Photodissociation dynamics of CF₃Br at 234 nm: An implication of symmetry reduction during photodissociation

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The photodissociation dynamics of CF₃Br in the A-band has been investigated utilizing a two-dimensional photofragment ion-imaging technique coupled with a state-selective resonance-enhanced multiphoton ionization scheme. The total translational energy distributions for the Br(2P₃/2) and Br⁺(2P₁/₂) channels are well characterized by Gaussian functions with average translational energies of 183 and 151 kJ/mol, respectively. The recoil anisotropies were measured to be β=0.66 for Br and 1.83 for Br⁺. It was found that Br⁺ production is preferred, with a relative quantum yield of 0.80. The reduction in the recoil anisotropy for Br results from nonadiabatic coupling between the 1Q₁ and 3Q₀ states. The fraction of molecules that dissociate via a distorted pathway induced by symmetry reduction from C₃ᵥ to Cᵥ is estimated to be 0.11.

I. INTRODUCTION

The photodissociation of a range of methyl halides (CX₃Y; X=H,D,F; Y=Br,I) in the UV region has been extensively studied because the behavior of these molecules can be used as a prototype for depicting numerous types of photodissociations in a variety of polyatomic molecules.¹–⁶ The diffuse absorption bands observed in the UV spectra of methyl halides are denoted as A-bands, and the photon absorption that gives rise to these bands stems from the promotion of a lone-pair electron on the Y atom into the antibonding σ* orbital localized on the C-Y bond. Hence, A-band absorption leads to bond-selective fission of the relatively weak C-Y bond in a direct/impulsive manner.⁷ The strong spin-orbit coupling energy of the heavy Y atom gives rise to two distinguishable reaction product channels:

\[
\text{CX₃Y} + hν \rightarrow \text{CX₃} + \text{Y}(2P₃/2),
\]

\[
\text{CX₃Y} + hν \rightarrow \text{CX₃} + \text{Y}⁺(2P₁/₂).
\]

Three repulsive electronic-excited states have been predicted to contribute to the A-band absorption, which have been identified as 3Q₁, 3Q₀, and 1Q₁ states in Mulliken’s notation, by analogy with the electronic structures of hydrogen halides.⁸,⁹ Of these three states, only the 3Q₀ state is correlated with the spin-orbit excited state Y⁺, and the corresponding transition dipole moment is aligned parallel to the C-Y bond. The other states are correlated with the spin-orbit ground state Y, and the corresponding transitions to these states are polarized perpendicular to the bond axis. The relative contributions of the three excited states to the absorption in the A-bands of methyl halides have been resolved by magnetic circular dichroism (MCD).¹⁰,¹¹

Many experimental¹²–¹⁷ and theoretical¹⁸–²²,²⁴ studies have investigated the photodissociation of CH₃I. A noteworthy conclusion drawn in these studies is that nonadiabatic dynamics plays an important role in the photodissociation process. The A-band absorption of CH₃I is centered near 260 nm, and the parallel 3Q₀–X transition carries most (~95%) of the oscillator strength at the absorption peak.¹⁰,¹¹ Although it would be expected that the initial transition exclusively to the 3Q₀ state should result in the I⁺ product channel adiabatically, a considerable amount of I has been detected.¹⁷ The 3Q₀ and 1Q₁ states correspond to the 2A₁ and 3E states in C₃ᵥ symmetry with a large spin-orbit interaction, and the difference in symmetry between the two states disallows an interaction in an adiabatic approximation. However, a distortion of the molecule to Cᵥ symmetry evolving from a bending vibration mode induces the 3E state to split into A’ and A” states, and causes the 2A₁ state to be reduced to the A’ state, as is displayed in Fig. 1. The coupling between the A’ states, which can be explained by the radial derivative terms in the Hamiltonian, causes an avoided crossing. This avoided crossing is enhanced by symmetry-lowering vibrational motions. The production of I is therefore attributed to the coupling of the 1Q₁ and the 3Q₀ states, which is induced by the reduction of the molecular symmetry from C₃ᵥ to Cᵥ during the photodissociation process.⁴,⁷

In comparison with the methyl iodides, the photodissociation dynamics of methyl bromides has received less attention, even though their study provides an opportunity to unravel the effects due to differences in mass and spin-orbit coupling energy. The A-band absorption spectrum of CH₃Br is blueshifted compared with that of CH₃I, and is centered near 200 nm.²⁸,²⁹ An MCD study has shown that in CH₃Br the intensity due to the 3Q₀ state is reduced, whereas that due to the 3Q₁ state is enhanced.¹⁰,¹¹ A study of CH₃Br and CD₃Br at 222 nm, employing a photofragment ion-imaging technique, which reported wavelength and channel-dependent angular distributions, has provided strong evidence for the photodissociation dynamics of CH₃Br. In the case of CF₃Br, however, many theoretical studies have not been performed, and have been restricted to the photodissociation dynamics of CF₃I.¹⁰,¹¹

