Bimodal distribution of Bal vibrational states from the reaction \( \text{Ba} + \text{CF}_3\text{I} \)

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Unrelaxed vibrational state distributions of Bal product are reported for the reaction \( \text{Ba} + \text{CF}_3\text{I} \rightarrow \text{BaI} + \text{CF}_3 \), using laser-induced fluorescence. Product state distributions were measured using a beam-gas arrangement and a primitive angular distribution was also determined using a crossed-beam configuration. The Bal vibrational distribution is bimodal with a low vibrational component peaking at \( v \sim 27 \) and a high vibrational component peaking at \( v \sim 47 \). At least 75\% of the Bal is produced in the high vibrational levels. The angular distribution indicates that the Bal formed in the high vibrational states is scattered in a forward direction with respect to the Ba beam, but the low vibrational component is not sharply forward scattered. The \( \text{Ba} + \text{CF}_3\text{I} \) reaction is thought to proceed by two mechanisms: (1) attack in the direction of \( 1-\text{CF}_3 \), leading to Bal product formation with low vibrational energy; and (2) attack in the direction of \( \text{CF}_3-1 \), either by initial attack of the \( \text{CF}_3 \) end followed by migration or by attack of the \( 1 \) end at large impact parameters, leading to Bal product formation with high vibrational energy.

I. INTRODUCTION

Recently, it has become possible through various spectroscopic means to observe directly the internal state distributions of unrelaxed products formed in bimolecular collisions. In particular, the vibrational distribution has been found to decrease monotonically, described roughly by a temperature, or to show a population inversion, described by a smooth bell-shaped form. An important exception is the observation in infrared chemiluminescence studies of bimodal internal state distributions. Bimodal rotational distributions characterize the HCl arising from the reaction \( \text{H} + \text{SCl}_2 \rightarrow \text{HCl} + \text{S} \) and, at enhanced collisional energies, from the reaction \( \text{CI} + \text{HI} \rightarrow \text{HCl} + \text{I} \). Recently, vibrational bimodality has also been observed by Nazar, Polanyi, and Skrlac in the reaction \( \text{H} + \text{ICl} \rightarrow \text{HCl} + \text{I} \). They find that the HCl product has a bimodal energy distribution, with approximately 82\% of the HCl in high vibrational, high rotational levels, while 18\% is in low energy levels. Observation of bimodality suggests that more than one reaction mechanism is operative. Nazar et al. interpret their results to indicate that most of the reactive encounters are attack of the I end by the H atom followed by subsequent migration of H to the Cl end, while some encounters involve direct attack of the Cl end. This contention is supported by trajectory studies they have done, which indicate a strong preference for a collinear intermediate.

In this paper, we present results indicating a bimodal vibrational energy distribution in the Bal product from the reaction \( \text{Ba} + \text{CF}_3\text{I} \rightarrow \text{BaI} + \text{CF}_3 \).

This reaction is studied using the laser-induced fluorescence technique. Primary experiments are done with a beam–gas arrangement, but some primitive angular distribution studies of the Bal product are reported as well. Following a presentation of the data, the origin of the bimodal distribution is discussed.

II. EXPERIMENTAL

For the determination of the total internal state distribution, a beam–gas arrangement was employed, as described previously. An effusive barium beam enters the scattering chamber through a slit, where it is crossed by an uncollimated stream of \( \text{CF}_3\text{I} \) issuing from a 3 mm i. d. tube at room temperature. During experiments, the scattering chamber pressure is in the range \( 2-6 \times 10^{-5} \) torr and no appreciable pressure dependence of the Bal vibrational distribution is observed in this range, indicating no relaxation of the Bal. The Bal product is detected by measuring the excitation spectrum using the \( \text{C}^2\Pi_{u/2} \rightarrow \text{X}^2\Sigma^+ \) band system in the region 5290–5360 Å.

The angular dependence of the scattering is measured by mounting the barium and \( \text{CF}_3\text{I} \) beam sources on a rotatable lid and observing the fluorescence from a particular Bal band over a range of laboratory scattering angles \( \theta \) at a fixed distance (22 cm) from the scattering center. Figure 1 details the experimental arrangement, which is similar to that employed in previous angular scattering studies of \( \text{H} + \text{BrCl} \) except for the addition of improved liquid-nitrogen-cooled shielding. The angular range over which measurements can be made is \(-30^\circ < \theta < 65^\circ\), where \( \theta \) is measured from the Ba beam toward the \( \text{CF}_3\text{I} \) beam. The angular distribution of a particular Bal band is recorded at a range of angles as the difference in signal with the \( \text{CF}_3\text{I} \) beam on and off. During these angular distribution experiments, the scattering chamber pressure is \( 1-2 \times 10^{-4} \) torr, the upper range of single-collision conditions.

