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13. ABSTRACT

Progress has been made in our understanding of oxygen and fluorine reaction chemistry through the study of several new reactions as well as the completed analysis of data obtained in the previous contract period. We have made further technological advances which will increase our ability to study O(^{3}P) reactions and we have taken the initial steps to develop an O(^{1}D) source.

In the first three sections, the developments in the source technology and chemistry are discussed. First, in the photofragmentation spectroscopy of O_3 to yield O(^{1}D), the vibronic states of the dissociation product was resolved. Then, a discussion of the O(^{3}P) source as used in the exciting studies of iodine abstraction reactions is presented. Lastly, we report the improvements which were made to increase the intensity, Mach number, and energy variability of the O(^{3}P) source.

Section four describes the completed high resolution study of the reaction of O(^{3}P) with ICl and CF_3I in which we were able to obtain an improved value of the IO bond energy.

The reactions of Cl and F with C_2H_3Br, discussed in section five, contribute significantly to our understanding of the dynamics of chemical reactions. The nonstatistical product energy distributions and unexpected coupling of angular and energy distributions shed light on the mechanism of radical reactions and the importance of angular momentum.

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By

Yuan T. Lee
Professor of Chemistry
Department of Chemistry
University of California
Berkeley, California 94720
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CROSSED MOLECULAR BEAM STUDY OF THE REACTIONS OF OXYGEN AND FLUORINE ATOMS

Reporting Period: January 1978 to February 1979

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I. Progress Report (January 1, 1978 to December 31, 1978)
Crossed Molecular Beam Study of the Reactions of Oxygen Atoms and Fluorine Atoms

N00014-75-C-0671
Principal Investigator:
Yuan T. Lee

Introduction

Substantial progresses have been made in the study of both oxygen atom and fluorine atom reactions during this period.

For the reactions of oxygen atoms, we have started to investigate the possibility of carrying out the reaction of $O(^1D)$ in a crossed molecular beams experiment. The best method of producing $O(^1D)$ is the photodissociation of O_3. Consequently, we have first investigated dynamics of photodissociation of O_3 by molecular beam photofragmentation translational spectroscopy. This study was carried out with our new high resolution universal molecular beam apparatus. Very exciting results were obtained, in which the electronic and vibration state of dissociation products is clearly resolved. These results will enable us to prepare the future studies of the $O(^1D)$ reaction and are briefly summarized in the first section.

The second section contains a paper presented at the XIth International Symposium on Rarefied Gas Dynamics on "Development of a Supersonic Atomic Oxygen Nozzle Beam Source for Crossed Beam Scattering Experiment". The third section is the up to data report on the recent improvement on the kinetic energy, intensity and Mach number of the oxygen atom beam source, mainly due to improved pumping speed and the seeding of O_2 in the He carrier gas. The development of the $O(^3P)$

beam source is now considered as satisfactory and we are preparing an article for publication in the Review of Scientific Instruments in the near future.

The fourth section contains a completed study on the reaction of oxygen atoms with ICL and CF_3I. Preliminary results of these works are briefly mentioned in last year's report. This paper will be published in the Don Bunker memorial issue of the Journal of Physical Chemistry.

The fifth section contains Molecular Beam Studies of Unimolecular Reactions: Cl, F + C_2H_3Br. This article was prepared for presentation in the Faraday Society Discussion in April 1979 and will be published in the Faraday Discussions of the Chemical Society. In the F + C_2H_3Br studies, we have further clarifed many important questions on the dynamics of the decomposition of chemically activated complexes, especially the aspect of the applicability of energy randomization assumption.

1. Dynamics of Photodissociation of O_3.

L. R. Carlson, R. K. Sparks, K. Shobatake and M. L. Kowalczyk

We have undertaken recently several studies on the photodissociation dynamics of small molecules. Since photodissociation mechanisms are poorly understood for systems other than diatomics, we have chosen ozone as a suitable molecule to study. Extensive theoretical efforts have been made by other workers as well as spectroscopic information obtained which renders a base of complimentary information to our studies. The photolysis of ozone is not only important from a theoretical view but is also an important source of metastable $O(^1D)$ atoms in the atmosphere in that $O(^1D)$ reacts rapidly with water to produce OH. The OH radical affects the concentration of important atmospheric trace quantities. The quantum efficiency for production of $O(^1D)$ has been estimated to be unity for the process

$$O_3(^1A_1) + h\nu(\lambda < 300\text{ nm}) \longrightarrow O_3(^1B_2) \longrightarrow O_2(^1\Delta_g) + O(^1D)$$

In our measurements we have shown that previous measurements are in considerable error. We find at $\lambda = 266$ n.m. a quantum efficiency for $O(^3P) + O_2(^3\Sigma_g)$ to be 12%. This neglected product channel can be significant in quantitative atmospheric modelings.

Detailed mechanisms for the photodissociation process of ozone can be obtained from the ozone time of flight data (Fig. 1) which was obtained on our general purpose, 34 cm. flight path crossed beam facility. Utilizing a supersonic ozone source, rotational temperatures of less than 10°K are produced which virtually eliminate complications from rotational and hot band excitations. Also enhanced resolution in energy is obtained from such a source due to the dramatic velocity spread narrowing in a supersonic expansion. As seen in Fig. 1, the vibrational levels of the product O_2 are clearly resolved. From the peak profiles, rotational energy distributions can also be deduced from the data produced with our facility.

With detailed energy distribution information, along with the measurements of signal intensities as a function of polarization angle, we find that the dissociation is highly impulsive. The energy distribution is non thermal although no population inversion is observed as shown in Fig. 2 after a transformation to center of mass energy coordinates has been made.

We further find from analysis of the polarization data (Fig. 3) that ozone fragments with an axis of recoil 36.8° from the direction of the transition dipole moment. This is in excellent agreement with ab initio calculations which yield an equilibrium bond angle of the excited $^1B_2$ state of 108.4°. From the data we obtained a fragmentation bond angle of 106.4° compared to 116.8° for the $^1A_1$ ground state of ozone.

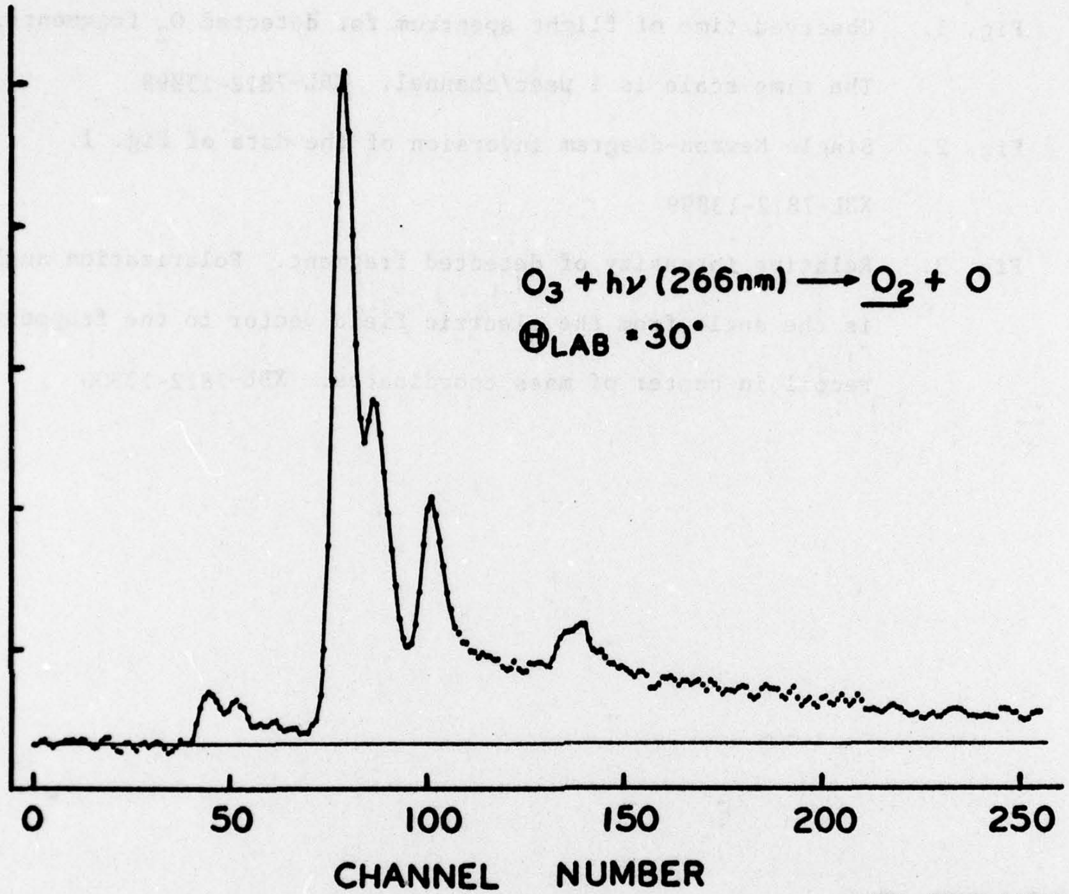
The analysis of the ozone fragmentation is continuing presently in order to elucidate details of the excited state potential surface. We are performing classical trajectory calculations with various excited state potentials thereby obtaining agreement with the fragment energy partitioning. We shall also continue our experimental studies in order to obtain wavelength dependences on this system. Thus we are incorporating a pulsed dye laser with nonlinear optical components to generate the desired tunable UV radiation.

FIGURE CAPTIONS

Fig. 1. Observed time of flight spectrum for detected O_2 fragments. The time scale is 1 μsec/channel. XBL-7812-13898

Fig. 2. Single Newton-diagram inversion of the data of Fig. 1. XBL-7812-13899

Fig. 3. Relative intensity of detected fragment. Polarization angle is the angle from the electric field vector to the fragment recoil in center of mass coordinates. XBL-7812-13900



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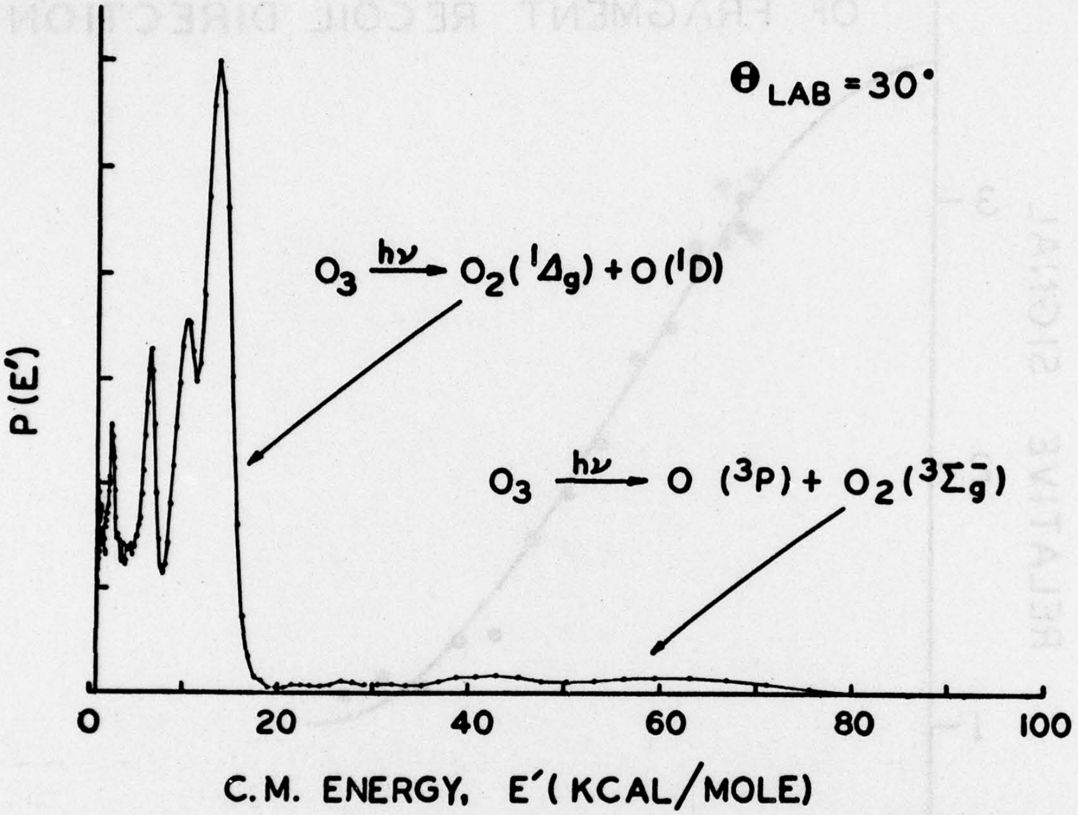

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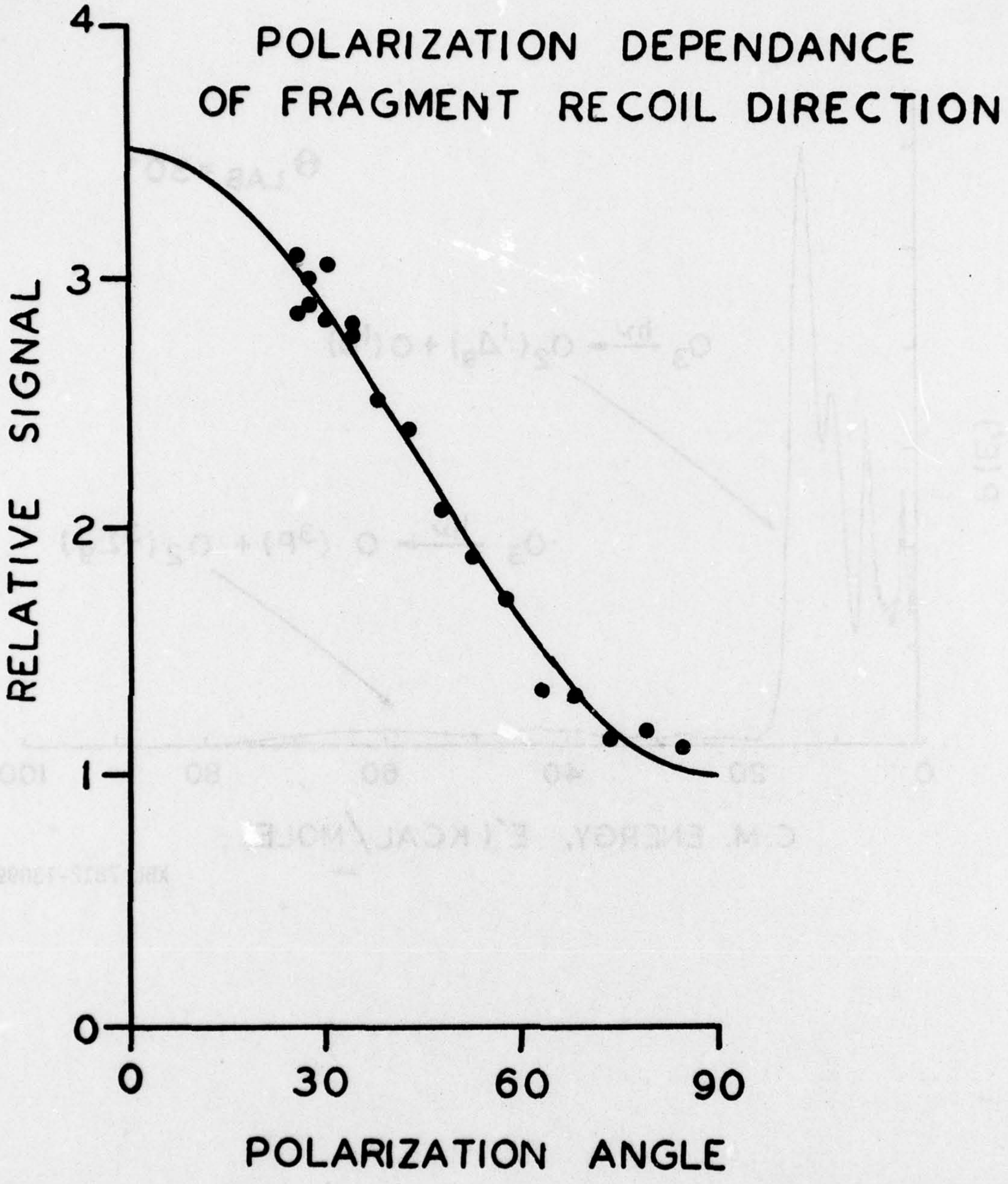

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2. DEVELOPMENT OF A SUPERSONIC ATOMIC OXYGEN NOZZLE BEAM SOURCE FOR CROSSED BEAM SCATTERING EXPERIMENTS

Steven J. Sibener, Richard J. Buss and Yuan T. Lee

Materials and Molecular Research Division
Lawrence Berkeley Laboratory and
Department of Chemistry
University of California, Berkeley, CA 94720 USA

ABSTRACT

A high pressure, supersonic, radio frequency discharge nozzle beam source has been developed for the production of intense beams of ground state oxygen atoms. An efficient impedance matching scheme has been devised for coupling the radio frequency power to the plasma as a function of both gas pressure and composition. Techniques for localizing the discharge directly behind the orifice of a water-cooled quartz nozzle have also been developed. The above combine to yield an atomic oxygen beam source which produces high molecular dissociation in oxygen seeded rare gas mixtures at total pressures up to 200 torr: 80-90% dissociation for oxygen/argon mixtures and 60-70% for oxygen/helium mixtures. Atomic oxygen intensities are found to be greater than 10^{17} atom sr^{-1} sec^{-1}. A brief discussion of the reaction dynamics of $O + ICl \rightarrow IO + Cl$ is also presented.

