Final Report

Product Imaging of Molecular Dynamics Relevant to Combustion Grant No. DE-FG02-88ER13934

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I. Introduction: Program Scope

Product imaging has been used to investigate several processes important to a fundamental understanding of combustion. The imaging technique produces a "snapshot" of the three-dimensional velocity distribution of a state-selected reaction product. Research in three main areas is planned or underway. First, product imaging has been used to investigate the reactive scattering of radicals or atoms with species important in combustion. These experiments, while more difficult than studies of inelastic scattering or photodissociation, are now becoming feasible. They provide both product distributions of important processes as well as angular information important to the interpretation of reaction mechanisms. Second, the imaging technique has been used to measure rotationally inelastic energy transfer on collision of closed-shell species with important combustion radicals. Such measurements improve our knowledge of intramolecular potentials and provide important tests of *ab initio* calculations. Finally, experiments using product imaging have explored the vacuum ultraviolet photodissociation of O₂, N₂O, SO₂, CO₂ and other important species. Little is known about the highly excited electronic states of these molecules and, in particular, how they dissociate. These studies provide product vibrational energy distributions as well as angular information that can aid in understanding the symmetry and crossings among the excited electronic states

II. Summary of Progress

In addition to the reports of new research results published or submitted during the previous grant period and described briefly below, we also published a review paper that is not discussed in detail. Brief summaries follow for the most recent work.

A. Quantum Yields for Product formation in the 120-133 nm Photodissociation of O₂

Oxygen is a molecule involved in all practical combustion processes, but surprisingly little is known about its highly excited electronic states. We have studied the photodissociation of O₂ in the region from 120-133 nm by using product imaging. The spectrum in this region is dominated by transitions from the ground state to the first three

vibrational levels of the $E^3\Sigma_u^-$ state. As shown in Figs. 1 and 2, the $O(^1D) + O(^3P)$ channel is the only product channel observed by product imaging for dissociation at either 124.4 nm or 120.4 nm. Fig. 1 shows the velocity distributions of the $O(^1D)$ product (top) and the $O(^3P_2)$ product (bottom) for dissociation at 124.4 nm. Peaks in both panels correspond to the production of the $O(^1D) + O(^3P_2)$ channel, but there are no peaks corresponding to other possible channels. Fig. 2 shows the velocity distribution of the $O(^1D)$ product for dissociation at 120.4 nm. Again, the peak in the distribution corresponds to production of $O(^1D) + O(^3P)$, but no peak is observed for the channel producing $O(^1D) + O(^1D)$. We conclude that the quantum yield for $O(^1D)$ production at both wavelengths is unity.

The $O(^1D_2)$ product is aligned in the molecular frame in such a way that its J vector is perpendicular to the relative velocity vector between the $O(^1D)$ and the $O(^3P)$. The repulsive part of the $O_2(E^3\Sigma_u^-)$ state is actually the continuation of the repulsive part of the $O_2(B^3\Sigma_u^-)$ state, which correlates to the observed $O(^1D) + O(^3P)$ products. According to the Wigner-Witmer rules, the combination of a 1D and 3P atoms to produce a Σ^- state can only occur with $m_J = 0$ or 1. This prediction is consistent with our finding that $m_J = 0$ is strongly preferred.

The variation in the anisotropy of dissociation is approximately predicted by considering transitions on individual lines and then taking into account the coherent excitation of overlapping resonances.

At a dissociation wavelength of 132.7 nm, both the $O(^1D) + O(^3P)$ and the $O(^3P) + O(^3P)$ channels are observed with branching ratios of 0.40 ± 0.08 and 0.60 ± 0.09 , respectively. At 130.2 nm, the quantum yield for production of $O(^1D)$ is 0.76 ± 0.28 .

B. Dissociation of sulfur dioxide by ultraviolet multiphoton absorption between 224 and 232 nm

Figure 1 Speed Distributions of $O(^1D)$ (upper panel) and $O(^3P_2)$ (lower panel) produced in the 124.4 nm photodissociation of O_2 .

Figure 2 Speed distribution of $O(^1D)$ produced in the 120.4 nm photodissociation of O_2 .

Multiphoton excitation and dissociation of SO_2 has been investigated in the wavelength range from 224-232 nm. Strong evidence is found for two-photon excitation to the $\tilde{H}$ Rydberg state, followed by dissociation to $\text{SO} + \text{O}$ and ionization of the SO product by absorption of a third photon. The two-photon excitation is resonantly enhanced via the $\tilde{C}^1\text{B}_2$ intermediate state, and the two-photon yield spectrum shown in Fig. 3 thus bears a strong resemblance to the spectrum of this intermediate.

Figure 3 Yield spectra from multiphoton dissociation of SO_2 in the range 42700-45000 cm^{-1} . (a) SO^+ and (b) S^+ .

Imaging of the $\text{O}(^3\text{P}_2)$, $\text{S}(^1\text{D}_2)$ and SO products suggests that, following dissociation of SO_2 from the $\tilde{H}$ state, SO is produced in the A and B electronic states. Figure 4 shows the kinetic energy release spectrum of the SO product.

$\text{S}(^1\text{D}_2)$ is produced both from two-photon dissociation of SO_2 to give $\text{S}(^1\text{D}_2) + \text{O}_2$ and by single-photon dissociation of SO^+ . In the former process, the O_2 is likely formed in all of its lowest three electronic states.

This work was performed in collaboration with Professor Edwin Quiñones and his (then) graduate student, Yuxiu Lei, both of the University of Puerto Rico in Rio Piedras.

