AD-A095 472 COLUMBIA UNIV NEW YORK F/G 7/5
ULTRAVIOLET PHOTODISSOCIATION OF MOLECULAR BEAMS.(U)
DEC 80 R BERSOHN DAAG29-78-G-0004
UNCLASSIFIED ARO-15014.3-C ML

1 OF 1
AD A095472

END
DATE FILMED
3-81
DTIC

ARO 15014.3-C

19 (12)

TITLE

ULTRAVIOLET PHOTODISSOCIATION OF MOLECULAR BEAMS.

TYPE OF REPORT (TECHNICAL, FINAL, ETC.)

FINAL REPORT FOR PERIOD 10/01/77 - 9/30/80

AUTHOR (S)

(10) R. BERSOHN

DATE

11 15 DEC [redacted] 80

U. S. ARMY RESEARCH OFFICE

CONTRACT / GRANT NUMBER

(15) DAAG29-78-G-0004

INSTITUTION

COLUMBIA UNIVERSITY
NEW YORK, N.Y. 10027

81 2 18 146

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: 1	2. GOVT ACCESSION NO.: AD-A095 472
3. RECIPIENT'S CATALOG NUMBER:	
4. TITLE (and Subtitle): Ultraviolet Photodissociation of Molecular Beams	5. TYPE OF REPORT & PERIOD COVERED: Final report for period 10/01/77 - 9/30/80
6. PERFORMING ORG. REPORT NUMBER:	
7. AUTHOR(s): R. Bersohn	8. CONTRACT OR GRANT NUMBER(s): DAAG29 78 G-0004
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Columbia University, New York, N.Y. 10027	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:
11. CONTROLLING OFFICE NAME AND ADDRESS: U. S. Army Research Office, Post Office Box 12211, Research Triangle Park, NC 27709	12. REPORT DATE: December 15, 1980
	13. NUMBER OF PAGES: 3
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office):	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE: NA

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Photodissociation, excimer laser, nitrocompounds, carbon disulfide, sulfur dioxide, aryl halides, hydrogen peroxide

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_2O_2. The translational energy distributions of the fragments were measured. In addition, the internal energy distributions of CS (from CS_2) and OH fragments from H_2O_2 were measured. The excess of photon energy over bond energy is released primarily as vibration for SO_2 and

(OVER)

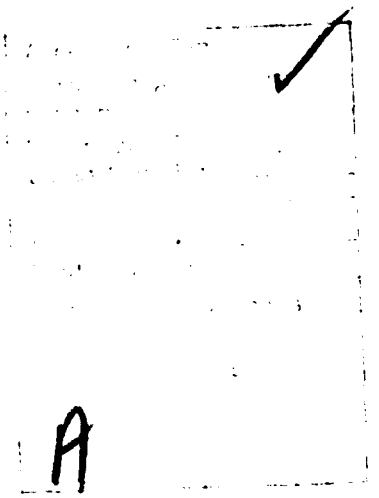
DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. continued

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.



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. N_2O and NO_2 - 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. SO_2 - 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. O_3 - 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. H_2S - Hawkins and Houston studied the photodissociation of H_2S at 193 nm (J. Chem. Phys. 72, 297 (1980)). and we therefore did not duplicate their effort.

6. H_2O_2 - Work on this molecule is still proceeding but the essential results are that two OH radicals are produced entirely in the v=o 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 O_2-H_1 repulsive force ($H_1O_1O_2H_2$) although weaker generates a comparable torque to the O-O repulsion.

7. CH_2O - 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. CF_3I - CF_3I like CH_3I turned out to produce mainly $I^*(^2P_{1/2})$ and vibrationally cold CF_3 radicals. Because CF_3 is pyramidal this was an expected result; CH_3 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 CH_3 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. CCl_2F_2 - Same comments as for 1,2

10. CCl_3F - Same comments as for 1,2

11. N_2F_4 was commercially available in 1976 but was not in 1979. The somewhat hazardous synthesis made other molecules more attractive.

12. CS_2 - 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 $R\text{-}NO_2 + h\nu(193\text{ nm}) \longrightarrow R\cdot + NO_2^*$

The excited NO_2^* 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 H_2O_2 and the nitrocompounds.

Scientific Personel Supported by the Project

Principal investigator:	R. Bersohn
Postdoctoral fellows:	A. Freedman
	S. C. Yang
Graduate Students:	S. J. Lee - Ph.D. awarded in 1978
	S. Kanfer
	G. Ondrey


DATE
ILME