Commercial trifluoromethyl iodide (Columbia Organic
During experiments, the CF$_3$I vapor pressure characteristics to CF$_3$I but comparison was run from a reservoir at $-77^\circ$C, at which temperature I$_2$ has negligible vapor pressure. HI has similar vapor pressure characteristics to CF$_3$I but comparison of the Bal vibrational distribution of this work with that from Ba + HI$_2$ shows no feature attributable to any HI impurity.

III. RESULTS

Laser excitation of the $C^2\Pi_{1/2}-X^2\Sigma^+$ Bal band system in the region 5295-5360 Å is used to determine the internal state distribution of the reaction product. Figure 2 shows the variation of total fluorescence intensity with excitation wavelength for the Bal $\Delta v = v' - v = 0$ sequence. The bands are identified using the least squares fitting parameters given in Ref. 9. The bimodal nature of the Bal vibrational distribution is immediately apparent from the fluorescence spectrum; there is a low vibrational component peaking at $v \approx 27$ and a more intense high vibrational component peaking at $v \approx 47$. Contributions from the least intense $\Delta v = -1$ sequence (arising from the most intense bands in the low and high vibrational components) overlap and obscure the $\Delta v = 0$ spectrum in two regions, as indicated in the figure.

There is insufficient spectroscopic information available to accurately calculate the Franck-Condon factors for the Bal $C-X$ system. As in previous work, we assume that the Franck-Condon factor array is a delta function, $q_{\Delta v} = \delta_{\Delta v}$. This is known to be accurate for low vibrational levels; however, as $v$ increases, this assumption becomes progressively less valid. Using this approximation, we have obtained relative vibrational populations for the Bal product in the usual manner, estimating the population in the regions obscured by the $\Delta v = -1$ overlap. The delta function assumption will have the effect of underestimating the population of the high vibrational component relative to the low vibrational part since the Franck-Condon factors certainly become less than unity as $v$ increases. However, the general shape of the bimodal distribution is clear. The high vibrational component comprises $\geq 75\%$ of the total Bal product.

No BaF product from the reaction Ba + CF$_3$I could be detected even though this channel is energetically accessible. Nor were any bands observed in the region 4900-5600 Å that could be ascribed to BaIF or any other species. However, this is not evidence that BaIF is not formed as its electronic spectrum is unknown.

An attempt was also made to see if the two vibrational components of the BaI reaction product could be separated dynamically by their angular distributions using the crossed-beam arrangement of Fig. 1. The signal-to-noise ratio is much poorer in this case than for the alkaline earth—alkali halide exchange reactions of previous angular studies. This is in part because the reaction Ba + CF$_3$I is of smaller cross section and populates more product vibrational states. This allowed a primitive angular distribution to be obtained only for the high vibrational component of BaI product. The variation in fluorescence intensity of the Bal (47,47) band as a function of laboratory scattering angle is shown in Fig. 3, together with the Newton diagram constructed from the most probable reactant beam velocities. This distribution is seen to peak quite close to the Ba beam ($\theta \sim 5^\circ$). However, a measurement of the BaI beam profile under identical conditions (also shown in Fig. 3) indicates that the Ba beam peaks symmetrically about $\theta = 0^\circ$. Thus the Bal angular scattering distribution does not follow the Ba beam, and suggests that the BaI product formed in high vibrational levels scatters preferentially in a forward direction with respect to the center of mass.

A search for the Bal low vibrational component was unsuccessful, partly because the signal is a factor of 2
or 3 lower than for the high vibrational component. This would give an even more unfavorable signal-to-noise ratio. In addition, the low vibrational levels will be associated with higher recoil energies, making the scattering less confined. If the low vibrational component scattered forward with a similar distribution to the high vibrational one, the expected factor of 2 or 3 reduction in signal would still have allowed its observation. We thus conclude that the Bal produced in low vibrational levels is not sharply forward peaked. The increased translational energy available to the Bal products in low vibrational levels allows a wider range of angular scattering. However, without a direct measurement, we cannot know if the product is scattered backwards, sideways, or isotropically.

