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Major Goals: Reliable strategies for predicting the environmental fate, long-term stability, and mitigation of aerosolized compounds and chemical warfare agents (CWAs) requires a detailed understanding of the physical and chemical interactions that occur at the gas-surface interface. Therefore, instrumental methods have been developed for the purpose of studying the vapor-phase chemistry, characteristics of liquid aerosols, and the surface chemistry of model aerosols. These two instrumental methods will be critical in the collection of fundamental spectroscopic data important for the study of particulate and aerosol chemistry. The instruments will be employed to study simulant (at Virginia Tech) and agent (at Edgewood Chemical Biological Center) chemistry under real-world atmospheric conditions.

The specific achievements for this project have been two-fold:

(1) Designed and constructed a rotating drum environmental chamber (atmospheric cloud simulation chamber, ACSC) for suspending aerosols and studying the vapor via stand-off spectroscopic methods. The rotating drum enables experiments that probe chemistry in the presence of a prolonged suspension of aerosolized agent or simulant. The drum is coupled with cavity ring down spectroscopy (CRDS) for highly sensitive in situ absorbance spectra. Ambient environments with varying concentrations of pollutants (e.g., CO2, NOx, SOx, etc.) can be introduced for direct observation of reactive processes that aerosols may undergo in the atmosphere. The rotating drum and CRDS instruments have been fully constructed, tested, and used for initial studies employing CWA simulants at Virginia Tech. Following these initial tests, an identical system was transported to Edgewood Chemical Biological Center, where it has been re-assembled and installed into a surety hood for agent work.

(2) Designed and constructed a complimentary instrument to the rotating drum for the study of molecules adsorbed to the surface of particulates. While the rotating drum capability highlighted here enables one to track gas-phase species formed during the evaporation of products from an aerosol, another instrument has been developed to monitor molecules adsorbed to the surface of particulates. This has been accomplished by employing transmission infrared spectroscopic methods through a sample of particles that is suspended within an environmental chamber. In this instrument, infrared spectroscopy tracks bond breaking and formation on the surface while a mass spectrometer monitors products desorbing from the surface and into the gas phase. The instrument has been installed at ECBC following appropriate benchmark testing at Virginia Tech.

Accomplishments: See Uploaded Document

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Training Opportunities: During the period of performance, a Cecilia Smith, now a fifth-year graduate student, completed her training in the design, construction, and operation of the rotating drum/CRDS instrument. In addition, a research scientist from ECBC, Monica McEntee, visited our group at Virginia Tech to be trained on the operation of the stationary-particle instrument for gas-surface particulate chemistry. Darren Driscoll, the primary architect responsible for the design and construction of the instrument, trained Monica. Once trained, Monica led the effort, along with Darren, in the disassembly, move, and re-construction of the instrument at ECBC.

Results Dissemination: Our work has been disseminated through presentations at scientific meetings (ACS National Meeting), seminars at universities (Washington State University), and in scientific publications (Technical Report at Edgewood Chemical and Biological Center). Most importantly, I was co-chair and organizer for a symposium at the Spring 2016 Meeting of the American Chemical Society on the topic of Catalysis a the Sub-Nanometer Scale. This meeting served as an excellent venue to discuss our science, learn about other work in the field, and develop new ideas.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: This program involved extensive interactions and collaborations with Edgewood Chemical and Biological Center. Most importantly, Dr. Erin Durke and Dr. Monica McEntee were technical advisors during the course of instrument design, construction, and benchmark testin. Two graduate students from Virginia Tech, Mr. Darren Driscoll, and Ms. Cecilia Smith, visited ECBC to help complete instrument construction within the laboratories at ECBC.

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)
Participant: Darren Driscoll
Person Months Worked: 5.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Cecilia Smith
Person Months Worked: 5.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
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Participant: John Morris
Person Months Worked: 2.00 **Funding Support:**
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National Academy Member: N
Other Collaborators:

RPPR Final Report
as of 13-Jun-2018

Development of Instrumental Methods for Particulate and Aerosol Surface Science

Final Report

W911NF1420074

John R. Morris, Virginia Tech

I. Overview

Reliable strategies for predicting the environmental fate, long-term stability, and mitigation of aerosolized compounds and chemical warfare agents (CWAs) require a detailed understanding of the physical and chemical interactions that occur at the gas-surface interface. Therefore, instrumental methods have been designed and constructed that will be employed to study the vapor-phase chemistry, characteristics of liquid aerosols, and the surface chemistry of model aerosols. The two instruments developed under this program will be critical in the collection of fundamental spectroscopic data important for the study of particulate and aerosol chemistry.

Below, the two instruments developed under this grant are described in detail. Key experimental measurements are also reviewed, which provide benchmarks for each instrument.

II. Atmospheric Cloud Simulation Chamber

Currently, researchers are using a variety of techniques to study aerosol chemistry in the atmosphere through direct monitoring, fundamental vacuum studies, and cloud chambers. Each approach has drawbacks: atmospheric monitoring lacks experimental control, vacuum studies are generally performed on a fixed particle bed under non-atmospheric conditions, and particles quickly settle out or deposit on the walls of cloud chambers. The atmospheric cloud simulation chamber (ACSC) provides the opportunity to study heterogeneous reactions between volatile organic compounds and solid or liquid aerosols. We designed our instrumentation to extend particle suspension lifetime while monitoring *in situ* gas composition spectroscopically under "operando" atmospheric conditions.

The ACSC, designed for studying particle growth and chemistry under atmospheric conditions, is based on the concept of a *Goldberg Drum*. For the past 50 years, Goldberg Drums have been used to achieve particle suspensions in air (e.g., days, months). The drum enables one to observe, in a laboratory setting, aerosol dynamics in an environment analogous to our atmosphere, where particles remain suspended for extended periods of time. The basic concept is that a slowly rotating cylinder (1 m × 0.6 m) prevents particles from settling and creates a stable atmosphere.

II. A. Instrumental Design

Project Criteria. The ACSC employs a rotating drum and cavity ring down spectrometer to create a stable particle suspension while monitoring the gas composition *in situ*. Key design criteria, and the corresponding design solutions are provided in Table 1. The following paragraphs detail each aspect of the design. Figure 1 provides an assembly drawing of the rotating drum component of the instrument.

Table 1. List of experimental criteria and approaches for studying heterogeneous chemistry of aerosols.

Project Criteria	Experimental Design and Approach
Long term particle suspensions	Rotating drum
Monitor gas phase species	Cavity ring down spectroscopy
Minimal particle contamination of optics	Isolated on-axis optical components
Uniform aerosol introduction	Distributed injection ports
Ability to alter and monitor humidity	MFC controlled humidity introduction and relative humidity probe
Adaptable to future experiments	Modifiable ports at four radii

Particle Suspension. Aerosol suspensions in experimental chambers are affected by a variety of phenomena including electrostatic forces, pressure gradients, inter-particle collisions, gravity and viscous drag from surrounding gas molecules. Slowly rotating the cylindrical chamber (0.5 – 10 RPM) increases the centrifugal viscous drag force to the same magnitude as the opposing gravitational force, resulting in an extended particle suspension lifetime. The extended lifetime permits multi-day experiments that simulate atmospheric particle transport over time. Optimal rotation speed varies depending on the density and size of the particles in question; however, ultrafine and fine particles have similar ideal rotation rates–between 1-2 RPM.

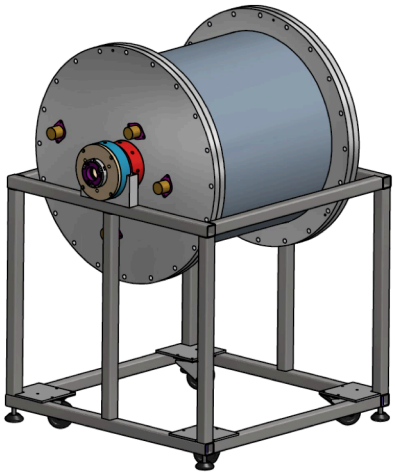

Figure 1. CAD schematic of the Atmospheric Cloud Simulation Chamber. The motor, belt, specific gas lines and gas-handling manifold are omitted for clarity.

Gas-phase Spectroscopy. The ACSC employs cavity ring down spectroscopy (CRDS) for sensitive *in situ* monitoring of gas molecules. CRDS is a multi-pass spectroscopic method that effectively increases the path length of the sample cell to enable detection below 10 ppb for certain species.

