

Final Report for Period: 04/2010 - 03/2011**Submitted on:** 04/13/2011**Principal Investigator:** Houston, Paul L.**Award ID:** 0852482**Organization:** GA Tech Res Corp - GIT**Submitted By:**

Houston, Paul - Principal Investigator

Title:

Product Imaging of Photodissociations and Reactions of Atmospherically Important Molecules

Project Participants**Senior Personnel****Name:** Houston, Paul**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** North, Simon**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Collaborated on project resulting in publication (From Texas A&M, Welch Foundation support. Did not receive salary from project

Name: Hall, Gregory**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Collaborated on project resulting in publication (from Brookhaven, DOE support) Did not receive salary from this NSF project.

Name: Kable, Scott**Worked for more than 160 Hours:** Yes**Contribution to Project:**

From U. Sydney, Australia; collaborated on project but did not receive any salary from NSF sources.

Name: Stranges, Domenico**Worked for more than 160 Hours:** Yes**Contribution to Project:**

From University of Rome 'La Sapienza'; collaborated on project but did not receive any salary from NSF grant.

Name: Chen, Jun**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Dr. Chen is a research scientist helping to run the group. He is working part time on this project but supported from other funds.

Name: Bowman, Joel**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Collaborated on Allyl papers but did not receive salary from this project

Post-doc**Name:** Kim, Hahkjoon**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Collaborated on project resulting in publication (From Texas A&M, Welch Foundation Support); did not receive any salary from NSF project

Name: O'Keeffe, Patrick

Worked for more than 160 Hours: Yes

Contribution to Project:

From University of Rome 'La Sapienza'; did not receive salary from this NSF project

Graduate Student

Name: Dooley, Kristin

Worked for more than 160 Hours: Yes

Contribution to Project:

Collaborated on project resulting in publication (From Texas A&M, Welch Foundation Support)

Name: Davis, Eric

Worked for more than 160 Hours: Yes

Contribution to Project:

From Cornell, NSF support from this grant

Name: Tokel, Onur

Worked for more than 160 Hours: Yes

Contribution to Project:

From Cornell, NSF support from this grant

Name: Kelleher Ulrich, Clarice

Worked for more than 160 Hours: Yes

Contribution to Project:

Undergraduate Student

Technician, Programmer

Other Participant

Research Experience for Undergraduates

Organizational Partners

The Texas A&M University System

Three people from Texas A&M worked collaboratively on a paper jointly authored by the PI and others

Brookhaven National Laboratory

One person from BNL worked collaboratively on a paper co-authored by the PI and others

University of Rome

Two people from the University of Rome 'La Sapienza' worked collaboratively on a paper co-authored by the PI and these two people

University of Sydney, Australia

One person from the University of Sydney, Australia co-authored a paper with the PI

Emory University

Joel Bowman and other members of his group collaborated on the Allyl papers.

Other Collaborators or Contacts

No other collaborations

Activities and Findings

Research and Education Activities:

One published paper in the general area of photodissociation, photoionization dynamics. One invited talk at the Dynamics of Molecular Collisions conference (July, 2007). Ongoing progress on the reactions of O(1D) with N₂O. Invited talk at Gordon Research Conference on Atomic and Molecular Interactions (July, 2008). Invited talk at the ACS meeting in Washington (August, 2009). Invited talk to take place at Emory University (May, 2010). Invited talk at the Workshop on 'Roaming Radical and Multiple Mechanism Reactions,' Argonne National Laboratory (April, 2010). Invited talk at Stereodynamics Conference (11/10)

Findings: (See PDF version submitted by PI at the end of the report)

Discovered that dissociative ionization of I₂ leads to high-n Rydberg states of the iodine fragment

We have observed highly vibrationally excited NO produced in the reaction of O(1D) with N₂O. The attached findings file summarizes our results.

We have observed and characterized the methyl elimination channel in allyl dissociation and discovered that vinylidene is an intermediate

Training and Development:

Trained two graduate students at Cornell University

Established research group at Georgia Institute of Technology following move from Cornell University

Laboratory has been moved to Georgia Tech, along with a research associate and four graduate students. One Georgia Tech student has joined the group to date.

Two students are writing their theses and are defending on May 12 and 13, 2011.

Outreach Activities:

Spoke at Siemens Science Regional Awards Dinner, honoring high school regional winners (Nov., 3, 2007)

Spoke at Georgia Tech High School Math Competition (Feb. 28, 2009).

Developing collaborative project with Peter Chen, a professor at Spelman College in Atlanta.

