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MOLECULAR DYNAMICS OF UPPER ATMOSPHERIC CHEMICAL REACTIONS

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During the period of June 14, 1999 – August 31, 2000, I worked at the Air Force Research Laboratory at Hanscom AFB under the Laboratory Scholar Postdoctoral Program and contract F19628-98-C-0029. In this time, I conducted experiments to investigate the molecular dynamics of chemical reactions that produce visible or infrared radiation in the upper atmosphere. The experiments were performed using laser pump-probe methods and detection techniques such as laser induced fluorescence (LIF) and resonantly enhanced multiphoton ionization (REMPI). The focus of this work was to gain a better understanding of some of the important processes that produce or destroy infrared-active species such as OH and NO in the mesosphere and thermosphere. During this time, I also researched and designed a new set of experiments to investigate the molecular dynamics of the interactions of $O(^3P)$ atoms with hydrocarbons. These experiments will be important for understanding how hydrocarbons released by space vehicles traveling through the upper atmosphere will interact with $O(^3P)$ atoms, a dominant atmospheric species above 90 km.

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Final Report

Jennifer B. Lipson

Introduction

During the period of June 14, 1999 – August 31, 2000, I worked at the Air Force Research Laboratory at Hanscom AFB under the Laboratory Scholar Postdoctoral Program and contract F19628-98-C-0029. In this time, I conducted experiments to investigate the molecular dynamics of chemical reactions that produce visible or infrared radiation in the upper atmosphere. The experiments were performed using laser pump-probe methods and detection techniques such as laser induced fluorescence (LIF) and resonantly enhanced multiphoton ionization (REMPI). The focus of this work was to gain a better understanding of some of the important processes that produce or destroy infrared-active species such as OH and NO in the mesosphere and thermosphere. During this time, I also researched and designed a new set of experiments to investigate the molecular dynamics of the interactions of $O(^3P)$ atoms with hydrocarbons. These experiments will be important for understanding how hydrocarbons released by space vehicles traveling through the upper atmosphere will interact with $O(^3P)$ atoms, a dominant atmospheric species above 90 km.

OH Experiments

In the upper atmosphere, the reaction of $H + O_3$ leads to the production of OH in highly excited vibrational states ($v \leq 9$). This reaction is an important source of OH and has a strong influence on the atmospheric radiative energy balance. The OH formed by this reaction produces intense, spectrally highly structured, nighttime emission in both the visible and the infrared near the mesopause (~87 km). Laboratory measurements of the $OH(v)$ nascent product distribution from the $H + O_3$ reaction are necessary in order to accurately model the spectral distribution and radiance level produced by the OH Meinel bands. Previous studies of this reaction have used infrared chemiluminescence detection to monitor OH. This technique is experimentally straightforward, but is not nearly as sensitive as laser-based techniques such as LIF. A number of experiments and field measurements have employed the $A^2\Sigma^+$–$X^2\Pi$ LIF transition for OH detection. However, this method is limited to the detection of $OH(v \leq 5)$, which is not useful for detecting the highly excited vibrational levels of OH (v = 7-9) that are responsible for most of the Meinel band emission. The OH $B^2\Sigma^+$ state has a much larger internuclear separation than the ground state, and so improved Franck-Condon overlap makes the B state more suitable for LIF detection of OH ($v \geq 6$).

During the period of the contract, I assisted with a set of experiments to investigate the production of highly vibrationally excited OH from the $H + O_3$ reaction using the $B^2\Sigma^+$–$X^2\Pi$ electronic transition for the LIF detection of OH. In these experiments, H atoms were produced by the microwave dissociation of H_2. H atoms and O_3 were introduced into a low-pressure flow cell using a concentric injector which

allowed the reactants to mix just above the detection region. A Nd:YAG pumped dye laser was used to produce light in the 426-474 nm region, and then frequency doubling crystals were used to create a tunable source of ultraviolet light for the B-X LIF detection of OH. This set-up enabled us to monitor OH (v = 7-9) formed by the H + O_3 reaction. The wavelength required for excitation of OH (v = 6) is difficult to achieve with conventional laser dyes. However, we were able to set up a wavelength tripling experiment to produce light at 202 nm in order to probe this vibrational level. The measurements were conducted at pressures between 3 x 10^{-5} and 3 x 10^{-4} Torr. A number of OH(B-X) v'= 0–v''= 6-9 vibration-rotation spectra were obtained, with the v'', J''-dependent populations characterized through synthetic spectral fitting. OH(B-X) 0-v'' relative band intensities and OH(B, v = 0) J-dependent collision-free lifetimes were also measured. Preliminary analysis suggests that the $B^2\Sigma^+$ state is weakly predissociated through gyroscopic and spin-orbit perturbation interactions with the nearby $2^2\Pi$ state. These results should add confidence in deriving accurate OH v, J-dependent populations from B-X spectra.

