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Investigation of Ionic Liquid Monopropellant Plasma using Optical Diagnostic Techniques

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

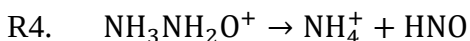
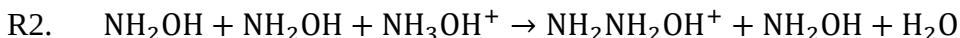
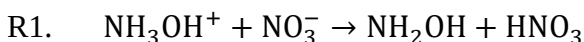
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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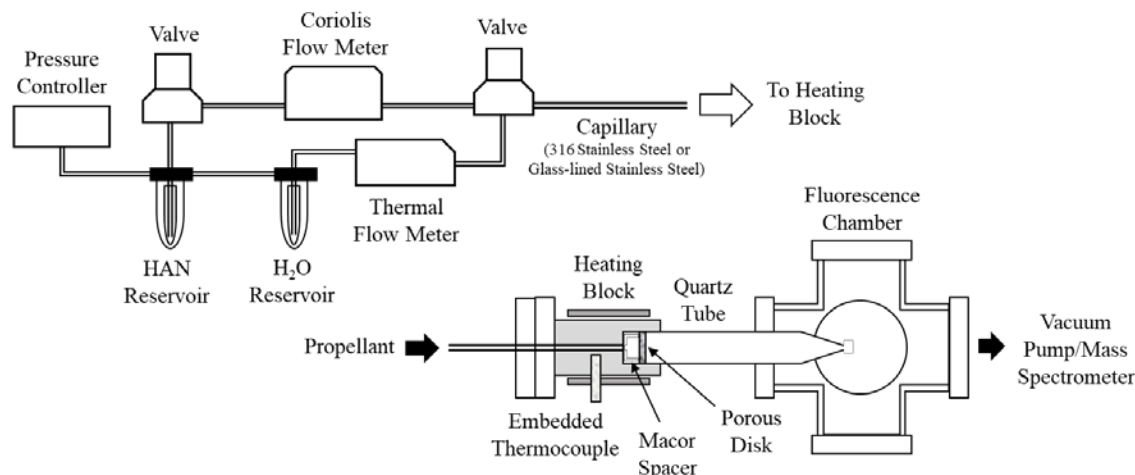


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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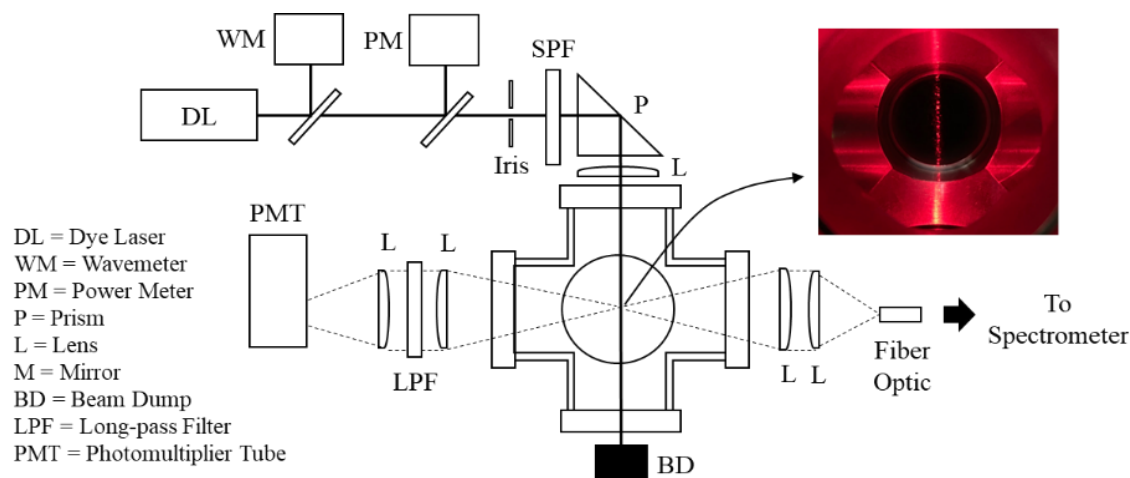


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680$ nm) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6$ Hz), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at ~624 nm, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at ~626 nm, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~642 nm. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

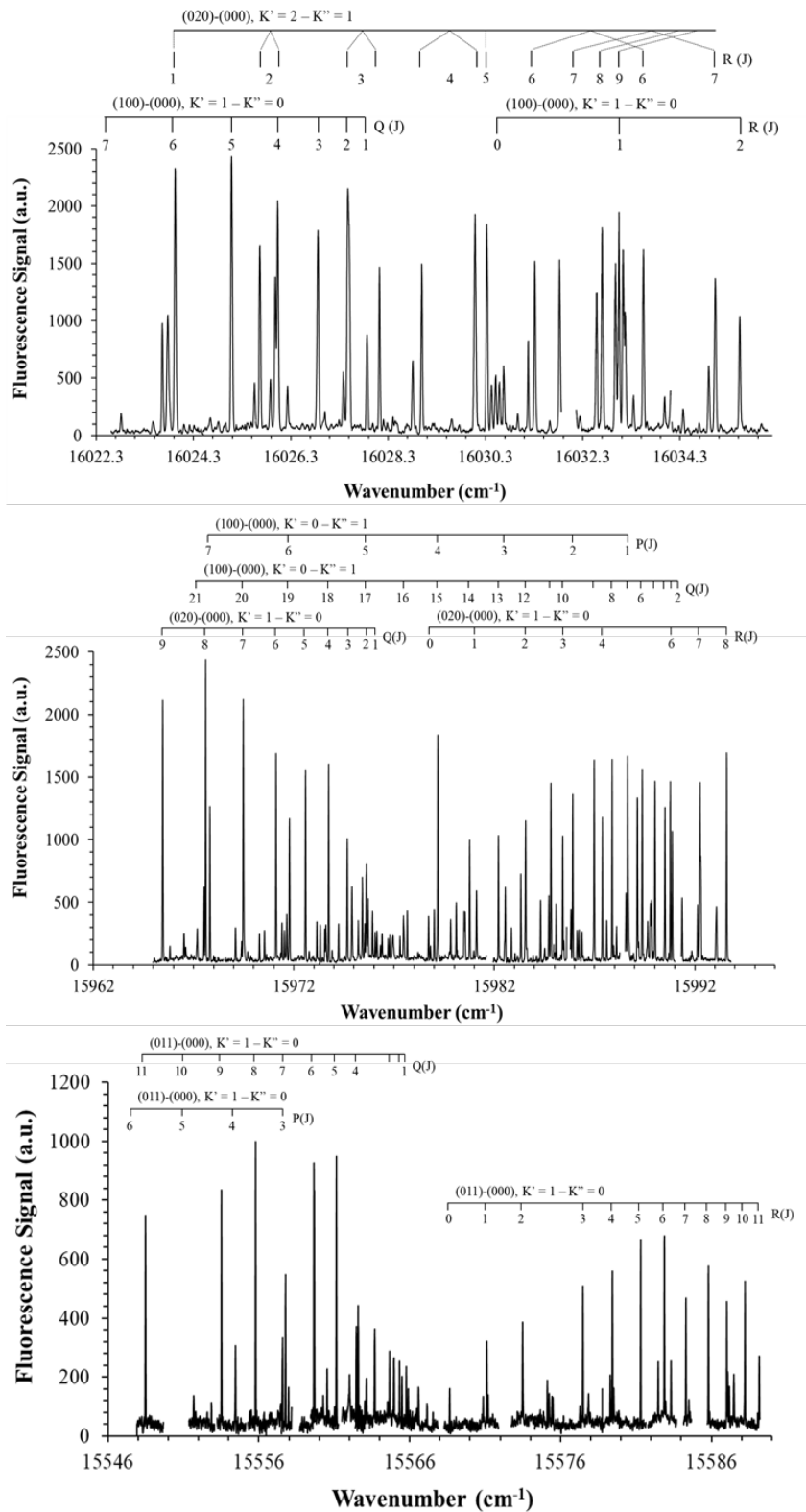


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) and $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

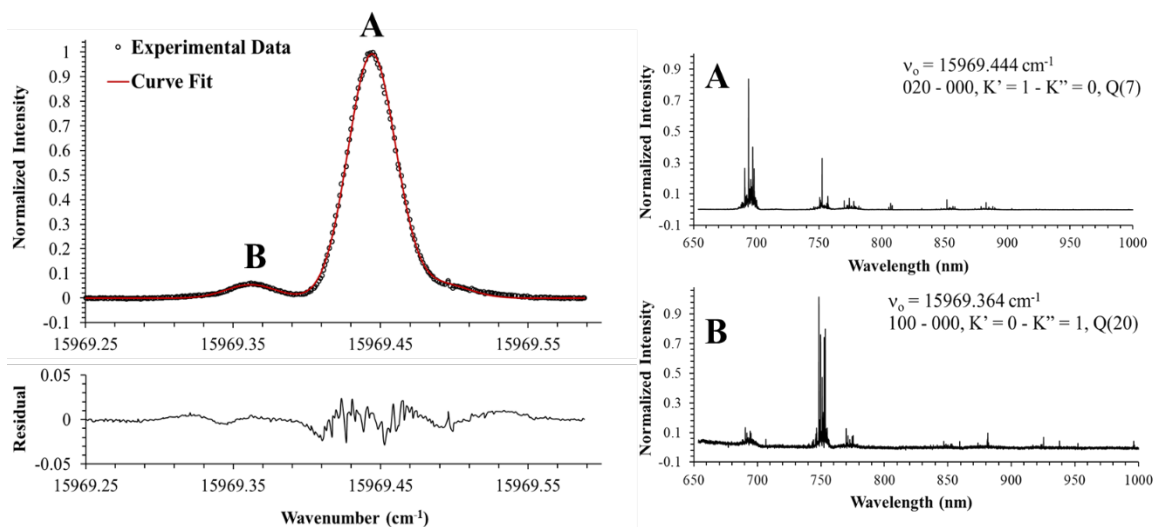


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition denoted as **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition denoted as **B**. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, **A** and **B**. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347$ K and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

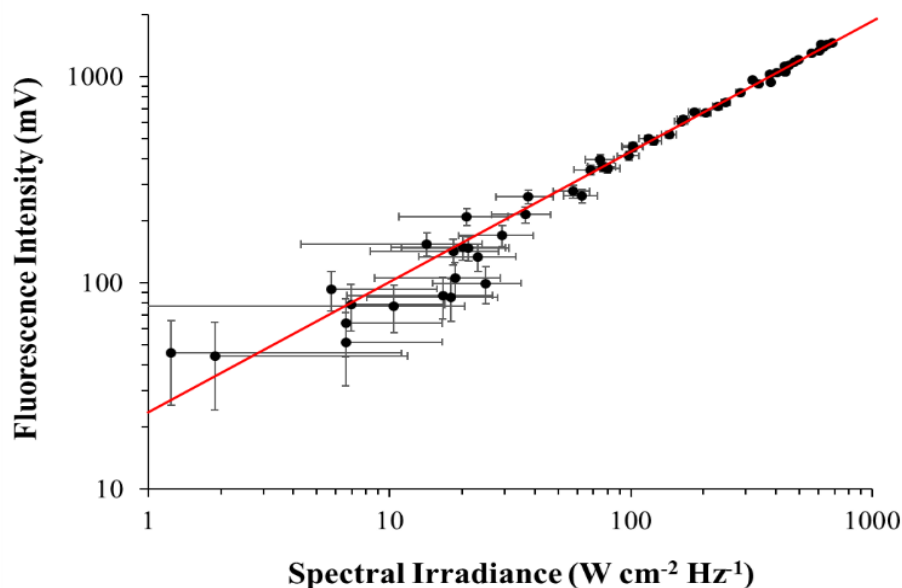


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

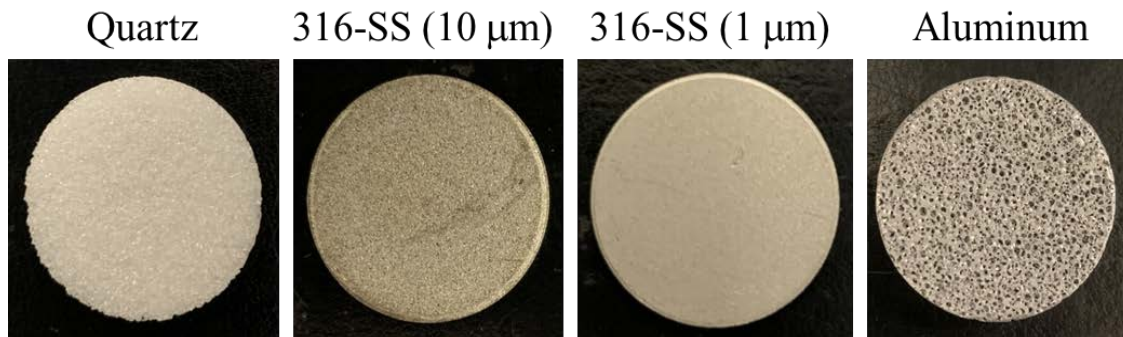


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

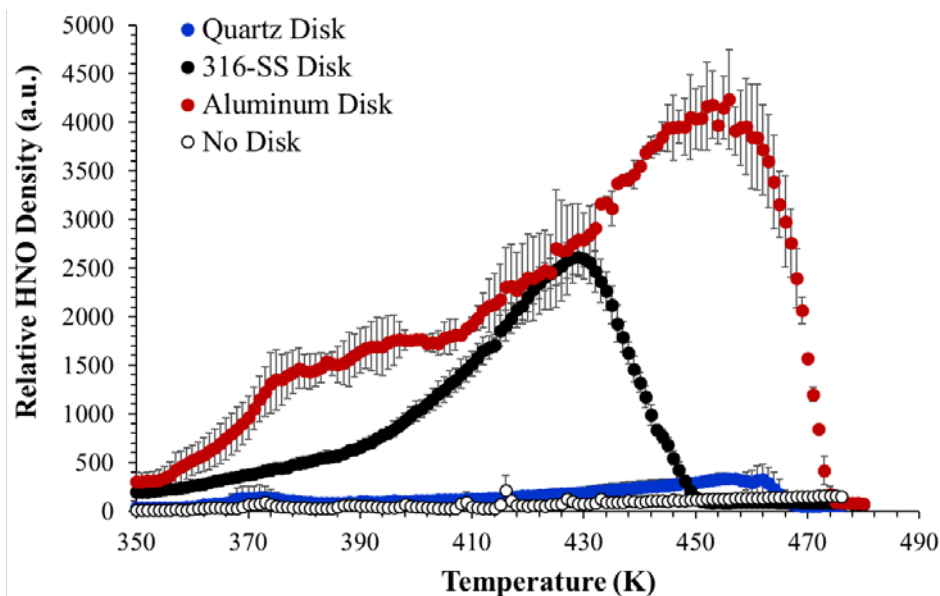


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2.Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

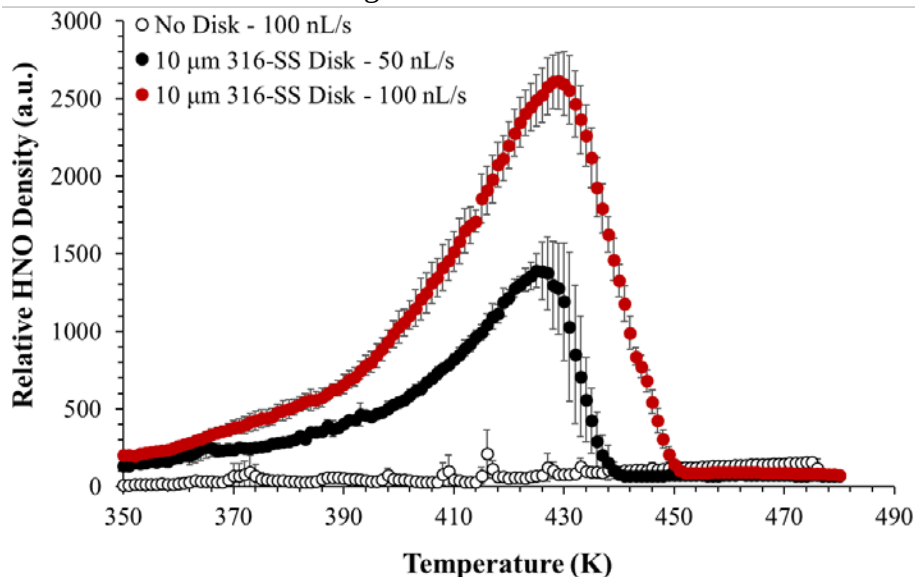


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

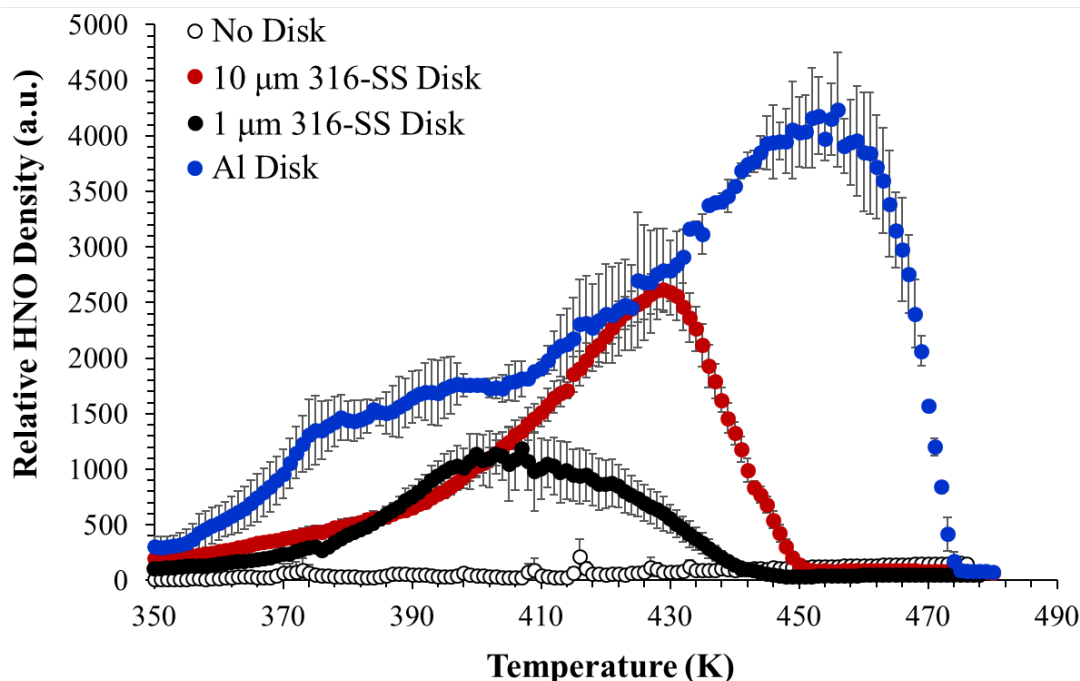


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

Acknowledgments

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

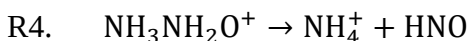
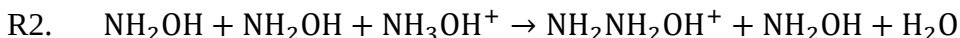
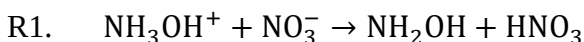
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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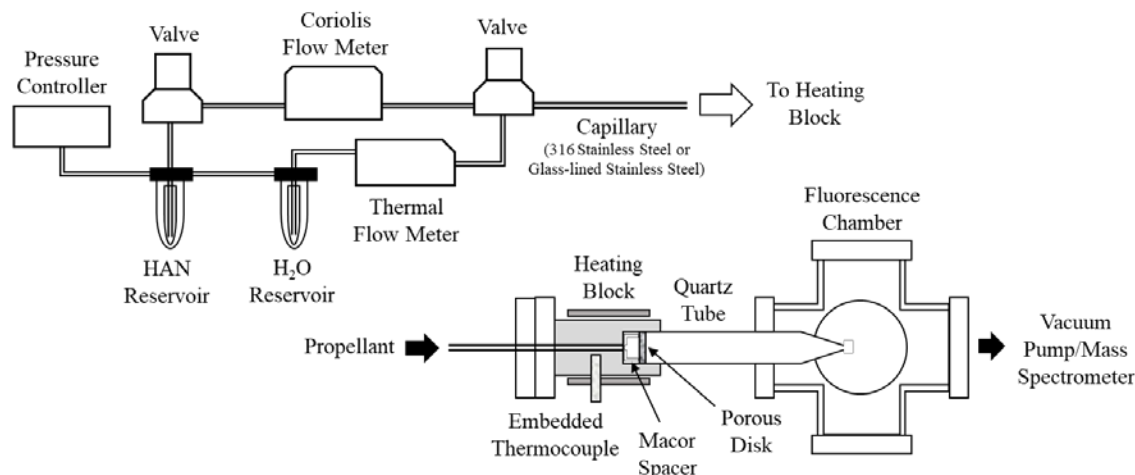


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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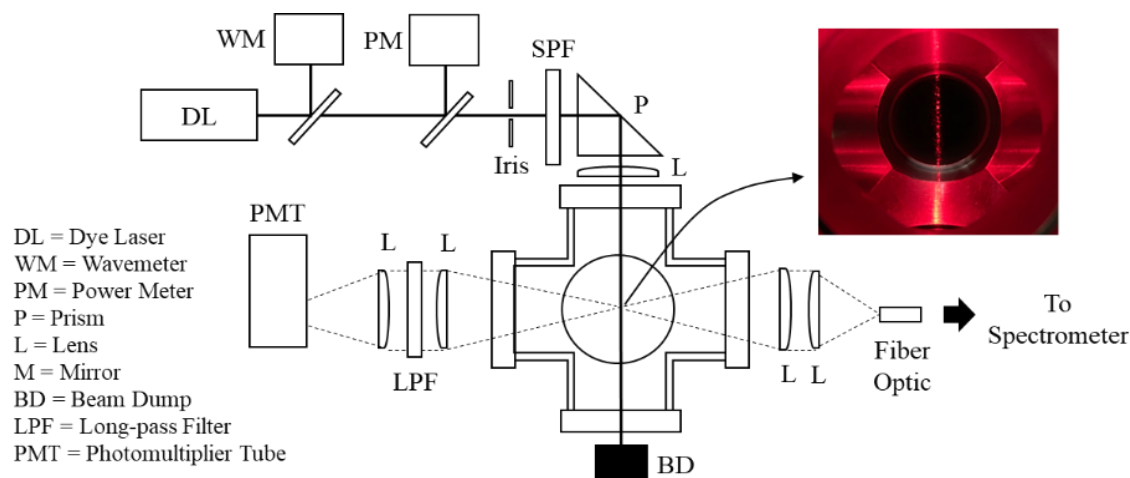


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680$ nm) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6$ Hz), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at ~624 nm, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at ~626 nm, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~642 nm. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

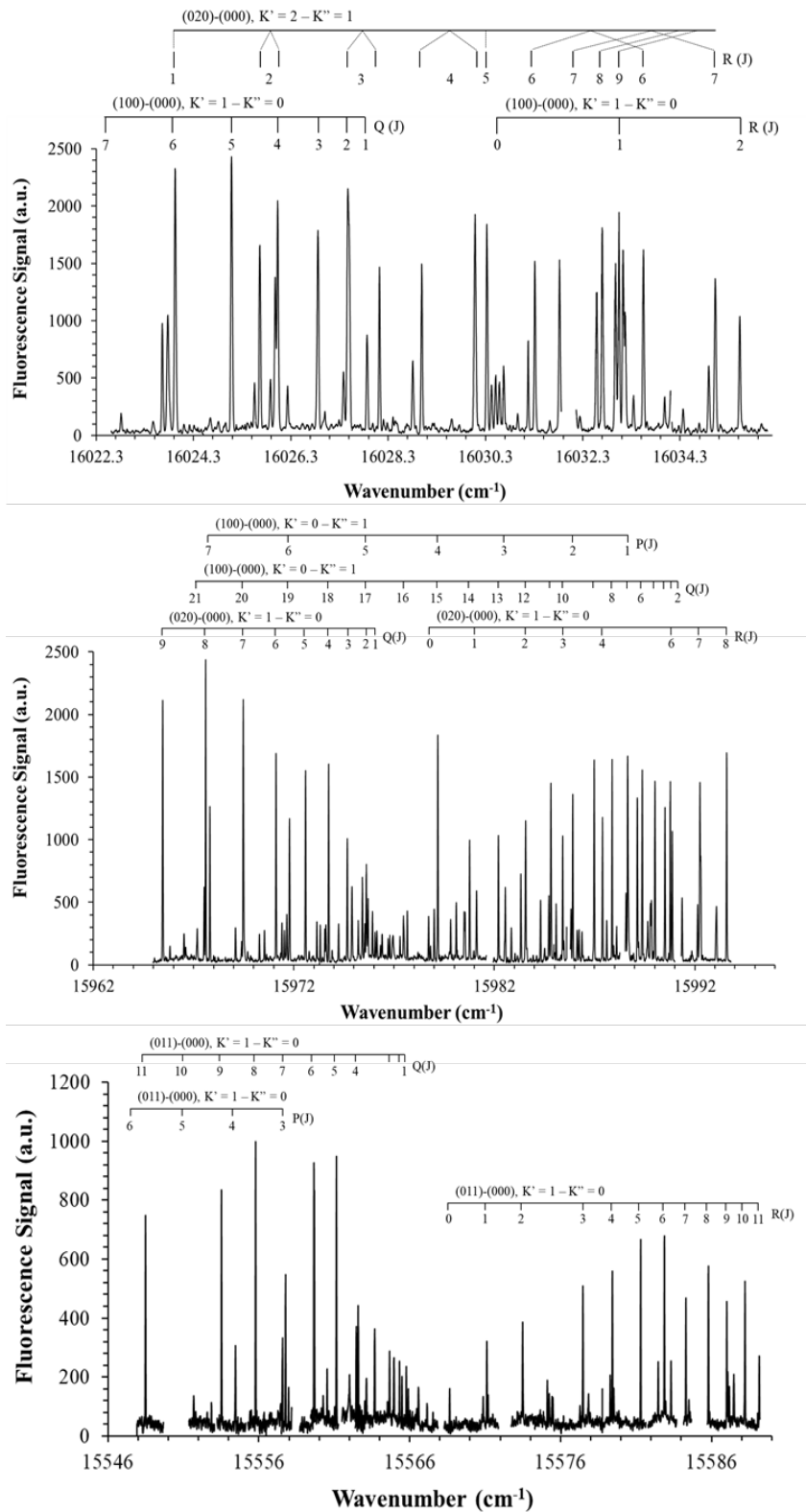


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) and $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

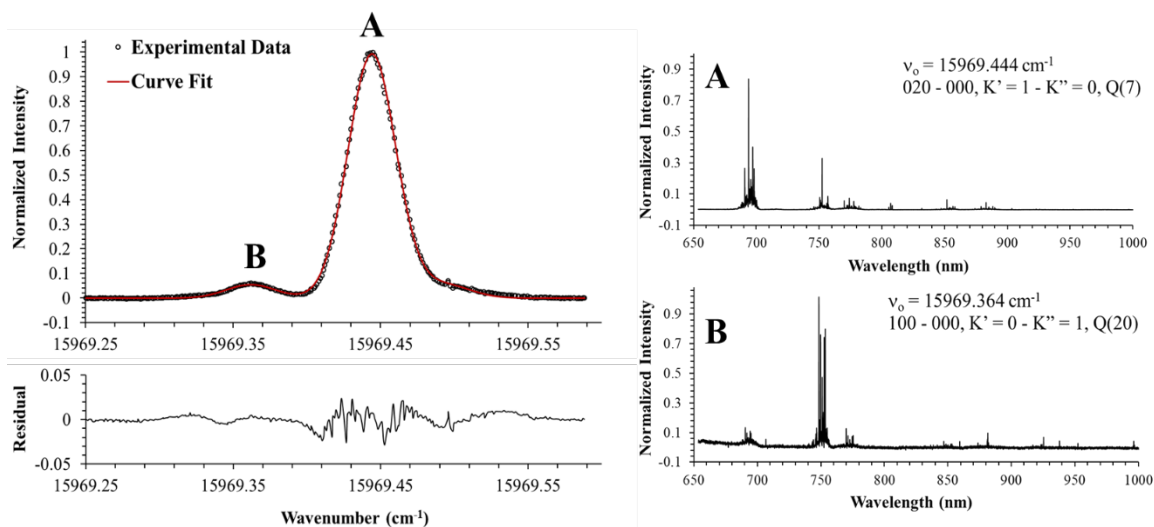


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition denoted as **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition denoted as **B**. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, **A** and **B**. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347$ K and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

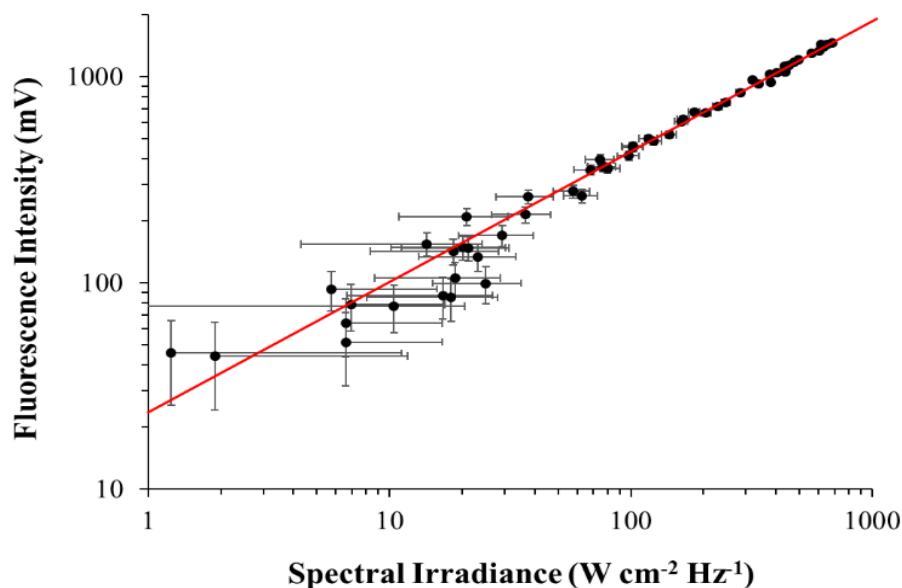


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

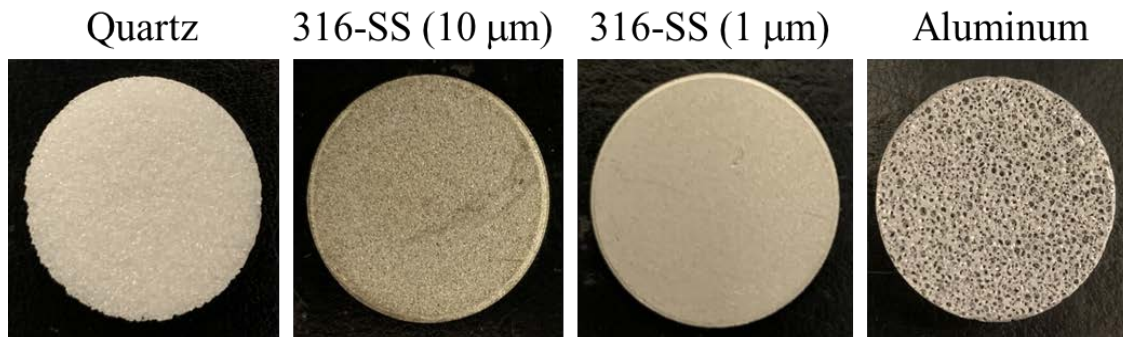


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

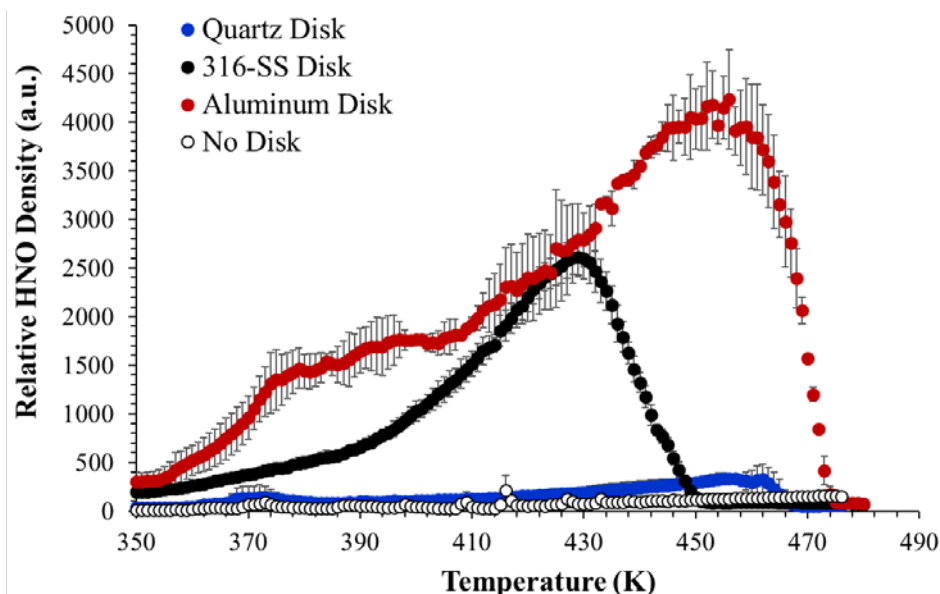


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2. Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

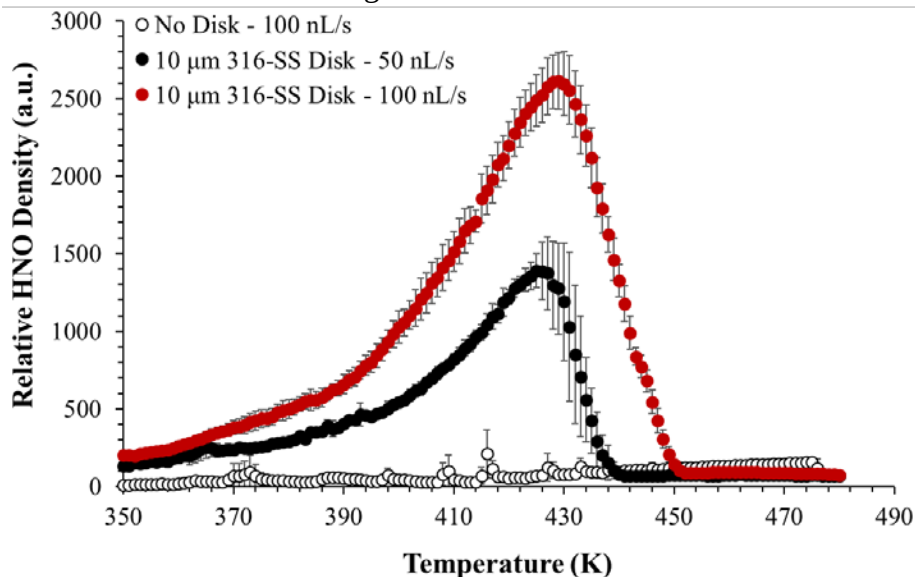


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

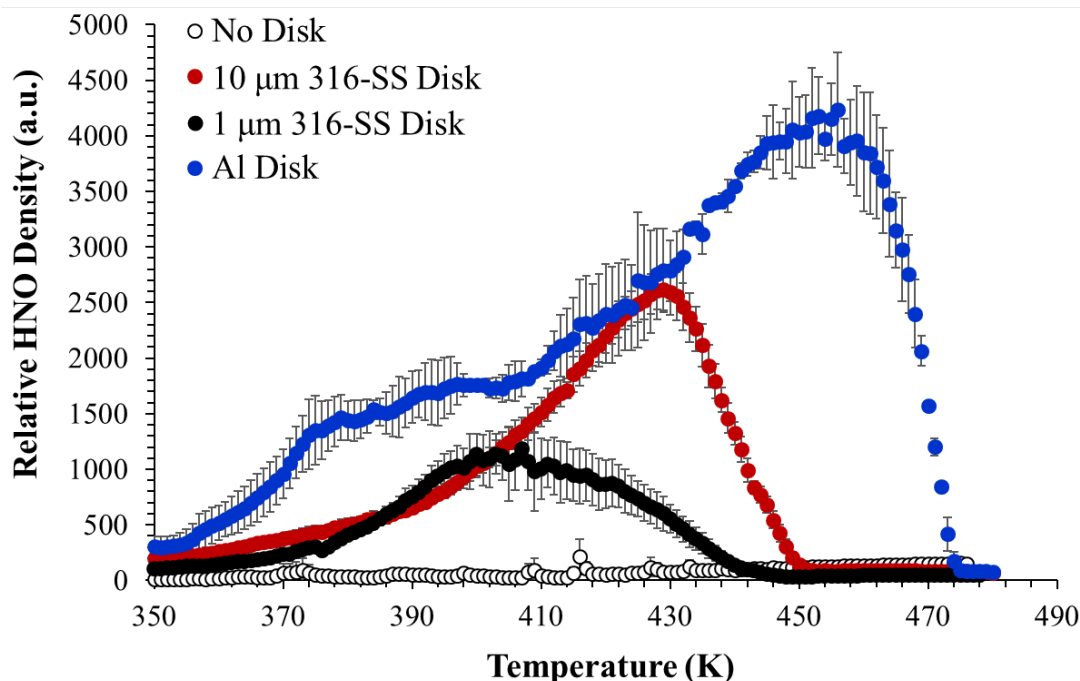


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

Acknowledgments

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

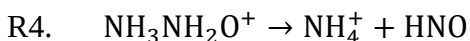
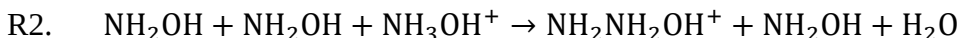
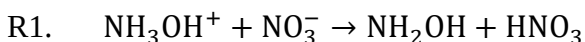
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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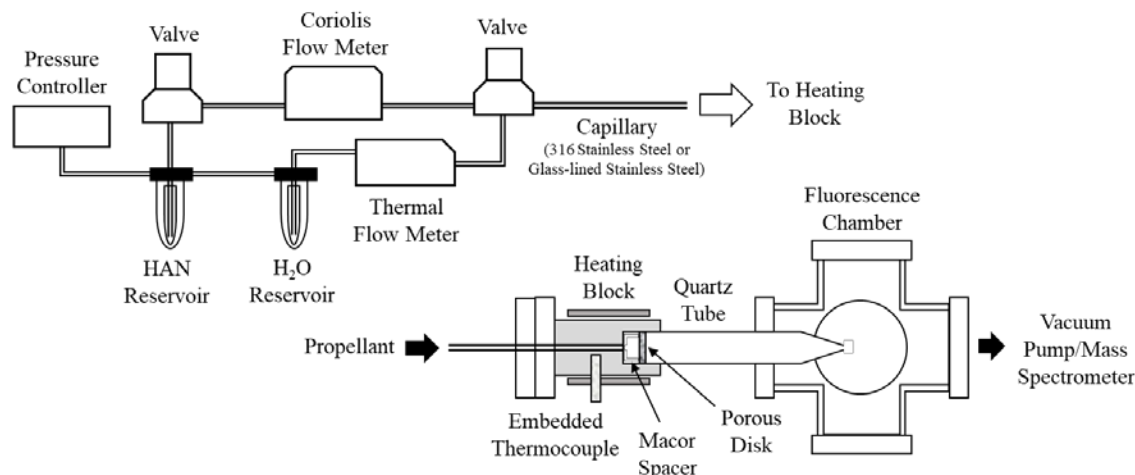


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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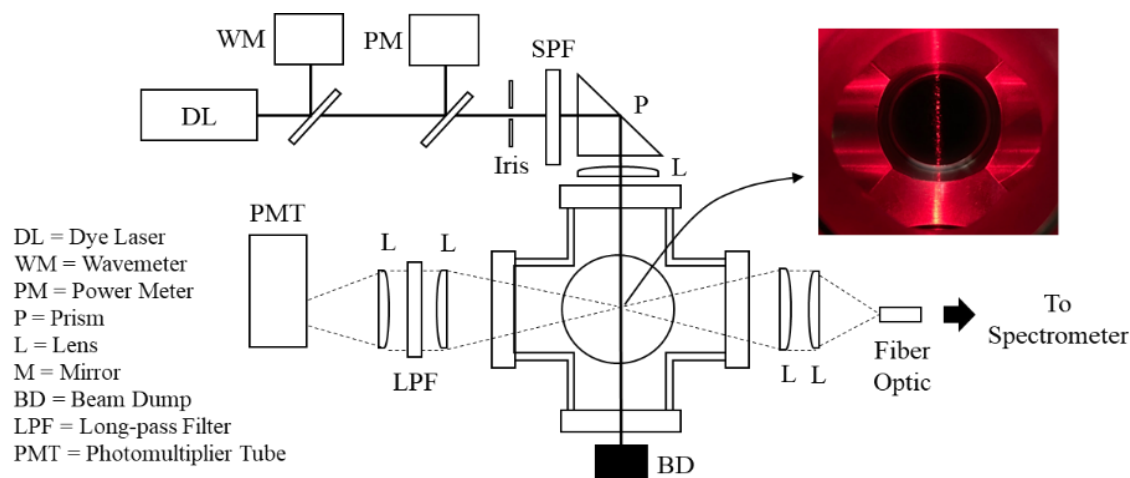


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680$ nm) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6$ Hz), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at ~624 nm, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at ~626 nm, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~642 nm. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

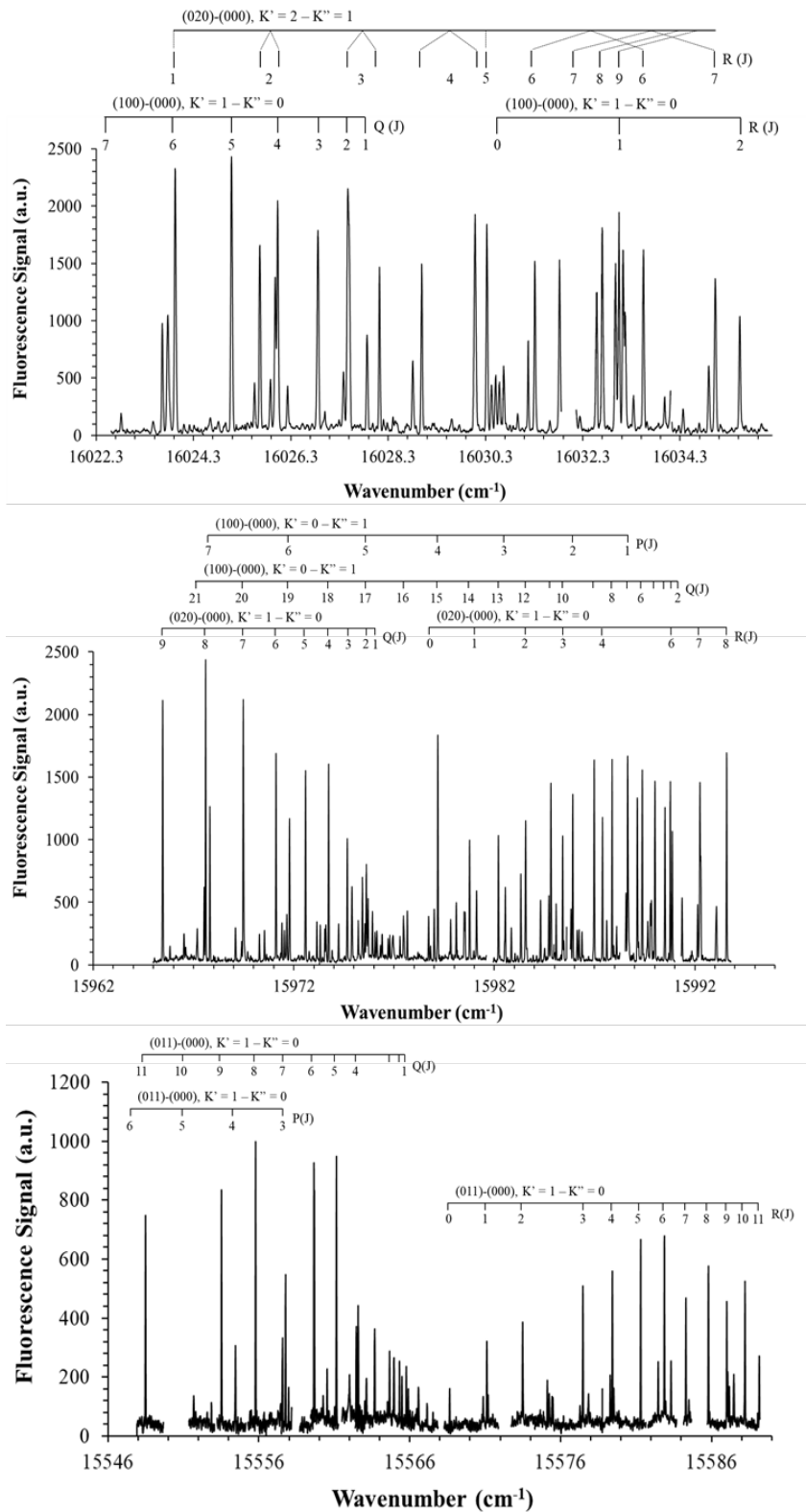


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) and $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