The spectrometer injects light from a pulsed tunable quantum cascade laser into an optical cavity that was established along the central axis of rotation for the drum. The intensity light within the cavity naturally decreases over time due to mirror losses and the absorbing medium present in the chamber. Equation 1 describes the exponential decrease of light intensity over time,

$$\frac{\mathrm{I}(\nu)}{\mathrm{I}_0(\nu)} = \mathrm{e}^{-(\frac{\mathrm{tc}}{\mathrm{L}}(\ln \mathrm{R}(\nu) - \sigma(\nu)\mathrm{Nd}))} \qquad (1)^1$$

where $I(\nu)$ is the intensity of light at a specific frequency, $I_0(\nu)$ is the initial light intensity after one pass through the optical cavity, t is time in microseconds, c is the speed of light in cm/μs, L is the distance between the highly reflective mirrors that define the optical cavity, $R(\nu)$ is the reflectivity of the mirrors at a particular frequency, $\sigma(\nu)$ is the frequency-dependent absorption cross section for one absorbing

medium, N is the number density or concentration of the absorbing medium, and d is the effective path length the light traveled.

Cavity ring down time describes the frequency dependent inverse decay constant ($1/k$), referred to as the "ring down time" or $\tau(\nu)$. Equation 2 describes the relationship between $\tau(\nu)$, mirror reflectivity ($R(\nu)$) and absorbing medium ($\sigma(\nu)Nd$). When the chamber contains no absorbing medium, only the highly reflective mirrors decrease the light intensity over time.

$$\frac{I(\nu)}{I_0(\nu)} = e^{-kt} \text{ where } \frac{1}{k} = \tau(\nu) = \frac{L}{c(1 - R(\nu) + \sigma(\nu)Nd)} \quad (2)$$

Equation 3 is used to extract absorbance due to the absorbing medium ($\sigma(\nu)Nd$) from $\tau(\nu)$, where $\tau_0(\nu)$ is the initial ring down time in the absence of an absorbing medium.

$$\frac{(\tau_0(\nu) - \tau(\nu))}{\tau_0(\nu)\tau(\nu)} \frac{L}{c} = \sigma(\nu)Nd \quad (3)$$

According to Beer's Law, individual components in a mixture additively absorb light and scale linearly with concentration of the absorbing medium (equation 4).

Chamber Design. The main chamber (MJ5GG28196) and faceplates (QF630-BF) were designed during the first several months of this program and machined by Kurt J. Lesker, Inc. Mountain Precision Tool Inc. modified the faceplates and custom manufactured the axle, fixed tube extension, end caps and aerosol ports, as highlighted in Figure 2. One end flange houses a Rotronic humidity/temperature probe (HC2-IE302) and a male VCR port (6LV-4-HVCR-1-6TB7) for an MKS absolute capacitance manometer pressure gauge (727A13TCE2FB). All welded VCR ports are high flow, solid construction, male, VCR fittings (6LV-4-HVCR-1-6TB7).

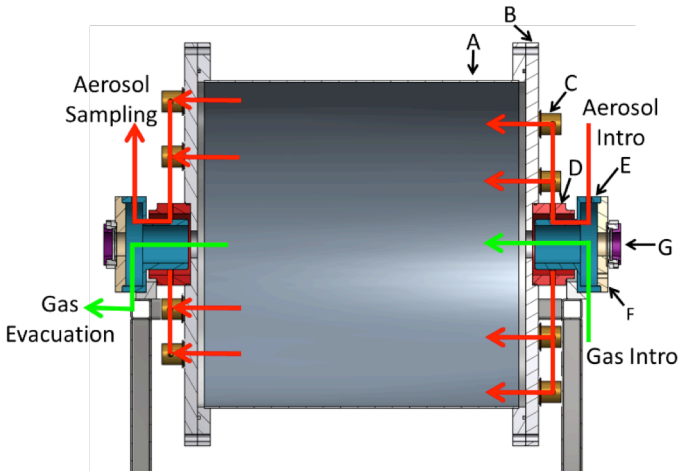

Figure 2. Cross-sectional schematic of the main ACSC chamber. Part A is the 600 L main chamber. Part B is the end plate modified to mount four aerosol ports (C) and the aerosol introduction port (D). The stationary tube extension (E) has six male VCR ports equally spaced around the larger diameter section. The CRDS optical mounts for the highly reflective mirrors (G), RH/T probe (not pictured here), and pressure gauge (not pictured here) are attached to the end plate (F). Aerosols flow through a 90^{O} tube welded between the introduction port and a hole bored in the smaller diameter section of the tube extension, which is aligned with a separate channel in the axle. The ports (C), connected to the axle via stainless steel tubing, are located at radii of 5", 7", 9" and 11". Background and analyte gases flow through ports on the tube extension and into the main chamber through a 2" hole in the end plate.

A VCR fitting is welded to each aerosol port and mounted to the faceplate. Aerosols are introduced directly into the chamber through stainless steel tubing connecting the port VCR fittings to the VCR fittings on the axle. A channel machined into the axle intersects with the fixed tube extension port allowing for aerosol introduction and sampling while the drum rotates. The fixed tube extension has five additional ports for various uses including gas introduction and chamber evacuation. One port is dedicated to evacuating the chamber.

Two double-walled ball bearings (VXB Bearing KA050CP0) pressed onto the outside of each axle provide smooth rotation. Three rotary seals (SKF 36740 LDS) hydraulically pressed into the axle keep the chamber airtight. The drum is rotated using a 1/8 HP parallel shaft DC gear motor (McMaster 6470K87) powered by an AC to DC, variable speed controller. A cut-to-length, ¾" wide timing belt (1840k4) and L-series quick disconnect pulley ensures minimal slipping while rotating the drum.

Optics Construction. The cavity ring down spectrometer (MIRVOC 2, Los Gatos Research, Inc.) was created by focusing pulsed laser light from a tunable quantum cascade laser (Daylight Solutions 11100-UT, 9 µm to 12 µm) through a 5 mm hole in the reinjection mirror (Newport 20DC500ER.1) and into the optical cavity formed by two-2" highly reflective ZnSe mirrors (II-VI Infrared, Inc.). The reinjection mirror reflects light transmitted through the introduction mirror with each round trip of the laser pulse, increasing the sensitivity by an order of magnitude. A 2" diameter ZnSe meniscus lens (ULO Optics 20ZLF43/10.0 µm) collected and focused light transmitted through the exit mirror onto a photovoltaic HgCdTe (MCT, Teledyne J19D11-M204-R01M-60) detector. The MCT signal is amplified by 10^5 then digitized by a National Instruments acquisition board (NI-DAQ). A LabVIEW program on the computer records the decrease in light intensity over time for approximately 20,000 traces at each frequency before calculating the ring-down time, (τ). The program plots the ring-down time (τ) versus time (s) or wavenumber (cm^{-1}) depending on the scan type. Figure 3 depicts the optical arrangement.

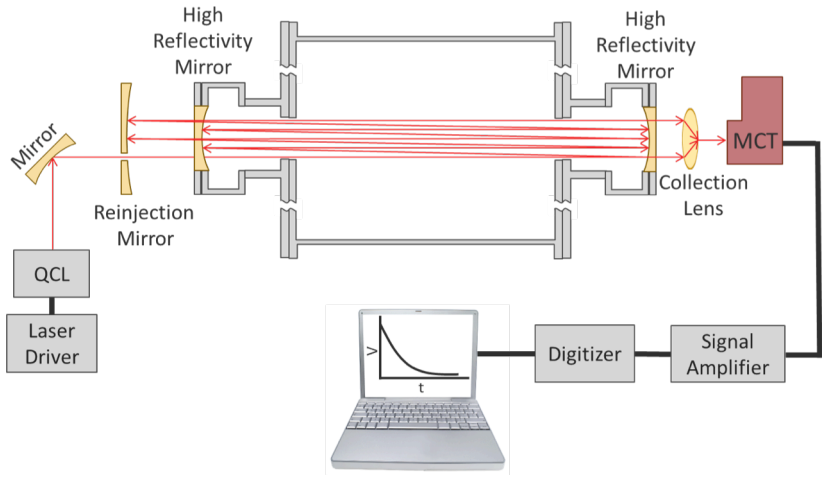

Figure 3. Schematic of the optics involved in acquiring CRDS spectra. The laser light is focused into the cavity through a 3 mm hole in the reinjection mirror using flat mirrors. Two highly reflective mirrors create the optical cavity that produces the ring-down. A lens collects the exiting laser light for detection by an MCT detector.

II. B. ACSC Benchmarks

Aerosol Suspension Characteristics: monodisperse 1 µm particles. Fine particulate matter ($PM_{2.5}$) research requires the ability to extend the lifetime of the aerosol suspension. The ACSC instrument addresses this issue with the rotating main chamber. A series of experiments rotating the chamber at different rates demonstrates the ACSC capability to study particle suspensions for extended durations.

