**Title and Subtitle**: Vacuum Ultraviolet Studies of Molecular Dynamics

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**Abstract**: Tunable vacuum ultraviolet radiation generated by four-wave mixing will be used to probe collisional energy transfer and photodissociation. Collisional relaxation of the S'(D) velocity distribution by rare gases has been measured to learn to what extent this simple process can be described by a hard-sphere, elastic interaction. E→V transfer was studied from S'(D) to CO and N₂, both by examining the Doppler profile of the relaxed atoms and by direct measurement of the CO(v,J) distribution. Finally, the photodissociation of O₃ and N₂O have been investigated by monitoring the Doppler profiles of the resulting O(D) lines. This integrated program of molecular dynamics studies using vacuum ultraviolet radiation has enhanced our knowledge both of the chemical physics of these basic processes and of the interaction of high energy photons with small molecules found in the upper atmosphere.

**Subject Terms**: Vacuum Ultraviolet Light, Molecular Dynamics, Ozone, Nitrous Oxide, CO
ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Tunable vacuum ultraviolet radiation generated by four-wave mixing will be used to probe collisional energy transfer and photodissociation. Collisional relaxation of the S(1D) velocity distribution by rare gases has been measured to learn to what extent this simple process can be described by a hard-sphere, elastic interaction. E→V transfer was studied from S(1D) to CO and N2, both by examining the Doppler profile of the relaxed atoms and by direct measurement of the CO(v,J) distribution. Finally, the photodissociation of O3 and N2O have been investigated by monitoring the Doppler profiles of the resulting O(0D) lines. This integrated program of molecular dynamics studies using vacuum ultraviolet radiation has enhanced our knowledge both of the chemical physics of these basic processes and of the interaction of high energy photons with small molecules found in the upper atmosphere.
Abstract

Tunable vacuum ultraviolet radiation generated by four-wave mixing will be used to probe collisional energy transfer and photodissociation. Collisional relaxation of the S(1D) velocity distribution by rare gases has been measured to learn to what extent this simple process can be described by a hard-sphere, elastic interaction. E→V transfer was studied from S(1D) to CO and N₂, both by examining the Doppler profile of the relaxed atoms and by direct measurement of the CO(v,J) distribution. Finally, the photodissociation of O₃ and N₂O have been investigated by monitoring the Doppler profiles of the resulting O(1D) lines. This integrated program of molecular dynamics studies using vacuum ultraviolet radiation has enhanced our knowledge both of the chemical physics of these basic processes and of the interaction of high energy photons with small molecules found in the upper atmosphere.

A. Summary of Completed Work (Projects in 1992 and 1993 with AROSR Support)

1. The S(1D) + N₂ Quenching Process: Determination of the Branching Ratio among Triplet Fine Structure Products

The quenching by N₂ of S(1D) to the S(3P₂), S(3P₁), and S(3P₀) levels has been investigated by using tunable vacuum ultraviolet laser-induced fluorescence to probe the initial and final levels following creation of S(1D) by pulsed 222-nm photolysis of OCS. The total quenching rate is (7.1 ± 1.0) x 10⁻¹¹ cm³ molec⁻¹ s⁻¹, while the branching ratios were found to be 0.143 ± 0.006 for 3P₀, 0.085 ± 0.012 for 3P₁, and 0.77 ± 0.02 for 3P₂. The total rate is in good agreement with previous measurements. The branching ratios contrast to the inverted distribution found by Stout, Andrews, Bevilacqua, and Weisman for quenching of S(1D) by argon [Chem. Phys. Lett. 1988, 151, 156].
2. Product Distributions in the 157-nm Photodissociation of CO

The vibrational and rotational distributions of CO (\(^{1}Σ^+\)) produced in the 157 nm photodissociation of CO\(_2\) have been determined by measuring vacuum-ultraviolet laser-induced fluorescence spectra of the CO photoproduct. The photodissociation of CO\(_2\) is known to occur via two pathways; one yielding O('D) and the other yielding O('P). Spin conservation and previous experimental studies confirm that dissociation via the O('D) channel is the dominant process. The available energy for this channel is sufficient to populate only the ground and first excited vibrational levels of CO. We measured the rotational distributions for CO in \(v=0\) and \(v=1\) and found them to be non-Boltzmann. In fact, a highly structured distribution with distinct peaks at \(J=10, 24, 32\) and \(39\) is observed for CO in \(v=0\). A less structured population is displayed by molecules in \(v=1\). The relative vibrational population (\(v=0/v=1\)) was determined to be \(3.7 \pm 1.2\). Doppler spectra of individual rovibronic transitions were also recorded. The profiles have widths in accord with the available translational energy, display the expected \(v \perp J\) correlation, and are best described by an isotropic distribution of the velocity vectors with respect to the polarization direction of the dissociation light.

3. Velocity Relaxation of S('D) by Rare Gases Measured by Doppler Spectroscopy

Velocity relaxation of S('D) by He, Ar, and Xe has been monitored by measuring the Doppler profile of the S('D) for variable collision partner pressures at a fixed time delay following creation of S('D) by pulsed laser photolysis of OCS at 222 nm. The nascent S('D) has a mean speed about three times that at room temperature and an effective anisotropy parameter of \(β=0.5\). A calculation assuming elastic hard-sphere collisions is performed to model the process. The data are in qualitative agreement with the model in that the angular distribution relaxes more rapidly with collision number as the mass
ratio between the collision partner and sulfur approaches infinity, whereas the speed
distribution relaxes more rapidly as the mass ratio approaches zero. Helium behaves as
predicted by the hard-sphere model with a collision cross section of $\sigma_{\text{col}} = 26 \pm 2 \text{ Å}^2$.
However, the cross sections for argon and xenon are found to depend on the collision
energy. The dependence allows an estimation of the following Lennard-Jones parameters:
for argon $\sigma = 3.6 \pm 0.5 \text{ Å}$ and $\varepsilon = 2.5 \pm 0.5 \text{ kJ/mol}$; for xenon $\sigma = 3.9 \pm 0.5 \text{ Å}$ and $\varepsilon = 3.9 \pm 0.8 \text{ kJ/mol}$.

