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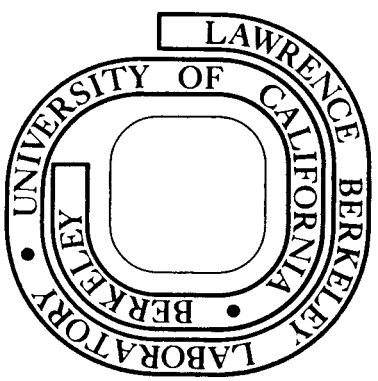
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MOLECULAR BEAM STUDY OF $F_2 + I_2$

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Crossed molecular beam techniques have been used to study the endoergic reaction between F_2 and I_2. Above a threshold energy of 4 kcal/mole the observed products are I_2F and F. At higher energies IF is also produced. Angular and velocity distributions indicate that the IF does not result from a four-center reaction.

*National Science Foundation Predoctoral Fellow.

MOLECULAR BEAM STUDY OF $F_2 + I_2$

It has long been believed that exchange reactions involving halogen molecules proceed either via a bimolecular four-center mechanism, whereby two product molecules are formed simultaneously, or via atom-molecule reactions initiated by thermal decomposition of halogen molecules into atoms. However, orbital symmetry considerations indicate that the four-center mechanism is thermally forbidden, while the generation of atoms in the gas phase also requires a high activation energy. In a crossed molecular beam study of $Cl_2 + Br_2$ no BrCl product was detected at collision energies up to 30 kcal/mole [1], indicating that high kinetic energy alone is not sufficient to produce four-center reactions of this type.

The recent observation of the formation of stable CH_3IF from the crossed beam reaction of F_2 and CH_3I at collision energies above 10 kcal/mole [2] suggests, however, that stable trihalogen molecules might be produced in the direct reaction of two halogen molecules, for example:

$$F_2 + I_2 \longrightarrow I_2F + F. \qquad (1)$$

I_2F is expected [3] to be more stable than CH_3IF, and therefore should be detectable in a molecular beam experiment employing crossed beams of F_2 and I_2 of moderate energy. I_2F will only be observed if reaction (1) is less endoergic than the reaction

$$F_2 + I_2 \longrightarrow I + IF + F, \qquad (2)$$

that is, if I_2F decomposition into IF and I is endoergic.

Indeed, the present investigation shows that above a threshold energy of approximately 4 kcal/mole collisions between F_2 and I_2 do

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produce principally I_2F and F as in (1). As the collision energy is increased reaction (2) also becomes important. The IF product detected in this experiment is closely related to the formation of I_2F, and could result from decomposition of an excited long-lived I_2F intermediate,

$$I_2F^{\ddagger} \longrightarrow IF + I, \qquad (3)$$

but not from IF_2,

$$IF_2^{\ddagger} \longrightarrow IF + F. \qquad (4)$$

IF_2 is not expected to be stable, and was not observed in this experiment. A previous crossed beam study of $I + F_2$ and $F + I_2$ reactions [4] showed evidence for a stable I_2F collision complex, but not an IF_2 complex.

The crossed molecular beam apparatus used in this study has been described previously [5]. Both reactant beams were generated by supersonic expansion using differentially pumped nozzle sources. A mixture of molecular fluorine (1-2%) in a He or He/Ne carrier gas was used to vary the collision energy. Additional control of the fluorine beam energy was provided by a resistance heated nickel oven operated between 300 and 900 K, without appreciable F atom production. The iodine beam energy was fixed by maintaining the glass nozzle at 380 K and using a 10-15% mixture of I_2 in Ar. This arrangement resulted in a range of collision energies from 3 to 30 kcal/mole. Product molecules were detected in the plane of the reactant beams using a rotatable, triply differentially pumped quadrupole mass spectrometer, equipped with an electron bombardment ionizer and utilizing ion counting techniques. In addition to measurement of the angular distribution of the products, the product velocity distributions were also determined by means of a cross correlation time-of-flight method [6]. This technique provided a

velocity resolution of better than 10%.

Figure 1 shows the measured angular distributions of both the I_2F (m/e 273) and IF (m/e 146) products resulting from reaction at collision energies of 12.6 and 18.7 kcal/mole. In each case, part of the measured IF signal resulted from the break-up of I_2F in the detector ionizer, hence a fraction of the I_2F signal has been subtracted from the IF signal, and the corrected angular distributions of IF are also shown.

These results indicate that reaction (1) does not proceed via a four-center mechanism, as shown by the energy schematic in figure 2. Such a mechanism is exoergic by more than 60 kcal/mole. If even a relatively small fraction of this energy appeared as product translation, the IF angular distributions would be much broader. Also, since the four-center reaction produces two identical molecules, the product distributions would have forward-backward symmetry in the center-of-mass coordinate system, and be roughly symmetric about the center-of-mass (C.M.) angle in the laboratory system under our experimental conditions. A preliminary analysis of the angular and velocity distributions of the IF product does suggest that at least at higher energies some of the IF is produced by decomposition of highly excited I_2F intermediate.