I. INTRODUCTION

The reactions of ground-state oxygen atoms are of considerable interest and importance due to their fundamental role in combustion processes and atmospheric chemistry. A high pressure, supersonic, radio frequency discharge nozzle beam source has been developed in order to determine the products and reaction dynamics of $O(^3P)$ reactions in crossed molecular beam experiments. Our motivation for constructing this beam source is that supersonic nozzle sources characteristically produce beams of greater intensity, and have lower translational velocity dispersion than effusive sources.[1] Also the translational energy of the atomic beam can be varied using the seeded beam technique.[2]

The production of a stable and efficiently coupled high pressure discharge for the generation of atomic species is much more difficult than the production of a low pressure (~1 torr) discharge. Impedance matching of the plasma to the radio frequency power as a function of both gas pressure and composition is required. Plasma localization directly behind the orifice must also be achieved in order to limit atomic recombination before the expansion. Finally, sufficient cooling of the nozzle in order to prevent meltdown and to limit wall recombination - while not interfering with power coupling to the plasma - is mandatory. The beam source described in this paper meets all of the above criteria. A boron nitride skimmer is used and is found to be completely stable with respect to the atomic oxygen beam.

Miller and Patch[3] have previously reported an atomic oxygen radio frequency discharge beam source with ~35% dissociation at 60 torr for a 5% O_2/He mixture. Grice[4] has recently reported a microwave discharge source with dissociation characteristics similar to those of Miller and Patch. The impedance matching scheme, nozzle construction and, in particular, plasma localization techniques described in this paper permit a higher degree of molecular dissociation to be achieved at total pressures of 200 torr. A brief description of the reaction dynamics of $O + ICl \rightarrow IO + Cl$ is included in the latter part of this paper as evidence of this beam source's applicability to crossed beam reactive scattering studies.

II. SOURCE CONSTRUCTION AND OPERATION

A cross-sectional view of the source mounted in the differential pumping region of our universal scattering machine is shown in Fig. 1, with an enlarged view of the internal source components and nozzle tip appearing in Fig. 2. Low conductivity water is used as the nozzle coolant and is flowed through the concentric quartz water jacket at a rate of 10 cm^3/sec. Use of regular conductivity water as the coolant is precluded due to excessive radio frequency power loss to the water.

The orifice is blown on a spinning glassblowers lathe in an operation requiring two people. One person locally heats the tip of the quartz nozzle and actually blows the hole while the other simultaneously views the hole diameter with a 60X power measuring-microscope. Hole size readjustment can be carried out with this procedure to within 0.005 mm of the desired diameter. When an orifice of the desired size is achieved its straightness is always checked by placing a small positive pressure of oxygen behind the nozzle, which produces a small oxygen jet at the orifice. This jet is then ignited with a small torch flame while the entire nozzle is rotated on the lathe. If any wobble or precession of the flame jet is detected the orifice is reblown. Nozzle diameters are typically 0.075 mm for oxygen/argon discharges and 0.200 mm for oxygen/helium discharges. Nozzle preparation is completed by briefly etching the inner quartz tube with a dilute solution

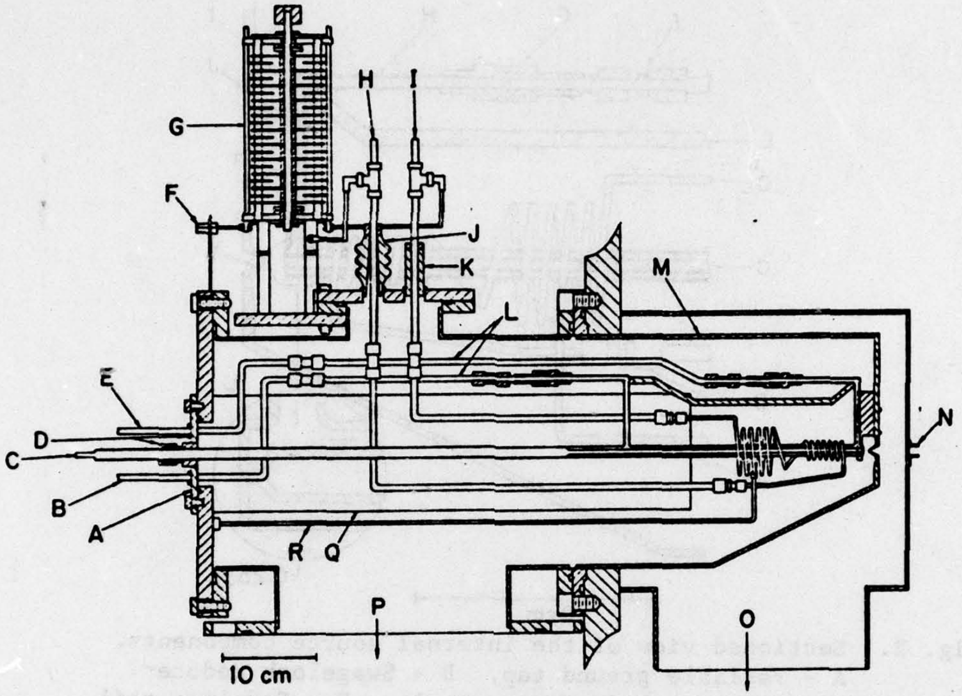

Fig. 1. Sectioned view of the plasma beam source mounted in a differentially pumped chamber. A-Lucite insulating flange. B-Nozzle coolant return. C-Quartz nozzle gas inlet. D-Cajon ultra-torr fittings. E-Nozzle coolant inlet. F-RF power input from RG-213/u coaxial cable. G-Variable air capacitor. H-Coupling coil coolant outlet. I-Coupling coil coolant inlet. J-Ceramic feedthrough for RF return and coil coolant. K-Ceramic feedthrough for RF input and coil coolant. L-Poly-Flo tubing sections. M-Stainless steel source chamber. N-Plates for 5000 V/cm ion deflecting field. O-1200 ℓ/sec diffusion pump, differential region. P-4200 ℓ/sec diffusion pump, source region. Q-Epoxy resin mechanical support. R-Electrical ground wire. Not shown:_ Wire mesh RF shielding which covers the air capacitor/RF feedthrough assembly.

of hydrofloric acid. This is believed to inhibit atomic recombination at the walls of the tube.

The radio frequency power (hereafter, RF) is generated by a Viking radio transmitter which can deliver a maximum output of approximately 150 watts over a continuously variable frequency range of several hundred kilohertz centered at a frequency of 14 megahertz. A linear amplifier can also be operated to produce RF levels in excess of 1000 watts. However,

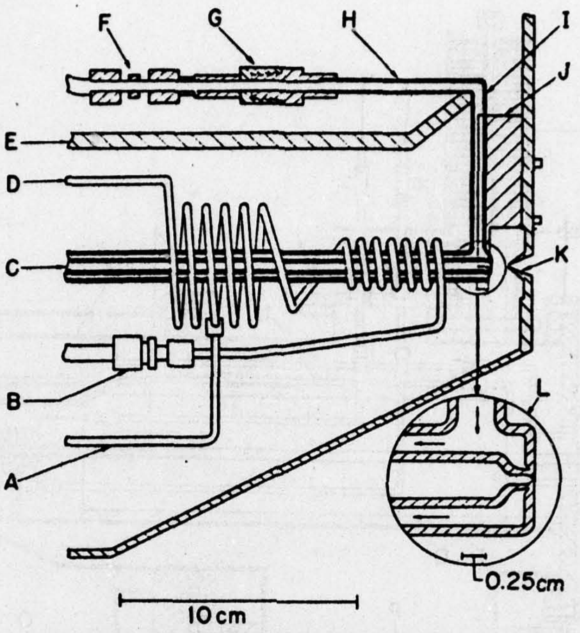

Fig. 2. Sectioned view of the internal source components. A - Variable ground tap. B - Swagelock reducer. C - Water-cooled quartz nozzle. D - Coupling coil. E - Quartz support rod for water inlet/outlet assembly. F - Swagelock union joining copper and Polyflow tubing. G - Cajon VCO fitting. H - Kovar-pyrex section. I - Graded seal, pyrex to vycor. J - Aluminum support block at electrical ground. K - Boron nitride skimmer, 0.88 mm. L - 4X enlargement of nozzle tip; arrows indicate low conductivity water flow direction.

power levels on the order of only 100-200 watts seem to be adequate for atomic oxygen generation. The plasma coupling tank coil and capacitor can be clearly seen in Fig. 1. The variable air capacitor (0-75 pf) is mounted outside of the vacuum to facilitate initial frequency matching of the tank circuit to the electronics. A grid-drip meter is used for this preliminary frequency tuning of the beam source.

We have developed a novel impedance matching scheme which enables the source to routinely operate at a standing wave ratio (SWR) of less than 1.05:1. Figure 3 presents a schematic outline of the impedance matching circuitry, which can best be viewed in two stages. First, a variable ground tap on the tank coil (Fig. 2, A) produces a large stepdown of the plasma impedance, as seen by the final RF amplifier, to approximately 50Ω. This allows the RF power to be delivered by coaxial cable (RG 213/u) to the beam source from a remote location. Then a PI-network,[5] series capacitor arrangement is used to critically

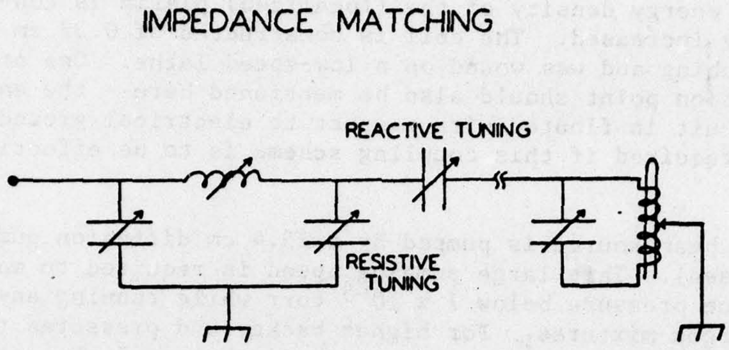

Fig. 3. Schematic outline of the impedance matching circuitry.

tune the impedance match. This circuit is capable of remotely tuning out any reactive or resistive impedances presented to the RF electronics by the plasma coupling tank circuit. Impedance variation occurs when the plasma is first started, and as the pressure is raised from 1 torr to the desired value-usually 200 torr. Tuning of the impedance matching circuitry is greatly facilitated by continuous use of an inline RF wattmeter and a standing wave ratio bridge. Power coupling to the plasma is extremely efficient (> 99%) and power levels must be limited in order to avoid meltdown of the quartz nozzle. The beam source is doubly interlocked to protect both the nozzle and the electronics. The nozzle coolant flow rate is monitored with a waterwheel flowswitch, which turns off the RF power if the coolant rate drops belows a preset point. The electronics are protected by a fast electronic switch which continuously monitors the SWR level.

Finally, we have been successful in localizing the plasma directly behind the orifice. This is of critical importance in order to achieve high molecular dissociation in a high pressure discharge. This localization is achieved by placing around the nozzle tip (outside of the water jacket, not along the front surface of the nozzle) a carefully shaped, electrically grounded block of aluminum (Fig. 2, J). We observe that the discharge changes from an inductively coupled plasma at low pressures to a capacitively coupled discharge at high pressures - with this coupling occuring between the front, small diameter coil turns and the grounded aluminum block. As this capacitive coupling becomes stronger the plasma localizes towards the front of the discharge tube. The tank coil has also been differentially wound (Fig. 2, D) in order to further localize the plasma and increase its energy density. The first seven coil turns nearest the orifice are of 1.37 cm I.D. while the six further coil turns are of 5.08 cm I.D. These larger turns decouple from the plasma as the pressure is increased, and thus the energy density of the (localized) plasma is considerably increased. The coil is constructed of 0.32 cm O.D. copper tubing and was wound on a low-speed lathe. One other construction point should also be mentioned here - the entire tank circuit is floated with respect to electrical ground. This is required if this coupling scheme is to be effectively used.

The beam source is pumped by a 25.4 cm diffusion pump (4200 l/sec). This large pumping speed is required to maintain the source pressure below 7×10^{-5} torr while running any oxygen/argon mixtures. For higher background pressures the RF decouples from the nozzle and a glow discharge of the entire source region occurs. This glow discharge problem is what ultimately constrains the orifice size to 0.075 mm diameter for gas mixtures containing argon. A larger diffusion pump will soon be added to this beam source with hopes of increasing nozzle throughput - allowing higher Mach numbers and intensities to be obtained. Fluxes are presently $10^{17} - 10^{18}$ atoms sr^{-1} sec^{-1}.

III. BEAM CHARACTERIZATION

The beam characteristics for four oxygen/rare gas mixtures are listed in Table I. The time-of-flight apparatus used in these studies consisted of a 17.78 cm diameter aluminum disk having four equally spaced 1 mm slots around its circumference. The disk was rotated at either 300 or 350 Hz. The detector aperature was narrowed to 0.125 mm diameter, and the distance between the TOF disk and the electron bombardment ionizer was 18.4 cm. The ionizer/quadrupole mass spectrometer has previously been described in detail.[6] A 256-channel scaler interfaced to an on-line minicomputer was used to record signal intensity as a function of flight time. The scaler channel width was set at 2.2 μs for the helium mixtures and 4.2 μs for the argon mixtures. Corrections for instrumental broadening and ion flight times have been included in these reported values.

The molecular dissociation was calculated with the following two equations:

$$R = \frac{N_o}{N_{o_2}} = \frac{(\sigma_D/\sigma_{o_2})}{\eta} \left(\frac{\sigma_{o_2}}{\sigma_o}\right) \left(\frac{I_o - \eta I_{o_2}}{I_{o_2}}\right) \tag{1}$$

$$\text{Percent Dissociation} \simeq \frac{R}{R+2} \tag{2}$$

where I_o and I_{o_2} are the experimentally observed mass 16 and 32 number densities, η is the observed I_o/I_{o_2} count ratio with the discharge off, and the cross sections represent the following processes:

$$\sigma_{O_2} : O_2 + e \rightarrow O_2^+ + 2e$$

$$\sigma_O : O + e \rightarrow O^+ + 2e$$

$$\sigma_D : O_2 + e \rightarrow O + O^+ + 2e$$

For bombardment by 250 eV electrons $\sigma_{O_2} = 1.52$ Å^2, $\sigma_O = 1.15$ Å^2, and $\sigma_D = 0.88$ Å^2.[7,8] An equivalent expression has been used by Miller[3] where the approximations leading to the use of Eq. 1 are also explained. The $(\sigma_D/\sigma_{O_2})/\eta$ term corrects for any differential detection of masses 16 and 32 by our detector - which is due, in part, to differential transmission of masses 16 and 32 through our quadrupole mass filter.

Table I
Beam Characterization

Gas Mixture	Pressure (torr)	RF Power (watts)	Mach Number	Dissociation (percent)	Oxygen Velocity (10^5 cm/sec)
$5\%O_2/Ar$	100	140	1.3	86	1.43
	150	140	2.1	84	1.30
	200	140	3.0	80	1.20
$10\%O_2/Ar$	100	140	1.1	77	1.43
	150	140	2.2	74	1.30
	200	140	3.0	71	1.28
$5\%O_2/He$	100	140	4.9	58	2.39
	150	140	6.1	70	2.47
$10\%O_2/He$	100	140	4.5	58	2.20
	150	140	5.8	70	2.25

Table I indicates a novel property of our oxygen beam source: even at total pressures of 200 torr the dissociation percentage remains very high. The intense discharge located at the nozzle tip undoubtedly contributes to this. The questions of actual nozzle temperature, the dependence of dissociation on RF power, and further analysis of beam characteristics will appear elsewhere in the literature. However, an analysis of nozzle temperature for $10\%O_2/He$ and $10\%O_2/Ar$ discharged by 140 watts at 150 and 200 torr, respectively, is now presented. Assuming the overall energy balance:[9,10]

$$(\Sigma X_i C_{P_i}) T_n = \Sigma X_i C_{P_i} T_i + \tfrac{1}{2}\Sigma X_i M_i V_i^2 \qquad (3)$$

(where X_i is the mole fraction, Cp_i the heat capacity, V_i the terminal velocity, M_i the mass, and T_i the terminal temperature of each component of the beam), we can calculate T_N, the nozzle temperature using the data presented in Table II.

Table II

Gas Mixture	Component	Velocity (10^5 cm/sec)	Temperature (K)
10% O_2/Ar (200 torr)	O	1.28	207
	O_2	1.23	250
	Ar	1.17	200
10% O_2/He (150 torr)	O	2.25	176
	O_2	2.13	256
	He	2.53	244

The O_2/Ar discharge is found to produce $T_N = 1400$ K, and the O_2/He discharge yields $T_N = 1100$ K.

IV. REACTIVE SCATTERING: $O + ICl \rightarrow IO + Cl$

We would like to conclude this paper by presenting the experimental data, and its convolution into the center-of-mass reference frame, for the reaction $O + ICl \rightarrow IO + Cl$. The oxygen atoms for this study were produced by discharging a 5% O_2/Ar mixture, and were found to have a peak translational velocity of 1.29×10^5 cm/sec. The atomic oxygen Mach number was 3.8 for these studies. The ICl was seeded in argon to a velocity of 4.95×10^4 cm/sec and a Mach number of 7.0. Figures 4,5, and 6 present the laboratory angular distribution, velocity distributions, and center-of-mass contour map, respectively, for this experiment. The high degree of forward-backward symmetry apparent in the contour map about the center-of-mass indicates that this reaction proceeds *via* a long-lived complex whose lifetime exceeds one rotational period of the OICl complex. Analysis of the IO product translational energy distribution reveals that the decomposition follows RRKM-AM[11] statistical predictions when an IO bond strength of 53 kcal/mole is assumed. This is in excellent agreement with Grice's[12] proposed bond strength for the IO radical obtained in a similar manner.