Each experiment began by filling the main chamber with ultrahigh purity nitrogen to atmospheric pressure, approximately 705 Torr, using a metal sealed mass flow controller (MKS GM50A013503SBV020). The nitrogen-filled chamber served as the spectroscopic and particle background. The chamber was evacuated to approximately 350 Torr while rotating at the desired speed in preparation for aerosol introduction. Ultra high purity nitrogen flowed through a Collison 6-jet nebulizer filled with 30 mL deionized water and 5-10 drops of 1% monodisperse 0.994 ± 0.012 µm polystyrene particles (Duke Standards 4009A) at 20 psi. The aerosols were then flowed through a TSI 3062 diffusion dryer before entering the main chamber. A TSI 3080 Aerodynamic Particle Sizer (APS) sampled the particle suspension approximately every hour for 12-36 hours. Particle sizers require atmospheric pressure upstream while sampling at 1 SLPM; therefore a port opposite of the particle sizer was opened to lab air with a Parker Balston particulate matter filter (9922-05-CQ), which filtered 99.98% of the particles >0.5 µm. A series of control studies using the CRDS and particle sizers showed that opening the filter to lab air while sampling had negligible effect on the gas-phase composition inside

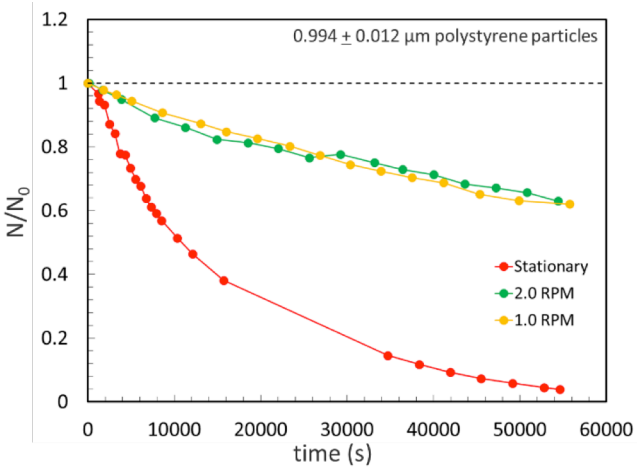

Figure 4. Long-term particle suspension efficiency (N/N_0) while the chamber rotates at 1 RPM (yellow) and 2 RPM (green) compared to a stationary chamber (red). The particles are 0.994 ± 0.012 µm monodisperse polystyrene latex spheres. Each data point represents a sample taken with the APS and the lines are added to help guide the eye.

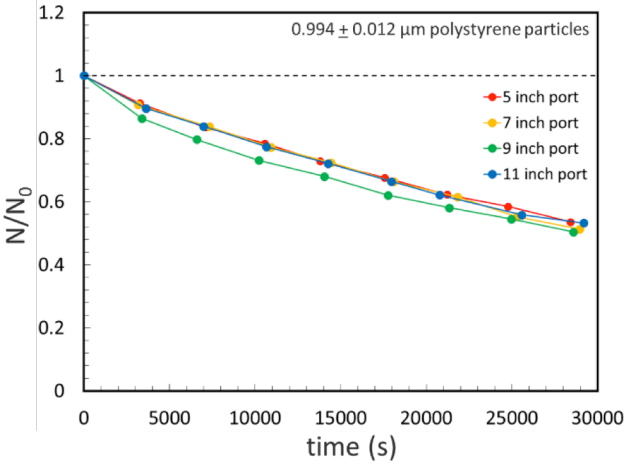

Figure 5. Number suspension efficiency (N/N_0) of 0.994 ± 0.012 µm polystyrene latex particles measured at different radii while rotating the drum at 2 RPM. The plot confirms that the distribution of particles is uniform throughout the main chamber. Each data point represents a sample taken with the APS and the lines are added to help guide the eye.

the chamber.

The particle suspension efficiency was benchmarked at various drum rotation speeds. Here, three speeds are highlighted: 0 RPM, 1 RPM and 2 RPM. Figure 4 provides a plot of the number suspension efficiency (N/N_0) versus time for each speed. The 1 μm particles settle out of the suspension much more rapidly for the stationary drum (0 RPM) relative to the moving drum. The 1 and 2 RPM rotation speeds resulted in particles remaining suspended for over 14 hours. More rapid rotation speeds were avoided due to stress imposed on the motor and belt system. Slower speeds resulted in motor instability. Therefore, once adequate suspension times were demonstrated for 2.0 RPM, the same speed was employed throughout subsequent testing.

The particles were found to uniformly fill the chamber, as demonstrated by radial sampling. Figure 5 provides a plot of the number suspension efficiency at the four sampling radii specified in the drum design: 5 in, 7 in, 9 in and 11 in from the central axis. Close agreement among the four radii indicates an even distribution of particles throughout the chamber.

Aerosol Suspension Characteristics: polydisperse nanoparticles. Monodisperse solid spheres only represent one small subset of atmospheric particles. For that reason, it is necessary to characterize polydisperse particle distributions within the rotating ACSC to characterize the impact of composition or heterogeneous reactions on aerosol dynamics. The series of experiments described below were designed to determine the effect of rotation and concentration on the particle distributions.

Experimental measurements typically begin with spectroscopic and particle background measurements recorded with the drum filled to atmospheric pressure with ultra-high purity nitrogen. Following background measurements, the chamber was evacuated to approximately 600 Torr in preparation for ammonium sulfate aerosol introduction. Particle injection was achieved by flowing ultrahigh purity nitrogen through a Collison 6-jet nebulizer containing 30 mL of 0.6833 g/L aqueous ammonium sulfate solution at 20 psi. The newly generated salt aerosols flowed through a TSI 3062 diffusion dryer to remove excess water until the chamber returned to atmospheric pressure. The ammonium sulfate introduction process resulted in aerosols between 18.8 – 881 nm aerodynamic diameter. Submicron suspensions were sampled in triplicate every 20-60 minutes using an electrostatic classifier (TSI 3080) and water

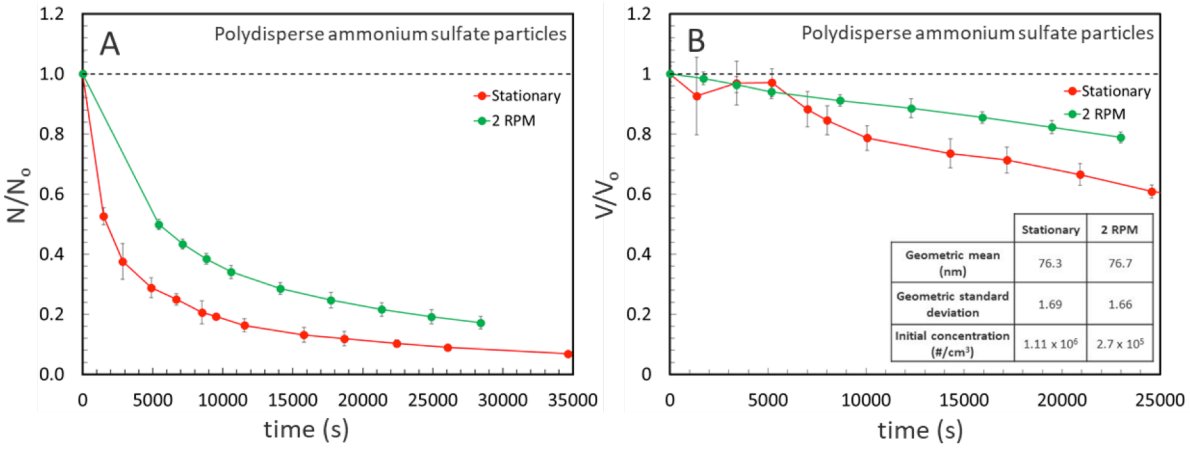

Figure 6. A) Long term number suspension efficiency (N/N_0) for polydisperse size distribution of ammonium sulfate particles while the drum rotates at 2 RPM (green) and while stationary (red). B) Long-term volume suspension efficiency (V/V_o) for polydisperse size distribution of ammonium sulfate particles while drum rotates at 2 RPM (green) and while stationary (red). The table inset describes the initial distribution of the stationary and 2 RPM experiments. Each data point represents the average of three samples taken with the SMPS and the lines are added to help guide the eye. Error bars represent absolute error of the average value, error bars smaller than the data point markers are not displayed.

condensation particle counter (TSI 3782) in scanning mobility particle sizing (SMPS) mode at 0.40 SLPM flow rate simultaneously through the four radial ports. One of the ports opposite of the particle sizer was opened to lab air with a Parker Balston particulate matter filter (9922-05-CQ), which filtered 99.98% of the particles >0.5 µm to maintain atmospheric pressure within the chamber.