Journal Publications

Hahkjoon Kim, Kristin S. Dooley, Simon W. North, G. E. Hall, and P. L. Houston, "Anisotropy of photofragment recoil as a function of dissociation lifetime, excitation frequency, rotational level and rotational constant", Journal of Chemical Physics, p. 133316, vol. 125, (2006). Published,

P. L. Houston and S. H. Kable, "Photodissociation of acetaldehyde as a second example of the roaming mechanism", Proc. Nat. Acad. Sci., p. 16079, vol. 103, (2006). Published,

P. O'Keeffe, D. Stranges, and P. L. Houston, "Neutral photodissociation of super-excited states of molecular iodine", Journal of Chemical Physics, p. 144309, vol. 127, (2007). Published, 10.1063/1.2777160

Paul L. Houston, "Product angular and alignment distributions in photodissociation from Rydberg states: NO, O₂, and N₂O", in Vector Correlation and Alignment in Chemistry, G. G. Balint-Kurti and M. P. de Miranda (eds.) (Collaborative Computational Project on Molecular Quantum Dynamics (CCP6), 2005, Daresbury Laboratory, UK), p. 23, vol. none, (2005). Published,

Stranges, D; O'Keeffe, P; Scotti, G; Di Santo, R; Houston, PL, "Competing sigmatropic shift rearrangements in excited allyl radicals", JOURNAL OF CHEMICAL PHYSICS, p. , vol. 128, (2008). Published, 10.1063/1.290771

C. Chen, B. Braams, D. Y Lee, J. M. Bowman, P. L. Houston, and D. Stranges, "Evidence for Vinylidene Production in the Photodissociation of the Allyl Radical", JPC Letters, p. 1875, vol. 1, (2010). Published,

O. Tokel, J. Chen, C. K. Ulrich, and P. L. Houston, "The O(1D) + N₂O reaction: NO vibrational and rotational distributions", Journal of Physical Chemistry A, p. 11292, vol. 114, (2010). Published,

C. Chen, B. Braams, D. Y Lee, J. M. Bowman, P. L. Houston, and D. Stranges, "The Dynamics of Allyl Radical Dissociation", Journal of Physical Chemistry A, p. , vol. , (2011). Accepted,

Books or Other One-time Publications

Paul L. Houston, "Chemical Kinetics and Reaction Dynamics", (1006). Book, Published
Bibliography: Dover Publications

Web/Internet Site

URL(s):

<http://people.ccmr.cornell.edu/~plh2/group/Betaofnu.htm>

Description:

A computer program is provided that accompanies one of the journal articles that we published

Other Specific Products

Contributions

Contributions within Discipline:

A better understanding of photodissociation dynamics has been provided, specifically concerning production of Rydberg states of atoms in dissociative ionization events.

This work has been presented at a National meeting (Dynamics of Molecular Collisions)

Contributions to Other Disciplines:

Contributions to Human Resource Development:

Two graduate students have been trained for one year each. One should graduate in 2009, another in 2010

Contributions to Resources for Research and Education:

Contributions Beyond Science and Engineering:

Conference Proceedings

Categories for which nothing is reported:

Any Product

Contributions: To Any Other Disciplines

Contributions: To Any Resources for Research and Education

Contributions: To Any Beyond Science and Engineering

Any Conference

NSF Final Report

Paul Houston

Our most important contributions during the past grant period¹ are provided in references 2-9 and summarized in this section. The goal of our research during this past period was to apply product imaging techniques to the study of photodissociations, particularly of systems that exhibit predissociative behavior. Briefly, we have 1) explained through theory and experimental examples how the angular distribution of products depends on the frequency of excitation, the lifetime of the dissociative state, the rotational level, and the rotational constant.² This leads to the possibility of oscillations in the anisotropy parameter hinted at in Fig. 1 (see below), and observed directly. 2) We have also found evidence for a “roaming” mechanism in the dissociation of acetaldehyde,³ augmenting the growing theoretical and experimental evidence for such processes. 3) We discovered direct evidence for the production of high- n Rydberg states of iodine atoms in the dissociative ionization of I_2 via the process $I_2 + h\nu \rightarrow I^+ + I^*(n) + e^-$.⁵ 4) We have performed several experimental and trajectory studies of the dissociation of the allyl radical, CH_2CHCH_2 , and its isotopolog CH_2CDCH_2 . An experimental study⁶ provided evidence that methyl elimination took place via two channels, with an intermediate $CH_3-CH_2CH_2$ formed by both a 1,3 hydrogen shift and a double 1,2 hydrogen shift. Trajectory calculations^{7,9} demonstrated that, in addition, methyl elimination was also accompanied by vinylidene (CCH_2) production, and that this species accounted for the bimodal methyl translational distribution observed in a previous experiment. 5) The NO vibrational distribution in the $O(^1D) + N_2O \rightarrow 2 NO$ reaction has been determined.⁸ Abbreviated abstracts of the publications follow.