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evidence for the importance of non-adiabatic transitions in the photodissociation dynamics of CH3Br as was found in the case of CH3I photodissociation.23

Unraveling the photodissociation dynamics of CF3Br is of importance because comparison of the results for CF3Br with those for CH3Br and CH3I provides physical and chemical insight into the electronic and mass effects caused by the substitution of H atoms with highly electronegative F atoms, and the effects due to the substitution of I with Br. A small number of experiments have investigated the photodissociation of CF3Br at 193 nm, the blue-edge of the A-band.30–32 The relative quantum yield of Br* at 193 nm was measured to be 0.56±0.0530 and 0.66±0.07.31 The angular distribution of the nascent Br* showed a mixture of the characteristics of parallel and perpendicular transitions with a ratio of 1.3:1, whereas the distribution of Br was featured by a purely parallel transition.32 From the measured recoil anisotropies and relative quantum yields, it has been proposed that at 193 nm roughly two-thirds of the molecules dissociate via a distorted geometry in which the C3v molecular symmetry is reduced to C1v through the effect of e-type bending vibrations.32

In the present study we investigate the photodissociation dynamics of CF3Br at 234 nm, the wavelength at which curve-crossing is expected to have a substantial effect. A photofragment ion-imaging technique was utilized to obtain the spatial distributions of the nascent bromine atoms. To achieve state-selective detection of Br and Br*, a [2+1] resonance-enhanced multiphoton ionization (REMPI) scheme was employed. Translational energy distributions, recoil anisotropies, and relative quantum yields were measured, and they are used to depict the photodissociation dynamics of CF3Br in the A-band. The experimental findings in this work elucidate the role of nonadiabatic curve-crossing in the photodissociation process following A-band excitation.

II. EXPERIMENT

The details of the experimental setup employed in this work have been described elsewhere.33 In brief, the ion-imaging spectrometer consisted of a molecular-beam source and a main chamber. The main chamber was composed of an electrostatic lens,34 a time-of-flight (TOF) tube, and a detection system. A pulsed valve (General valve, Series 9) with an 800 mm diameter orifice operated synchronously with the laser pulses, typically at 10 Hz. A supersonic molecular beam was skinned through a conical copper skimmer mounted 20 mm downstream from the nozzle. The skimmer divided the main chamber from the source chamber. The molecular beam was then collimated by a pinhole with an orifice of diameter 1 mm. The molecular beam perpendicularly intersected the laser beam, and photolysis of the sample occurred in the intersecting region.

The nascent bromine atoms were ionized in the main chamber. The resultant ion clouds were accelerated and focused by an electrostatic lens onto a position-sensitive detector, which was composed of a microchannel plate, a phosphor screen (Galileo, FM3040), an image intensifier (Stanford Computer Optic), and a charge-coupled device (CCD) camera (Photometric, CH250). A negative pulse was applied to trigger the image intensifier in order to distinguish the signals corresponding to ions with specific masses from those stemming from background noise and scattered light. The laser was scanned over a range of ±0.4 cm−1 to cover all ion velocity components. During the laser scan, over 100 000 shots were transferred from the CCD camera to a personal computer where they were integrated to construct an image. To acquire the REMPI TOF spectra, a photomultiplier tube (Hamamatsu, 1P21) and a digital oscilloscope (Lecroy 9310) were used in stead of the image intensifier and CCD camera. To minimize the noise due to nonresonant ionization of the fragments, images and spectra collected at off-resonance wavelengths under the same conditions were subtracted from those obtained at the resonance wavelengths.

The 355 nm output of a Nd:YAG laser (Spectra Physics, GCR-170) was used to pump a dye laser (Lumonics, HD-500), and the VIS output of the dye laser was frequency-doubled by a BBO crystal. The linearly polarized UV laser beam was vertically aligned using a half-wave retardation plate. The resulting laser beam was then focused onto the molecular beam by a lens with a focal length of 150 mm. CF3Br was photolyzed and the nascent bromine atoms were ionized within a single laser pulse. To achieve the state-selective ionization of Br+[2p3/2] and Br*[2p1/2], [2+1] REMPI at 233.69 nm via 6p 3P1/2 → 5p 3P3/2 1/2 intermediate state, and at 234.03 nm via 6p 4D3/2 1/2, were utilized, respectively.35,36 CF3Br (PCR, 99.9%) was used without further purification. Optimal expansion cooling was realized by seeding ca 20 Torr of CF3Br in He at a stagnation pressure of ca. 1500 Torr.

