Bal product state distribution from the reaction Ba+CF₃I

M. A. Johnson, a) J. Allison, b) and R. N. Zare
Department of Chemistry, Stanford University, Stanford, California 94305

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Under single-collision beam-gas scattering conditions the Ba + CF₃I → Bal + CF₃ reaction has been studied using laser induced fluorescence to detect the Bal X ²Σ⁺ product. The resulting Bal C ²Π−X ²Σ⁺ excitation spectrum has a complex appearance owing to the similarity of the upper and lower state rotational constants, causing a reversal in band shading, and owing to a predissociation in the upper state, causing a break off in the fluorescence of high vibrational levels in each spin-orbit subband. From the predissociation onset an upper bound of 78.5 ± 0.5 kcal/mol is placed on the BaI bond energy. The vibrational population distribution is shown to be bell shaped, peaking near ν' = 50, and accounts for most of the available energy. The average energy appearing in Bal rotation decreases with increasing Bal vibrational excitation. The Bal rotational distribution has a width comparable to that of the vibrational distribution.

I. INTRODUCTION

Among the earliest crossed molecular beam studies of chemical reactions are those involving an alkali atom (typically K or Rb) with an alkyl iodide molecule (CH₃I or CF₃I). These investigations demonstrated that the alkyl iodide product recoiled predominantly backwards with respect to the alkali atom direction (in the center of mass frame) caused by considerable repulsive energy release during the reactive encounter. 1,2 These reactions are referred to as "impulsive" and are interpreted in the DIPR-DIP (direct interaction-product repulsion-dissociation as in photodissociation) model 3,4 as resulting in Gaussian-shaped recoil energy distributions. 5 Interest in this class of reactions has been further heightened by the ability to orient the CH₃I or CF₃I reagent and hence to explore the influence of approach geometry on the subsequent dynamics. 6-8 Such studies have shown a strong preference for reaction at the iodine end of the alkyl iodide reagent. The alkaline earth analogs of this class of reactions, typically those involving Ba, have also received much attention. Lin, Mims, and Herm 9 (LMH) studied product translational energy distributions and found similar trends as for the alkali atoms. To obtain complementary information on the internal state distribution, Dagdigian, Cruse, and Zare 10 used laser induced fluorescence (LIF) to detect the Bal product formed in the reactions

\[ \text{Ba} + \text{CH₃I} \rightarrow \text{Bal} + \text{CH₃} \]  

and

\[ \text{Ba} + \text{CH₃I} \rightarrow \text{Bal} + \text{CH₂I}. \]

They found that the Bal product vibrational distribution was inverted and approximately Gaussian in shape.

An outstanding exception to the picture that emerges for alkali and alkaline earth atom reactions with the alkyl iodides is the system

\[ \text{Ba} + \text{CF₃I} \rightarrow \text{Bal} + \text{CF₃} \]

in which evidence has been put forward that the Bal product is formed by two reaction pathways. In the crossed molecular beam study of LMH, 9 the Bal product angular distribution shows two distinct peaks, suggesting the possibility of competing reaction channels. Unfortunately, alternative explanations involving microscopic branching could not be ruled out and the "bimodal" product distribution could have arisen as an artifact of the laboratory to center-of-mass transformation. In 1977, Smith, Whitehead, and Zare (SWZ) examined this reaction using LIF detection and reported a bimodal vibrational distribution of the Bal product having two inverted distributions, one peaking at high \( ν(ν' = 50) \), the other at low \( ν(ν' = 20) \).

Polanyi and co-workers 12-14 have addressed the issue of bimodal distributions in reaction dynamics and they have shown that certain reactions are capable of following different trajectories over the potential surface resulting in bimodal or multimodal distributions of product internal energy states. An example of such a reaction is found in the \( ν, T , R \) distributions for the reaction

\[ \text{Cl} + \text{HI} \rightarrow \text{HCl}(ν, T , R) + \text{I}. \]

In this reaction it was postulated that the bimodality in the product energy distribution was due to a geometrical effect in which attack at the H end of the HI resulted in high vibrational excitation while attack at the I end gave lower vibrational excitation. Analogous examples have been reported by Breckenridge et al. 15 who found a clearly bimodal distribution of MgH product rotation:

\[ \text{Mg}(1^1P) + \text{H}_2 \rightarrow \text{MgH} + \text{H}. \]

The authors postulated that the high \( N \) distribution results from Mg atom insertion while the low \( N \) distribution results from end-on attack.