As with the standard, well-defined 1 µm particles, we benchmarked the suspension efficiency of the rotating and stationary drum for aerosolized ammonium sulfate particles. Total volume suspension efficiency (V/V_0) is the most appropriate parameter for characterizing performance for a polydisperse cloud. A polydisperse distribution that maintains a constant total volume indicates a stable suspension. That is, the number density (N/N_0) may decrease due to particle coagulation rather than "wall loss". In this case, total volume remains constant. Figure 6 represents the comparison of particle number suspension efficiency (N/N_0, 6A, pervious page) and volume suspension efficiency (V/V_0, 6B) for a stationary and rotating chamber. The volume suspension efficiency demonstrates that ammonium sulfate total volume is maintained slightly more efficiently for the rotating, as compared to the stationary, drum.

Further insight into the dynamics of particle coagulation (and our ability to study it) comes from a key benchmark experiment in which we compared an atmosphere of low particulate density to one of high density. For the low density cloud created from the polydisperse particulate suspension, we found that number density remained constant for all sizes throughout the duration of our measurements (Figure 7A). A constant particle size distribution is expected for this case because the mean-free-path for particles at such low concentrations (~600 cm^{-3}) exceeds the dimensions of the ACSC. In stark contrast, Figure 7B shows how dramatically particle size changes at higher densities, where the particle mean-free-path is much lower. In this figure, we show that the smallest particles in the cloud are rapidly removed due to their high sticking (coagulation) probability to larger particles. This, coupled with the high mobility of smaller particles, results in slight growth of the larger particles at the expense of the number of small particles in the drum.

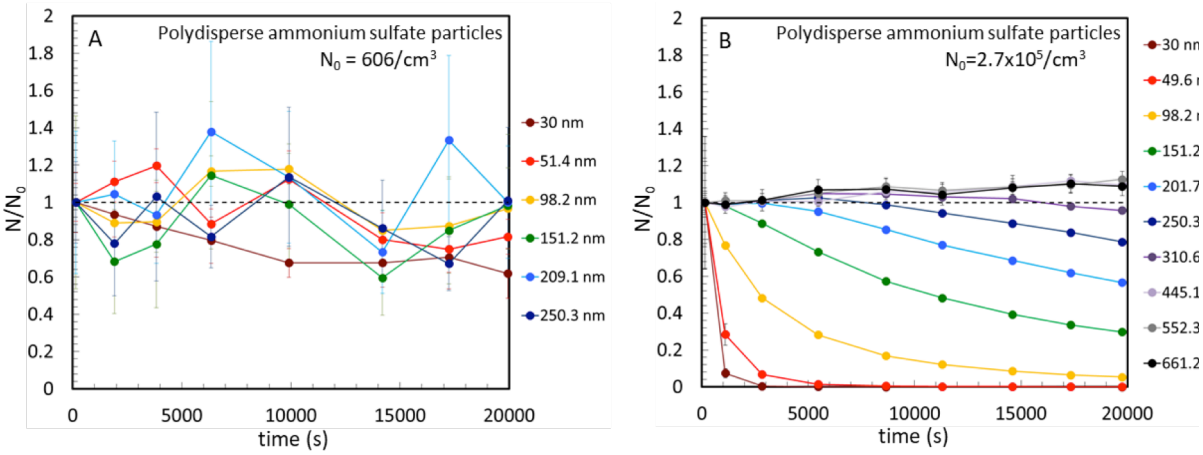

Figure 7. Polydisperse ammonium sulfate particle number suspension efficiency (N/N_0) versus time (s) for various size channels. The midpoint diameter for each channel plotted denoted in the legends. Plot A is the low concentration experiment (N_0 = 606/cm^3) and plot B is the high concentration experiment (N_0 = 2.7 x 10^5/cm^3). Each data point represents the average of three samples taken with the SMPS and the lines are added to help guide the eye. Error bars represent absolute error of the average value, error bars smaller than the data point markers are not displayed.

Cavity Ring Down Spectroscopy. Atmospheric research requires highly sensitive gas monitoring. Cavity ring down spectroscopy provides the ACSC with *in situ* non-destructive information on the gas-phase composition within the chamber. A highly detailed spectrum of water vapor illustrates the sensitivity of the spectroscopic technique.

After recording a background spectrum in a nitrogen atmosphere, water vapor was added to the ACSC using an elastomer sealed mass flow controller (MKS GE50A013503SBV020) to flow 2500 SCCM ultrahigh purity nitrogen through a nanopure water bubbler until the relative humidity inside the chamber reached the desired value. Figure 8 compares the recorded CRDS spectrum of 11.4 Torr water vapor, approximately 60.9% relative humidity, to calculated line positions and intensities. The P-branch of the asymmetric bending rovibrational band centered around 1595 cm^{-1} and pure rotational band centered at 204 cm^{-1} of water overlap in the 860-1010 cm^{-1} CRDS spectral window with intensities four orders of magnitude less intense than the rovibrational band. Figure 8 shows excellent agreement between the calculated lines and recorded spectra, which provides a good benchmark for the spectroscopic method.

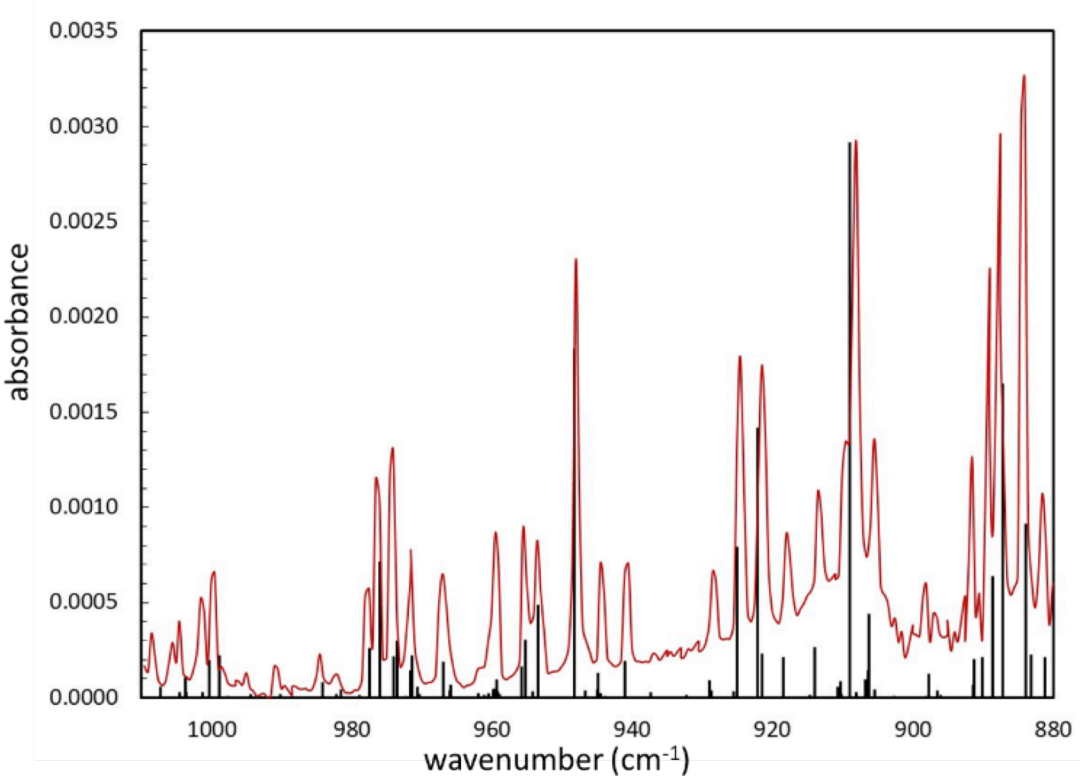

Figure 8. Absorbance spectra of 11.4 Torr of water vapor (60.9% relative humidity, red line) filled to 700 Torr with ultrahigh purity nitrogen gas. Scaled HITRAN calculated spectral lines for water are the black lines, showing excellent agreement between theoretical and experimental data.

