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TITLE: Molecular dynamics in the Vacuum Ultraviolet

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INCLUSIVE DATES: November 1, 1985 through October 31, 1988

CONTRACT/GRANT NUMBER: AFOSR 86-0017

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PUBLICATIONS:

1. G. E. Hall, N. Sivakumar, R. Ogorzalek, G. Chawla, H.-P. Haerri, P. L. Houston, I. Burak, and J. W. Hepburn, "Product Correlations in Photofragment Dynamics," Disc. Farad. Soc. **82**, 13 (1986).
2. P. L. Houston, "Vector Correlations in Photodissociation Dynamics," J. Phys. Chem. **91**, 5388 (1987).
3. G. E. Hall, N. Sivakumar, D. Chawla, P. L. Houston, and I. Burak, "Angular Correlations between Recoil Velocity and Angular Momentum Vectors in Molecular Photodissociation," J. Chem. Phys. **88**, 3682-3691 (1988).
4. N. Sivakumar, G. E. Hall, P. L. Houston, I. Burak, and J. W. Hepburn, "State-Resolved Photodissociation Dynamics of OCS Monomers and Clusters," J. Chem. Phys. **88**, 3692-3708 (1988).
5. G. E. Hall, R. Ogorzalek Loo, H.-P. Härrri, N. Sivakumar, G. K. Chawla, P. L. Houston, D. W. Chandler, J. W. Hepburn, and

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- I. Burak, "Vector Correlations in the Photodissociation of CH_3I , OCS, and Glyoxal," *Ber. bunsenges. Phys. Chem.* **92**, 281-288 (1988).
6. G. K. Chawla, G. C. McBane, P. L. Houston, and G. C. Schatz, "State-selective Studies of $\text{T} \rightarrow \text{R}, \text{V}$ Energy Transfer: the $\text{H} + \text{CO}$ System," *J. Chem. Phys.* **88**, 5481-8 (1988).
 7. G. E. Hall, N. Sivakumar, G. Chawla, P. L. Houston, I. Burak, I. M. Waller, H. F. Davis and J. W. Hepburn, "Photo-fragment Spectroscopy with Coherent VUV: Product Correlations and Alignment," *AIP Conference Proceedings* **160**, 1987 (*Adv. Laser Sci.* **2**), pp 170-178.
 8. R. Ogorzalek Loo, C. E. Strauss, H.-P. Haerri, G. E. Hall, P. L. Houston, I. Burak, and J. W. Hepburn, "Vector Correlations in the 157-nm Photodissociation of OCS and the 266-nm Photodissociation of Methyl Iodide," *Disc. Farad. Soc.*, accepted.
 9. C. E. Strauss, P. L. Houston, I. Burak, and J. W. Hepburn, "The 157-nm Photodissociation of OCS," *J. Chem. Phys.*, submitted.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

Tunable vacuum ultraviolet radiation generated by four-wave mixing was used to probe photodissociations, reactive encounters, and collisional energy transfer. Photodissociation studies of OCS at 222 nm were completed and studies at 157 nm were begun. Substantial progress was made in understanding and employing vector correlations to unravel the details of photochemical events. Energy transfer reactions of the type $\text{H} + \text{CO}(\text{v}=0, \text{J}=\text{low}) \rightarrow \text{H} + \text{CO}(\text{v}, \text{J})$ were investigated.

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Molecular Dynamics in the Vacuum Ultraviolet

Final Technical Report
November 1, 1985 through October 31, 1988
Paul L. Houston
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Ithaca, New York 14853

Summary

This report summarizes research progress under grant AFOSR-86-0017 for the three-year period 1985-1988. The photodissociation of OCS at 222-nm has been examined by using tunable vacuum ultraviolet laser radiation to probe the CO and S products. Products of both the monomer and polymer dissociation have been identified and characterized, with particular emphasis on vector correlations. The vacuum ultraviolet radiation used to probe the CO and S products is generated by four-wave mixing in magnesium vapor. The photodissociation of OCS at 157 nm and of CO₂ at the same wavelength have also been investigated. Energy transfer between hot hydrogen atoms and CO($v=0, J=0$) has been investigated by dissociating H₂S in a molecular beam containing CO and probing the CO product by VUV laser-induced fluorescence.

Work Statement

Tunable vacuum radiation generated by four-wave mixing was used to probe photodissociations, reactive encounters, and collisional energy transfer. Photodissociation studies of OCS, already underway at the beginning of the grant period, were completed, and a study of CO₂ was initiated. Energy transfer reactions of the type $H + CO(v=0, J=\text{low}) \rightarrow H + CO(v, J)$ were investigated. Further development of tunable vacuum ultraviolet sources has opened wide areas of molecular dynamics for study.

Completed Research

Photodissociation of OCS in the region from 222-248 nm has been investigated by monitoring the CO, and S(¹D₂) primary photoproducts as well as the secondary production of S(³P₂), S(³P₁), and S(³P₀) using fluorescence induced by a tunable vacuum ultraviolet laser source

based on four-wave mixing in magnesium vapor. The quantum yield of $S(^3P)$ was found to be 0.00 ± 0.02 at 222 nm. Thus, in contrast to our preliminary report, the present more detailed investigation shows that the sole sulfur product appears to be $S(^1D)$. The CO photofragment is produced almost exclusively in $v=0$ [$CO(v=1)/CO(v=0) \approx 0.02$], but the rotational distribution is inverted and peaked at very high rotational levels. The peak shifts from $J=56$ for dissociation at 222 nm to $J=31$ at 248 nm. Doppler profiles of the CO rotational transitions reveal 1) that all observed levels are produced in coincidence with $S(^1D)$, 2) that for 222-nm photolysis the fragment recoil anisotropy shifts from a distribution characterized by $\beta=1.9$ at $J=67$ toward one characterized by $\beta=0$ near $J=54$, 3) that the CO velocity vector is aligned nearly perpendicular to its angular momentum vector, and 4) that the CO angular momentum vector is also aligned parallel to that component of the transition dipole which lies perpendicular to the recoil velocity. These results are interpreted in terms of a model for the dissociation in which excitation takes place to two surfaces of A' and A'' symmetry derived from a bent $^1\Delta$ configuration.