These considerations suggest the possibility of a relationship between reagent approach geometry and the internal state distribution, an area of active research. Interestingly, recent work by Munakata and Kasuya 16 on the bromine analog of reaction (3):

\[ \text{Ba} + \text{CF₃Br} \rightarrow \text{BalBr} + \text{CF₃} \]

also found evidence in the BalBr LIF spectrum for a bimodal vibrational distribution. In the latter work, the "low ν" mode
of the product energy is shown to increase with increasing reactant translational energy. Because of the importance of reaction (3) as a prototypical example of microscopic branching, and because of the experimental possibility of controlling the collision orientation and determining the product vibration-rotation energy disposal, Bernstein and Wilcomb\textsuperscript{5} published in 1977 a detailed analysis and comparison of the experimental results. These authors made the important observation that for the three reactions:

\[
\begin{align*}
\text{K} + \text{CH}_3\text{I} & \rightarrow \text{KI} + \text{CH}_3, \quad (7) \\
\text{K} + \text{CF}_3\text{I} & \rightarrow \text{KI} + \text{CF}_3, \quad (8) \\
\text{Ba} + \text{CH}_3\text{I} & \rightarrow \text{BaI} + \text{CH}_3, \quad (9)
\end{align*}
\]

and

\[
\text{Ba} + \text{CH}_3\text{I} \rightarrow \text{BaI} + \text{CH}_3,
\]

the total energy appearing as product translation was consistent with the DIPR-DIP type momentum transfer constraint as discussed by Herschbach\textsuperscript{6} and others.\textsuperscript{3} In this model, the impulse delivered to the separating MX and CF\textsubscript{3} mities is governed by the energy release in the X$^\rightarrow$CF\textsubscript{3} bond-breaking step of the harpoon mechanism postulated to control these reactions. Crudely speaking, for a given amount of energy released in this step, heavier alkyl substituents result in proportionally less translational energy release. This energy appears as internal excitation, and in the reaction series:

\[
\begin{align*}
\text{Ba} + \text{CH}_3\text{I} & \rightarrow \text{BaI} + \text{CH}_3, \\
\text{Ba} + \text{CH}_3\text{I} & \rightarrow \text{BaI} + \text{CH}_3, \\
\text{Ba} + \text{CH}_3\text{I} & \rightarrow \text{BaI} + \text{CH}_3,
\end{align*}
\]

the BaI LIF spectra reveal bell-shaped vibrational distributions peaking at $v' = 15, 40, \text{ and } 62$, respectively.\textsuperscript{10,17} Moreover, Bernstein and Wilcomb\textsuperscript{5} showed that the position and shape of the BaI vibrational distribution from Ba $+ \text{CH}_3\text{I}$ was consistent with the momentum transfer model where the BaI vibrational distribution is derived from the translational distribution via energy balance. The conclusion of their paper is that the conservation of linear momentum controls the overall energy disposal in these reactions, and that with the exception of the Ba $+ \text{CF}_3\text{I}$ reaction, this series of reactions is well-characterized both with respect to the vibrational and translational energy disposal.

Shortly after Bernstein and Wilcomb's\textsuperscript{5} study, we reexamined the evidence of SWZ for a bimodal vibrational distribution and concluded that uncontrolled saturation effects\textsuperscript{18} in LIF coupled with an undetected predissociation in the BaI C$^2\Pi_{1/2}$ state caused complexities in the spectrum which were misinterpreted as a bimodal vibrational distribution.\textsuperscript{19} In this paper, we present the detailed analysis of the LIF spectrum and show that the vibrational distribution is actually bell-shaped, in accord with other members of this reaction family. Based on higher resolution, we are also able to extract the gross form of the rotational distribution of the BaI product as a function of vibrational level. We suggest that the breadth in the rotational distribution is related to the breadth in the vibrational distribution assuming that the product recoil energy is constant.