In situ Heterogeneous Chemistry. One of the key design objectives of the ACSC was to detect gas phase products from heterogeneous reactions at the vapor-particle interface. Benchmark testing involved exploring reactions between ammonium sulfate aerosols and gaseous alkyl amines. Previous studies have shown that ammonium sulfate particles release gaseous ammonia upon the reactive uptake of alkyl amines in the presence of at least 5% relative humidity (Reaction 1). This heterogeneous reaction was selected for our proof-of-concept study because of the critical role sulfate particles play in atmospheric chemistry.

$$2CH_3NH_2(g) + (NH_4)_2SO_4(s) \rightarrow 2NH_3(g) + (CH_3NH_3)_2SO_4(s) \qquad (1)$$

Experiments designed to study the heterogeneous chemistry of ammonium sulfate and alkyl amines began by introducing a polydisperse distribution of ammonium sulfate into the rotating main chamber using the same procedure described in the previous sections The aerosol suspension reached a stable distribution

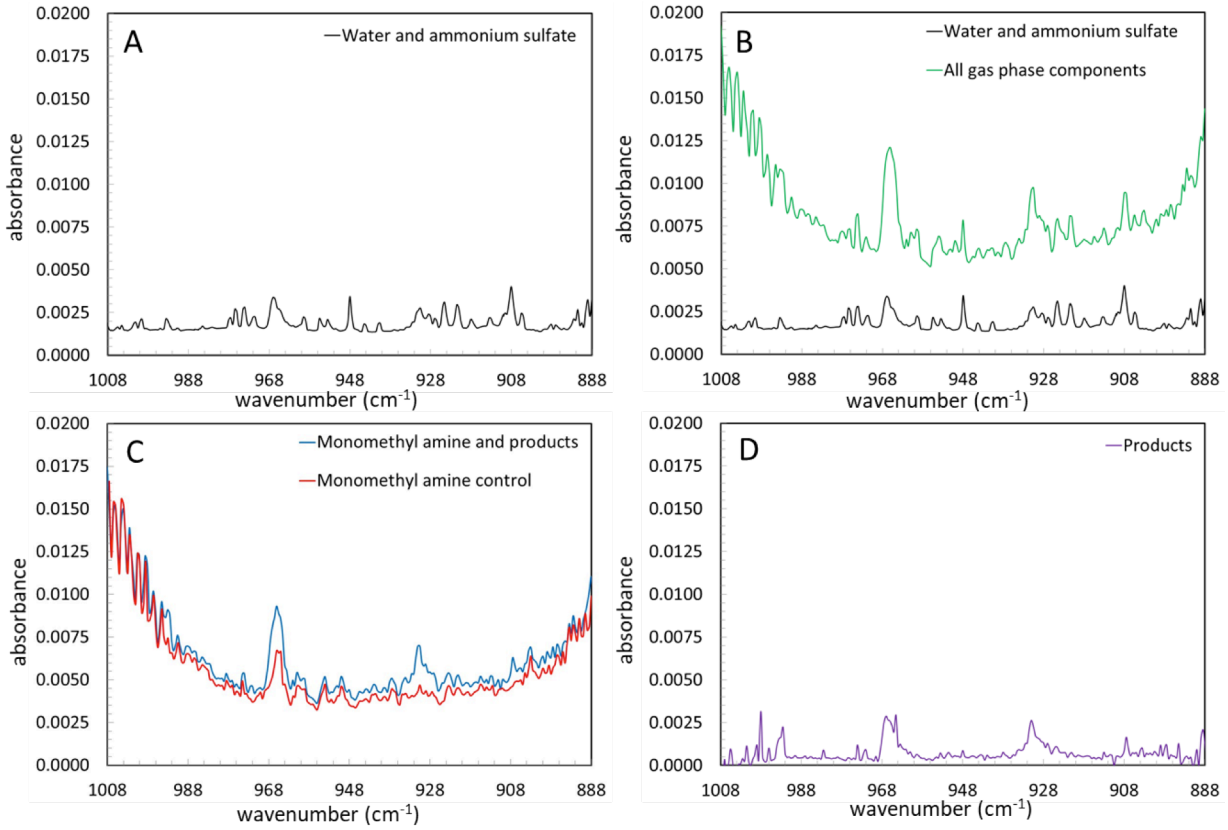

Figure 9. The spectra shown above represent the evolution of ammonia gas after exposing ammonium sulfate particles to monomethyl amine. A) Black spectrum verifies the presence the ammonium sulfate particles in approximately 60.9% relative humidity, or 11.4 Torr of water vapor. B) Green spectrum was recorded upon release of monomethyl amine into the simulated cloud, thus the spectrum contains features associated with the ammonium sulfate particles, water vapor, excess monomethyl amine, and the gas-phase reaction products. The black spectrum (same as in spectrum A) was subtracted from the green spectrum resulting in the blue spectrum representing excess monomethyl amine and gas-phase reaction products in figure C. The scaled monomethyl amine control spectrum (red) is then subtracted from the blue spectrum in figure C. D) Purple spectrum is the result from subtracting red spectrum from the blue spectrum in figure C, leaving a spectrum representative of the gas-phase reaction products.

after 1-2 hours in the rotating chamber. Once stabilized, monomethyl amine gas was introduced into the chamber using a metal sealed mass flow controller (MKS GM50A013503SBV020) and ultrahigh purity nitrogen was added until the chamber as make-up gas to re-establish atmospheric pressure. Spectroscopic measurements using cavity ring down spectroscopy provided information on the heterogeneous reaction that occurred within the drum. Figures 9A-D show spectral evidence supporting the evolution of ammonia as a result of reaction 1.

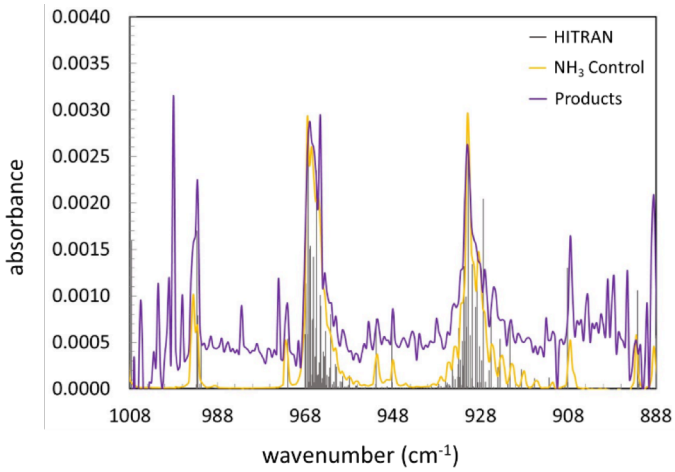

Figure 10. Comparison of the products spectrum (purple), ammonia control (yellow) and Scaled HITRAN calculated spectral line positions and intensities for ammonia (grey).

The final spectrum in Figure 9D appears to be due to the release of ammonia, the gas-phase product of reaction 1. Verification of the creation of ammonia comes from comparison to an ammonia standard (recorded with the same experimental configuration) and a computed spectrum for ammonia (see Figure 10). To our knowledge, this data represents the first demonstration of the *in situ* detection of a gas-phase reaction product released from atmospheric particles in a rotating drum system.

III. Mid-infrared aerosol chemistry chamber

III. A. Introduction

Ultra-high vacuum (UHV) based surface science instruments have revolutionized the field of gas-surface chemistry. Ranging from single-crystal metal surfaces to complex heterogeneous nanostructured systems, UHV environments have provided fundamental thermodynamic binding energies and single atom resolution imaging of the gas-surface interface. Unfortunately, the gap between typical materials studied within an UHV environment and the materials of practical relevance can be significant. To address this so-called "materials gap", we have a developed a controlled environmental apparatus to study complex materials with the ability to cover vast temperature and pressure ranges. The main goal of the instrument developed under this program is to better understand how materials, including polymers, atmospheric aerosols, and chemical warfare agents, function in realistic environments while quantifying fundamental thermodynamic energetics of the gas-material interactions.

The instrument was designed to address four key challenges and provide specific analytical capabilities:

(1) ***In situ* spectroscopic characterization.** Infrared spectroscopy has been incorporated into the instrument to interrogate the surface-adsorbed species, reaction intermediates, and emergence of products in real-time as atmospheric molecules collide on the surface of a material of interest.

(2) **Variable pressure environment.** Precision controlled vapor dosing, gas handling, and vacuum pump baffling have been applied to provide the ability to study interfacial reactions at pressures ranging from 100 Torr to 10^{-9} Torr.

(3) **Wide-range temperature control.** A sample mount for particles and other materials has been designed that provides the ability to rapidly heat and cool the sample from liquid nitrogen temperatures to 1000 K.

(4) **Gas phase detection.** Detection of gas-phase products released from a surface has been achieved via the implementation of a differentially pumped line-of-sight quadrupole mass spectrometer with a mass range from 1 to 300 amu.