NO Experiments

Space based spectrometers (e.g. CIRRIS 1A) have observed highly rotationally excited NO in the thermosphere during both daytime and nighttime measurements. The reaction of hyperthermal N(^{4}S) atoms with O_2 is one mechanism that has been proposed to explain this phenomena based on theoretical calculations. In the atmosphere, fast N(^{4}S) atoms are produced by the photodissociation of N_2 and the dissociative recombination of N_2^+ and NO^+. In the laboratory, it is very challenging to create a clean, abundant source of N(^{4}S) atoms with sufficient energy to overcome the 0.3 eV reaction energy barrier. As a result, experimental measurements of the NO rotational energy distribution from fast N(^{4}S) + O_2 have never been conducted.

During the period of the contract, I performed experiments to try to create a source of fast N(^{4}S) atoms to be used to study the N(^{4}S) + O_2 reaction. The fast N(^{4}S) atoms were produced by the photodissociation of NO around 142 nm. NO was excited to the high-lying, predissociative 4d Rydberg state $O^2\Sigma$, $O'^2\Pi$ (v = 1) using a tightly focused beam of light from a Nd:YAG pumped dye laser. Photodissociation of NO in this region produces N(^{4}S) atoms with up to 1.1 eV of kinetic energy, more than enough energy to overcome the N(^{4}S) + O_2 reaction barrier. The spectroscopy of the 4d Rydberg state of NO is quite complicated. The d Rydberg states are known to be split into three components: $^2\Sigma^+$, $^2\Pi$ and $^2\Delta$. The $^2\Sigma^+$ and $^2\Pi$ states are very close together in energy with splittings on the order of ~10 cm^{-1}. As a result of the interaction of these two states, a lambda splitting occurs in the $^2\Pi$ state producing two components: $^2\Pi^-$ and $^2\Pi^+$. In previous REMPI studies of the d Rydberg states, only the $^2\Pi^-$ component has been observed. These studies have proposed that the $^2\Sigma^+$ and $^2\Pi^+$ states predissociate so rapidly that very little ionization occurs.

In order to characterize the N(^{4}S) atom source, pump-probe laser experiments were conducted in which the N atoms produced by the photodissociation of NO were

detected directly using LIF. The N ($2p^2 3p\ ^4D_J^0$) ← ($2p^3\ ^4S_{3/2}^0$) transition was excited with a highly focused beam of 211 nm light produced by a Nd:YAG pumped dye laser. Using a 10 nm band pass filter on the photomultiplier tube, we monitored the fluorescence from the N ($2p^2 3s\ ^4P_J$) ← ($2p^2 3p\ ^4D_J^0$) transition at 869 nm. The production and detection of N(^{4}S) atoms in these experiments are both multiphoton processes, and so it was necessary to tightly focus both laser beams. At the center of the experimental cell, the spot size diameter of both beams is on the order of ~100 μm. Therefore, careful alignment and overlap of the beams was critical to the success of the experiments. By scanning the photolysis laser, we were able to identify the lines that produced the strongest N(^{4}S) atom signals.

Next, experiments were performed on the N(^{4}S) + O_2 → NO + O reaction using the fast N atom source from the photodissociation of NO. The goal was to investigate the nascent rotational distribution of NO produced by the reaction. Previous experiments from the COCHISE laboratory have shown that the N(^{4}S) + O_2 reaction produces NO $X^2\Pi$ in vibrational levels 0 through 7. As a result, there are many excitation and emission bands that can be used to probe the NO product with LIF detection via the A-X electronic transition. In order to distinguish between the NO product and the background thermal NO used to produce the N(^{4}S) atoms, only NO ($v \geq 3$) was probed. The experiments were conducted at low pressure (~500 mTorr) and at short delay times between the lasers (~60 ns) in order to ensure single collision conditions in our flow system, and thereby prevent rotational relaxation of the NO product. Unfortunately, under these conditions highly rotationally excited NO was observed without O_2 present in the system. After reviewing the literature, we discovered that NO_2, an impurity, is readily photolyzed at the wavelength of the NO photodissociation laser and yields highly vibrationally and rotationally excited NO.

