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May 1983

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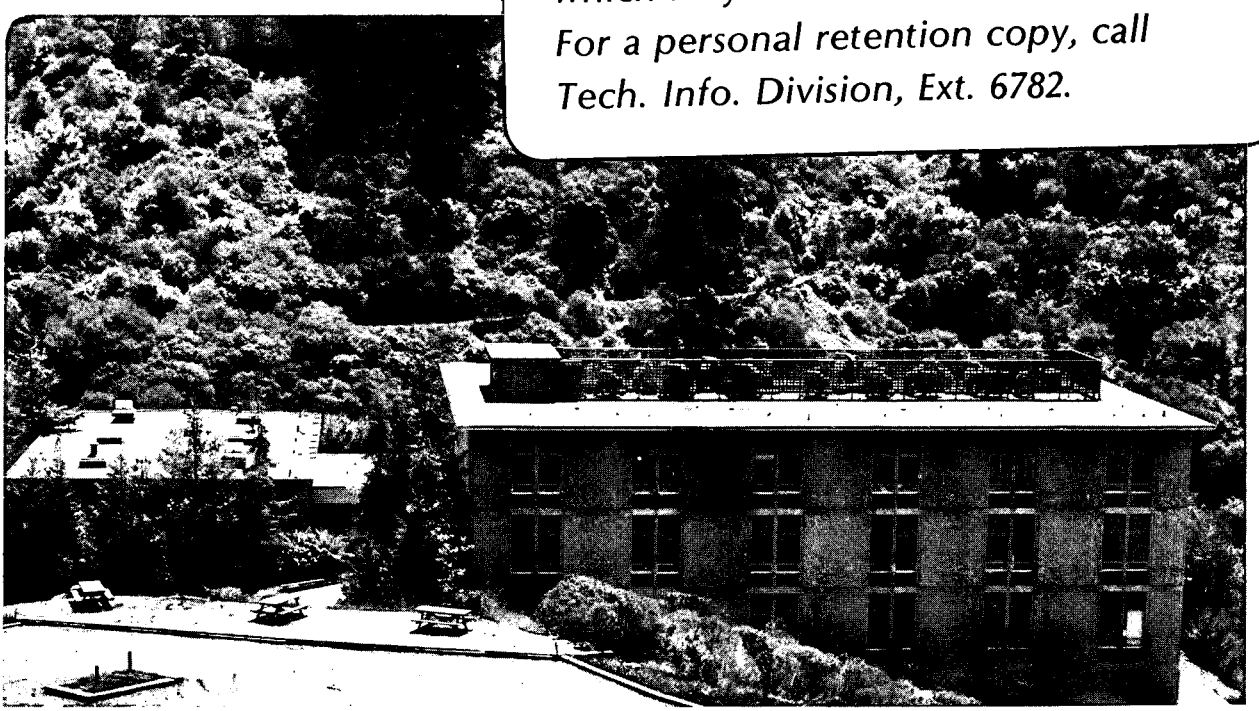

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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REACTIVE SCATTERING OF $O(^3P) + CF_3I$

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May 1983

ABSTRACT

The reaction of $O(^3P) + CF_3I$ has been studied using an RF discharge, supersonic oxygen atom beam source in a crossed beams arrangement. At a collision energy of 2.2 kcal/mole, the reaction yields exclusively $IO + CF_3$ radical products. The angular and velocity distributions of the product show that the reaction involves complex formation with the intermediate living greater than or equal to one rotational period. Only a small fraction of the available energy is partitioned into product translation, in good agreement with a statistical model. The reaction is believed to remain confined to the triplet surface forming a CF_3-I-O complex.

