MOLECULAR BEAM REACTION OF K ATOMS WITH SIDEWAYS ORIENTED CF$_3$I

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Reactive scattering is observed for K + CF$_3$I → KI + CF$_3$ where the CF$_3$I is oriented "sideways" with the I end pointing towards or away from the detector. Angular distributions are extremely broad and completely different from "heads" and "tails" orientations. Maximum signal corresponds to the "tails" orientation although reactivity of the two orientations is equivalent.

1. Introduction

Reactions of alkali metals have played a central role in the elucidation of the dynamics of chemical reactions [1–3], and many features of these reactions have been qualitatively correlated using "impulsive" or photodissociation models based on an electron transfer mechanism originally proposed by Polanyi and Magee [4]. According to this mechanism, an electron is transferred from the easily-ionized alkali metal to a species of high electron affinity, typically a halogen-containing molecule. The ultimate details of reaction, such as cross section, energy disposal, and angular distribution of products, depend on the stability of the nascent molecular ion.

This mechanism was invoked in a previous investigation of the reaction of K atoms with oriented CF$_3$I [5]. KI was found to be scattered forward in the center-of-mass (c.m.) system when the K atom attacked at the backside, or CF$_3$, end of the molecule ("tails" orientation), whereas the KI was scattered backward in the c.m. from the other, "heads", orientation. It was suggested that if the CF$_3$I" ion formed by electron transfer were in a repulsive electronic state, the ion would literally explode, sending the I$^-$ and CF$_3$ moieties along the instantaneous direction of the molecular axis. This predicted forward scattering for the "tails" orientation, and backward scattering for the "heads" orientation, and agreed semiquantitatively with experiment.

To test this hypothesis we have oriented the CF$_3$I molecules perpendicular to the relative velocity (i.e., "sideways"), so that the I end of the molecule can be directed towards or away from the detector, depending on the polarity of the applied electric field. This changes the view of the reaction as seen by the detector without changing the reaction dynamics. As expected, the angular distribution of scattered molecules is drastically changed. The result is in rough agreement with predictions of the electron-transfer model, but discrepancies still exist.

2. Experimental

Much of the apparatus and experimental method has been previously described [6,7]. Briefly, CF$_3$I expands from a nozzle in a separate cryopumped chamber, is collimated, modulated by a rotating chopper wheel, and then enters an inhomogeneous 6-pole electric field. This field selects molecules with $\langle \cos \theta \rangle < 0$, where $\theta$ is the average angle between the molecular dipole and the applied electric field. After state selection, the molecules enter a region of uniform electric field perpendicular to the nominal relative velocity (produced by parallel plates oriented 63° with respect to the CF$_3$I beam and perpendicular to the plane of the two beams). A small
transition field is required to ensure that molecules make adiabatic transitions into the uniform field.

In the uniform field, molecules are oriented about the electric field so that $\langle \cos \theta \rangle < 0$. Depending on the polarity of the field, the molecules are oriented perpendicular to the relative velocity with the I end towards the detector, "T", or away from the detector, "A". The K beam, formed by collimating an effusive beam, intersects the CF$_3$I beam in the uniform field, and the reactively scattered KI is detected in-plane by a differential surface ionization detector rotated about the scattering center by a stepping motor. The positive ions produced are measured by counting the output pulses from a Bendix crossed-field particle multiplier. The signal is the difference in counts between chopper open and chopper closed and is taken from both "T" and "A" orientations at a variety of scattering angles. A NOVA-2 computer with CAMAC interface is used to control the position of the detector and the polarity of the orienting field, and to record and reduce the data.

3. Results

The angular distribution of reactively scattered KI for a focusing voltage of 5 kV is shown in fig. 1 for the "T" and "A" orientations. These distributions are the difference between the signals on a W filament (detects K and KI) and the signal from a normalized Pt-W filament (detects K only). A small (10%) correction has been made to eliminate contributions from unoriented molecules that are transmitted when no high voltage is applied to the inhomogeneous 6-pole field. The "T" and "A" distributions are extremely broad, with fwhm$\approx 80^\circ$, compared to $\approx 45^\circ$ observed for the "heads" and "tails" orientations. Both the "T" and "A" distributions peak at essentially the same angle, which is in sharp contrast to the behavior observed for "heads" and "tails" where forward scattering was observed for the "tails" orientation and backward scattering was observed for the "heads" orientation. Higher voltages applied to the 6-pole field increase the reactively scattered signal because more molecules are transmitted, although the difference between the "T" and "A" distributions decreases because the extra molecules are more poorly oriented.

4. Discussion

We must emphasize that in both the "T" and "A" orientations, the molecule is oriented sideways with respect to the incoming atom so the reactive probability must be the same for both the "T" and "A" orientations. Any difference in experimental observation is a result of the detector having different views of the same process. Since a large difference is observed, a considerable correlation must exist between the scattered angle and the orientation. This rules out the formation of a long-lived collision complex (as does refs. [8,9]) and also provides evidence that substantial reorientation of the molecule does not occur during the collision.

The role played by orientation is complicated not only by the distribution of speeds in each beam and in the product, but also by the distribution of orientations. As a consequence, no attempt will be made to deconvolute the scattering data, but instead, it will be compared with the laboratory prediction of a simple "harpoon" model [10].