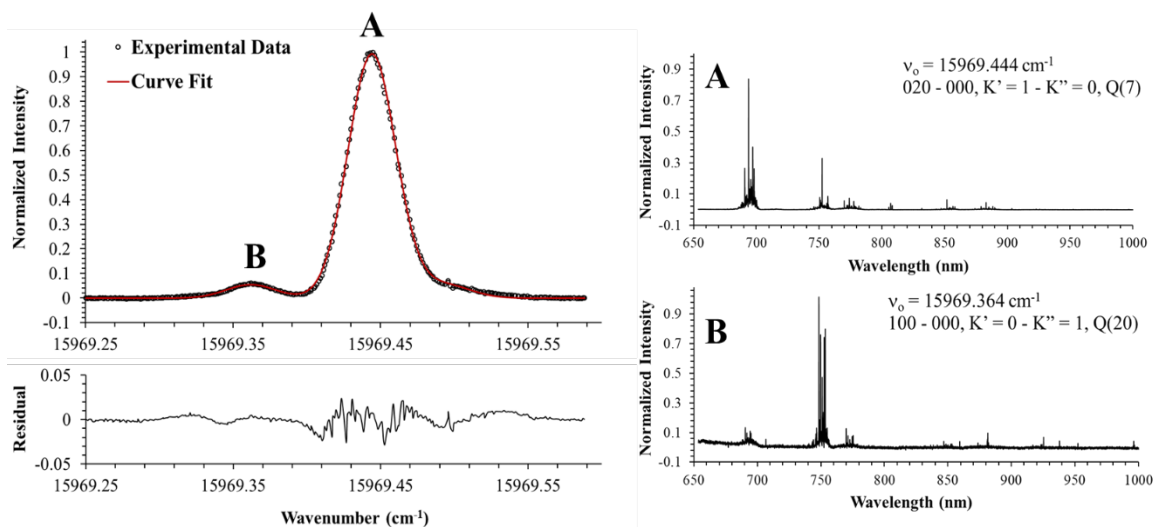


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition denoted as **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition denoted as **B**. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, **A** and **B**. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347 \text{ K}$ and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

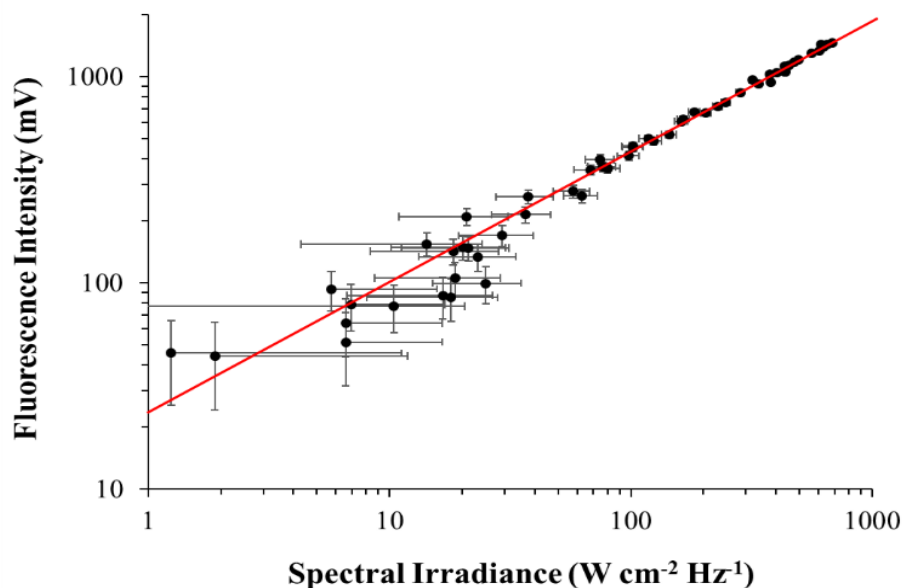


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

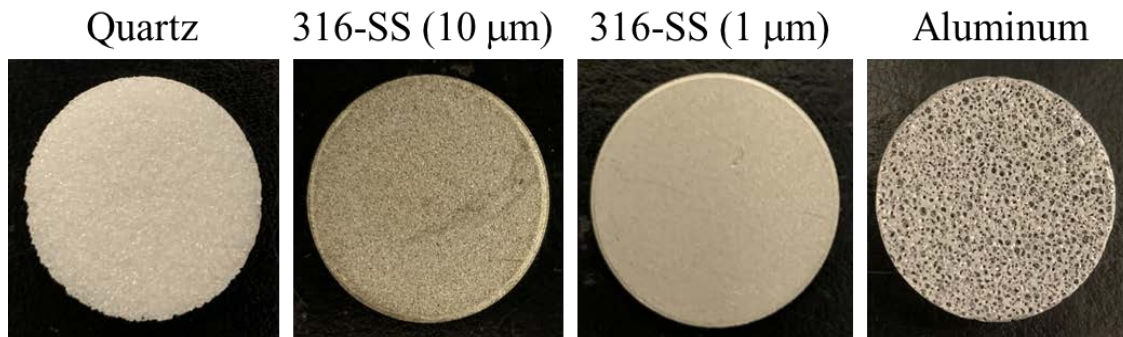


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

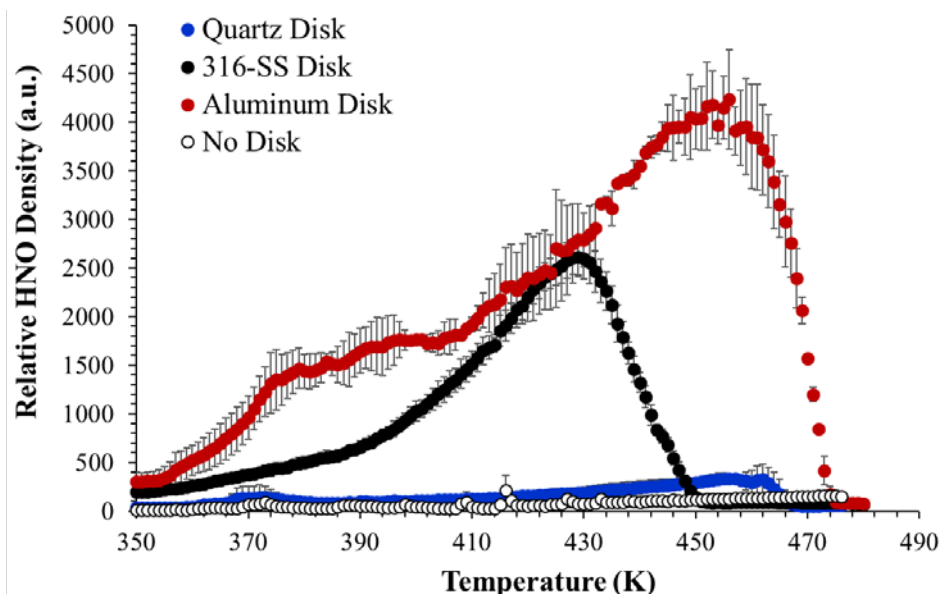


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2. Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

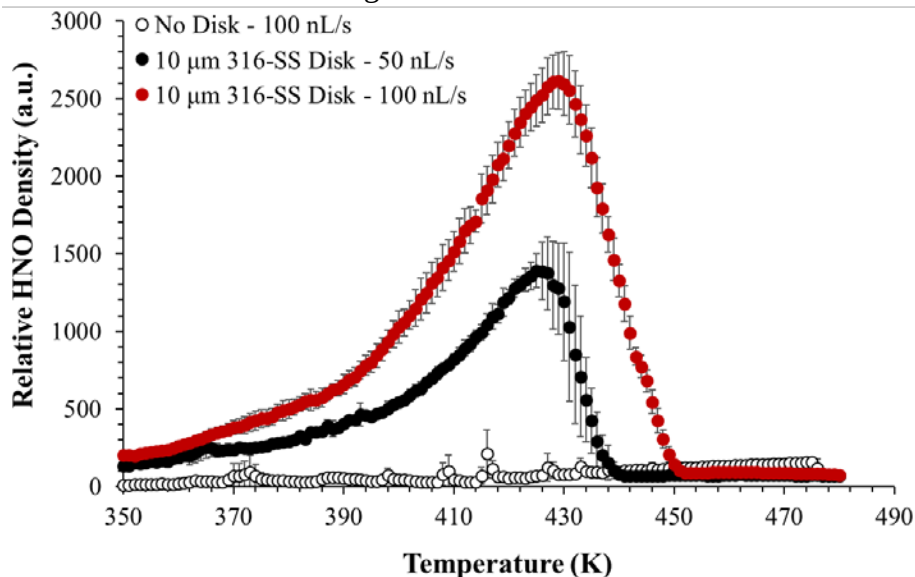


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

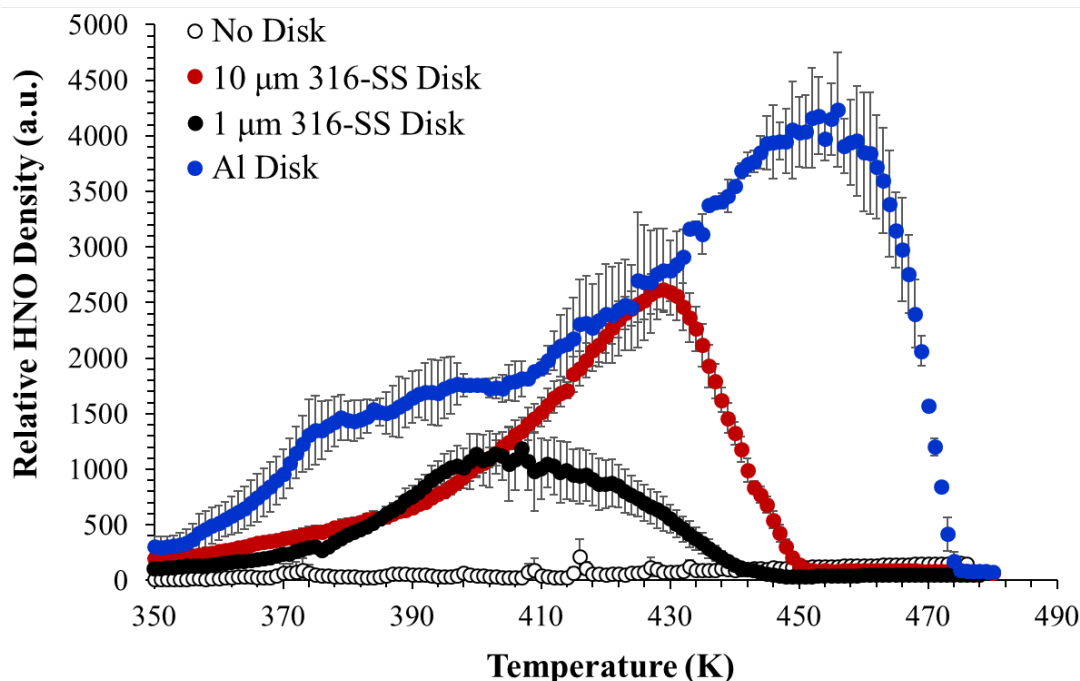


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

Acknowledgments

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

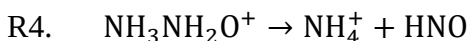
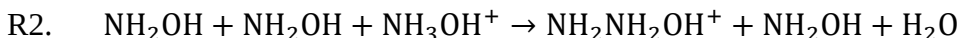
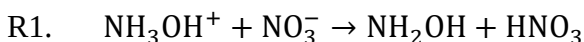
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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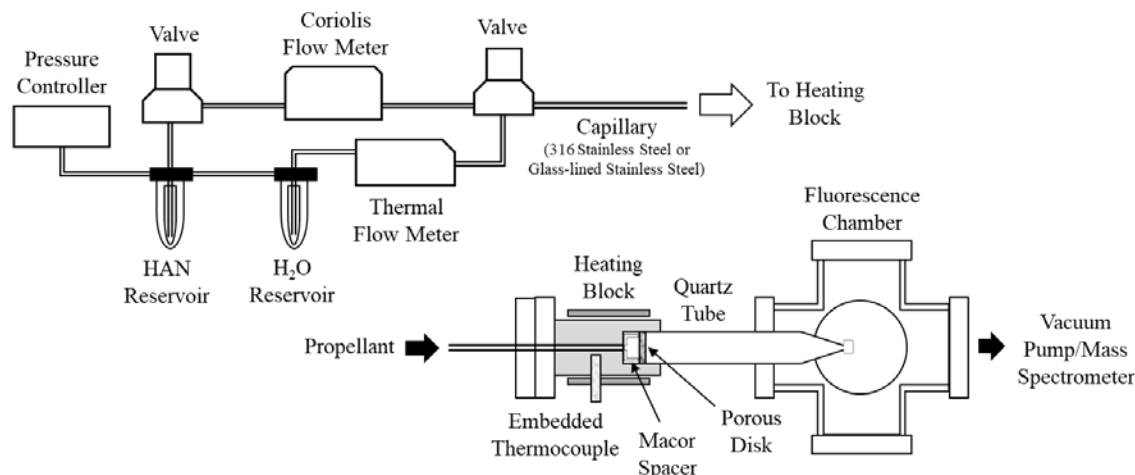


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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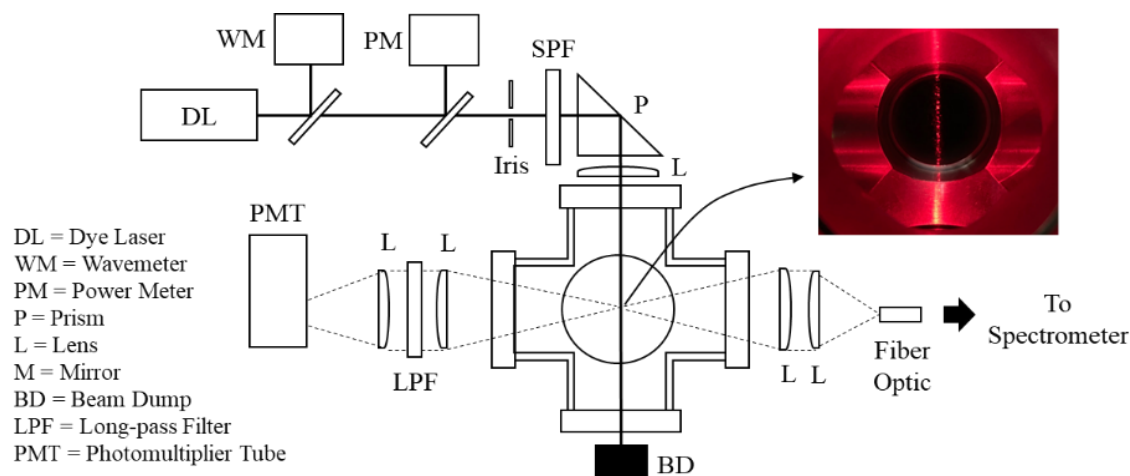


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680$ nm) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6$ Hz), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at ~624 nm, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at ~626 nm, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~642 nm. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

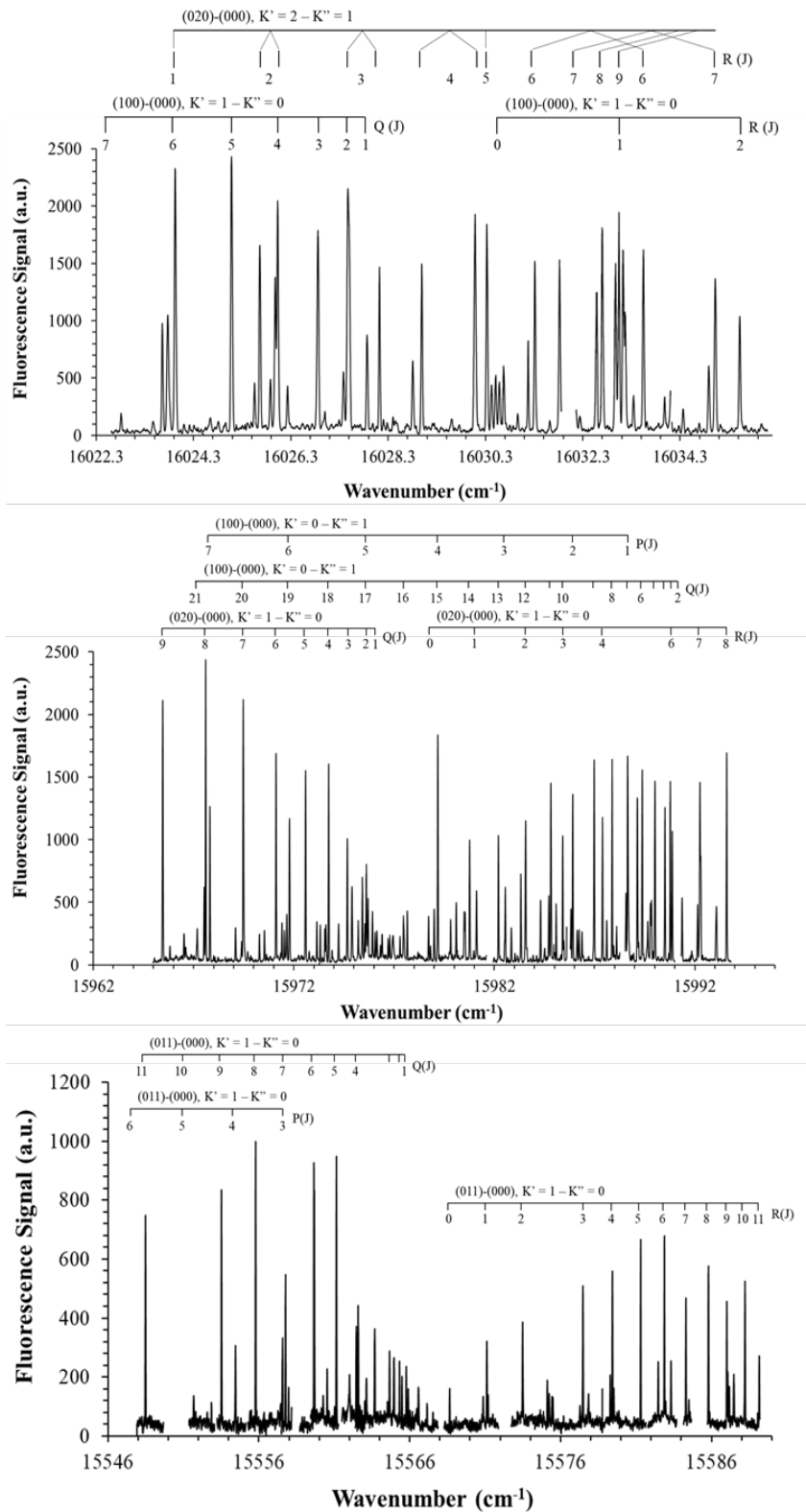


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) and $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

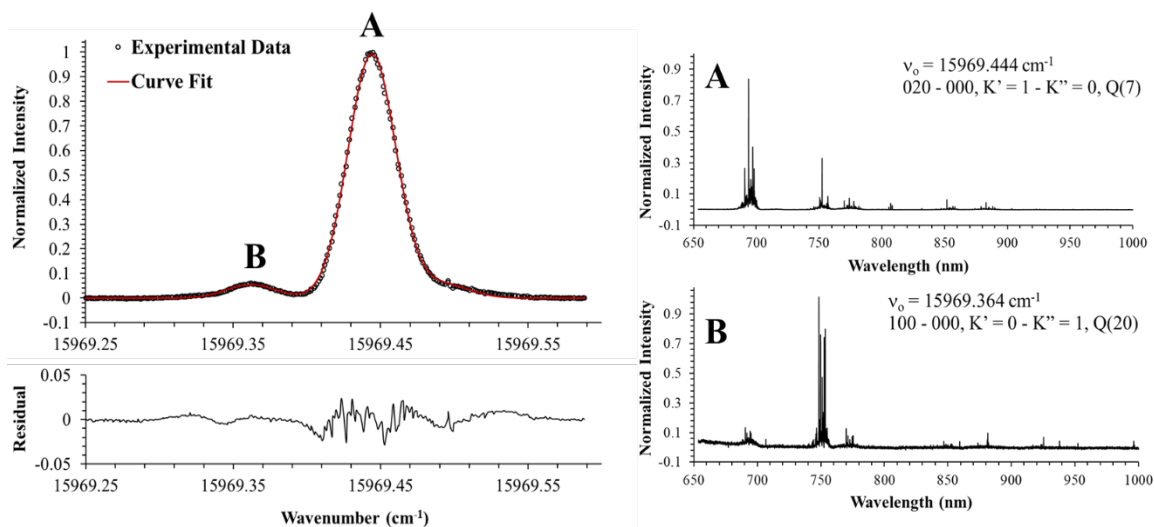


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition denoted as **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition denoted as **B**. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, **A** and **B**. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347 \text{ K}$ and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

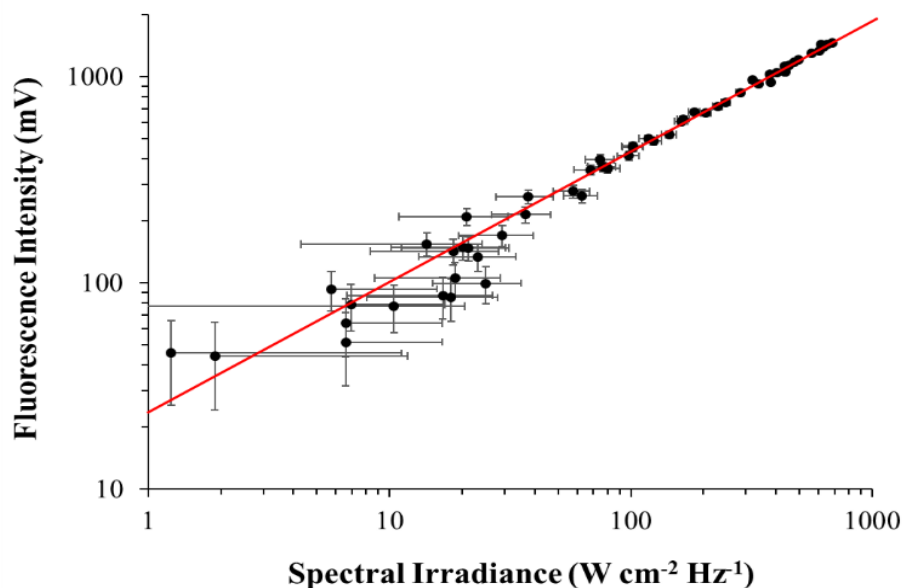


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

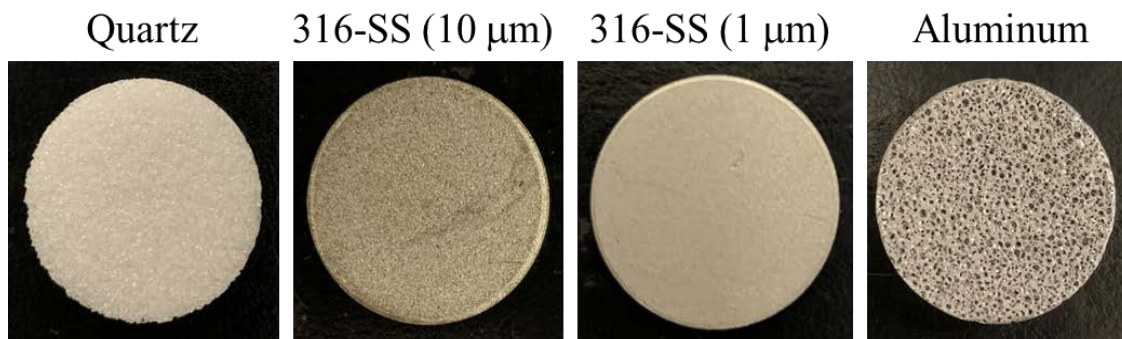


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

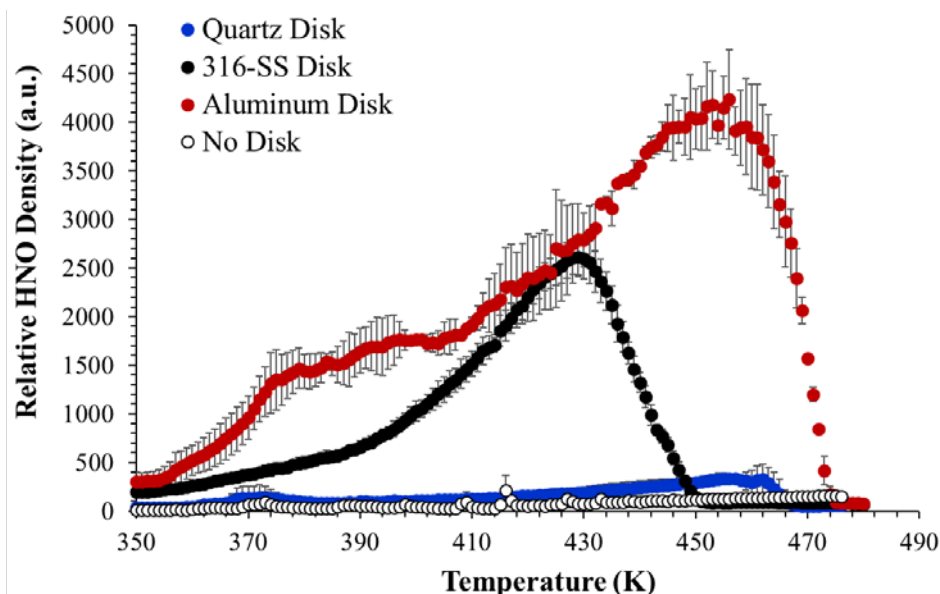


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2. Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

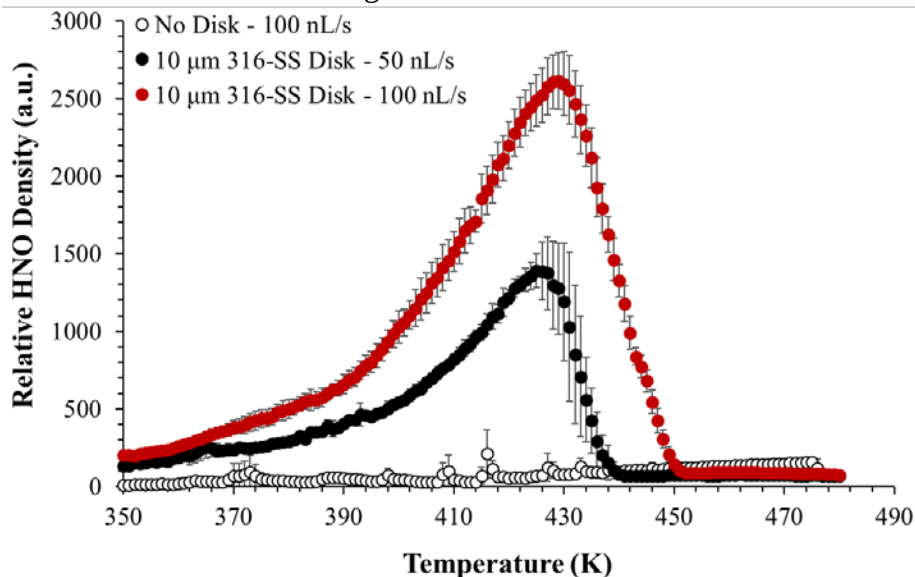


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

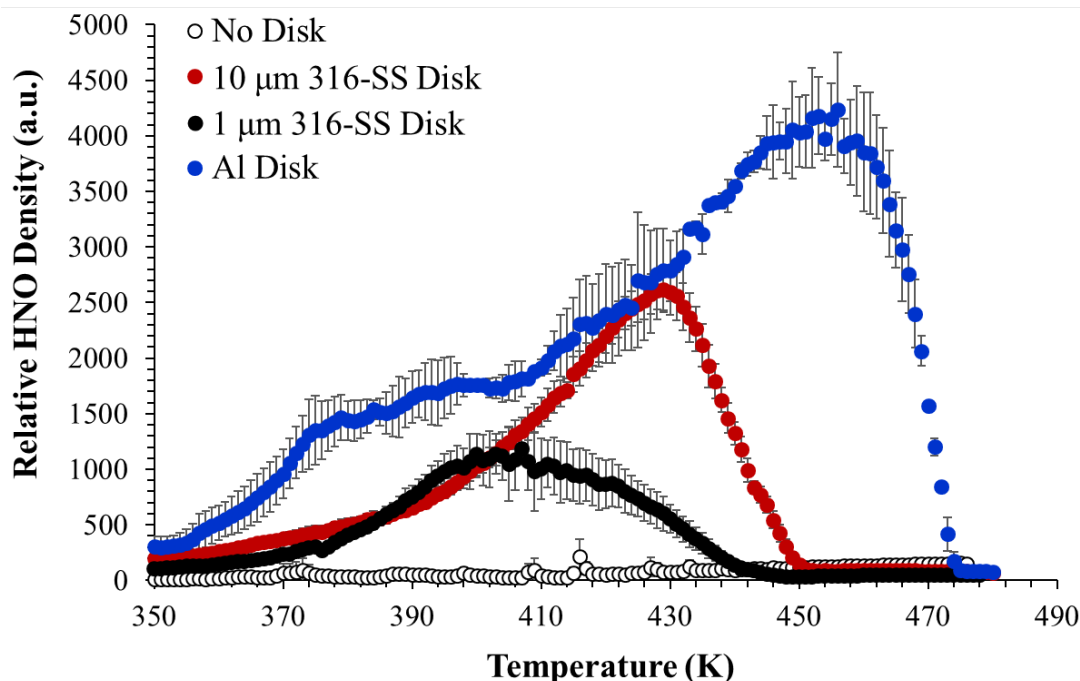


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

Acknowledgments

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

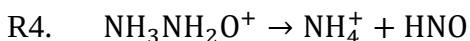
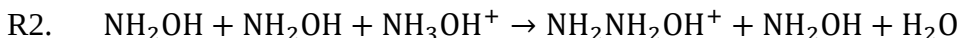
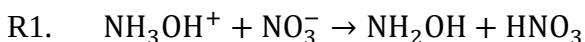
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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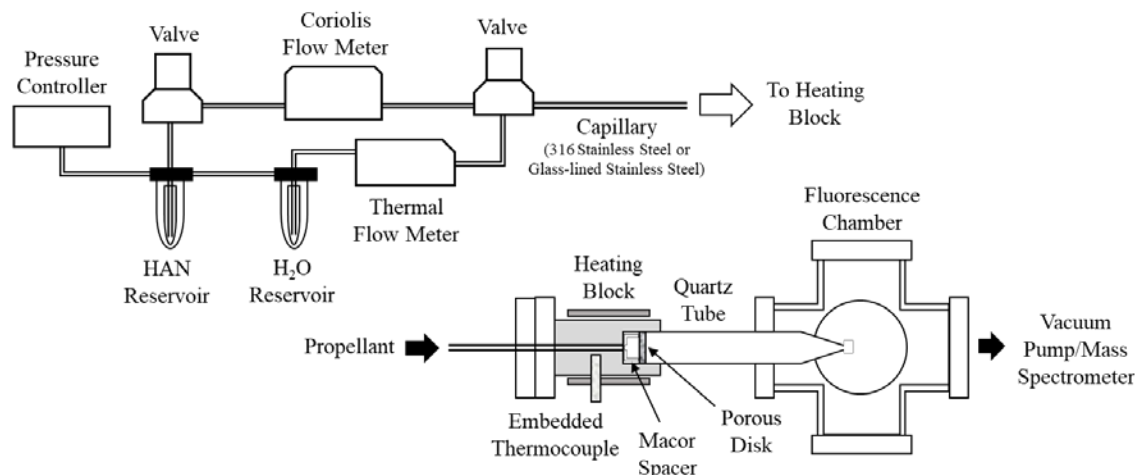


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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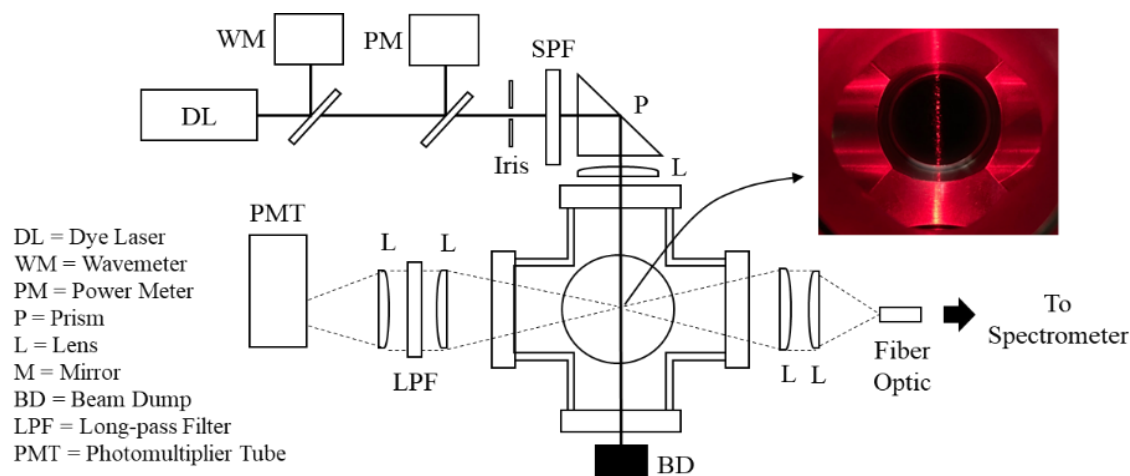


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680$ nm) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6$ Hz), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at ~624 nm, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at ~626 nm, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~642 nm. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

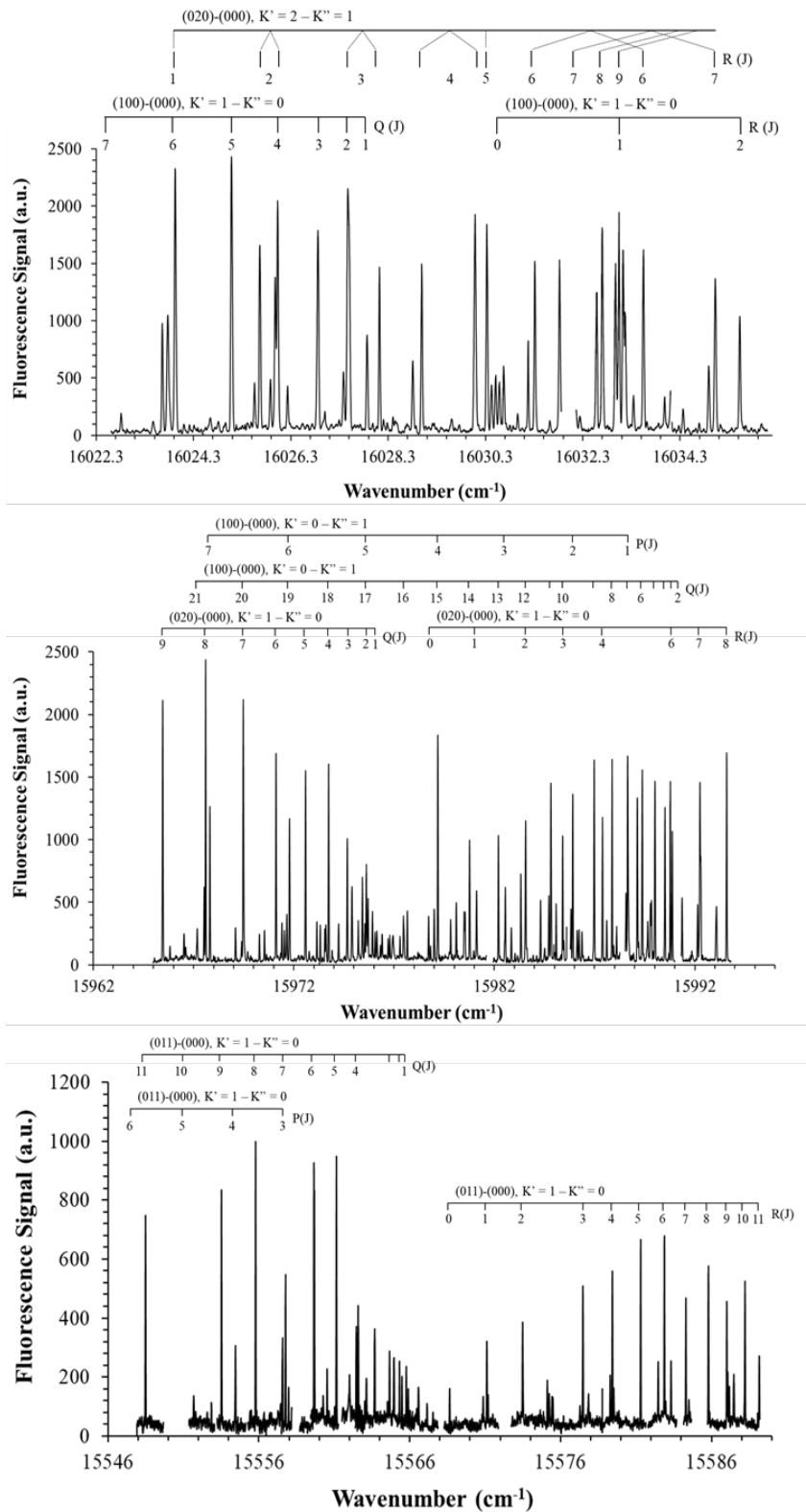


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

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In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) and $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

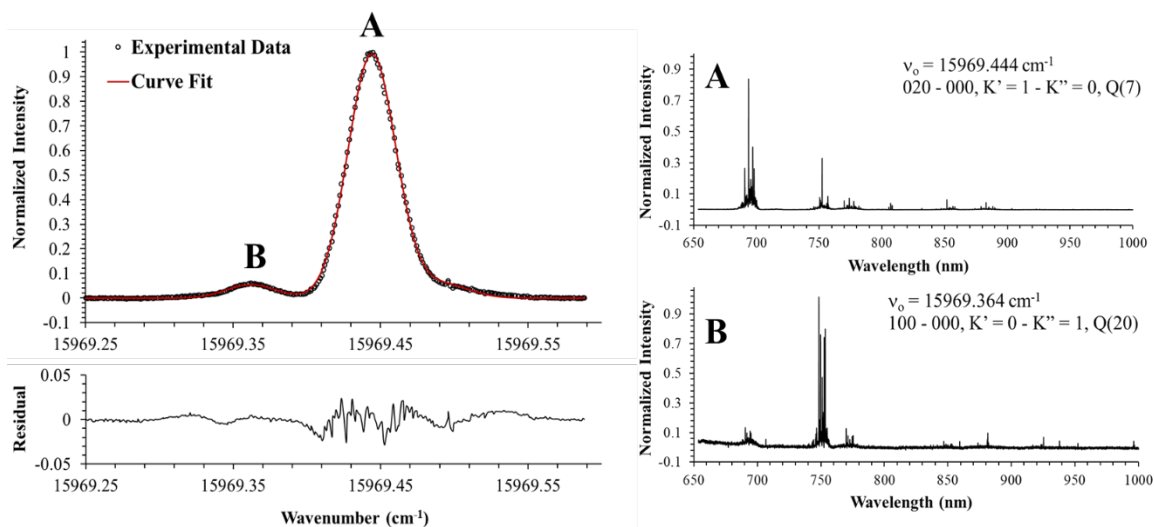


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition denoted as **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition denoted as **B**. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, **A** and **B**. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347 \text{ K}$ and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

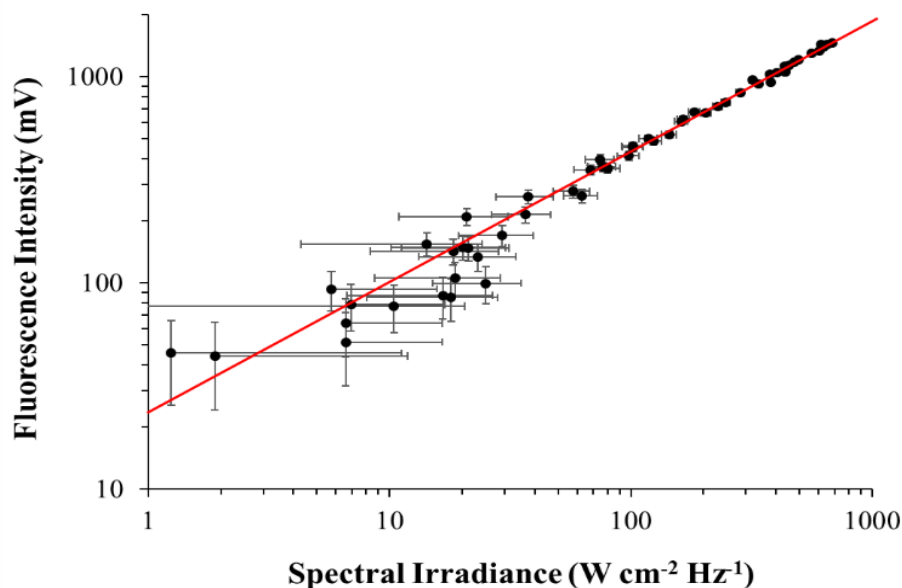


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

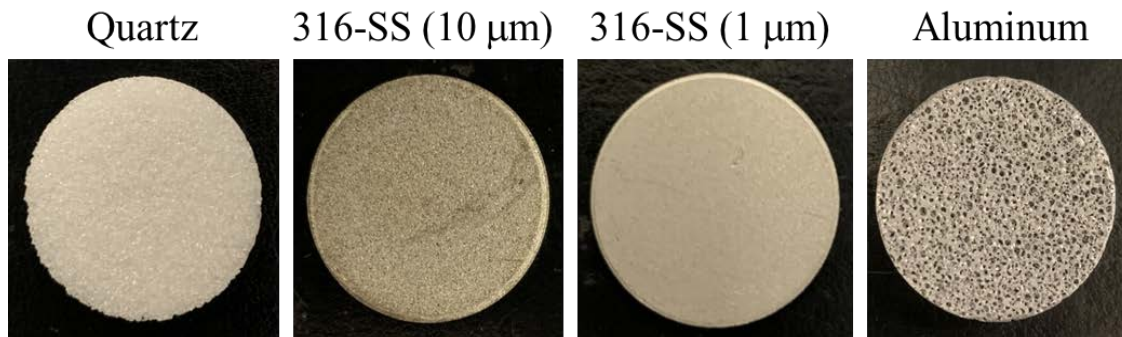


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

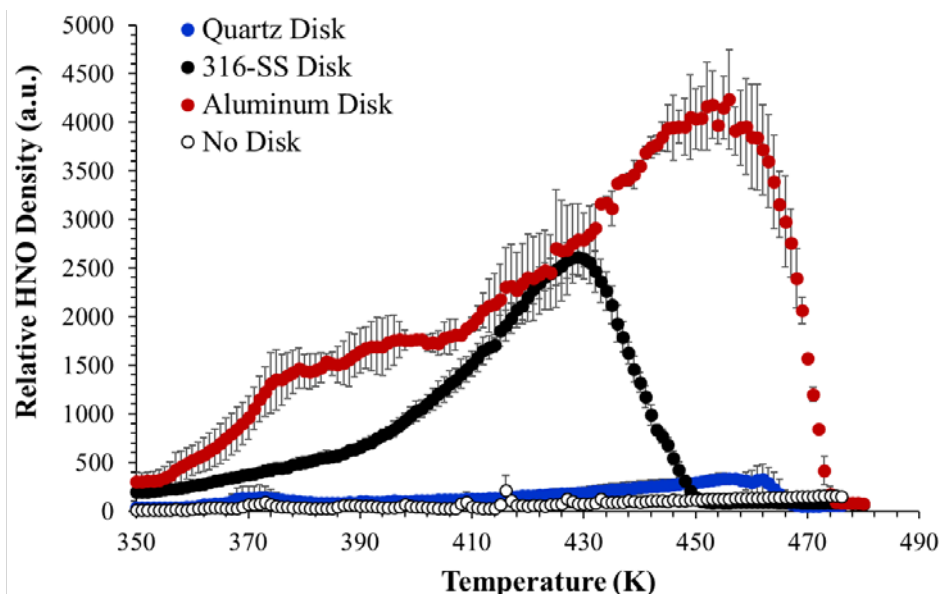


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2. Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