V. CONCLUSION

An atomic oxygen supersonic beam source has been constructed and its operating characteristics described for four rare gas mixtures. Plasma localization at the nozzle tip in

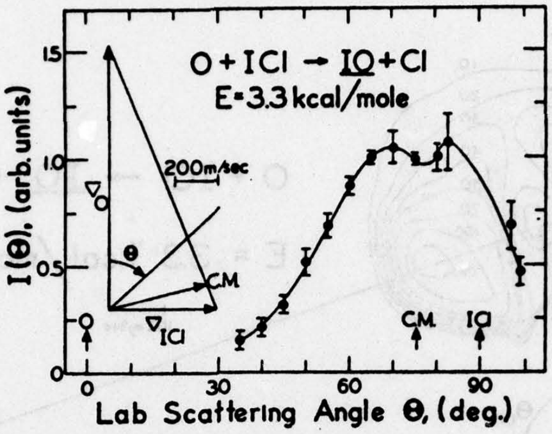

Fig. 4. Angular distribution of reactively scattered IO product.

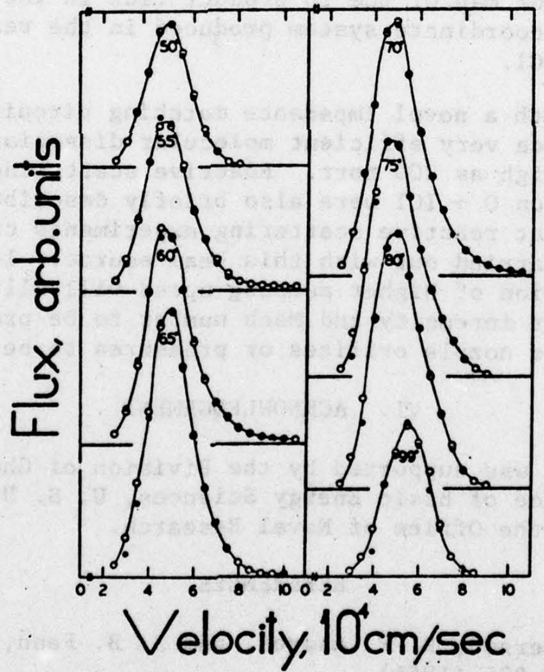

Fig. 5. Flux distributions for reactively scattered IO at eight laboratory angles. ● Experimental distributions obtained from cross-correlation TOF; o Calculated best fit distributions.

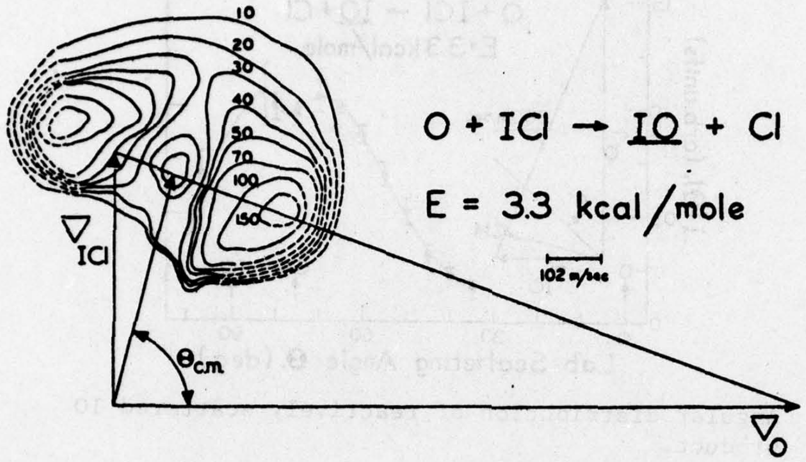

Fig. 6. Contour map of the IO product flux in the center-of-mass coordinate system produced in the reaction O + ICl.

conjunction with a novel impedance matching circuit has been shown to produce very efficient molecular dissociation at pressures as high as 200 torr. Reactive scattering results for the reaction O + ICl were also briefly described to demonstrate that reactive scattering experiments can be successfully carried out with this beam source. It is hoped that the addition of higher pumping speed will allow beams of still higher intensity and Mach number to be produced by allowing larger nozzle orifices or pressures to be used.

VI. ACKNOWLEDGEMENT

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REFERENCES

1. J. B. Anderson, R. P. Andres, and J. B. Fenn, Adv. Chem. Phys. 10, 275 (1966).
2. N. Abauf, J. B. Anderson, R. P. Andres, J. B. Fenn, and D. G. H. Marsden, Science 155, 997 (1967).
3. D. Miller and D. Patch, Rev. Sci. Instrum. 40, 1566 (1969).
4. P. A. Gorry, C. V. Nowikow, and R. Grice, Chem. Phys. Lett. 49, 116 (1977).
5. The Radio Amateur's Handbook, 46th Ed. (ARRL, Newington, 1969) p. 49.

6. Y. T. Lee, J. D. McDonald, P. R. Lebreton, and D. R. Herschbach, Rev. Sci. Instrum. 40, 1402 (1969).
7. W. L. Fite and R. T. Brackman, Phys. Rev. 113, 815 (1959).
8. D. Rapp, P. Englander-Golden, and D. D. Briglia, J. Chem. Phys. 42, 4081 (1965).
9. D. R. Miller and R. P. Andres, Sixth Rarefied Gas Dynamics, L. Trilling and H. Wachman, Eds. (Academic Press, New York, 1969) Vol. 2, p. 1385.
10. D. R. Miller and R. P. Andres, J. Chem. Phys. 46, 3418 (1967).
11. S. A. Safron, N. D. Weinstein, D. R. Herschbach, and J. C. Tully, Chem. Phys. Lett. 12, 564 (1972).
12. D. St. A. G. Radlein, J. C. Whitehead, and R. Grice, Nature 253, 37 (1975).

3. Atomic Oxygen Nozzle Beam Source Development

Steven J. Sibener and Richard J. Buss

During the past year the emphasis of our atomic oxygen research program has been directed towards obtaining still further improvement in the beam characteristics of our supersonic oxygen beam source, for which a preliminary description has now appeared in the literature. Our efforts have especially been directed towards increasing the intensity, decreasing the relative velocity spread, and extending the translational energy range of the atomic oxygen beam. We have succeeded in meeting the above goals by making some beam source modifications which are described below. These improvements should significantly enhance our ability to study the dynamics and energetics of ground state atomic oxygen reactions in well characterized crossed molecular beam scattering experiments.

Specifically, the addition of higher pumping speed to the source - an 8000 li/sec diffusion pump backed by a roots blower - has enabled us to operate at stagnation pressures up to 350 torr total pressure for seeded O_2/Ar mixtures with a 3 mil nozzle. This should be compared with an ultimate pressure of 200 torr with our old pumping arrangement. Temperatures of 1300 K have been reached in these O_2/Ar discharges. The actual intensity gain brought about by operation at these higher pressures exceeds a factor of two. However, the oxygen Mach numbers did not improve significantly, indicating that a limit has been reached in the Mach number obtainable for dilute O_2/Ar mixtures in our discharge beam source. The use of neon to reduce atomic oxygen slippage in the expansion may prove to be of some help here. Higher Mach numbers have been achieved in the O_2/He mixtures described below.

The major development of the past year has been the extension of the mean translational energy range of the oxygen beam to 0.5 eV. This has been achieved by generating for the first time a hot discharge (1100 K) of O_2/He mixtures at stagnation pressures up to 220 torr. The key modification that enabled us to generate a plasma of the correct temperature (1000 K < T < 1400 K) was to increase the nozzle orifice diameter from 3 mil to 7.5 mil. The larger gas flow rate evidently stabilizes the 1100 K discharge mode of the plasma with respect to cooler discharges modes - allowing for the successful generation of atomic oxygen. Atomic oxygen Mach numbers of 9 have been measured for these O_2/He mixtures with an intensity of ~10^{18} atoms sr^{-1} sec^{-1}. The intensity of the helium seeded beam is therefore seen to exceed by a factor of ~3 the intensity of the current argon seeded beam. The developments outlined above give us hope that the coming year should indeed be a fruitful one for our atomic oxygen research program here at Berkeley.

4. THE CROSSED BEAM REACTION OF ATOMIC OXYGEN WITH ICl and CF_3I

R. J. Buss, S. J. Sibener, and Y. T. Lee

Materials and Molecular Research Division
Lawrence Berkeley Laboratory

and

Department of Chemistry
University of California
Berkeley, California 94720

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ABSTRACT

An RF-discharge, supersonic oxygen atom beam source has been used to study the reactions of O + ICl and CF_3I. The IO bond strength determined from the product flux distribution in the ICl reaction, is 55.0 ± 2.0 kcal mol^{-1}, in modest agreement with an earlier measurement. The product from the CF_3I reaction differs in angular and velocity distribution from that of a previous study, and is found to agree well with statistical calculations using a long-lived complex model.

INTRODUCTION

The development of atomic oxygen beam sources in several laboratories has enabled the crossed molecular beam method to be applied to the study of oxygen reactions. The abstraction of an iodine atom from various iodine-containing molecules has the advantages of easy product detectability and large cross section and has been the subject of several crossed molecular beam studies. We report here our recent studies of the reactions of oxygen atoms with ICl and CF_3I using a supersonic oxygen atom beam source. These two reactions have been investigated by Grice and coworkers previously, though their ICl reaction was with an effusive oxygen atom beam source. In the study of ICl,[1] they applied a long-lived collision complex model to deduce a bond energy for the IO product, but the applicability of the long lived complex model for this reaction is not convincing. In particular the recent laser induced fluorescence studies of the similar F + ICl reaction[2] has shown that the IF vibrational distribution is highly inverted in contradiction to a statistical long lived model. In the work by Grice and coworkers,[3] the IO product from the $O + CF_3I$ reaction at two collision energies shows no evidence of the strong peaking on the relative velocity vector which is expected from the domination of orbital angular momentum in a reaction with a relatively large cross section and expected to go through a long lived complex. At both collision energies, some product is observed with energy in excess of the total available for translation, and hence the comparison with statistical theory is very poor.

The results of our investigation of the O + ICl reaction give a slightly higher IO bond energy, though not inconsistent with the value of Grice and coworkers in view of the uncertainties in the determination. On the other hand, our results of the reaction of O + CF_3I are not in line with the conclusion of the previous study of Grice and coworkers. They are, actually, found to be quite similar to the results of the F + CH_3I reaction.[4]

EXPERIMENTAL

The crossed beam apparatus and data acquisition techniques were similar to those described previously.[5] The oxygen atom source, described in detail elsewhere,[6] employs a high pressure RF plasma, carefully localized at the nozzle, to achieve a high oxygen flux with reasonably narrow velocity spread. With a 5% O_2 in argon mixture at 100 torr pressure, we produced a peak velocity 1050 ms^{-1} with a FWHM velocity spread of 40%. The ICl, practical grade from Matheson Coleman and Bell, at its vapor pressure at 315 K was mixed with argon to bring the total pressure to 240 torr. This mixture, approximately 50% ICl, was expanded from a 0.1 mm quartz nozzle at 329°K. The ICl beam was measured with the single shot time-of-flight method to have a peak intensity at 5.02 ms^{-1} and a FWHM velocity spread of 29%. The supersonic CF_3I beam was produced with the same nozzle conditions at 250 torr pressure of CF_3I

from PCR Research Chemicals Inc. without further purification. The beam velocity distribution peaked at 366 ms^{-1} with FWHM velocity spread of 30% corresponding to near complete relaxation of translation, rotation and two low frequency vibrations. Under these conditions the reacting CF_3I should have an average internal energy around 1 kcal mol^{-1}. The mean collision energy for the ICl reaction is 2.36 kcal/mol with FWHM = 0.8 while that for the CF_3I reaction is 2.18 kcal mol^{-1} with FWHM = 0.8. Laboratory angular distributions of product number density were taken by repeated scans of 100 second counts at each angle. The IO product signal intensity at the peak of the angular distribution was approximately 15 counts per second with background 30 counts per second. Velocity distributions at each angle were obtained with the cross-correlation time-of-flight technique[6] with 12 μsec per channel time resolution. Counting time varied from one to three hours at an angle.

RESULTS

The laboratory angular distributions of IO product are shown in fig. 1 with standard deviation of the mean of 10 measurements. The product from both reactions is seen to peak near the center of mass as a consequence of the strong enhancement of detecting molecules with low center-of-mass velocity due to the center-of-mass to laboratory coordinate transformation, though slight bimodality is observed in the ICl reaction. The product velocity distributions are shown in Figs. 2 and

3 together with the best fit calculations using the iterative deconvolution technique of Siska.[6] The contour maps of center-of-mass product flux distributions in Figs. 4 and 5 are deconvoluted distributions, which, when averaged over the reactant beam velocities, will produce the best-fit lines in Figs. 1, 2 and 3.

Some backscattered product is observed in both reactions but, in neither case is their sufficient intensity to produce symmetry about 90°. Fitting of the angular and velocity data with an uncoupled energy, P(E') and center-of-mass angular, T(θ) distribution indicates that the ratio of flux at 0° to that at 180° is about 2.0 for the ICl and 2.2 for the CF_3I reaction.

The product velocity and center-of-mass angular distributions exhibit rather strong coupling in both reactions. The velocity at which the flux peaks decreases smoothly as the center-of-mass angle increases from 0° to 90°.

The experimental P(E') shown in Figs. 6 and 7 are the average energy distributions between 0° and 90°. Each theoretical curve was obtained by calculating P(E') with the RRKM-AM model[8] for five collision energies spanning the experimental range and the P(E') were summed over the distribution of collision energies in the experiment. The curves are calculations for three values of the IO bond energy; all vibrational modes of the complex are assumed to participate in energy sharing. The treatment of angular momentum requires specification of a maximum centrifugal barrier, B_m'.[9] For the CF_3I reaction, B_m' has been estimated from the C_6 constants. A satisfactory fit to the ICl data required increasing B_m' to 0.454 E_c almost double the value calculated with the C_6 constants.

DISCUSSION

In attempting to deduce the exothermicity of a reaction from analysis of the product in a cross beam experiment, one looks to the high energy fall off to set a lower bound. The use of narrow velocity distributions of the reactants to produce a well-defined collision energy enables one to assign a minimum exothermicity necessary to give the observed product with proper energy conservation. The resolution limitations of the time of flight method introduce the greatest uncertainty for the molecules with highest speed and account has been taken of this in the analysis of the high energy data. For the reaction of O + ICl an approximate lower bound of 3.5 kcal mol^{-1} can be assigned the exothermicity. In general, it might be difficult to obtain a better knowledge of the reaction energetics without additional knowledge of the internal excitation of products, but this specific reaction is particularly well-suited for making a more definitive determination of exothermicity. Although the exact product translational energy distributions depend on both exothermicity and reaction dynamics for systems with a small number of internal degrees of freedom the observed fall-off of high energy product is more sensitive to the actual total energy available than to the reaction dynamics. Relying on fitting the fall-off region, we obtain an exothermicity $\Delta H = -5.5 \pm 2.0$ kcal mol^{-1} for the reaction $O + ICl \rightarrow IO + Cl$, from which, with the known ΔH_f of the other species,[10] we deduce an IO bond energy 55.0 ± 2.0 kcal mol^{-1}. As demonstrated in Fig. 6, calculations with the RRKM-AM model agree well with these conclusions if the maximum centrifugal barrier, B_m', is taken as a variable to achieve best fit.

The value of B_m' specifies the degree to which conservation of angular momentum causes energy to be stored in rotational motion of the complex to be partitioned to translation of the products. If the long-range dispersion force between the reactants determines the maximum impact parameter for capture, then B_m' is related simply to the ratio of entrance to exit channel C_6 constants.[9] In order to fit the experimental results, we have, effectively, increased this C_6 constant ratio by a factor of 4, a change which if associated with the entrance channel, corresponds to increasing the total cross section from 55 $Å^2$ to 90 $Å^2$. This appears to be an unreasonably large total cross section in view of the 2 $Å^2$ cross section determined experimentally[13] for the similar reaction $O + Br_2 \rightarrow OBr + O$.

Our slightly higher IO bond energy is not inconsistent with 53 ± 3 kcal/mole obtained by Grice and coworkers[11] although reliance on the statistical calculation to derive this value by comparing the overall features is questionable for this reaction. The RRKM lifetime is calculated to be exceedingly short, 0.3 ps, a region in which nonstatistical effects have been observed in several other reactions.[12] The density of states in the complex at the dissociation energy is very low, approximately 1 per cm^{-1}, hence the products might be expected to exhibit more dynamical effects. Additionally, the uncertainties in treatment of angular momentum may introduce too much flexibility to the model, making it unreliable for thermodynamic data determination. Finally, the use of the velocity distribution along the centroid in reference 11 is contraindicated because the severe Jacobian enhancement at this angle tends to overwhelm the information contained in the high energy tail.

The product from the CF_3I reaction is shown in Fig. 7 to agree well with statistical calculations using the IO bond energy determined above. The density of states for the CF_3I-O complex at the dissociation energy is about 10^7 per cm^{-1} and the calculated lifetime about 2 ps, although uncertainties in the energetics of the complex as well as its frequencies reduce the significance of these figures. Grice and coworkers[3] report their study of this reaction at two higher collision energies in which they observe high energy product far exceeding the total available for translation. The conditions of the reactants are too well specified to attribute this to uncertainty in internal energy, thus the explanation must lie in some systematic error. Their reported center-of-mass angular distribution shows no peaking on the relative velocity vector though the kinematics of the reactions almost require this. The contour map in

Fig. 5 shows the strong forward scattered product observed in our experiment. Although Jacobian enhancement of the product has produced strong peaking at the center-of-mass angle, transformation to the CM reference frame demonstrates the peaking on the relative velocity vector away from the center-of-mass.

The asymmetry of product about 90° in both reactions is not inconsistent with the statistical calculations. The rotational period is estimated to be 0.8 - 3.0 ps for the ICl and 1-5 ps for the CF_3I reactions, in each case comparable to the calculated lifetime. At a lower collision energy, 0.81 kcal mol^{-1} Radlein et al.[1] observed forward backward symmetry in the O + ICl reaction.

The coupling of product energy and angular distributions which is observed here can arise from several dynamical effects. The observation of such coupling in direct reactions with product repulsion has been reported,[14] but the energetics of these two reactions preclude this mechanism as an explanation. More pertinent is the coupling which should arise in long lived complexes from the distribution and the disposal of angular momentum.[12] Because both the product energy and angular distributions vary with impact parameter, the observed distributions, averaged over all possible impact parameters will retain the coupling.