Below, the instrumental capabilities are demonstrated and benchmarked. These studies show that the instrumental development is complete and the system is ready for exploring novel gas-surface processes of relevance to the Army mission of warfighter protection.

III. B. Experimental Design

A schematic representation of the experimental vacuum chamber is shown in Figure 11. The vacuum system is divided into two chambers separated by a pneumatic gate valve (VAT Valve). Each chamber is pumped by a magnetically levitated turbomolecular pump (400 L/s Pfeiffer Vacuum). A manual gate valve (VAT Valve) is placed below the main chamber (blue compartment, Figure 1) to isolate the sample and chemical reactants from the turbomolecular

pump. The manual gate valve serves as a pumping baffle that allows the main chamber to quickly cover pressure ranges between 1 x 10^{-9} Torr – 100 Torr. The main reaction chamber includes 16 Conflat® flange ports that are used to introduce chemicals, photons (green – Visible/UV and red- infrared lines), samples, and other instrumentation into the chamber. The entire apparatus is mounted on an aluminum framework (80/20 Inc.).

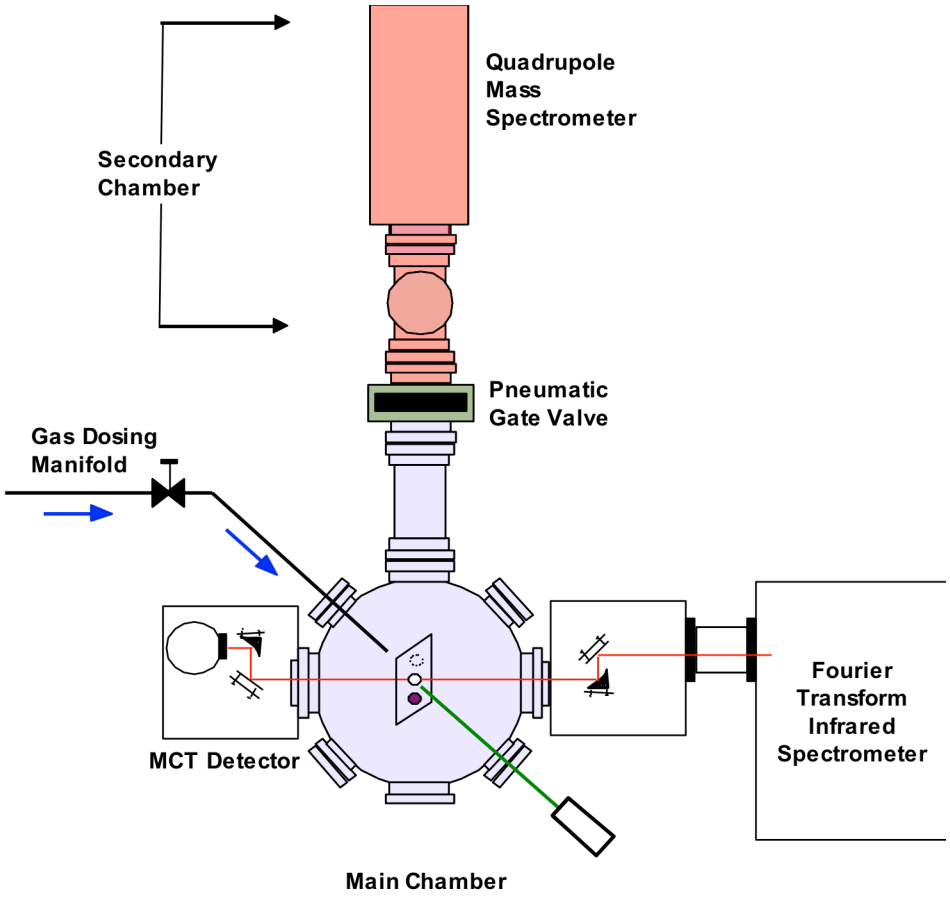

Figure 11. General schematic of the instrument. The main chamber, where the sample is located, is shown in blue. The secondary chamber is shown in red. The FTIR and mirror are not under vacuum and shown in white. Components not drawn to scale.

For the detection of surface species during experimental operation, transmission Fourier transform infrared spectroscopy is incorporated into the chamber (Red solid line, Figure 11). Two 4.5" CF flanges are fixed with KBr windows to allow for the transmission of infrared light through the chamber. In combination with the *in situ* detection of surface species, a quadrupole mass spectrometer is attached to the secondary chamber (red compartment, Figure 11) to monitor the gas phase reactants and products that desorb from the surface. Together, these methods provide simultaneous probes of reactants as they adsorb to a surface and products as they are released into the gas phase.

Infrared spectroscopy. The infrared light used to detect surface species is coupled to the instrument through two KBr windows and custom designed optics compartments. Infrared light is extracted from a commercial FTIR spectrometer through an external port. A dry-air purge is used to remove residual gas molecules and vapors from the custom optics compartments (Figure 12A). In the entrance optics compartment, one flat mirror (Edmund Optics) and one parabolic mirror (Thor Labs focal length = 228.6 mm) are inverted and attached to a micrometer stage (Newport) to allow for fine adjustment to or from the sample. The parabolic mirror is adjusted to focus the infrared energy onto a 1 mm^2 spot on the sample. Once focused, infrared light passes through the sample and enters a dry-air purged detector box where a flat mirror (Edmund Optics) reflects the light onto a parabolic mirror (Thor Labs, focal length = 152.4 mm) as shown in Figure 12B. Finally, the light is focused onto an external MCT/A detector for analysis.

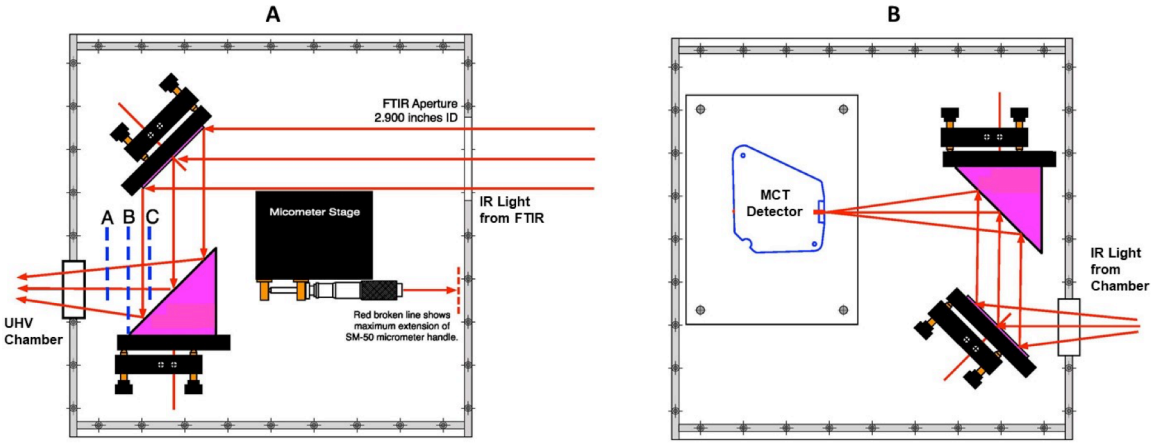

Figure 12. Infrared light mirror boxes. A. Mirror box that directs infrared light from the FTIR housing to the vacuum chamber. B. Mirror box that directs the infrared from the vacuum chamber into the MCT detector. Parabolic mirrors are depicted as pink triangles.

Mass spectrometer. While infrared spectroscopy characterizes surface adsorbates, the secondary vacuum chamber has been manufactured to provide detailed information on the gas products produced from surface desorption or reaction. The residual gas analyzer (RGA, SRS 300) is mounted to a custom six-way CF cross (Kurt J. Lesker) where the center of the ionizer is positioned directly in line with the center of the sample (located in the main chamber). This allows for line-of-sight detection of the gas phase products that desorb from the surface. The pneumatic gate valve between the two vacuum chambers can be actuated during high-pressure experiments to preserve the mass spectrometer. A gas leak valve is attached between the two chambers to allow for real time sampling by the RGA when the main chamber is held at high pressure for heterogeneous chemical reactions.

Sample Mount. The custom designed and constructed sample mount (Figure 13) utilizes stainless steel clamps that immobilize a tungsten grid. Samples can either be pressed into the voids of the grid or deposited onto the grid via an aerosol generator or nozzle. The grid allows

for a variety of materials to be integrated into the instrument for exposure to reactive species. The sample holder is mounted to an external manipulator (McAllister) for precision alignment at the intersection of the mass spectrometer and infrared beam. A pinhole aperture below the sample position is used to align the IR light by locating the beam path in the center of the chamber. For temperature control, the stainless steel clamps are attached to copper leads and resistively heated with applied current from an external power source. A k-type thermocouple is used to monitor temperature of the sample and is used as part of a feedback loop to the external power source for active and precise temperature control. Finally, a liquid nitrogen reservoir is used as a heat sink to cool the copper leads and grid. The liquid nitrogen and the resistive heating provide a working sample temperature range of < 90 K to 1000 K.