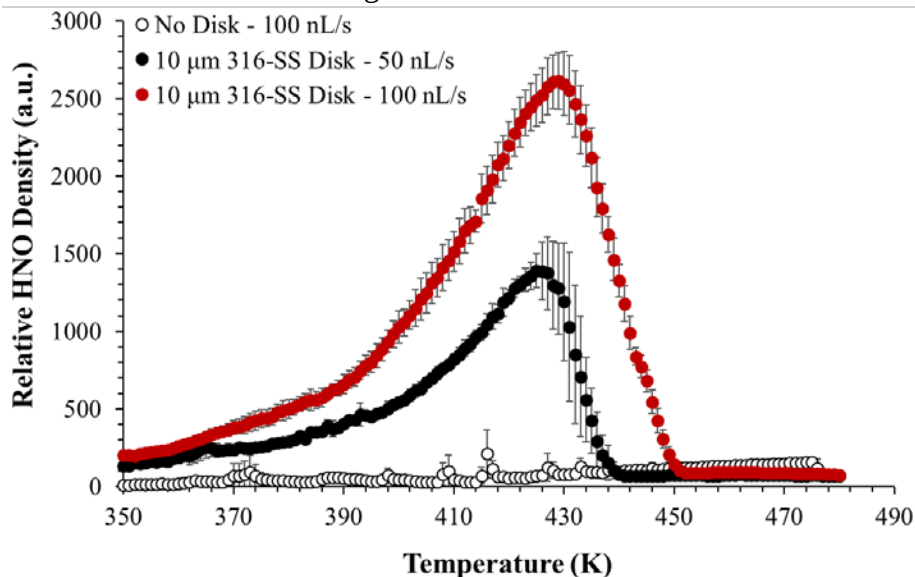


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

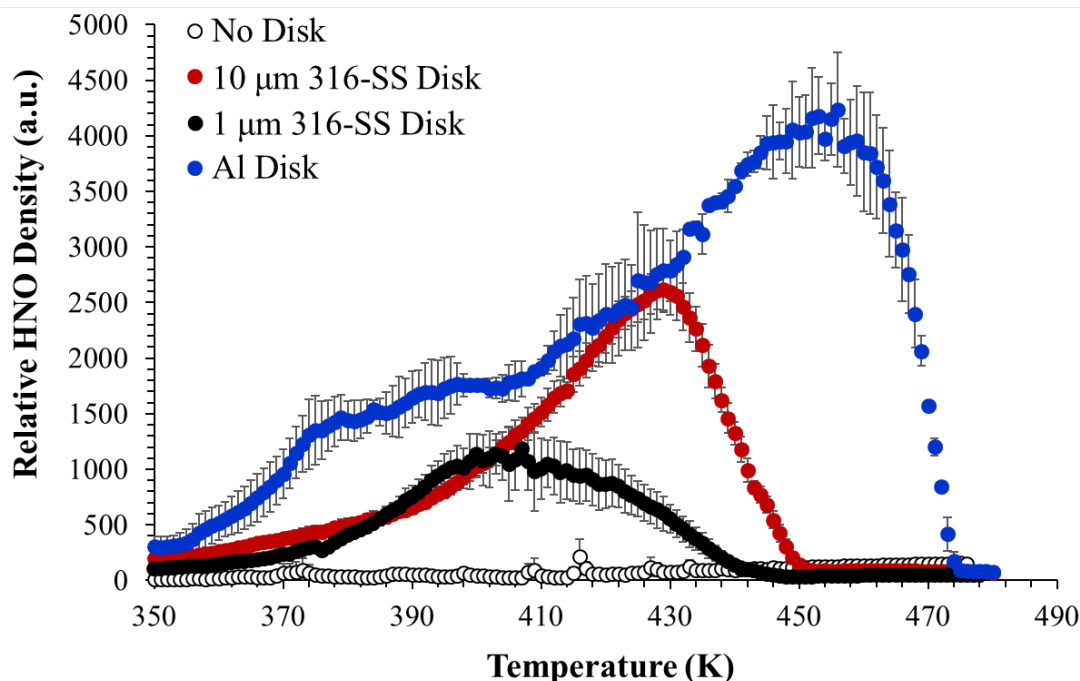


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

Acknowledgments

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

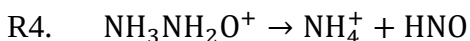
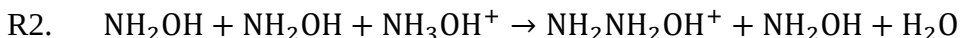
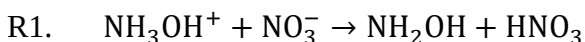
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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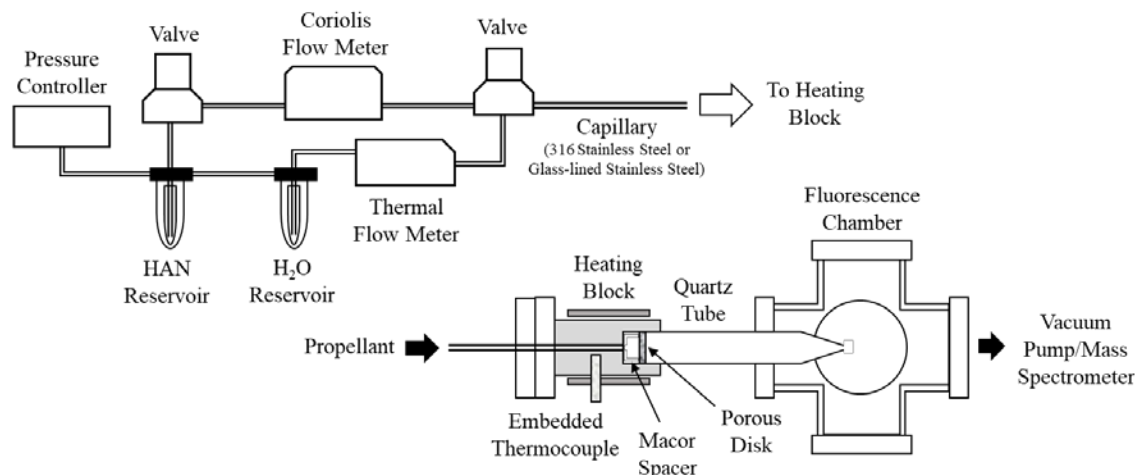


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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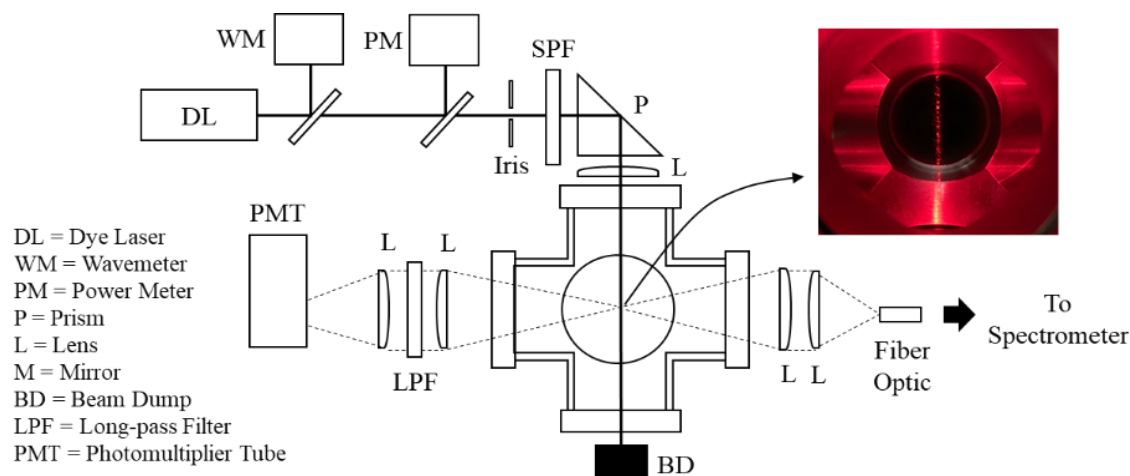


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680$ nm) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6$ Hz), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at ~624 nm, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at ~626 nm, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~642 nm. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

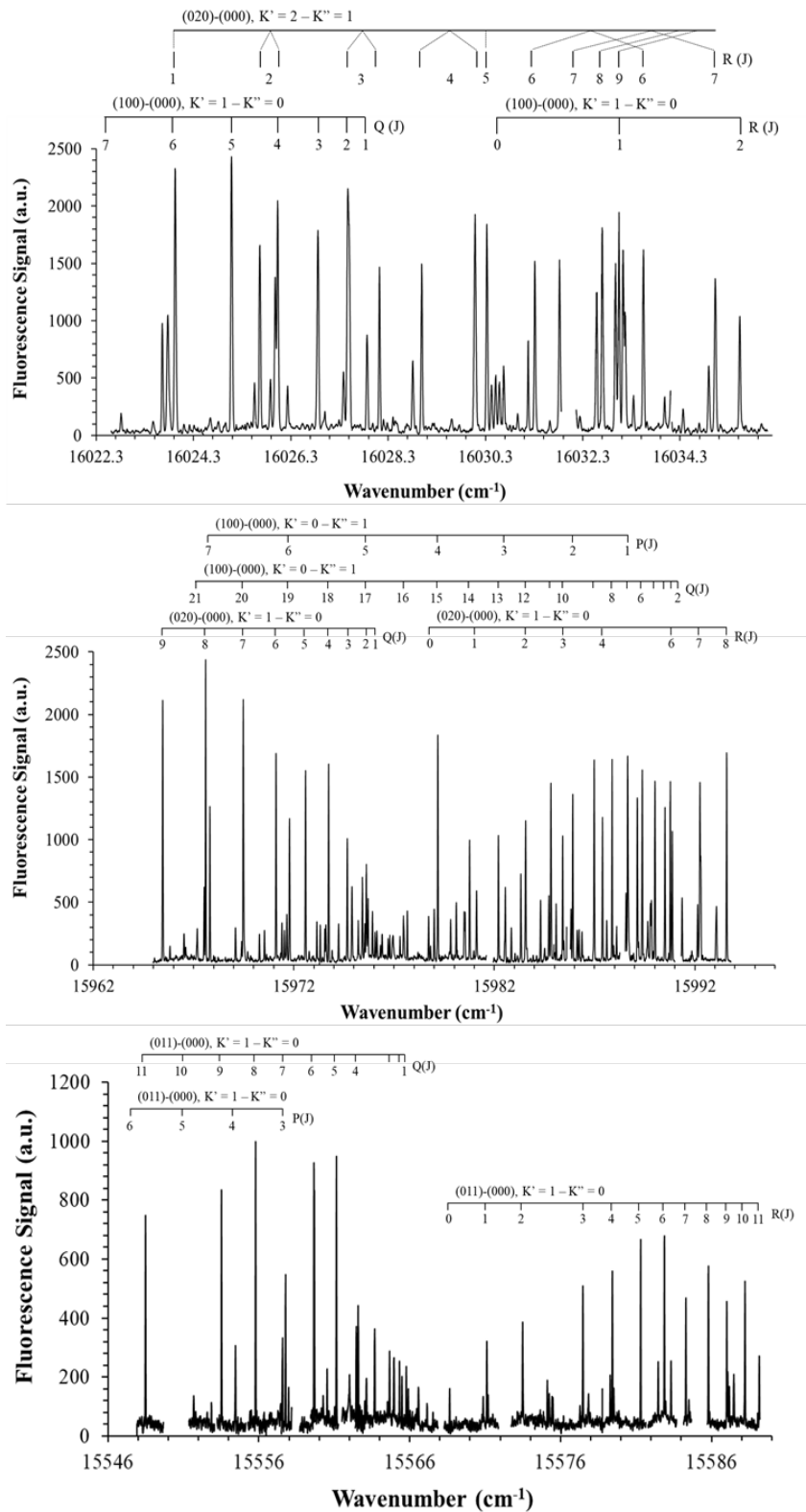


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

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In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' - X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' - X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' - X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' - X^1A'$ (020 – 000) and $\tilde{A}^1A'' - X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

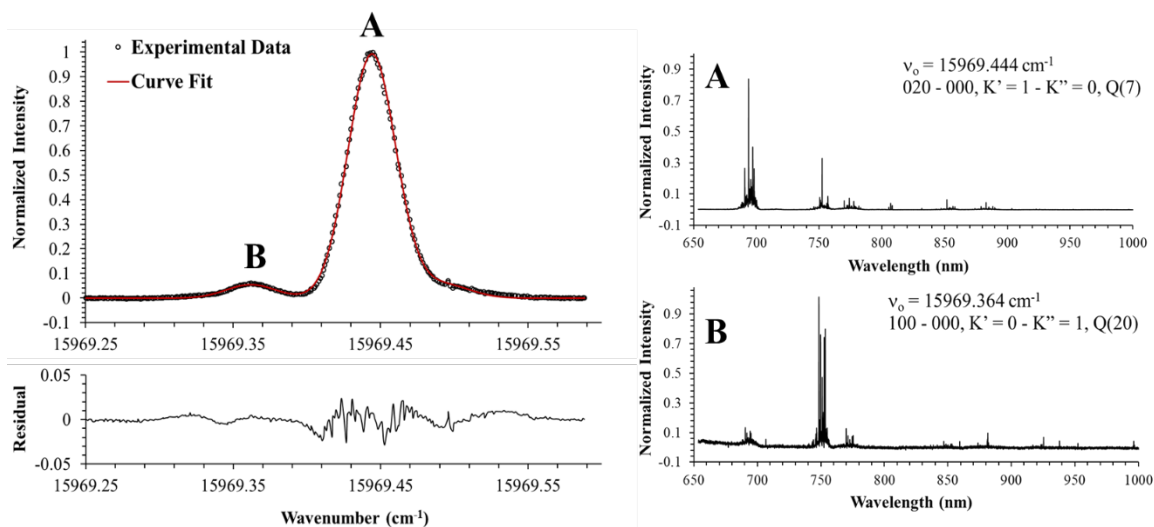


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition denoted as **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition denoted as **B**. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, **A** and **B**. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347$ K and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

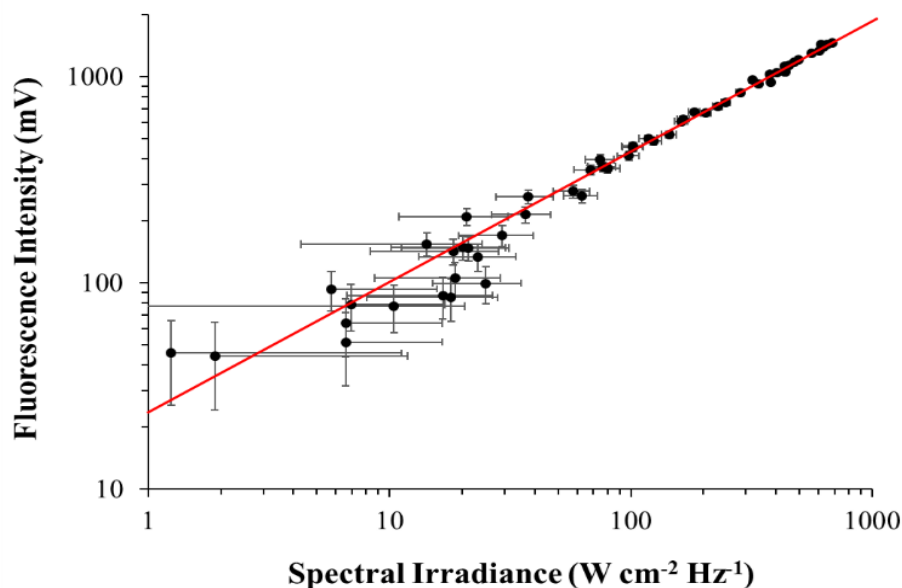


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

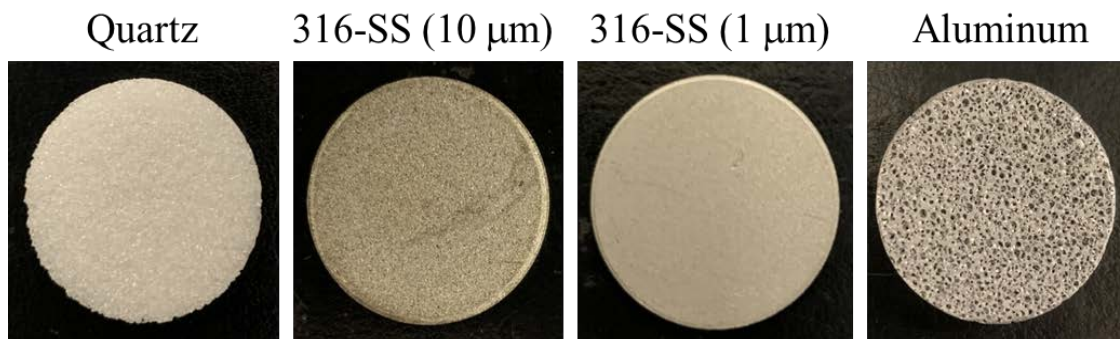


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\ \mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

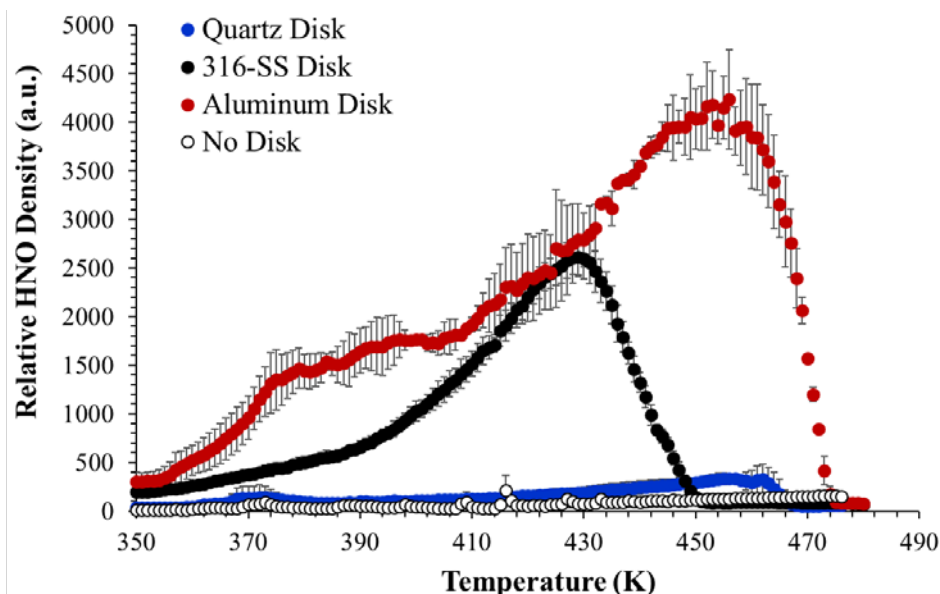


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2. Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

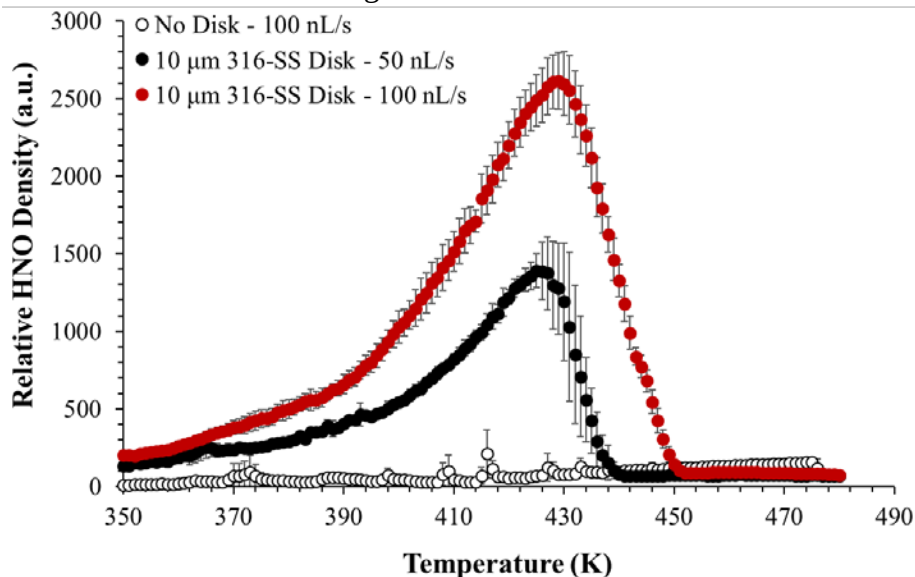


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

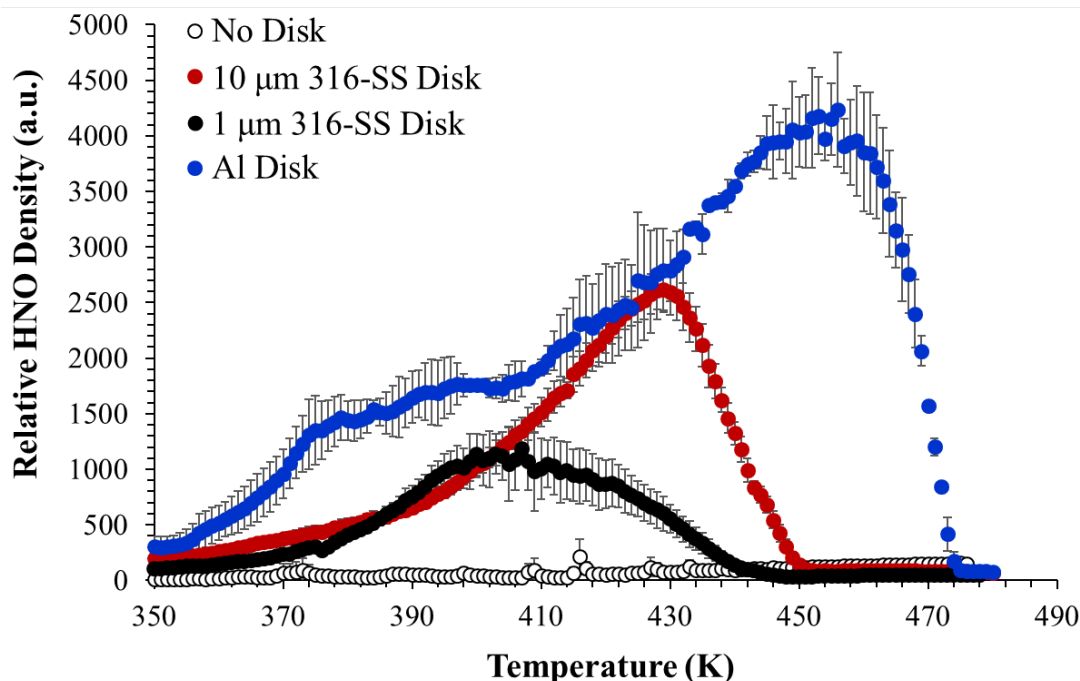


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

Acknowledgments

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

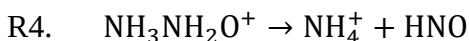
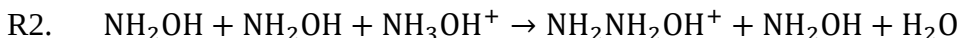
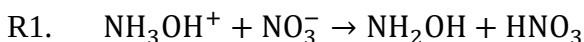
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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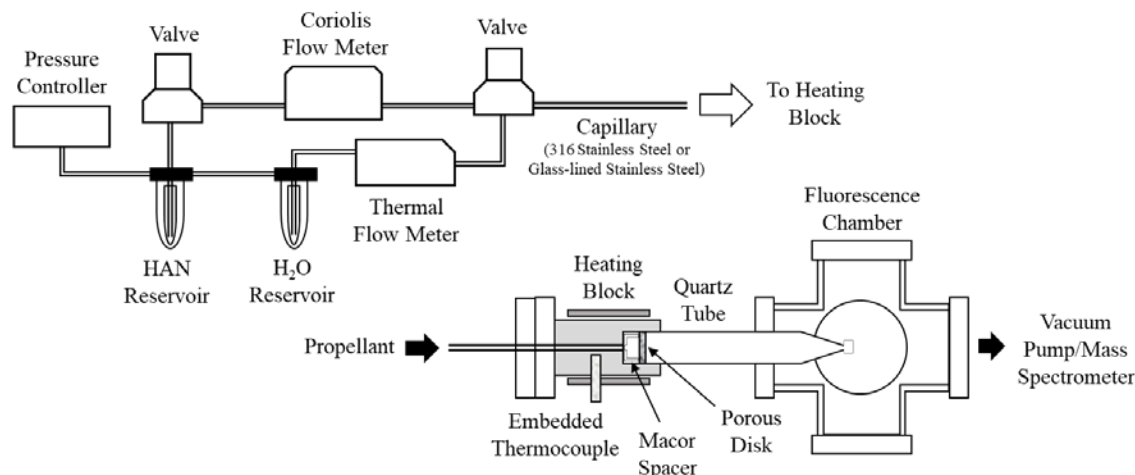


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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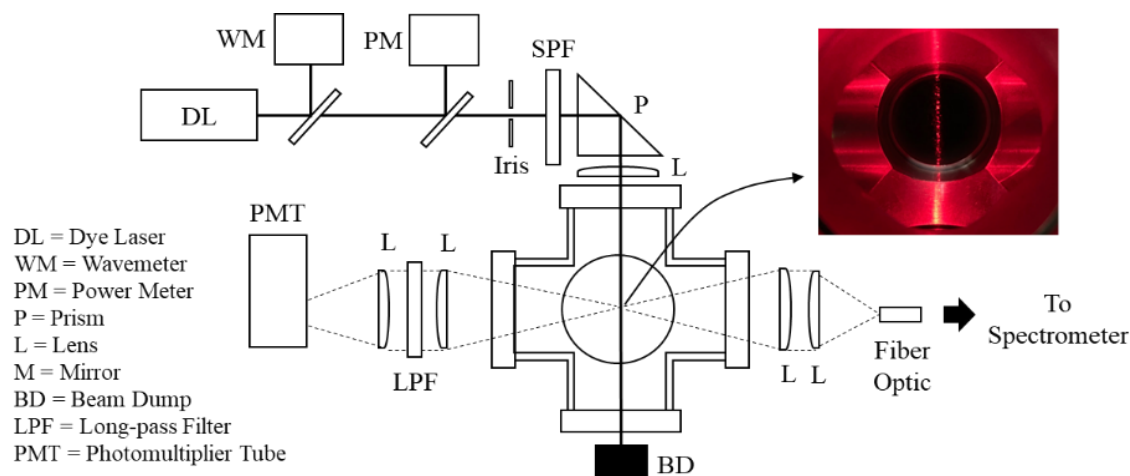


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680 \text{ nm}$) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6 \text{ Hz}$), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at $\sim 624 \text{ nm}$, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at $\sim 626 \text{ nm}$, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at $\sim 642 \text{ nm}$. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

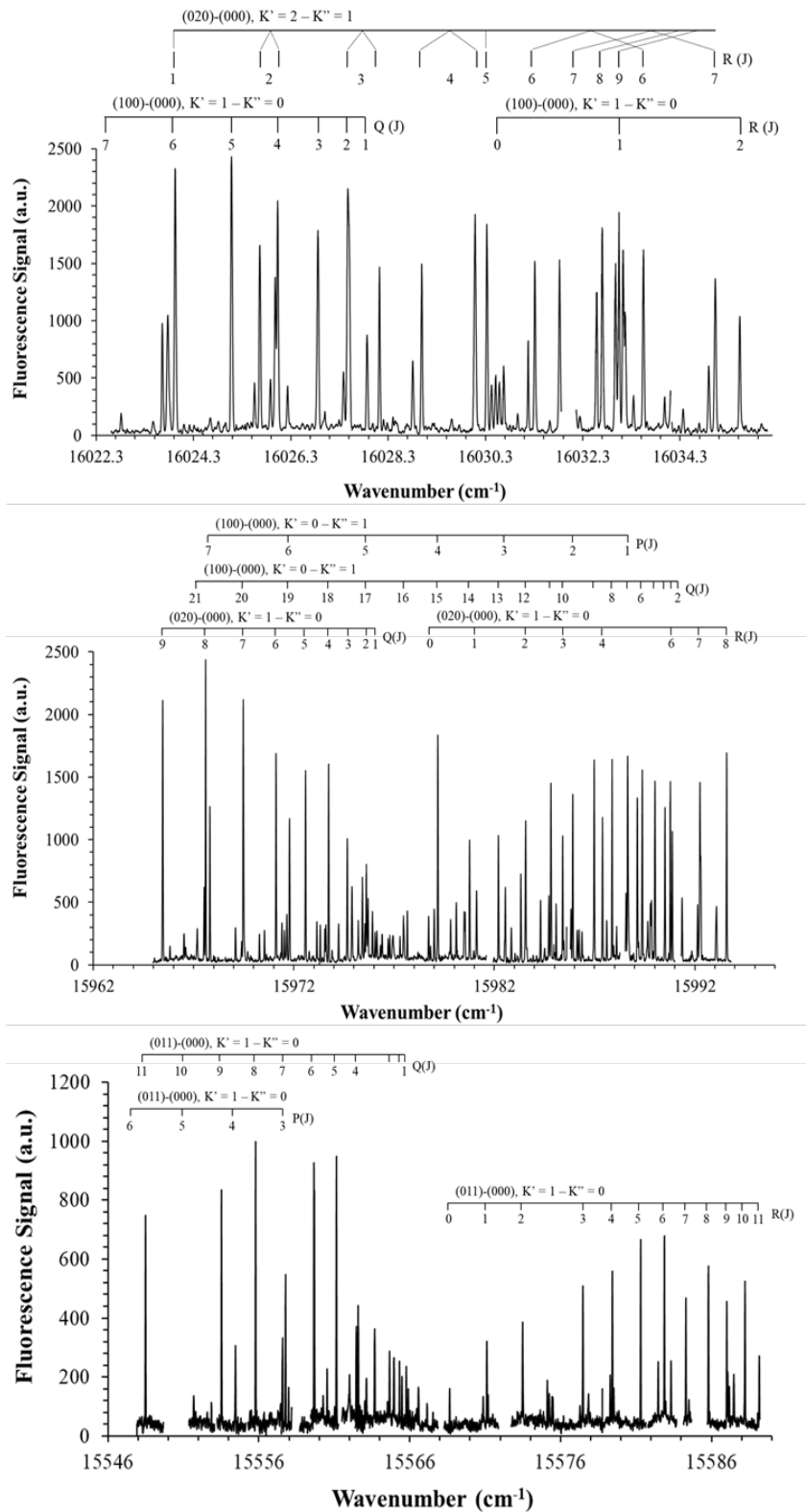


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

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In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) and $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

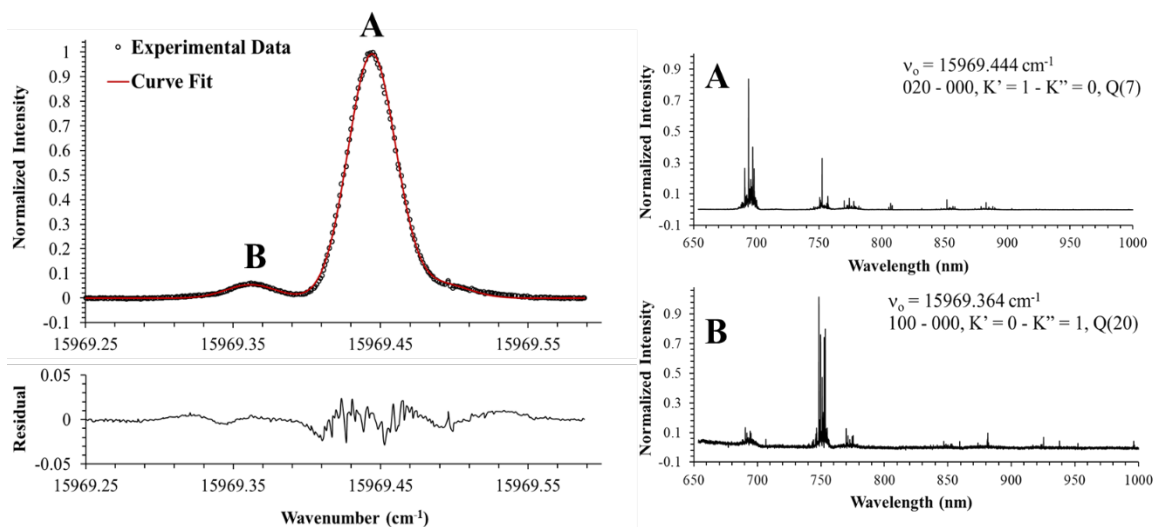


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020-000), $K' = 1 - K'' = 0$, Q(7) transition denoted as **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100-000), $K' = 0 - K'' = 1$, Q(20) transition denoted as **B**. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, **A** and **B**. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347$ K and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

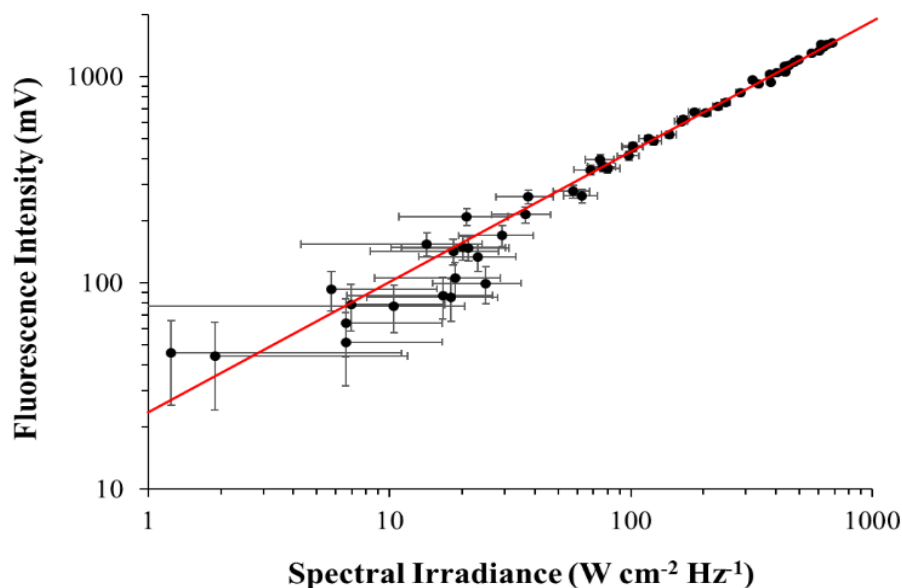


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

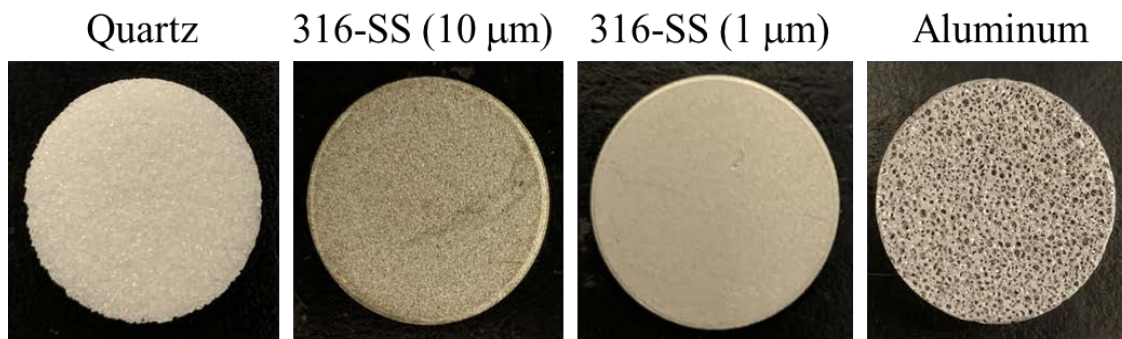


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

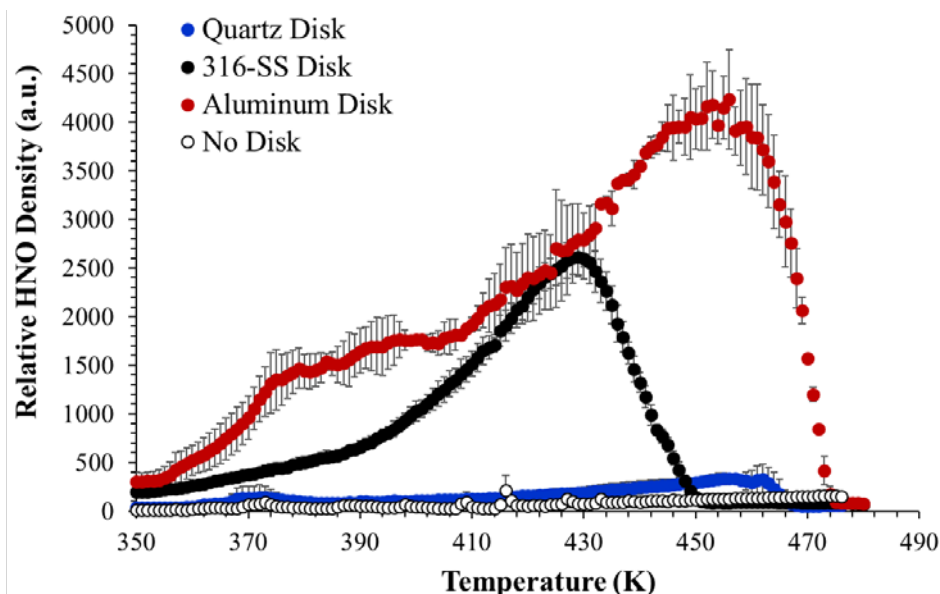


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2.Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

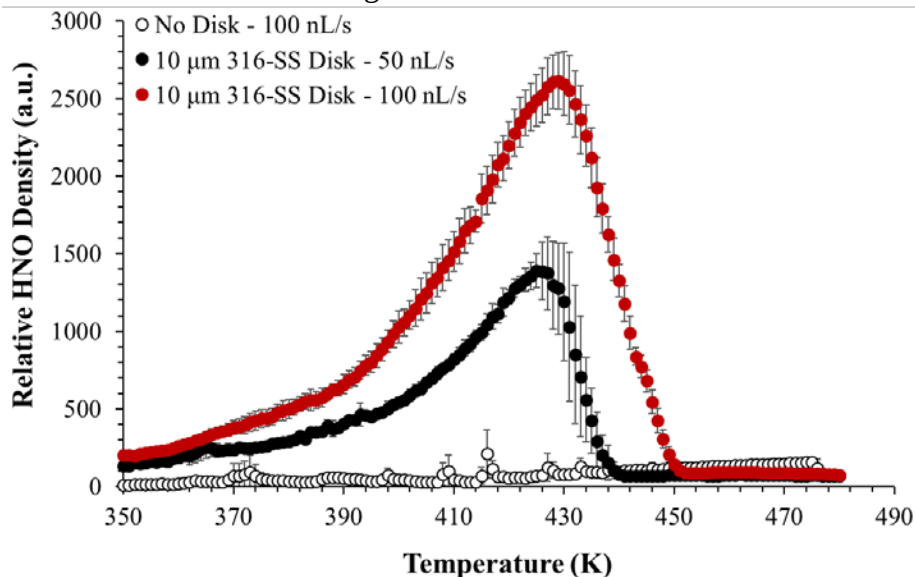


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

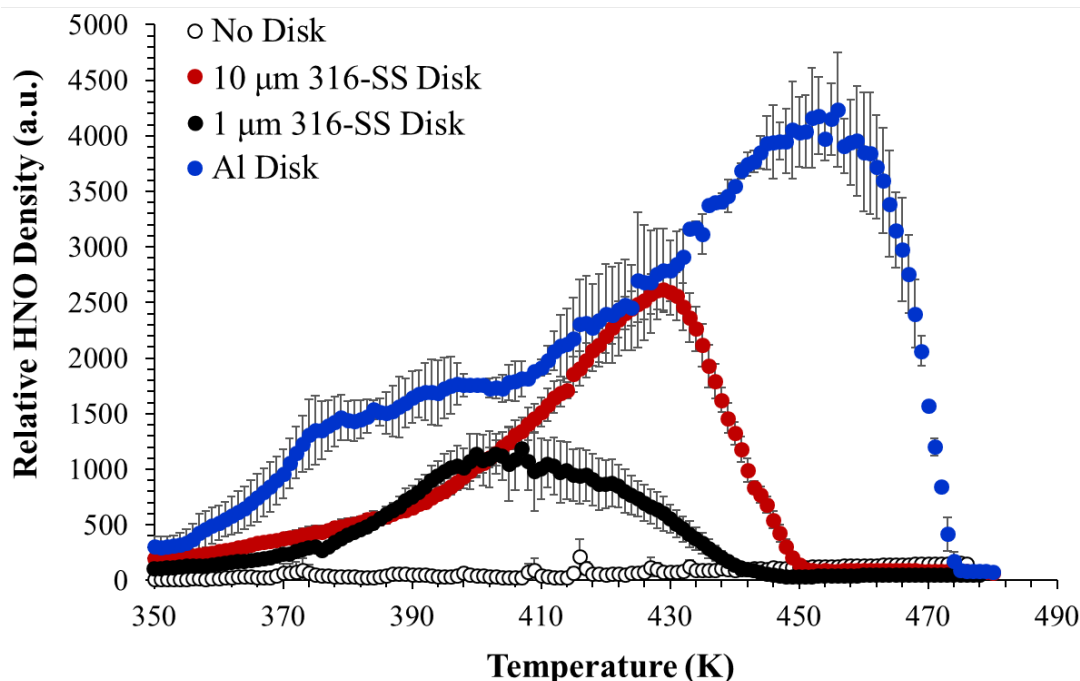


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

Acknowledgments

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

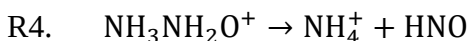
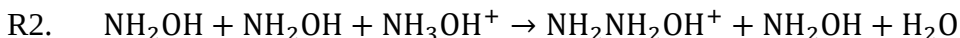
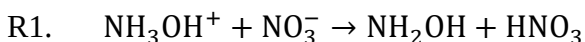
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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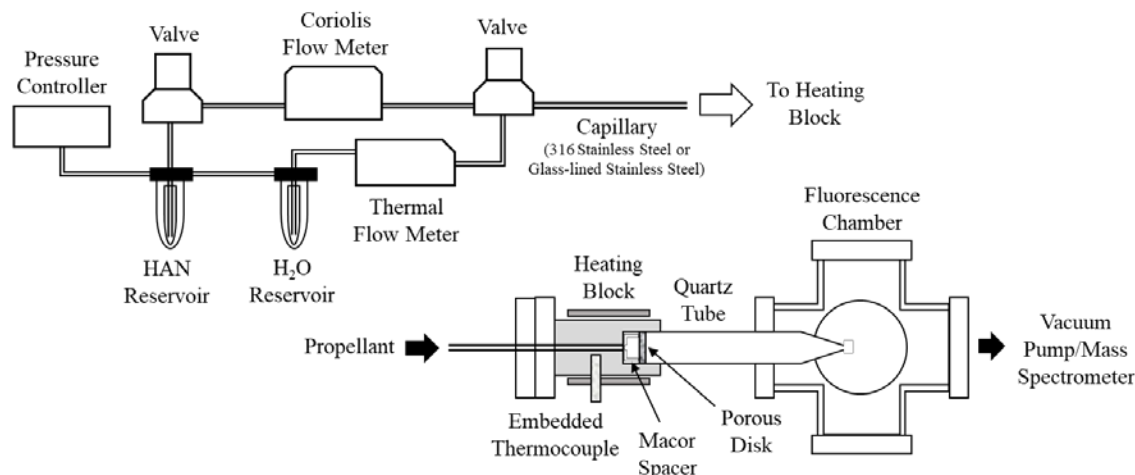