### II. EXPERIMENTAL

The results presented in this paper were all taken under so-called "beam-gas" conditions, where barium atoms from an effusive oven source are collimated into a beam and allowed to impinge on a low pressure ($5 \times 10^{-4}$ Torr) of CF\textsubscript{3}I gas at room temperature. We estimate the average relative translational energy as $3 \pm 1$ kcal/mol. Metal atom ovens of four radically different designs and construction materials were used and found to give identical results over the range 1000–1250 K.\textsuperscript{17} The overall intensity of the LIF spectra varied greatly, but the appearance of the spectra was unchanged. Excitation spectra were taken with a modified "folded cavity" oscillator in a nitrogen-pumped dye laser having a resolution of 0.1 cm$^{-1}$, continuously tunable from 5280 to 5700 Å (Coumarin dye 540 A). At this resolution, all bandhead splittings (e.g., spin-rotation) were resolved, and their positions were measured by simultaneously recording an I$_2$ excitation spectrum\textsuperscript{20} with the BaI spectrum. The LIF was collected with f/3 optics and imaged unfiltered onto a Centronic 9283 photomultiplier tube. The spectra of the off-diagonal sequences were taken in an optically saturated regime to enhance signal to noise, while spectra used for population analysis were confirmed to be linear in laser power and photomultiplier/gated-integrator response. Spectra were obtained using a PAR 162 boxcar averager. The CF\textsubscript{3}I reagent was obtained from PCR Research Chemicals, Inc., and subjected to freeze–pump–thaw cycles for purification. It was found that no difference in the spectra ensued when unpurified CF\textsubscript{3}I was used directly from the bottle. Barium metal was obtained from Alpha Products and stored under oil. The oil was removed just prior to loading the oven by washing with ether.

### III. RESULTS AND DISCUSSION

#### A. Analysis of the Bal C–X spectra

As previously discussed, the excitation spectrum used by Smith, Whitehead, and Zare\textsuperscript{11} is displayed in Fig. 1, along with the BaI vibrational population distribution extracted by these authors. In a short comment,\textsuperscript{19} we have presented optical saturation data which showed that the "low $v'$" feature identified by SWZ was actually the $\Delta v = -1$ sequence of a high $v'$ distribution; therefore, the evidence for vibrationally bimodality in reaction (3) must be dismissed. In this section, the peculiarities of the BaI vibrational spectroscopy which ultimately lead to this misassignment are discussed. In Fig. 2, an entire scan over the BaI C$^2\Pi_{1/2}--X^2\Sigma^-$ band is presented where the region used by SWZ has been indicated by the dashed box. It is noteworthy that the detailed bandhead structure of the two spin-orbit subbands for BaI formed by the Ba $+ \text{CF}_3\text{I}$ reaction is drastically different. The vibrational sequences in the C$^2\Pi_{1/2}--X^2\Sigma^-$ band are quite regular, with an even spacing between bandheads, although there is a strong vibrational dependence to the head intensities for the two heads formed within each vibronic band. In the C$^2\Pi_{3/2}--X^2\Sigma^+$ subband, however, which was used for population analysis by SWZ, the bandhead structure is complicated and involves a loss of head structure around $v = 50$.\textsuperscript{19}
FIG. 1. Excitation spectrum and vibrational distributions of the BaI product resulting from the reaction Ba + CF3I → BaI + CF3, as reported by Smith, Whitehead, and Zare (Ref. 11). In the upper trace, the structure on the red side of the main sequence was incorrectly identified as the \( \Delta v = -1 \) sequence. This actually belongs to the \( \Delta v = 0 \) sequence. The spectrum resulting from the reaction BaI + CF3 is overlapped by bands resulting from the reaction Ba + CF3I → BaI + CF3. The old \( D_g^0 \) value of 102 kcal/mol would have implied that the \( C^2 \Pi \) state was still well below the energy of separated atoms at \( \nu = 54 \) and hence unable to interact with repulsive electronic states. The \( \Omega = 1/2 \) subband, on the other hand, lies 740 cm\(^{-1}\) below the \( \Omega = 3/2 \) state and can therefore support about six more vibrational levels before encountering these repulsive states at \( \nu \approx 69 \). In fact, we have investigated the onset of head-loss behavior for higher vibrational levels of the \( \Omega = 1/2 \) state and find similar behavior to the \( \Omega = 3/2 \) subband, this time at \( \nu \approx 77 \) (see Fig. 3). Once again, we see that the head structure is rapidly lost as the energy of the \( C^2 \Pi_{1/2} \) state nears the energy of the separated atoms.

In the normal rotational structure of a \( ^3 \Pi - ^2 \Sigma \) transition, this rapid change of head structure in only one subband is atypical. It will be shown that this behavior is caused by predissociation of the \( \Omega = 3/2 \) component of the BaI \( C^2 \Pi \) state.