Anisotropy of photofragment recoil as a function of dissociation lifetime, excitation frequency, rotational level and rotational constant²

Quantum mechanical calculations of photofragment angular distributions have been performed as a function of the frequency of excitation, the lifetime of the dissociative state, the rotational level and the rotational

constant. In the limit of high J values and white, incoherent excitation, the general results are found to agree exactly with both those of Mukamel and Jortner and those of Jonah. Example calculations describe how the anisotropy is dependent on the degree of broadening, the rotational constant, the initial rotational level, and the frequency of excitation. Applications are also made to interpret experimental results on the photodissociation of ClO via the 11-0, 10-0 and 6-0 bands of the $A^2\Pi_{3/2} - X^2\Pi_{3/2}$ transition, as shown in Fig. 1 for the 10-0 band, and on the photodissociation of O_2 via the 0-0 band of the $E^3\Sigma_u^- - X^3\Sigma_g^-$ transition. **Photodissociation of acetaldehyde as a second example of the roaming mechanism³**

Product state distributions of the CO produced in the 308 nm photolysis of acetaldehyde

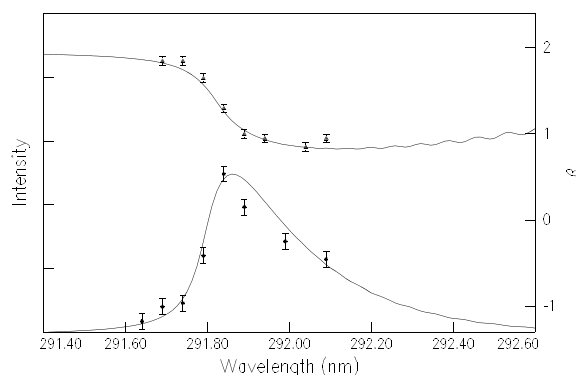


Figure 1 Experimental data for the 10-0 band of ClO and calculated spectrum and variation in β . The upper data give the experimental values of β (right hand ordinate), while the lower data give the experimental photofragment excitation spectrum. The calculations (solid lines) were done for $\Delta\nu=4.00$ cm.

show clear evidence of two dissociation mechanisms. One is attributed to the conventional transition state mechanism predicted by theory, with high rotational and translational energy of the CO and a pronounced $\mathbf{v} \perp \mathbf{J}$ vector correlation. However, as much as 15% of the reaction flux proceeds via another pathway that produces low CO rotational and translational energy, very high CH₄ internal energy, and no correlation between the CO velocity and angular momentum vectors. The attributes of this channel are dynamically similar to the recently reported “roaming atom” mechanism in formaldehyde. We therefore speculate that the second pathway in acetaldehyde also occurs via a roaming mechanism in the CH₃ + HCO exit channel that decays into the CH₄ + CO channel.

Product angular and alignment distributions in photodissociation from Rydberg states: NO, O₂, and N₂O⁴

A conference paper has been prepared that summarizes NSF-supported work on the dissociation of NO,¹⁰ O₂,¹¹ and N₂O.¹²

Neutral photodissociation of super-excited states of molecular iodine⁵

Formation of high-*n* Rydberg atoms from the neutral dissociation of superexcited states of I₂ formed by resonant two-photon excitation of molecular iodine using an ArF laser has been investigated. The high-*n* Rydberg atoms I* are formed by predissociation of the optically excited molecular Rydberg states I₂^{*} R[B ²Σ_g⁺] converging on the I₂⁺ B ²Σ_g⁺ state of the ion. Measurement of the kinetic energy release of the Rydberg I* fragments allowed the identification of the asymptotic channels to be I*[R(³P_J)] + I(²P_{3/2}), where the I*[R(³P_J)] are Rydberg atoms converging on the I*(³P_J) states of the ion with *J* = 2, 1, and 0. In the case of the I*[R(³P₂)] fragments, the average Rydberg life time is observed to be 325 ± 25 μs. Based on observations of the variation in the Rydberg atom signal with field ionizing strength, the distribution of Rydberg levels peaks about 25 - 50 cm⁻¹ below the ionization limit.

Competing Sigmatropic Shift Rearrangements in Excited Allyl Radicals⁶

The competition between rearrangement of the excited allyl radical via a 1,3 sigmatropic shift vs. sequential 1,2 shifts has been observed and characterized using isotopic substitution, laser excitation, and molecular beam techniques. Both rearrangements produce a 1-propenyl radical that subsequently dissociates to methyl + acetylene. The 1,3 shift and the 1,2 shift mechanisms are equally probable for CH₂CHCH₂, whereas the 1,3 shift is favored by a factor of 1.6 in CH₂CDCH₂. The translational energy distributions for the methyl and acetylene products of these two mechanisms are substantially different. Both of these allyl dissociation channels are minor pathways compared to hydrogen atom loss.

