

AD-A166 257

LASER STUDIES OF HALOGENS AND OXYGEN(U) CORNELL UNIV
ITHACA NY DEPT OF CHEMISTRY P L HOUSTON 81 JAN 86
AFOSR-TR-86-0105 F49620-83-K-0012

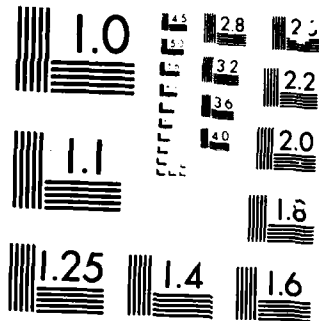
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Laser Studies of Halogens and Oxygen

Final Scientific Report

November 1, 1982 through October 31, 1985

Period Covered by this Report:

November 1, 1984 through October 31, 1985

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A. Research Objectives

Interconversions of energy between the metastable species of halogens, interhalogens, and oxygen [$I^*(^2P_{1/2})$, $O_2(^2\Delta, ^2\Sigma)$, $I_2(X, A, B)$, $IF(X, A, B)$] are important to the determination of the mechanisms for the chemical oxygen/iodine and IF lasers and to the development of a better fundamental understanding of electronic energy transfer. Previous research by our group in this broad area has investigated the kinetics of the equilibrium $I^* + O_2 = I + O_2(^1\Delta)$, has measured electronic-to-vibrational energy transfer from I^* to I_2^v , and has determined the rates of deactivation of I^* by alkyl and perfluoroalkyl iodides. During the past three years our efforts have focused on better ways to detect $O_2(^1\Delta)$, on the deactivation kinetics of I^* by Cl_2^v , and on the photodissociative generation of iodine atoms.

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B. Status of the Research Effort

1. Deactivation Kinetics of I* by Cl₂

Collisional quenching of excited iodine atoms by Cl₂ in a flow system has been investigated [J. Chem. Phys. **82**, 2590 (1985)]. Time-resolved emission from photolytically generated I*(²P_{1/2}) has been studied in a slow flow apparatus. The total rate of deactivation of I* by Cl₂ has been measured to be no more than $8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, substantially slower than previous reports. Evidence is presented for a very fast ($k = 2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) relaxation of I* by Cl atoms, which can account for both the earlier and the present observations.

2. Photodissociation of ICN

CN(v=0) rotational distributions as a function of photolysis wavelength have been probed by laser-induced fluorescence following photodissociation of ICN prepared in very low rotational levels by expansion through a supersonic jet [J. Phys. Chem. **88**, 6658 (1984)]. In most cases, the rotational distributions can be described by a superposition of low-temperature and high-temperature Boltzmann distributions. A semiclassical model has been used to interpret the results. Potential surfaces are proposed which reproduce both the deconvoluted ICN absorption spectrum and the major features of the variation in average rotational energy disposal as a function of photolysis energy. Minor discrepancies between the theory and experiment are likely to be caused by nonadiabatic transitions between dissociative surfaces.

3. Multiphoton Ionization Detection of O_2

Multiphoton ionization has been used to detect sensitively both $O_2(^3\Sigma)$ and $O_2(^1\Delta)$. The two-photon resonant ionization of $O_2(^3\Sigma)$ show a vibrational progression ($v'=0, 1, 2, 3$) which can be assigned to the $C^3\Pi_g$ intermediate state. Only the (2,0) band shows rotational structure, while the broad bands corresponding to the other vibrational levels can be understood as resulting from the dissociation by repulsive states which cross the $^3\Pi_g$ state. $O_2(^1\Delta)$ was detected both in a microwave discharge and as the photolysis product of O_3 dissociation at 266 nm. The spectrum shows several vibrational levels for each of two Rydberg transitions in the 260-245 nm region (single photon), as well as near 340 nm. None of the states reached from $O_2(^1\Delta)$ has previously been reported. Manuscripts for publication of this work are currently in preparation.

4. Photodissociation of CH_3I

A new photofragment spectrometer has been used to measure both the internal energy distribution in the CH_3 and I/I^* fragments of photodissociation of CH_3I at 266 nm. Multiphoton ionization of the CH_3 group provides vibrational and rotational resolution, while ionization as a function of position provides translational resolution. This work is still in progress.