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INTRODUCTION

Among the earliest applications of the molecular beam method to the study of oxygen atom chemistry were reactions with halogen molecules.[1] These are chemically interesting in that the ground state reactants approach each other on a triplet potential energy surface which is an excited state of the triatomic intermediate with one electron promoted from the $3\pi^*$ to the $3\sigma^*$ orbital. The atomic arrangement in the ground singlet state of a triatomic molecule containing two halogen atoms and an oxygen atom (X_2O) cannot be predicted easily from the electronegativity rule[2] which states that the most electronegative atom will be located in the position of highest electron density. For these 20 electron systems, the 3π and the $3\pi^*$ molecular orbitals are completely filled in the ground state, resulting in no region of particularly high electron density. F_2O, Cl_2O and Br_2O are all found to have an XOX arrangement although the relative electronegativity of oxygen has changed from most positive in F_2O to most negative in Cl_2O and Br_2O. In the triplet state, however, with one electron promoted to a $3\sigma^*$ molecular orbital, the highest electron density should be on the end atoms, directing the most electropositive atom to the center. In the reaction of O + ICl, the intermediate would be expected to have the arrangement OICl if there is no intersystem crossing to the ground electronic surface. The arrangement ClOI would be more likely on the singlet surface in analogy with BrOBr. In a molecular beam study of O + ICl by Grice and coworkers,[3] it was reported that IO is the only product, and that the angular distribution of product was consistent with a long-lived complex model. Insertion of the oxygen into the ICl bond would be expected

to lead to formation of OCl product which is energetically more favorable. Thus this study suggests that the reaction is confined to the triplet surface.

The reaction of oxygen with CF_3I is expected to be similar to the O + ICl system. The oxygen atom approaching on the triplet surface should form a complex with a central iodine atom, while intersystem crossing to the ground singlet surface might lead to the oxygen atom inserting in the C-I bond. However, the O + CF_3I reaction differs from O + ICl in that the CF_3IO complex has a greater number of vibrational degrees of freedom than ClIO. These additional modes would be expected to cause the CF_3IO complex to have a longer lifetime than ClIO if these complexes are of comparable stability, and if there is a statistical redistribution of the energy released during complex formation.

Grice and coworkers[4] have reported a study of O + CF_3I at two collision energies in a crossed molecular beam arrangement. The results which we present here for O + CF_3I differ qualitatively in several important ways from those of Grice and coworkers. In particular, the translational energy distribution of the products is found to agree well with statistical calculations, in contrast to the previous study which reported highly non-statistical results.

EXPERIMENTAL

The crossed beam apparatus and data acquisition techniques were similar to those described previously.[5] The reaction is studied under single collision conditions by crossing two molecular beams at right angles in a region with background pressure about 10^{-7} torr. Products are detected by an electron bombardment ionization quadrupole mass spectrometer which rotates about the collision region in the plane of the two beams.

The oxygen atom source, described in detail elsewhere,[6] employs a high pressure RF plasma, localized near the nozzle, to achieve a high oxygen flux with reasonably narrow velocity spread and 80 percent dissociation. With a 5 percent O_2 in argon mixture at 100 torr pressure, the peak velocity was found to be 1050 ms^{-1} with a FWHM velocity spread of 40 percent. The CF_3I beam was an expansion of 250 torr pure gas from a 0.1 mm quartz nozzle at room temperature. The CF_3I was obtained from PCR Research Chemicals, Inc., and was used without further purification. The beam velocity distribution was determined by the time-of-flight method to have a peak velocity of 366 ms^{-1} with FWHM velocity spread of 30 per cent. This terminal velocity implies that the supersonic expansion effectively converted translational, rotational, and two low frequency vibrational degrees of freedom to beam kinetic energy. Under these conditions the reacting CF_3I should have an average internal energy around 1 kcal mol^{-1}. The mean collision energy for the CF_3I reaction is 2.18 kcal mol^{-1} with FWHM = 0.8 kcal mol^{-1}. Laboratory angular distributions of IO product number density were taken by repeated scans of 100 second counts at each angle. The oxygen beam was modulated at 150 hz with a

tuning fork and the signal obtained by subtracting the chopper-closed count from the chopper-open count. 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 with 12 μsec per channel time resolution. For this purpose a disk with a pseudorandom sequence of 255 slots was placed in front of the detector to modulate the product. Counting time varied from one to three hours at an angle.