At the time the SWZ work was undertaken, an erroneous value for the BaI bond dissociation energy, \( D_g^0 \) (BaI) = 102 kcal/mol, was accepted because the role of Ba metastables in the beam-gas chemiluminescence experiments \(^{21}\) had not been uncovered. \(^{22} \) The more correct value of \( D_g^0 \) (BaI) = 74.6 \( \pm \) 2 kcal/mol was used by SWZ for evaluation of the reaction energetics, but these authors failed to appreciate how this value affects the stability of the BaI \( C^2 \Pi \) state. In particular, excitation of the \( \Delta v = 0 \) sequence at \( \nu = 54 \) results in a total of approximately 75 kcal/mol in the BaI molecule, very close to the dissociation energy to ground state atoms. The old \( D_g^0 \) (BaI) value of 102 kcal/mol would have implied that the \( C^2 \Pi \) state was still well below the energy of separated atoms at \( \nu = 54 \) and hence unable to interact with repulsive electronic states. The \( \Omega = 1/2 \) subband, on the other hand, lies 740 cm\(^{-1}\) below the \( \Omega = 3/2 \) state and can therefore support about six more vibrational levels before encountering these repulsive states at \( \nu \approx 69 \). \(^{23} \) In fact, we have investigated the onset of head-loss behavior for higher vibrational levels of the \( \Omega = 1/2 \) state and find similar behavior to the \( \Omega = 3/2 \) subband, this time at \( \nu \approx 77 \) (see Fig. 3). Once again, we see that the head structure is rapidly lost as the energy of the \( C^2 \Pi_{1/2} \) state nears the energy of the separated atoms.

FIG. 2. BaI \( C^2 \Pi \rightarrow X^2 \Sigma^+ \) excitation spectrum obtained from the reaction Ba + CF3I → BaI + CF3 in this work. In this partially saturated spectrum, many \( \Delta \nu \neq 0 \) sequences are evident for both subbands. The spectrum isolated in the boxed area corresponds to the region analyzed by SWZ in Fig. 1.

FIG. 3. BaI \( C^2 \Pi \rightarrow X^2 \Sigma^+ \) excitation spectrum obtained from the reaction Ba + CH3I → BaI + CH3. The \( \nu \) numbering for the \( \Delta \nu \neq 0 \) sequences is uncertain, as is the assignment at high \( \nu \) in the \( \Delta \nu = 0 \) sequence. Uncertain assignments are shown in parentheses.
Aside from the head structure of the \( C^2\Pi_{1/2} \rightarrow X^2\Sigma^+ \) band, there is another interesting feature in the intensity profile. In all the vibrational sequences, vibrational levels in the range \( \nu = 67 \) to 72 are anomalously weak, where the excitation spectrum dips down and then increases in intensity above about \( \nu = 72 \). In the spectrum of both the \( \Omega = 1/2 \) and 3/2 components of the \( C^2\Pi \) state, the bandheads grow closer together and finally the intensity drops precipitously at a specific \( \nu' \).

To investigate further this high \( \nu \) behavior, we have taken extensive excitation spectra of the \( C^2\Pi_{3/2} \rightarrow X^2\Sigma^+ \) system, with representative spectra shown in Fig. 4. These spectra were taken at a resolution of \(-0.1 \text{ cm}^{-1}\), where the rotational contours of the vibronic sequences are clearly visible. Recall that in the branch structure of a \( ^2\Pi \rightarrow ^2\Sigma^+ \) system, generally three bandheads are formed—two which are closely spaced and are separated by the \( ^2\Sigma^+ \) state spin-rotation interaction energy \( |\gamma(N + 1/2)| \), and one isolated head which is formed at about three times the rotational quantum number as that of the double head.\(^{24}\) When \( B' \geq B'' \), the low \( J \) double head is formed by the \( Q_2 \) and \( P_{21} \) branch members while the high \( J \) single head is formed in the \( P_2 \) branch. When \( B' < B'' \), the low \( J \) double head is in the \( Q_{21} \) and \( R_2 \) branches while the high \( J \) single head is in the \( R_{21} \) branch. The heads forming the backbone of the \( \Omega = 3/2 \) subband are clearly seen to be doublets and are in fact lost near \( \nu = 50 \) and reappear shaded in the opposite direction above \( \nu' = 54 \). This behavior where the bandhead reverses in shading is caused by the relative magnitudes of the upper and lower state rotational constants. When \( B' > B'' \), no head is formed in the absence of centrifugal distortion. In fact, much of the \( \Omega = 3/2 \) spectrum in the region of \( \nu' = 48–55 \) is characterized by vibrational-level dependent rotational structure. Figures 5(a) and 5(b) present spectra of the \( \Delta \nu = +2 \) and \( \Delta \nu = -2 \) sequences at a resolution of about \( 1.0 \text{ cm}^{-1} \). Under high resolution \( \sim 0.1 \text{ cm}^{-1} \), it is seen that both isolated and spin-rotation-split bandheads appear and that their relative intensity changes markedly over a few vibrational levels. The brackets in Fig. 5 connect the low-\( J \), spin-rotation split head with its corresponding high-\( J \), isolated head. The sequences have a complex appearance because both the rotational distributions and the rotational band structure change rapidly with vibration.