Dissociation of OCS clusters was also investigated and was found to produce a photochemistry completely different from that of the monomers. Rotationally cold CO as well as S_2 in both the $X^3\Sigma_g^-$ and $a^1\Delta_g$ states was observed.

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 780 K for $v=3$. Measurements of the CO Doppler profiles demonstrate that the dissociation takes place from a transition of predominantly parallel character ($\beta=1.8 \pm 0.2$) and that the CO velocity and angular momentum vectors are perpendicular to one another.

A preliminary investigation of the photodissociation of CO_2 at 157 nm has been undertaken. Laser-induced fluorescence signals have been observed for the CO products, but analysis of the spectrum has not been completed. The CO product is observed primarily in $v=0$ and $v=1$.

Collisional energy transfer from H atoms to CO($v=0, J \approx 2$) has been studied at a collision energy of 1.58 ± 0.07 eV by photolyzing H₂S at 222 nm in a nozzle expansion with CO and probing the CO(v'', J'') levels using tunable VUV laser-induced fluorescence. The ratio CO($v''=1$)/CO($v''=0$) is found to be 0.1 ± 0.008 . The rotational distribution of CO($v''=0$) peaks at $J'' \approx 11$ and decays gradually; population is still observed at $J'' > 45$. The rotational distribution of CO($v''=1$) is broad and peaks near $J''=20$. The experimental results have been compared to quasi-classical trajectory calculations performed both on the H+CO surface of Bowman, Bittman and Harding (BBH) and on the surface of Murrell and Rodriguez (MR). The experimental rotational distributions, particularly those for CO($v''=1$), show that the BBH surface is a better model than the MR surface. The most significant difference between the two surfaces appears to be that for energetically accessible regions of configuration space the derivative of the potential with respect to the CO distance is appreciable only in the HCO valley for the BBH surface, but is large for all H atom approaches in the MR potential. Because the H-CO geometry is bent in this valley, vibrational excitation on the BBH surface is accompanied by appreciable rotational excitation, as observed experimentally. Current efforts are underway to investigate the dynamics at somewhat higher collision energy (2.3 eV) and to learn from the Doppler profiles of the scattered CO any possible information about the differential scattering cross section and about the correlation between velocity and rotational angular momentum vectors in the CO product.

Publications During Support Period

1. G. E. Hall, N. Sivakumar, R. Ogorzalek, G. Chawla, H.-P. Haerri, P. L. Houston, I. Burak, and J. W. Hepburn, "Product Correlations in Photofragment Dynamics," *Disc. Farad. Soc.* **82**, 13 (1986).
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6. G. K. Chawla, G. C. McBane, P. L. Houston, and G. C. Schatz, "State-selective Studies of $T \rightarrow R, V$ Energy Transfer: the $H + CO$ System," *J. Chem. Phys.* **88**, 5481-8 (1988).
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8. R. Ogorzalek Loo, C. E. Strauss, H.-P. Haerri, G. E. Hall, P. L. Houston, I. Burak, and J. W. Hepburn, "Vector Correlations in the 157-nm Photodissociation of OCS and the 266-nm Photodissociation of Methyl Iodide," *Disc. Farad. Soc.*, accepted.
9. C. E. Strauss, P. L. Houston, I. Burak, and J. W. Hepburn, "The 157-nm Photodissociation of OCS," *J. Chem. Phys.*, submitted.

Participating Scientists

Dr. Itamar Burak (Univ. Tel Aviv)
 Dr. G. Chawla
 Dr. G. E. Hall
 Prof. J. W. Hepburn (Waterloo)
 Prof. G. Schatz (Northwestern)
 G. E. McBane
 C. E. Strauss
 N. Sivakumar (Ph.D. Cornell University, 1986)
 R. Ogorzalek Loo (Ph.D. Cornell University, 1989)

Interactions (PLH Only)

1. The Hebrew University of Jerusalem, Department of Physical Chemistry, November 13, 1986.
2. Workshop on Dynamical Aspects of Stereochemistry, Hebrew University, Jerusalem, Israel, November 16-24, 1986.
3. Sandia National Laboratories, Livermore, California, Combustion Research Facility, December 12, 1986.
4. University of Colorado at Boulder, Department of Chemistry, February 13, 1987.
5. University of New Hampshire, Department of Chemistry, April 2, 1987.
6. University of Southern California, Department of Chemistry, April 6, 1987.
7. Brookhaven National Laboratory, Department of Chemistry, April 21, 1987.
8. Conference on Molecular Energy Transfer, Emmetten, Switzerland, August 23-28, 1987.
9. International Conference on Laser and Optical Science, Atlantic City, NJ, November 1-5, 1987.
10. Laser and Lightwave Centre, University of Toronto, February 23, 1988.
11. University of Maryland, Department of Chemistry, May 12, 1988.
12. Gordon Conference on Atomic and Molecular Interactions, Plymouth, NH, August 1-5, 1988.

13. Rice University, Department of Chemistry, September 14, 1988.
14. Wayne State University, Department of Chemistry, Frontier Seminar, October 3, 1988.
15. Air Force Office of Scientific Research Contractors' Meeting, Newport Beach, CA, October 31-Nov. 2, 1988.

Inventions

None