State Resolved Differential Cross Sections for Reactions Important to the Decomposition of Energetic Materials

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13. ABSTRACT *(Maximum 200 words)*

This final report describes the research whose goal was to develop a new technique for characterizing the velocity distributions of state-selected reaction products and to use this technique to study reactions of importance to the decomposition of energetic materials. In this technique, the three-dimensional product velocity distribution is determined by ionizing the appropriate species, waiting for a delay while the species separate along their trajectories, and then projecting the spatial distribution of ions onto a two-dimensional screen. The technique was developed and tested using photodissociation of molecules such as NO_2 and CH_3NHNO_2. Further advances were made by investigating the crossed beam dynamics of the collision of argon with NO. Initial attempts were made at investigating the reactions of H with NO_2, CH_3NHNO_2, and H_2NNO_2: an intense hydrogen atom source has been developed.

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1. Foreword

This report describes progress in developing and applying a new technique, product imaging. In this technique, the three-dimensional product velocity distribution is determined by ionizing the appropriate species, waiting for a delay while the species separate along their trajectories, and then projecting the spatial distribution of ions onto a two-dimensional screen. Examples of its use are described.

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List of Illustrations:

4. Final Report

A. Statement of Problem Studied

The goal of the research was to develop a new technique for characterizing the velocity distributions of state-selected reaction products and to use this technique to study reactions of importance to the decomposition of energetic materials. In this technique, the three-dimensional product velocity distribution is determined by ionizing the appropriate species, waiting for a delay while the species separate along their trajectories, and then projecting the spatial distribution of ions onto a two-dimensional screen. The technique was developed and tested using photodissociation of molecules such as NO_2 and CH_3NHNO_2. Further advances were made by investigating the crossed beam dynamics of the collision of argon with NO. Initial attempts were made at investigating the reactions of H with NO_2, CH_3NHNO_2, and H_2NNO_2: an intense hydrogen atom source has been developed.

B. Summary of the Most Important Results

1. The Photodissociation of NO_2

Two dimensional photofragment imaging has been applied to the 355 nm photodissociation of NO_2 in a supersonic beam. The NO fragments are state-selectively ionized and projected onto a two dimensional position-sensitive detector, resulting in an image which can be reconstructed mathematically to provide the velocity distribution shown in Figure 1. This figure was obtained by performing an Abel transform of the observed image of the fragments. The speed distribution of a single rovibrational state of NO consists of a single peak as expected from conservation of momentum and energy.

The angular distribution of the NO and O products is shown in Figure 2. The anisotropy parameter, β, of the NO photofragments is found to be 1.40 ± 0.20, which is significantly larger than previously reported values measured with effusive molecular beams. This discrepancy is explained by the effect of the rotation of the parent molecule.

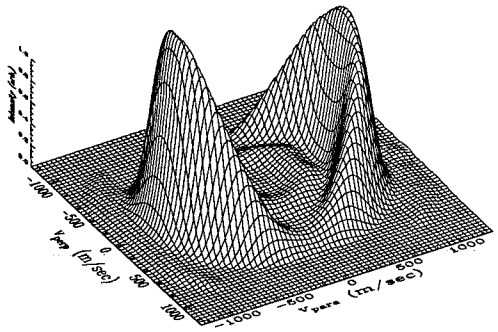

Figure 1 Abel transform of the image from NO_2 photodissociation showing a slice of the three-dimensional distribution.

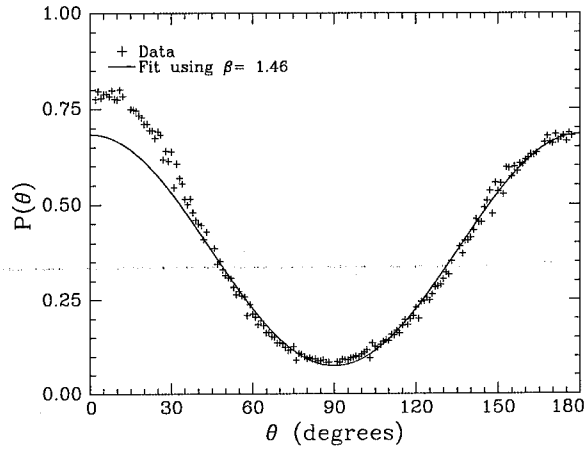

Figure 2 Angular distribution of NO(v″= 0,J″= 25½). The symbols correspond to the distribution obtained by integrating over all the speeds in Fig 1.