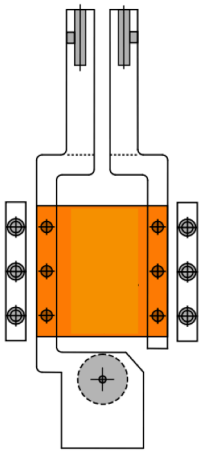

Figure 13. Schematic representation of the sample used for gas-surface studies. The yellow region indicates the mesh that is coated with the samples. A pinhole aperture is located below the sample (circle, shadowed).

III. C. Sample Installation and System Benchmarking. The instrumental system has been benchmarked by measurements on a test polymeric sample of polyvinylidene fluoride (PVDF) and the response of the polymer to a gas-phase challenge of NH_3 and O_2.

The polymer samples used in these studies were prepared such that *in situ* techniques could interrogate their structure when exposed to gas of interest. Samples of β-PVDF and α-PVDF were acquired commercially. In addition to the bulk polymer materials, two metal organic frameworks ($UiO_{66}NH_2$ & Cu-HKUST1) were mixed with the PVDF such that a 10% concentration of MOF was incorporated into the polymeric matrix. Each PVDF and MOF/PVDF sample was electrospun directly onto the tungsten grid and installed into the chamber. A clean tungsten grid was placed directly below the polymer and installed at the same time. The sample mount only allows for one sample coated mesh and one clean mesh to be installed simultaneously. Both the polymer and clean mesh samples were heated in vacuum to 380 K prior to each gas exposure and no changes in the infrared spectra were detected during this thermal treatment.

The characterization of each PVDF material in vacuum was accomplished through infrared spectroscopy. Figure 14 displays the infrared spectra for the $UiO_{66}NH_3$ incorporated into the β-PVDF sample. Spectra were recorded over the temperature range of 298 K to 116 K. The final spectrum recorded at low temperature (Figure 4, red spectrum) has a few minor differences in infrared absorbance around 740-760 cm^{-1} and 790 – 805 cm^{-1} compared to the material at room temperature (Figure 14, black spectrum).

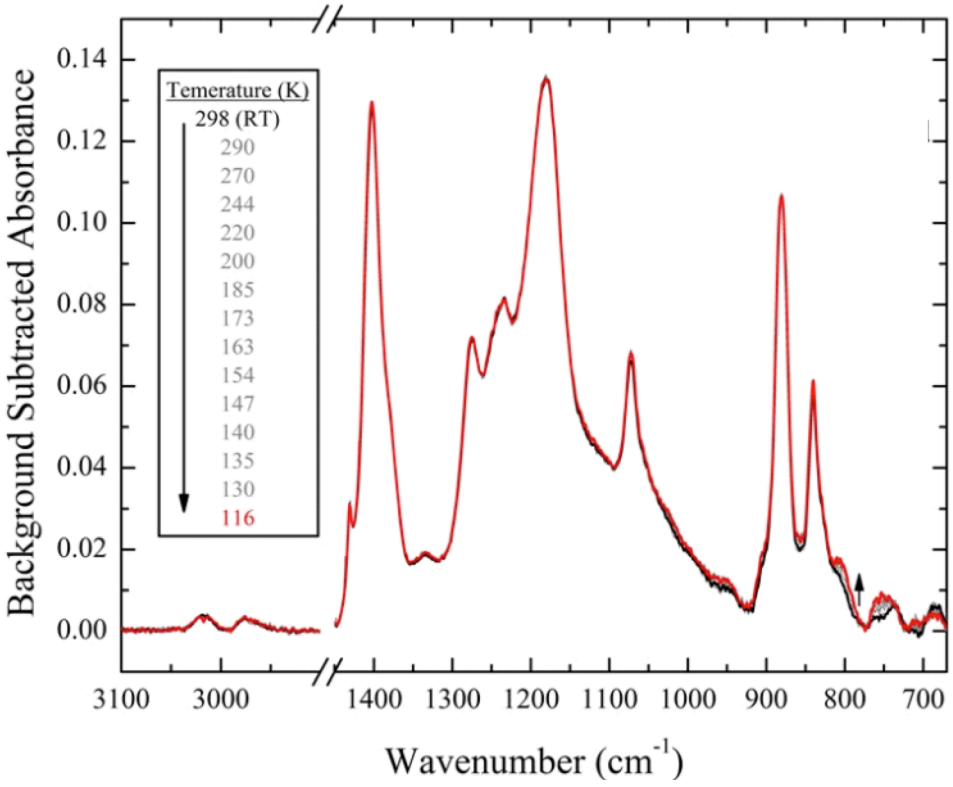

Figure 14. Infrared spectra of the $UiO_{66}NH_3$ incorporated into β-PVDF at decreasing

In situ monitoring of small molecule uptake on PVDF. Initial small molecule uptake studies utilized *in situ* infrared spectroscopy as the molecules interacted with the CuBTC incorporated into β-PVDF sample. Figure 5 provides the infrared spectra when an increasing amount of oxygen is placed inside the main chamber at 115 K. In the low wavenumber region (Figure 15A), the CuBTC/PVDF sample exhibits significant increases in absorbance values for each vibrational signature. This change in absorbance upon oxygen introduction is attributed to the uptake of O_2 into the polymer. Figure 15B illustrates infrared spectra in the high wavenumber region when oxygen is in the chamber. While the increase in absorbance at high oxygen pressures is less significant compared to the low wavenumber region, the evidence for oxygen uptake is clear.

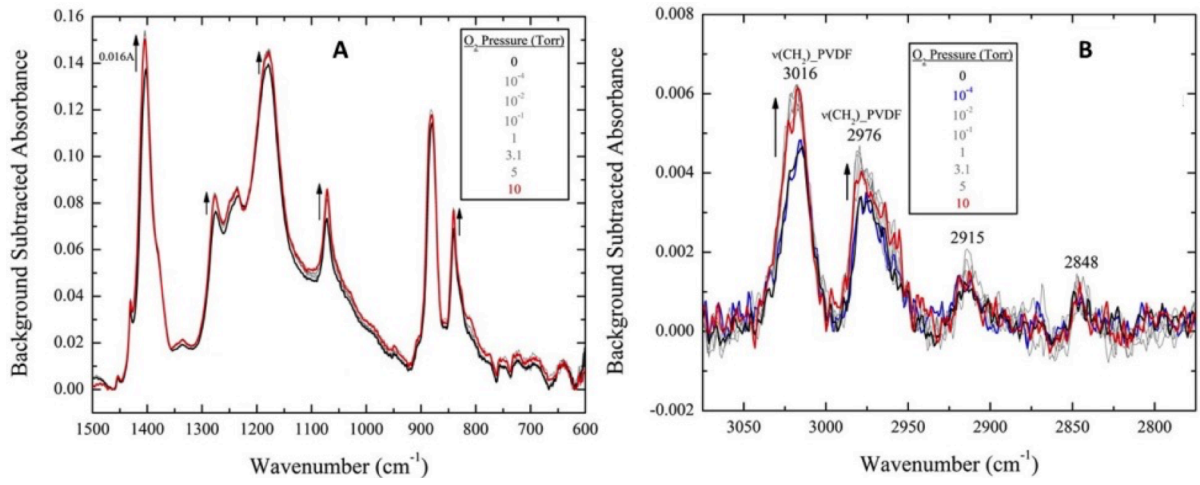

Figure 15. Infrared spectra acquired at increasing pressures of O_2 upon exposure to the CuBTC incorporated into β-PVDF sample. Panel A provides the low wavenumber region (1500 – 600 cm^{-1}). Panel B provides the high wavenumber region (3075 – 2775 cm^{-1}).

The reversibility of the adsorption process was also monitored utilizing *in situ* infrared spectroscopy. Oxygen was introduced into the main chamber and then subsequently removed from the chamber at 115 K. Infrared spectra, shown in Figure 16, illustrate the change in IR absorbance due to the oxygen in the chamber (Figure 16, blue & green spectra) and then once the chamber was evacuated and the sample returned to its original state. The result is consistent with a weak physical interaction between the oxygen and polymer that is reversible even at low temperatures. The oxygen molecules interact with the polymer under an atmosphere of gas and once the system is under vacuum the oxygen rapidly desorbs from the polymer.

