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Vacuum Ultraviolet Studies of Molecular Dynamics

Final Report
to the
Air Force Office of Scientific Research
by

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Table of Contents

Title Page	1
Table of Contents	1
I. Introduction	2
II. Summary of Completed Work	3
A. Collisional Excitation of CO by 2.3 eV H Atoms	3
B. Quenching of S(¹ D) by N ₂	4
C. Photodissociation of CO ₂ at 157 nm	4
D. Dissociation Dynamics of C ₃ O ₂ Excited at 157 nm	5
E. The 157 nm Photodissociation of OCS	6
COMPLETED PROJECT SUMMARY	7

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I. Introduction

The study of molecular dynamics using vacuum ultraviolet (VUV) laser sources has become an increasingly important activity over the past five years. To be sure, the increase is partly due to the greater availability of VUV sources, but there are several other reasons as well. VUV sources carry chemically significant energies, so that the availability of lasers in this spectral region opens up a whole range of bond-breaking photochemistry. VUV sources also allow sensitive, state-resolved detection of atoms and molecules either by laser-induced fluorescence (LIF), in which easily detectable photons are produced, or by multiphoton ionization (MPI), in which easily detectable ions are created. Finally, the field of molecular dynamics has grown in importance because of a practical need to learn about the interaction of energetic photons with matter, particularly as such dynamics pertain to the creation of short wavelength lasers and to the propagation of radiation through the atmosphere.

This research grant used tunable vacuum ultraviolet radiation generated by four-wave mixing to probe collisional energy transfer, reactive encounters, and photodissociations. Translation-to-vibration/rotation energy transfer was examined in the $\text{H} + \text{CO}$ system to learn how the extent of transfer depends on the collision energy. The quenching of $\text{S}(^1\text{D})$ by N_2 was studied to learn the branching ratio for quenching to each of the $^3\text{P}_0$, $^3\text{P}_1$, and $^3\text{P}_2$ components as well as to determine the rates of equilibration among these components. Photodissociations of OCS , CO_2 , and C_3O_2 at 157 nm were studied to learn the distribution of energy in the S, O, and CO products and to investigate vector correlations and velocity distributions of these products. 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 likely to be found in the upper atmosphere.

II. Summary of Completed Work

A. Collisional Excitation of CO by 2.3 eV H Atoms

Vibrational and rotational distributions of CO excited by collisions with 2.3 eV H atoms have been obtained by monitoring the products with VUV laser induced fluorescence. Translational-to-vibrational (T→V) transfer is dominated by the dynamics of collisions occurring in the two wells on the H+CO potential energy surface, one characterizing the HCO radical and the other characterizing COH. The measured vibrational distributions agree well with the results of trajectory calculations performed on the *ab initio* potential energy surface of Bowman, Bittman, and Harding (BBH). The measured rotational distributions show two significant differences from the calculated ones, as shown in Figure 1. First, for $v=0$ the experiments find more population in $J<15$ than predicted.

The source of this discrepancy is not yet known, but the trajectories reach locations on a part of the BBH potential that is thought to be calculated accurately. Second, for $v=1$, the experimental distribution is flat from $J=0$ to $J=10$, whereas the calculated one rises from near zero at $J=0$ to a peak at $J=12$. This discrepancy appears to be the result of placing the barrier to the COH metastable well about 0.2 eV too high. An article on this work has appeared in the *Journal of Chemical Physics*.

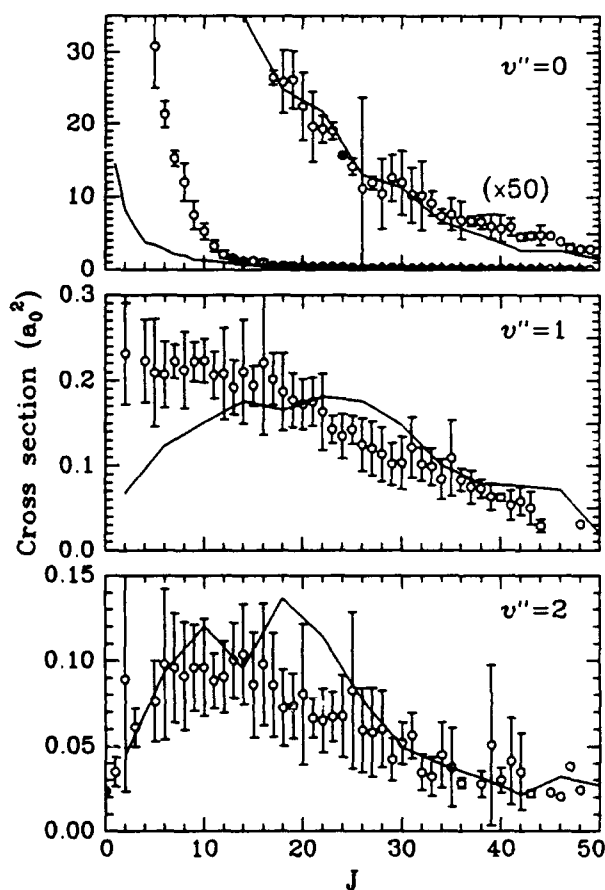


Figure 1 Relative populations for $v=0, 1$, and 2 scattered CO. The Circles give experimental measurements, while the solid line gives the result predicted by the classical trajectory calculations.