RESULTS

The only observed product of the O + CF_3I reaction was the IO radical. Taking into account uncertainties in the relative detection efficiencies of CF_3O and IO, we estimate that if the more exoergic channel producing I + CF_3O ($\Delta H \sim -40$ kcal/mole) is occurring at all, it accounts for less than 10 percent of the reaction.

The laboratory angular distribution of IO product is shown in Fig. 1 with error bars showing two standard deviations of the mean of ten measurements. The product is found to peak strongly near the center-of-mass (CM) angle with no evidence of bimodality, suggesting that little of the available energy has gone to translation. The product time-of-flight (TOF) distributions at seven laboratory angles are shown in Fig. 2. A single peak close to the center of mass velocity is observed at each angle reinforcing the impression that the translational energy of the product is low.

The angular and velocity data were analyzed by two techniques. A direct inversion of the data using the iterative deconvolution technique of Siska[7] produces a two dimensional map of product flux in the CM reference frame. From this map, one can observe the overall features of the reaction, such as symmetry of the product about the relative velocity vector and whether there is coupling of the CM angular distribution ($T(\theta)$) and the product translational energy ($P(E)$). The Siska method is very sensitive to noise in the raw data and typically results in high energy tails on the derived $P(E)$, particularly for systems in which the spread in the center-of-mass velocities is large and the product detected is much more massive than the leaving group. Thus we also generally fit the data by

direct convolution of a trial P(E) and T(θ) over the beam velocity spread with automatic variation of the functions to achieve the best fit. This technique also greatly facilitates the derivation of error bars for the P(E), without which the distributions are less meaningful.

In Fig. 3 is the contour map of CM flux for IO product which was derived from the data. The contours represent the deconvoluted flux which, when averaged over the reactant beam velocities and other machine broadening effects in the transformation of CM to the laboratory coordinate system, will produce the best-fit solid lines shown in Figs. 1 and 2.

The distribution function P(E) and T(θ) are shown in Fig. 4. The peak of the translational energy is quite low, and represents only 10 percent of the available energy. Also shown is a statistical calculation of the P(E) using the phase space theory of Light.[8] The agreement between calculated and observed distributions is seen to be excellent.

The function T(θ) shows strong peaking on the relative velocity vector as is characteristic of reaction in which orbital angular momentum plays a larger role than molecular angular momentum. The observed T(θ) exhibits fairly good symmetry with possibly very slight preference for forward scattering of the IO product with respect to the oxygen atom direction.

DISCUSSION

The $O(^3P)$ atom approaches CF_3I on a triplet surface, the features of which have not been well characterized. Because many reactions of $O(^3P)$ have been found to resemble those of ground state fluorine atoms we look to the analogous reaction $F + CH_3I$ for similarities. The existence of a CH_3-I-F molecule was deduced from reactive scattering experiments[9] and the complex was later synthesized in a crossed beam experiment.[10] The CH_3-IF and CH_3I-F bond energies were found to be 13 and 26 kcal/mole respectively. Thus, in analogy we might expect a moderate well on the CF_3I-O triplet surface. The addition complex would be predicted to have the more electropositive iodine atom in the central position.

The CM angular distribution which is measured here suggests that a complex is formed which lives greater than or approximately equal to a rotational period. The strong peaking on the relative velocity vector, at 0° and 180°, is characteristic of reactions in which orbital angular momentum (L) predominates in the entrance channel and the product orbital angular momentum is strongly correlated to it. Because the CF_3I beam is a supersonic expansion in which rotational cooling is extensive, the molecular angular momentum (J) of the reactants is low, and L is likely to dominate the entrance channel with a moderate size of reaction cross section.

Donovan has suggested[11] that the dynamics of this reaction may be dominated by the well in the singlet surface, with the reaction always proceeding with intersystem crossing. This mechanism cannot be ruled out by our data. However, we believe that the singlet complex is more likely to have the oxygen atom inserted between the CF_3 and the I. The CF_3 often

behaves like a halogen atom and the structure of the complex might be expected to resemble the other halogen-oxygen singlet species, BrOBr or ClOCl. General rules of atomic ordering in triatomics[2] do not lead to a clear picture for those species because there is no region of dramatically higher electron density. If it is true that the singlet species has the configuration CF_3-O-I, then the decomposition would surely favor production of CF_3O + I which is far more exoergic. Absence of CF_3O product leads to the conclusion that the preferred geometry of the complex is CF_3-I-O.