NO_2 is a common impurity in NO gas cylinders due to the reaction of O_2 impurity with NO over long periods of time. When making a bulb of NO, we attempt to remove the NO_2 impurity by flowing the NO from the cylinder through a copper coil immersed in a precooled pentane bath at a temperature of -120° C. NO_2 condenses at a much higher temperature than NO, and therefore should be trapped out by this process. In order to determine the level of NO_2 impurity in the NO gas, we calibrated our background NO LIF signal using a bulb with a known concentration of NO_2. From this experiment, we determined that the NO_2 impurity level in the NO bulb was ~ 0.1%. This calibration also served to define our sensitivity limits for the detection of vibrationally and rotationally excited NO in which the population is spread over many different levels. In order to further reduce the impurity level, we set up an in-line cold trap on our flow system which successfully scavenged the NO_2. Unfortunately, no signal was observed when O_2 was added to the flow system. Calculations based on the NO_2 experiments indicate that we were probably not making enough N(^{4}S) atoms in order to successfully detect the NO product from the N(^{4}S) + O_2 reaction.

In the course of choosing an N(^{4}S) source, photolysis of NO via the $C^2\Pi$ state was also considered. The $C^2\Pi$ state ($v = 0$) lies just at the level of the NO dissociation threshold, and the rotational and vibrational levels above the threshold are known to be

predissociative via the $a^4\Pi$ state. In order to create $N(^4S)$ atoms with sufficient energy to overcome the $N(^4S) + O_2$ barrier, it is necessary to excite NO to at least the third or fourth vibrational level of the $C^2\Pi$ state. In choosing the N atom source, the higher-lying Rydberg state had the advantage of creating atoms with significantly more kinetic energy than the reaction barrier. However, in the process of investigating the $C^2\Pi$ state literature, it became clear that there were a number of unanswered questions related to the predissociation of this state.

In the atmosphere, the photodissociation of NO occurs primarily via excitation to the $C^2\Pi$ ($v = 0,1$) states in the same spectral region as the O_2 discrete Schumann-Runge bands (~175-195 nm). The photolysis of NO in this wavelength range is an important process in the upper and middle atmosphere that contributes to atmospheric opacity, and thereby influences the photodissociation rate of NO and other species at lower altitudes. In the mesosphere, photodissociation is the main loss process for NO. Uncertainties in several NO $C^2\Pi$ state parameters remain and lead to uncertainties in atmospheric models. For example, the variation of the predissociation rate with rotational quantum number has not been fully investigated. Current models assume that absorption of radiation leads to uniform predissociation in all rotational levels of the $C^2\Pi$ state that lie above the NO dissociation energy threshold. Sensitivity analyses have shown that atmospheric models of radiative transfer are strongly influenced by the assumed predissociation widths of the NO $C^2\Pi$ states. Since there are no reports of direct observations of the $N(^4S)$ atoms produced by the photolysis of the C state in the literature, we decided to use our current experimental set-up to conduct these experiments. Similar to our previous experiments, the $N(^4S)$ atoms produced by the photodissociation of the C state are monitored using LIF detection as a function of the photolysis wavelength. At the end of the contract period, these experiments were still in progress. These measurements should provide new insight into the predissociation of the $C^2\Pi$ state and help to improve atmospheric models.

Future Hydrocarbon Experiments

Hydrocarbons released by space vehicles traveling through the upper atmosphere will predominantly be consumed by reactions with $O(^3P)$ atoms, a major atmospheric constituent above 90 km. The hydrocarbons will impact the $O(^3P)$ atoms at high collision energies due to the speed of the space vehicle. The products of these interactions will likely be formed in both rotationally and vibrationally excited states resulting in significant infrared background emissions. The nascent rovibrational energy distributions and branching ratios of the products of hyperthermal $O(^3P)$-hydrocarbon reactions have not been well characterized. Reactions of O atoms with alkenes or alkynes, hydrocarbons containing carbon-carbon double or triple bonds, are particularly interesting because they proceed through complex mechanisms leading to multiple product channels. The branching ratios of the product channels and the energy distributions within the products are strongly influenced by the overall collision energy of the reaction.