Because the only peak we found lies so close to the parent Ba beam, it could possibly arise from reaction of Ba with background CF₃I gas within the observation chamber. Were this the case, however, a clear Bal(v = 27) signal between 5° and 15° would have been observed. Its absence confirms our confidence in the Bal(v = 47) angular distribution. Clearly a better angular study needs to be done, but this was not possible with the present apparatus.

The energetics for Reaction (1) depend on a knowledge of the Bal dissociation energy. We adopt the value $D_{0}^{2}(\text{Bal}) = 74,6 \pm 2$ kcal mole⁻¹, which is based on the observation 13 of the chemiluminescent reaction

$$\text{Bal}^{*}(D_{0}^{2}) + I_{2} \rightarrow \text{Bal} + I \quad (2)$$

under beam conditions. This work corrects a previous value 14 which was based on the incorrect assumption that Reaction (2) involved ground state barium atoms. The production of barium metastables is pulsed on and off and the Bal* emission is observed as a function of elapsed time. From this simple time-of-flight measurement, the contribution of the reactant relative translational energy to the population of the highest $v'$ level observed in the Bal C ½ state is determined. 13 The resulting value of 74.6 ± 2 kcal mole⁻¹ for the Bal bond energy compares favorably with a recent mass spectrometric determination, $D_{0}^{2}(\text{Bal}) = 71 \pm 3$ kcal mole⁻¹. The bond energy of CF₃I has been determined 16 to be 53.5 kcal mole⁻¹. We estimate the sum of the initial relative kinetic energy of the reactants and the internal energy of CF₃I as 3 ± 1 kcal mole⁻¹. Thus the energy available to the products is calculated to be $\Delta E = 24.1 \pm 3$ kcal mole⁻¹. This is consistent with the energy necessary to populate the highest Bal vibrational level observed, $v = 56$, for which $E_{\text{vib}}(\text{Bal}) = 22.0$ kcal mole⁻¹. The maximum Bal$(v = 47)$ channel recoil energy is 5 ± 3 kcal mole⁻¹ derived from the above energetics; a recoil energy of 8 kcal mole⁻¹ does not place any angular constraints on the Bal$(v = 47)$ scattering inconsistent with the observed distribution. The peak of the Bal$(v = 47)$ angular distribution gives a minimum product translational energy of 5 kcal/mole. Giving due consideration to the uncertainties in the energetics, we estimate the internal energy of CF₃ product associated with the predominant, high $v$ Bal component of the reaction to be 0–3 kcal mole⁻¹. Clearly, most of the available energy in the reaction goes into vibrational motion of the newly formed Bal.

IV. DISCUSSION

The most striking feature of the Ba + CF₃I reaction dynamics is the internal energy distribution of the Bal products. Most Bal products are formed with high vibrational excitation peaking at $v \sim 47$, while some are with low vibrational excitation peaking at $v \sim 27$. Such a bimodal distribution has been observed previously for other reaction systems, 15 and the Ba + CF₃I reaction is conveniently discussed by comparing it with these other investigations. This leads us to propose a model to explain the observed reaction dynamics. We compare this model with the conclusions and interpretations of related experiments on K + CF₃I, Ba + CF₃I, +CH₃Cl, and Ba + CH₃I. The proposed model is then examined in terms of an election jump mechanism.

In their study of the bimodal HCI product internal distribution from H + ICI + HCI + I, Nazar et al. 4 assigned the major channel giving high vibrational excitation of the HCI to an initial attack by the hydrogen on the iodine end of the ICI molecule, followed first by migration to the chlorine end and then insertion into the ICI bond. This causes the departing HCI to be vibrationally excited, in contrast to the direct attack on the CI end which releases energy into product translation rather than internal excitation. These two distinct outcomes result from different paths across a single reaction potential energy surface and imply that initial approach of the H to the I end is more attractive than to the CI end, which may be associated with a small barrier.

Reasoning by analogy, we attribute the low vibrational component to "head-on" collisions in which Ba directly attacks the I end of CF₃I. 4, 15 To produce Bal with the release of energy largely into translation, and we attribute the high vibrational component to collisions in which Ba initially attacks the CF₃ end of CF₃I.
and then migrates to the I end to produce BaI with high vibrational excitation. Note that the direct attack is characterized by smaller impact parameters and hence a smaller cross section than the indirect attack. Further consideration suggests that the high vibrational component may also be formed by a glancing attack on the I end where the Ba atom passes near to I and then the BaI product continues much in the same direction as the Ba atom [Fig. 4(c)].