The amount of energy appearing as translation is quite low, with the peak in the distribution occurring at about 0.4 kcal/mole. In comparing this with statistical predictions, it is necessary to assume several features of the reaction which are not well established. The distribution of angular momenta in the complex depends on the reactivity as a function of impact parameter, the opacity function, which can only be roughly estimated. If the long range force is estimated from polarizabilities, and used to calculate a capture cross section, the result is 59 $Å^2$. This seems inconsistent with the relatively small observed room temperature rate constant, $k = 1 \times 10^{-11}$ cm^3 $molec^{-1}$ s^{-1} (corresponding to about 2 $Å^2$ cross section if the activation energy is near zero). A strong orientation dependence of the reactants could cause the opacity function to deviate markedly from that predicted by a simple long range force treatment. Indeed the phase space calculation for the P(E), in which the angular momentum distribution is determined by the C_6 constant, predicts slightly more translational energy than is observed. When the angular

momentum effects are decreased by assuming a cross section of 34 $Å^2$, the calculated P(E) gives a reasonably good fit to the experimental angular and velocity distributions. It is assumed in these calculations that the reaction is exothermic by 2 kcal/mole, estimated from published heats of formation.[12]

A previous study of O + CF_3I using the crossed molecular beams technique has been reported by Grice et al.[4] The results which we report here directly contradict the findings of the Manchester group in several important ways. Of particular significance is the difference in P(E) for reaction at similar collision energy. In contrast to the slow product in good agreement with statistical theory which we observe, Grice reports product with average energy more than twice the statistical average. In fact, they report some product with translational energy exceeding twice the available energy, a physical impossibility. There is also no agreement between the T(θ) distributions in the two studies. The strong peaking on the relative velocity vector which we attribute to correlation of reactant and product orbital angular momentum was not seen in the previous study. Instead, a broad angular distribution favoring backscattering at low energies and becoming isotropic at higher collision energies was reported. The dashed lines in Figs. 1 and 2, calculated using the P(E) and T(θ) from Ref. 4, demonstrate the poor agreement between the two studies.

The reason for the major discrepancy between the results of the two studies is not readily apparent. There are significant differences in the raw data which cannot be reconciled by comparing the reported operating conditions. Deconvolution of the data requires precise and accurate

knowledge of the beam conditions, because high energy tails on the molecular beam, unaccounted for in the analysis, would manifest themselves as impossibly high energy products. Dimers in the beam may also result in skewing of the product angular distribution because the center of mass of the dimer reaction is located closer to the reactant beam.

While the difference between tne two studies remains a mystery, our results make a strong case for the existence of a relatively stable intermediate. We believe the excellent agreement between our P(E) and the statistical calculation is not simply fortuitous but indicates energy redistribution in a long lived intermediate. The near symmetry of $T(\theta)$ about 90° argues for the existence of a complex with a lifetime comparable to or longer than a rotational period. The strong peaking of $T(\theta)$ on the relative velocity vector reflects the expected dominance of L over J in the reaction.

CONCLUSION

The reaction of O + CF_3I is found to give IO product exclusively, apparently because the reaction remains confined to the triplet surface. A reaction complex having the structure CF_2I_O is formed which has a lifetime greater than or equal to one rotational period. The translational energy of the products agrees well with the results calculated using statistical theory.

ACKNOWLEDGMENT

This work was supported by Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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12. H. M. Rosenstock, K. Draxl, B. W. Steiner and J. T. Herron, J. Phys. Chem. Ref. Data, 1977, 6, Suppl. 1. The heat of formation of IO can be obtained from the IO bond energy 53 ± 3 kcal/mole which was measured in a crossed beam experiment of O + ICl, (D. St. A. G. Radlein, J. C. Whitehead and R. Grice, Nature 253, 37 (1975)). We have studied the same reaction in crossed molecular beams and prefer a slightly higher IO bond energy 55 ± 2 kcal/mole.