C. Photodissociation of N_2O near 130 nm

Nitrous oxide is an important component of Earth's natural atmosphere produced primarily by biological processes in soils and oceans but also as a by-product of combustion. Mostly inert in the troposphere, it is transported to the stratosphere where it is destroyed both by photodissociation (at $\lambda \approx 200$ nm),

and by reaction with $\text{O}(^1\text{D})$ produced either in (1) or from the dissociation of ozone,

Figure 4 Total translational energy distribution obtained for dissociation via the intermediate $(0, 0, 6)$ band of the $\tilde{C}^1\text{B}_2$ state by analyzing the image for SO^+ .

NO produced in (3) is the primary catalytic agent destroying stratospheric ozone in the natural atmosphere, as noted by Crutzen.

At shorter wavelengths, N_2O can be excited to the $\text{C}(^1\Pi)$ state near 145 nm or to the $\text{D}(^1\Sigma^+)$ state near 130 nm. The absorption coefficient for the latter transition is high, about 80 Mb ($1 \text{ Mb} = 10^{-18} \text{ cm}^2$). Although dissociation process (1) near 200 nm has been extensively studied, that at shorter wavelengths is both more complex and less well understood. At 130 nm, the following channels are thought to be important:

We have investigated channels (4) - (8) by using product imaging to detect the angular distributions for the five channels as well as the kinetic energy release for each of the product atoms or diatoms. The atomic products were probed by resonant ($1 + 1'$) ionization using ultraviolet excitation for the first step, while the diatomic products were probed by non-resonant ionization. Our work is part of a larger effort at Cornell to characterize this photodissociation process. Witinski, Ortiz-Suárez, and Davis, whose work is also supported by DOE, have used oxygen Rydberg time-of-flight spectroscopy to study channels (7) and (8), with results that are in reasonable agreement with ours.

Figure 5 shows the total kinetic energy release for the $\text{O} + \text{N}_2$ products based on measurements of the $\text{O}(^1\text{S})$, $\text{O}(^3\text{P}_0)$, $\text{O}(^3\text{P}_2)$, and N_2 products. In each case, conservation of momentum is assumed to determine the total kinetic energy release. The good match for the N_2 and $\text{O}(^3\text{P})$ peaks in the lower panel shows that these are indeed momentum matched. Figure 6 shows similar data for the $\text{N} + \text{NO}$ channel, where $\text{N}(^2\text{D})$, $\text{N}(^2\text{P})$, and NO were probed. In each of these figures, the energy release data provides information about the vibrational distribution of the diatomic fragment.

Figure 5 Total kinetic energy released for $\text{O} + \text{N}_2$ products from the dissociation of N_2O at 130.2 nm: a) $\text{O}(^1\text{S})$; b) $\text{O}(^3\text{P}_2)$ top solid curve; $\text{O}(^3\text{P}_0)$ top dashed curve; N_2^+ bottom curve.

Information about the branching ratio between various channels has also been obtained. The ratio of O^+ and NO^+ can be converted to a branching ratio between the dissociation channels leading to $O(^3P) + N_2$ vs. $N + NO$ by calibrating against the O^+ and NO^+ peaks obtained from the dissociation of NO_2 at 355 nm, assuming that the vibrational distributions for NO in the NO_2 dissociation and the $N + NO$ products are not too different. The reaction appears to favor the $O(^3P) + N_2$ channel by a ratio of 1.4 ± 0.5 . Vacuum ultraviolet line strengths for $O(^3P)$ and $O(^1S)$ are known, so that correcting for laser power variations and assuming similar ionization efficiencies, we find that the $O(^1S) + N_2(X)$ channel has about 10 ± 1.5 times the quantum yield of the $O(^3P) + N_2(A,B)$ channel. Spin-orbit distributions have also been obtained for all atomic products, and the ratio of quantum yields for the $N(^2D) + NO$ vs. $N(^2P) + NO$ channels is about 3.

Figure 6 Total kinetic energy released for N+NO products from the dissociation of N_2O at 130.2 nm: $N(^2P_{3/2})$ top solid curve (at 131.054 nm); $N(^2D_{5/2})$ top dashed curve; NO^+ bottom curve.

D. Summary of Papers Based on DOE Support, 2002-2005

P. L. Houston, "Charged Particle Imaging in Chemical Dynamics: An Historical Perspective," in *Imaging in Molecular Dynamics: Technology and Applications*, B. Whitaker, ed. (Cambridge University Press, Cambridge, 2003).

Bogdan R. Cosofret, H. Mark Lambert, and Paul L. Houston, " $N(^2D)$ Product Velocity Mapped Imaging in the VUV Photolysis of Nitrous Oxide at 118.2 nm," *Bull. Korean Chem. Soc.* **23**, 179-183 (2002). (K.-H. Jung commemorative issue).

Bogdan R. Cosofret, H. Mark Lambert, and Paul L. Houston, "Two-photon Photodissociation of NO through Rydberg Levels in the 265-278 nm region: Spectra and Photofragment Angular Distributions," *J. Chem. Phys.* **117**, 8787-8799 (2002)

Amitavikram A. Dixit, Yuxiu Lei, Keon Woo Lee, Edwin Quiñones, and Paul L. Houston, "Dissociation of sulphur dioxide by ultraviolet multiphoton absorption between 224 and 232 nm," *J. Phys. Chem. A* **109**, 1770-1775 (2005).

H. M. Lambert, A. A. Dixit, E. W. Davis and P. L. Houston, "Quantum Yields for Product Formation in the 120-130 nm Photodissociation of O_2 ," *J. Chem. Phys.* **121**, 10437-10446 (2004).

M. Lambert, E. W. Davis, O. Tokel, A. A. Dixit, and P. L. Houston, "Photodissociation Channels for N₂O near 130 nm Studied by Product Imaging," J. Chem. Phys. **122**, 174304-7 (2005).

These publications may be accessed at

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

More information about our research group is available at

<http://people.ccmr.cornell.edu/~plh2/group/hrghome.html>