The detailed explanation of the BaI \( C^2\Pi \rightarrow X^2\Sigma^+ \) band structure was not possible at the time of our first report\(^1\) of the Ba + CF\(_3\) reaction since there were no rotationally resolved spectra available nor were spectroscopic constants available for any of the BaI electronic states. This situation was improved when we analyzed the \( C-X \) (0,0) band using molecular beam techniques together with optical–optical double resonance.\(^{23,25}\) From these studies, we now have a complete set of rotational constants for the \( C \) and \( X \) vibrationless levels on which to build the bandhead analysis of the higher vibronic transitions. In this analysis, we have fixed the known spin-rotation splitting for the \( X \) state and lambda doubling for the \( C \) state at their \( \nu = 0 \) values. The constants \( B^* \) and \( D^* \) were allowed to vary with vibration. The vibrational dependence was modeled assuming a Morse potential for the \( X^2\Sigma^+ \) state. The \( B' \) and \( D' \) constants were determined from the measured bandhead splittings in the \( \Delta \nu = 0 \) and \( \Delta \nu = -1 \) sequences. These splittings are shown in Fig. 6 by brackets connecting the heads corresponding to a particular vibronic band. A minimum of two vibronic sequence bands are required for this analysis to obtain \( B' \) and \( D' \) uniquely. Table I presents a listing of the bandhead positions used in this analysis as well as for the \( \Omega = 3/2 \) bands.

The results of these fits are given in Fig. 7, which shows the vibrational dependence of the \( B' \) value for each \( C \) state component. This figure actually summarizes a great deal of information about the appearance of the BaI \( C-X \) spectrum since the relative disposition of the upper and lower state \( B \) constants determines the shading and splitting for all \((\nu', \nu'')\).
TABLE I. Bandhead positions (cm⁻¹) for the Bal $^2\Pi\rightarrow X^2\Sigma^+$ system.

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TABLE I. (continued).

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bands as well as indicates whether a head exists or not for a given $(\nu', \nu'')$ sequence member. As an example, the crossing of the $B'$ and $B''$ curves at approximately $\nu' = 15$ has not been recognized previously. It is now apparent that both subbands will have a headless region around $\nu = 15$ in the $\Delta\nu = 0$ sequence, with heads degraded to the red below $\nu = 15$ and to the blue above $\nu = 15$. This fact implies that previous vibrational assignments are actually incorrect since a simple counting of the "bumps" through the headless region results in skipping over vibrational levels. In the Bal...
C–X system, the spacing between the heads in the Δν = 0 sequences is nearly the same as the displacement of the head from the vibronic origin. Hence, previous assignments above ν = 15 in the Δν = 0 sequence must be increased by two vibrational quanta. This counting correction also applies to the head reversal in the Ω = 3/2 subband near ν′ = 52. High resolution spectroscopy was required to establish even the vibrational numbering for the C–X band system in this molecule. Interestingly, SWZ reexamined the BaI Δν = 0 excitation spectrum for the Ba + CHI3 reaction and argued for a possible bimodality in the vibrational distribution, where levels ν* = 0–40 are populated. The “bimodal” feature in this spectrum coincides with the vibrational levels around ν = 24—those levels where the heads are just reforming according to Fig. 7. Therefore this vibrational product distribution is also likely bell shaped. In this regard, it is important to bear in mind the subtleties of the underlying rotational structure of the vibrational spectra even if only a crude distribution of product vibrational energy is desired.

