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ULTRAVIOLET PHOTODISSOCIATION OF MOLECULAR BEAMS, (U)

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The Ar-F laser (193 nm) was used to photodissociate molecular beams of SO ₂ , CS ₂ , aryl halides, phenyl cyanide and isocyanide, nitroalkenes and nitrobenzene, and H ₂ O ₂ . The translational energy distributions of the fragments were measured. In addition, the internal energy distributions of CS (from CS ₂) and OH frag- ments from H ₂ O ₂ were measured. The excess of photon energy over bond energy is released primarily as vibration for SO ₂ and		

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primarily as translation for H_2O_2 . For CS_2 , comparable amounts of energy appear in translation and vibration; 80% of the S atoms appear in the 1D state. Both phenylcyanide, C_6H_5CN and phenylisocyanide, C_6H_5NC gave $\cdot CN$ and $C_6H_5\cdot$ fragments. In spite of the greater energy available, C_6H_5NC yielded slower CN fragments. The iodobenzene fragmentation occurred by two processes, one from the initially excited state which gave fast fragments and the other from a lower energy state which gave slower fragments and, of course, more internal energy.

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Ultraviolet Photodissociation of Molecular Beams

In our proposal in 1977, we listed a baker's dozen of molecules whose photodissociation dynamics we wished to study. Our final report will consist of a list of these molecules with comments on each.

- 1,2. N₂O and NO₂ - We did not have the signal intensity to study these weakly absorbing molecules. Toward the end of the research grant period we began to install a nozzle beam and a stronger excimer laser which may make such an experiment possible.
3. SO₂ - The translational energy distribution of the SO and O fragments produced at 193 nm were measured. Most of the available energy is present as vibration, i.e. most of the SO fragments are formed in the $v = 3,4$ states. Results are reported in
 (1) A. Freedman, S.C. Yang and R. Bersohn, J. Chem. Phys. 70 6313 (1979).
4. O₃ - Yuan Lee and his group at Berkeley have thoroughly studied the photodissociation of ozone (J. Chem. Phys. 72, 1401 (1980)) and we therefore did not duplicate their effort.
5. H₂S - Hawkins and Houston studied the photodissociation of H₂S at 193 nm (J. Chem. Phys. 72, 297 (1980)). and we therefore did not duplicate their effort.
6. H₂O₂ - Work on this molecule is still proceeding but the essential results are that two OH radicals are produced entirely in the $v=0$ states and predominantly in states of low rotational quantum number. This is surprising because the O-O repulsive force generates a torque around the center of mass. The conclusion is that the O₂-H₁ repulsive force (H₁O₁O₂H₂) although weaker generates a comparable torque to the O-O repulsion.
7. CH₂O - A very weak absorber. We did not have the signal intensity to study this weakly absorbing molecule. Toward the end of the research grant period we began to install a nozzle beam and a stronger excimer laser which may make such an experiment possible.

8. CF₃I - CF₃I like CH₃I turned out to produce mainly I*(²P_{1/2}) and vibrationally cold CF₃ radicals. Because CF₃ is pyramidal this was an expected result; CH₃ is planar and should have been strongly vibrationally excited. The observed slight vibrational excitation can be explained by a potential which preserves the pyramidal structure of the CH₃ radical after dissociation and only gradually allows it to become planar as the fragments recede (M. Shapiro and R. Bersohn, J. Chem. Phys. 73, 3810 (1980) aided primarily by NSF).
9. CCl₂F₂ - Same comments as for 1,2
10. CCl₃F - Same comments as for 1,2.
11. N₂F₄ was commercially available in 1976 but was not in 1979. The somewhat hazardous synthesis made other molecules more attractive.
12. CS₂ - This molecule was studied most completely. At 193 nm distributions over translation, electronic and vibrational energies were measured by time of flight and laser induced fluorescence studies. In contrast to previous findings, our data show that 80% of the S atoms are produced in the ¹D state.
The results were described in
(2) S.C. Yang, A. Freedman, M. Kawasaki and R. Bersohn
J. Chem. Phys. 72, 4058 (1980)

Studies have also been carried out on the photolysis of nitroalkanes and nitrobenzene at 193 nm. The dominant process is

$$\text{R-NO}_2 + h\nu(193 \text{ nm}) \rightarrow \text{R}\cdot + \text{NO}_2^*$$

The excited NO₂* emits a very broad spectrum extending from the upper energy limit at 395 nm out to the cutoff of the photomultiplier tube near 850 nm. φCN and φNC both gave the same product but the higher energy compound φNC yielded, paradoxically, slower fragments.

With the joint help of the Army and the NSF, studies were completed on the photodissociation of aryl and aryl-alkyl halides at 193 nm. This work was reported in

- (3) A. Freedman, S.C. Yang, M. Kawasaki and R. Bersohn,
J. Chem. Phys. 72, 1028 (1980)

The three papers so far published describing work supported by the Army are listed as (1), (2), (3) above. Support of the U.S. Army will, of course, be acknowledged in future publications on H₂O₂ and the nitrocompounds.

Scientific Personel Supported by the Project

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