Evidence for Vinylidene Production in the Photodissociation of the Allyl Radical⁷

A combination of experimental and theoretical work strongly implicates the production of vinylidene (Fig. 2) in the photodissociation of the allyl radical, CH_2CHCH_2 , an important intermediate in hydrocarbon combustion. The evidence comes from a study of the dissociation of 2- d_1 -allyl, which yields distinctly different translational energy distributions and mechanisms for the products $\text{HCCH} + \text{CH}_2\text{D}$ and $\text{DCCH} + \text{CH}_3$. In one mechanism, a 1,3 hydrogen shift takes place to give the CH_3CDCH intermediate, which then dissociates to yield $\text{CH}_3 + \text{DCCH}$, whereas in the second, one of two branches occurs after a 1,2 hydrogen shift. The shift forms $\text{CH}_2\text{D}-\text{C}-\text{CH}_2$, which either dissociates directly to $\text{CH}_2\text{D} + \text{CCH}_2$ (vinylidene) or undergoes a second 1,2 shift to give $\text{CH}_2\text{D}-\text{CH}-\text{CH}$, which subsequently dissociates to $\text{CH}_2\text{D} + \text{HCCH}$.

The Dynamics of Allyl Radical Dissociation⁹

Dissociation of the allyl radical, CH_2CHCH_2 , and its deuterated isotopolog, CH_2CDCH_2 , have been investigated using trajectory calculations on an *ab initio* ground-state potential energy surface calculated for 97418 geometries at the coupled cluster single and double and perturbative treatment of triple excitations, with the augmented correlation consistent triple zeta basis set level (CCSD(T)/AVTZ). At an excitation energy of 115 kcal/mol, corresponding to optical excitation at 248 nm, the primary channel is hydrogen loss with a quantum yield of 0.94 to give either allene or propyne in a ratio of 6.4 to 1. The total dissociation rate for CH_2CHCH_2 is $6.3 \times 10^{10} \text{ s}^{-1}$, corresponding to a $1/e$ time of 16 ps. Methyl and C_2H_2 are produced with a quantum yield of 0.06 by three different mechanisms: a 1,3 hydrogen shift followed by CC cleavage to give methyl and acetylene, a double 1,2 shift followed by CC cleavage to give methyl and acetylene, or a single 1,2 hydrogen shift followed by CC cleavage to give methyl and vinylidene. In this last channel the vinylidene eventually rearranges to give internally excited acetylene, and the kinetic energy distribution is peaked at much lower energy (6.4 kcal/mol) than that for the other two channels (18 kcal/mol), as shown in Fig. 3. The trajectory results also predict the $\mathbf{v}\text{-}\mathbf{J}$ correlation, the anisotropy of dissociation, and distributions for the angular momentum of the fragments. The $\mathbf{v}\text{-}\mathbf{J}$ correlation for the $\text{CH}_3 + \text{HCCH}$ channel is strongest for high rotational levels of acetylene, where \mathbf{v} is perpendicular to \mathbf{J} . Methyl elimination is anisotropic, with $\beta = 0.66$, while hydrogen elimination is nearly isotropic. In the hydrogen elimination channel, allene is rotationally excited with a distribution peaked near $J = 17$. In the methyl elimination channel, the peak of the methyl rotational distribution is at $J \approx 12$, whereas the peak of the acetylene rotational distribution is at $J \approx 28$.

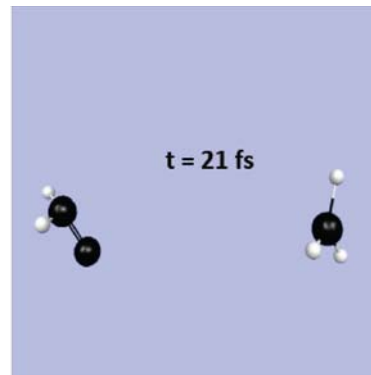


Figure 2 Vinylidene produced in the dissociation of allyl

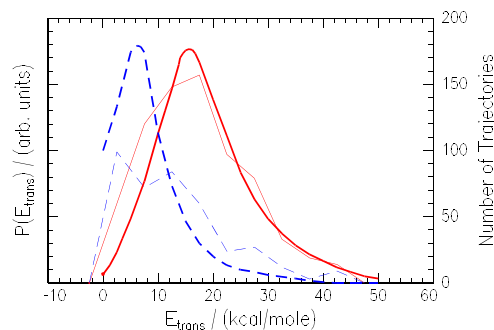


Figure 3 The smooth curves give the experimental kinetic energy distributions for HCCH (dashed, $\times 3$) and DCCH (solid) from ref. 6. The remaining curves give the corresponding distributions for trajectories starting at the allyl global minimum for C_3H_5 (the HCCH distribution has been multiplied by 3).