B. Evidence for predissociation in the Bal C state

We summarize here the evidence for identification of a perturbation in the C 2Π state as a predissociation rather than a simple formation of a vibrational head of heads.24 In Fig. 8 the rotational constant and vibrational origin spacing of the C state spin-orbit components are shown as a function of vibrational level. In both B(ν) and ΔG(ν) plots, a sharp drop-off occurs at approximately ν = 50, as expected when a potential curve is distorting rapidly at the outer wall. The observed spread of ν over which this drop-off occurs is, however, quite wide (about eight vibrational levels) indicating that the matrix element for the interaction must be large (200–500 cm⁻¹). Also, note that the nature of the perturbation is such that the Ω = 3/2 and Ω = 1/2 states are not equally perturbed. This indicates that ΔΩ = 0 crossings are favored, possibly implying a Hund’s case (c) coupling for these states at large internuclear distances. Note that the distortion of the potential in the Ω = 3/2 state accounts for the rapidly increasing Franck–Condon factor for the Δν ≠ 0 sequences with increasing vibration, and that the Ba + CF3I reaction produces a high level of vibrational excitation. The rapid change in the ΔG(ν) vs ν plot for the Ω = 3/2 component accounts for the compressed appearance of the heads at high ν in the Ω = 3/2 subband (see Fig. 2).

It remains to be determined whether the sharp falloff in the Δν = 0 spectrum at ν = 62 arises because of a vibrational head of heads or because of predissociation. To settle this point, we obtained BaI excitation spectra from the Ba + CHI₃→BaI + CHI₃ reaction which creates an even more highly excited vibrational distribution, ν = 50 to 80 (see Fig. 3). Spectra of the Δν = + 2 and Δν = 0 sequences of the Ω = 3/2 subband are presented in Fig. 9, which show no additional features arising from higher vibrational levels. Consequently we conclude that the drastic drop in fluorescence intensity results from a predissociation of the C 2Π state at ν ≈ 62 in the Ω = 3/2 component and at ν ≈ 78 in the Ω = 1/2 component (see Fig. 3).

Inspection of Fig. 3 shows a dip in the fluorescence intensity near ν′ ≈ 70 in the Ω = 1/2 subband for the Δν = 0,1,2 sequences. This occurs at the same region where the Ω = 3/2 component is completely predissociated. It is interesting to speculate that this effect may arise from interaction with the same repulsive states. If indeed the Ω = 3/2 and 1/2 components share a common perturber, then this suggests the perturbation is a repulsive 2Π state with an in-
C. Extraction of the Bal vibrational population distributions

The vibrational population analysis is based on the \( \Delta v = 0 \) sequence, recorded in a regime in which the intensity varies linearly with laser power. The \( \Omega = 1/2 \) subband is used for most \( v' \)'s since this component of the upper state is predissociated at \( v' \) levels not populated in the \( \text{Ba} + \text{CF}_3 \text{I} \) reaction. For the \( \Delta v = 0 \) sequence, the Franck–Condon factor is assumed to be essentially unity. The presence of the \( \text{BaI}^1P_{3/2}-1S_{0+} \) resonance line obscures the \( \Delta v = 0 \) sequence near \( v' = 47 \). Consequently for \( v' \leq 45 \) the \( \Omega = 3/2 \) subband is used. Because the relative intensities of the high \( J \) and low \( J \) heads vary with \( v' \), it is necessary to correct bandhead intensities for changing rotational distributions.

At a first glance (see Fig. 6) the \( \Delta v = -2 \) sequence appears to be very simple and isolated. A more detailed analysis shows, however, that the heads in this sequence result from a chance overlap of the bandheads among nearest vibronic members, so that this band is not suitable for population analysis. The \( \Delta v = +1 \) sequence (see Fig. 2) does not form a head at the rotational levels generated in the reaction and the \( \Delta v = +2 \) sequence forms well populated heads, but is badly overlapped by the \( \Delta v = -4 \) sequence of the \( \Omega = 3/2 \) subband. The \( \Delta v = -1 \) sequence of the \( \Omega = 1/2 \) subband is suitable for population analysis, but the effect of the vibration-dependent rotational bandhead structure is severe for this sequence (see Fig. 11) and had to be taken into account.

Our strategy is to use the bandhead intensities in the \( \Delta v = 0 \) and \( \Delta v = -1 \) sequences to establish the form of the rotational distributions and then to use these distributions to extract the vibrational distribution from the bandhead intensities in the \( \Delta v = 0 \) sequence.