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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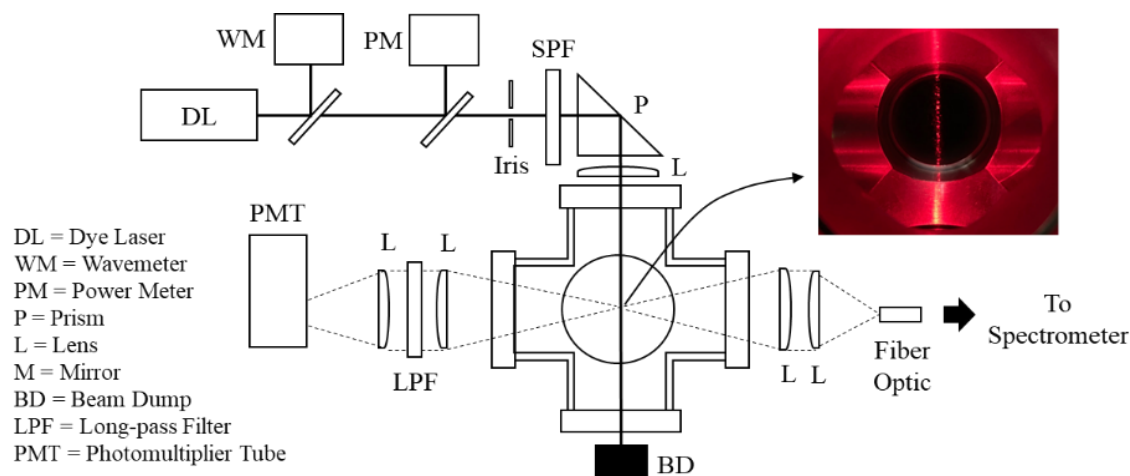


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680$ nm) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6$ Hz), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at ~624 nm, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at ~626 nm, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~642 nm. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

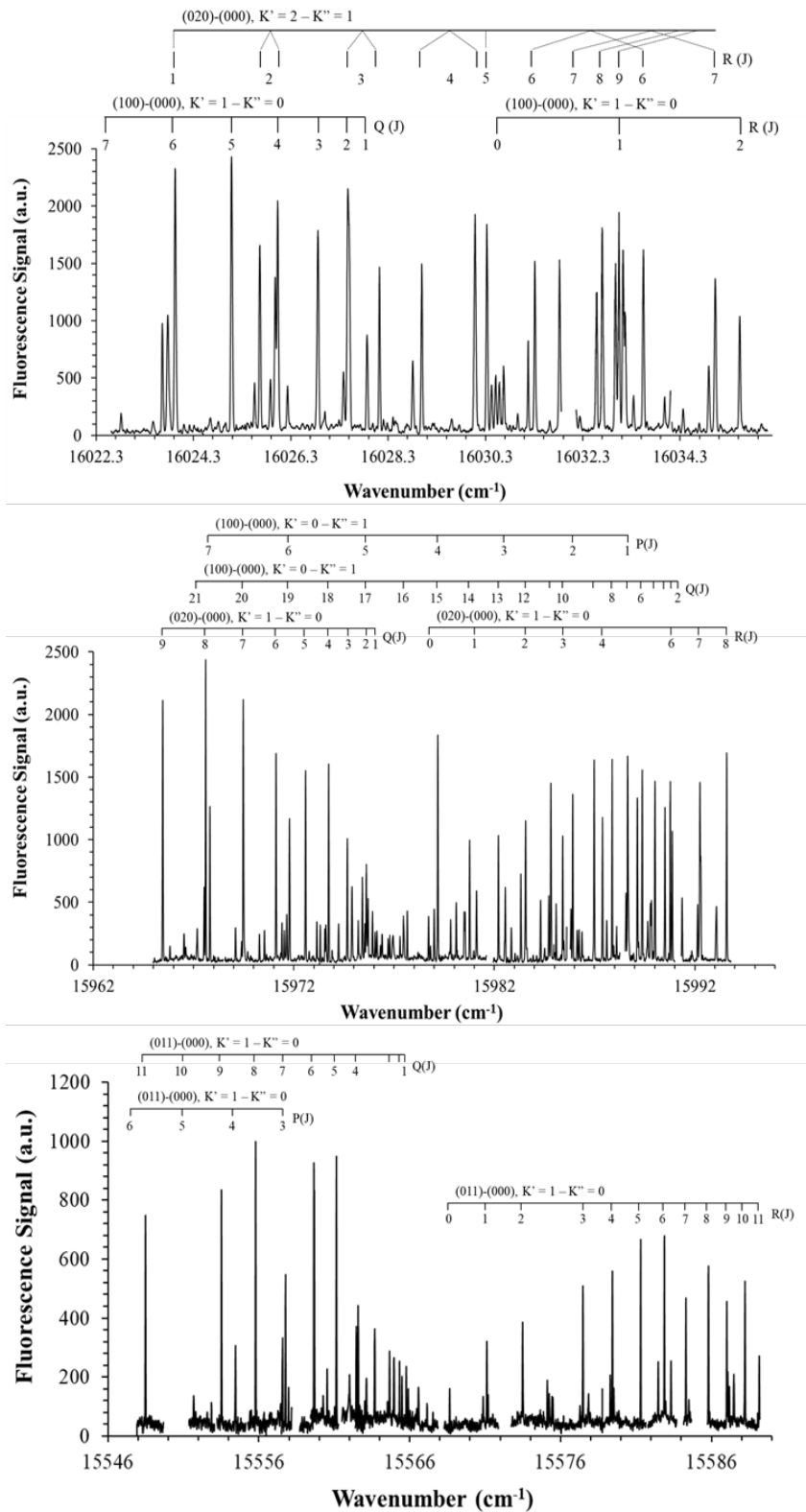


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

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In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' - X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' - X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' - X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' - X^1A'$ (020 – 000) and $\tilde{A}^1A'' - X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

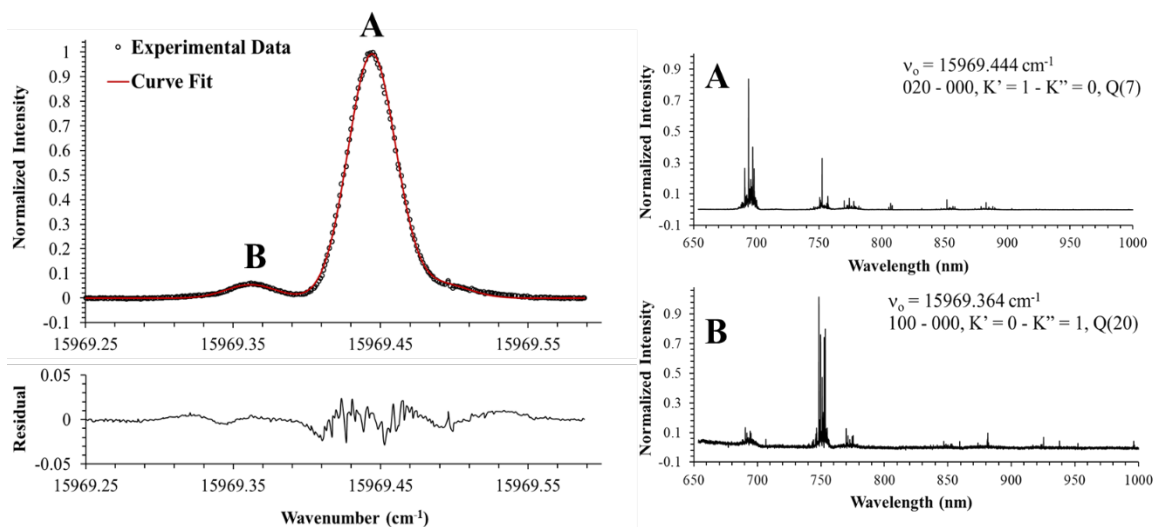


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition denoted as **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition denoted as **B**. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, **A** and **B**. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347 \text{ K}$ and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

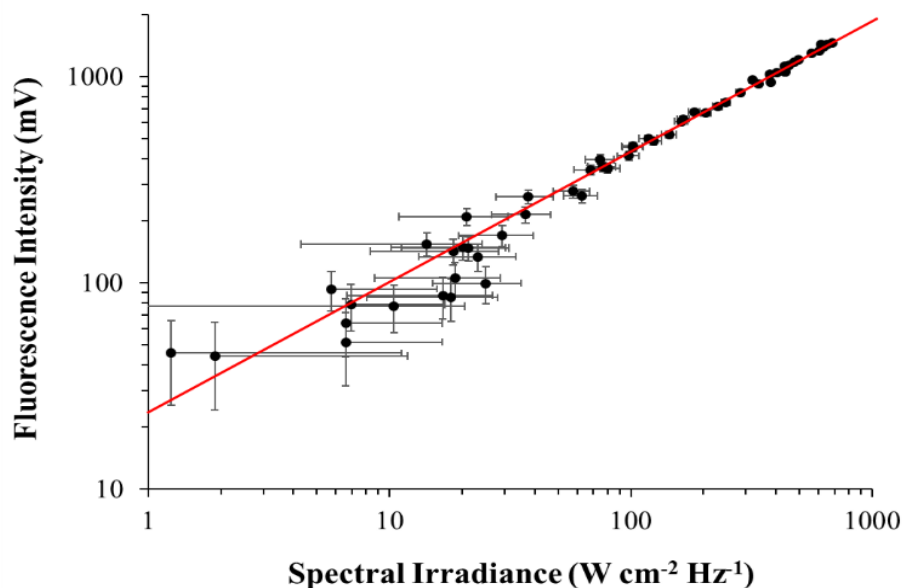


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

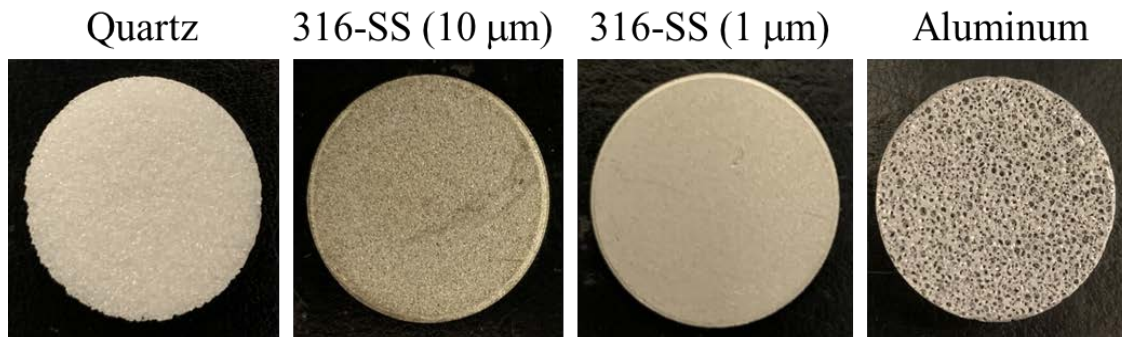


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

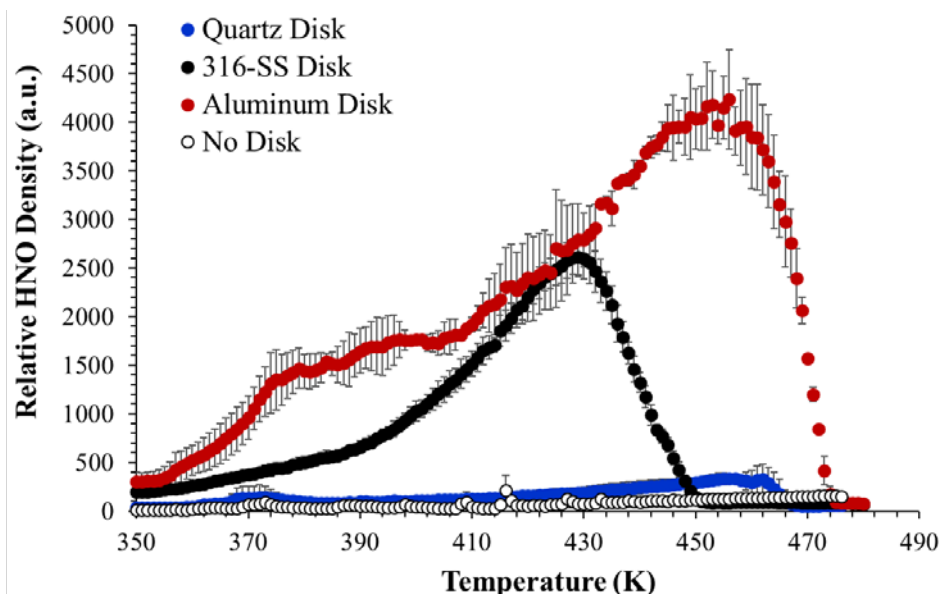


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2. Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

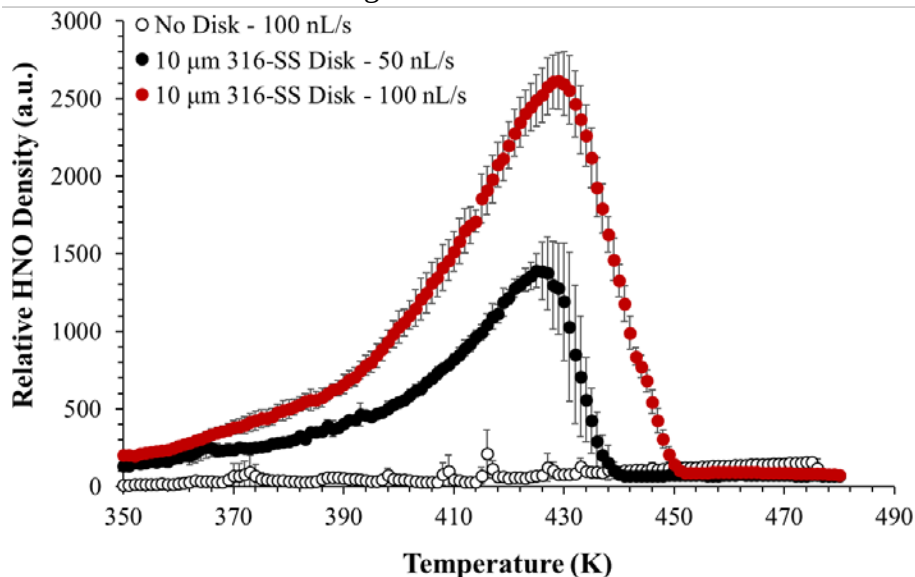


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

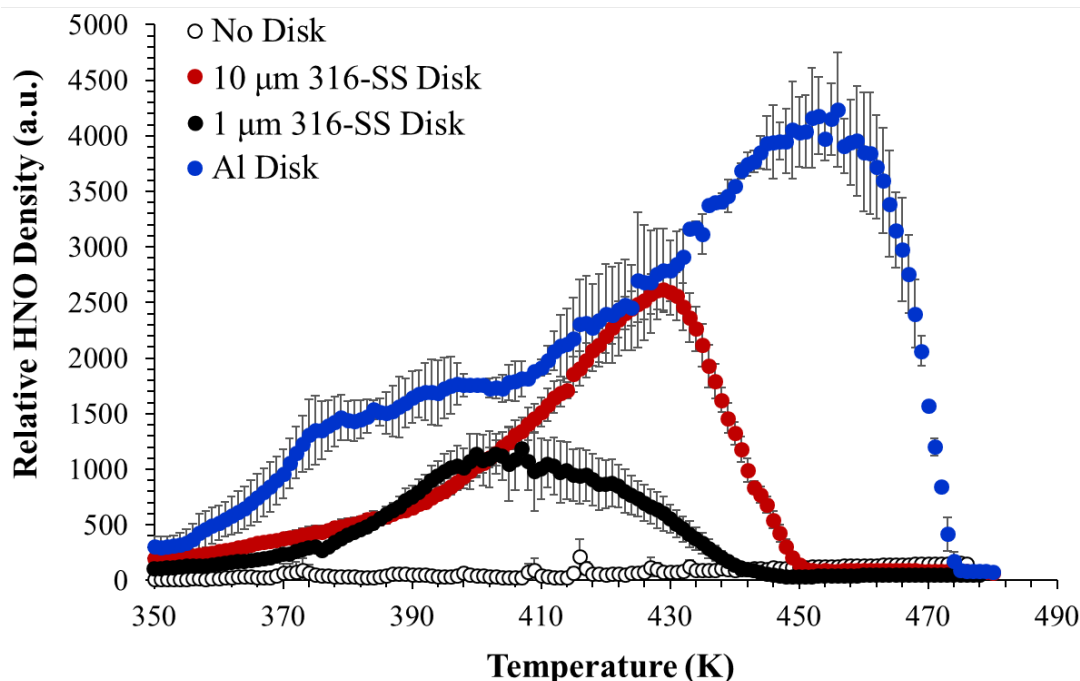


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

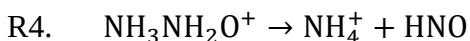
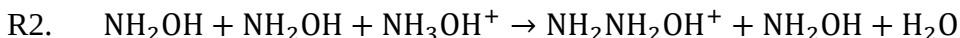
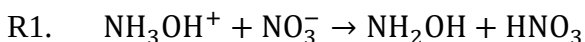
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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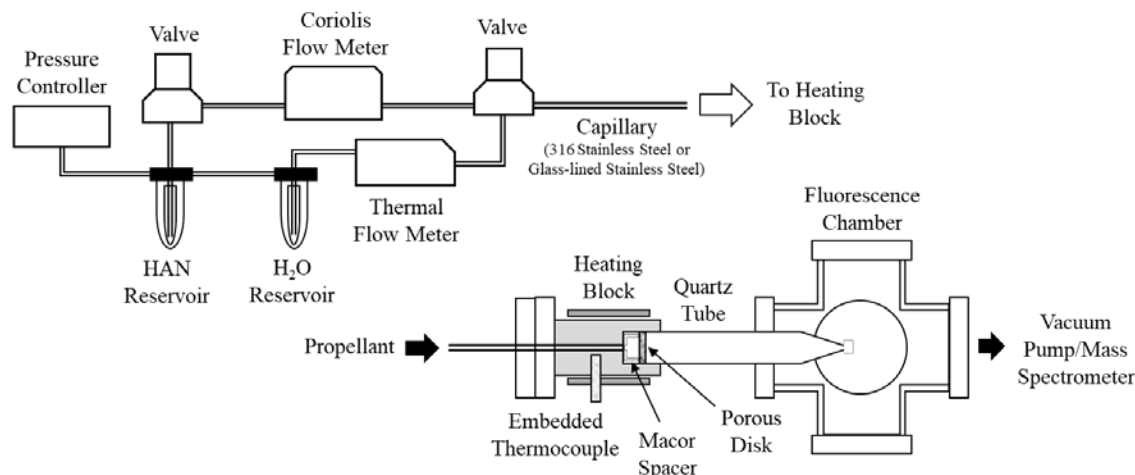


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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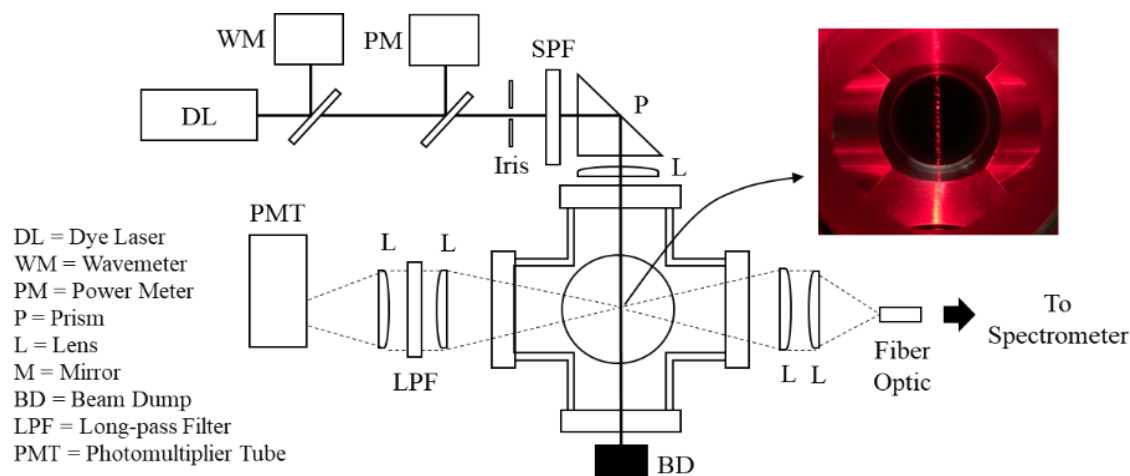


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680$ nm) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6$ Hz), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at ~624 nm, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at ~626 nm, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~642 nm. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

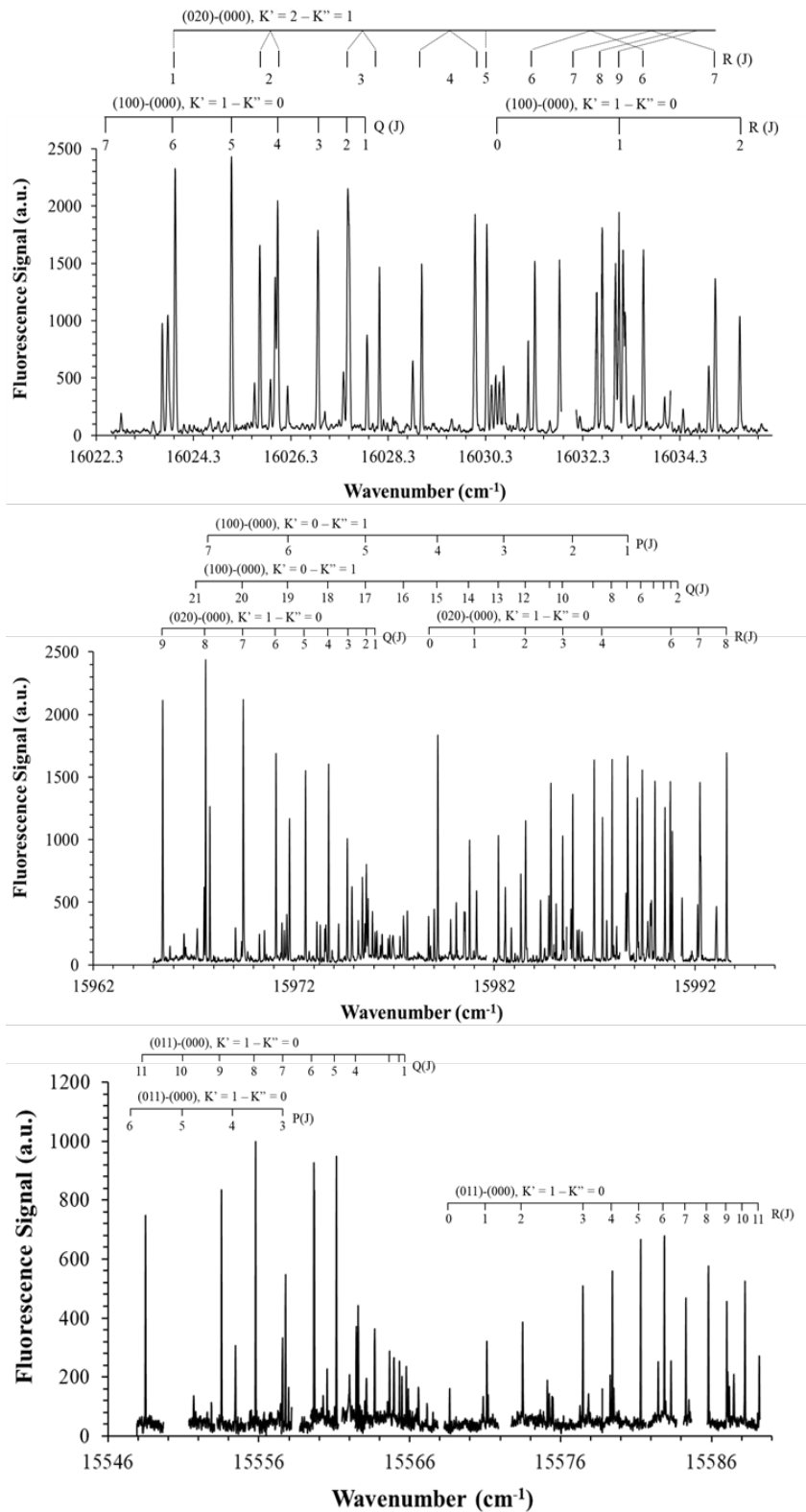


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

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In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' - X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' - X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' - X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' - X^1A'$ (020 – 000) and $\tilde{A}^1A'' - X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

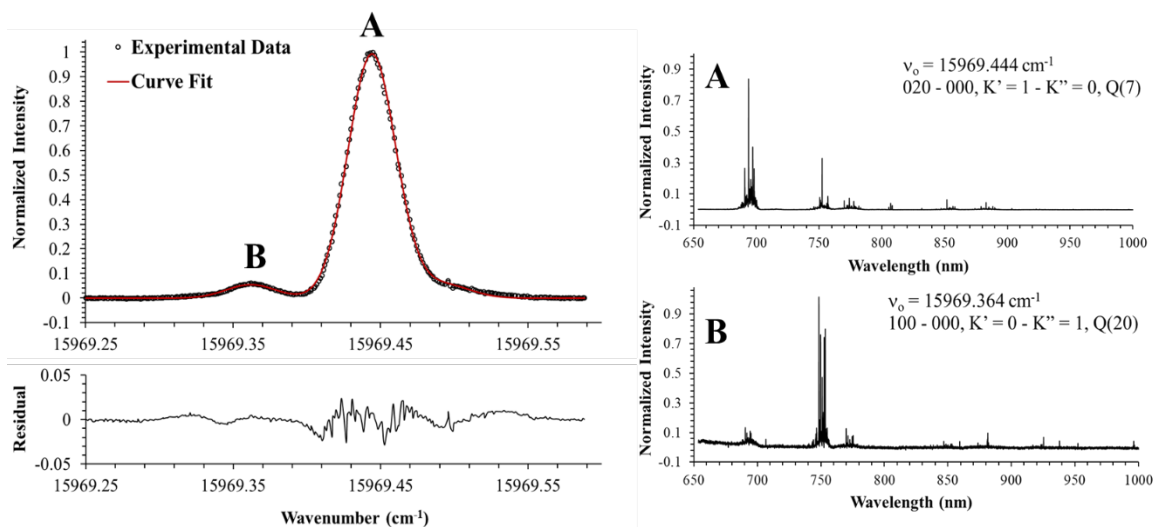


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition denoted as **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition denoted as **B**. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, **A** and **B**. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347 \text{ K}$ and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

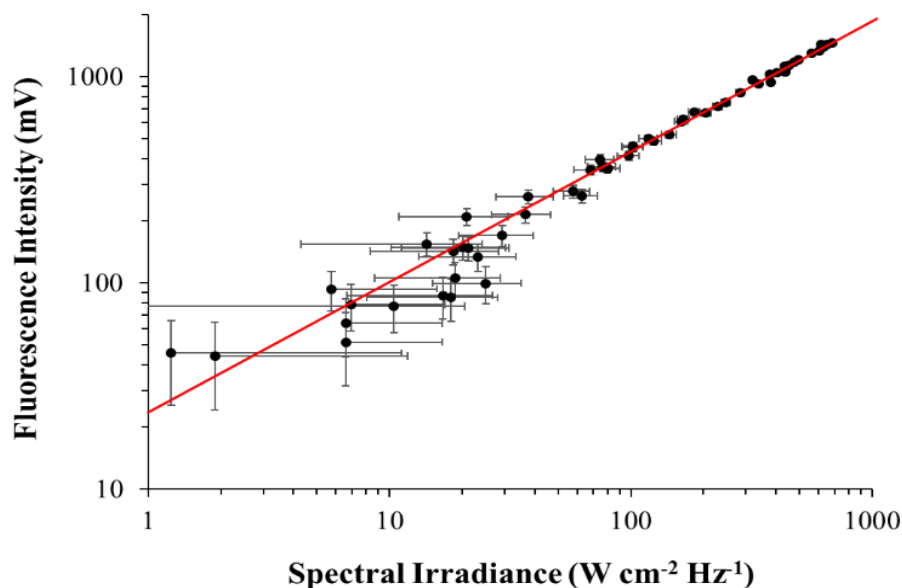


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

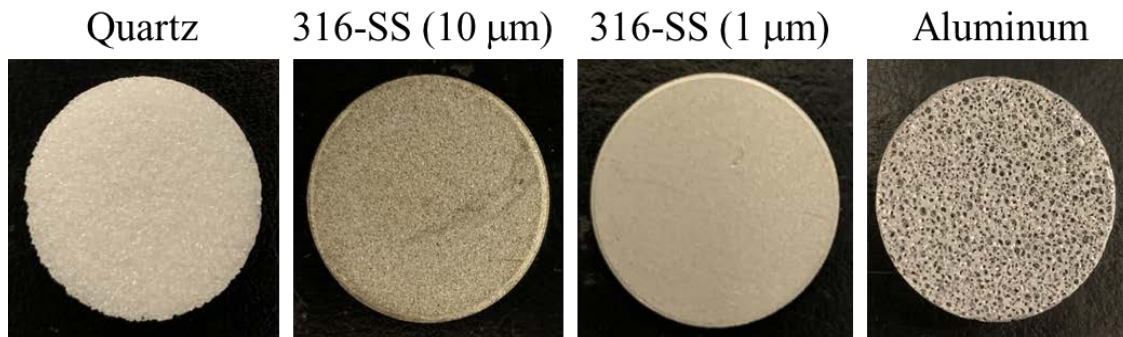


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

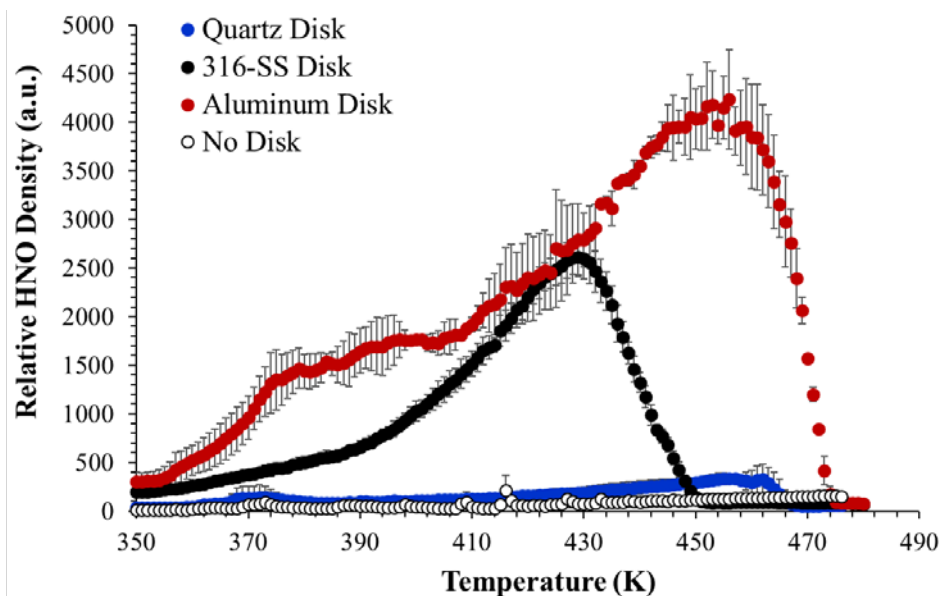


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2. Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

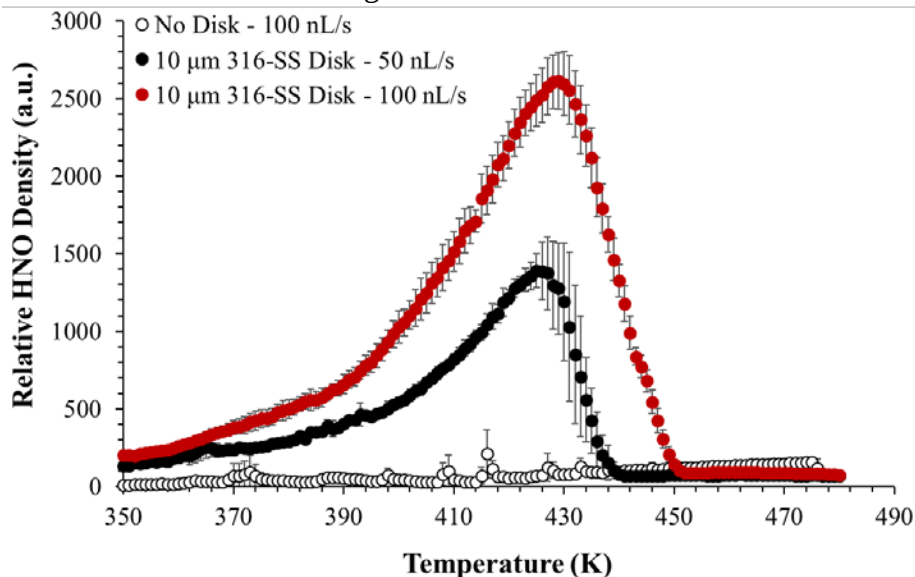


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

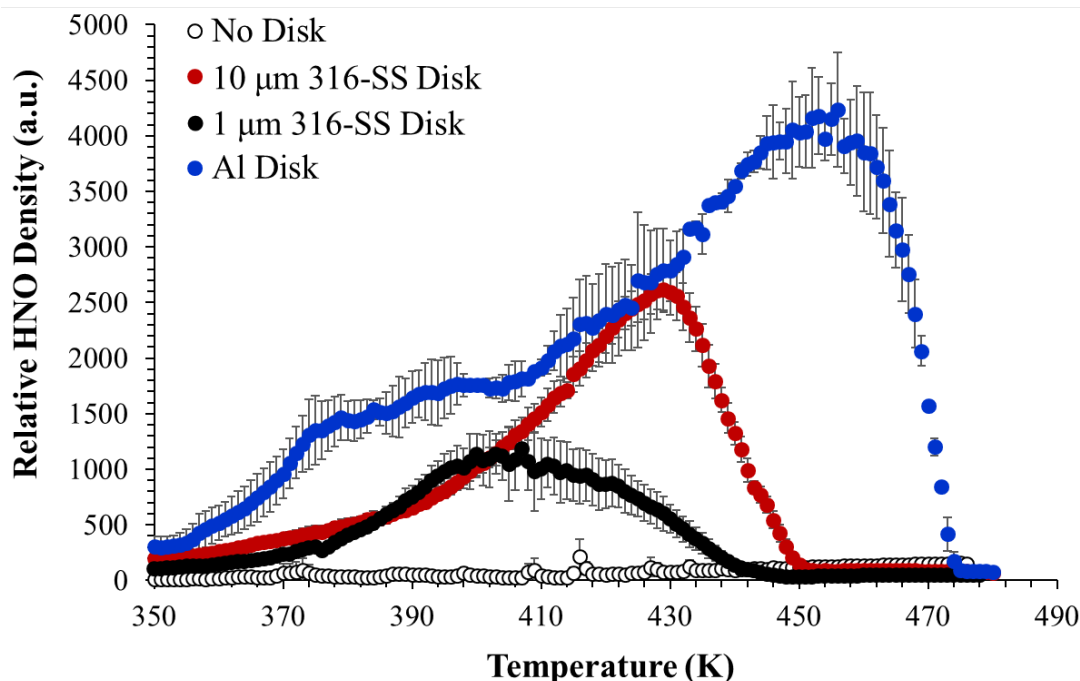


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

Acknowledgments

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

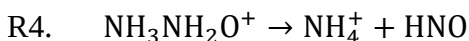
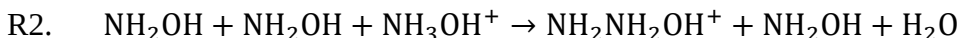
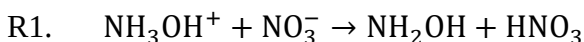
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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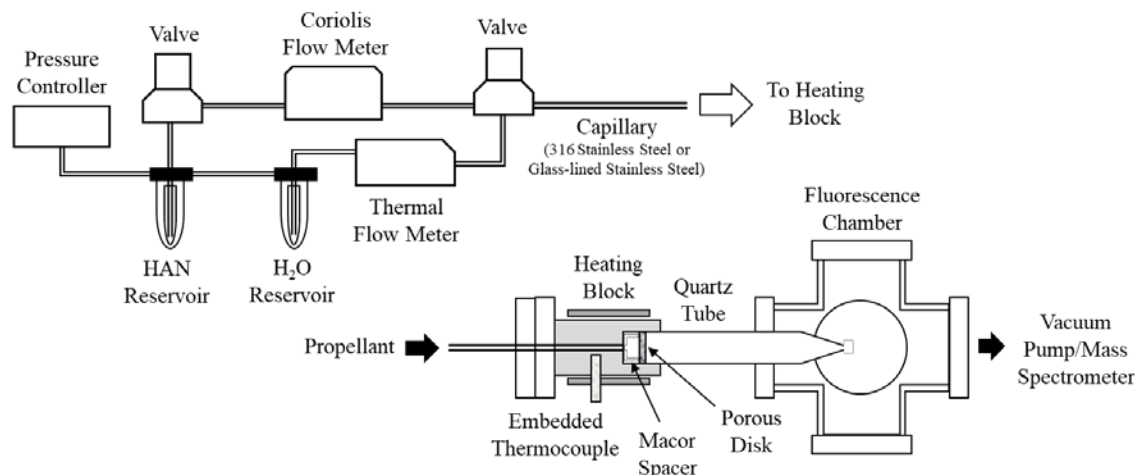


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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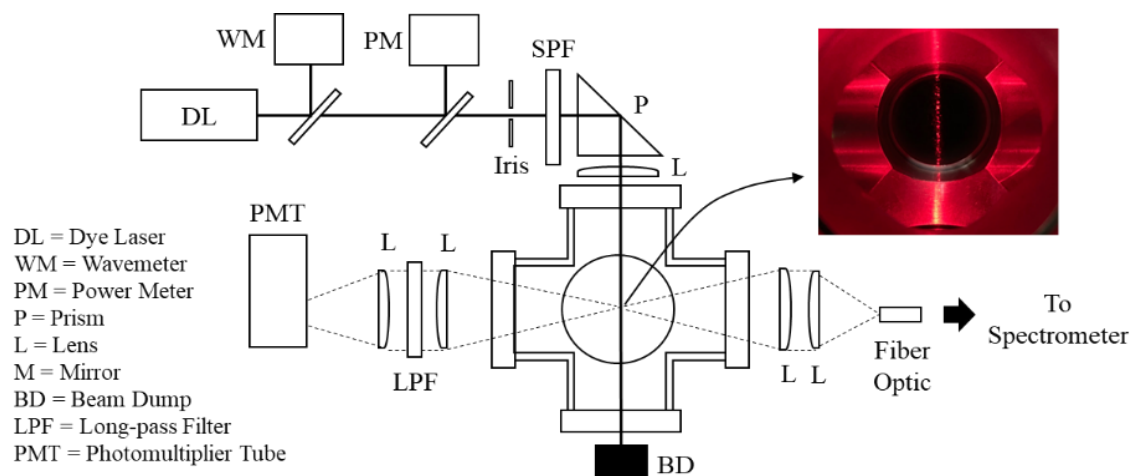


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680$ nm) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6$ Hz), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at ~624 nm, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at ~626 nm, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~642 nm. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