The $O(^1D) + N_2O$ reaction: NO vibrational and rotational distributions⁸

The $O(^1D) + N_2O \rightarrow 2 NO(X^2\Pi)$ reaction has been studied in a molecular beam experiment in which O_3 and N_2O were co-expanded. The precursor $O(^1D)$ was prepared by O_3 photodissociation at 266 nm, and the $NO(X^2\Pi)$ molecules born from the reaction as the $O(^1D)$ recoiled out of the beam were detected by 1+1 REMPI over the 220-246 nm probe laser wavelength range. The resulting spectrum was simulated to extract rotational and vibrational distributions of the $NO(X^2\Pi)$ molecules. The product rotational distribution is found to be

characterized by a constant rotational temperature of ≈ 4500 K for all observed bands, $v = 0-9$. An inverted vibrational distribution is observed, as shown in Fig. 4. A consistent

explanation of this and previous experimental results is possible if there are two channels for the reaction, one producing a nearly statistical vibrational distribution for low $O(^1D)$ - N_2O relative velocity collisions and a second producing the inverted distribution observed here for high relative velocity collisions. The former might correspond to an insertion/complex-formation reaction, while the latter might correspond to a stripping reaction. Velocity relaxation of the $O(^1D)$ is argued to compete strongly with reaction in most bulb studies, so that these studies see predominantly the nearly statistical distribution. In contrast, the beam experiments do not detect the part of the vibrational distribution produced in low relative velocity reactions because the $O(^1D)$ is not relaxed from its initial velocity before it either reacts or leaves the beam.

Publications supported by previous NSF grant

References 2-9 were supported entirely or partially by the previous NSF grant. These and other publications from the group can be accessed at <http://www.cosbkup.gatech.edu/group/PLHPublicat.htm>

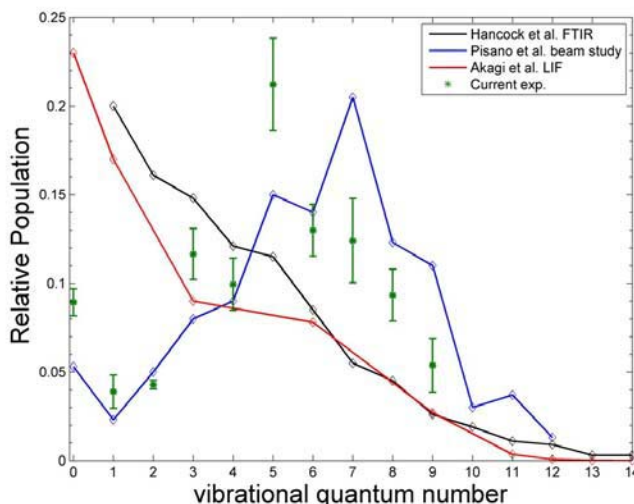


Figure 4 Comparison of the relative $NO(X^2\Pi)$ vibrational level population results from the current experiment with those from previous molecular beam and bulk studies. A shoulder is observed at the $v=4-8$ range in the bulk studies, whereas an inverted population is observed in the molecular beam studies.

Broader Impacts: Education and Human Resource Development

Four graduate students (one female), and one senior research associate have been directly associated with this NSF-sponsored project. One additional graduate student and three senior investigators have collaborated on two of the publications. Similar human resource development is expected to occur during the next funding period.

Graduate Students: Clare Kelleher Ulrich, David Lee, and Ben Strangfeld, from the Department of Chemistry and Chemical Biology at Cornell, and Onur Tokel from the School of Applied Physics at Cornell, are graduate students who have worked on NSF supported research during the last period. (David Lee was partially supported by ACS PRF during this period.) David Lee and Onur Tokel are expected to receive their doctorate degrees in

early 2011.

Research Scientist: Dr. Jun (Jack) Chen, who received his Ph.D. from U. C. Santa Barbara joined the group at Cornell first as a postdoctoral research associate and then moved with the group to the Georgia Institute of Technology, where he is a research scientist supported entirely by Georgia Tech funding. In addition to working on NSF projects, he has also helped to direct graduate students, keep equipment running, and represent the research group. He has also worked with the PI on outreach projects (see below).

Other Collaborators: We continue to collaborate closely with Professor Domenico Stranges of the University of Rome on projects concerning the allyl radical. Since arriving in Atlanta, we have also benefitted greatly from our collaboration with the group of Professor Joel Bowman, especially with Chao Chen (undergraduate) and Bastiaan Braams (research associate). This group calculated a surface for the allyl radical and got us started on a collaborative trajectory study carried out both at Emory and Georgia Tech.