During the period of the contract, I helped to design a new set of experiments on the interactions of hyperthermal $O(^3P)$ atoms with hydrocarbons, and I also contributed to

the writing of a research proposal for AFOSR on this topic. In the proposed experiments, the $O(^3P)$ atoms will be produced by the photolysis of NO_2 using a Nd:YAG pumped dye laser, and the O atom translational energy will be varied by changing the photolysis wavelength. LIF detection will be used to investigate the distribution of energy in the products of the reactions. LIF is a highly sensitive technique that can detect a variety of products (e.g. CH_2CHO, CH_3CHCHO, CH_2O, HCO, CH_2 and OH) from the reactions of atomic oxygen and small hydrocarbons. The reactions of oxygen atoms with hydrocarbons form highly reactive free radicals that can rapidly initiate secondary chemistry. Using a laser detection technique will make it possible to probe the reaction products on very short time scales which will enable us to investigate the fundamental reaction steps as well as the nascent distributions of energies in the products.

HCO is a common product of a variety of O + hydrocarbon reactions, and so the experiments will begin by focusing on the detection of this molecule. HCO has three infrared-active vibrational modes including a bending mode, a CO stretching mode and a CH stretching mode. The HCO B^2A'–X^2A' electronic transition is suitable for LIF detection and has been used to observe the production of HCO in methane-air flames. HCO is also produced by the photolysis of aldehydes such as CH_3CHO and has been shown to be formed in both rotationally and vibrationally excited states using LIF detection. We intend to use LIF detection in order to investigate the distribution of energy in HCO due to the reactions of fast $O(^3P)$ atoms with hydrocarbons. The experiments will begin with the simplest alkene, ethylene (C_2H_4), and then proceed to more complicated hydrocarbons. The $O(^3P) + C_2H_4$ reaction occurs by addition of the O atom to the carbon-carbon double bond followed by 1,2-hydrogen migration and fragmentation of the carbon-carbon bond to produce HCO and CH_3. This reaction has a rate constant that varies from $\sim 5 \times 10^{-13}$ to $\sim 1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} over a temperature range of 300 to 1500 K, and so it seems likely that varying the $O(^3P)$ translational energy will have a significant effect on the distribution of rotational and vibrational energy in the HCO product. These experiments should provide new insights into the mechanisms and dynamics of fast O + hydrocarbon reactions.

Conclusions

During the period of contract F19628-98-C-0029 under the Laboratory Scholar Postdoctoral Program, I conducted experiments on reactions that form infrared-active species and produce infrared background emissions in the atmosphere, such as $H + O_3$ and $N(^4S) + O_2$. In this time, I also performed some complementary experiments on the photodissociation of NO. Finally, I designed a new set of experiments on the reactions of fast $O(^3P)$ atoms with hydrocarbons. In these experiments, I plan to investigate the rotational and vibrational energy distributions of the products as a function of the $O(^3P)$ translational energy using laser pump-probe methods developed in the previous studies.

Publications

Hwang, E. S., J. B. Lipson, R. W. Field, and J. A. Dodd, Detection of OH(X, v'', J'') via the $B^2\Sigma^+$–$X^2\Pi$ Transition and Properties of the $B^2\Sigma^+$ State, *J. Phys. Chem. A*, **105**, 6030, (2001).

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Hwang, E. S., J. B. Lipson and J. A. Dodd, New Studies of the OH(v=6-9) Nascent Population Distribution from $H + O_3 \rightarrow OH + O_2$, *American Geophysical Union Spring Meeting*, Washington, D.C. June 1, 2000.

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Miller, S. M., W. Chen, R. B. Lockwood and J. B. Lipson, Production of 0.1 to 0.4 eV Nitrogen Atoms for the Reaction of Fast Nitrogen Atoms with Oxygen to Produce Rotationally Excited Nitric Oxide, *American Geophysical Union Fall Meeting*, San Francisco, CA. December 15, 1999.