5. Detection by Tunable Vacuum Ultraviolet Lasers

A vacuum ultraviolet source tunable in the 140-160 nm region has been used to detect the CO product distributions from OCS and glyoxal dissociation as well as from the collision of hot hydrogen atoms with CO.

Translation to vibration/rotation energy transfer has been investigated in the collision $H + CO$. H_2S is dissociated at 193 nm in an pulsed nozzle beam containing CO. The H atoms make 1-2 collisions with the cold CO and excite it vibrationally and rotationally. The CO products are then probed by vacuum ultraviolet laser induced fluorescence using a tunable VUV source made by four-wave mixing in Mg vapor. Because of the photolysis conditions for the H_2S , the initial translational energy is well-specified, and because of the expansion, nearly all of the CO is initially in $v=0, J=0$. Thus, the initial conditions are (nearly) completely specified. The final product distribution can be completely determined by the VUV laser-induced fluorescence; vibrational and rotational analysis is currently underway.

C. Complete List of Publications Supported by this Grant

1. Z-N. Gu, A. T. Young, and P. L. Houston, "Deactivation of $I(5^2P_{1/2})$ by CF_3I , CH_3I , C_2H_5I , and CH_4 ," *Int. J. Chem. Kin.* **16**, 669-677 (1984).
2. W. J. Marinelli, N. Sivakumar, and P. L. Houston, "Photodissociation Dynamics of Nozzle-Cooled ICN," *J. Phys. Chem.* **88**, 6685-6692 (1984).
3. G. E. Hall, S. Arepalli, P. L. Houston, and J. R. Wiesenfeld, "Collisional Quenching of Excited Iodine Atoms ($5p^5\ ^2P_{1/2}$) by Cl_2 in a Flow System," *J. Chem. Phys.*, accepted.
4. G. E. Hall, W. Marinelli, Sivaram Arepalli, A. T. Young, P. L. Houston, and J. R. Wiesenfeld, *J. Photochemistry* **25**, 551 (1984).
5. A. Sivaram, W. J. Marinelli, R. Ogorzalek, P. L. Houston, and J. R. Wiesenfeld, "Multiphoton Ionization Spectra of $O_2(^3\Sigma)$ and $O_2(^1\Delta)$: New Rydberg and Valence States," in preparation.

6. R. Ogorzalek, P. L. Houston, and R. W. Field, "Spin-Orbit Coupling in the $(3d\pi_g)$ Rydberg Levels of O_2 ," in preparation.

D. Personnel During FY 85

1. Paul L. Houston, Ph.D., 1973, Massachusetts Institute of Technology.
2. H.-P. Härrli, Ph.D. 1980, University of Bern, Switzerland.
3. G. E. Hall, Ph.D., 1980, University of Toronto.
4. R. Ogorzalek, graduate student, Cornell University.

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Unclassified

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR- 86-0105	
6a. NAME OF PERFORMING ORGANIZATION Cornell University	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION AFOSR/NC	
6c. ADDRESS (City, State and ZIP Code) Department of Chemistry Ithaca, New York 14853		7b. ADDRESS (City, State and ZIP Code) Bldg. 410 Bolling AFB, D. C. 20332-6448	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR	8b. OFFICE SYMBOL (If applicable) NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F49620-83-K-0012	
8c. ADDRESS (City, State and ZIP Code) Bldg. 410 Bolling AFB, D. C. 20332-6448		10. SOURCE OF FUNDING NOS.	
		PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2303
		TASK NO. 157	WORK UNIT NO.
11. TITLE (Include Security Classification) Laser Studies of Halogens and Oxygen			
12. PERSONAL AUTHOR(S) Paul L. Houston			
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 11/01/84 to 10/31/85	14. DATE OF REPORT (Yr., Mo., Day) 1/1/86	15. PAGE COUNT 5
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	Iodine Laser Vacuum Ultraviolet, Energy Transfer, Electronic State Quenching	
	SUB GR.		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Sensitive detection of O ₂ (¹ Δ) by multiphoton ionization is reported. The deactivation of I* by Cl ₂ is found to be much slower than previously thought. The photodissociation of ICN and CH ₃ I have been examined. The relaxation of I* by alkyl iodides and perfluoroalkyl iodides is reported.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input checked="" type="checkbox"/> DTIC USERS <input type="checkbox"/>		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL Francis J. Wodarczyk	22b. TELEPHONE NUMBER (Include Area Code) 202-767-4963	22c. OFFICE SYMBOL NC	

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