CONCLUSION

We have used the reaction of O + ICl to obtain an improved value of the IO bond energy. The reactions of oxygen atoms with CF_3I appear to proceed through a complex with a mean lifetime comparable to the rotational period. The product translational energy for both systems shows no marked deviations from the RRKM-AM calculations.

ACKNOWLEDGEMENT

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REFERENCES

1. D. St. A. G. Radlein, J. C. Whitehead, and R. Grice, Mol. Phys. 1975, 29, 1813.
2. J. Wanner, private communication.
3. P. A. Gorry, C. V. Nowikow and R. Grice, Chem. Phys. Lett. 1978, 55(1), 24.
4. J. M. Farrar and Y. T. Lee, J. Chem. Phys. 1975, 63(8), 3639.
5. Y. T. Lee, J. D. McDonald, P. R. LeBreton and D. R. Herschbach, Rev. Sci. Instrum. 1969, 40, 1402. For data acquisition, see J. J. Valentini, Ph.D. dissertation, University of California, Berkeley, California 1976.
6. S. J. Sibener, R. J. Buss, and Y. T. Lee, XIth International Symposium on Rarefied Gas Dynamics, Cannes France, 1978 (also to be published S. J. Sibener, R. J. Buss, and Y. T. Lee, Rev. Sci. Instrum.).
7. V. L. Hirschy and J. P. Aldridge, Rev. Sci. Instr. 1971, 42, 381.
8. P. J. Robinson and K. A. Holbrook, Unimolecular Reactions, Wiley-Interscience, New York, 1972. See also reference 9 for angular momentum treatment.
9. S. A. Safron, N. D. Weinstein, D. R. Herschbach, and J. C. Tully, Chem. Phys. Lett. 1972, 12, 564.
10. H. M. Rosenstock, K. Draxl, B. W. Steiner, J. T. Herron, J. Phys. Chem. Ref. Data, 1977, 6, Suppl #1.
11. D. St. A. G. Radlein, J. C. Whitehead, R. Grice, Nature, 1975, 253, 37.

12. R. J. Buss and Y. T. Lee, Faraday Discussions, Birmingham, England, April 9-11, 1979.

13. M. A. A. Clyne, P. B. Monkhouse, and L. W. Townsend, Int. J. Chem. Kin. 1976, 8, 425.

14. N. D. Weinstein, Ph.D. dissertation, Harvard University, Cambridge, Massachusetts, 1972.

FIGURE CAPTIONS

Fig. 1. Laboratory angular distribution of IO intensity from the reactions of O + ICl, CF_3I. Error bars are one standard deviation of the mean of 10 measurements at each angle.

Fig. 2. Product IO flux distribution from the reaction O + ICl at eight laboratory angles. Solid lines are the best fit from the deconvolution procedure.

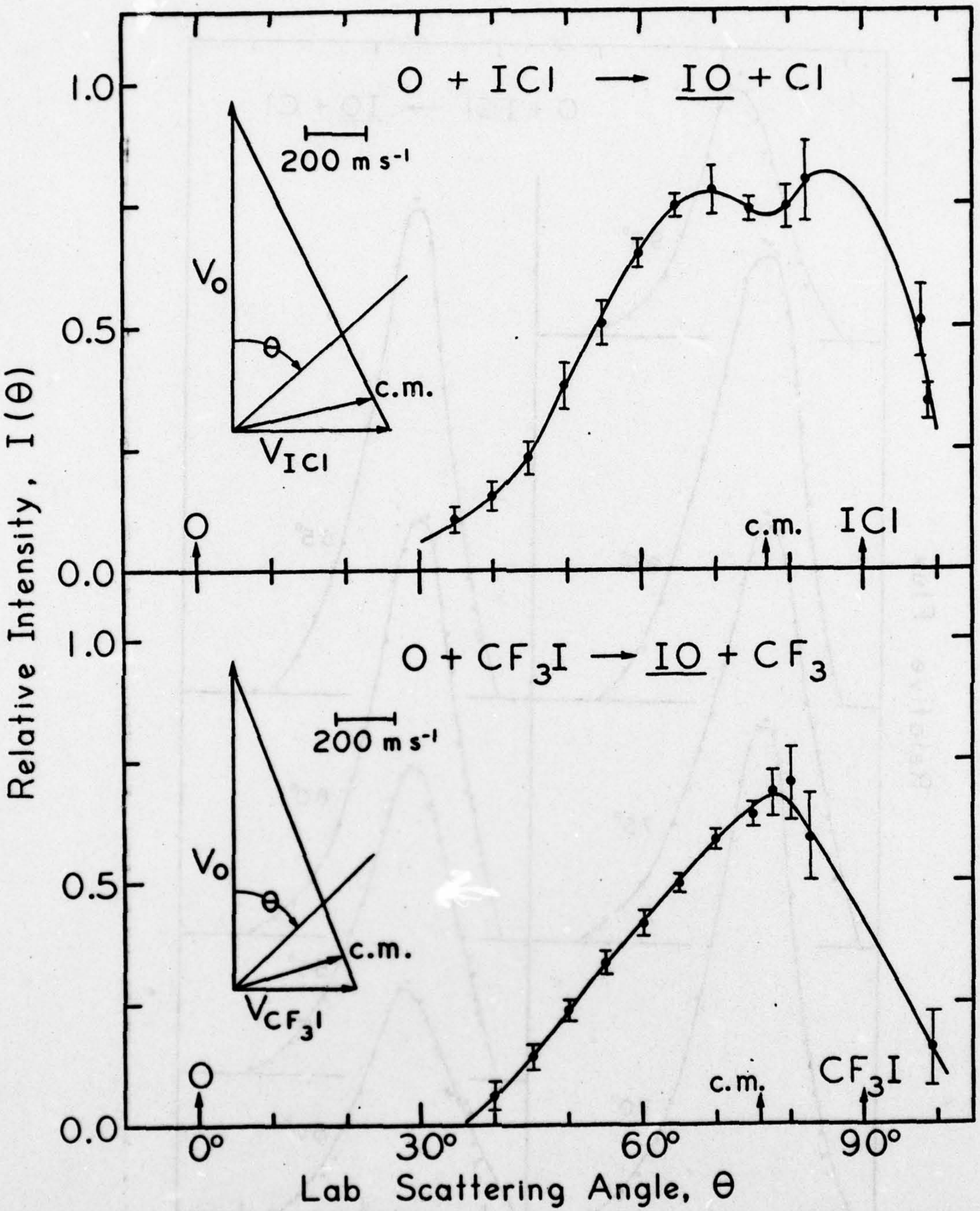
Fig. 3. Product IO flux distributions from the reaction O + CF_3I at seven laboratory angles.

Fig. 4. Contour map of center of mass product IO flux with the most probable Newton diagram.

Fig. 5. Contour map of center of mass product IO flux.

Fig. 6. Product translational energy distributions. ••• experimental, lines are RRKM-AM calculations for three values of the IO bond energy. - - - - E_{IO} = 53, ——— E_{IO} = 55 and - —— - —— E_{IO} = 57 kcal mol^{-1}.

Fig. 7. Product translational energy distributions. ••• experimental, lines are RRKM-AM calculations for three values of the IO bond energy. - - - - E_{IO} = 53, ——— E_{IO} = 55 and - —— - —— E_{IO} = 57 kcal mol^{-1}.



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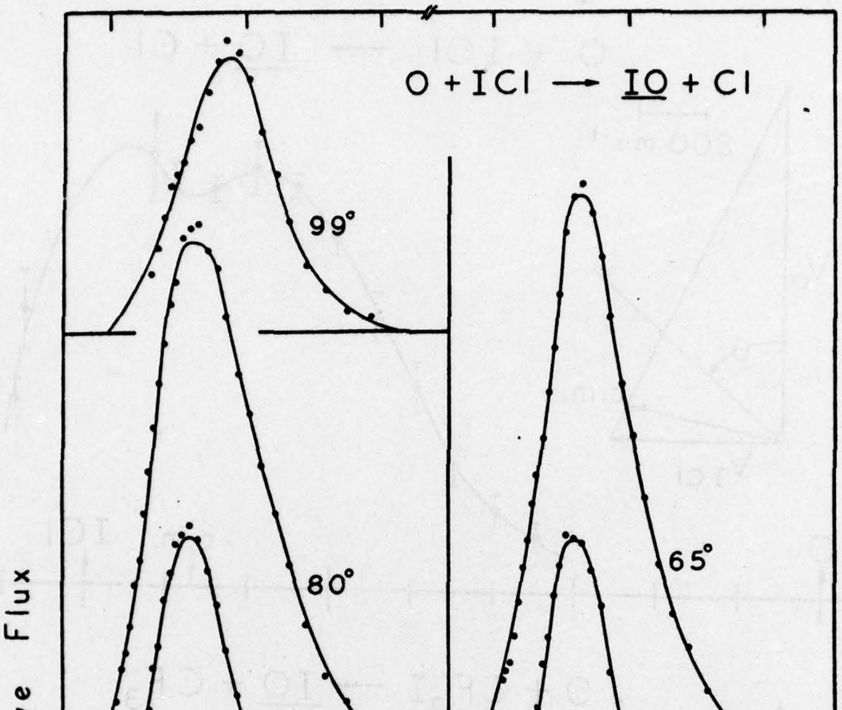

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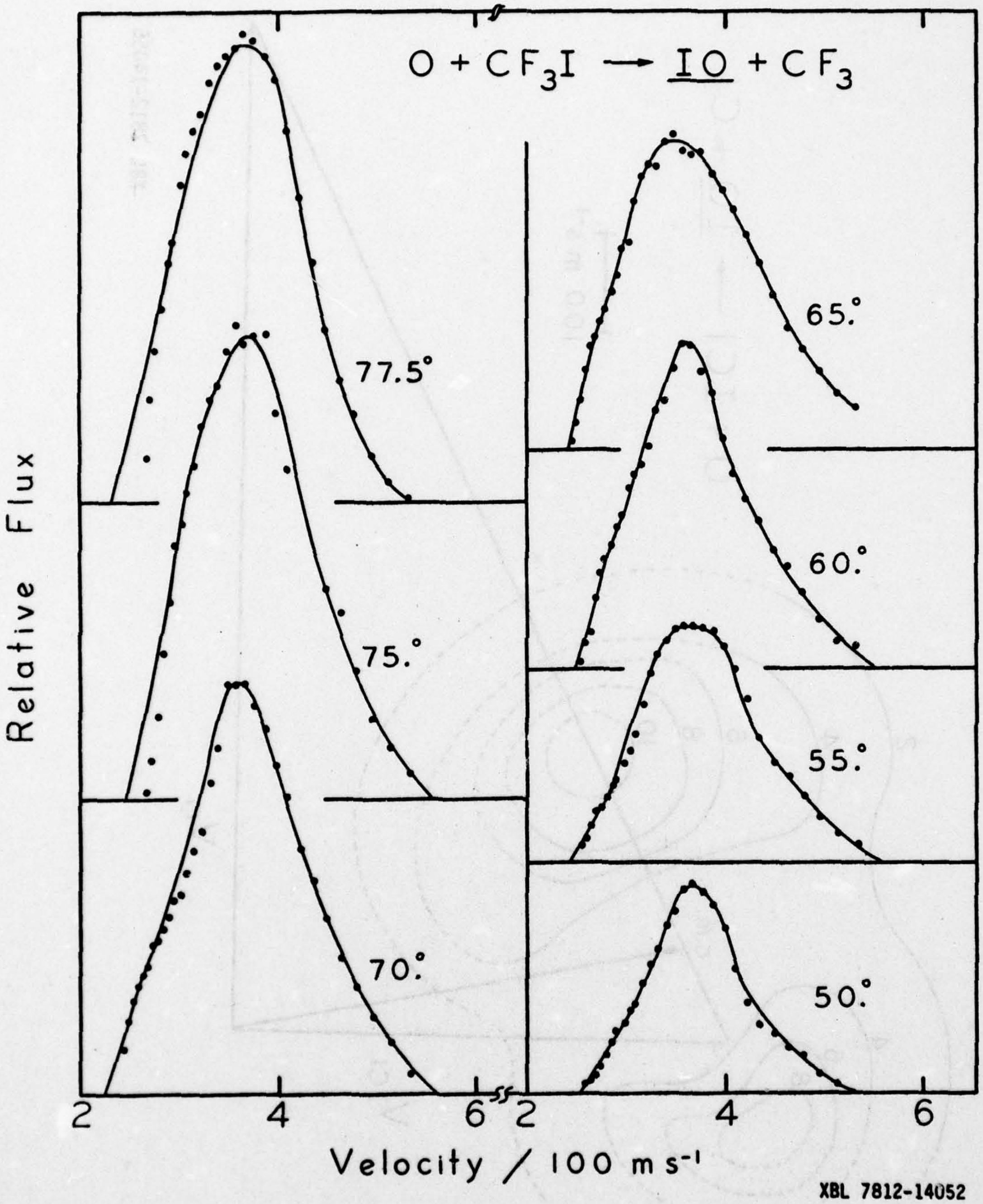

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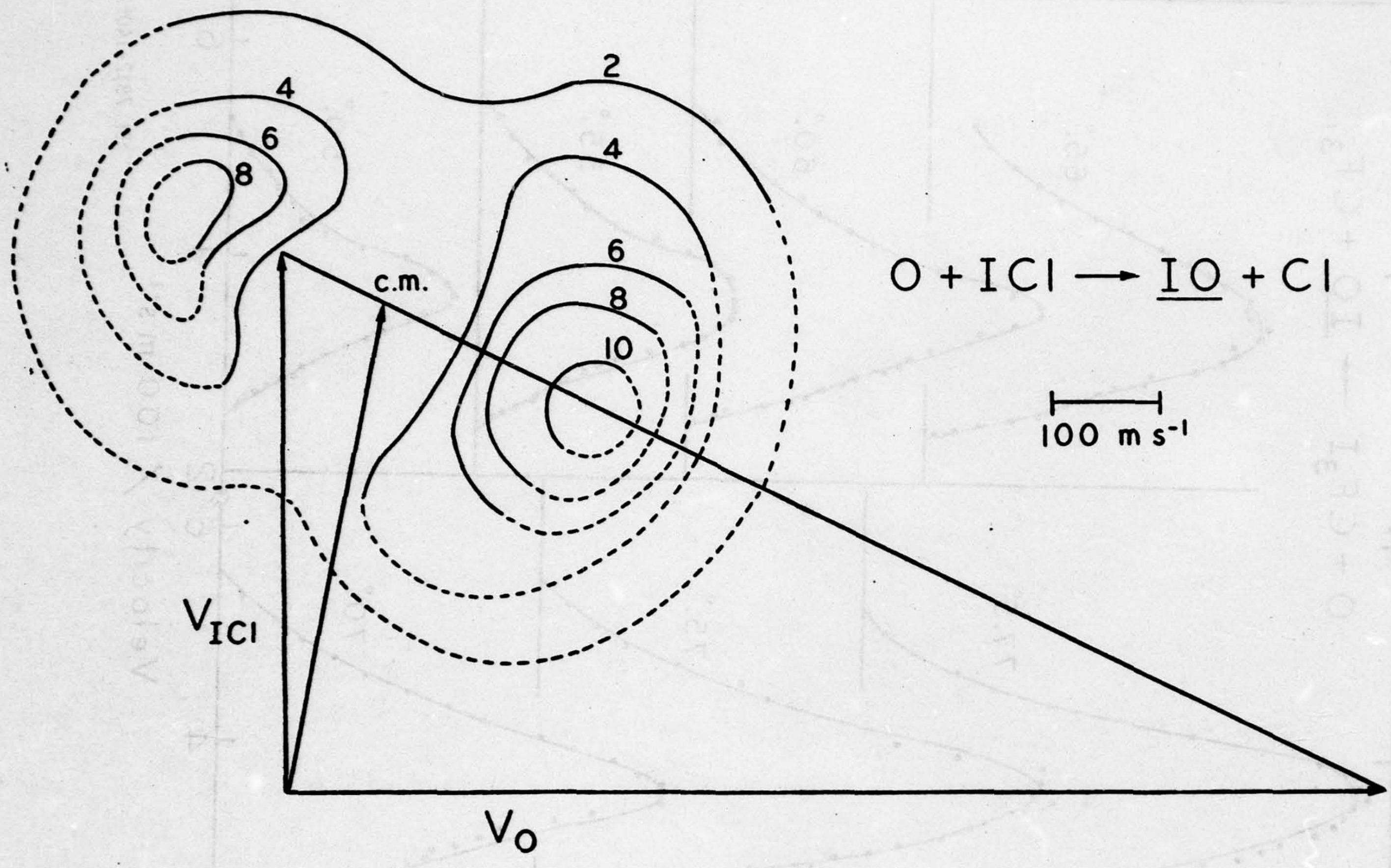