To determine the vibrational dependence of the rotational distribution, the intensities of the high-\( J \) and low-\( J \) heads were fit by a convolution program simulating the \( \Delta v = 0 \) and \( \Delta v = -1 \) sequences for a given \( v' \) level. The rotational distribution was then adjusted to achieve reasonable agreement. The high-\( J \) head dominates the \( \Delta v = -1 \) spectrum for \( v' < 54 \), as shown in Fig. 11. A fit could be obtained with a Gaussian form for the \( J \) distribution:

\[
P(\nu,J) = (2J + 1) \exp\left\{- \frac{(F_J - F_\nu)^2}{\sigma_\nu^2}\right\},
\]

(10)

where \( F_J \) is the fraction of the total available energy appearing in rotation. The total energy available was taken as 12,000 cm\(^{-1}\). The parameters \( F_\nu \) and \( \sigma_\nu \) describe the vibrational dependence of the rotational distributions and were adjusted for each \( \nu \). \( F_\nu \) and \( \sigma_\nu \) were varied until the rotational distributions given by Eq. (10) give the observed ratio of bandhead intensities for the \( \Delta v = 0 \) and \( \Delta v = -1 \) sequences of the \( \text{C}^2\Pi_{3/2} - \text{X}^2\Sigma^+ \) subband. Two sequences are used in the fit since \( J \) values where the two main bandheads form in each vibronic branch (i.e., in the \( Q_{12} + P_{12} \) and \( P_{12} \) branches) vary strongly with vibrational sequence (see Table II). This procedure significantly constrains the form of the rotational distributions since four ranges of \( J \) are sampled from \( J = 140 \) to \( J = 370 \) using the two heads in two sequences. The values of \( F_\nu \) and \( \sigma_\nu \) which reproduce the
bandhead intensities are given by the following empirically determined formulas:

\[ F_v = 0.125 - 0.0085(v - 50) \] (11)

and

\[ \sigma_v = 0.46 - 0.01075v + 7.5 \times 10^{-5}v^2. \] (12)

Figure 12 displays the resulting rotational distributions for three vibrational levels, \( v'' = 40, 50, \) and 60. It is seen that increasing vibrational excitation of the product is correlated with decreasing rotational excitation. It is also apparent that the width of the rotational distribution increases proportionally to the most probable \( J \) value. These rotational distributions should be regarded as first-order estimates rather than a rigorous fit to contours. These distributions are introduced here primarily to correct the vibrational distributions for changes in the rotational distribution. In fact while the rotational distributions shown in Fig. 12 do reproduce the intensities of the bandheads, they systematically underestimate the population at low \( J \), away from the heads. Consequently, we are hesitant to make firmer conclusions about the rotational energy disposal. In particular, we are unable to rule out more complex rotational distributions such as bimodal ones.

The rotationally corrected vibrational distribution for the reaction \( \text{Ba} + \text{CF}_3I \rightarrow \text{Ba}^+ + \text{CF}_3 \) is shown in Fig. 13. It has the expected bell-shaped appearance seen previously for reactions of barium with alkyl halides, except the reaction \( \text{Ba} + \text{CF}_3\text{Br} \). Naaman\textsuperscript{27} has suggested that this remaining anomaly might be caused by unrecognized \( \text{CF}_3\text{Br} \) dimers in the seeded reactant beam used by Munakata and Kasuya.\textsuperscript{16} In Naaman's study of \( \text{Ba} + (\text{CF}_3\text{I})_2 \), the BaI product is formed in much lower vibrational states than the reaction with monomer. Under our conditions (ambient low-pressure \( \text{CF}_3\text{I} \) gas) the dimer concentration is negligible. Munakata and Kasuya have considered this possibility,\textsuperscript{28} and they consider the vibrational distribution.
argue against the presence of dimers based on mass spectrometric identification of their beam species.