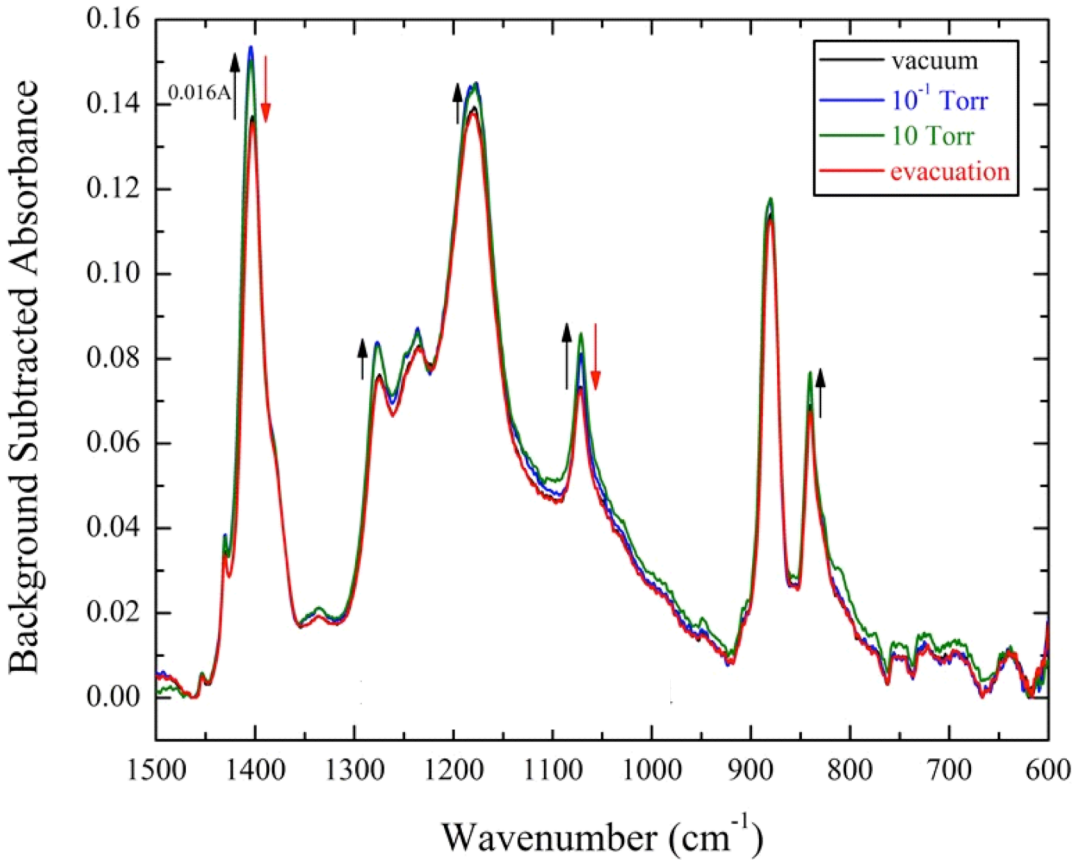

Figure 16. Infrared spectra acquired before, during, and after O_2 exposure of the CuBTC-incorporated β-PVDF sample.

In situ molecular desorption monitoring. The desorption of gas molecules from the polymeric coating was tracked in a test experiment by heating the sample while monitoring product desorption with the line-of-sight mass spectrometer. Initially, the PVDF sample was exposed to NH_3 at 123 K. Once equilibrated, the temperature of sample was increased linearly while the mass analyzer was used to monitor the gas phase composition. As shown in Figure 17, the gas phase m/z for NH_3 (17) increased over time as the temperature of the gas-saturated sample increased. Monitoring other gas phase species such as H_2O, CO_2, and CO did not exhibit this same trend during the temperature ramp.

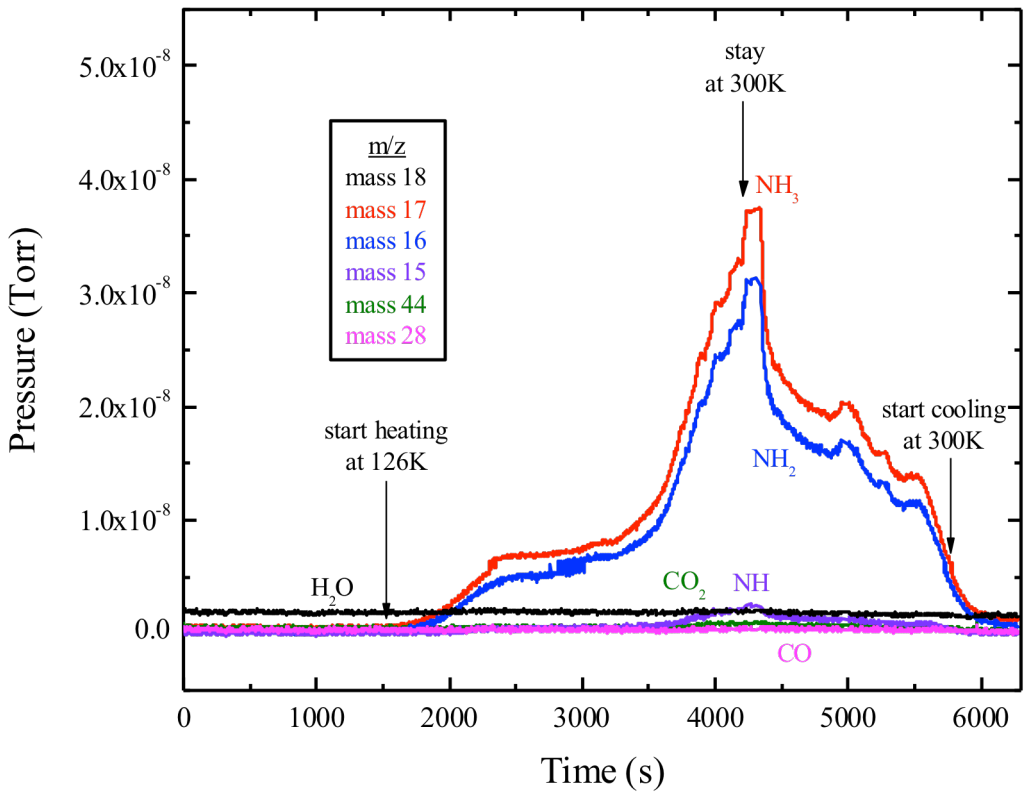

Figure 17. Temperature programmed desorption profile of NH_3 bound to PVDF. Pressures of each mass fragment over time were acquired with the RGA.

Summary. Reliable strategies for predicting the environmental fate, long-term stability, and mitigation of aerosolized compounds and chemical warfare agents (CWAs) requires a detailed understanding of the physical and chemical interactions that occur at the gas-surface interface. Therefore, instrumental methods have been developed for the purpose of studying the vapor-phase chemistry, characteristics of liquid aerosols, and the surface chemistry of model aerosols. These two instrumental methods will be critical in the collection of fundamental spectroscopic data important for the study of particulate and aerosol chemistry. The instruments will be employed to study simulant (at Virginia Tech) and agent (at Edgewood Chemical Biological Center) chemistry under real-world atmospheric conditions.

The specific achievements for this project have been two-fold:

(1) Designed and constructed a rotating drum environmental chamber for suspending aerosols and studying the vapor via stand-off spectroscopic methods.

The rotating drum enables experiments that probe chemistry in the presence of a prolonged suspension of aerosolized agent or simulant. The drum is coupled with cavity ring down spectroscopy (CRDS) for highly sensitive *in situ* absorbance spectra. Ambient environments with varying concentrations of pollutants (e.g., CO_2, NO_x, SO_x, etc.) can be introduced for direct observation of reactive processes aerosols experience in the atmosphere. The rotating drum and CRDS instruments have been fully constructed, tested, and used for initial studies employing CWA simulants at Virginia Tech. Following

these initial tests, an identical system was transported to Edgewood Chemical Biological Center, where it has been re-assembled and installed into a surety hood for agent work.

(2) Designed and constructed a complimentary instrument to the rotating drum for the study of molecules adsorbed to the surface of particulates

While the rotating drum capability highlighted here enables one to track gas-phase species formed during the evaporation of products from an aerosol, another instrument has been developed to monitor molecules adsorbed to the surface of particulates. This has been accomplished by employing transmission infrared spectroscopic methods through a sample of particles that is suspended within an environmental chamber. In this instrument, infrared spectroscopy tracks bond breaking and formation *on the surface* while a mass spectrometer monitors *products desorbing from the surface* and into the gas phase. The instrument has been installed at ECBC following appropriate benchmark testing at Virginia Tech.