The sharply peaked I_2F angular distributions show only slight variation as the collision energy is increased by a factor of two. It is quite clear that the stable trihalogen is produced only within a narrow band of recoil velocities, that is, when the excess energy channeled into the translational motion of product molecules is such that internal excitation of I_2F is not sufficient to dissociate it into IF and I. From the observed threshold of 4 kcal/mole, and the dissociation

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energy of fluorine, 36.7 kcal/mole [7], a lower limit on the II-F bond energy of 33 kcal/mole is obtained.

Additional studies of molecular halogen reactions have also been carried out using ICl and HI in place of I_2. In both cases, similar reaction products were detected, that is, ClIF and HIF. The measured thresholds for the ICl and HI reactions to yield ClIF and HIF give lower limits on the I-F bond strength of 31 and 19 kcal/mole, respectively.

The important role played by stable radicals in promoting bimolecular chemical reactions such as $F_2 + I_2$ had not been suspected previously. The fact that a fluorine atom, which can initiate a chain reaction in F_2/I_2 mixtures, can be generated in a collision between F_2 and I_2 at a relative kinetic energy as low as 4 kcal/mole is intriguing. This is especially so considering that 37 kcal/mole is necessary to dissociate either F_2 or I_2. It is also interesting to note that a subsequent reaction,

$$F + I_2F \longrightarrow 2\ IF, \qquad (5)$$

is exoergic by 64 kcal/mole. The recently studied IF chemiluminesence from the gas phase reaction of I_2 with F_2 [8] may be exclusively due to reaction (5).

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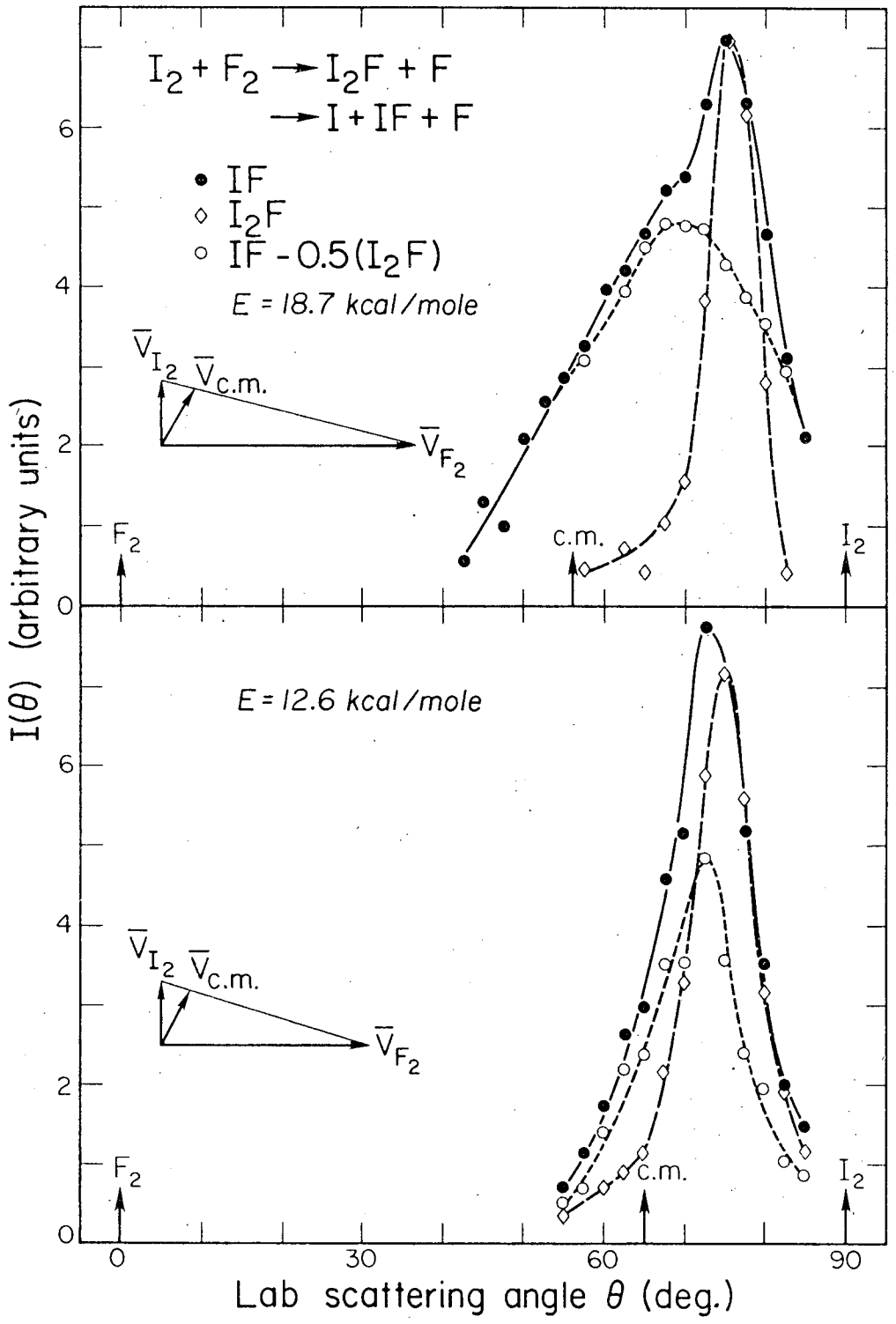
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FIGURE CAPTIONS