4. **Electronic-to-vibrational, -Rotational, and -Translational Energy Transfer:**

$S(^1\text{D}) + \text{CO, N}_2, \text{O}_2, \text{and CO}_2$ Measured by Doppler Spectroscopy

Collisions of $S(^1\text{D})$ with CO, N$_2$, O$_2$ and CO$_2$ have been investigated to estimate the
fraction of the sulfur electronic energy that is deposited in the internal degrees of freedom
in the collision partner during the quenching of $S(^1\text{D})$ to $S(^3\text{P})$. The experiment measures
the Doppler profile of the $S(^3\text{P})$ product, a profile that depends both on the amount of
energy disposed into the internal degrees of freedom and on the differential scattering
cross section for the inelastic collision. For CO and N$_2$ the results are consistent with a
collision complex model for which the scattering is assumed to be isotropic in the collision
plane and for which the energy is partitioned statistically into the degrees of freedom.
Under the assumption of isotropic scattering, the results suggest that less energy than
the statistical prediction is partitioned into translation for collisions with O$_2$, whereas
more energy is partitioned into translation for CO$_2$.

5. **Anisotropy and Energy Disposal in the 193-nm N$_2$O Photodissociation**

Measured By VUV Laser-Induced Fluorescence of O($^1\text{D}$)

Laser-induced fluorescence near 115 nm has been used to measure the Doppler profile of
the O($^1\text{D}$) product of 193-nm N$_2$O photolysis. The anisotropy of product recoil vectors is
characterized by the parameter $\beta = 0.50 \pm 0.05$. The measured velocity distribution can
be used to calculate a distribution of recoil energies that is in reasonable agreement with
that reported recently by Felder, Haas, and Huber; an average of 27.3 kcal/mole is deposited into translation, leaving ~37 kcal/mole for the internal excitation of the \( N_2 \) fragment.

6. Photodissociation of OCS at 222 nm: The Triplet Channel

The dissociation of OCS at 222 nm produces both \( S(1D) \) and \( S(3P) \). By monitoring the Doppler profile of the minor \( S(3P) \) product on the \( ^3D_1 \leftarrow ^3P_2 \) transition we have determined that the branching ratio for this triplet channel is 5% relative to the singlet channel. The Doppler profiles change as the angle between the polarization direction of the photolysis light and the propagation direction of the probe light is varied, indicating that the excited state lifetime of the OCS is short compared to its rotation period. Detailed analysis of the Doppler profiles provides an anisotropy parameter of \( \beta = 0.3 \pm 0.2 \) and a recoil speed distribution with an average of 37% of the 19,881 cm\(^{-1}\) available energy. The remainder of the energy, 12,525 cm\(^{-1}\), is deposited into CO vibration and rotation. The distributions for both the relative translation and the CO internal energy are broad.

B. Unpublished Projects

1. Photodissociation of \( O_3 \)

The Hartley band photodissociation of ozone has been extensively investigated and is known to occur via two pathways; one yielding \( O(1D) + O_2(a^1\Delta_g) \) and the other \( O(3P) + O_2(X^3\Sigma_g^-) \). Studies indicate that the quantum yields for the excited singlet and ground state triplet product channels are .85 to .90 and .15 to .10, respectively. Recently, Turnipseed et al., examined the dissociation of ozone at 193 nm and determined that the quantum yield for excited state \( O(1D) \) atoms is .46 ± .29. Molecular oxygen in the \( b^1\Sigma_g^+ \) state was also detected and quantified, \( \Phi(b^1\Sigma_g^+) = .50 \pm .38 \). It was therefore suggested that
$O(^1\text{D})$ and $O_2(\text{b}^1\Sigma_u^+)$ are coproduced in the 193 nm photolysis of $O_3$. We have measured the Doppler spectra of $O(^1\text{D})$ products from the 248 and 193 nm photolysis of ozone in order to investigate further the transition from Hartley band dissociation channels and those observed in the vacuum ultraviolet. The $O(^1\text{D})$ fragments produced were detected by laser-induced fluorescence via the one photon $2p^4(^1\text{D}_2)-3s^1(^1\text{D}_2^0)$ transition at 115.2 nm. Two-photon resonantly enhanced four-wave sum mixing in mercury yielded the required VUV radiation. The angular distributions and translational energy for the $O(^1\text{D})$ atoms were deduced from the profiles. Present results indicate that ozone dissociation at 248 nm can be described by a parallel transition, whereas photolysis at 193 nm appears to result in an isotropic distribution of the velocity vectors with respect to the polarization direction of the dissociating light. It was also determined that $O(^1\text{D})$ fragments produced in the 248 nm photolysis of $O_3$ have more energy in translation than the excited atomic oxygen fragments produced when $O_3$ is dissociated at 193 nm. These results and their implications concerning the existence of the $O(^1\text{D}) + O_2(\text{b}^1\Sigma_u^+)$ channel are still under analysis.