Alkali halides can best be described as ionic, $M^+X^-$, for bond distances near equilibrium, but since the molecule dissociates into neutral fragments, a covalent $M=X$ description is more appropriate at large distances. The zero-order potential curves must cross at distance
The crossing distance is a measure of reactivity and, through $E_v(X)$, offers a way of correlating reactivity with molecular properties. The dynamics of reaction will, however, depend on the exit valley interactions, and in particular, the properties of the molecular ion. Frequently, the ionic states are purely repulsive, or as expected [11] for CF$_3$I$, the equilibrium bond length is longer for the ion than the neutral, so that a vertical transition results in a purely repulsive configuration, which will dissociate in less than one vibrational period in a fashion resembling photo-dissociation [12]. As suggested earlier, such a repulsion would result in the instantaneous ejection of fragments along the direction of the molecular axis. If the direction of the molecular axis were changed, the angular distribution of reactively scattered product would also change.

The qualitative implications of this electron transfer dissociation model can be seen in fig. 2 where we show Newton diagrams for nominal beam speeds and orientations. The average dipole moment makes an angle with respect to the defining electric field (shown by an arrow in fig. 2) and precesses slowly around the field. The ensemble average distribution of dipoles describes a cone of half angle $\theta$, with the field as an axis. If the molecular ion dissociates in a time short compared to the rotation, the velocities of the I$^-$ and CF$_3$ fragments will lie along a generator of this cone. Since the recoil energy is rather high [8,9] and the detector measures in-plane scattering, the c.m. direction of KI is approximately that defined by the intersection of the precessional cone with the plane containing the two beams. The lab velocity of KI is then given by vector addition of the c.m. velocity and the velocity of the c.m.

The precessional cone cuts the plane in two places, and as shown in fig. 2, each orientation of the molecule is predicted to show two reactively scattered peaks, although some of these (shown by dotted lines) are in regions inaccessible to the detector. As observed, this predicts a single (detectable) peak in the backward direction for the "heads" orientation, and a single (detectable) peak in the forward direction for the "tails" orientation. This simple model predicts a drastic change for sideways orientation, but for the "towards" sideways orientation, two detectable (and resolvable) peaks are predicted, whereas only one is observed.

In an attempt to try to resolve the difference between this simple model and experiment, we have performed computer simulations which average over the range of beam speeds, recoil speeds, and orientations which could be expected. A typical result of this averaging is shown in fig. 3. It is clear that even after extensive averaging, two peaks persist in the "T" orientation, and two detectable peaks appear in the "A" orientation as well. But if we ignore for a moment the minimum in the simulated curves, we note that this very simple model accounts for the gross features of the scattering: "A" is less intense than "T"; the angular position and
Fig. 3. Laboratory angular distributions predicted by simple “harpoon” model for Boltzmann speed distributions peaking at 2.5 x 10^6 and 5 x 10^6 cm/s for CF_3I and K. Recombination speed distribution is that of ref. [9]; molecular orientation distribution is obtained by previously described [6] calculations. Solid line and dashed line denote “T” and “A” orientations, respectively.

breadth is roughly correct, and the “A” distribution might possibly be bimodal. No experimental evidence exists to suggest that the “T” distribution could be bimodal, however.

Different computational parameters affect the calculated angular distributions in different ways. As will be discussed in detail elsewhere, modification of the initial speeds slightly changes the shape of the angular distribution, but the minimum still persists. The minimum can be “filled in” only by drastically modifying the distribution of recoil speeds (to have a peak close to zero) or by modifying the distribution of orientations to have many nearly perfectly oriented molecules. The recoil speeds have been measured, and a low speed peak is not present [8,9]. The orientation distribution should peak for \( \theta \approx 90^\circ \), not the \( \theta \approx 180^\circ \) required. We are left to conclude that no reasonable choice of parameters removes the minimum in the calculated angular distribution.

Our inability to reproduce the experimental data suggests, of course, a defect in the model. (As will be discussed elsewhere, the computer simulation includes effects due to the perturbation of the I” trajectory by the K+ ion, precession of the molecule about the total angular momentum vector, and the effects of not having the electric field perpendicular to the relative velocity.) The model assumes that all orientations are equally reactive, that the molecule remains oriented in the laboratory during the approach of the atom, and that the molecular ion decomposes in a time much less than a rotation. The most questionable of these assumptions is that all the molecules remain oriented during approach of the incoming atom. The laboratory field (\( \approx 60 \text{ V/cm} \)) can be easily overcome by the field from the induced-dipole in the K atom and a small amount of reorientation might take place during the course of the collision. (Of course, for sufficiently small distances, one cannot even identify the molecule, let alone its orientation.)

This would have the same effect as twisting the applied field to be more parallel to the relative velocity and would tend to “fill-in” the minimum in the predicted curves. This reorientation would also tend to broaden the “heads” and “tails” peaks, and this is currently under investigation.

5. Summary

Reaction has been observed between K atoms and “sideways” oriented CF_3I molecules. Two different “sideways” orientations are observed: the I end of the molecule can be pointed either “towards” the detector or “away” from the detector. The reaction probability is identical for these two sideways orientations, but a considerable difference in scattering is observed. This is attributed to the detector having a different view of the reaction for the two cases. A simple “harpoon” model suggests that the differences are mainly a result of coordinate transformations and qualitatively accounts for the difference in the two orientations. Important unresolved differences between model and experiment still remain, however, and suggest that a small fraction of molecules may twist under attack of the incoming K atom.

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