It is interesting to examine this model for the Ba + CF3I reaction in the light of previous experiments on K + CF3I and Ba + CF3I. Brooks18 studied the crossed-beam reaction of potassium atoms with CF3I molecules oriented by an electric hexapole field. He found that KI product is formed from reaction of K with either end of the CF3I molecule. However, the angular distribution of scattered KI from each configuration is different. The KI scattered from the low-impact-parameter direct attack on the I end is scattered backwards (rebound mechanism), whereas the KI formed from the initial attack of K on the CF3 end is scattered forwards. Nevertheless, the angular distribution for the reaction of K with unoriented CF3I shows substantial sideways peaking, which is not simply the superposition of scattering from the two orientations. These findings seem to support the reaction model shown in Fig. 4.

However, the analogy is not perfect. Rulis, Wilcomb, and Bernstein19 made a velocity analysis of the KI product from the reaction of K with unoriented CF3I. They determined that most of the KI formed is scattered into the backward hemisphere and has low recoil energy (~30% of the total energy available). Evidently the fraction of forward scattering is much larger for Ba + CF3I than K + CF3I. If a similar fraction of the available energy were released into translation for Ba + CF3I, the product recoil energy would be about 7.5 kcal mole-1. For the peak of our low vibrational component, 12.5 kcal mole-1 is available for product translation and CF3 internal excitation. Certainly, 5 kcal mole-1 is not an unreasonable amount of excitation for CF3 resulting from a rebound collision, although a higher product translational energy is possible. Thus the low vibrational component of BaI may be associated with reactive collisions of the type shown in Fig. 4(a) (rebound mechanism).

Lin, Mims, and Herm50 have studied the angular scattering distribution from the reaction Ba + CF3I using mass-spectrometric detection. In contrast to the other reactions of Ba with halomethanes in their study, the laboratory angular distribution of BaI from Ba + CF3I shows two peaks, leading the authors to suggest that there might be two competing reaction mechanisms. However, the laboratory angular scattering could also be accounted for by sideways peaking in the center-of-mass scattering distribution. Product velocity analysis would be required to distinguish these possibilities. Based on a nominal laboratory to center-of-mass transformation, they determine a mean product recoil energy of 9 kcal mole-1 (compared to our value of ~5.3 kcal mole-1 for the high v component of BaI) if only BaI product is formed. Because they observe a small BaF* as well as BaI* signal, Lin et al. suggest that the major reaction product is not BaI but rather BaIF, which would ionize in the detector to give predominantly BaI*, although some BaI might be produced in the reaction. The forward peak in their angular distribution may correspond to the forward-peak distribution for BaI (v = 47) given in Fig. 3. This would leave a second peak in the distribution of Lin et al. peaking symmetrically about the direction of the centroid vector. We have no positive information about the angular scattering of the low vibrational component of BaI product to exclude it as the centroid peak, although a large sideways peaked barycentric BaI velocity would be required to explain its nonobservation. It is likely that the peak at the centroid results from BaIF product. Indeed, this peak is of comparable magnitude to the forward peak in Ref. 20, whereas we find that the low vibrational component of BaI comprises only ~25% of the total scattering. This situation is similar to the finding in the reaction Ba + CH3I22 in that the cross-beam angular distribution might be mainly due to BaI2 scattering, in contrast to the laser-induced fluorescence observation of BaI as a product.

A striking contrast emerges between the BaI energy disposal for the reactions Ba + CF3I and Ba + CH3I. These two reactions have almost identical exoergicities, but the mean BaI vibrational energy in Ba + CF3I is 15.9 kcal mole-1 (432 ± 0.59 kcal mole-1), whereas for Ba + CH3I the value is 8.8 kcal mole-1 (351 ± 0.44). This additional vibrational energy arises from the high vibrational component of the BaI in Ba + CF3I. The low vibrational component from Ba + CF3I is only slightly shifted to higher vibrational levels than the BaI distribution in Ba + CH3I but is of similar form. The methyl end of CH3I is unlikely to present an attractive target for Ba attack or to promote glancing attack of the I atom (CF3 is more electronegative than CH3); thus, mainly direct attack on the iodine end will occur, populating lower BaI vibrational levels. This situation parallels the analogous reaction K + CH3I where 65% of the available energy goes into product translation,21 and studies with oriented CH3I52 show that reaction takes place predominantly at the iodine end.
There is, however, some evidence of bimodality in the BaI vibrational distribution from Ba + CH4I at higher levels \( n = 24 \), but the situation is by no means as clearly resolved as in Ba + CF3I.