In the light of these results, it is of interest to reexamine the circumstances that lead SWZ to conclude that the Ba + CF$_3$I reaction yielded a BaI bimodal vibrational distribution. The Ba + CF$_3$I reaction produces BaI with more vibrational excitation than had been previously seen in studies of Ba + HF$_2$ and Ba + CH$_3$I and CH$_3$I$_2$. Smith, Whitehead, and Zare were thus faced with a much bigger contribution to the LIF spectrum from the $\Delta v = -1$ sequence than occurs for a distribution peaking just ten vibrational levels lower (i.e., from Ba + CH$_3$I$_2$). The $\Delta v = -1$ spectrum overlaps the region in which the low-v portion of the $\Delta v = 0$ sequence would appear as an isolated feature. This accounts for the misassignment by SWZ of the $\Delta v = -1$ sequence as belonging to $\Delta v = 0$. It is worth emphasizing that in the present study the capability of resolving the spin-rotation doublet in the head structure was invaluable in producing unambiguous sequence assignments. Because the $J$ values at which the bandheads occur are strongly dependent on vibrational sequence, even in highly congested regions of the spectrum, the sequence identity of a given bandhead feature is readily established. In this way, we can conclusively state that the $\Delta v = -1$ feature of both subbands are not contaminated by low-v members of the $\Delta v = 0$ sequence.

Figure 14 displays a typical region in the $\Delta v = -1$ sequence at the C$^2\Pi_{1/2}$, X$^2\Sigma^+$ subband at a laser bandwidth of 0.1 cm$^{-1}$. The heads corresponding to the $\Delta v = 0$ sequence bands at low $v$ are easily distinguishable from $\Delta v = -1$ members at high $v$ since the spin-rotation splitting is much more pronounced for the $\Delta v = 0$ bands. Additionally, the high-$J$ heads are evident by their single-headed character. These results confirm our earlier suggestion that the $\Delta v = -1$ feature of both subbands are not contaminated by low-v members of the $\Delta v = 0$ sequence.

D. The Ba + CF$_3$I reaction dynamics

Until the Ba bond energy is more firmly established, we are unable to make quantitative statements on the energy partitioning for this reaction. Nevertheless, it is clear that the available energy $\Delta E$ for product excitation is in the range 24 $< \Delta E < 30$ kcal/mol. The peak in the vibrational distribution corresponds to $\sim 19.9$ kcal/mol, indicating the BaI vibrational excitation is the major channel for energy disposal. Note that the fits to the rotational distributions presented in Sec. III C required a total available energy of 34 kcal/mol, indicating that a significant portion of the rotational energy must arise from the collision energy. At the most probable product vibration, $v' = 50$, the most probable $J'$ value is about 270 (see Fig. 12) corresponding to a rotational energy of about 5 kcal/mol. Based on the DIPR-DIP model, the most probable translational energy is $\sim 5.7 \pm 2.3$ kcal/mol, which is comparable to the rotational energy. Hence the sum of the energy in product translation, BaI vibration and BaI rotation seems to account for nearly all available energy, suggesting that the CF$_3$ product has little internal energy. Geometrical arguments support this inference since the structure of CF$_3$ is pyramidal and the electron-jump reaction mechanism is not expected to exert a torque on the departing CF$_3$ fragment.

Conservation of angular momentum implies that the BaI rotation arises from the orbital angular momentum of the reagents. Furthermore, the width of the rotational distribution ($\sim 5.4$ kcal/mol) closely matches the width of the vibrational distribution ($\sim 5.1$ kcal/mol). This last observation, combined with a model where the product recoil energy is assumed constant, suggests that the width of the BaI vibrational distribution may be a consequence of the dynamics of the Ba + CF$_3$I reaction, i.e., the reaction probability as a function of translational energy and impact parameter. This picture should be contrasted with the model where the width is assumed to mirror only the photodissociation recoil distribution. If BaI rotation plays an important role in determining the BaI vibrational distribution, then experiments with velocity selected reagents are necessary to elucidate more deeply the reaction dynamics.

ACKNOWLEDGMENTS

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Johnson, Allison, and Zare: Ba + CF, reaction dynamics

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28. T. Munakata and T. Kasuya (private communication).
31. This estimate is based on the relation \( E_{\text{com}} (\text{Bal}) = \frac{P^2(\text{Bal})}{2\mu(\text{Bal}, \text{CF}_3)} \), where \( P(\text{Bal}) \) is the center of mass momentum and \( \mu(\text{Bal}, \text{CF}_3) \) is the reduced mass of Bal and CF, (see Ref. 5). In the DIPR-DIP, \( P(\text{Bal}) = P(KI) \) from the reaction \( K + \text{CF}_3 \rightarrow KI + \text{CF}_3 \) and \( P(KI) \) is taken from Ref. 5 to be 12.9 \( \text{A} \, \text{amu}^{-1} \). The error estimate represents the spread in C-I' energy release for the reactions Bal + CH, I and K + CH, I.