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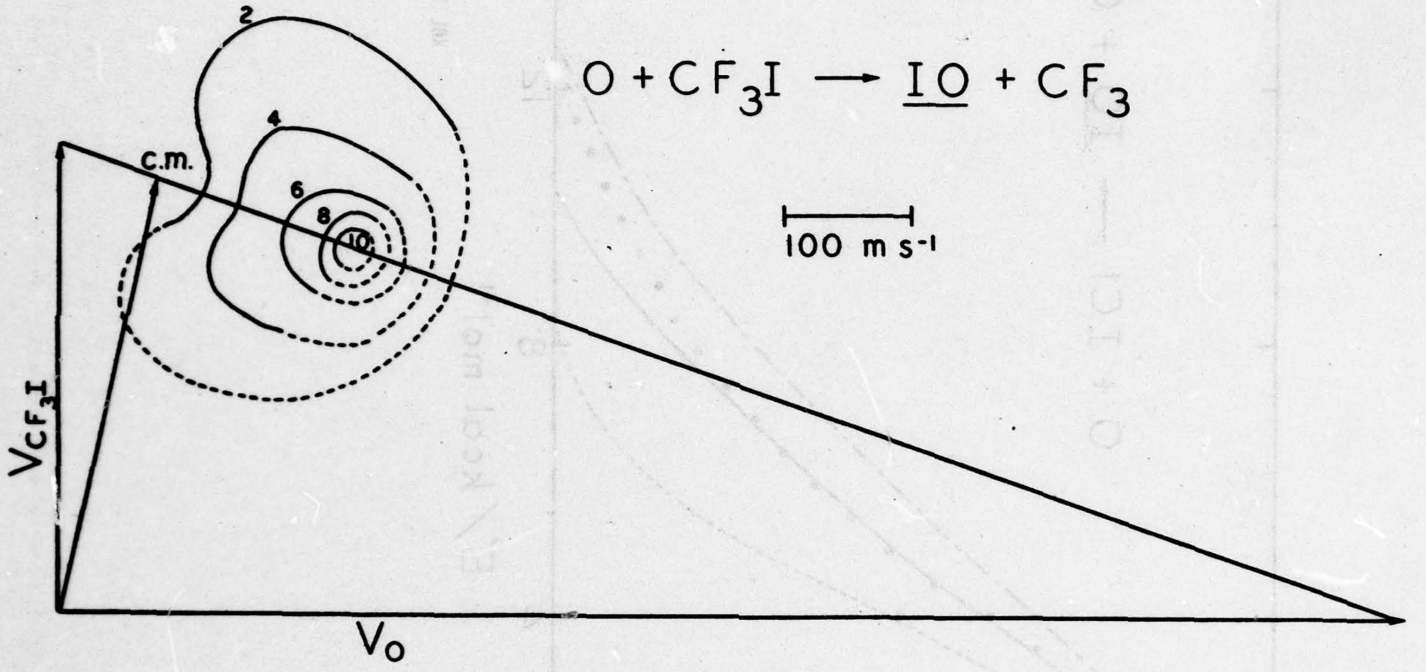

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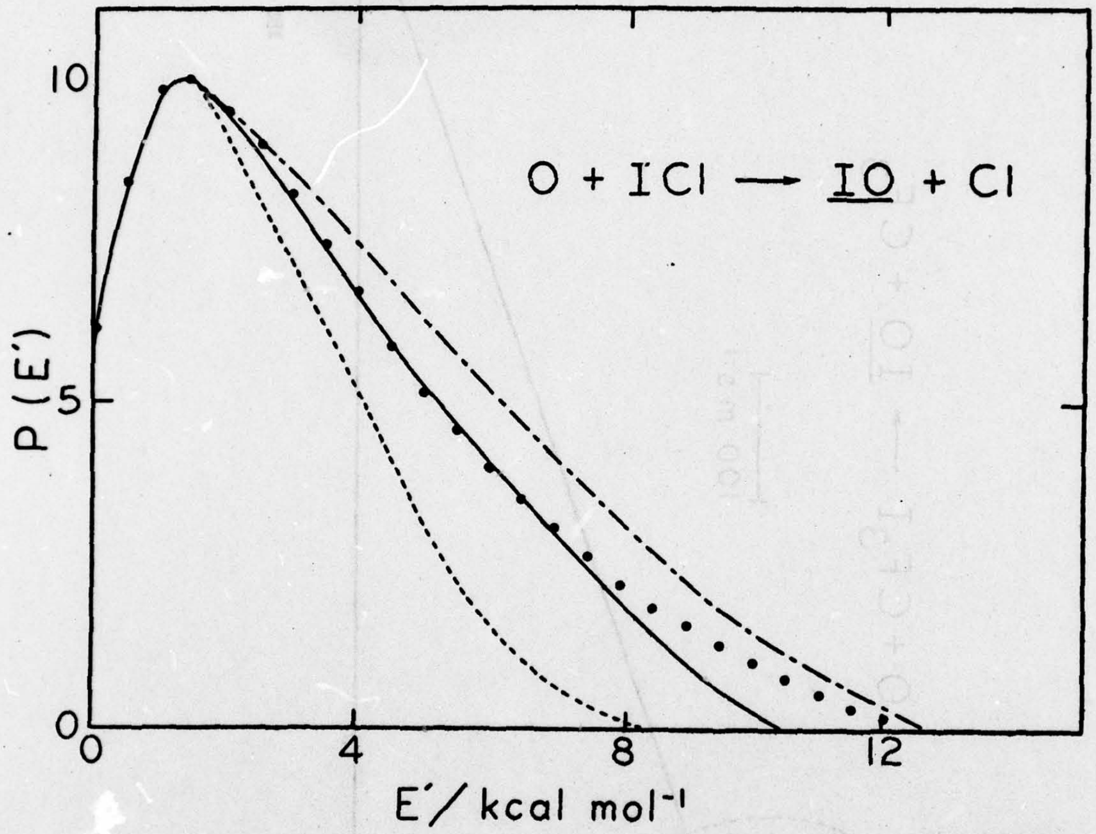

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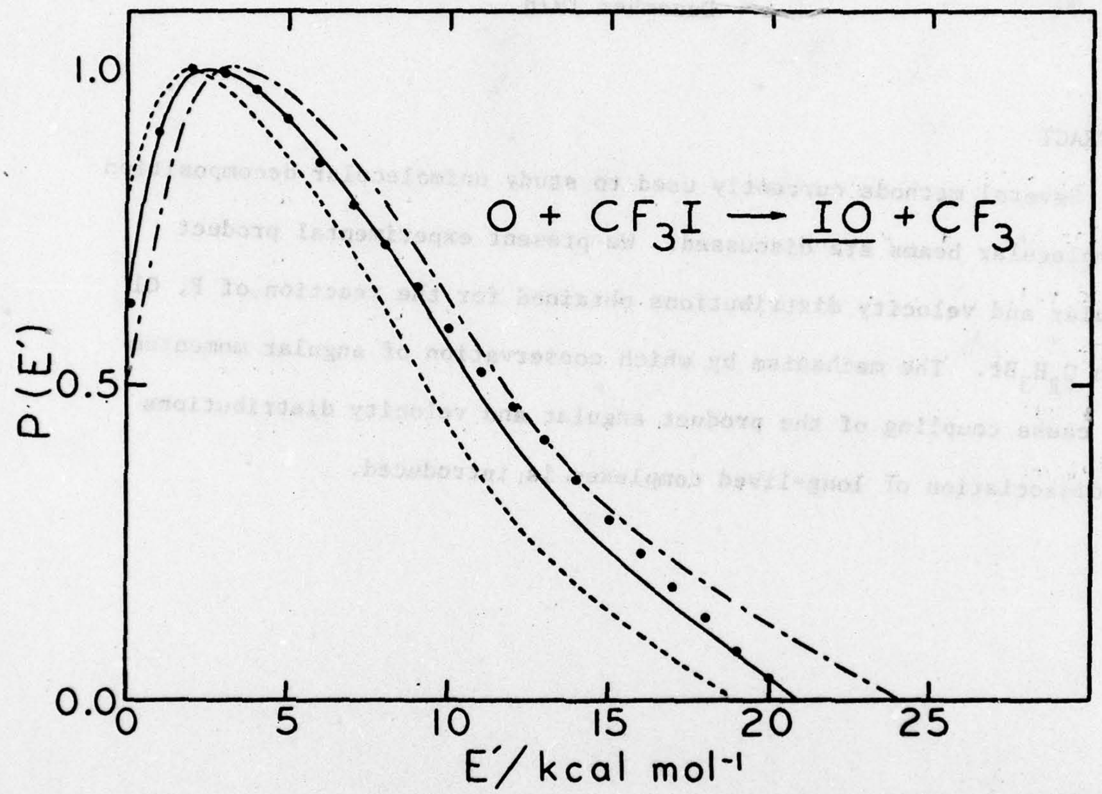

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5. Molecular Beam Studies of Unimolecular Reactions: Cl, F + C_2H_3Br

Richard J. Buss, Michael J. Coggiola and Yuan T. Lee

Materials and Molecular Research Division
Lawrence Berkeley Laboratory and
Department of Chemistry
University of California, Berkeley, CA 94720

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ABSTRACT

Several methods currently used to study unimolecular decomposition in molecular beams are discussed. We present experimental product angular and velocity distributions obtained for the reaction of F, Cl with C_2H_3Br. The mechanism by which conservation of angular momentum can cause coupling of the product angular and velocity distributions in dissociation of long-lived complexes is introduced.

Slightly over a decade ago, evidence for the existence of long-lived intermediates from reactive encounters of molecules in beams was presented at a Faraday Discussion meeting. This suggested the attractive possibility of studying the dynamics of unimolecular decomposition by the measurement of angular and velocity distributions of products in a collision free environment after preparing long-lived complexes by chemical activation. In the years since, a great number of reactions which appear to proceed via persistent complex have been studied in molecular beams. Although the early experiments frequently employed thermal beams and, hence, provided poor characterization of the collision energy, later refinement in beam techniques, especially the use of supersonic nozzle sources, has greatly increased the effectiveness of the method in providing insight into reaction dynamics.

More recently, a new technique, infrared multiphoton excitation in beams, in which molecules are excited under collision free conditions by absorbing tens of photons during an intense single laser pulse, has proven to be an excellent way to prepare excited molecules and to gain dynamical information about unimolecular decomposition. The study of some forty reactions ranging from simple bond rupture to three and four center eliminations has revealed trends which can likely be generalized to large classes of unimolecular decay.

These two methods, chemical activation and multiphoton excitation, differ substantially in several important respects. As a consequence the information obtained is complementary rather than overlapping.

The nature of the excitation process places limitations on the certainty with which we know the total energy of the dissociating molecules. With chemical activation in crossed beams, the total energy is simply the sum of internal energy of the reactants, energy released in formation of the new chemical bond, and the collision energy. The principal uncertainty, arising from the spread in collision energies, can be reduced to a small fraction of the total energy. With the use of two supersonic nozzle beams, the collision energy may typically be defined to FWHM = 5-10 kJ mol^{-1} which is often only 2-3% of the total excitation energy of the complex. This excellent energy characterization, combined with the variability of collision energy obtainable by seeding of the reactants with rare gases, make this technique a sensitive probe to the dynamics of unimolecular decomposition.

In sharp contrast, infrared multiphoton absorption produces excited molecules with a spread in excitation energies which can be an exceedingly large fraction of the average total energy. This problem is fundamental to the process, being governed by the mechanism of absorption of many photons. In the sequential absorption of photons, after an initial excitation through a region of discrete transitions, the molecule is excited to a region referred to as the quasi-continuum. The density of states, here, is sufficiently high that all transitions are near-resonant, essentially independent of laser frequency. A fairly adequate description of the population distribution of each level is given by a set of rate equations with transition rates depending on laser intensity, energy level dependent infrared absorption cross sections and density of states.[1] The result is somewhat similar to thermal excitation with a simple dependence of average excitation level on the energy fluence of the laser pulse. When the laser fluence is sufficient to drive the molecules above the dissociation threshold, an extra term must be added to the rate equations, to account for depletion by dissociative processes. At some high excitation level, the dissociation rate becomes much faster than the rate of excitation and population of higher states will not be significant. For a large molecule with high density of states around the dissociation levels, the unimolecular rate constant will increase gradually with excitation. Substantial dissociation will occur over a large range of levels. SF_6, for example, is calculated[1] to undergo detectable multiphoton dissociation (MPD) at levels from 4 to 13 photons above threshold, the total energy in the system then being defined to FWHM = 60 kJ mol^{-1} or about 15%. For smaller molecules, in which the rate constant increases more rapidly with excitation energy, the uncertainty in energy of the reacting molecules will be much narrower since most of the molecules dissociate from a level only a few photons above threshold.

The degree to which angular momentum affects the outcome of the unimolecular decay is also considerably different for the two processes. In both cases, cooling of the rotational degrees of freedom during supersonic expansion of the beams results in a low and relatively well-defined rotational temperature. In the bimolecular collision which produces the chemically activated species, orbital angular momentum can be very large, even at thermal energies, and sometimes dominating in its effects on the product translational energy distribution. Although the theoretical treatment of the effect of angular momentum on product energy distributions is fairly well developed, it remains a fundamental limitation in the analysis of this type of experiment that the probability of formation of the complex as a function of impact parameter which governs the distributions of angular momentum of the complexes is indeterminant. In consequence, it is incumbent on the theory to account correctly for angular momentum conservation, though this may require knowledge of dynamical features of the reaction, such as preferred orientation of reactants.

In MPD, angular momentum is found to play a much less significant role in the unimolecular decay. The depletion of low translational energy product expected for reaction with an exit channel centrifugal barrier associated with rotational motion is not observed in halogen atom detachment reactions using this technique. This indicates that the absorption of some forty photons does not appreciably increase the originally low average rotational energy. This greatly facilitates the comparison of product translational energy with statistical calculations.

The two methods lend themselves, most conveniently, to the study of different chemical systems. MPD in beams has been used extensively to study unimolecular decay of closed-shell molecules.[2] In particular, molecules with huge barriers to dissociation, for example, the three-center elimination of HCl from CHF_2Cl with approximately 225 kJ mol^{-1} barrier, are accessible with the energy fluence attainable in a high power CO_2 laser pulse. Indeed, MPD has been applied to systems ranging from such highly endoergic reactions to the nearly thermoneutral dissociation of ammonia dimers.[3]

Chemical activation has been applied principally to the investigation of open-shell systems. The addition of a radical species, eg. halogen atom, oxygen atom or methyl radical, to an unsaturated hydrocarbon to produce an excited radical intermediate constitutes the majority of long-lived complex reactions studied in crossed beams. The study of closed-shell systems by radical-radical combination collisions should become more frequent as these beam sources are developed.

A final aspect which distinguishes MPD from chemical activation is the time domain of the reactions. The multiphoton excitation always raises the molecules to a level at which the dissociation rate approximately equals the up-pumping rate. For the typical energy fluences attainable in a 50 nsec CO_2 laser, this fixes the upper limit of the average lifetime of the system at close to a nanosecond, fairly independent of the chemical nature of the molecule or type of dissociation process occurring. Using chemical activation, with its rapid deposition of bond-formation energy into the molecule, systems with average lifetimes shorter than a picosecond can be studied using the rotational period of the complex as an indicator. The method offers the possibility of finding a range of applicability of the statistical model for unimolecular decay. By studying reactions with a wide range of lifetimes, one can hope to place a bound on the time necessary for memory of the excitation event to be lost, though this time would undoubtedly be dependent on the exothermicity of the reaction, the stability and complexity of the intermediate.

The MPD of a large number of systems in which a single halogen atom is detached from a halocarbon has convincingly demonstrated the statistical nature of the process.[4] The primary pathway for decomposition is always found to be the statistically most favorable. The product translational energy distribution peaks at zero energy and has the correct statistical fall-off. Because the molecules undergoing dissociation have an average lifetime around one nanosecond after absorbing the final photon, we can conclude that the time for energy to be effectively randomized over all internal degrees of freedom should be much less than one nanosecond. Unfortunately, due to the limitation in the multiphoton excitation, it is not likely that these experiments will reveal exactly how fast the energy randomizes in the highly excited molecules.

In order to investigate the extent of intramolecular relaxation before chemical decomposition in a shorter time span than that of multiphoton decomposition, reactions of Cl and F with C_2H_3Br have been carried out in molecular beam experiments. In these chemical activation studies, as mentioned before, the product translational energy distributions, henceforth denoted P(E'), may be strongly influenced by angular momentum conservation, as well as by any potential barrier in the exit channel. The substitution reactions of fluorine and chlorine atoms with vinyl bromide are known to proceed with negligible potential barrier to bromine elimination. Angular momentum effects are large, though, and careful consideration of this is necessary in order to draw conclusions concerning the statistical nature of the process. Some important consequences of angular momentum, especially the coupling of angular and energy distributions of products will be discussed below.

EXPERIMENT

The crossed beam scattering apparatus and data acquisition methods used for these experiments has been described in detail.[5] The supersonic fluorine beam was produced by thermal dissociation of a 1% F_2 in argon mixture in a resistively heated nickle oven at about 1080°K. The chlorine source was similar, except the oven was high density graphite, and the mixture, 10% Cl_2 in argon, was heated to 1400°K. Vinyl bromide, undiluted, at a pressure of 250 torr was expanded from a 0.2 mm glass nozzle at room temperature. Time of flight characterization of the beams gave the information listed in

Table I. The spread in collision energies is determined from these parameters to be FWHM = 7.1 kJ mol^{-1} or 5.6% of the total energy for the chlorine reaction and FWHM = 4.2 kJ mol^{-1} or 2.2% of the total energy for the fluorine reaction. The laboratory angular distributions of product, shown in Fig. 1, were obtained by repeated scans with 100 second counts at each angle. In the fluorine experiment, elastic scattering of impurity from the secondary beam contributed to the signal at angles greater than 30°. The intensities at these angles were corrected by subtracting from them, the signal measured with a pure hot argon beam replacing the F/Ar mixture. The product flux distributions shown in Fig. 2 and 3 were obtained by the cross correlation time of flight method. The best fit lines in Fig. 1, 2 and 3 were obtained using the ratio method iterative deconvolution procedure.[6] The angular and velocity data have been combined to produce center of mass flux contour plots shown with the canonical Newton diagram in Fig. 4 and 5.