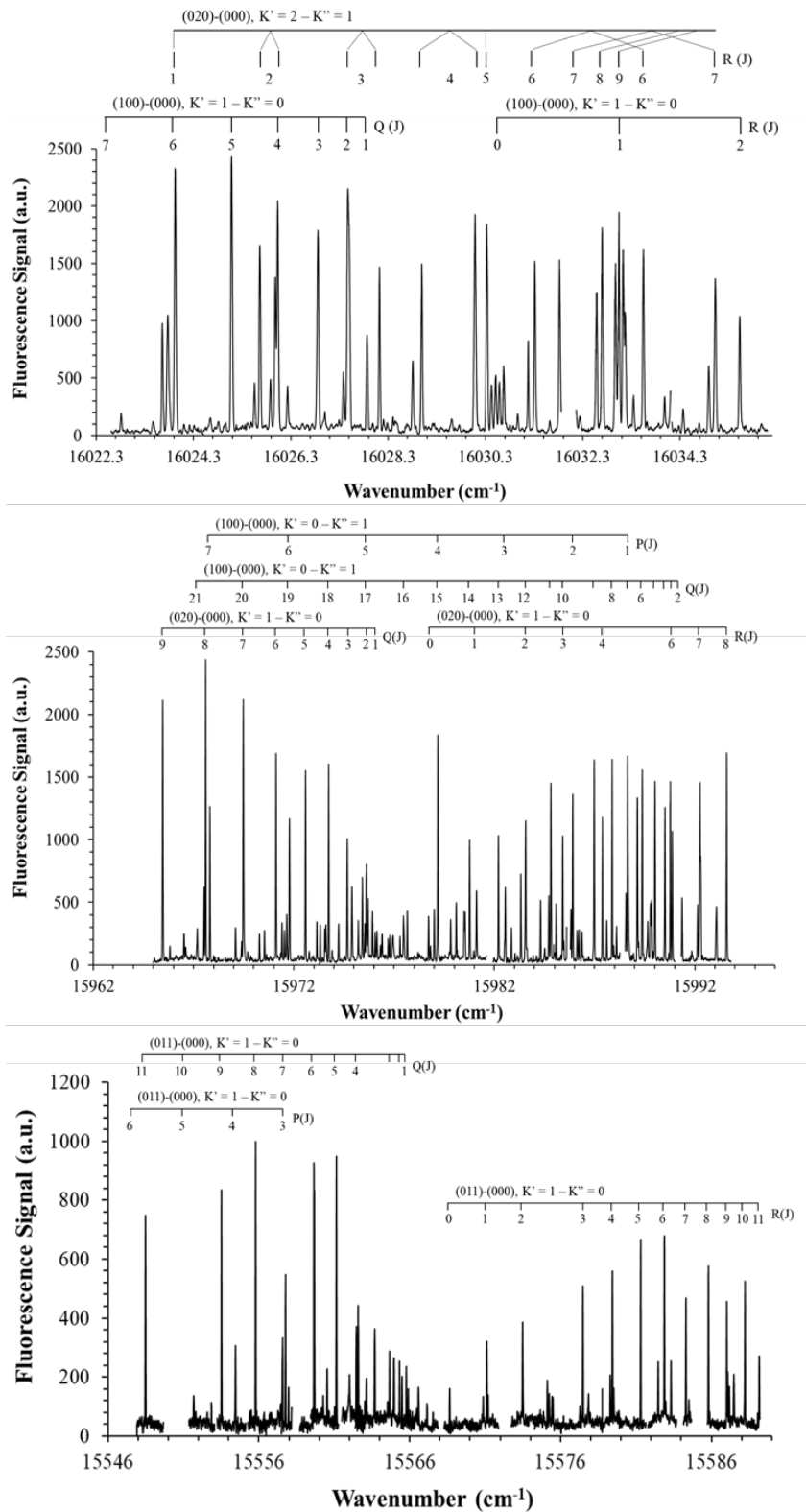


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

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In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) and $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

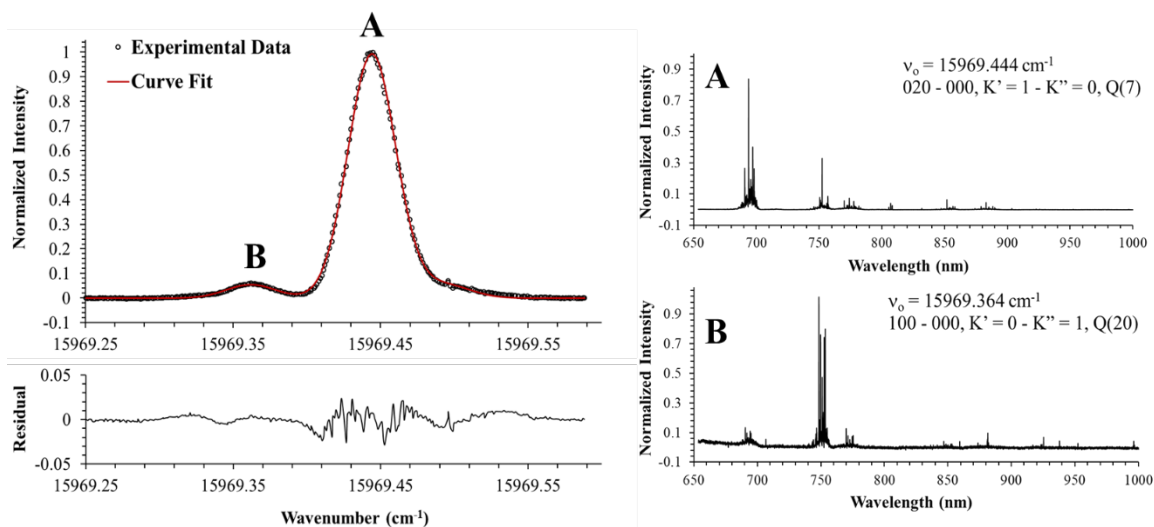


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020-000), $K' = 1 - K'' = 0$, Q(7) transition denoted as A. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100-000), $K' = 0 - K'' = 1$, Q(20) transition denoted as B. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, A and B. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347 \text{ K}$ and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

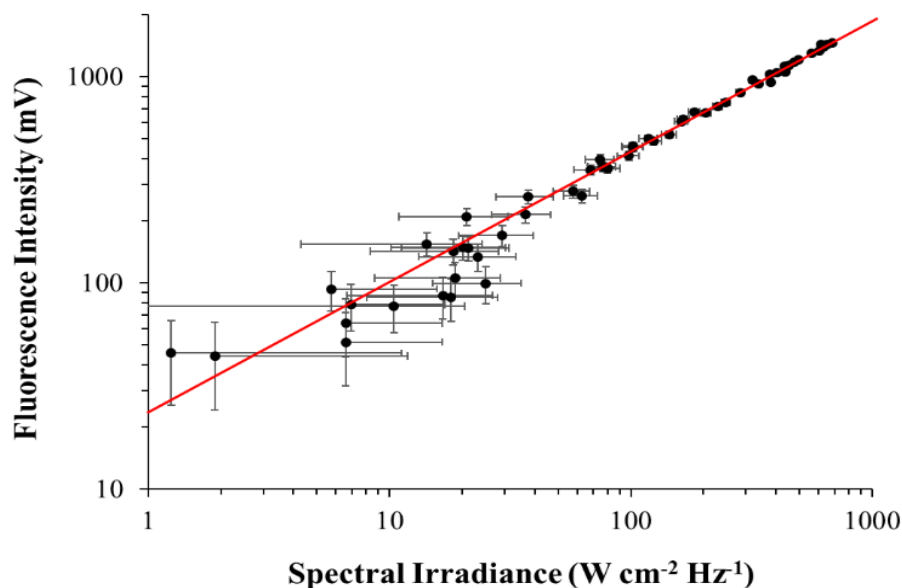


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

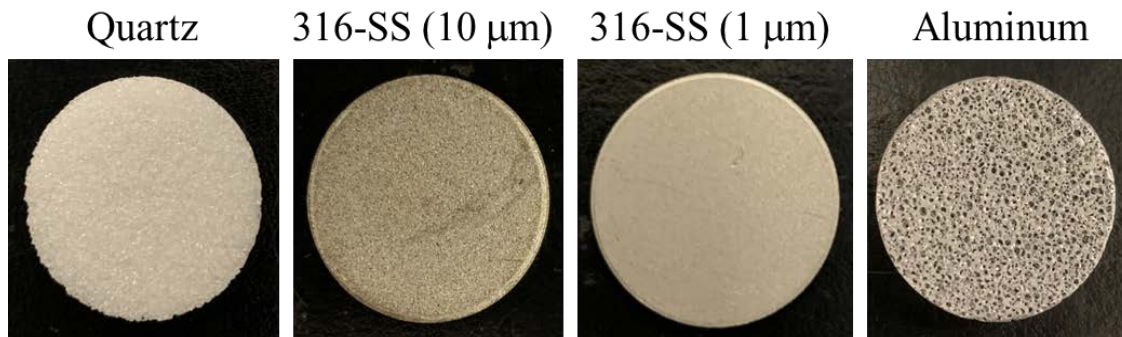


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

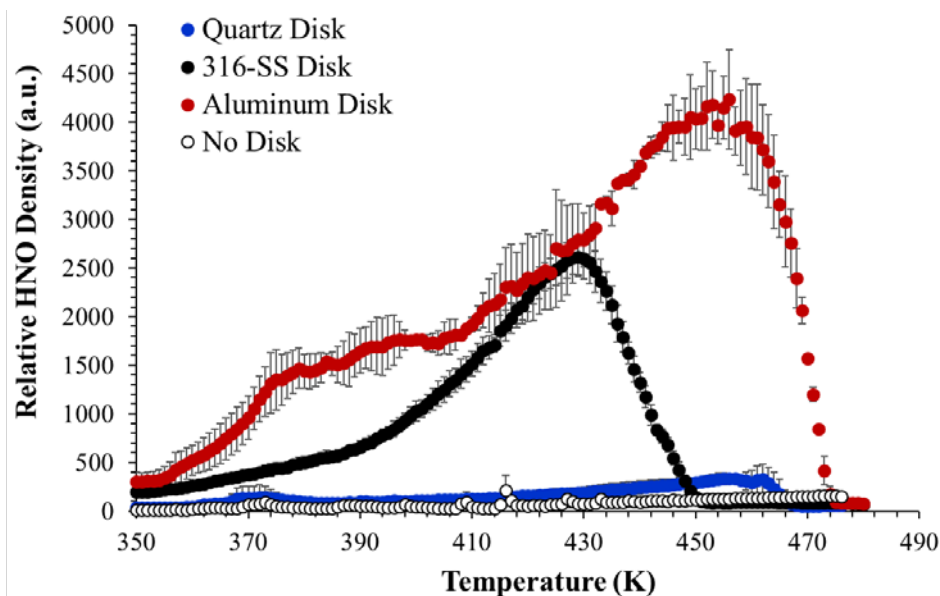


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2. Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

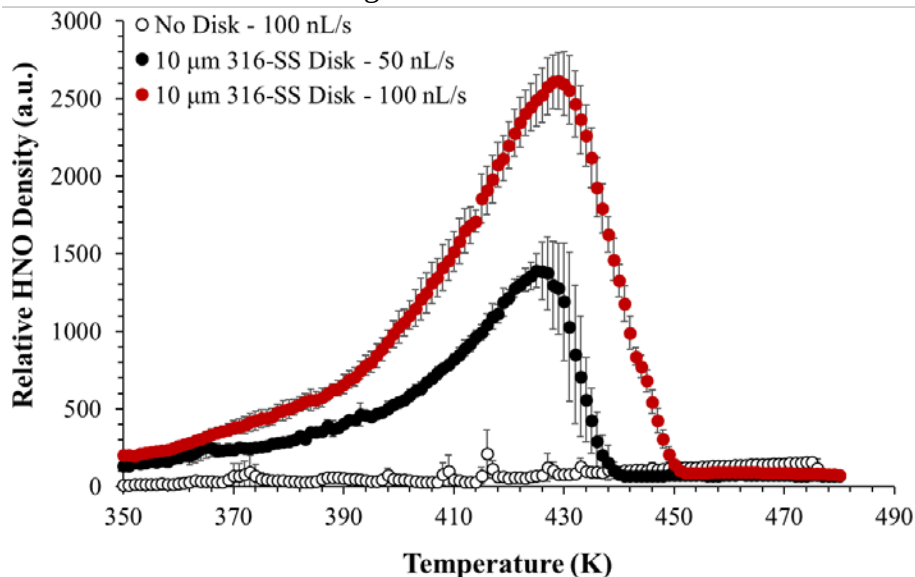


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

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production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

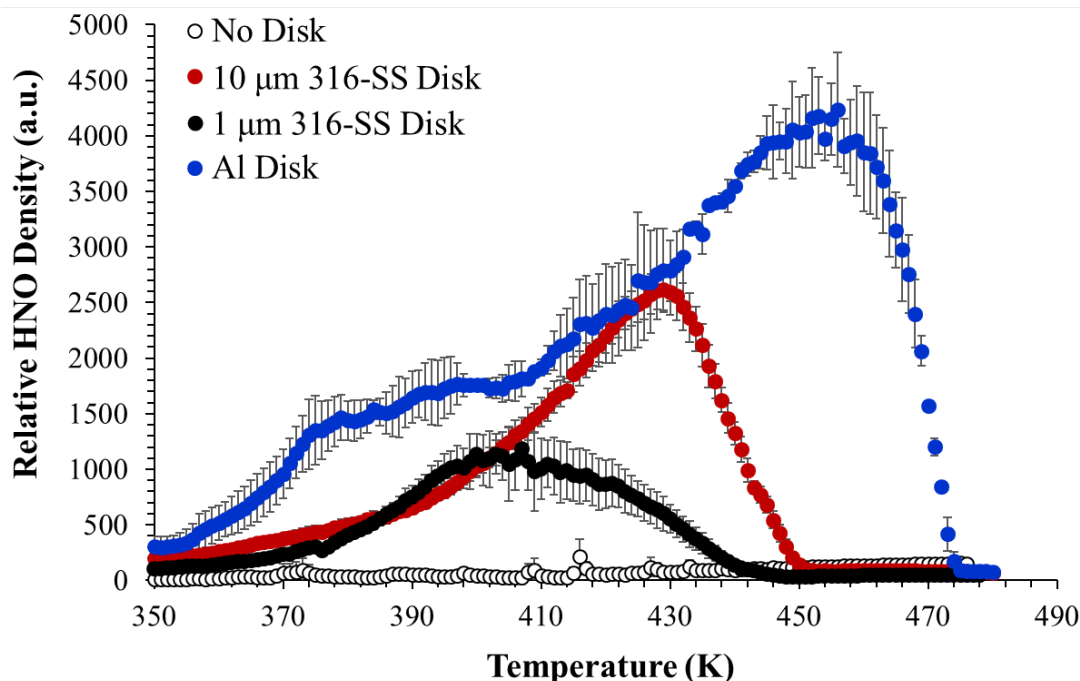


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

Acknowledgments

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

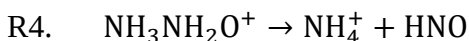
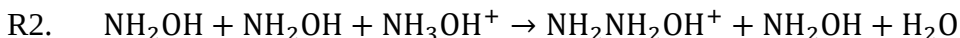
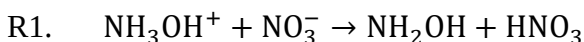
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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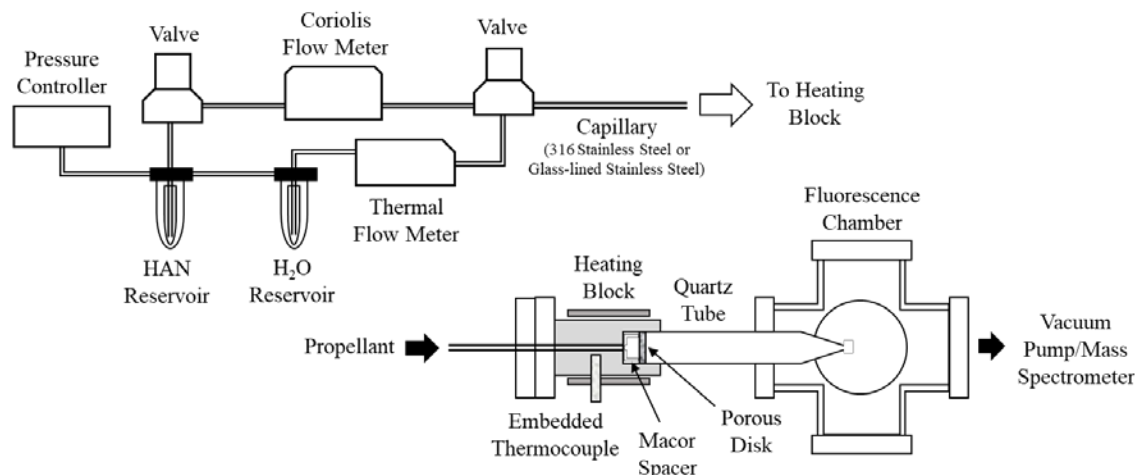


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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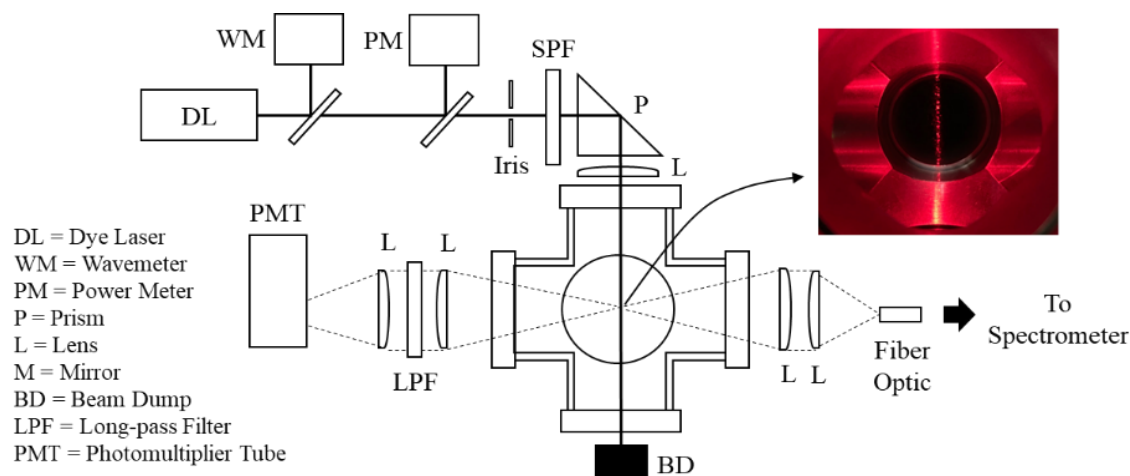


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680$ nm) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6$ Hz), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at ~624 nm, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at ~626 nm, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~642 nm. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

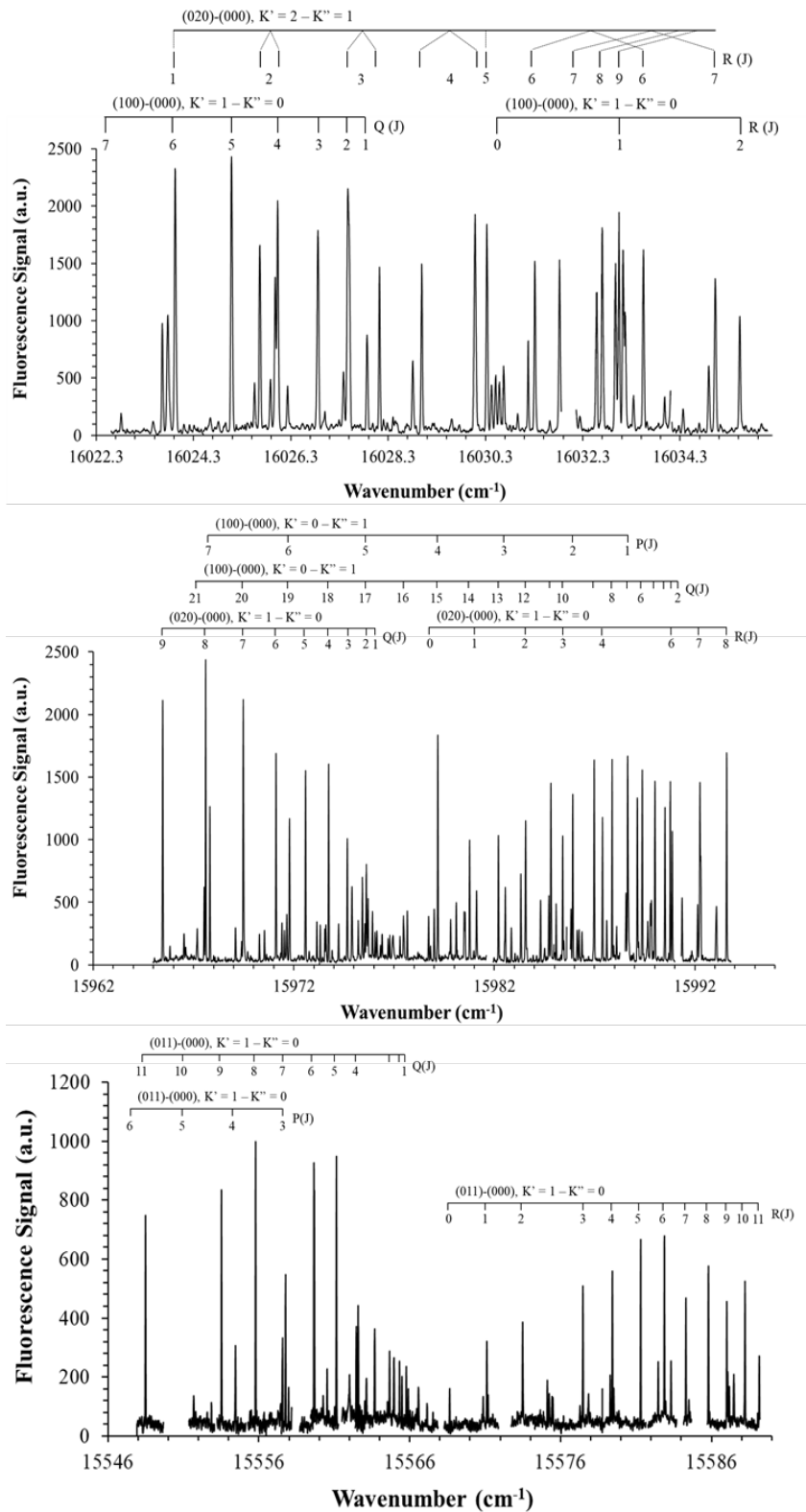


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

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In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' - X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' - X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' - X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' - X^1A'$ (020 – 000) and $\tilde{A}^1A'' - X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

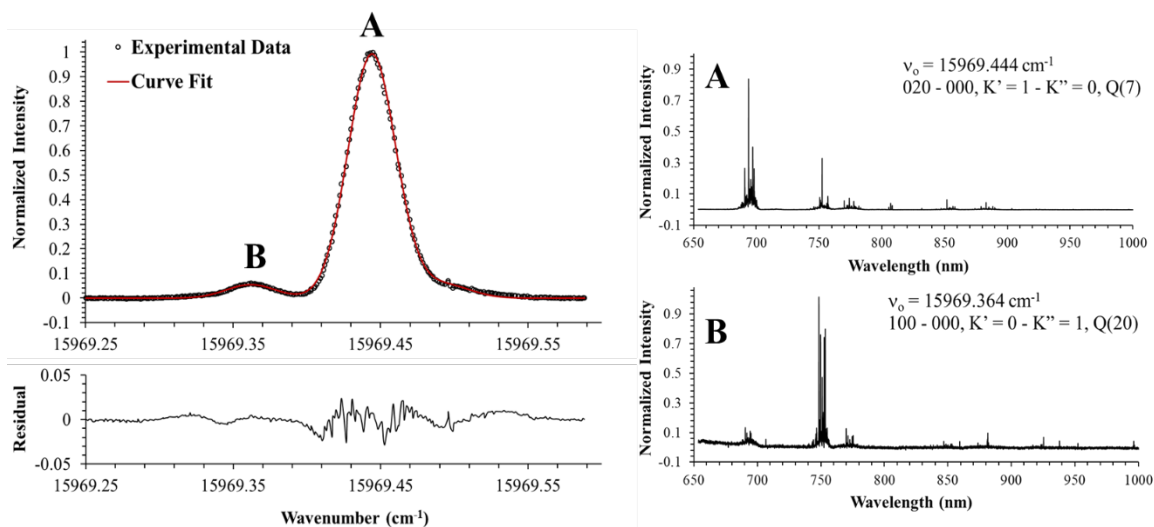


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020-000), $K' = 1 - K'' = 0$, Q(7) transition denoted as **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100-000), $K' = 0 - K'' = 1$, Q(20) transition denoted as **B**. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, **A** and **B**. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347 \text{ K}$ and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

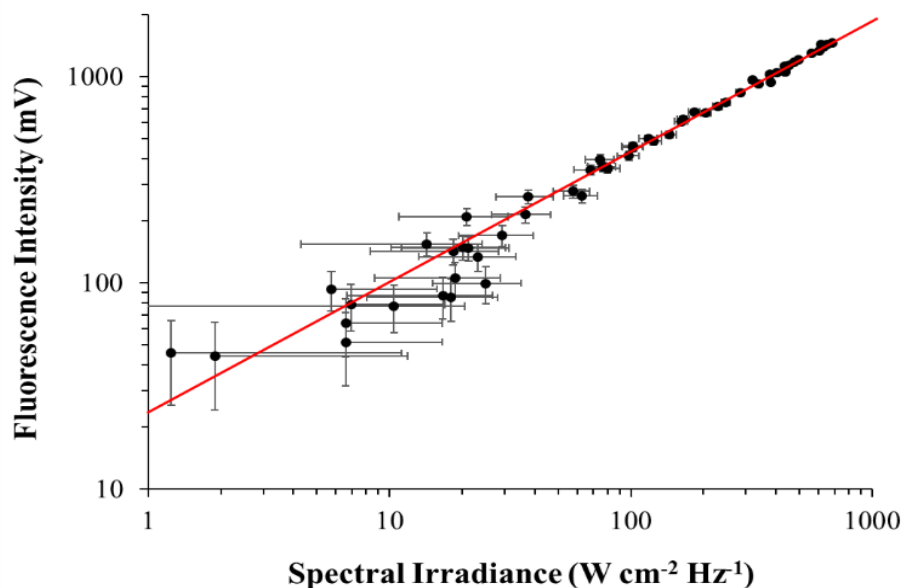


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

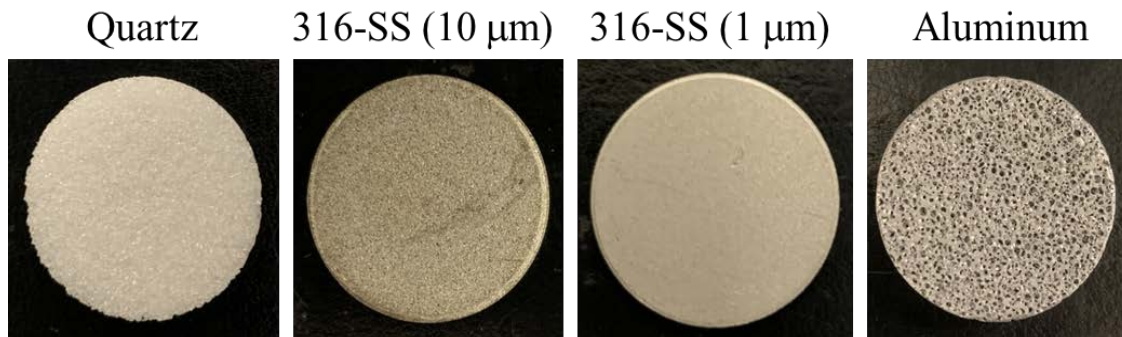


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

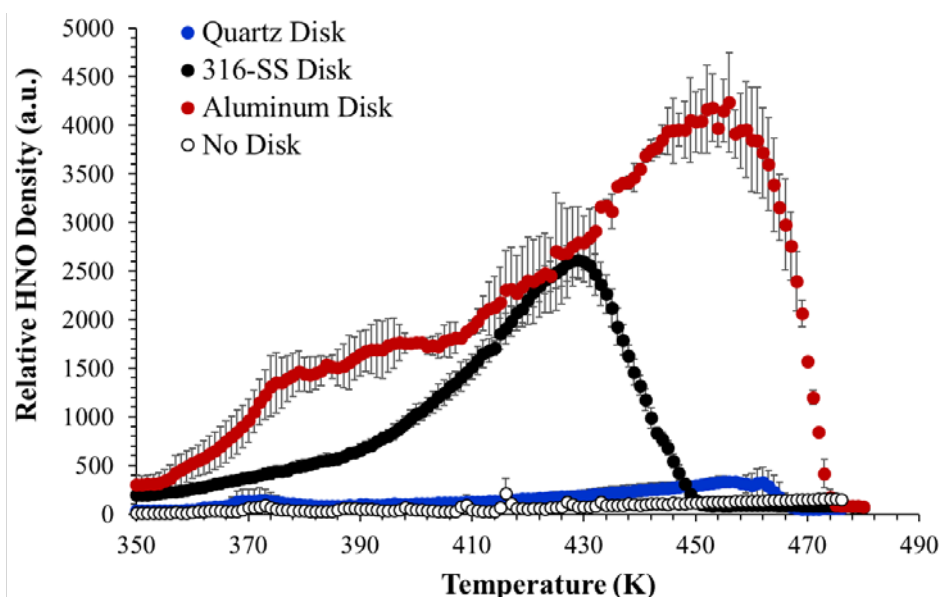


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2.Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

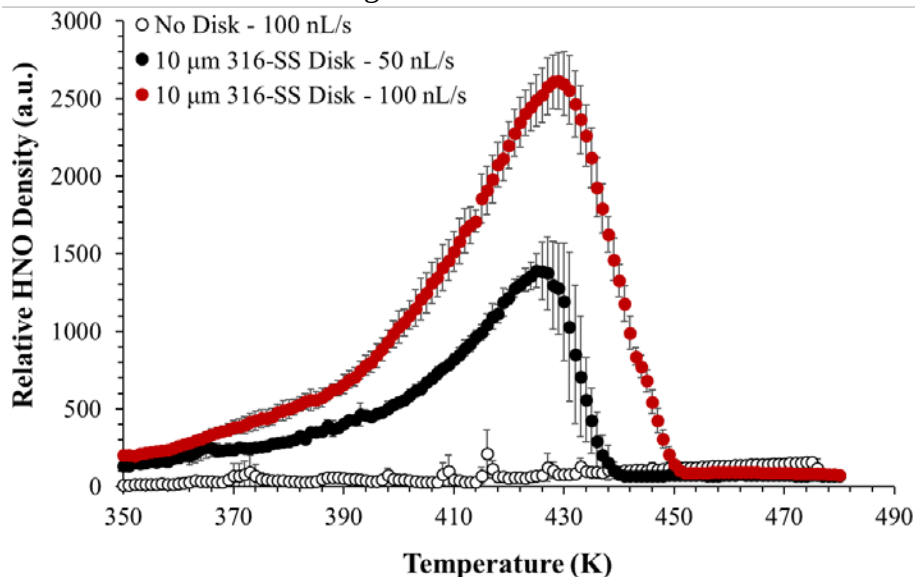


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

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production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

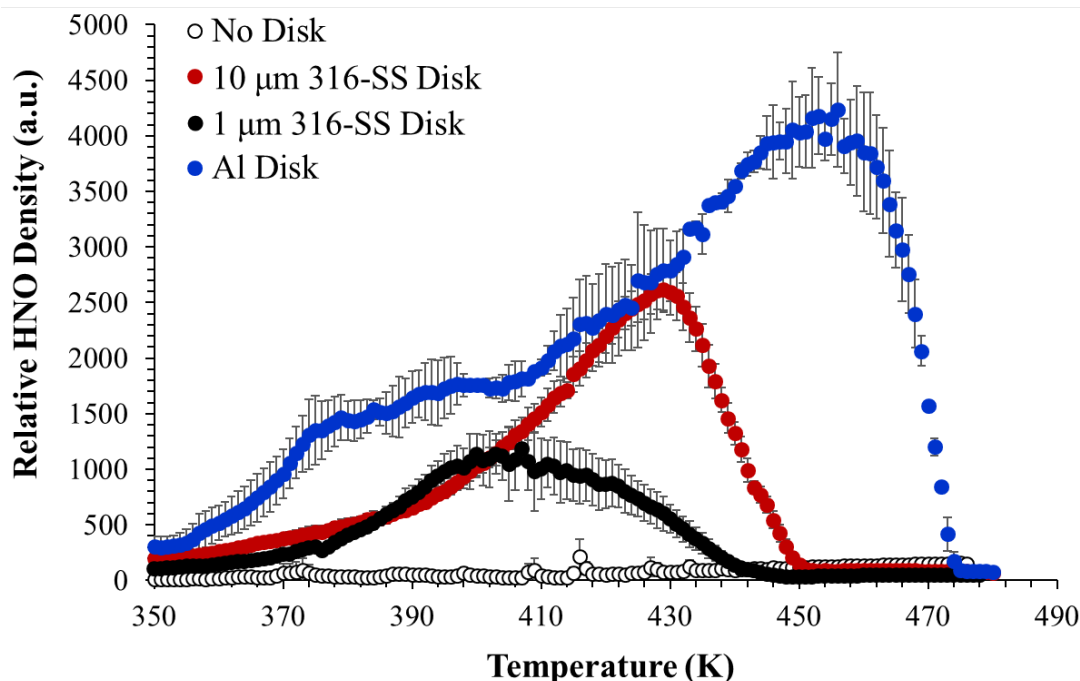


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

Acknowledgments

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

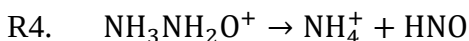
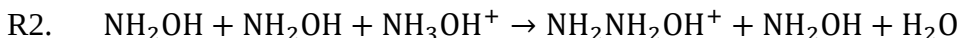
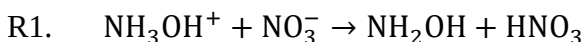
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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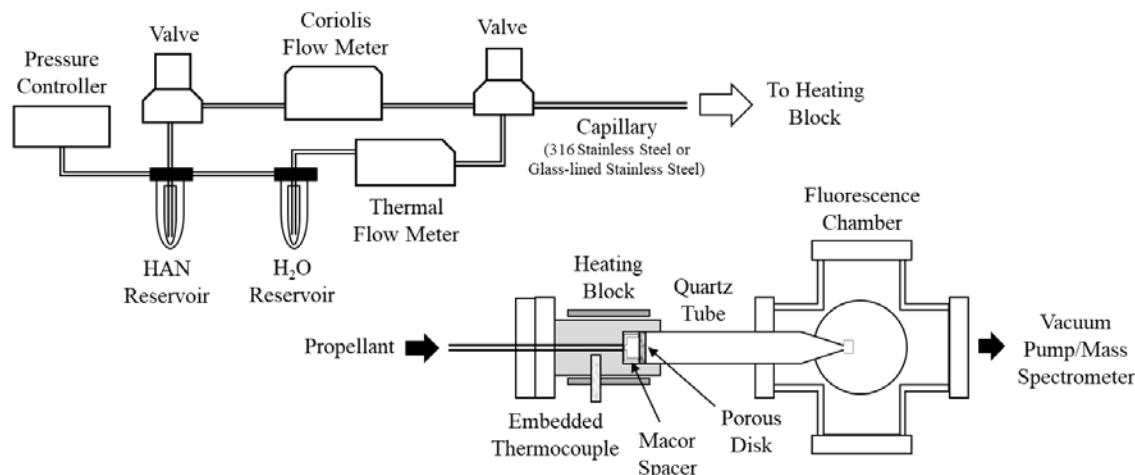


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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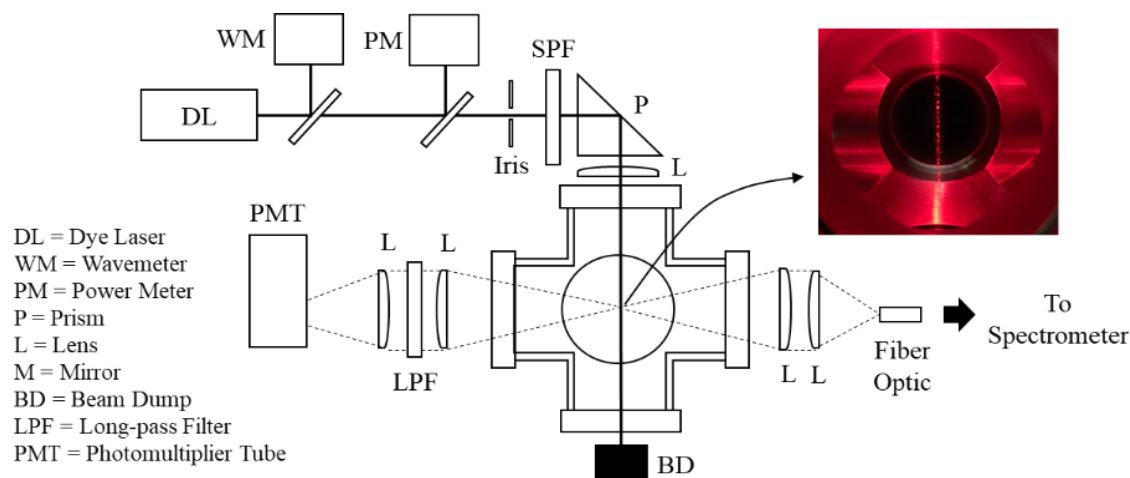


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680$ nm) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6$ Hz), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at ~624 nm, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at ~626 nm, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~642 nm. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

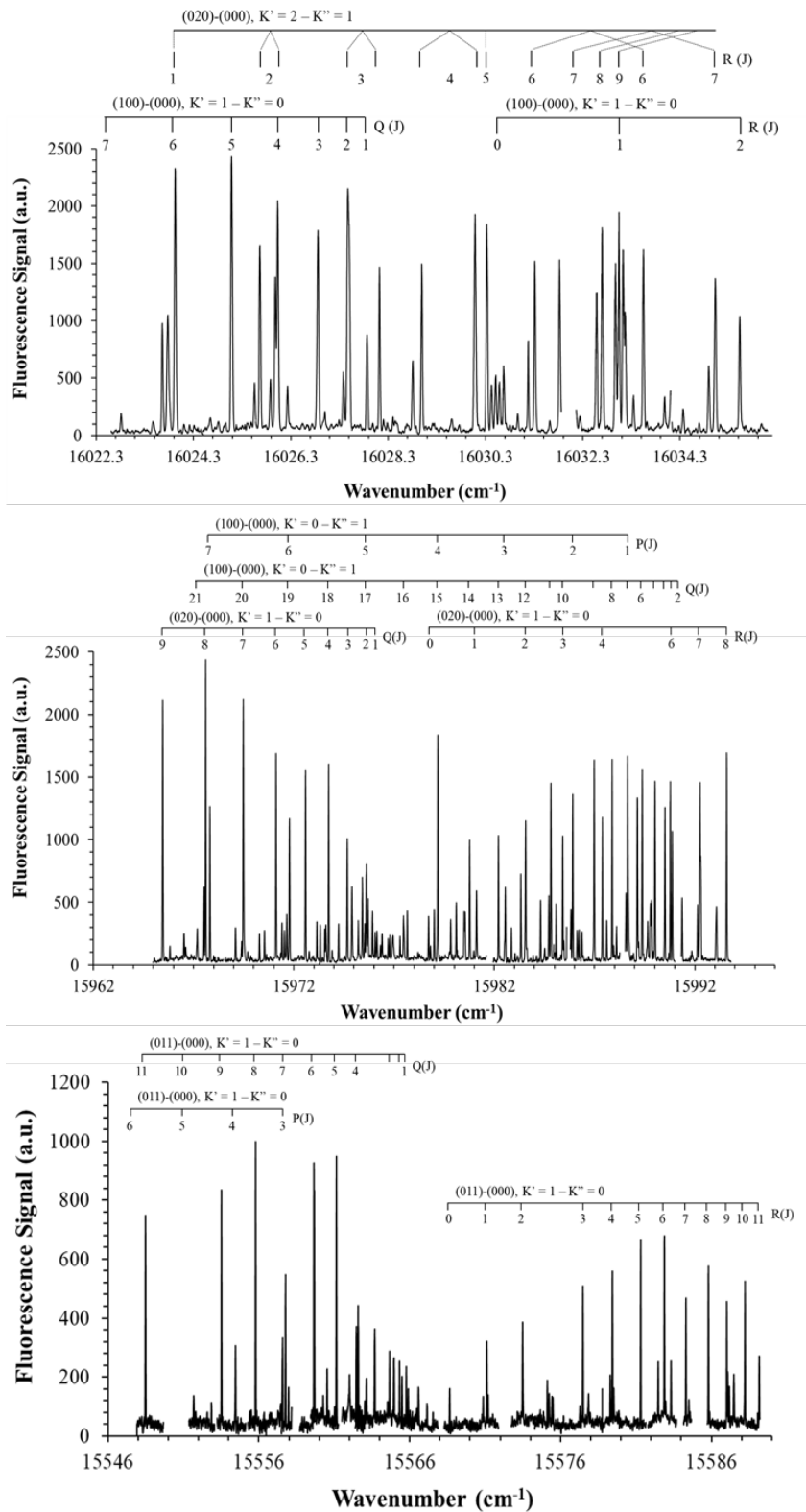


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

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In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' - X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' - X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' - X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' - X^1A'$ (020 – 000) and $\tilde{A}^1A'' - X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

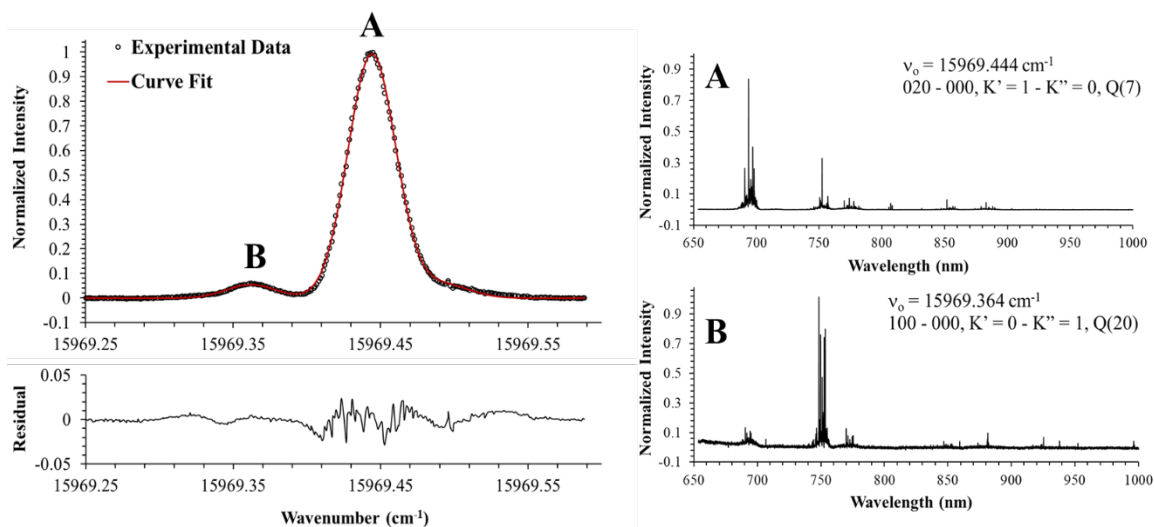


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020-000), $K' = 1 - K'' = 0$, Q(7) transition denoted as A. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100-000), $K' = 0 - K'' = 1$, Q(20) transition denoted as B. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, A and B. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347$ K and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