Figure 1. Angular distributions of reactively scattered I_2F and IF products formed from $F_2 + I_2$ at collision energies of 12.6 and 18.7 kcal/mole. The IF distribution (solid line) was obtained by subtraction of a fraction of the I_2F distribution (dot-dashed line) from the measured (dashed line) IF signal. The appropriate Newton diagrams are shown for each collision energy.

Figure 2. Schematic diagram of the reaction energetics for $F_2 + I_2$.



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Fig. 1

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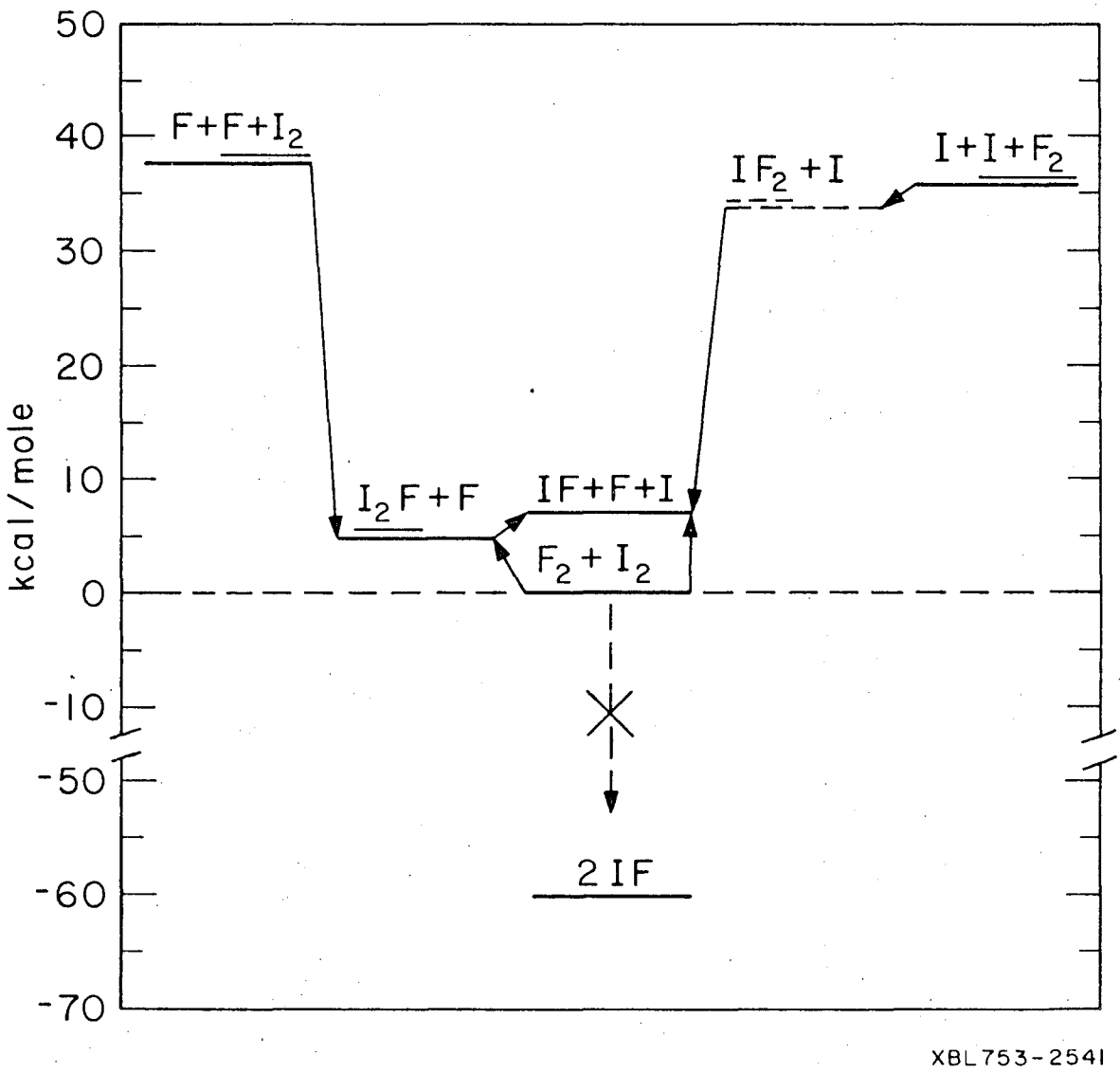


Fig. 2

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