Additional Activities: Paul Houston gave seven invited lectures during this grant period and presented several posters. During this period he also served as Chair of the APS Division of Chemical Physics Nominating Committee. In 2007, Professor Houston moved with his group to the Georgia Institute of Technology, where he is Professor in the School of Chemistry and Biochemistry and Dean of the College of Sciences. Despite his administrative duties, he has, on average, 40% of his time for research and some teaching. He recently taught an honors course on the topic "The Art of Talking Science," whose aim it was to help undergraduate students communicate about science. In addition to seven academic schools, an activity that reports to him is the Center for Education Integrating Science, Mathematics, and Computing (CEISM), a K-12 STEM outreach organization serving the entire institute and the State of Georgia. The PI and Dr. Jack Chen also have an ongoing collaboration with Professor Peter Chen of Spelman College and his student Thresa Wells to study multidimensional spectroscopy in molecular jets.

References

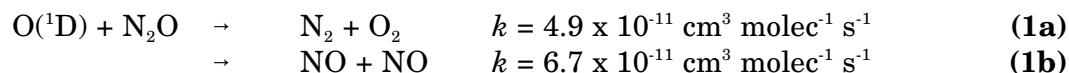
1. CHE-0548867, 2006-2010, \$687,240, "Product Imaging of Photodissociation and Reactions."
2. Hahkjoon Kim, Kristin S. Dooley, Simon W. North, G. E. Hall, and P. L. Houston, "Anisotropy of photofragment recoil as a function of dissociation lifetime, excitation frequency, rotational level and rotational constant," J. Chem. Phys. 125, 133316 -26 (2006).
3. P. L. Houston and S. H. Kable, "Photodissociation of acetaldehyde as a second example of the roaming mechanism" Proc. Nat. Acad. Sci. 103, 16079-16082 (2006).
4. P. L. Houston, "Product angular and alignment distributions in photodissociation from Rydberg states: NO, O₂, and N₂O," in Vector Correlation and Alignment in Chemistry, G. G. Balint-Kurti and M. P. de Miranda (eds.) (Collaborative Computational Project on Molecular Quantum Dynamics (CCP6), 2005, Daresbury Laboratory, UK).
5. P. O'Keeffe, D. Stranges, and P. L. Houston, "Neutral photodissociation of super-excited states of molecular iodine," J. Chem. Phys. 127, 144309 (2007).
6. P. O'Keeffe, D. Stranges, P. L. Houston and R. Di Santo, "Competing Sigma-

- tropic Shift Rearrangements in Excited Allyl Radicals," J. Chem. Phys. 128, 151101 (2008).
7. C. Chen, B. Braams, D. Y Lee, J. M. Bowman, P. L. Houston, and D. Stranges, "Evidence for Vinylidene Production in the Photodissociation of the Allyl Radical," JPC Letters, 1, 1875-1880 (2010).
 8. O. Tokel, J. Chen, C. K. Ulrich, and P. L. Houston, "The $O(^1D) + N_2O$ reaction: NO vibrational and rotational distributions," J. Phys. Chem. A 114, 11292–11297 (2010).
 9. C. Chen, B. Braams, D. Y Lee, J. M. Bowman, P. L. Houston, and D. Stranges, "The Dynamics of Allyl Radical Dissociation," accepted.

NSF Progress Report, Mar. 31, 2010

Paul L. Houston, Principal Investigator

The major focus of our effort during the past year is on the details of the reaction between $O(^1D)$ and N_2O :



These reactions increase in rate as the relative velocity between the $O(^1D)$ and reactant decreases. The reaction between $O(^1D)$ and N_2O is important because the branching ratio between the two channels is fundamental to the steady-state concentration of ozone. N_2 and O_2 are normal major constituents of the stratosphere, so reaction to this channel is neutral to the concentration of ozone. Production of 2 NO molecules, however, decreases ozone because NO is a catalyst in a scheme which converts two ozone molecules to three molecules of oxygen.

There is considerable uncertainty concerning the vibrational distribution of the NO products from reaction (1b). Brouard et al.¹⁻² reported the stereochemistry of the reaction by probing NO in $v=15$ and 16. Akagi et al.³⁻⁴ reported that two different NO molecules were formed, a “new” one from the abstraction of an N atom by $O(^1D)$ from N_2O and the other from the “old” NO left behind. The new NO had a peak in the vibrational distribution at high vibrational levels, whereas the old one peaked at $v=0$. Pisano, Westley, and Houston reported in 2000 that the distribution ranged from $v=0$ to $v=12$ and that it peaked at $v=7$.⁵ Hancock and Haverd looked at time resolved infrared emission of $NO(v=1-14)$ and concluded that the vibrational distribution was monotonically decreasing from a maximum population at $v=0$ or 1.⁶ Thus it is unclear what the vibrational distribution actually is and why so many measurements differ from one another.