RESULTS AND DISCUSSION

The product angular distribution provides some information about the average lifetime of the reaction intermediate. The existence of symmetry of the product angular distribution about 90° in the center of mass reference frame, reflects a complex lifetime which is longer than the average rotational period of the molecule. An approximation to the mean rotational period is obtained by assuming a geometry for the complex to generate moments of inertia, and estimating the average angular momentum of the complex. For the chlorine reaction, the mean rotational period is estimated to be 3 ps. The RRKM theory predicts a mean lifetime of 0.1 ps, though this number is rather sensitive to the frequencies used in the calculation. We would expect, then, that the reaction should not exhibit forward backward symmetry if its lifetime is entirely determined by a statistical distribution of internal energy. In the laboratory reference frame, for this reaction, the back-scattered product is de-emphasized in the center of mass to laboratory transformation, and most back-scattered product is also beyond the range of the detector. The single datum at 99° was compared with a detailed calculation in which the RRKM-AM P(E') calculated for a range of collision energies and weighted by calculated total cross sections, with assumed forward backward symmetry, was transformed to the laboratory reference frame. The calculated intensity at 99° was a factor of 1.7 times the observed intensity, or six standard deviations away, thus strongly suggesting that the lifetime is indeed less than a rotational period. Were the product to exhibit a longer lifetime than statistical, one might conclude that there was decoupling of the reaction coordinate from the major excitation modes causing a bottleneck in the energy transfer or possibly a slow atomic migration limiting the rate of decomposition.[11] The statistical calculations for the fluorine reaction also predict asymmetry in the angular distribution, but the impurity in the vinyl bromide beam prevented detection of any back-scattered vinyl fluoride product. Although use of the rotational period for measuring the lifetime in these experiments provides only the crudest estimate of the statistical behavior of the system, the product translational energy distribution gives a far more sensitive test, if careful attention is paid to the treatment of angular momentum conservation.

One of the most interesting observations in the reaction of chlorine and vinyl bromide is the presence of coupling of the product angular and energy distributions. In Fig. 4 the dashed line through the peak in product flux at 0° is contrasted with the dotted line through the observed peak at each center of mass angle as the average translational energy of the products becomes smaller at wide angle. Considerable attention has been paid to this type of coupling arising in direct reactions with a large impulsive force in the exit channel.[7] The effect has been observed in a number of alkali atom reactions with halomethanes,[8] but in the analysis of long lived complexes, it has always been assumed that the energy distribution is independent of scattering angle. In fact, angular momentum conservation is also expected to create such coupling in reactions proceeding through long-lived complexes. When the impact parameter is large, the orbital angular momentum will often dominate the molecular angular momentum in the reaction, the angular momentum of the activated complexes will be highly polarized, perpendicular to the relative velocity, and a large fraction of the initial relative kinetic energy will become rotational energy of the complex as a consequence of the conservation of angular momentum. If most of the angular momentum of the complex is carried away as orbital angular momentum of the products, the product angular distribution will be strongly peaked in the forward and backward direction and most of the rotational energy of the complex will be converted to translational energy, such that the product energy distribution will be shifted to higher average energy than that released along the reaction coordinate from the sharing of excess vibrational energy. On the other hand, if the impact parameter is small, the orbital angular momentum will no longer dominate the molecular angular momentum. Consequently, the angular momentum of the complex will be distributed more isotropically due to random orientation of the molecular angular momentum of the reactants and the angular distribution of products will tend to be more isotropic. In addition, with a small impact parameter, most of the initial translational energy will become vibrational energy of the complex, the rotational to translational energy release in the formation of product molecules is less important and the energy distribution will be closer to what one would expect from simple statistical considerations with a translational energy distribution peaking closer to zero energy. This coupling of angular and energy distributions due to the constraint of the conservation of angular momentum should be observable in the experiment if the contribution from large impact parameter collisions does not overwhelm the small impact parameter collisions.

A simple calculation to demonstrate this effect is shown in Fig. 6. The contour map of product flux distributions compare a calculation of RRKM-AM product energy distribution decoupled from the angular distribution with one including coupling. The latter calculation is the sum of fifty distributions in which P(E') and P(θ) are varied together considering the magnitude and polarization of angular momentum, simulating the range of impact parameters expected in the chlorine reaction with vinyl bromide as shown in Fig. 7. Despite the lack of sophistication of the model, the major features of this coupling are evident. At 0° the flux peaks at higher velocities with coupling while the reverse is true at 90°. The effect would be less noticeable in reactions with larger cross sections in which large impact parameter collisions dominated. Of course, this demonstration of the existence of coupling in the angular and energy distribution of product molecules in the long-lived complex does not imply the existence of a long-lived complex between chlorine and vinyl bromide.

Comparison of the product energy distributions with RRKM-AM calculations for the two reactions is shown in Fig. 8. The experimental curve for the chlorine reaction is the average P(E') for the product scattered between 0 and 90 degrees in the center of mass frame. Parameters used in the calculations are shown in Table II. The vinyl chloride product from the chlorine reaction is seen to be in poor agreement with the statistical calculation, the product energy being substantially higher than calculated. Extensive testing with the model demonstrated that the failure is not the result of the chosen vibrational frequencies, the energetics, or the choice of maximum centrifugal barrier B'_m in the angular momentum treatment. The calculated P(E') is very insensitive to the first and second within reasonable range of the parameters. The dotted curve is produced with the parameter B'_m having been set at an unreasonably high value, 60 kJ mol^{-1}, beyond which its effect is negligible.

There are two principle explanations for the discrepancy observed. The first is the much-discussed possible failure of the energy randomization hypothesis. The lifetime for this reaction is calculated by the statistical theory to be approximately 0.1 ps. It would not be improbable that this reaction is beyond the scope of a unimolecular decay theory since, if statistical theory is applicable here, intramolecular energy transfer must be faster than 0.1 psec. The second explanation is that the treatment of angular momentum is inadequate. The theory assumes a distribution of angular momentum which is linear in impact parameter with a cutoff determined by the long range forces.[9] In practice, the relative cutoff for entrance and exit channel has been treated as a variable to obtain best fit. The linearity with impact parameter may be questioned. For this reaction, dynamical constraints may require that the atom attack at the double bond which is removed from the center of mass of the vinyl bromide. Approach at small impact parameter could be less favorable for reaction. A simple calculation based on this idea suggest that the angular momentum distribution might be more nearly quadratic in impact parameter. Assuming this distribution, the statistical calculation is found to fit the observed P(E') quite well, though this is likely fortuitous. In the fluorine reaction, again, the agreement with theory is poor. While the experimental energy distribution below 5 kJ mol^{-1} has large uncertainty resulting from the elastic impurity in the

C_2H_3Br beam, it is clear that the observed intensity of both low and high energy product is reduced. This is not easy to explain with a simple model and will probably require more information about dynamical effects of the potential energy surface for a thorough understanding, but it is quite clear for this system that the reaction lifetime is shorter than the intermolecular relaxation time.

SUMMARY AND CONCLUSION

McDonald and coworkers[10] have measured the infrared chemiluminescence from these reactions. They find that the product vibrational energy distribution is statistical for the fluorine reaction and non-statistical for the chlorine. While an earlier crossed beam study of the chlorine reaction using a beam of chlorine atoms with a thermal velocity distribution[11] seemed to indicate that product translation was statistical, our higher resolution results suggest that product translational is not statistical in either reaction. One explanation for the discrepancy for the fluorine reaction lies in the different energetics of the two systems. The greater exothermicity of the fluorine reaction leaves about 170 kJ mol^{-1} in internal excitation of the product compared to about 60 kJ mol^{-1} for the chlorine reaction. The chemiluminescence experiment measures the product emission milliseconds after reaction. If the vibrational energy is large enough that the molecule is above the ergodic limit, even if the initial distribution is not statistical, energy will be redistributed before the emission of the infrared photon is observed. Perhaps the higher internal excitation of the vinyl fluoride product allows randomization before the emission is detected while the vinyl chloride product retains its non-statistical distribution. The lifetime of the activated complex in the fluorine with vinyl bromide reaction is only 0.05 psec, according to statistical theory. If such a treatment is applicable, as implied in the chemiluminescence experiment, the intramolecular energy transfer has to be faster than 0.05 psec which is highly unlikely.

The two techniques of MPD and chemical activation in beams are seen to produce complementary results. MPD has demonstrated that, without exception, energy appears to be randomized in the nanosecond time period of the reaction. Chemical activation in beams has revealed non-*statistical effects* appearing *for reactions* with sub-picosecond lifetimes. These observations are not in contradiction to the general conclusion obtained by Rabinovitch and coworkers[12] that the intramolecular relaxation time of highly excited molecules is on the order of several picoseconds. The lifetime range available with chemical activation, together with its good energy specification should make it the method of choice for investigation of the efficiency of intramolecular energy transfer and detailed dynamics of unimolecular decay. Nevertheless, the MPD method should prove valuable for the study of exit channel dynamical effects in the highly endoergic three and four-center elimination reactions.

REFERENCES

1. E. R. Grant, P. A. Schulz, Aa. S. Sudbø, Y. R. Shen and Y. T. Lee, Phys. Rev. Letters, 1978, 40, 115.
2. Aa. S. Sudbø, P. A. Schulz, Y. R. Shen and Y. T. Lee, J. Chem. Phys., 1978, 69, 2312.
3. Aa. S. Sudbø, D. J. Krajnovich, P. A. Schulz, Y. R. Shen and Y. T. Lee, in preparation.
4. Aa. S. Sudbø, P. A. Schulz, E. R. Grant, Y. R. Shen and Y. T. Lee, J. Chem. Phys., 1979 (in press).
5. Y. T. Lee, J. D. McDonald, P. R. LeBreton and D. R. Herschbach, Rev. Sci. Instrum., 1969, 40, 1402. See also reference 6.
6. J. J. Valentini, Ph.D. dissertation, University of California, Berkeley, California, 1976.
7. N. D. Weinstein, Ph.D. dissertation, Harvard University, Cambridge, Massachusetts, 1972.
8. S. J. Riley, Ph.D. dissertation, Harvard University, Cambridge, Massachusetts, 1970.
9. S. A. Safron, N. D. Weinstein, D. R. Herschbach and J. C. Tully, Chem. Phys. Letters, 1972, 12, 564.
10. J. C. Moehlmann and J. D. McDonald, J. Chem. Phys., 1975, 62, 3052; J. F. Durana and J. D. McDonald, J. Chem. Phys., 1976, 64, 2518.
11. J. T. Cheung, J. D. McDonald and D. R. Herschbach, J. Am. Chem. Soc., 1973, 95, 7889.
12. J. D. Rynbrandt and B. S. Rabinovitch, J. Chem. Phys., 1970, 74, 4175; J. Chem. Phys., 1971, 54, 2275.

Table I.

	Peak Velocity x 10^4 cm/sec	Mach Number	Mean Collision Energy kJ mol^{-1}	Energy Spread FWHM kJ mol^{-1}
Cl	11.5	9.1	20.54	7.1
F	10.9	8.3	11.55	4.2
C_2H_3Br	4.9	7.7	---	---

Table II

	Cl + Vinyl Bromide		F + Vinyl Bromide	
	Complex	Critical Configuration	Complex	Critical Configuration
Total internal energy/kJ mol^{-1}	144.5	78.8	191.5	128.7
Moments of inertia/AMU Å^2	76.8	71.0	41.7	40.2
	207.5	385.5	254.4	563.5
	271.2	571.3	296.1	603.5
Frequencies/ wavenumbers	3125	3125	3150	3150
	3086	3086	3115	3115
	3030	3030	3080	3080
	1437	1586	1479	1612
	1374	1374	1380	1380
	1281	1281	1306	1306
	1036	1036	1097	1156
	897	897	929	929
	648	706	863	863
	621	621	711	711
	274	122	458	483
	103	46	450	500
	450	500	285	63
	250	102	177	30
	426	---	389	---
Ratio of maximum entrance to maximum exit channel impact parameter	dashed curve in Fig. 8	.77		.67
	dotted curve in Fig. 8	4.0		2.0

FIGURE CAPTIONS

Fig. 1. Laboratory angular distribution of vinyl fluoride product from the reaction F + $C_2H_3Br \rightarrow Br + C_2H_3F$, above, and vinyl chloride product from the reaction Cl + $C_2H_3Br \rightarrow Br + C_2H_3Cl$, below. The solid lines are best fits obtained by the ratio deconvolution method of Siska.

Fig. 2. The vinyl chloride product flux distribution measured at 15 laboratory angles. Solid lines are best fits obtained by the ratio deconvolution method. Dashed lines connect data points for clarity.

Fig. 3. The vinyl fluoride product flux distribution at 4 laboratory angles. Lines are best fit calculated curves.

Fig. 4. Center of mass C_2H_3Cl product flux, deconvoluted for beam velocity spread, shown with the most probable Newton diagram. The dotted line is through the peak flux at each center of mass angle. The dashed line is at constant center of mass velocity 580 m s^{-1} for comparison.

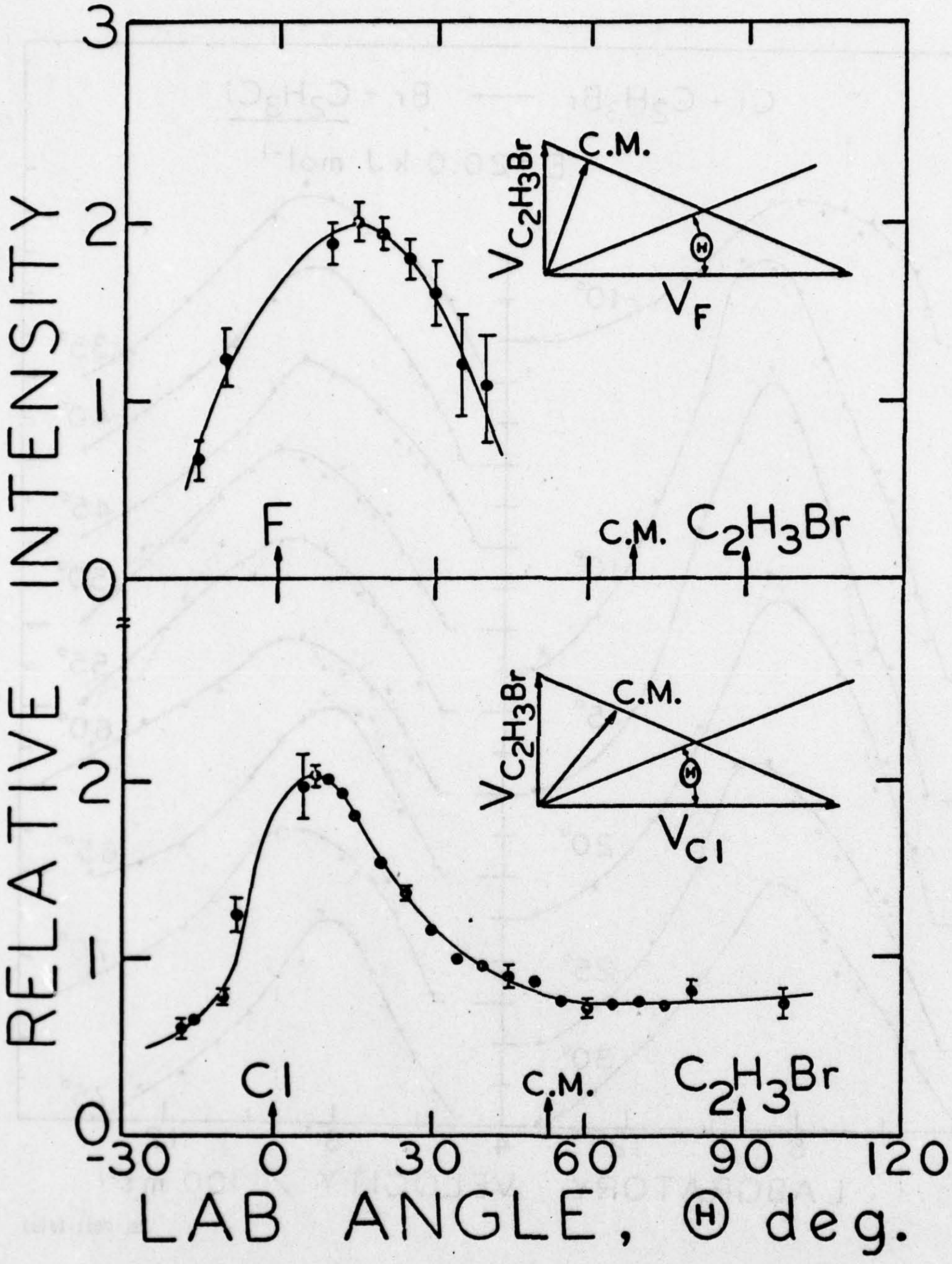
Fig. 5. Contour map of center of mass C_2H_3F product flux, shown with the most probable Newton diagram.

Fig. 6. Model calculation of product flux distributions. Dashed curves are generated from a single RRKM-AM P(E') with a single angular distribution. Solid curves are the sum of fifty P(E') with coupled T(θ) distribution.

Fig. 7. P(E') and T(θ) used to compare effect of angular momentum coupling. Shown are the RRKM-AM distributions for the uncoupled calculation. Also shown are three P(E') and

$T(\theta)$ for orbital angular momentum $L = \ell h$.

Fig. 8. Product translational energy distribution. Solid curves are experimental. Dashed curves are RRKM-AM with B_m' determined by C_6 constants. Dotted curves show calculations with B_m' increased to unphysically large values.