2. Photodissociation of Nitromethane

Multiphoton ionization spectroscopy and time-of-flight mass spectrometry have been used to determine nascent photofragment energy distributions for several of the products of the 193 nm photolysis of nitromethane (CH_3NO_2). Internal energy distributions have been obtained for CH_3 and NO(X $^2\Pi$), and translational energy distributions for CH_3, NO(A $^2\Sigma^+$), and O(^{3}P). The production of two NO electronic states (X and A) and the appearance of two peaks in the translational energy distributions of the CH_3 and O fragments are consistent with earlier proposals of a two channel dissociation. The major channel produces CH_3 and NO_2(1 $^2B_2$), some of the latter having sufficient internal excitation to further dissociate to NO(X) and O. The minor channel is believed to produce NO_2 in a different electronic state which subsequently absorbs a second 193 nm photon and dissociates to yield NO(A) and O. The major channel NO_2 dissociation dynamics are fit well by an impulsive model, while the minor channel apparently partitions much of the available energy into NO (A) vibration and/or rotation.

3. Differential Cross Sections for Ar + NO Collisions

State-to-state differential cross sections for inelastic collisions of NO with Ar have been measured in a crossed-beam experiment using time-of-flight ion imaging. Rotational rainbow peaks are observed in the angular distributions, and these move to backward scattering angles with increasing final rotational level. The images, examples of which are shown below, are analyzed using a Monte Carlo forward convolution program that accounts for the transformation from the center-of-mass differential cross sections to the experimental image.

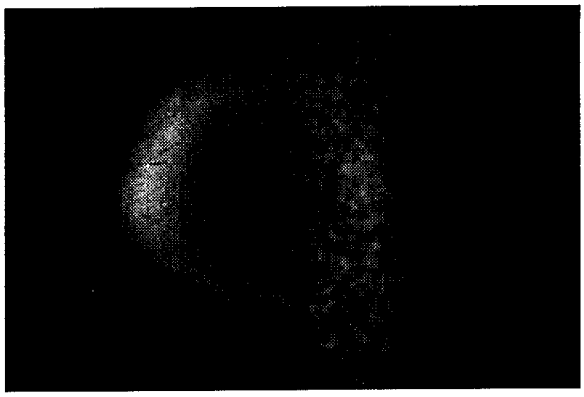

Figure 3 NO (J=9.5)

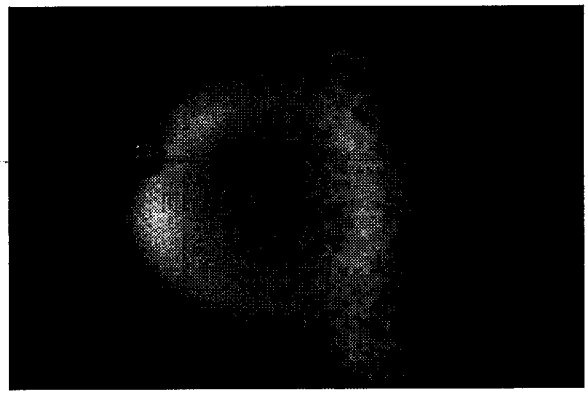

Figure 4 NO (J=11.5)

Figure 5 NO (J=15.5)

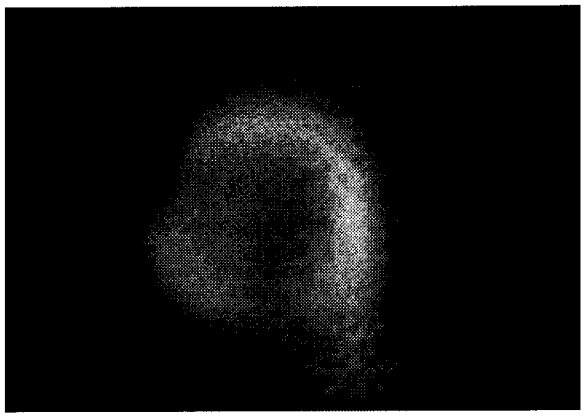

Figure 6 NO (J=18.5)

The figures show the inelastic scattering for different probed final states in the collision, Ar + NO($J_{initial}$=0.5) $\rightarrow$ Ar + NO(J), where J=9.5, 11.5, 15.5, and 18.5. Although there is some background signal that shows up as a stripe from bottom to top (where the laser propagates), the scattering is clearly distinguishable. Several features should be noted. The scattering is roughly symmetric about the relative velocity vector, a line running from lower right to upper left in each of the images. More importantly, as higher J values are probed the angular distribution moves from forward scattering (in Fig. 3) toward the backward part of the sphere ("backward" being defined as toward the lower right of the Newton sphere). Such "rotational rainbows" are exactly what are expected on the basis of calculations using model potentials.[1]

The results are interpreted using a simple two-dimensional hard ellipse model to provide quantitative insight into the anisotropy of the potential energy surface. For NO (j' = 18.5),

two rainbow peaks are observed. These double rainbows have been predicted for scattering of atoms from heteronuclear molecules, but they have not previously been directly observed in the angular distributions. The analysis is also used to obtain the eccentricity of the hard ellipse potential from the positions of the two rainbow peaks. The angular distributions for the spin-orbit conserving collisions and spin-orbit changing collisions are remarkably similar, even though they were thought to involve two different potential energy surfaces. An alternative mechanism is proposed to account for the spin-orbit changing collisions through non-Born-Oppenheimer coupling of nuclear and electronic motion.