All attempts to measure the rotational distribution find that it is very hot. Kawai et al.⁷ report temperatures up to 20,000 K, while Tsurumaki et al.⁸ found 10,000 K.

We have examined the vibrational and rotational distribution of the NO produced in (1b) by using a single beam of our apparatus, which is shown in Fig. 1. A mixture of O_3 (1%) and N_2O (6%) seeded in He (-78 C, backing pressure 2 psi) was expanded supersonically through a 500 mm diameter nozzle, and collimated with a 500 mm diameter skimmer, at 2 cm distance from the nozzle. Two counter-propagating laser beams intersect the molecular beam at right angles, in the

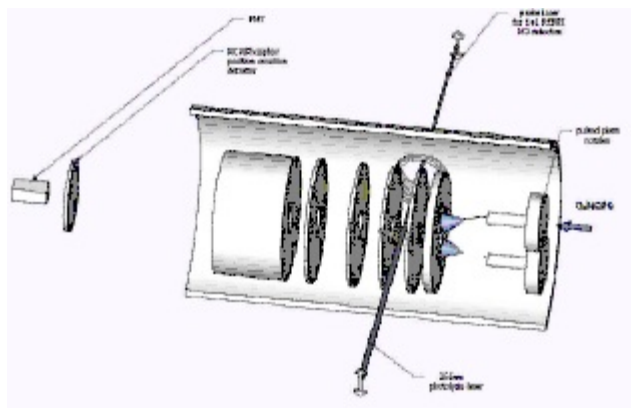


Figure 1 Schematic of Apparatus

center of repeller and extractor electrodes and 7 cm from the nozzle. One laser dissociates the O_3 molecules to generate $O(^1D)$ atoms, and the other state-selectively ionizes the resulting $NO(X^2\Pi)$ molecules from the $O(^1D) + N_2O \rightarrow 2 NO(X^2\Pi)$. The ion cloud is then extracted through an optimized velocity-map spectrometer onto a gated dual micro-channel plate coupled to a fast phosphor screen (Galileo, P-47) at the end of the TOF tube. The ion intensity was measured with a PMT (Thorn EMI) and passed to a computer, where a boxcar records the NO signal.

The O_3 molecules are dissociated by the linearly polarized 266 nm laser light, generated by the fourth harmonic of a Nd-YAG laser (Spectra-Physics GCR-6) operating at 10 Hz. Typical energies were 5-6 mJ/pulse. The laser beam size was cut to 5 mm, which gave the maximum signal to noise ratio under our detection conditions. The polarization axis is vertical to the plane defined by the molecular beam and the 266 laser direction.

The $O(^1D)$ ions created by 203.7 nm 2+1 REMPI processes, were used to check the molecular beam properties (and as a precursor to the reaction). The 203.7 nm light was generated by doubling the output of a Nd-YAG (Spectra-Physics GCR-270) pumped dye laser (PDL-2) in a KDP crystal, and then summing the fundamental with the doubled light in a BBO crystal. Typical powers were 0.9 mJ/pulse at 10 Hz.

NO molecules were state-selectively detected by 1+1 REMPI processes.⁹⁻¹⁰ The tunable NO molecule 220-246 nm probe laser light was generated by doubling the output of a Nd-YAG (GCR-230) pumped Scanmate OPPO laser (Lambda Physik). The probe laser polarization is the same as that of the 266 nm laser. In order to generate the appropriate light three types of dyes were used, i.e. Coumarin 450, 460 and 480. Typical energies were 0.9-1 mJ or 0.5-0.6 mJ/pulse. Energies of both lasers were monitored before and after each scan. The energy levels were chosen so that the NO ion signal never saturates.