B. Quenching of $S(^1D)$ by N_2

The quenching by N_2 of $S(^1D)$ to the $S(^3P_2)$, $S(^3P_1)$, and $S(^3P_0)$ 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 $(7.1 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, while the branching ratios were found to be $0.143 \pm .006$ for 3P_0 , $0.085 \pm .012$ for 3P_1 , and $0.77 \pm .02$ for 3P_2 . 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]. A manuscript on this work has recently been accepted for publication in the *Journal of Physical Chemistry*.

C. Photodissociation of CO_2 at 157 nm

The vibrational and rotational distributions of CO ($^1\Sigma_g^+$) from the 157 nm photodissociation of CO_2 have been measured by obtaining vacuum-ultraviolet laser-induced fluorescence spectra of the CO photoproduct. The photodissociation of CO_2 is known to occur via two pathways; one resulting in the formation of $O(^1D)$ and the other in $O(^3P)$. Spin conservation

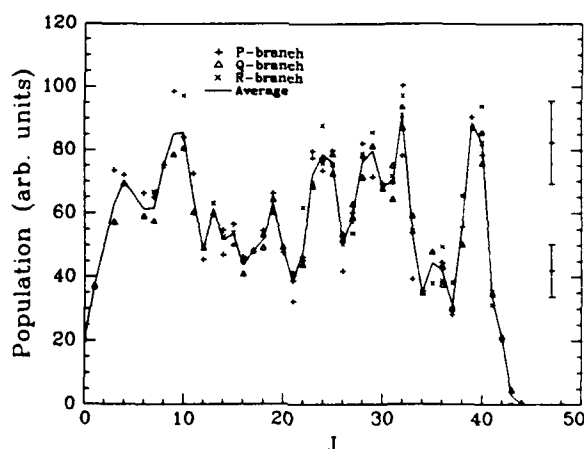


Figure 2 Rotational Distribution of $CO(v=0)$ produced in the 157-nm photodissociation of CO_2 .

and previous experimental studies confirm that dissociation via the $O(^1D)$ channel is the dominant process, providing sufficient energy 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-thermal. In fact, a highly structured distribution with distinct peaks at $J''=10, 24, 32$ and 39 is observed for CO in $v''=0$, as shown in Figure 2. A structured population is also displayed by molecules in $v''=1$. The relative vibrational population [$v''=0/v''=1$] was determined to be 2.5. Doppler spectra of individual rovibronic transitions were recorded. The profiles have widths in accord with the

available translational energy, display the expected $v \perp J$ correlation, and are best described by a β parameter of zero, where β is a measure of the anisotropy of the photofragment recoil. A manuscript on this work has recently been accepted for publication in the Journal of Physical Chemistry.

D. Dissociation Dynamics of C_3O_2 Excited at 157 nm

The dissociation of carbon suboxide by single photon absorption at 157 nm has been studied in the collisionless environment of a molecular beam. The primary products are $2CO + C(^3P(97\%) \text{ or } ^1D(3\%))$. The m_j levels of the 3P carbon were statistically distributed. The CO rotational populations in the first three vibrational levels are found to be well described by Boltzmann distributions with temperatures 3430 K, 4120 K, 4674 K, and 2339 K for $v = 0, 1, 2, 3$ respectively.

A second low temperature component in the $v=0$ rotational distribution was attributed CO produced in coincidence with $C(^1D)$. Significant population was found in the first four vibrational levels, as shown in Figure 3, with less than 3% estimated in the higher levels; a vibrational temperature of 3700 K fit the distribution. The Doppler profiles were nearly Gaussian with evidence of slightly anisotropic recoil directions in the CO ($\beta > 0$) but not the carbon fragments. The mean CO fragment speeds were nearly constant for all rotational levels, though slightly faster for $v'=1$ than $v'=0$. From the translational energetics of the CO, at least a small amount of stable C_2O is inferred to exist at an energy below that of the \bar{c} state. The overall energetics place the stable C_2O quantum yield under 2% assuming that excited C_2O is not radiatively stabilized. We were unable to detect C_2O directly in any electronic state. The dissociation of C_3O_2 into $C(^3P) + 2 CO$ appears to be best described as a stepwise reaction that produces a nearly statistical partitioning into all fragment