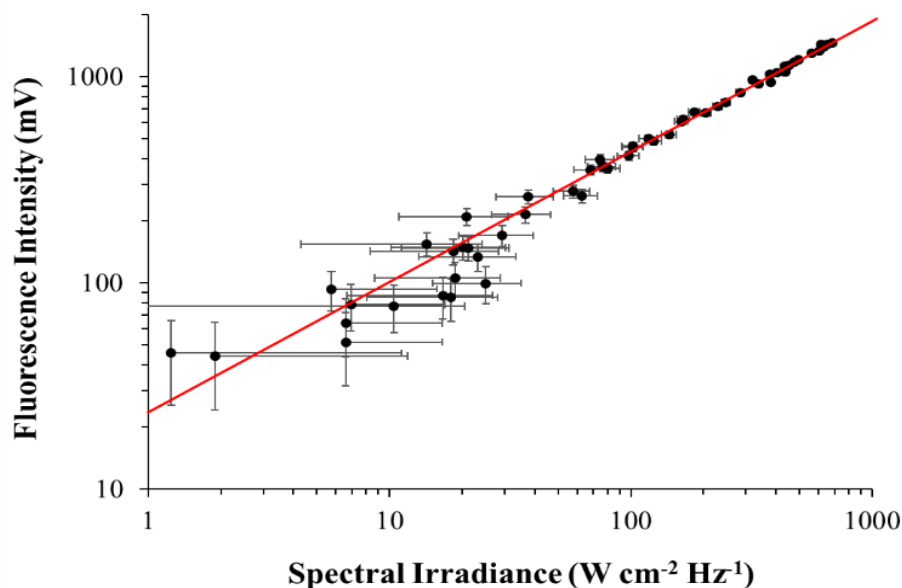


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

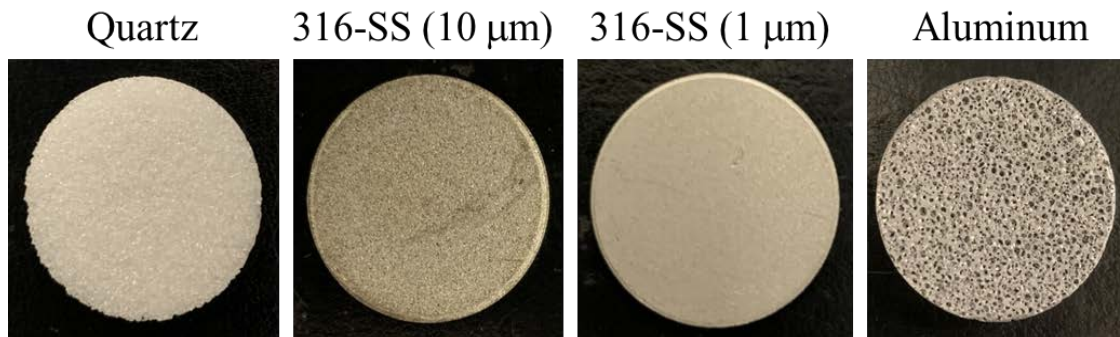


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

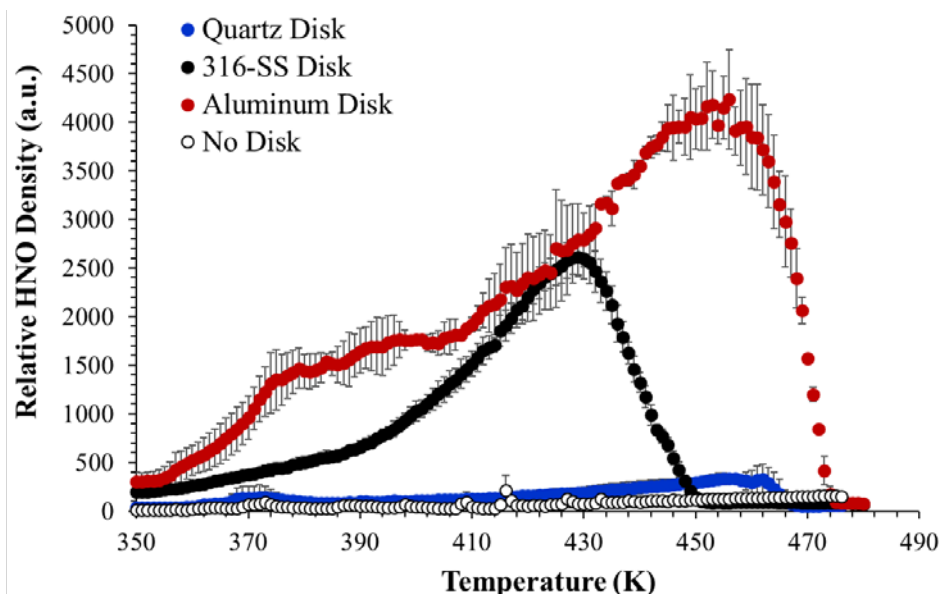


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2.Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

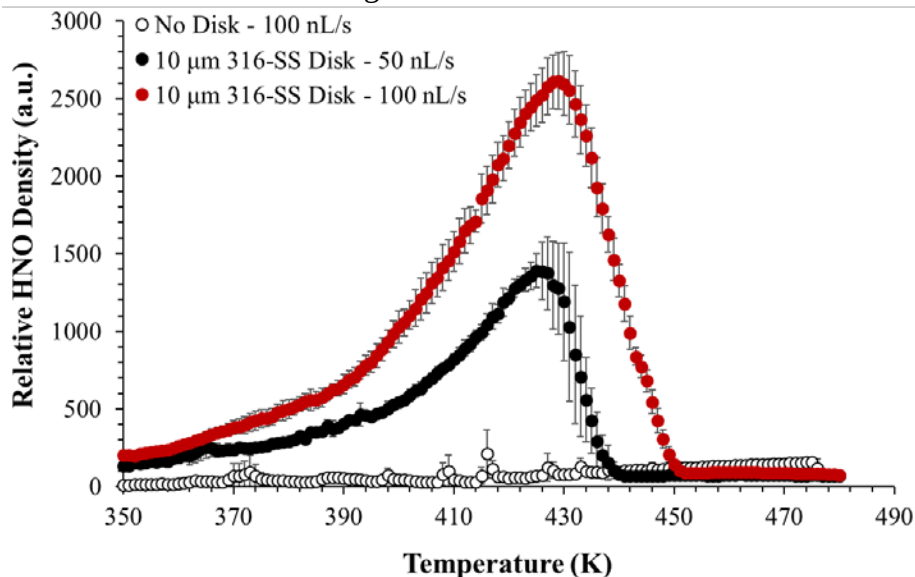


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

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production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

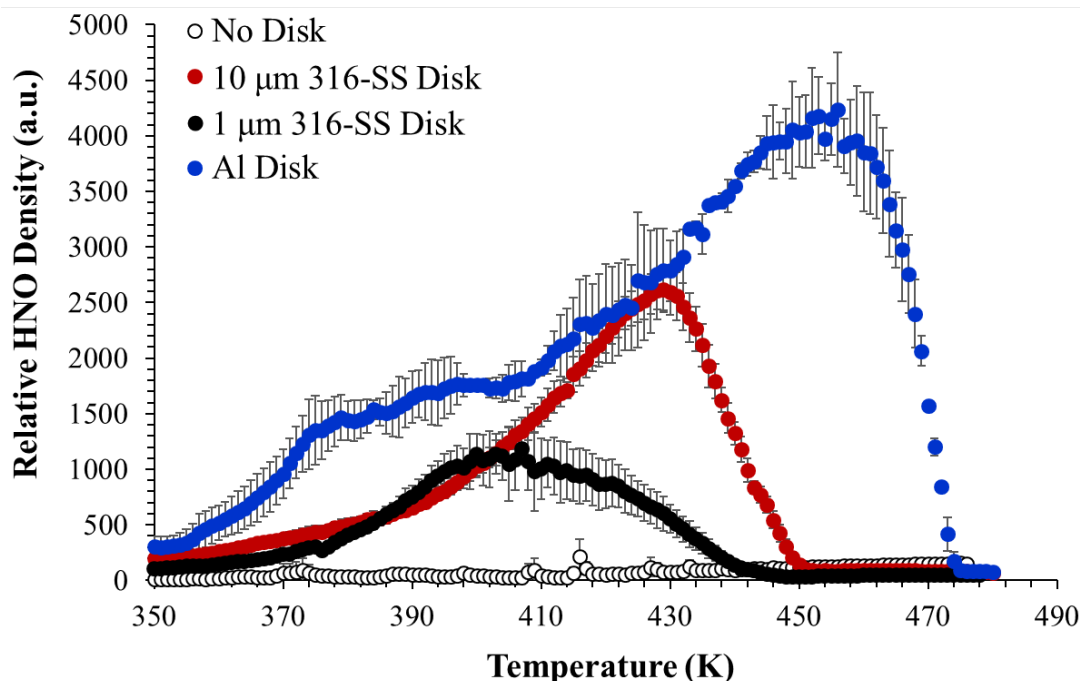


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

Acknowledgments

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

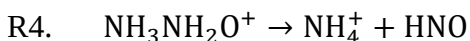
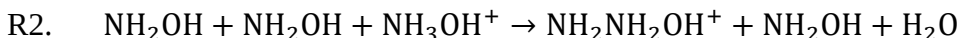
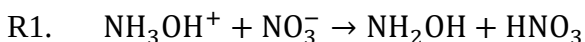
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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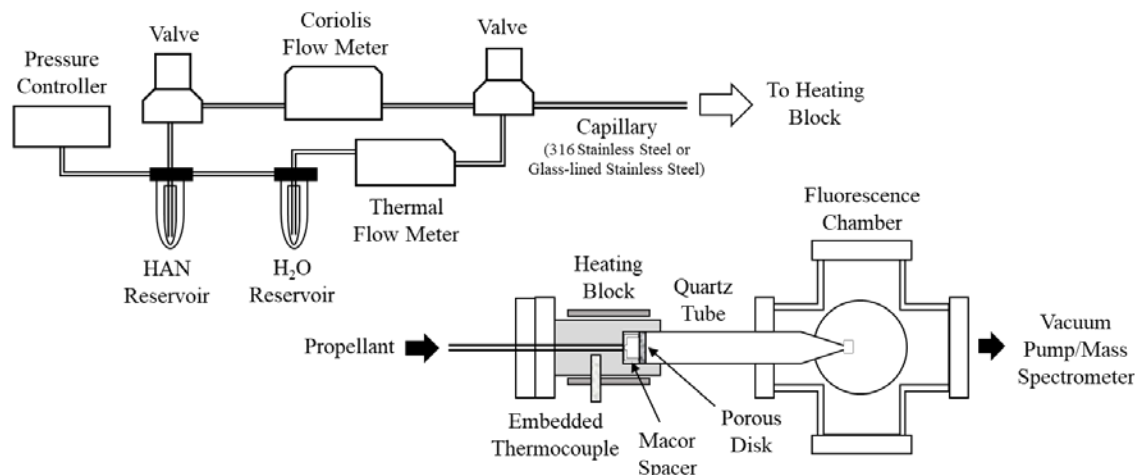


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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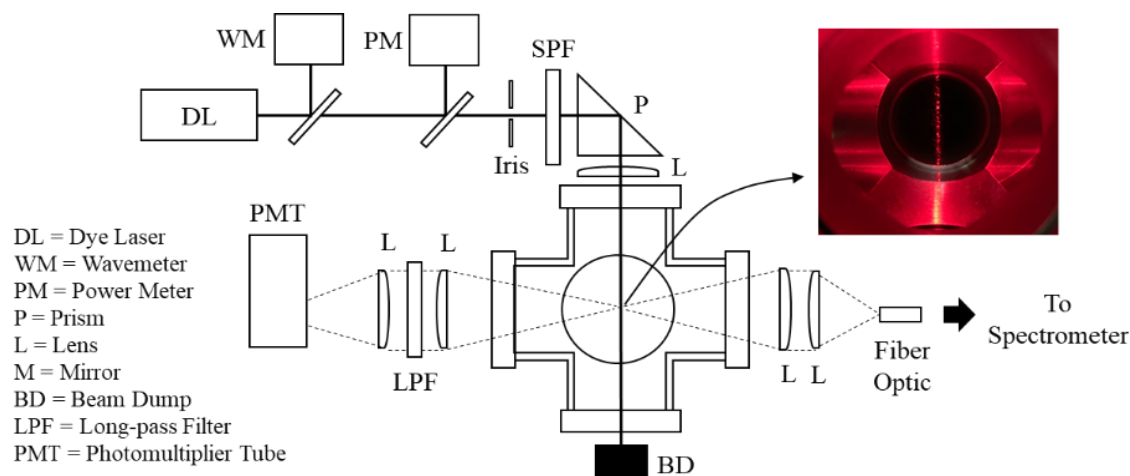


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680 \text{ nm}$) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6 \text{ Hz}$), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at $\sim 624 \text{ nm}$, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at $\sim 626 \text{ nm}$, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at $\sim 642 \text{ nm}$. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

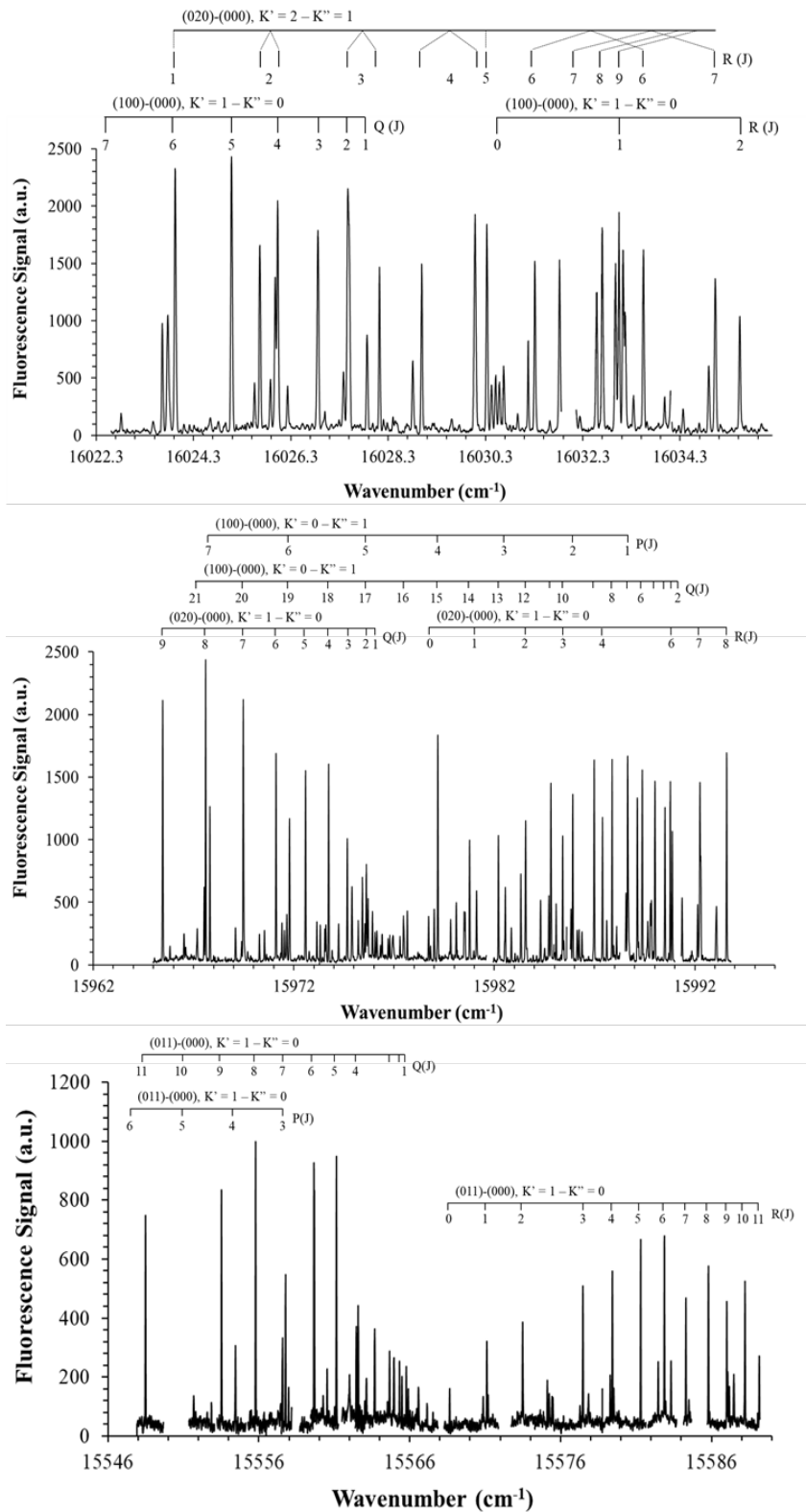


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

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In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' - X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' - X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' - X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' - X^1A'$ (020 – 000) and $\tilde{A}^1A'' - X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

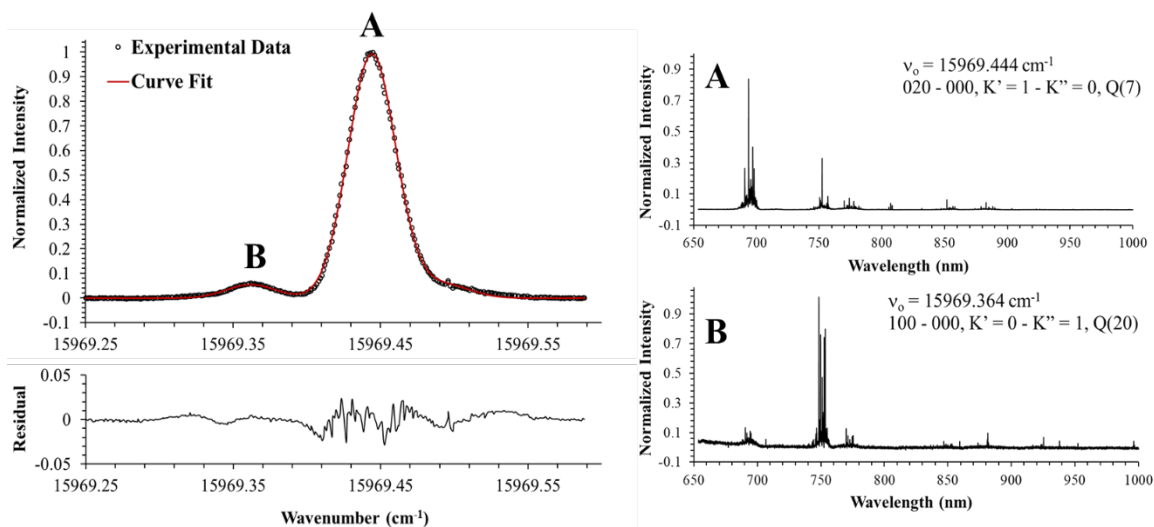


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020-000), $K' = 1 - K'' = 0, Q(7)$ transition denoted as A. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100-000), $K' = 0 - K'' = 1, Q(20)$ transition denoted as B. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, A and B. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347 \text{ K}$ and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

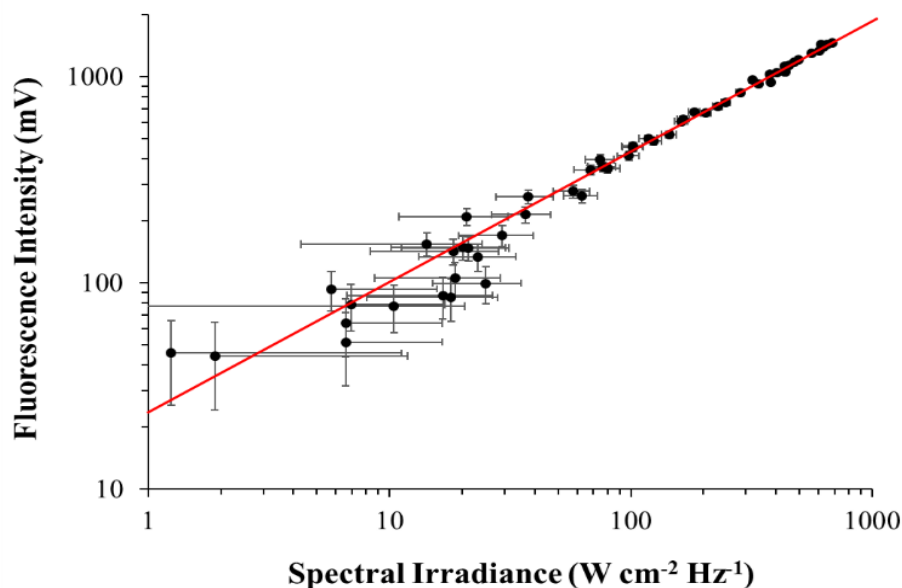


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

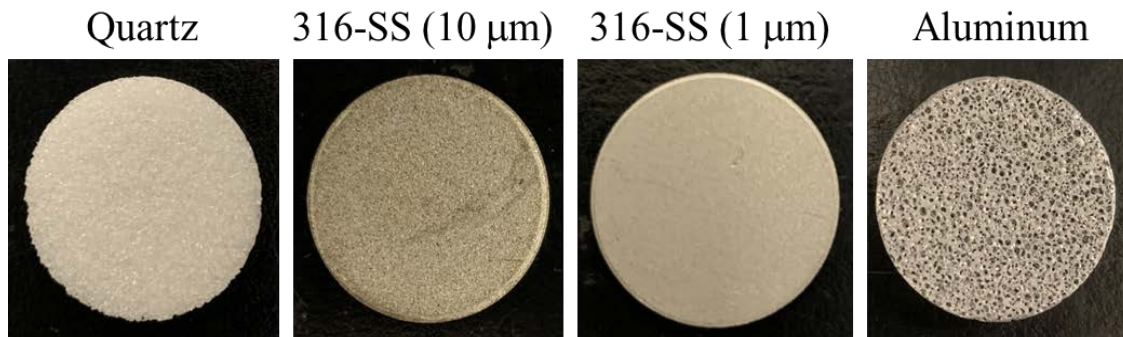


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

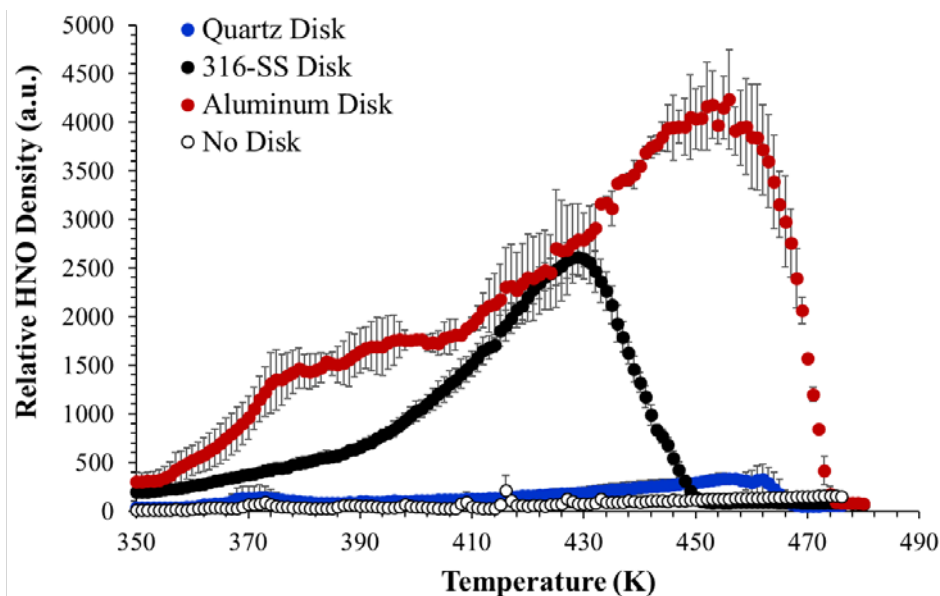


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2.Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

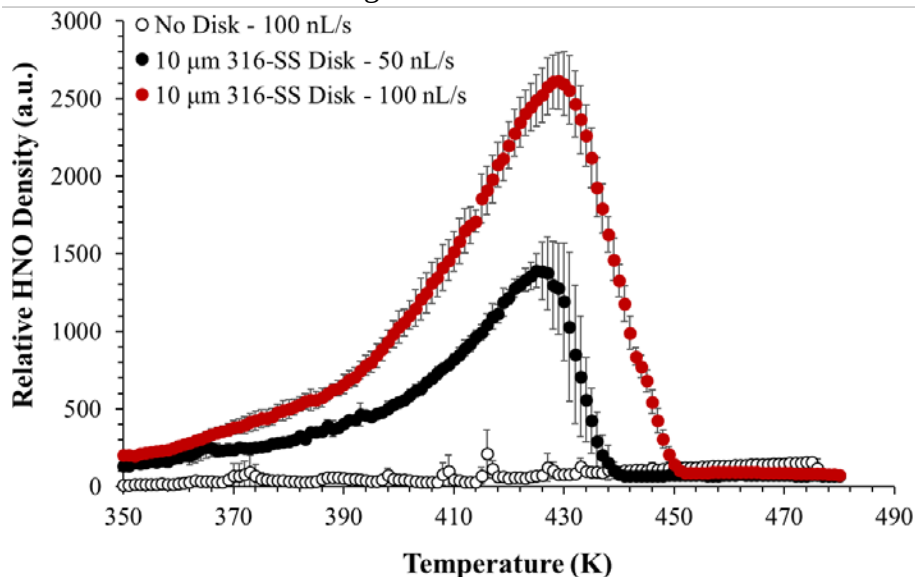


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

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production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

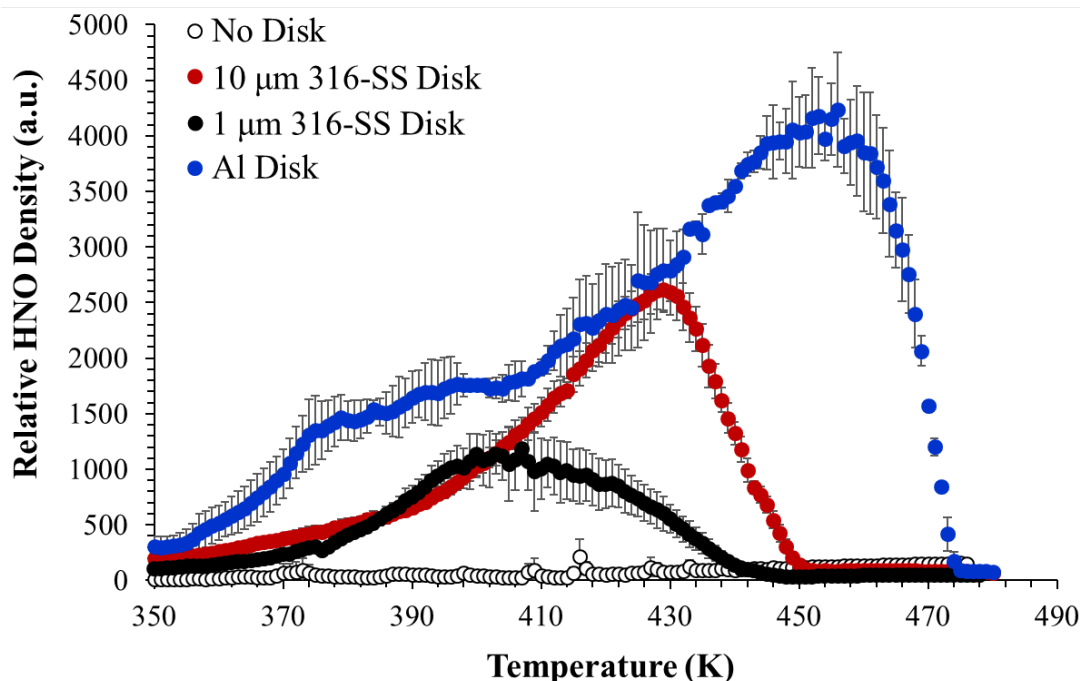


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

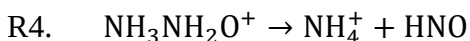
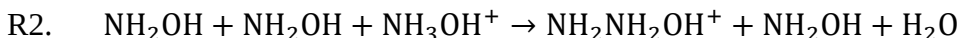
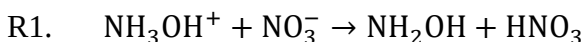
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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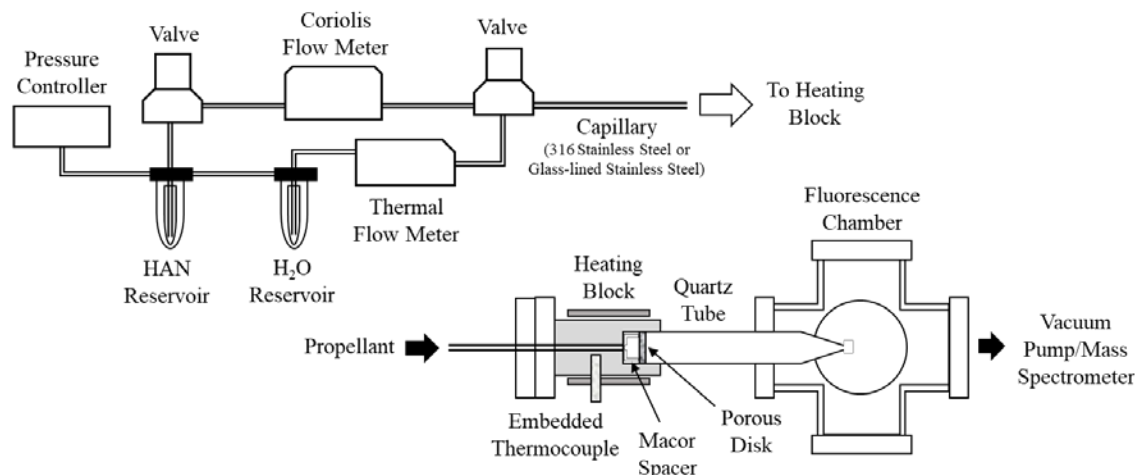


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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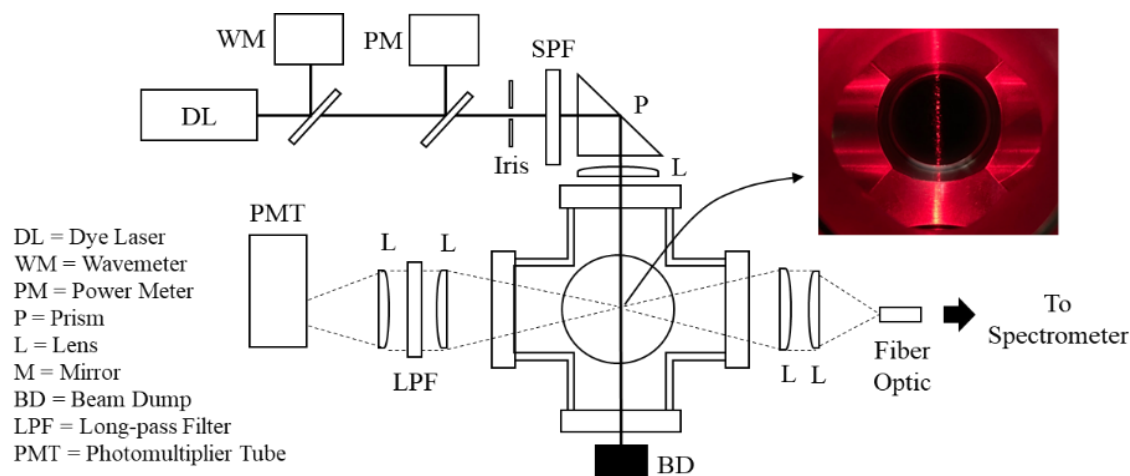


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680$ nm) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6$ Hz), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at ~624 nm, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at ~626 nm, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~642 nm. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

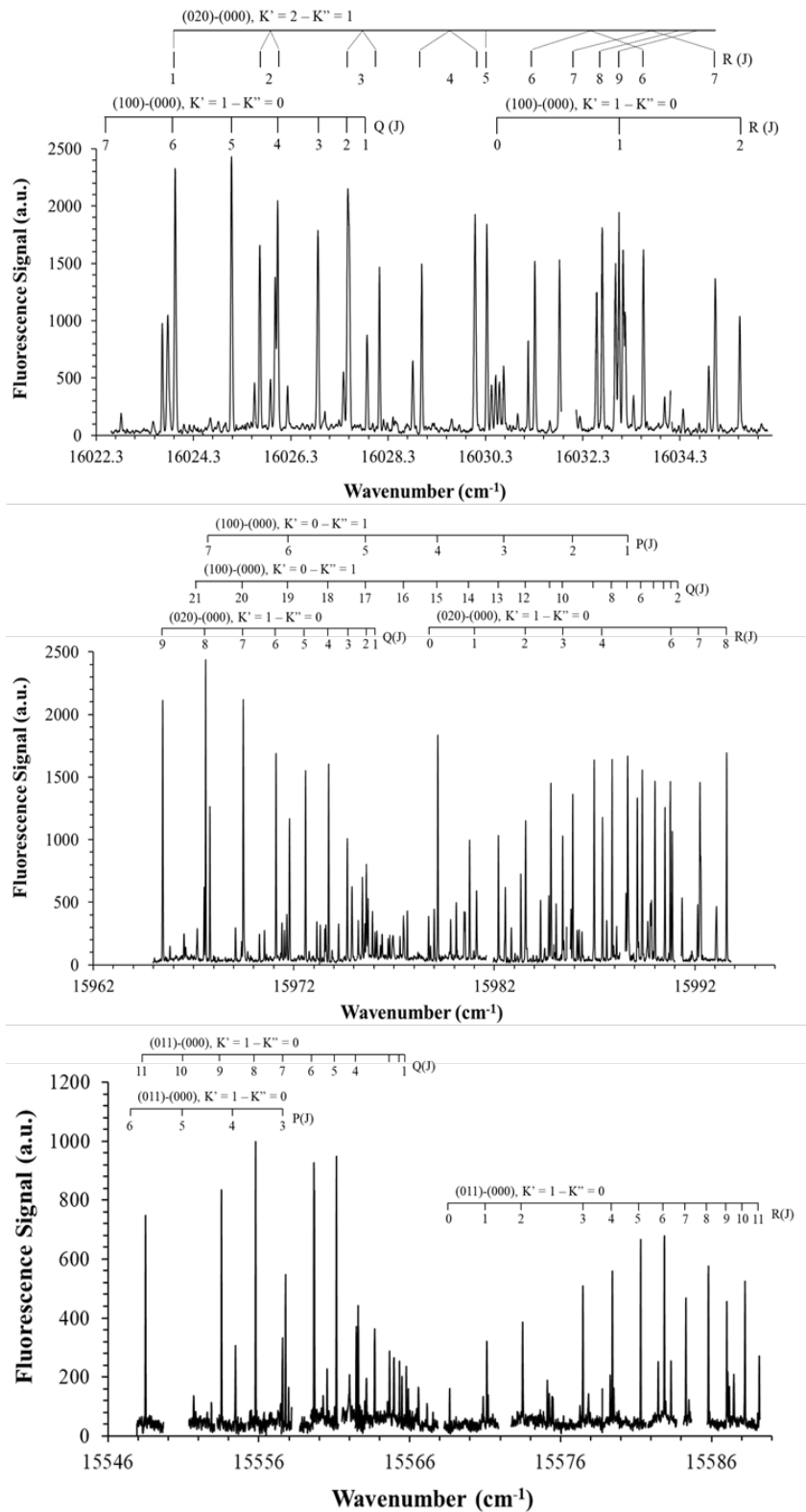


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

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In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' - X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' - X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' - X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' - X^1A'$ (020 – 000) and $\tilde{A}^1A'' - X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

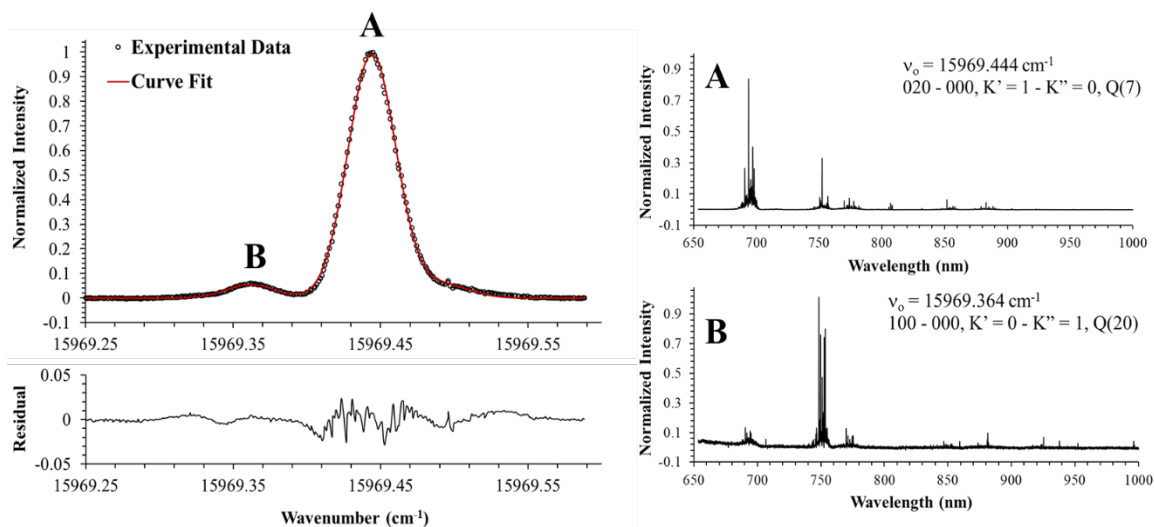


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition denoted as **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition denoted as **B**. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, **A** and **B**. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347 \text{ K}$ and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

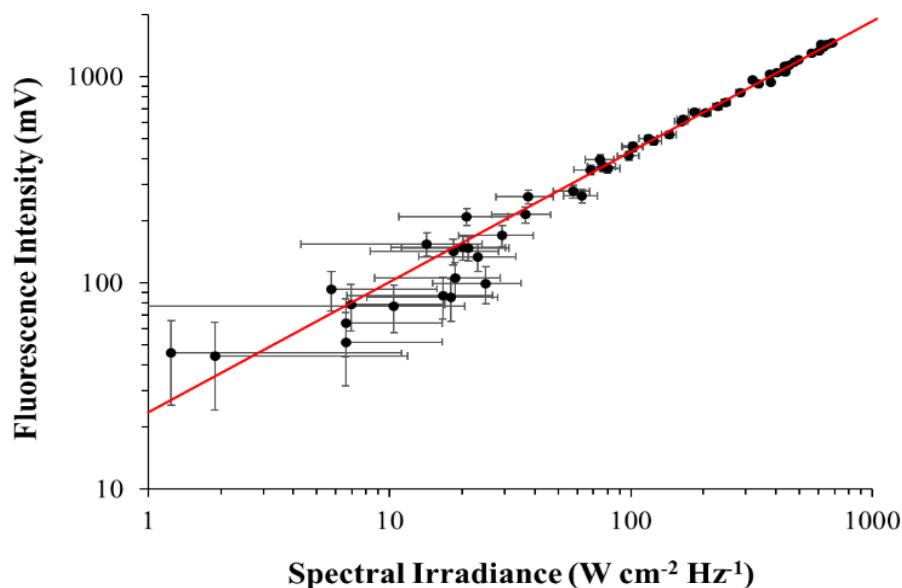


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

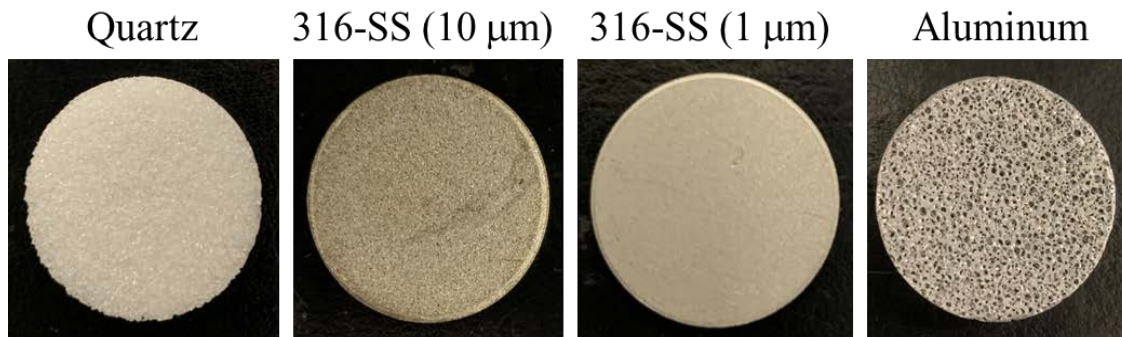


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

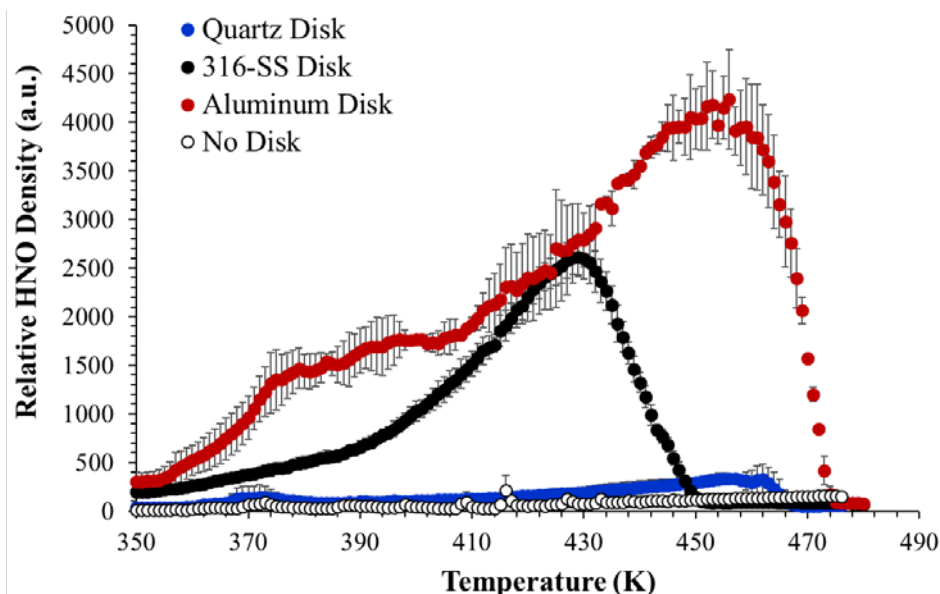


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2. Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

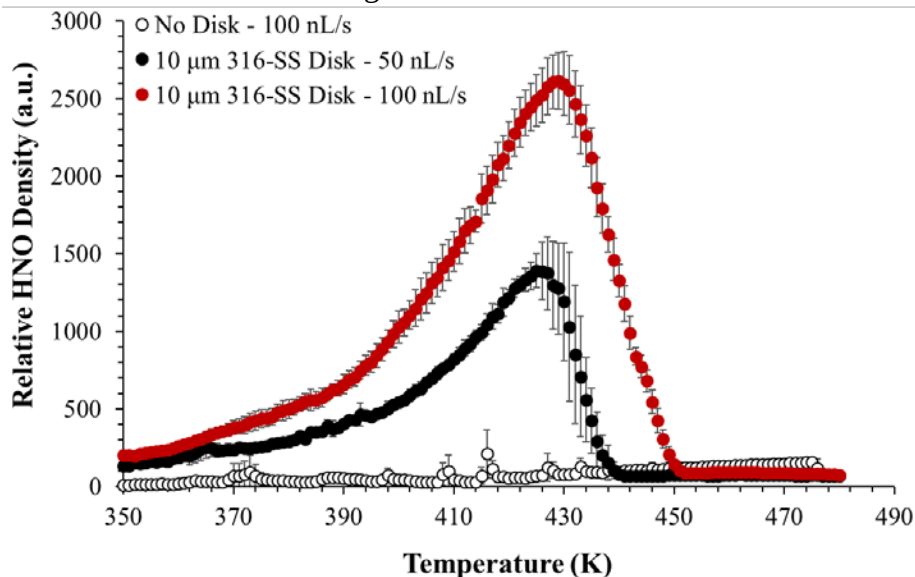


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

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production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