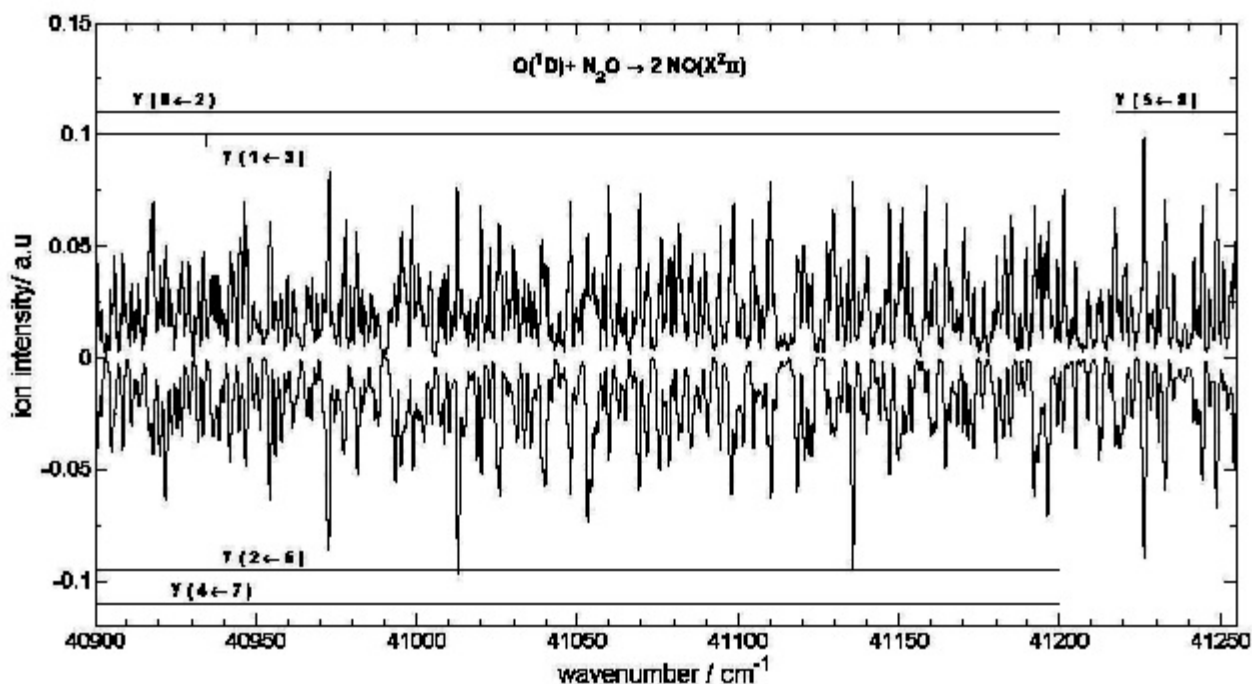


Figure 2

Figure 2 shows the 1+1 REMPI spectra of NO($X^2\Pi$) from $O(^1D)+N_2O \rightarrow 2\ NO(X^2\Pi)$ reaction. A ← X (0,2) ; (1,3); (2,5); (4,7) band features span the whole range. (5,8) bandhead and (1,3) band origin are also shown. The upper plot shows the data, while the lower one is the simulation with $T_{rot}=4500\ K$.

LIFBASE¹¹ and Pgoher¹² software were used to analyze the spectrum of Figure 2. Figure 3 shows the vibrational energy distribution obtained for the reaction. Levels where there are more than one measurements are based on different bands in the spectrum. It is clear that there is a peak in the distribution near $v=5$.

We are currently working to try to understand the relationship of this measurement to others mentioned in the introduction.

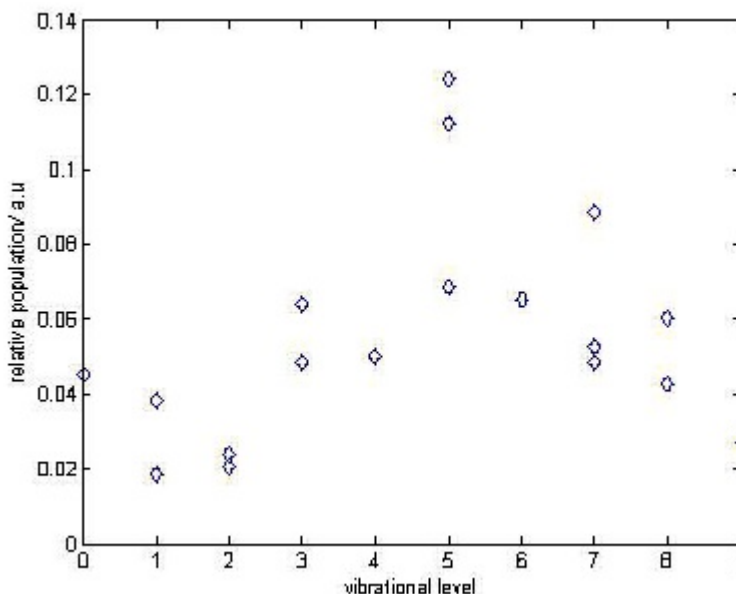


Figure 3 Relative NO vibrational level population from reaction (**1b**).

Another avenue of research has also proven successful. We are monitoring reaction (**1a**) by monitoring the vibrational and rotational distribution of the N_2 product using REMPI. Although there is considerable background at a mass of 28, we are hopeful that we can correct this problem to determine the energy disposal into the N_2 product.

In summary, substantial progress has been made on both branches of the reaction between $O(^1D)$ and N_2O . Reports are in preparation and should be submitted for (**1b**) this spring.

In another line of research, we have investigated the photodissociation of the allyl radical both experimentally, using product imaging, and theoretically, using trajectory calculations on an ab initio potential energy surface. This paper is now being prepared and will be described in our next report. A talk on this work will be presented at a workshop at Argonne National Laboratories this April.

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