FIGURE CAPTIONS

Fig. 1. Laboratory angular distribution of mass 143, IO product. Error bars are two standard deviations of the mean. Solid line is the calculated best fit. Dashed line is calculated using the reported P(E) and T(θ) from reference 4.

Fig. 2. Time-of-flight distributions for mass 143, at seven lab angles. Solid lines are the calculated best fit. Dashed lines are calculated using the P(E) and T(θ) from reference 4.

Fig. 3. Product translational energy distribution, P(E) and CM angular distribution, T(θ), obtained in this experiment. Shaded region shows experimental uncertainty in T(θ).

Fig. 4. Contour map of CM flux of IO product in velocity space. The canonical Newton diagram is superimposed.

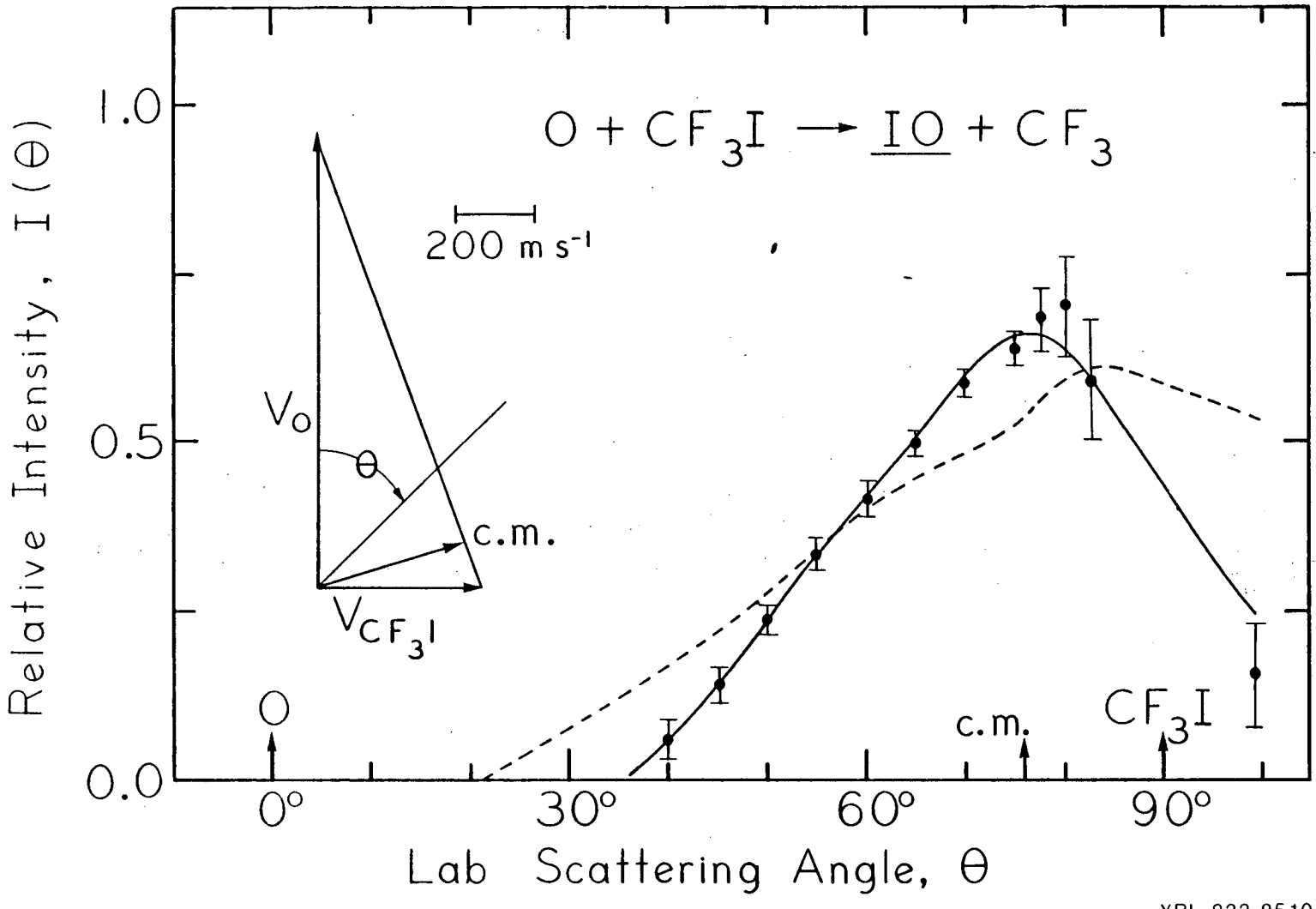

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Fig. 1

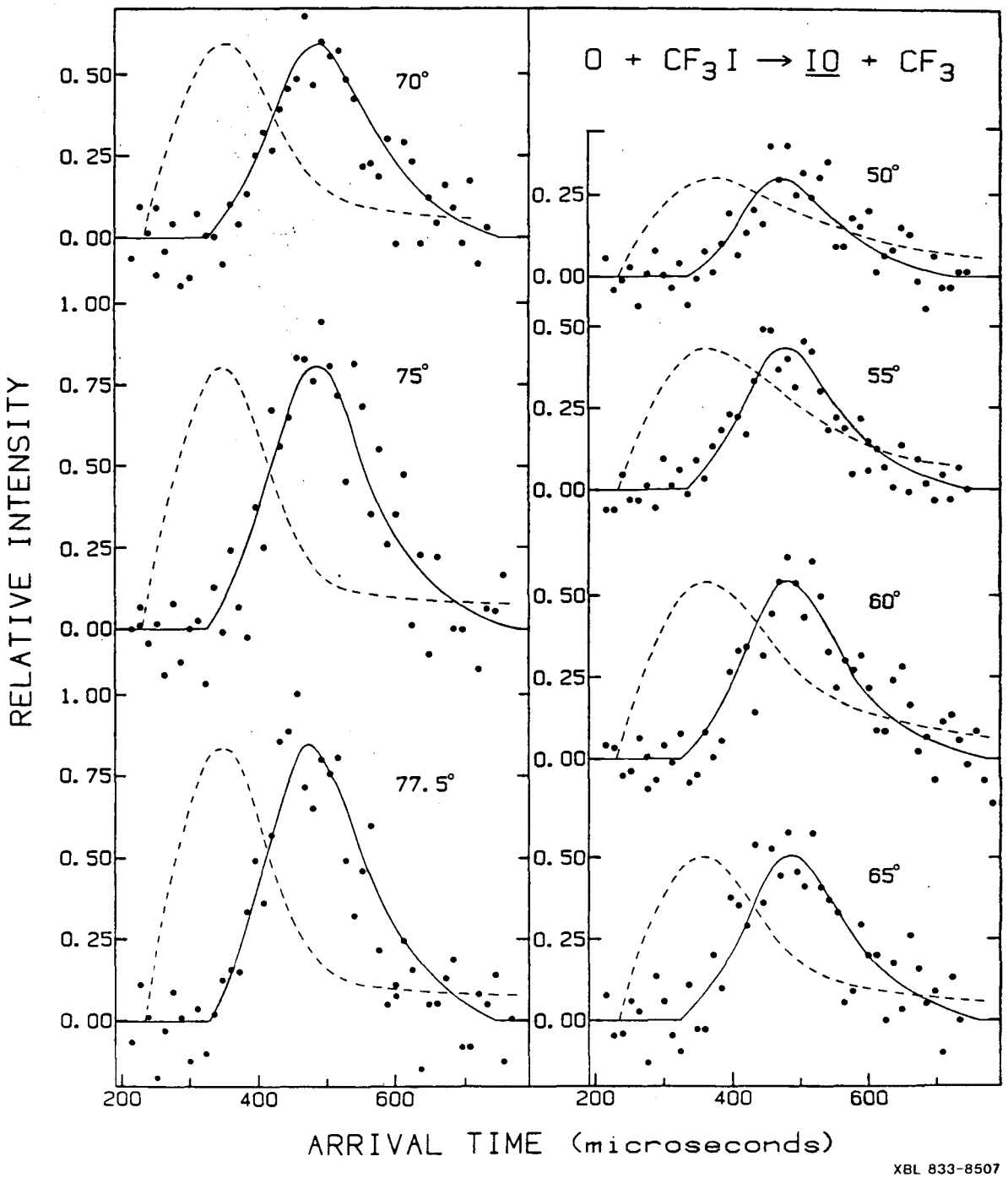
O + CF3I → IO + CF3
70°
75°
77.5°
50°
55°
60°
65°
RELATIVE INTENSITY
ARRIVAL TIME (microseconds)
0.50
0.25
0.00
1.00
0.75
200
400
600
XBL 833-8507