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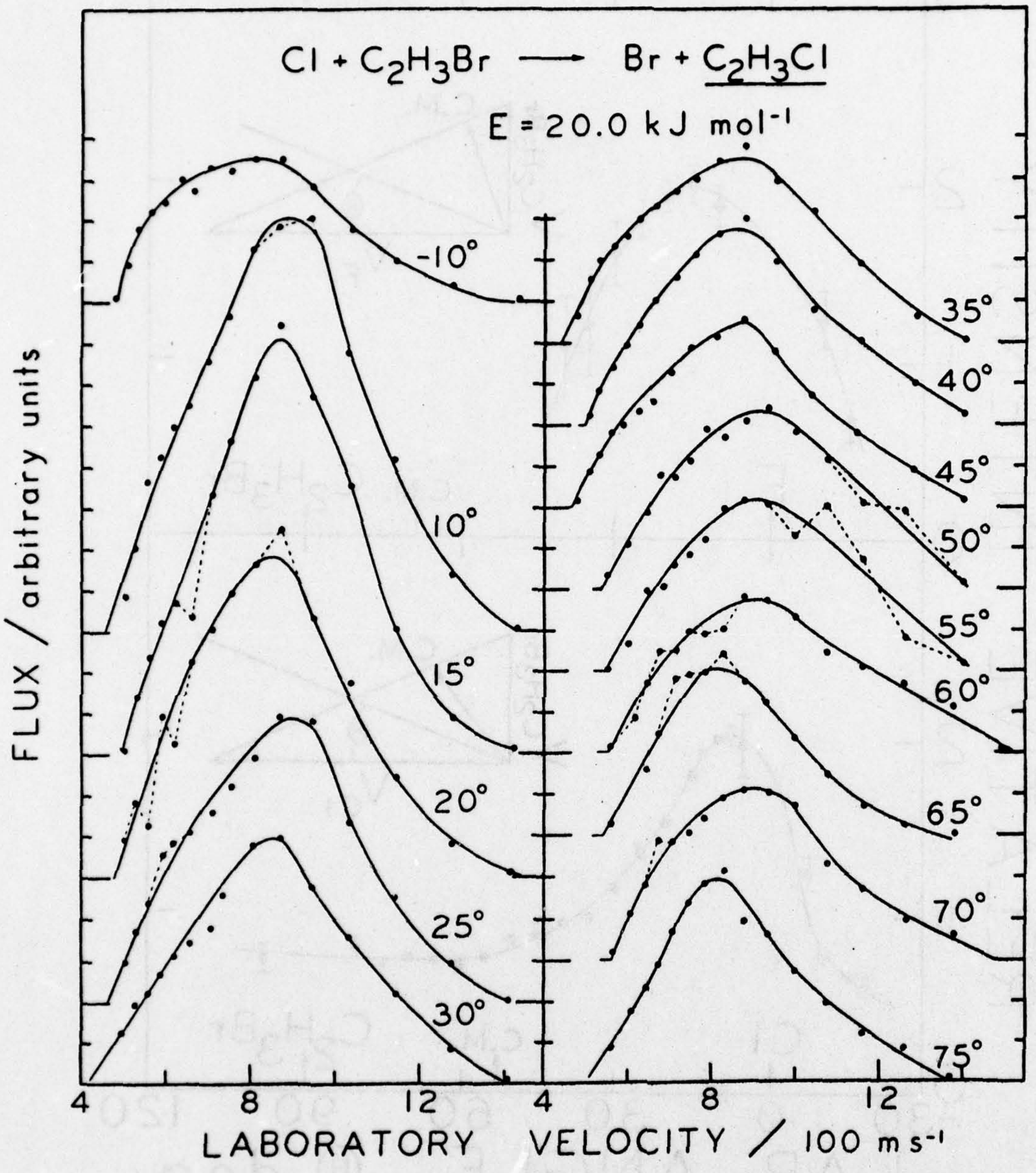

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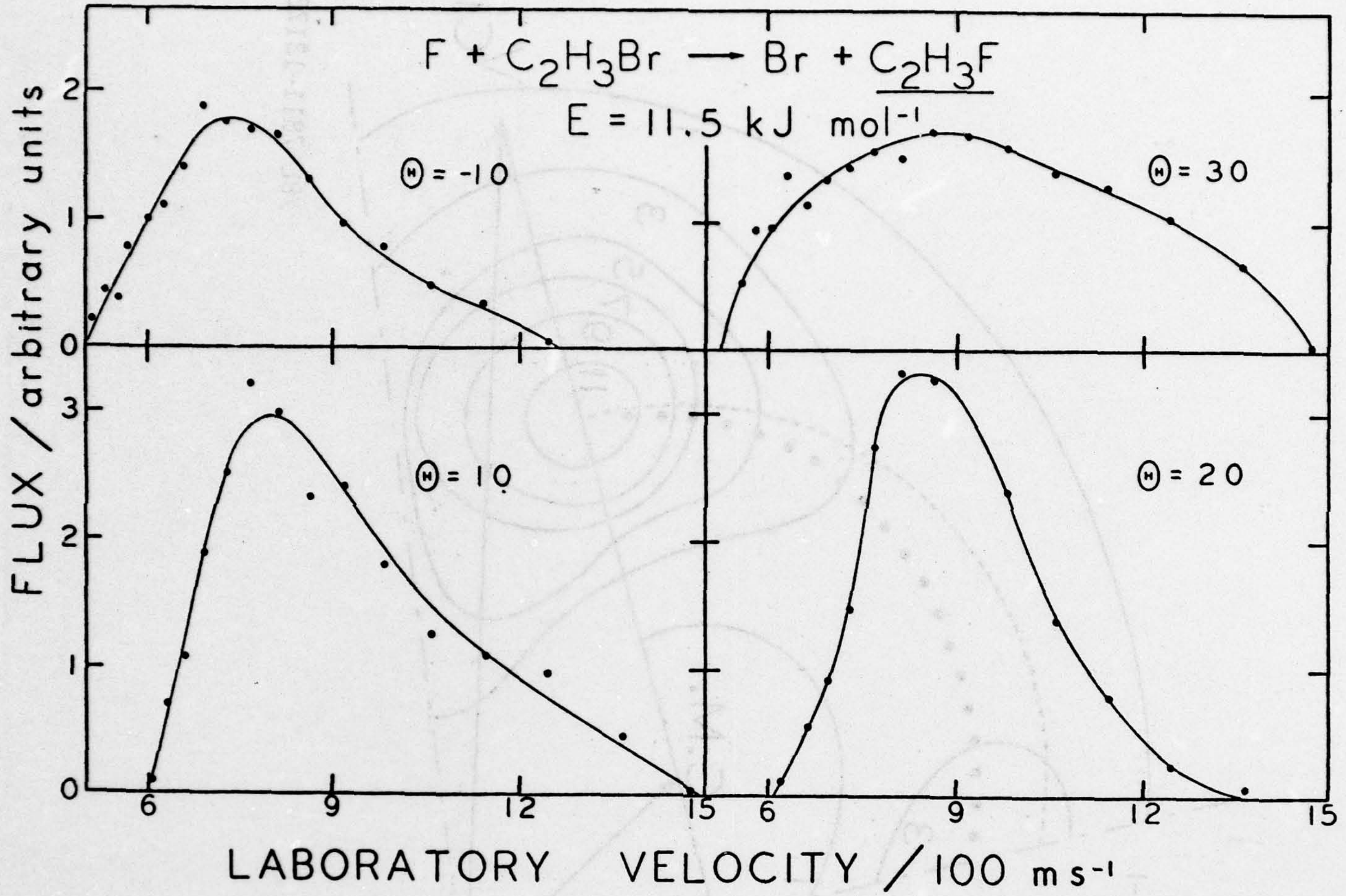

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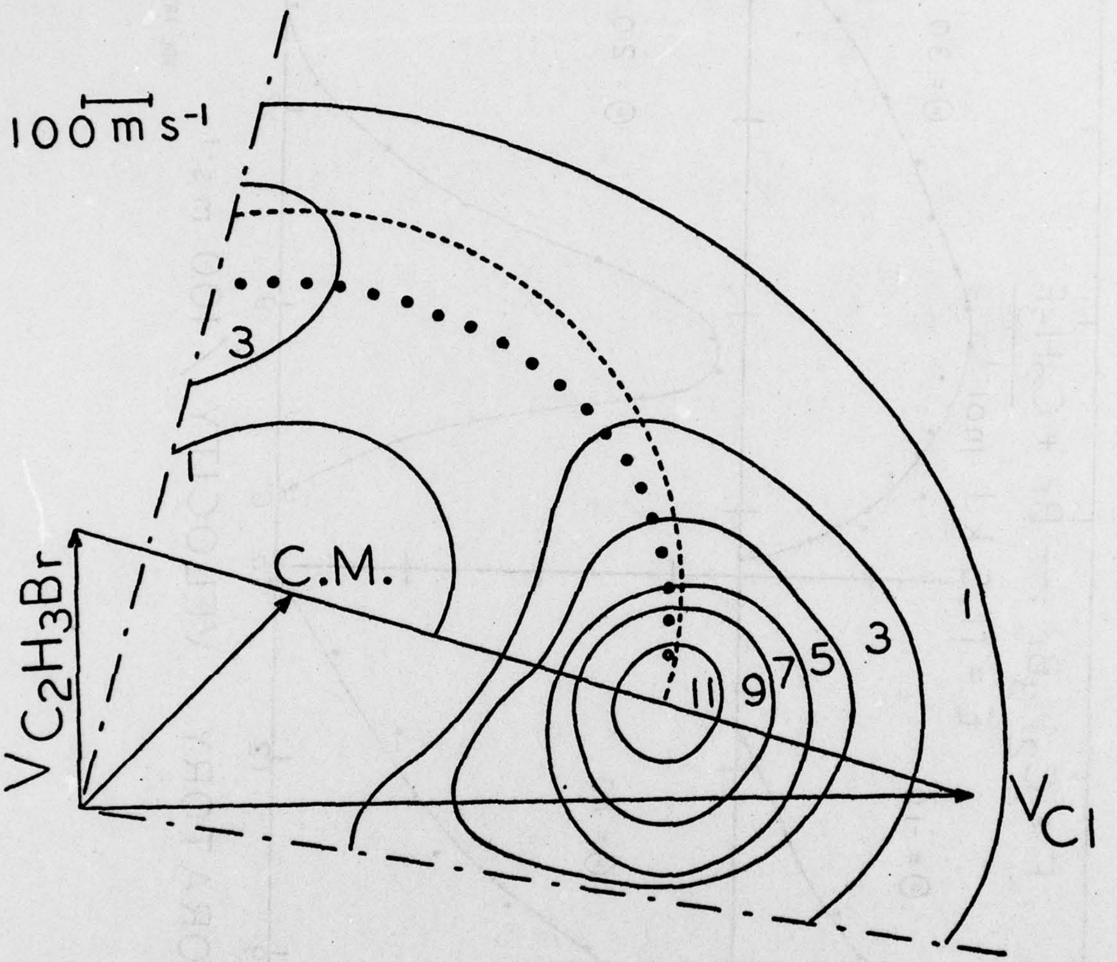

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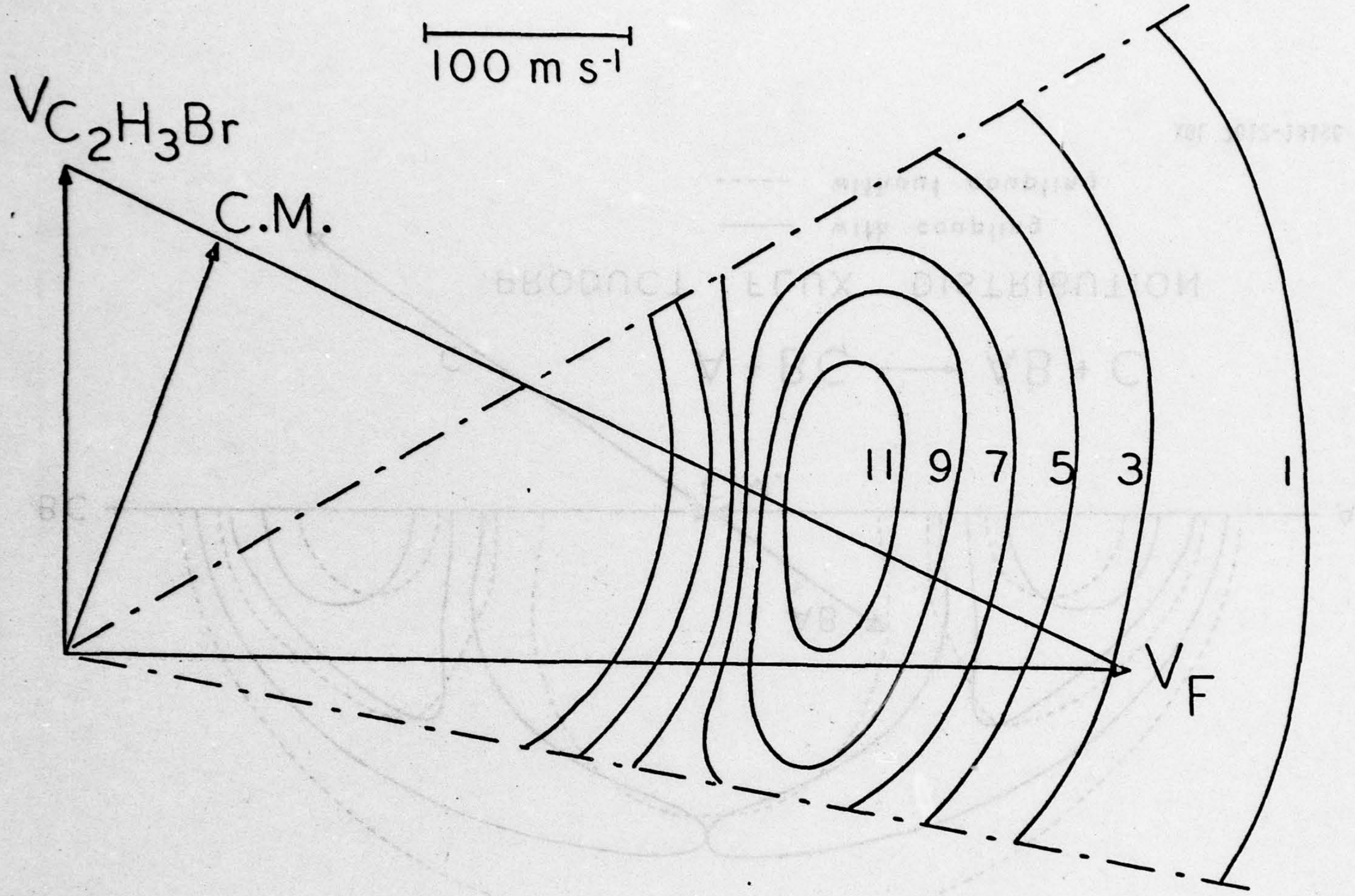

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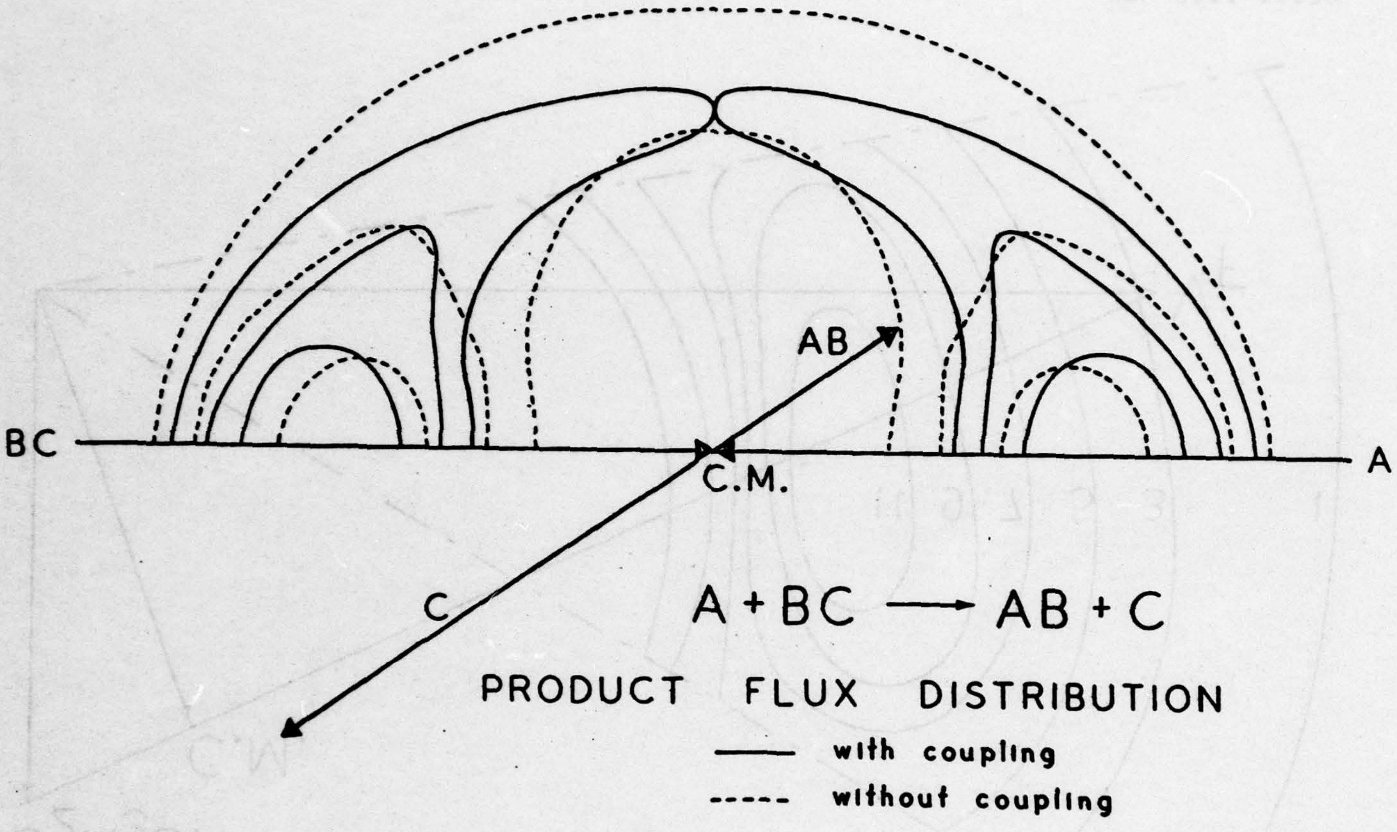