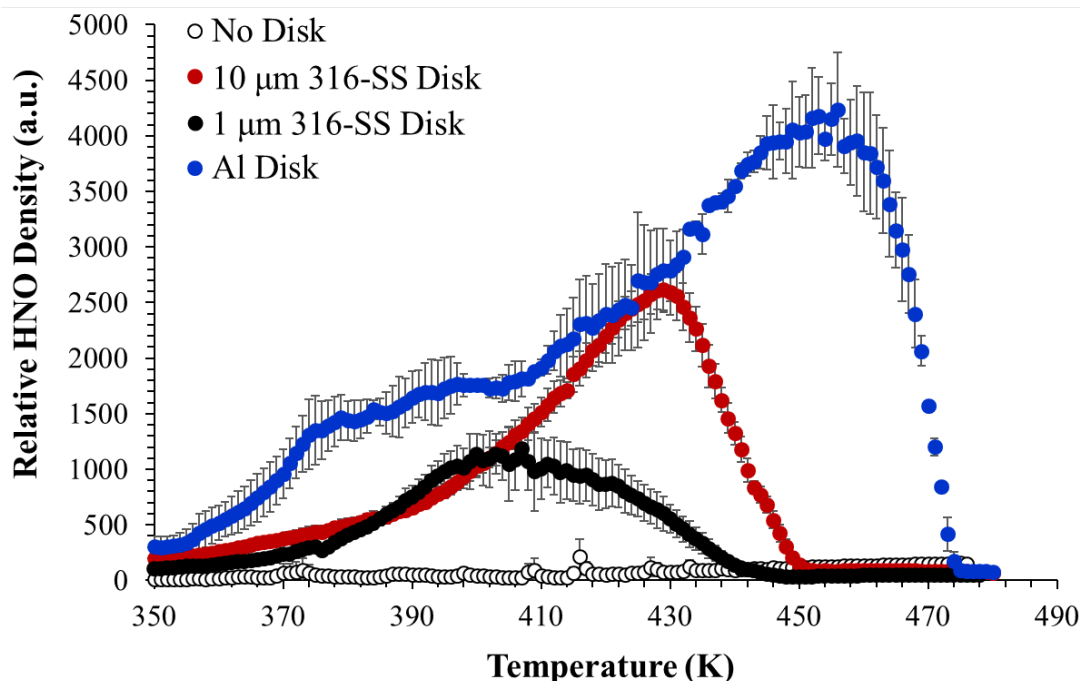


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

Acknowledgments

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

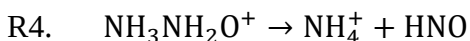
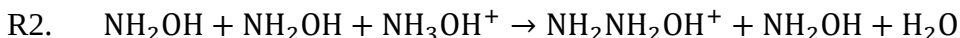
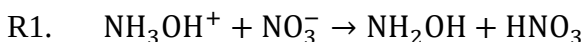
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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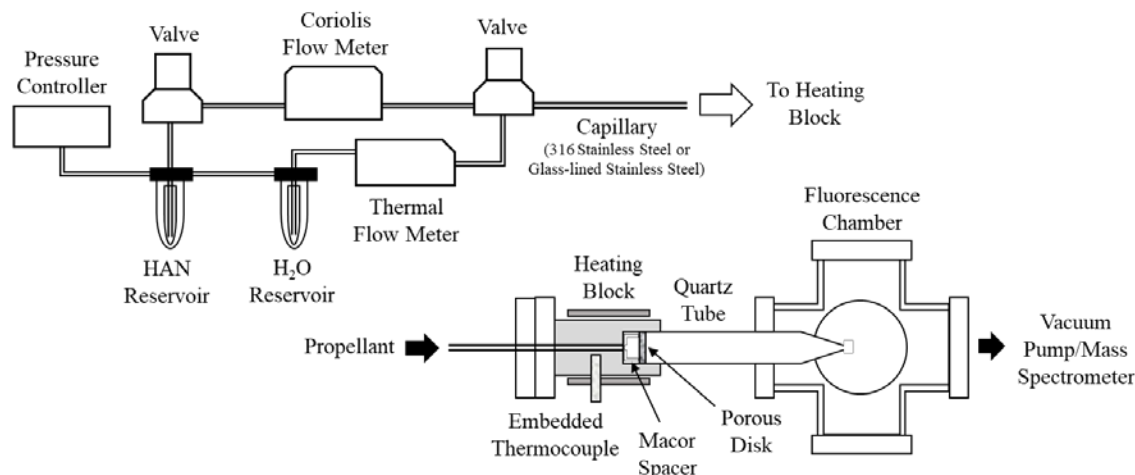


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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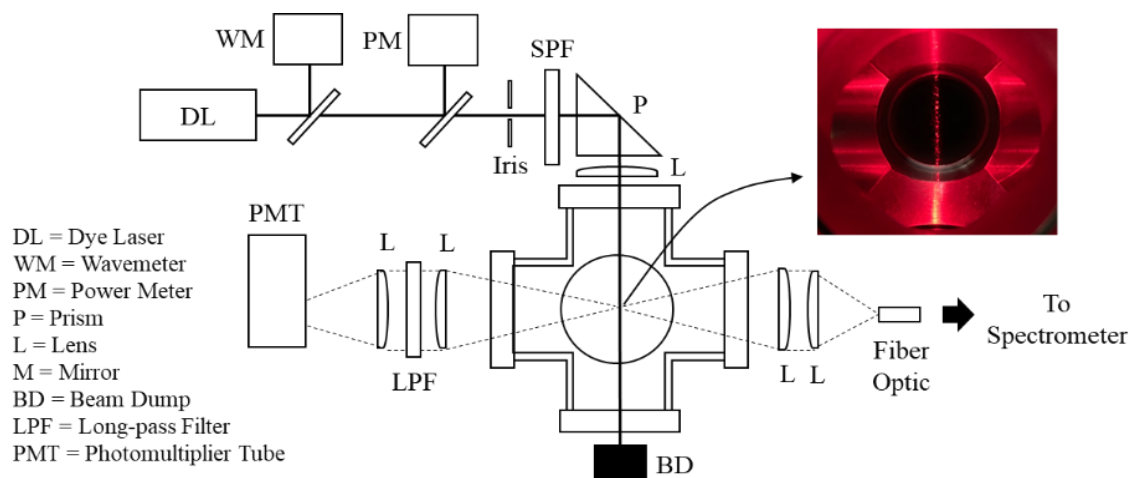


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680$ nm) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6$ Hz), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at ~624 nm, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at ~626 nm, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~642 nm. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

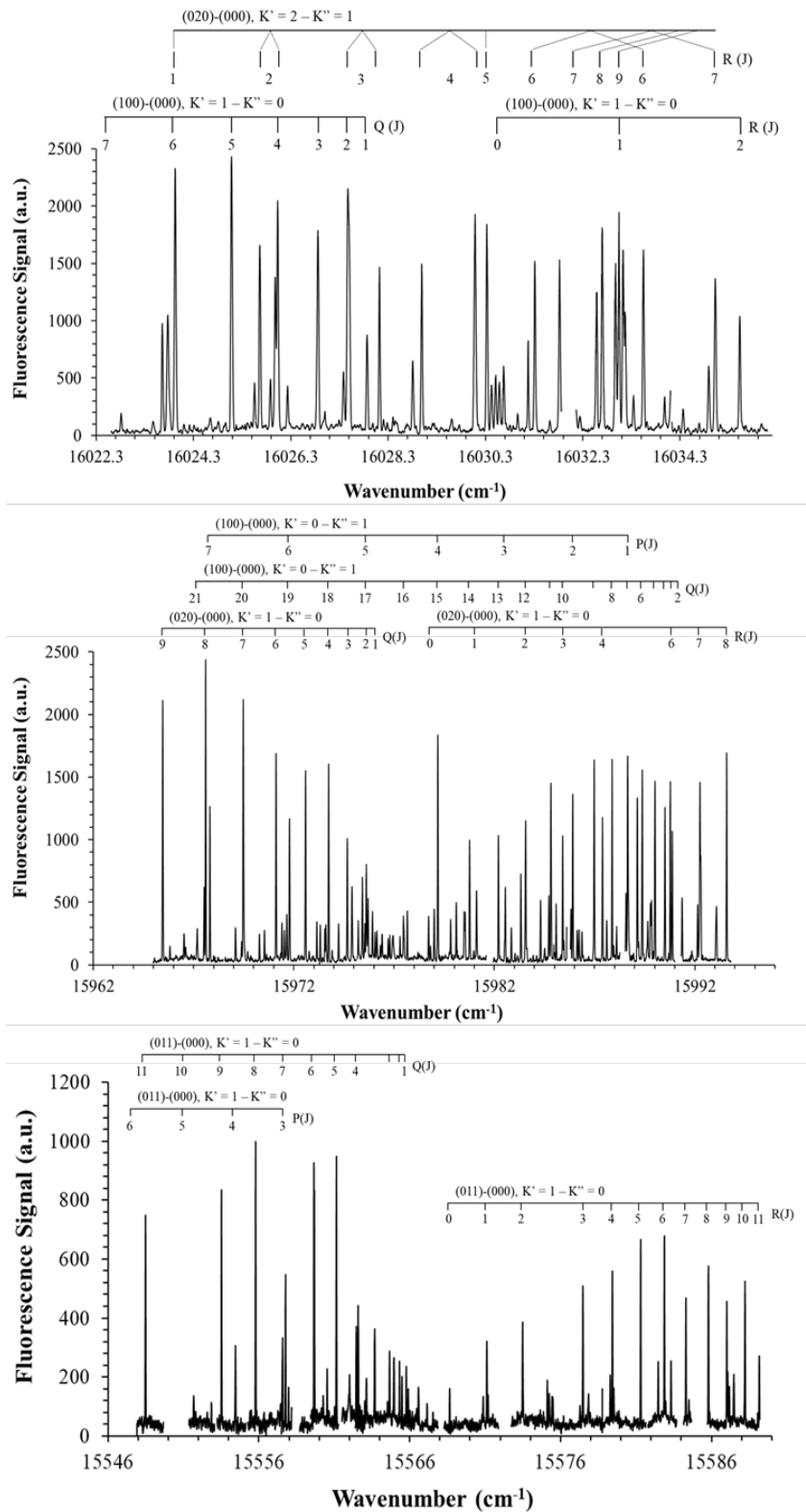


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

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In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' - X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' - X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' - X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' - X^1A'$ (020 – 000) and $\tilde{A}^1A'' - X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

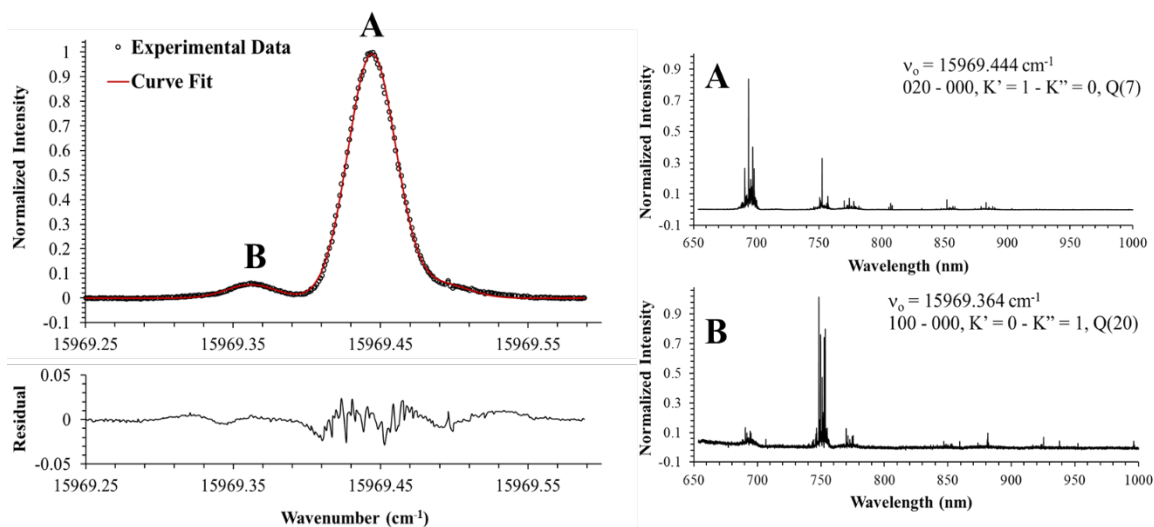


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020-000), $K' = 1 - K'' = 0$, Q(7) transition denoted as **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100-000), $K' = 0 - K'' = 1$, Q(20) transition denoted as **B**. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, **A** and **B**. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347 \text{ K}$ and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

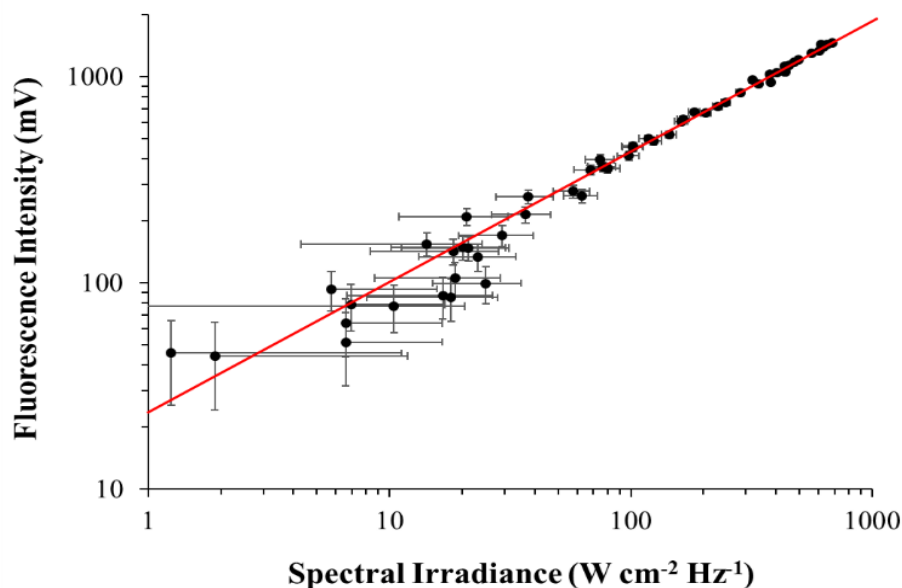


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

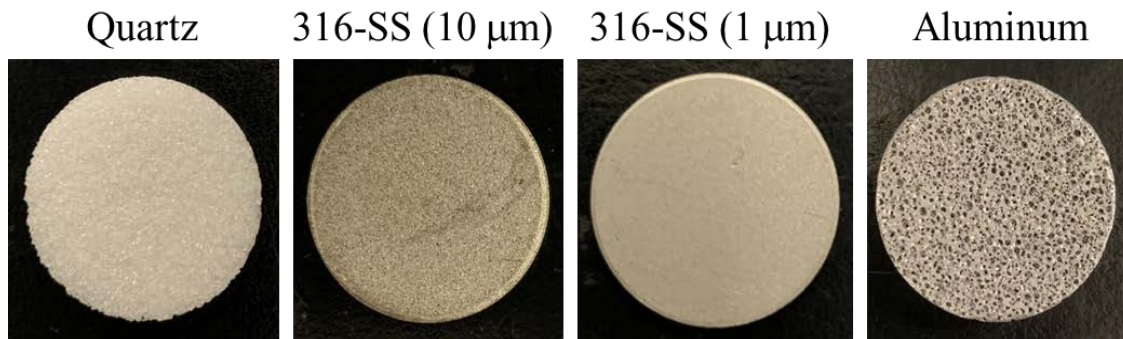


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

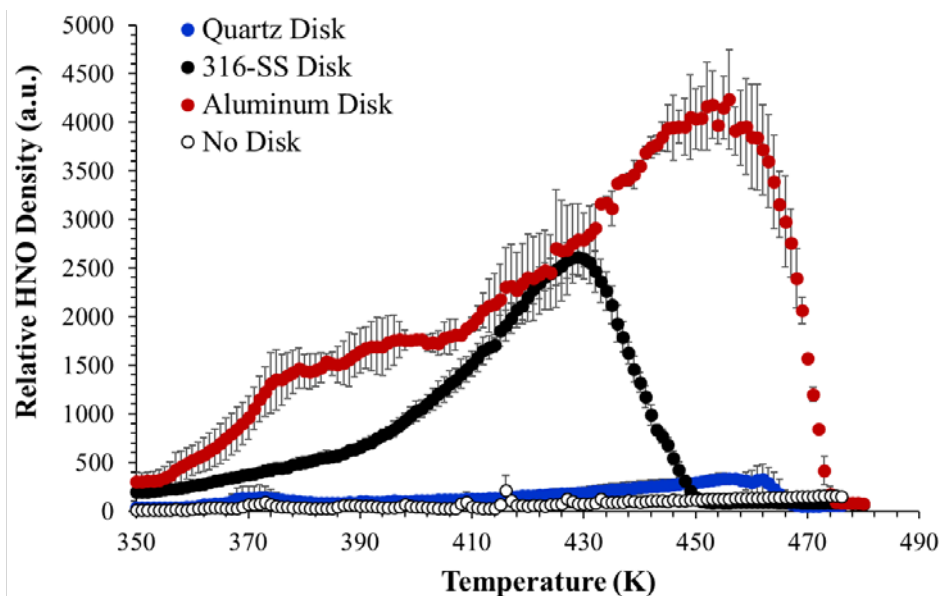


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2. Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

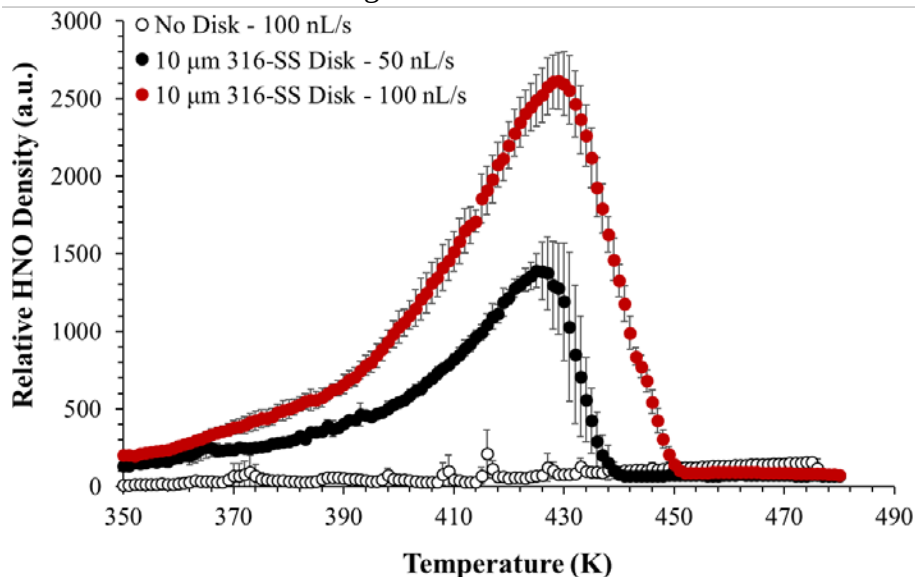


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

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production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

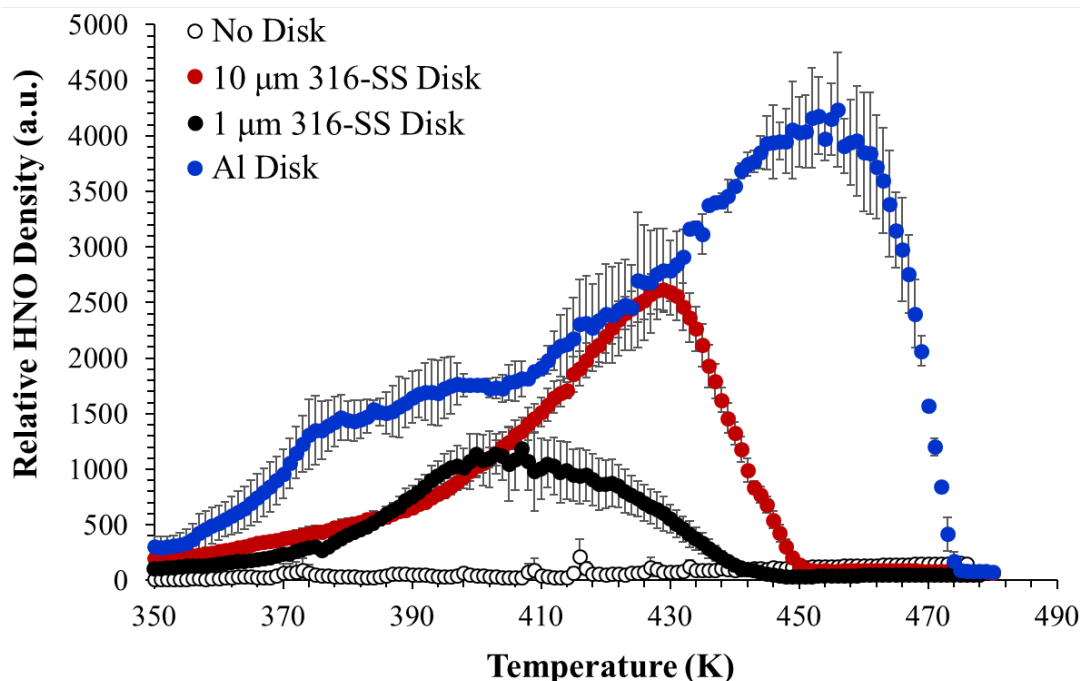


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

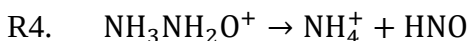
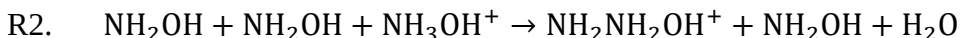
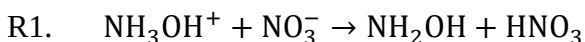
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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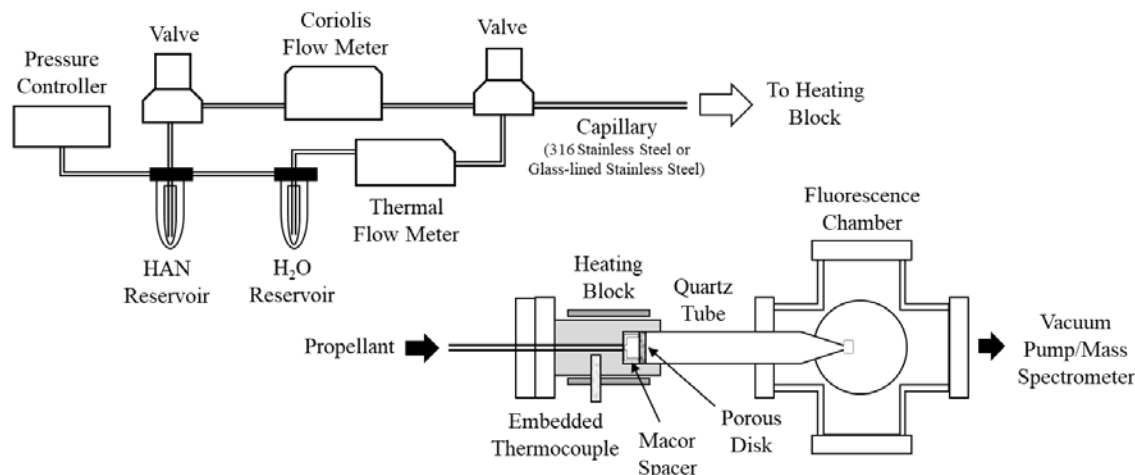


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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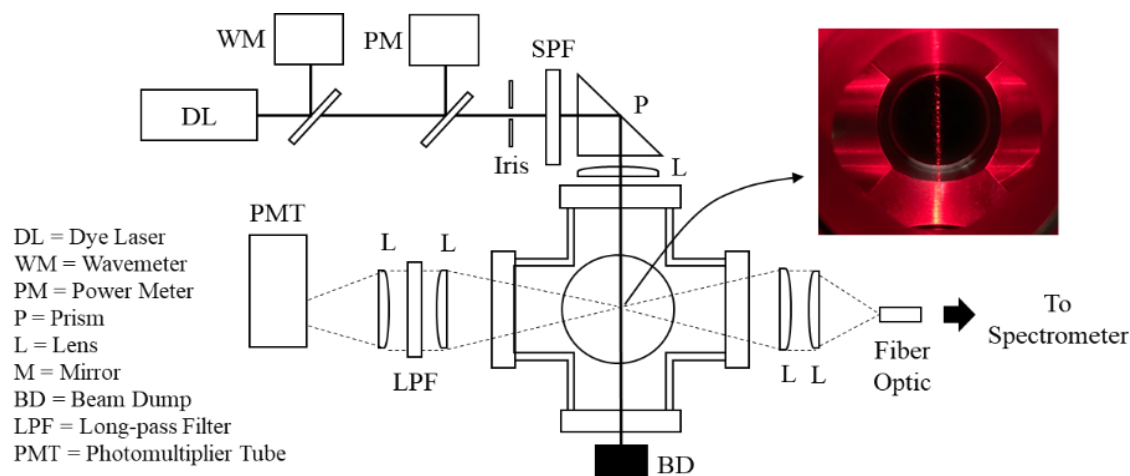


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680$ nm) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6$ Hz), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at ~624 nm, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at ~626 nm, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~642 nm. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

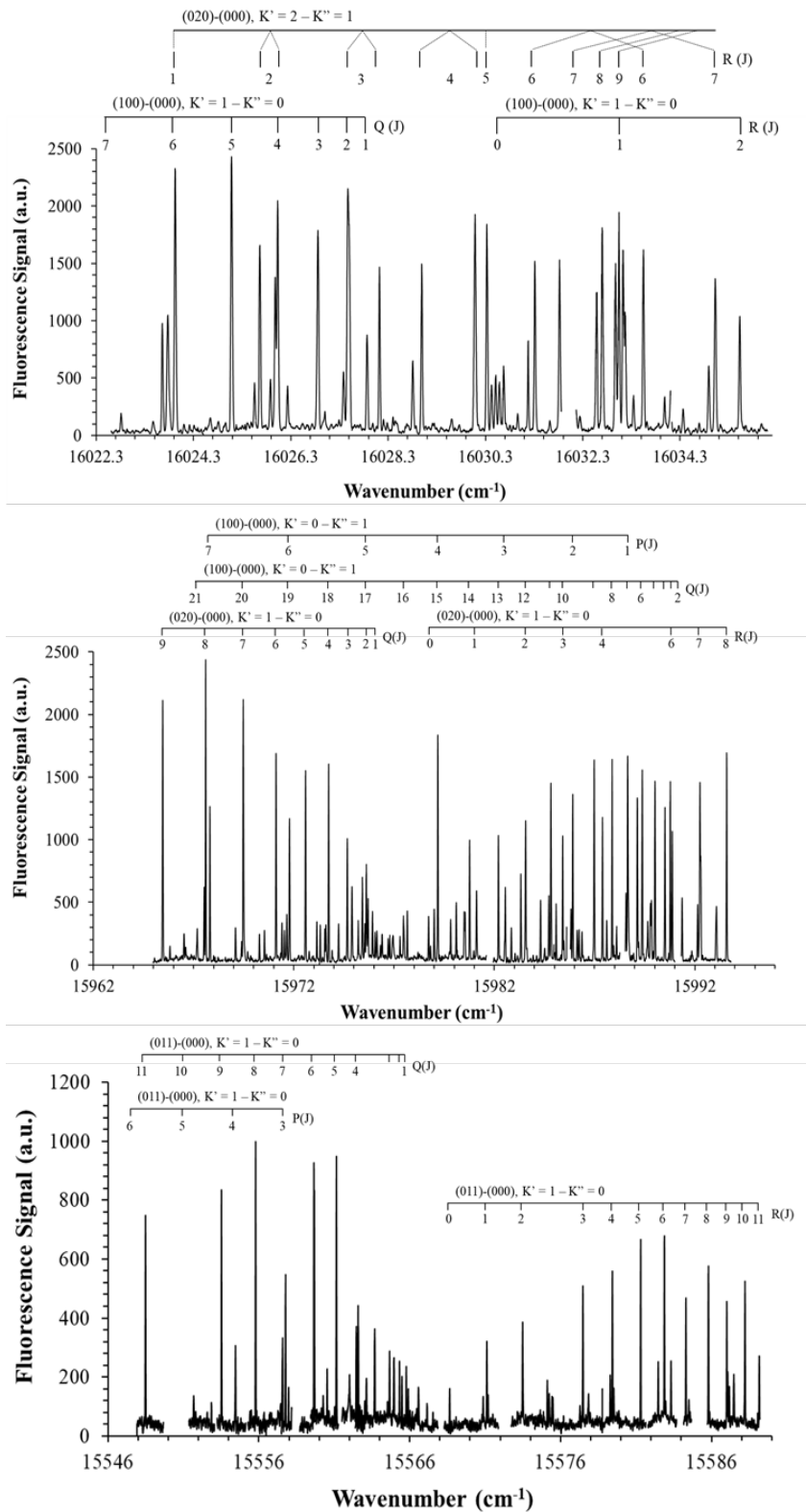


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

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In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' - X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' - X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' - X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' - X^1A'$ (020 – 000) and $\tilde{A}^1A'' - X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

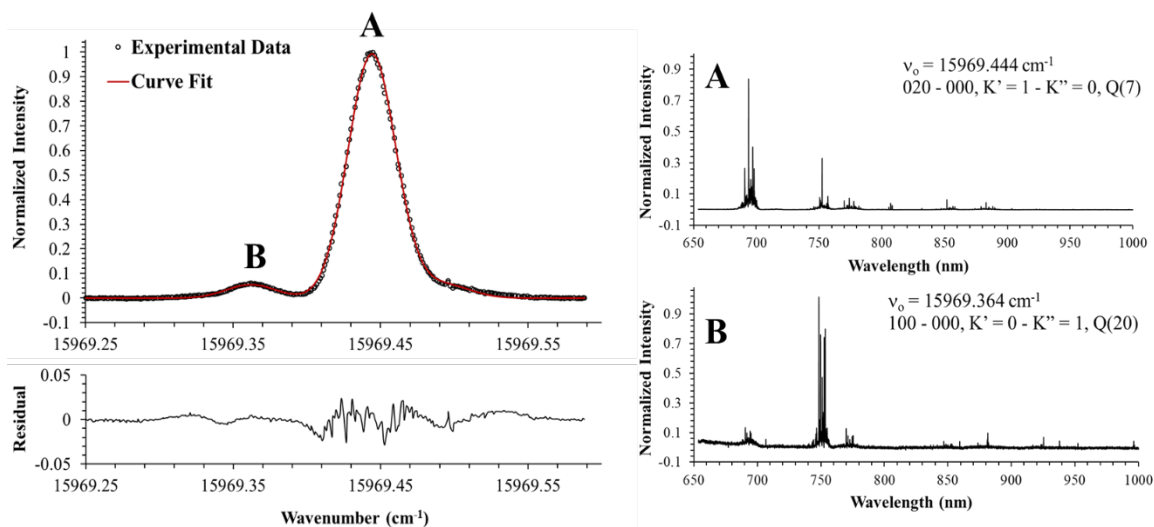


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020-000), $K' = 1 - K'' = 0$, Q(7) transition denoted as **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100-000), $K' = 0 - K'' = 1$, Q(20) transition denoted as **B**. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, **A** and **B**. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347 \text{ K}$ and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

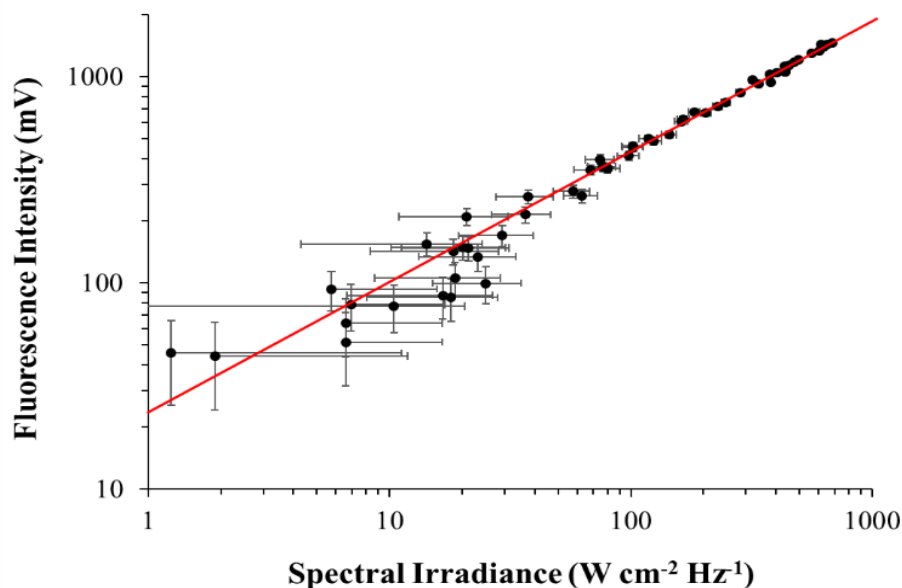


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

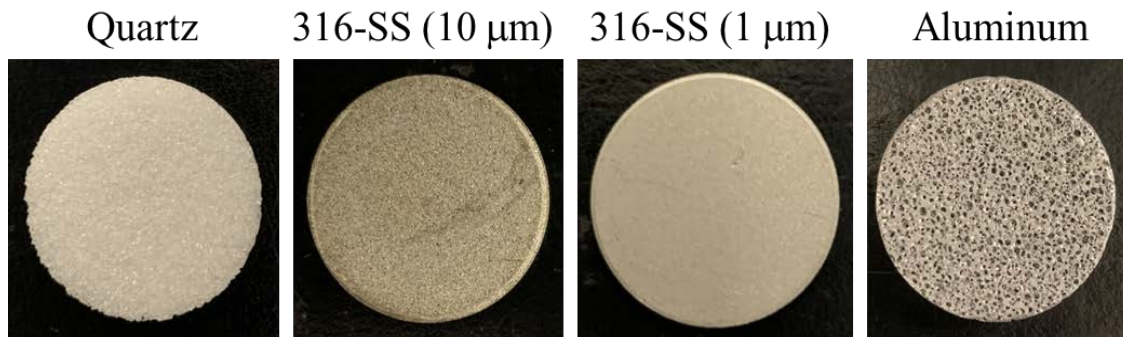


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

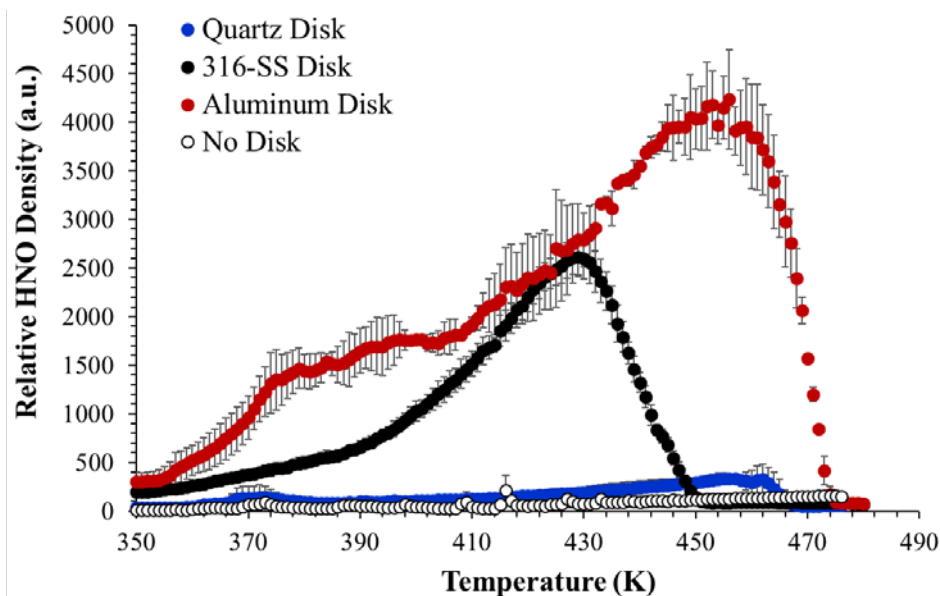


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2. Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

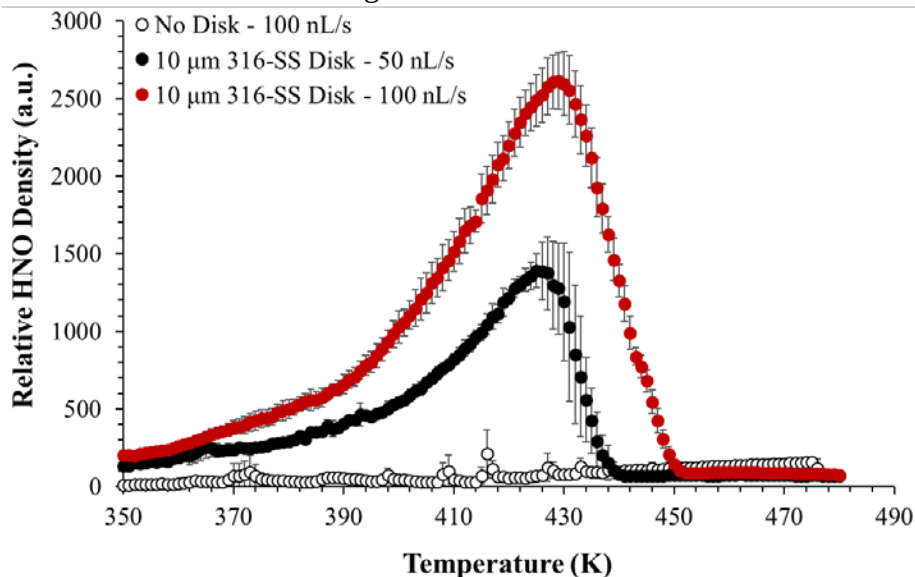


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

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production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

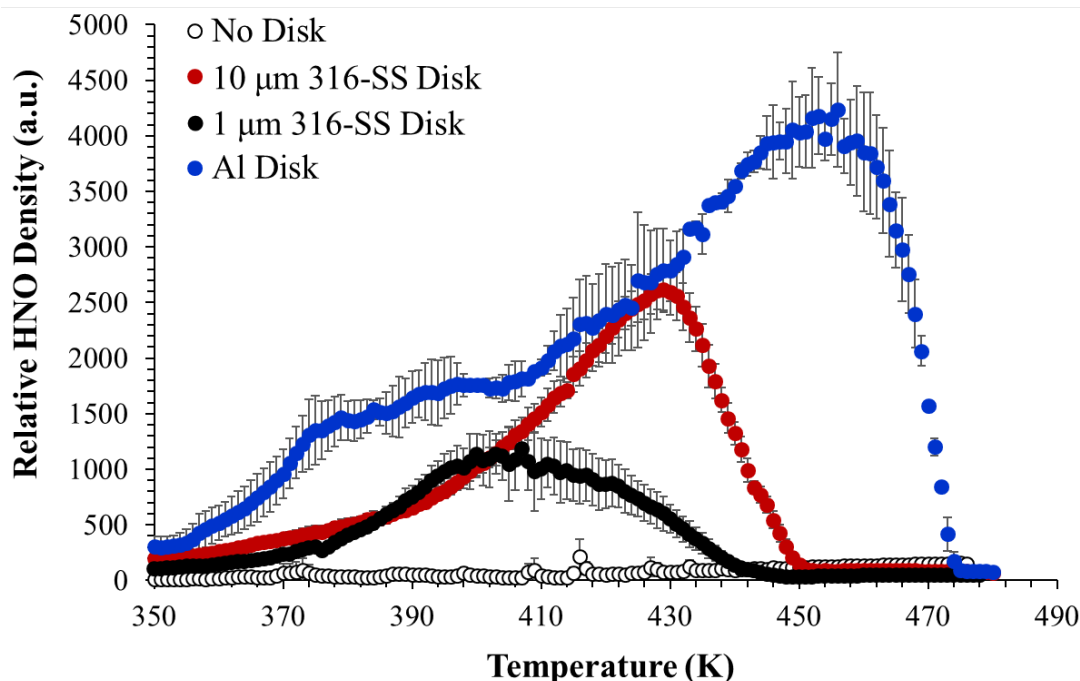


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

Acknowledgments

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Laser-Induced Fluorescence Detection of the Nitroxyl (HNO) Radical via Thermal Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract

The ionic liquid hydroxylammonium nitrate (HAN) is a promising monopropellant for various types of spacecraft propulsion systems. With regards to plasma-based electric propulsion applications, the ionic liquid is thermally and/or catalytically decomposed into a vapor and subsequently ionized. Among the various species generated from HAN decomposition is the formation of nitroxyl (HNO), an important molecule with implications in both chemical and electric propulsion applications. This work will describe the use of a laser-induced fluorescence (LIF) platform to detect the HNO radical. A single-mode dye laser was used to acquire LIF excitation spectra involving three excitation transitions: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. From these extended scans we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) ro-vibrational excitation transition to be the most optimal optical line for system diagnostics. Analysis on the production of HNO will be discussed with respect to decomposition temperature and porous heated disks used to interact with the vaporized HAN. Relationships between heated disk material composition, disk physical characteristics, and temperature dependent HNO density profiles will be discussed.

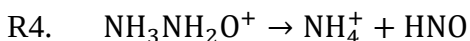
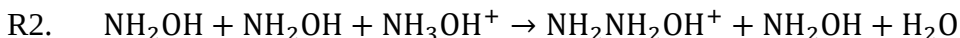
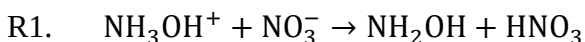
1. Introduction

Ionic liquids (ILs) have received significant interest in recent years as a potential dual-mode propellant replacement in electric propulsion devices.^{1,2} ILs possess many attractive properties including being environmentally benign, stable, and exhibit low-toxicity. ILs relatively high densities and near zero vapor pressures have led to them being widely utilized as propellants in electrospray thrusters.³⁻¹² Moreover, ILs are known to thermally decompose into gas phase species which can be utilized in gas-fed electric propulsion devices.^{2,13,22-31,14-21} In order to maximize the propellant's utility, the parameters that influence the chemical composition of the emitted gas phase species must be well characterized.

One particular IL that has received notable attention is hydroxylammonium nitrate (HAN). In 1985 Cronin and Brill examined the decomposition of HAN and speculated that the initial reaction involved proton transfer from the hydroxylammonium ion (NH_3OH^+) to the nitrate ion (NO_3^-) to form hydroxylamine (NH_2OH) and nitric acid (HNO_3).²¹ They postulated that hydroxylamine would further degrade into nitrous oxide (N_2O) and ammonia (NH_3). In 1988 Oxley and Brower conducted a comprehensive chemical gas analysis on the thermal decomposition of HAN and proposed several chemical mechanisms for the generation and reaction of observed species.³¹ Among these species was nitroxyl, HNO, which they treated as both a product of HAN decomposition, and a reactant for subsequent chemical reactions. Included in their mechanisms were reactions involving the formation of nitrous oxide as a final product. Later studies by Schoppelrei and Brill would

examine the production of nitrous oxide as a product of the dimerization of nitroxyl produced from HAN decomposition under high pressure conditions.³²

In recent years there have been a number of computational studies examining the decomposition of hydroxylamine.^{33–35} Most notable is the extensive study conducted by Izato *et al.* where they examined the early decomposition pathways of hydroxylamine in aqueous solutions.³⁵ Based on their computational analysis they concluded that a cation-catalyzed reaction was the likely initial decomposition pathway, as shown in reactions R1–R5, with R6 being the overall reaction.



Despite nitroxyl being predicted as a decomposition product of HAN, there have been no direct experimental observations of HNO, rather, its production has been implied due to the subsequent formation and detection of nitrous oxide. Moreover, we have found no reported studies which examine the thermal decomposition of HAN in the vapor phase. The goal of the work presented is to heat HAN flowing through a capillary which induces a proton transfer reaction, creating flowing solution of hydroxylamine and nitric acid. The subsequent vapor, composed of gas phase hydroxylamine and nitric acid (from here on referred to as HAN vapor), will be passed through various heated porous materials and the production of HNO will be assessed. The research presented here has two primary objectives. The first objective is to experimentally assess the validity of laser-induced fluorescence spectroscopy (LIF) as a means to selectively and sensitively observe the production of HNO from the thermal decomposition of HAN. The second objective is to utilize the optimized experimental LIF system to examine the production of HNO from the thermal decomposition of vaporized HAN. HNO production with respect to material-propellant interaction will be discussed.