4. An Intense Hydrogen Atom Source

We have recently developed an H atom source of roughly ten times the flux that we might have obtained by simply dissociating H_2S in a molecular beam. The source is based on the observation by Harrison *et al.*[2] that intense beams of hydrogen atoms are emitted from a LiF surface that has been covered with H_2S and irradiated at 193 nm. Figure 7 displays an image of H atoms generated in a similar manner, where a probe laser operating on the Lyman-α transition has been used as the first step in a two-photon ionization of the atoms. The arrow on the figure shows the origin of the H atoms, the point at which a 193 laser dissociated a beam of H_2S. The beam has a well defined velocity and width, and is intense enough so that we anticipate good signal to noise for the H + NO_2, CH_3NHNO_2, and H_2NNO_2 reactions.

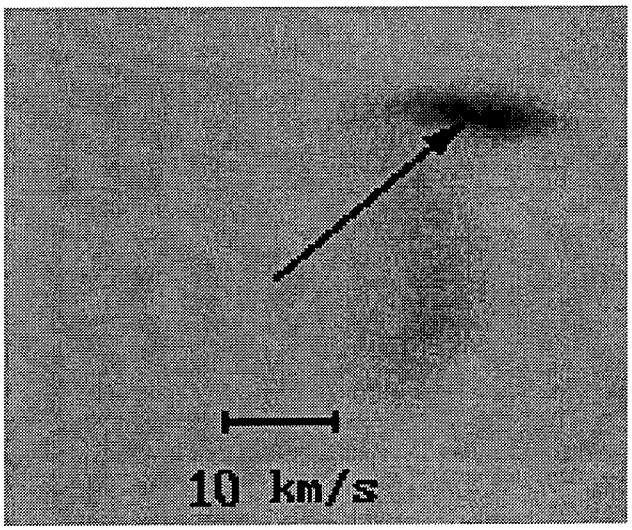

Figure 7 Image of H atom beam.

C. List of Publications and Technical Reports

1. D. B. Moss, K. A. Trentelman, and P. L. Houston, "193 Photodissociation Dynamics of Nitromethane," J. Chem. Phys. **96**, 237-247 (1992).

2. T. Suzuki, V. P. Hradil, S. A. Hewitt, P. L. Houston and B. J. Whitaker, "Two-dimensional Imaging of State-selected Photofragments: The 355 nm Photolysis of NO_2," Chem. Phys. Lett. **187**, 257-262 (1991).

3. A. G. Suits, L. S. Bontuyan, P. L. Houston, and B. J. Whitaker, "Differential Cross Sections for State-Selected Products by Direct Imaging: Ar + NO," J. Chem. Phys. **96**, 8618-8620 (1992).

4. L. S. Bontuyan, A. G. Suits, P. L. Houston, and B. J. Whitaker, "State-resolved Differential Cross Sections for Crossed-beam Ar-NO Inelastic Scattering by Direct Imaging," J. Phys. Chem. **97**, 6342-6350 (1993).

D. List of Participating Scientific Personnel and Degrees

Toshinori Suzuki, postdoctoral associate, now at the Institute of Molecular Science, Okazaki, Japan.

Arthur Suits, postdoctoral associate, now at the Lawrence Berkeley Laboratory.

Benjamin Whitaker, visiting scientist, now at Leeds University, United Kingdom.

Lizla Bontuyan, graduate student who obtained her Ph.D. on this project in August, 1993, now at the Institute of Molecular Science, Okazaki, Japan.

Vince Hradil, graduate student who obtained his Ph.D. on this project in May, 1992, now with Packer Engineering, Naperville, IL 60566.

Arthur Hewitt, postdoctoral associate, now at California State University, Fullerton.

David Moss, postdoctoral associate, now at Providence College, Providence, RI.

Karen Trentelman, graduate student who obtained her Ph.D. in May, 1989, now at the State University of New York at Buffalo.

5. Report of Inventions

There were no inventions during the course of this project.

6. Bibliography

1. R. Schinke and J. M. Bowman, "Rotational Rainbows in Atom-Diatom Scattering," in *Molecular Collision Dynamics*, Chapter 4, J. M. Bowman, ed., (Springer-Verlag, Berlin, 1983).

2. I. Harrison, J. C. Polanyi, and P. A. Young, J. Chem. Phys. **89**, 1498 (1988).

7. Appendixes

None