The reaction \( \text{Ba} + \text{CX}_3\text{I} (X = \text{H}, \text{F}) \) may be viewed as proceeding by means of an electron jump from the cova lent \( \text{Ba} + \text{CX}_3\text{I} \) surface to the ionic \( \text{Ba}^+ + \text{CX}_3\text{I}^- \) surface. These surfaces will intersect at an internuclear separation

\[
R_0(\AA) = 14.47 \left[ I.P. (\text{Ba}) - E.A. (\text{CX}_3\text{I}) \right],
\]

where \( I.P. (\text{Ba}) \) is the ionization potential of Ba and \( E.A. (\text{CX}_3\text{I}) \) the vertical electron affinity of \( \text{CX}_3\text{I} \), both in eV. There is little information on the vertical electron affinities of \( \text{CX}_3\text{I} \). However, \( E.A. (\text{CH}_3\text{I}) \) is assumed to be negative or close to zero, but \( E.A. (\text{CF}_3\text{I}) \) is thought to be larger. Thus the electron jump will take at a larger distance for Ba + CF3I than for Ba + CH3I and reaction can take place at correspondingly larger impact parameters, favoring either of the two mechanisms shown in Figs. 4(b) and 4(c).

The electron in \( \text{CX}_3\text{I}^- \) is placed in an antibonding orbital centered on I, causing the molecule to decompose to \( \text{CX}_3 + \text{I}^- \). For the alkali reactions with \( \text{CX}_3\text{I} \), Herschbach\(^2\) has shown the repulsion in the \( \text{CX}_3\text{I}^- \) and subsequent recoil energies can be explained by comparison with the photodissociation dynamics of \( \text{CX}_3\text{I}^- \). Photofragment studies\(^2\) show that most of the energy released goes into recoil energy rather than \( \text{CX}_3\text{I}^- \) internal excitation. The decomposition of \( \text{CF}_3\text{I}^- \) into \( \text{CF}_3 + \text{I}^- \) rather than \( \text{CF}_4 + \text{F}^- \) may explain why BaF is not observed as a reaction product, although the reaction \( \text{Ba} + \text{CF}_3\text{I} \rightarrow \text{BaF} + \text{CF}_3 \) is exoergic by \(-18\) kcal mole\(^{-1}\).

Following the attack of the \( \text{CF}_3 \) site by Ba, we do not know whether the Ba atom, on migrating toward the I end, forms the BaI by insertion or by far-side attack (variation on glancing attack). The electron jump to \( \text{CF}_3\text{I}^- \) may facilitate the separation of the \( \text{CF}_3 \) and I moieties and hence assist insertion of the comparatively large Ba atom between \( \text{CF}_3 \) and I. This may result from charge migration\(^2\) in which one pictures the following sequence of steps for Ba attack along the \( \text{CF}_3^- \) direction:

\[
\begin{align*}
\text{Ba} + \text{CF}_3^- & \rightarrow \text{Ba}^+ + \text{CF}_3^- \rightarrow \\
& \rightarrow \text{CF}_3^*- \rightarrow \text{Ba}^- \rightarrow \text{I}^-. \\
& \rightarrow \text{CF}_3 + \text{Ba}^+ - \text{I}^-.
\end{align*}
\]

Essentially, the same model has been previously proposed by Polanyi\(^8\) to explain the forward-scattered KI in the reaction of K + CF3I. Unlike the case of an alkali atom, with a divalent alkaline earth atom stable dihalide formation is possible. Thus the formation of BaIF may result during insertion when a fluorine atom on \( \text{CF}_3 \) is close to the nascent BaI product before the BaI separates from the collision intermediate.

The complex behavior of this reaction and its investigation by many techniques present an opportunity to probe the details of reactive scattering. We may look forward to a better understanding of the dynamics as more knowledge of the product channels giving BaI and BaIF and their angular scattering and recoil energies becomes known. This will allow comparison with the other alkaline earth and alkyl halide reactions, particularly in terms of understanding the stereospecific role in reaction dynamics played by the orientation of reactants.

ACKNOWLEDGMENT

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