2. Experimental Design

2.1. Thermal Decomposition System

The experimental platform used to examine the production of HNO is shown in figure 1. Controlled quantities of an aqueous HAN solution (24% wt.) are injected into the thermal decomposition system with a combined piezoelectrically controlled pressure controller and sensitive mass flow meters. Automated 3-way valves are used to control the sequence and timing of each fluid injected into the system. Water is used here to flush the system when necessary and assess background signal levels. Two flow meters are used in the current work, a Coriolis flow meter used to measure the HAN flow rate, and a thermal flow meter calibrated to measure the flow rate of water. The resulting liquid is injected into a capillary with the final 25 mm portion confined within an aluminum heating block. An alumina tube (id = 1/16", od = 1/8") is used to maintain separation between the metal capillary and the aluminum house, which was found to be necessary to provide good thermal contact while

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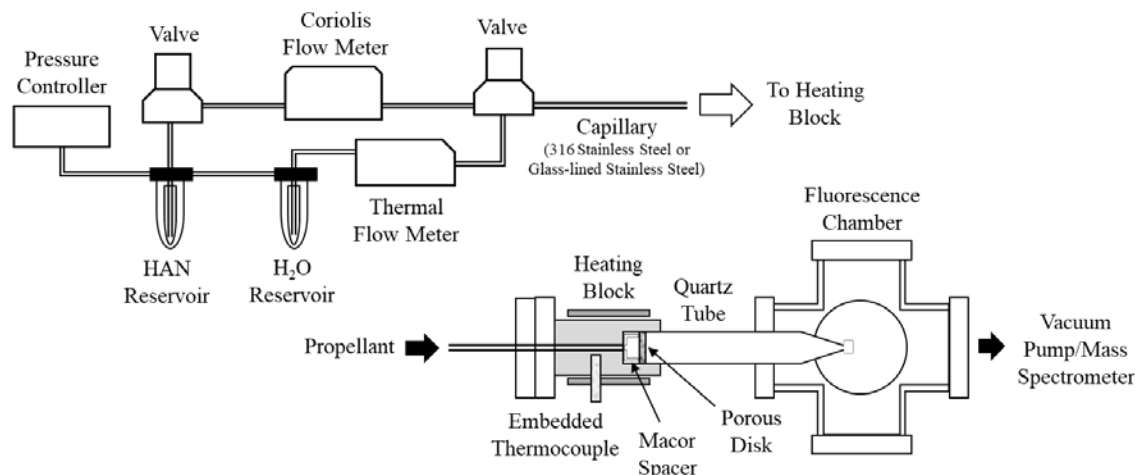


Figure 1: Illustration of the experimental platform used for propellant injection, thermal decomposition, and HNO detection.

preventing the two metals from seizing. A glass-lined stainless-steel capillary (id = 100 μm , od = 1/16", L = 20 cm) was used throughout the work presented here. The temperature of the heating block is controlled with thermal tape and a temperature controller. Four embedded K-type thermocouples positioned along the heating block (only one shown) are used to acquire temperature measurements along the heated portion of the capillary. Immediately following the end of the heated capillary and positioned within the heating block cavity is a Macor spacer and a porous disk. The Macor spacer shields the vaporized propellant from the aluminum heating block, avoiding unwanted Al-propellant reactions, and provides a consistent 10 mm spacing between the end of the capillary and the face of the various porous disks used throughout this work. The initial purpose of the porous disk was to help homogenize the gas vapor that emerges from the capillary, providing a fairly uniform distribution of vaporized species for subsequent injection into a plasma for ionization. An additional feature of these porous disks is the potential for reactive and/or catalytic studies. The decomposed vapor products emerging from the disk flows through a 20.3 cm (8") long fused quartz tube with an outer diameter of 25.8 mm and inner diameter of 22 mm. The end of the fused quartz tube has been tapered to a final inner diameter of 5 mm in order to funnel and focus the gas species into the LIF chamber. The chamber vacuum system and an in-line mass spectrometer were positioned downstream from the fluorescence chamber.

2.2.Laser-Induced Fluorescence System

The laser-induced fluorescence system is constructed of a 6-way 2.75-inch con-flat flange cube fitted with viewports with anti-reflection coated windows. An illustration of the optical system is shown in figure 2. A single-mode cw dye laser with a linewidth of $\sim 75 \pm 5$ kHz was used as the excitation source. A wavemeter is used to stabilize the laser's absolute frequency about a frequency setpoint or to acquire laser frequency values during acquisition of spectra profiles. The laser power was measured with a power meter and is used in post-processing the data to correct the acquired fluorescence signals. A short pass filter ($\lambda_0 = 650$ nm) is positioned prior to injection into the fluorescence chamber and is used to pass the laser beam and block the higher wavelength fluorescence generated from the DCM dye within the laser cavity. The laser beam is directed into the fluorescence

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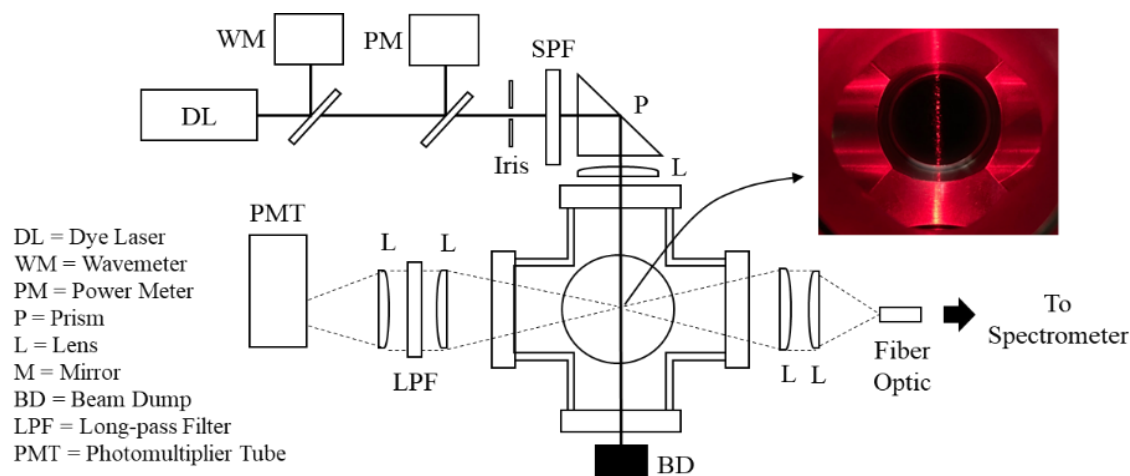


Figure 2: Illustration of the optical excitation and detection system. An image of the fluorescence chamber with the laser beam is shown.

chamber with a combination of beam steering and focusing optics. A beam dump located at the bottom of the chamber blocks the further propagation of the laser beam. HNO fluorescence photons were collected and detected with two co-linear arms positioned orthogonal to the incident laser beam. The first arm filtered the fluorescence with a long pass filter ($\lambda_0 = 680 \text{ nm}$) and detects all fluorescent photons with a photomultiplier tube (PMT). The electrical current output from the PMT is passed through an RC low-pass electronic filter ($\Delta f = 0.6 \text{ Hz}$), suppressing large quantities of high frequency noise. The final signal voltage is recorded with a DAQ. The second arm collects and launches the resulting fluorescence photons into a fiber optic coupled to a high-resolution spectrometer equipped with a cooled CCD. The spectrometer arm provides additional spectral selectivity, allowing LIF emission spectra to be measured.

The entire experimental system is controlled with an in-house written LabVIEW vi which records all relevant data including temperature, chamber pressure, water flow rate, HAN flow rate, laser frequency, laser power, mass signal at $m/z = 30$, mass signal at $m/z = 44$, and the fluorescence signal from the PMT. The acquisition of LIF emission spectra was accomplished with Lightfield software (Princeton Instruments) in separate experiments.

3. Results and Discussion: HNO Fluorescence Detection

3.1. Laser-Induced Fluorescence Excitation Profiles of Nitroxyl (HNO)

The first comprehensive spectroscopic analysis of HNO was conducted by Dalby in 1958.³⁶ Later works by Ramsay³⁷ and Dixon^{38–40} expanded on this early work and provided the necessary spectroscopic data for line assignments conducted within this work. Based on these early works, as well as other reports,^{38,41–47} three optical regions were selected for investigation. The first involves the $\tilde{A}^1A'' - X^1A'$ (100 – 000) transition at $\sim 624 \text{ nm}$, the second involves the $\tilde{A}^1A'' - X^1A'$ (020 – 000) transition at $\sim 626 \text{ nm}$, and the third involves the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at $\sim 642 \text{ nm}$. The standard (v_1, v_2, v_3) formalism used here represents the vibrational modes v_1 (N-H stretching), v_2 (N=O stretching), and v_3 (H-N=O bending).

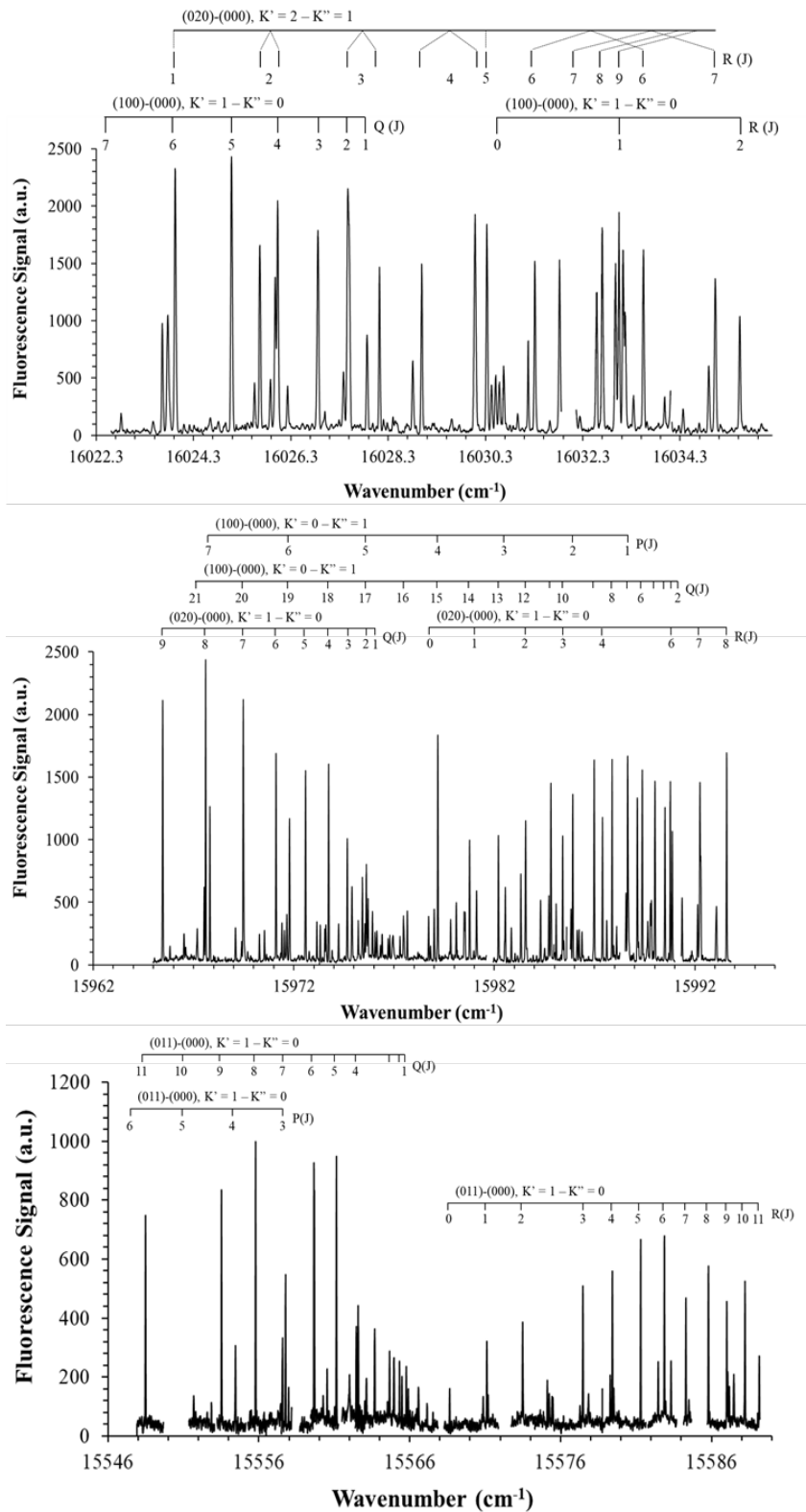


Figure 3: HNO fluorescence excitation profiles: TOP) $\tilde{A}^1A'' \leftarrow X^1A'$ (100 - 000), MIDDLE) $\tilde{A}^1A'' \leftarrow X^1A'$ (020 - 000), BOTTOM) $\tilde{A}^1A'' \leftarrow X^1A'$ (011 - 000). Flow rate = 150 nL/s, Temperature = 440 K.

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In a preliminary study, we acquired extended LIF excitation scans of HNO covering the three spectroscopic regions noted above. This was necessary in order to identify the most analytically optimal excitation transition. For this study, the thermal decomposition system consisted of a 40 μm porous 316-stainless-steel (316-SS) disk, a flow rate of 150 nL/s, and a temperature of 440 K. The resulting HNO fluorescence signal from the PMT and absolute frequency from the wavemeter were recorded. Since the single-mode dye laser used for the current study has a maximum 60 GHz mode-hop free tuning range, multiple 60 GHz scans from each region were necessary.

The resulting LIF excitation spectra for the three spectral regions are shown in figure 3 (Top = $\tilde{A}^1A'' - X^1A'$ (100 – 000), Middle = $\tilde{A}^1A'' - X^1A'$ (020 – 000), Bottom = $\tilde{A}^1A'' - X^1A'$ (011 – 000)). Unfortunately, a few spectral gaps exist in the data, however, this was not considered limiting to the data analysis and consideration of optimal excitation transition. Upon examination for excitation spectra acquired, the $\tilde{A}^1A'' - X^1A'$ (011 – 000) transition at ~ 642 nm yielded the weakest fluorescence signal relative to the $\tilde{A}^1A'' - X^1A'$ (020 – 000) and $\tilde{A}^1A'' - X^1A'$ (100 – 000) transitions. Furthermore, it was observed that tuning the laser to 642 nm increased the amount of background signal.

Upon closer experimental inspection of the most intense lines observed in figure 3 (Top and Middle), the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition at $15969.444 \text{ cm}^{-1}$ was determined to be the most optimal for our system. It should be noted that this transition was selected for our specific system given the distribution of populations among the lowest rotational levels and quantum state transition probabilities. Systems with different thermal and collisional environments relative to the one examined here may require a different transition to probe and would have to be determined independently.

It is important to note here that not all spectral lines observed in figure 3 have been identified. While its likely these lines are unidentified HNO lines from higher rotational quantum states, it is possible these lines originate from a molecular species other than HNO. The identification of these lines is important and the subject of ongoing research, however, such work is beyond the scope of the current study.

3.2. The HNO $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) Transition

To obtain reliable HNO fluorescence data over long experimental timescales requires locking the dye laser's frequency to the center of the desired optical excitation transition. The work reported here involved the use of a wavemeter, as shown in figure 2, to lock the laser absolute frequency to a predetermined setpoint. To determine this frequency setpoint, accurate and precise knowledge of the transitions profile center is required. To achieve this, we measured the spectral profile of the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition with a slow frequency scan, thus obtaining a high density of experimental data for the selected spectral transition. The fluorescence excitation profile for the selected transition is shown in figure 4 (left) and is denoted **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000), $K' = 0 - K'' = 1$, Q(20) transition and is denoted **B**. This profile was post processed with an in-house written Matlab curve fitting routine which provided the center of the transition, ν_0 . Given the low-pressure ($P \sim 85 \text{ mTorr}$) and low temperature ($T \sim 300 \text{ K}$) environment of the experimental chamber, Doppler broadening was assumed to dominate the spectral profile. The residual to the curve fit is shown below the profile and indicates a reasonably good fit. From analysis of the spectral profile, the transition centers were found to be $\nu_0 = 15969.444 \text{ cm}^{-1}$ and $\nu_0 = 15969.364 \text{ cm}^{-1}$ for **A** and **B**

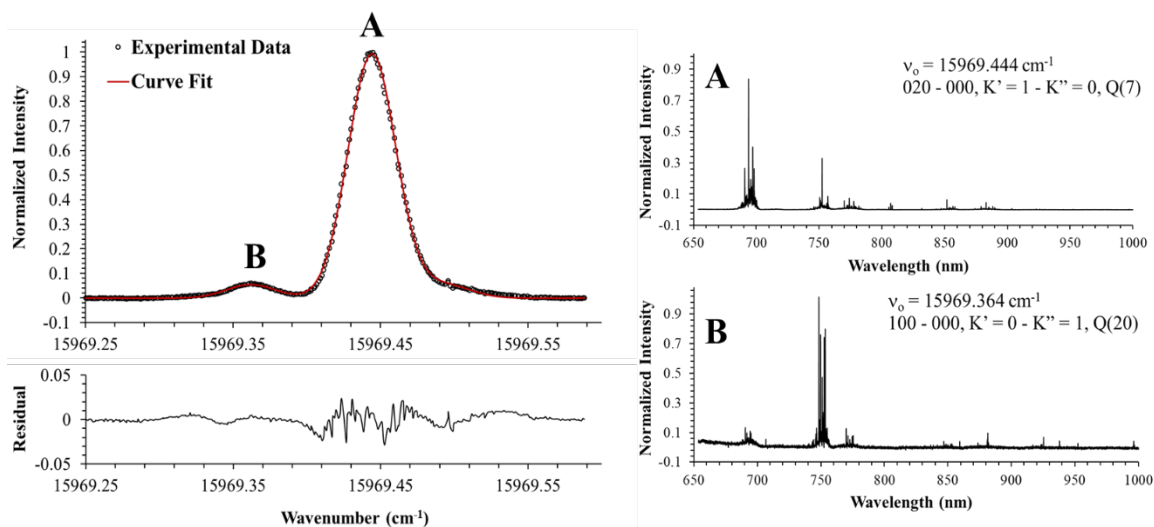


Figure 4: (Left) HNO fluorescence excitation profile for the selected $\tilde{A}^1A'' \leftarrow X^1A'$ (020-000), $K' = 1 - K'' = 0$, Q(7) transition denoted as **A**. Also shown is the $\tilde{A}^1A'' \leftarrow X^1A'$ (100-000), $K' = 0 - K'' = 1$, Q(20) transition denoted as **B**. (Right) HNO fluorescence emission profiles measured with the laser tuned to the center of each respective transition, **A** and **B**. Data was collected with a flow rate of 150 nL/s and temperature of 440 K.

respectively. Furthermore, profile analysis determined the gas kinetic temperature to be $T = 347 \text{ K}$ and is considered a reasonable value give a decomposition temperature of 440 K.

Also shown in figure 4 (right) are fluorescence emission profiles measured from the spectrometer arm of the fluorescence detection chamber. These spectra were acquired with the laser tuned to the center of each respective transition. Line analysis of the emission spectra shown in figure 4 (right) further confirms the signal collected originates from the HNO radical and highlights the selectivity of the LIF detection method utilized for this work. Finally, from both fluorescence excitation and emission profiles, no spectral interferences have been observed confirming the resulting signal measured is due to HNO fluorescence.

3.3.Laser-Induced Fluorescence Saturation Curve for Nitroxyl (HNO)

The magnitude of a molecular fluorescence signal is directly related to the amount of energy deposited into the system, with the signal increasing linearly until the signal deviates from linearity. These linear deviations can manifest from a number of mechanisms such as optical saturation, photo-bleaching, photo-ionization, or photo-dissociation to name a few. Typically, it is ideal to saturate the probed transition since this condition produces the maximum fluorescence signal and is independent of laser intensity fluctuations, yielding an optimal signal-to-noise ratio (SNR). To diagnose our system, fluorescence was measured for a fix set of experimental conditions as a function of incident laser spectral irradiance, with the results shown in figure 5. These results indicate the system has not reached saturation with a maximum incident laser spectral irradiance of $684 \text{ W cm}^{-2} \text{ Hz}^{-1}$. While it is sometimes preferred to saturate the optical transition, the small level of background signal from laser scatter results in a non-optimal signal-to-background ratio (SBR) under saturation conditions. It was found experimentally that the ideal spectral irradiance to use is between $150\text{-}200 \text{ W cm}^{-2} \text{ Hz}^{-1}$ which resulted in the most ideal SBR.

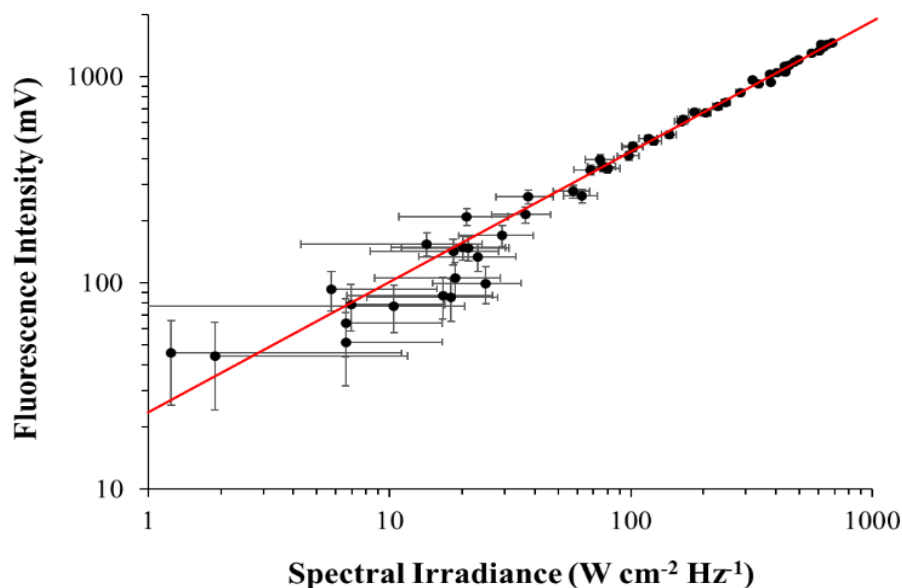


Figure 5: Fluorescence saturation curve for the $\text{HNO } \tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition.

Since the laser power is recorded throughout each experiment, all fluorescence data has been corrected to account for slight differences in laser powers used between experiments.

4. Results and Discussion: HNO from Decomposed HAN Vapor

4.1. Material Interaction

Examination of the generation of HNO from the thermal decomposition of vaporized HAN was initiated with the detection system set to optimal experimental conditions. We limited this preliminary study to examine quartz, 316-stainless steel (316-SS), and aluminum. Images and properties of the porous disks used are shown in figure 6. HAN was injected into the thermal decomposition system at a controlled flow rate of 100.0 nL/s and the temperature of the heating block was slowly ramped from 350 K to 480 K at a rate of 4.3 K min⁻¹. Currently our system possesses an upper limit of 480 K and is due to the

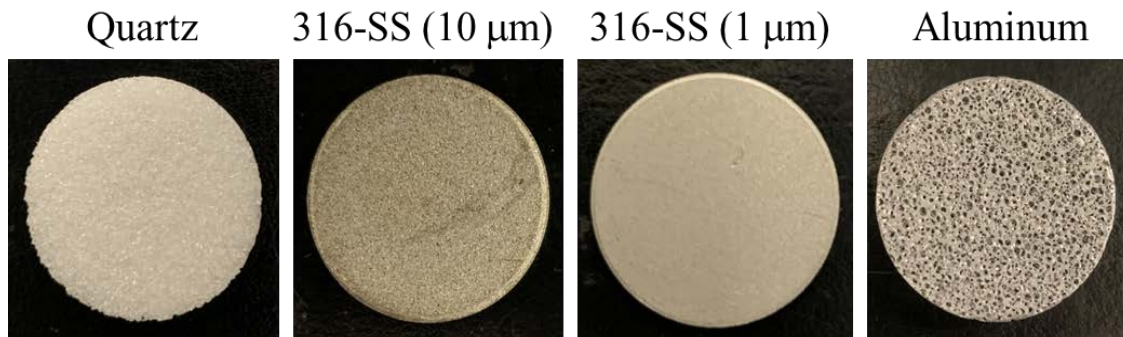


Figure 6: Images of the porous disks used to evaluate HNO production from HAN decomposition. Quartz porosity = 160-250 μm, thickness = 4 mm. 316-SS porosity = 10 μm and 1 μm, thickness = 1.6 mm. Aluminum porosity = 1.6 mm, thickness = 4 mm. All disks have a 25 mm diameter.

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thermal limitations of the Kyflon o-rings used to secure a vacuum tight seal around the quartz tube and aluminum heating block.

The results from the examination of each material is shown in figure 7. Initially, data was collected with no porous disk inserted into the system. This provides a baseline of HNO production due to either HAN decomposition occurring in the bulk liquid or a potential interaction between vaporized HAN and the quartz tube and/or Macor spacer. Interestingly, HNO is still easily detected when no disk is inserted at temperatures as low as 350 K. As the temperature is increased, HNO production increases with a maximum value at 480 K which is the maximum temperature allowed by the experimental system.

The first material examined was a porous quartz disk as shown in figure 4. Quartz material was chosen since it is commonly considered a chemically inert material. Therefore, examining the temperature dependent production of HNO using a porous quartz disk would allow us to examine the magnitude of HNO production due to the interaction of vaporized HAN and a thermal surface in the absence of a reactive and/or catalytic reaction. The data in figure 7 shows that the HNO density from a quartz disk increases with temperature and is enhanced by a factor of ~ 2 relative to no disk present. Interestingly, temperatures above ~ 455 K showed a loss in HNO production with densities returning to near baseline levels. The HNO loss mechanism is currently unknown but can be attributed to two general possibilities 1) HNO produced continues to react with the surface or other molecular gas phase species to produce additional decomposition products or 2) vaporized HAN is no longer producing HNO and is now producing other decomposition products. Indeed, additional studies would be required to identify the decomposition products.

To examine the potential of a reactive and possibly catalytic reaction between vaporized HAN and a heated surface, two porous metal disks were examined. For this study 316-SS and aluminum were chosen. The data in figure 7 clearly shows vaporized HAN exhibits strong reactivity with both metals examined. The porous 316-SS disk, with a pore size of $10\text{ }\mu\text{m}$, demonstrates a significant HNO density enhancement with increasing temperature until ~ 430 K after which an HNO loss mechanism begins to dominate. As with

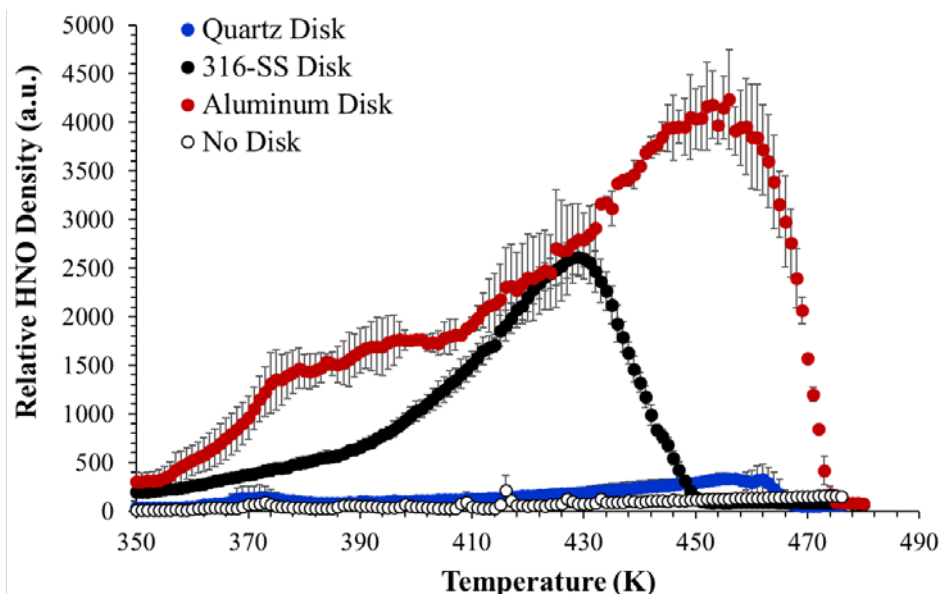


Figure 7: Relative HNO density measured with no disk, 316-SS, aluminum, and quartz disks. Flow rate for all data was 100 nL/s.

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the quartz data, this loss mechanism is currently unknown and would require further experiments. For perspective, the insertion of a 316-SS disk increased the density of HNO by a factor of ~1960% relative to no disk present.

The choice of aluminum was based on a HAN material compatibility study where various materials were immersed in a 60% HAN solution and heated to 338 K (65 °C).⁴⁸ The results from this compatibility study showed that aluminum was by far the most reactive material, thus, it was chosen for this initial study. Consistent with the reported material compatibility study, the aluminum data in figure 7 resulted in the largest relative density of HNO, with an enhancement of ~3150% relative to the no disk data. The shape of the HNO profile with an aluminum disk is quite different compared to the 316-SS data. The aluminum data peaks at ~455 K before an HNO loss mechanism begins to dominate. This behavior is similar to the quartz data which also peaks at ~455 K before a loss mechanism dominates. As noted in figure 6, the quartz and aluminum disks have large pore sizes while the 316-SS disk is significantly smaller. The thickness of the quartz and aluminum disks are also similar, 4 mm, while the 316-SS disk is much thinner, 1.6 mm. Since the generation of HNO from vaporized HAN is clearly a surface interaction, it is reasonable to infer the shape and magnitude of the HNO curves in figure 7 are influenced by the physical dimensions of the porous disk. This possibility will be explored below.

4.2. Generation of HNO from HAN Decomposition: HNO Density vs. Flow Rate

The HNO data presented in figure 7 was collected with a flow rate of 100 nL/s. One concern developed during the course of this study was the possibility of a cooling effect imposed on the porous disk as the HAN vapor flow through the system. As noted in the experimental section (2.1.) the systems temperature was recorded from an embedded thermocouple positioned within the heating block and close the capillary. While these values accurately reflect the temperature the capillary and bulk HAN liquid flowing through the capillary, it may not represent the true temperature of the inserted disk as the HAN solution is vaporized. Therefore, the flux of vaporized HAN and water passing through the disks could have a cooling effect which would influence the kinetics of HNO

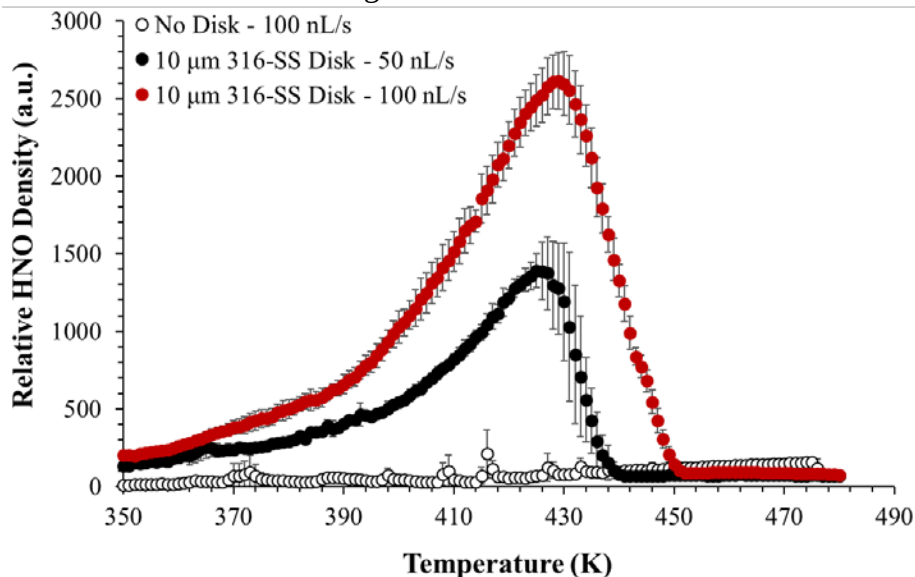


Figure 8: Relative HNO density measured with 316-SS disk with 10 μm pore size and two flow rates.

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production and by extension the magnitude and shape of the resulting HNO density curves shown in figure 7. To explore this possibility, HNO density data was collected with the 316-SS disk at two different flow rate, 50 nL/s and 100 nL/s, with results shown in figure 8. If a cooling effect is occurring, then the ratio of the relative HNO densities will differ from the ratio of the flow rates. The ratio of 100 nL/s data to the 50 nL/s data is found to be 1.9 ± 0.3 and is statistically identical to the expected value of 2. From this experiment we conclude that the HNO density produced from the thermal decomposition of vaporized HAN is linear with flow rate, thus, there is a negligible cooling effect occurring at flow rates less than 100 nL/s. A similar experiment would be required if higher flow rates are required.

While the possibility of a cooling effect was initially assumed to be negligible, it was necessary to validate this assumption. Since the entire thermal decomposition system is heated to the desired setpoint at any given time, including the HAN solution within the capillary, the vaporized HAN and water molecules will have some residual thermal energy before interacting with the heated porous disk. While this appears to be the case with the current experimental configuration with a capillary-disk spacing of 10 mm, larger distances may allow the vaporized molecular species to thermally cool and potentially induce a mild cooling effect. This could be compensated for by simply adjusting the temperature with flow rate, however, the system would need to be calibrated prior to operation.

4.3.Generation of HNO from HAN Decomposition: HNO Density vs. Porosity

As noted above, it is reasonable to expect the production of HNO from the surface decomposition of vaporized HAN to be dependent on the physical structure of the porous disks. In order to assess this possibility, we examined two 316-SS disks with different pore sizes, 1 μm and 10 μm , and equal thicknesses. As shown in figure 9, both the shape and magnitude of the HNO density produced from the two disks are significantly different. From an assessment of the results in figures 7 and 9, there appears to be a relationship between the temperature which HNO density production peaks and the pore size of the disks used. The larger disks utilized in this work, quartz and aluminum, both produced a peak HNO density at a temperature of ~ 455 K, while the 10 μm and 1 μm disks produced HNO density peaks at ~ 430 K and 405 K, respectively. It should also be noted that the quartz and aluminum disks are 4 mm thick while the 316-SS disks are 1.6 mm thick. Regardless, there appears to be a correlation which could potentially be connected to the available surface area.

A final interesting observation made from the data in figure 9 are the rates at which the HNO density decreases as the temperature exceeds its peak production. Similar to the mechanism which produces the observed HNO density, the HNO loss mechanism is similarly influenced by the physical structure of the porous disks utilized. The largest pore size, aluminum, has a rapid loss in HNO production followed by the 10- and 1- μm disks, respectively. Clearly this preliminary data induces a number of very interesting questions which are difficult to answer with the limited data collected to date. Indeed, additional experiments are currently being designed to provide insight into the mechanism of HNO production from a heated porous material.

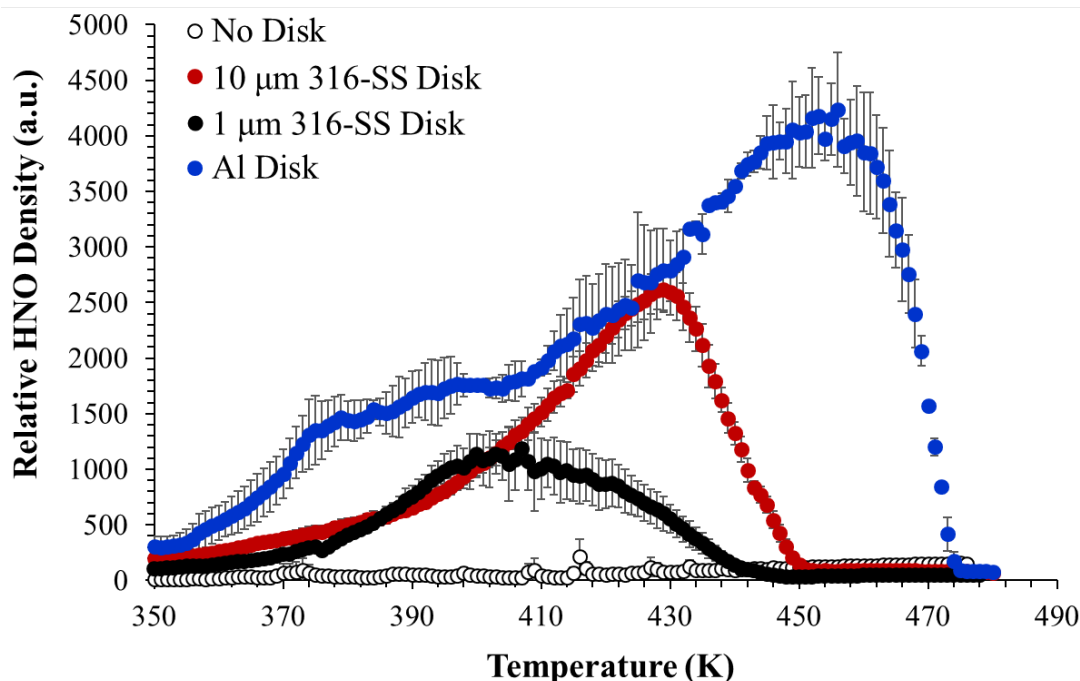


Figure 9: Relative HNO density as a function of temperature for two 316-SS disk, aluminum disk, and no disk. The flow rate for each experiment was 100 nL/s.

4.4. Comment on HNO Detection vs Quantification

Throughout this work we reported on the relative density of HNO produced from the interaction of vaporized HAN with heated porous disks. Ideally, we would like to acquire absolute HNO number densities in order to compare the amount of HAN injected into the system, providing an estimate on the molar conversion of hydroxylamine to HNO. Typically, an analytical standard is used to calibrate the detection system, thus allowing the acquired voltage signal to be converted into a number density. Unfortunately, HNO is a highly reactive radical with no off-the-self analytical standards available. Furthermore, calibrating the system with analytical standards will only yield concentration values for the input solution and would not apply to the absolute number density in the vapor phase at the point LIF is occurring.

A common approach to converting an acquired LIF signal to an absolute number density is to optically calibrate the detection system and then convert the voltage signal to a spectral radiance, $\text{W cm}^{-2} \text{Hz}^{-1}$. These spectral radiance values can then be used in appropriate fluorescence equations to calculate the absolute number density. Unfortunately, this approach is both experimentally challenging and requires knowledge of HNO spectroscopic constants. While we possess both the experimental equipment and expertise to optically calibrate our detection system, the spectroscopic constants for the HNO molecule are unknown, thus, precluding this approach.

In the absence of known HNO spectroscopic constants, another common approach to calibrate the system is to use absorption spectroscopy to quantify HNO and cross-calibrate the LIF detection system. Absorption is advantageous since it does not require calibration of the optical system and experimentally only requires the ratio of signal with and without the absorber present. Additionally, if the path length and absorption cross-section are known, calculation of the HNO number density is fairly straightforward. Unfortunately,

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the only HNO absorption cross-section reported in the literature is small and does not allow for direct standard absorption measurements to be applied. Fortunately, cavity enhanced absorption techniques (cavity ring-down spectroscopy, off-axis integrated cavity output spectroscopy, laser intracavity absorption spectroscopy, and incoherent broadband cavity enhanced absorption spectroscopy) and frequency modulation spectroscopy techniques have been utilized to directly measure the absolute number density of HNO molecules. Moreover, initial calculations based on estimated HNO number densities suggest cavity enhanced absorption techniques should be more than sufficient to detect and quantify HNO within our experimental system. Assuming the experimental system is designed properly, absorption and LIF measurements can be acquired simultaneously, thus allowing the LIF detection system to be cross calibrated with the calculated absorption number density values. The primary reason LIF detection and quantification is preferred over cavity enhanced absorption is the potential for LIF to be more sensitive and possess a lower detection limit. Additionally, the analog output from the current LIF system demonstrates a linear dynamic range at least 4 orders of magnitude with the current filtering and data processing techniques utilized.

Unfortunately, the cavity enhanced absorption techniques noted require expensive high reflectivity mirrors, high precision mirror mounts, and additional system components which are currently inaccessible to our lab. An effort is currently underway to explore this approach.

5. Summary and Conclusions

We have conclusively demonstrated for the first time that the nitroxyl radical, HNO, is produced from the thermal decomposition of HAN. We have presented an assessment on the use of LIF detection of HNO generated from the thermal decomposition of HAN. Three excitation regions were examined: $\tilde{A}^1A'' \leftarrow X^1A'$ (100 – 000) at $\lambda \sim 624$ nm, $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000) at $\lambda \sim 626$ nm, and $\tilde{A}^1A'' \leftarrow X^1A'$ (011 – 000) at $\lambda \sim 642$ nm. Based on extended spectral excitation scans of these three regions we determined the $\tilde{A}^1A'' \leftarrow X^1A'$ (020 – 000), $K' = 1 - K'' = 0$, Q(7) transition to be optimal for our specific system. Furthermore, from the optical saturation curve and assessment of the background signal, we determined a region of laser spectral irradiances which provide optimal SNR and SBR, providing the best achievable detection limit for our system. The contribution to the background signal was primarily from small levels of laser scatter leaking through long-pass filter and reaching the PMT.

Initial examination of the production of HNO from the thermal decomposition of HAN utilizing a glass-lined stainless-steel capillary and heated porous disks yielded significantly different results depending on whether the disk was present or absent. In the absence of a heated material, HNO was still detectable albeit at relatively low levels. In the presence of a porous quartz disk, HNO production was enhanced but only by a factor of ~ 2 , suggesting a mild reactivity between vaporized HAN and glass/Macor material. Conversely, when 316-SS and aluminum disks were inserted, the production of HNO was significantly enhanced, with aluminum producing a maximum 3150% HNO density enhancement relative to no disk present and 316-SS producing a 1960% HNO enhancement. Indeed, the experimental results presented here indicate a strong propellant-material interaction in a catalytic manner.

The HNO density profiles reported here have also revealed that the physical characteristics of the porous material influences the magnitude of the temperature dependent profiles. Specifically, there appears to be a correlation between the shape of the HNO density profile and the pore size, or available surface area, of the heated material, although, more work is needed in order to confirm this observation. We also examined the possibility of a cooling effect imposed by the vaporized HAN and water emerging from the heated capillary. Examination of HNO density at two different flow rates confirmed that the system behaves linearly with flow rate and any cooling effect is negligible at flow rates less than 100 nL/s.

6. Future Work

The research reported here clearly demonstrated the ability to use LIF to detect HNO generated from the vaporization and decomposition of HAN. Unfortunately, we did not possess the ability to convert the relative HNO density values into absolute HNO number densities. Future work will focus on developing a cavity enhanced absorption spectrometer capable of sensitively measure the absorption signal from HNO. This signal will be converted into an absolute number density via Beer-Lambert Law and utilized to cross calibrate the LIF optical system. A complete analytical assessment of the two detection and quantification systems will be conducted, with linear dynamic ranges and detection limits determined.

As discussed above, the material interaction study was preliminary and conclusively demonstrated that a heated porous material can be used to generate substantial quantities of HNO. However, the materials utilized were limited in scope due to fiscal constraints. Future work will examine additional porous materials as well as the physical characteristics of these materials, with the goal of producing the largest quantity of HNO at the lowest possible temperature. Indeed, these would be the ideal application conditions were a feed gas is produced at the lowest temperature, reducing the power requirements of the spacecraft.

Finally, while the current study focused the detection of HNO, various other molecular species are expected to be generated from the interaction between a HAN vapor and a heated porous material. Among these species includes nitrous acid (HONO), nitrogen dioxide, and nitric oxide. Each of these molecules could be detected and quantified with the cavity enhanced absorption spectrometer currently under development. The combination of these data would provide an enhanced understanding of the molecular integrity of HAN, its decomposition products, and its potential future as an electric propulsion monopropellant.

Acknowledgments

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