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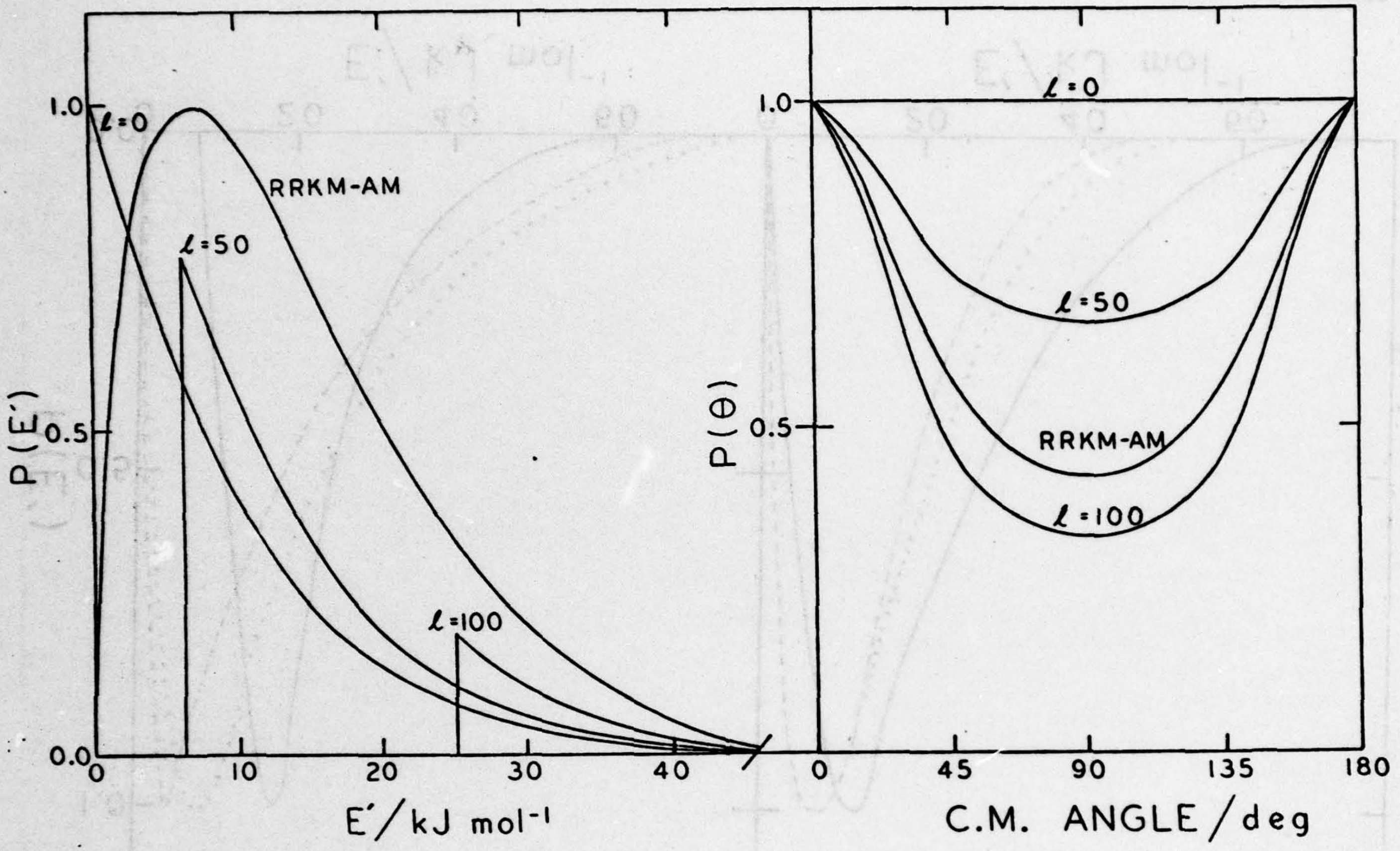

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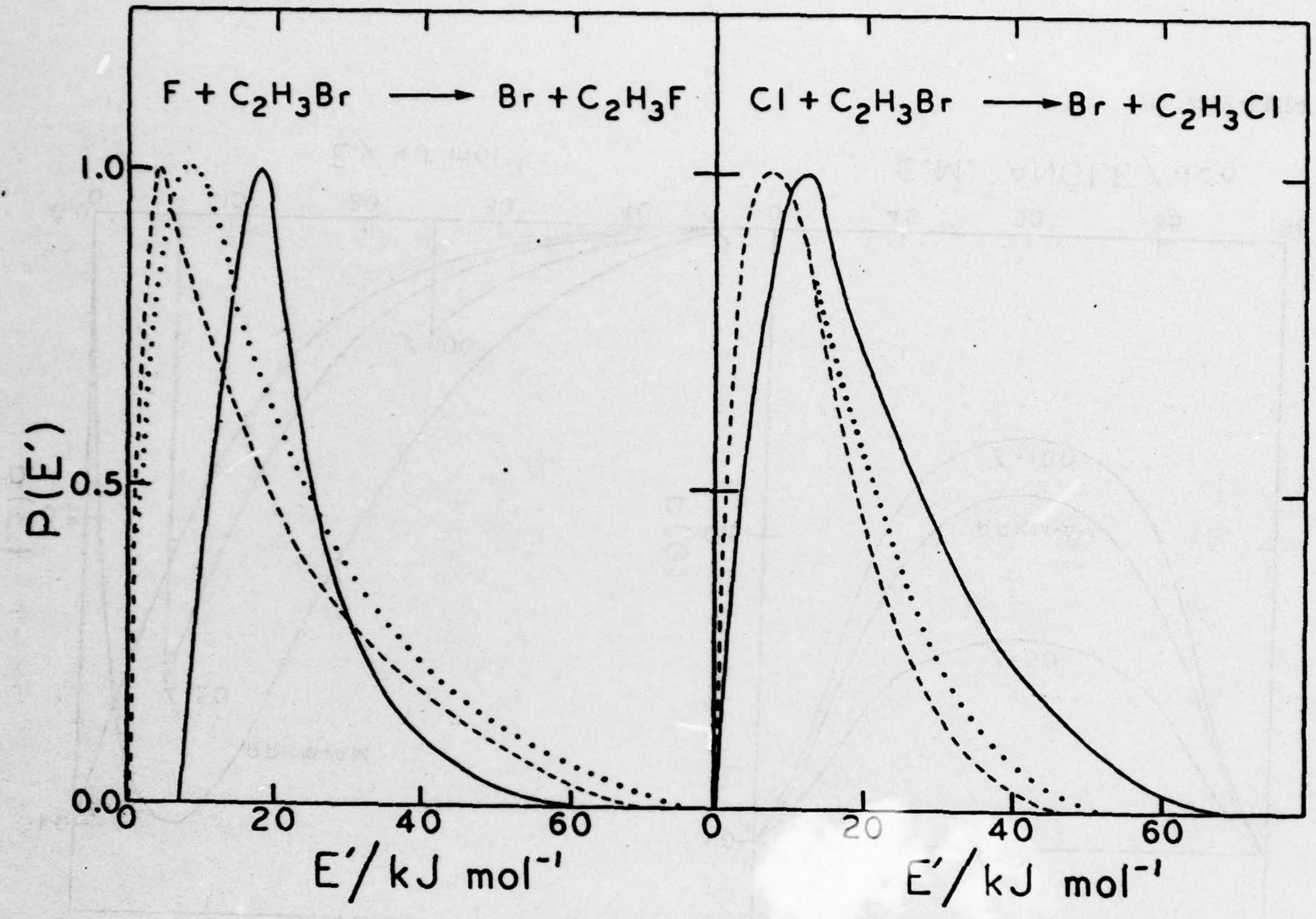

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II. Publication of ONR Supported Research

A. Papers submitted for publication

1. Development of a Supersonic Atomic Oxygen Nozzle Beam Source for Cross Beam Scattering Experiments.
Steven J. Sibener, Richard J. Buss and Yuan T. Lee
XI Proceedings of XIth International Symposium on Rarefied Gas Dynamics, Cannes, France, July 3-8, 1978.

Abstract

A high pressure, supersonic, radio frequency discharge nozzle beam source has been developed for the product of intense beams of ground state oxygen atoms. An efficient impedance matching scheme has been devised for coupling the radio frequency power to the plasma as a function of both gas pressure and composition. Techniques for localizing the discharge directly behind the orifice of a water-cooled quartz nozzle have also been developed. The above combine to yield an atomic oxygen beam source which produces high molecular dissociation in oxygen seeded rare gas mixtures at total pressures up to 200 torr: 80-90% dissociation for oxygen/argon mixtures and 60-70% for oxygen/helium mixtures. Atomic oxygen intensities are found to be greater than 10^{17} atom sr^{-1} sec^{-1}. A brief discussion of the reaction dynamics of $O + ICl \rightarrow IO + Cl$ is also presented.

2. Molecular Beam Studies of Unimolecular Reactions: Cl, F + C_2H_3Br, Richard J. Buss, Michael J. Coggiola and Yuan T. Lee, Faraday Society Discussions of Chemical Society, April 1979.

Abstract

Several methods currently used to study unimolecular decomposition in molecular beams are discussed. We present experimental product angular and velocity distributions obtained for the reaction of F, Cl with C_2H_3Br. The mechanism by which conservation of angular momentum can cause coupling of the product angular and velocity distributions in dissociation of long-lived complexes in introduced.

3. Molecular Beam Studies of Reactins of Oxygen Atoms with ICl and CF_3I, Richard J. Buss, Steven J. Sibener and Y. T. Lee

Abstract

Crossed molecular beam studies of reactions of O + CF_3I and O + ICl were carried out with a high intensity supersonic oxygen atom beam source developed recently in our laboratory. From the measured translational energy distributions of the IO product and the known dissociation energy of ICl bond energy, the IO bond energy is estimated to be 55 ± 3 kcal/mole. The reaction dynamics of O + ICl is not consistent with the formation of the long lived OICl complex, on the other hand, in the reaction of $O + CF_3I \rightarrow IO + CF_3$, the decomposition dynamics of chemically activated CF_3IO could be very well described by a statistical theory of unimolecular decomposition. The information on the dynamics of chemical reactions are mainly derived from the measurements of the translational and angular distributions of product molecules.

B. Invited lectures presented by principal investigator, Y. T. Lee, during contract period.

1. Y. T. Lee, Molecular Beam Photoionization Spectroscopy, Department of Chemistry, Tohoku University, Sendai, Japan, December 19, 1977.

2. Y. T. Lee, Crossed Molecular Beam Chemical Kinetics, College of General Education, University of Tokyo, Japan, December 22, 1977.

3. Y. T. Lee, Infrared Multiphoton Dissociation of Polyatomic Molecules, Department of Chemistry, University of Tokyo, Japan, December 23, 1977.

4. Y. T. Lee, Recent Advancement of Molecular Beams Experiment, Department of Chemistry, University of Kyoto, Japan, December 24, 1977.

5. Y. T. Lee, Laser Induced Chemistry by a High Power CO_2 Laser, Department of Chemistry, Tsinghua University, Taiwan, China, December 29, 1977.

6. Y. T. Lee, Multiphoton Dissociation of Polyatomic Molecules, Department of Chemistry, National Taiwan University, Taipei, Taiwan, China, December 30, 1977.

7. Y. T. Lee, Dynamics of Multiphoton Dissociation of Polyatomic Molecules by Infrared Lasers, Department of Chemistry, University of Southern California, Los Angeles, California, January 6, 1978.

8. Y. T. Lee, Recent Crossed Molecular Beam Studies of Elementary Chemical Reactions, Symposium on Experiments and Trajectories in Chemical Kinetics, 175th ACS National Meeting, Anaheim, California, March 13, 1978.

9. Y. T. Lee, Energetics of Molecule Ions by the Molecular Beam Photoionization Method, Symposium on Gas Phase Ion Thermochemistry, 175th ACS National Meeting, Anaheim, California, March 14, 1978.

10. Y. T. Lee, Dynamics of Infrared Multiphoton Dissociation of Polyatomic Molecules, Symposium on Laser Induced Chemistry, 175th ACS National Meeting, Anaheim, California, March 16, 1978.

11. Y. T. Lee, Dynamics of Multiphoton Dissociation by the Molecular Beams Method, Symposium on Laser Chemistry and Reaction Dynamics, California Institute of Technology, Pasadena, California, March 21, 1978.

12. Y. T. Lee, Molecular Beam Studies on Infrared Multiphoton Dissociation of Polyatomic Molecules, Joint Institute Laboratory Astrophysics, Boulder, Colorado, March 22, 1978.

13. Y. T. Lee, Crossed Molecular Beam Chemical Kinetics, Institute of Chemistry, Chinese Academy of Science, Peking, People's Republic of China, May 22, 1978.

14. Y. T. Lee, Laser Induced Chemical Reactions, Institute of Chemistry, Chinese Academy of Science, Peking, People's Republic of China, May 23, 1978.

15. Y. T. Lee, Investigation of Elementary Processes by the Molecular Beams Method, Institute of Chemical Physics, Chinese Academy of Science, Darien, People's Republic of China, May 24, 1978.

16. Y. T. Lee, Molecular Beam Studies of Multiphoton Dissociation of Polyatomic Molecules, Institute of Applied Chemistry, Chinese Academy of Science, Changchun, People's Republic of China, May 26, 1978.

17. Y. T. Lee, Molecular Beam Chemistry, Shanghai Association of Science and Technology, Shanghai, People's Republic of China, June 2, 1978.

18. Y. T. Lee, Elementary Atomic and Molecular Processes by the Molecular Beams Method, Institute of Chemical Physics, Chinese Academy of Science, Lanchow, People's Republic of China, June 9, 1978.

19. Y. T. Lee, Recent Advances of Multiphoton Dissociation of Polyatomic Molecules, Griffith University, Brisbane, Australia, August 25, 1978.

20. Y. T. Lee, Molecular Beam Studies of Infrared Multiphoton Dissociation of Polyatomic Molecules, XI Australian Spectroscopic Conference, Brisbane, Australia, August 28 - September 1, 1978.

21. Y. T. Lee, Dynamics of Infrared Multiphoton Dissociation of Polyatomic Molecules, University of Sydney, Sydney, Australia, September 4, 1978.

22. Y. T. Lee, Multiphoton Dissociation of Polyatomic Molecules, University of California, Santa Barbara, California, October 26, 1978.

23. Y. T. Lee, Interaction Potentials and Molecular Collisions, Haverford College, Haverford, Pennsylvania, November 8, 1978.

24. Y. T. Lee, Crossed Molecular Beam Studies of Reaction Dynamics, Haverford College, Haverford, Pennsylvania, November 9, 1978.

25. Y. T. Lee, Laser Induced Unimolecular Decomposition, Haverford College, Haverford, Pennsylvania, November 10, 1978.

III. Proposed Research (April 1, 1979 to March 31, 1980)

A. Crossed Molecular Beam Studies of the Reaction of Oxygen Atoms with Aliphatic and Aromatic Hydrocarbons.

The increase of the intensity by a factor of more than three, the reduction of the FWHM velocity spread to better than 15% and the intention of the range of collision energy to 25 kcal/mole were all accomplished during the past 10 months together with the recent reduction of background by a factor of four makes crossed molecular beams investigation of reaction dynamics involving oxygen atoms one of the most exciting areas of research for years to come. The completed work on a oxygen atom with iodine containing molecules included in this report clearly indicates a new era of understanding the dynamics oxygen atom reactions has indeed arrived. We have already initiated the investigation of long awaited reactions of oxygen atoms with unsaturated hydrocarbons. During this contract period we will concentrate our efforts on reaction dynamics of oxygen with medium size (2 to 8 carbons) aliphatic and aromatic hydrocarbons. We expect to complete at least three systems before the end of this contract period.

B. State Resolved Detection of OH and Other Simple Radicals by Multiphoton Ionization Processes.

Our next goal in the investigation of elementary reactions involved in combustion processes is the measurement of exact quantum state distributions of product molecules as a function of scattering angle. The laser induced fluorescence method is certainly one of the possible approaches, but in a crossed molecular beam experiment measuring angular distribution, the level of OH radicals is so low that it is often overwhelmed by high photon background produced by a oxygen atom beam source. A method which we want to develop and it is likely to be much superior is the multiphoton (2-3 photon) ionization using a tunable high power laser source. Recently, we acquired a high power Nd-Yag pumped TDL system in our laboratory and we plan to set up a beam apparatus to develop multiphoton ionization detection of a OH radical. Detection sensitivity will be compared with the laser induced fluorescence method. If the multiphoton ionization process is shown to be a viable state resolved detection method, we will set up a crossed molecular beams apparatus with rotatable beam sources for coupling to laser equipment. A quadrupole mass spectrometer is requested for this period.

C. Initiation Processes of Combustion.

One of the most important questions in the combustion phenomena is the initiation process of combustion. The hydrogen atom transfer from hydrocarbons to O_2, forming HO_2 and the dissociation of hydrocarbons followed by reactions of alkyl radicals with O_2 are generally understood to be the two most likely initation steps.

We intend to study the first process by using the high energy O_2 beam source. In order to understand the energy requirement in overcoming 50 kcal/mole endothermicity, vibrational temperature and translational energies of O_2 will be changed independently.

D. The Development of the $O(^1D)$ Beam Source.

The successful investigation of the dynamics of photodissociation of O_3 by photofragmentation spectroscopy provided us with a sufficient data base for developing the $O(^1D)$ beam source. Several approaches will be tried to produce a pulsed $O(^1D)$ beam source using pulsed 266 nm photons from a quadrupled Nd-Yag pulsed laser.

E. Substitution Reactions of Halogen Atoms with Unsaturated Halogenated Hydrocarbons.

Contrary to the conclusion of McDonald and coworkers, the F + C_2H_3Br product energy distribution is not statistical. Apparently, the excitation energy of C_2H_3F products are so high in this reaction, the energy redistribution took place after the reazction but before the emission of infrared photons. This observation, as described in this report, raises many interesting questions on the nature of intramolecular energy transfers. Especially, the ergodic limit of excited moelcules. In this period we will pursue this question further by looking at systems with more than one substitution channel.

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Professor S.N.B. Murthy 5
Technical Director, Project SQUID
Purdue University
Lafayette, IN 47907