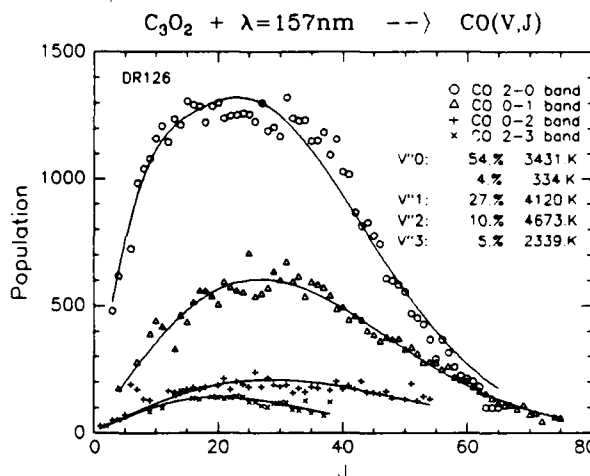


Figure 3 The CO rotational distributions for each vibrational level. The first four vibrational levels are shown with the proper relative scaling and the best Boltzmann fit.

degrees of freedom. The best agreement is obtained for an intermediate C_2O electronic state in the vicinity of the \tilde{b} (e.g., \tilde{b} , \tilde{a} or \tilde{A}); a ground state C_2O intermediate is unlikely. The deviations from a statistical distribution are consistent with a picture in which the exit channel is impulsive but the initial conditions are widely dispersed in phase space. The spin forbidden triplet to singlet crossing most likely occurs in the C_2O system on a time scale longer than a rotation (a few picoseconds). An article on this work has been published in the *Journal of Chemical Physics*.

E. The 157 nm Photodissociation of OCS

The photodissociation of OCS at 157 nm has been investigated by using tunable vacuum ultraviolet radiation to probe the CO and S photoproducts. Sulfur is produced almost entirely in the $S(^1S)$ state, while CO is produced in its ground electronic state and in vibrational levels from $v=0-3$ in the approximate ratio $(v=0):(v=1):(v=2):(v=3) = (1.0):(1.0):(0.5):(0.3)$. The rotational distribution for each vibrational level is found to be near Boltzmann, with temperatures that decrease from 1350 K for $v=0$ to

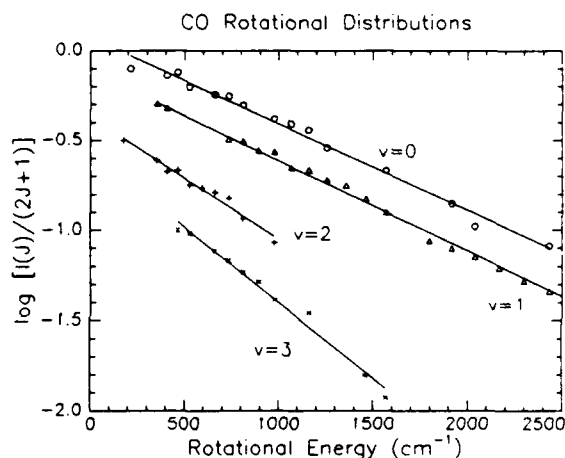


Figure 4 Boltzmann plots for CO produced in the photodissociation of OCS at 157 nm.

780 K for $v=3$, as shown in Figure 4. Measurements of the CO Doppler profiles demonstrate that the dissociation takes place from a transition of predominantly parallel character ($\beta=1.8\pm0.2$) and that the CO velocity and angular momentum vectors are perpendicular to one another. A report of this work has been published in the *Journal of Chemical Physics*.

COMPLETED PROJECT SUMMARY

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PUBLICATIONS:

1. C. E. Strauss, P. L. Houston, I. Burak, and J. W. Hepburn, "The 157-nm Photodissociation of OCS," J. Chem. Phys. **90**, 5364-5372 (1989).
2. R. Ogorzalek Loo, A. Sivaram, W. J. Marinelli, G. E. Hall, P. L. Houston, J. R. Wiesenfeld, and R. W. Field, "Multiphoton Ionization of $O_2(^2\Sigma^-)$ and $O_2(^1\Delta_g)$: The $3s\sigma_g$ and $3d\pi_g$ Rydberg Levels," J. Chem. Phys. **91**, 5185-5200 (1989).
3. G. C. McBane, S. H. Kable, P. L. Houston, and G. C. Schatz, "State-selected T \rightarrow R,V scattering of H from CO at 2.3 eV," J. Chem. Phys. **94**, 1141-1149 (1991).
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6. R. L. Miller, S. H. Kable, P. L. Houston, and I. Burak, "Product Distributions in the 157-nm Photodissociation of CO_2 ," J. Chem. Phys. **96**, 332-338 (1992).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research grant used tunable vacuum ultraviolet radiation generated by four-wave mixing to probe collisional energy transfer, reactive encounters, and photodissociations. Translation-to-vibration/rotation energy transfer was examined in the H + CO system to learn how the extent of transfer depends on the collision energy and to determine the vibrational and rotational distribution of the product. The quenching of S(¹D) by N₂ was studied to learn the branching ratio for quenching to each of the ³P₀, ³P₁, and ³P₂ components as well as to determine the rates of equilibration among these components. Photodissociations of OCS, CO₂, and C₃O₂ at 157 nm were studied to learn the distribution of energy in the S, O, and CO products and to investigate vector correlations and velocity distributions of these products. 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 likely to be found in the upper atmosphere.