Fig. 2

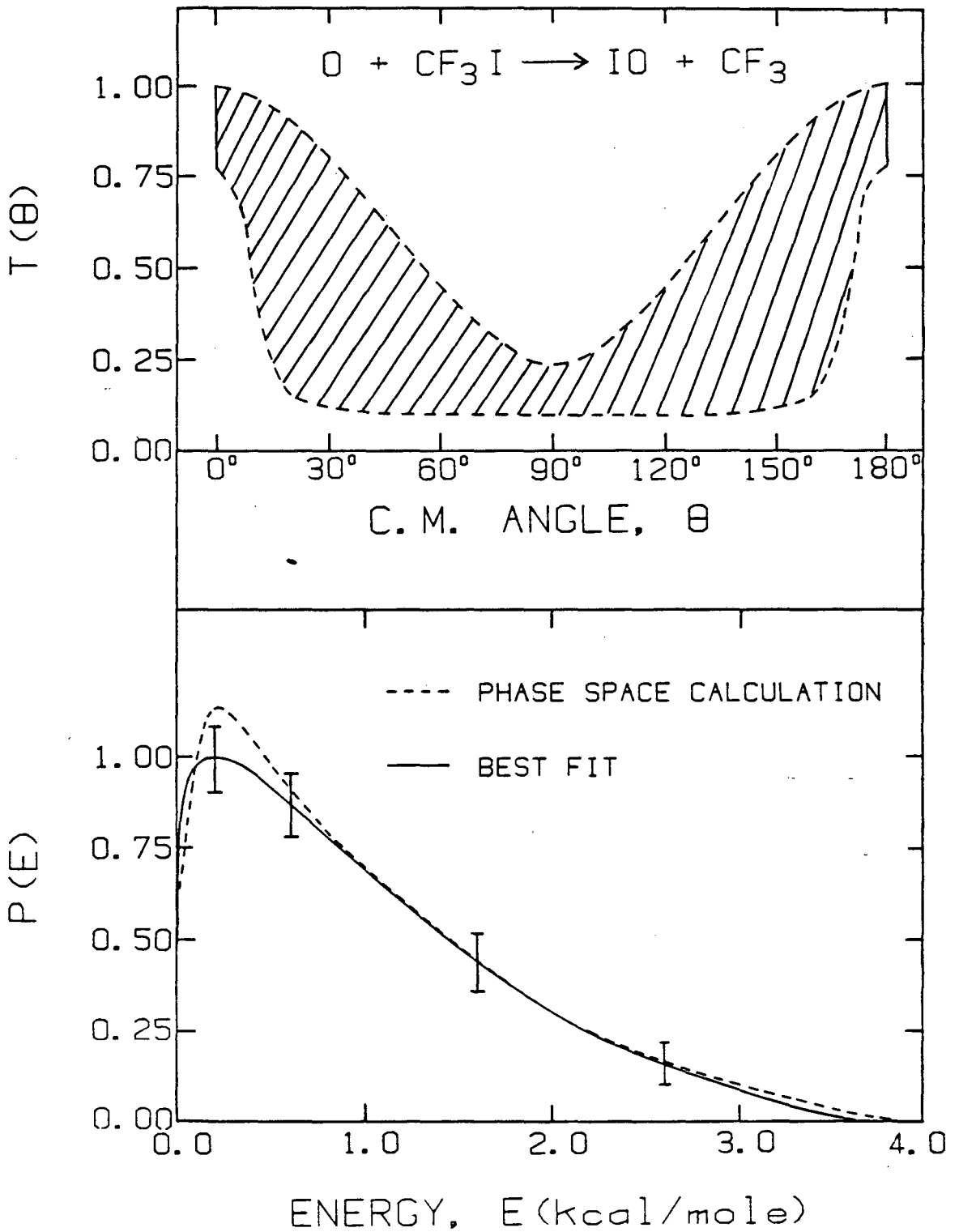

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Fig. 3

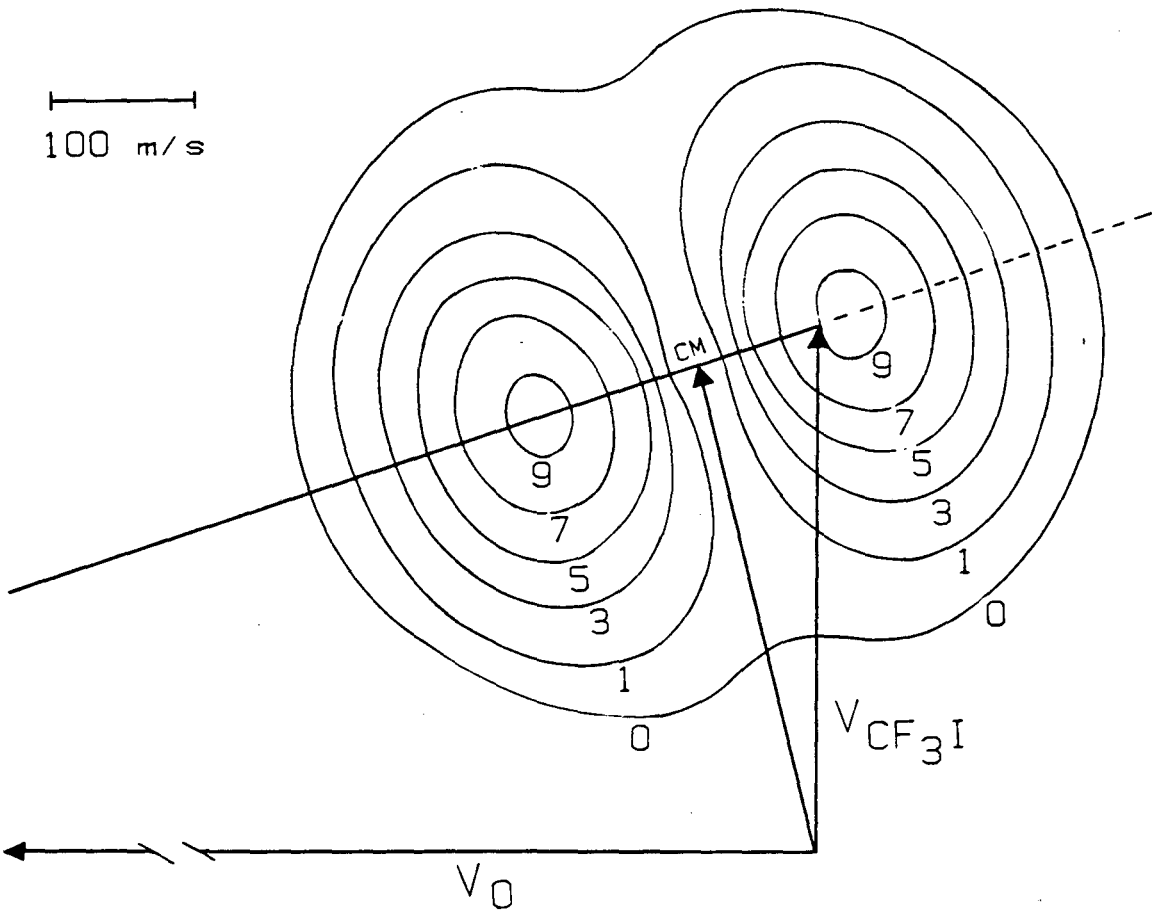

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Fig. 4

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