III. RESULTS AND ANALYSIS

The raw images of Br and Br* are displayed in Figs. 2(a) and 2(b), respectively. The polarization vectors of the laser beams were vertically aligned in both cases. Both images
have polar caps, implying that an electronic transition with dipole moment parallel to the recoil axis (C-Br) provides the main contribution to the generation of Br and Br*. The more distinct structure in the raw image of Br* in comparison to that of Br indicates a higher anisotropy in the angular distribution of Br*.

An angular distribution can be characterized by an anisotropy parameter $\beta$, which is obtained from the standard formula:

$$P(\theta) = 1 + \beta P_2(\cos \theta),$$  \hspace{1cm} (3)$$

where $P(\theta)$ and $P_2(\cos \theta)$ are the angular distribution of fragments and the second order Legendre polynomial, respectively. The parameter $\theta$ represents the angle between the laser polarization axis and the recoil velocities of fragments. Each raw image represents a two-dimensional projection of the three-dimensional spatial distribution of the fragments, which is cylindrically symmetric along the laser polarization axis. Therefore, the original spatial (angular and speed) distribution of the fragments can be reconstructed through an inverse Abel transformation. $P(\theta)$ was extracted by integrating the reconstructed speed distribution over an appropriate range of speed at each angle. The anisotropy parameter $\beta$ is estimated by fitting $P(\theta)$ with the standard formula given in Eq. (3). The angular distributions of Br and Br* are plotted in Fig. 3 along with the relevant curve-fits. Anisotropy parameters of $\beta=0.66\pm0.05$ for Br and $1.83\pm0.05$ for Br* were calculated from the fitted curves.

The speed distribution of bromine fragments, $P(v)$, was extracted by integrating the reconstructed three-dimensional speed distribution over all angles at each speed. $P(v)$ can be converted into the total center-of-mass translational energy distribution using the relationship:

$$P(E) = P(v) \frac{dv}{dE},$$  \hspace{1cm} (4)$$

$$E_T = \frac{1}{2}(m_{Br} + m_{CF_3}) \frac{m_{Br}}{m_{CF_3}} v_{Br}^2,$$  \hspace{1cm} (5)$$

where $P(E)$, $E_T$, $m_X$, and $v_{Br}$ denote the total translational energy distribution, the total energy, the mass of $X$ ($X=Br$, $CF_3$), and the velocity of the bromine fragments, respectively. The total translational energy distributions for the Br and Br* channels are illustrated in Fig. 4. Each distribution can be modeled by a narrow single-peaked Gaussian curve, which coincides well with the prompt/impulsive fission of the C-Br bond after UV absorption. Using the data in Fig. 4,
the average translational energies were calculated to be $\langle E_T \rangle = 183$ kJ/mol for Br and 151 kJ/mol for Br*. The available energy for the dissociation process was calculated using:

$$E_{av} = E_{hv} - D_0 - E_e + E_{int},$$

$$f_T = \frac{\langle E_T \rangle}{E_{av}},$$

where $E_{av}$, $E_{hv}$, $D_0$, $E_e$, and $E_{int}$ indicate the available energy, the photon energy, the bond dissociation energy of C-Br, the electronic energy of the bromine atom, and the internal energy of the parent molecules in the supersonic molecular beam. A bond dissociation energy of $D_0 = 287$ kJ/mol was adopted from Ref. 39, and $E_e$ is 0 kJ/mol for Br and 44.1 kJ/mol for Br*. Using these values, the fractions were calculated to be $f_T = 0.81$ for Br and 0.84 for Br*.

The relative quantum yields of Br and Br* were extracted from the relative signal intensities of Br and Br* in the REMPI TOF spectra:

$$\frac{N_{Br*}}{N_{Br}} = k \frac{I_{Br*}}{I_{Br}},$$

where $N_X$ and $I_X$ ($X=Br$, Br*) are the number and signal intensity of X, respectively. The parameter $k$ is a factor related with the experimental setup and the relative REMPI intensities. A value of $k = 0.26$ was obtained for the experimental conditions used in this study. Therefore, the measured intensity ratio of 15.40 gives $N_{Br*}/N_{Br} = 4.00$, resulting in relative quantum yields of $\Phi_{Br} = 0.20 \pm 0.05$ and $\Phi_{Br*} = 0.80 \pm 0.05$ which favor Br*.

### IV. DISCUSSION

The calculated anisotropy parameters, $\beta = 0.66 \pm 0.05$ for Br and of $\beta = 1.83 \pm 0.05$ for Br*, imply that both dissociation channels originate mainly from electronic transitions that are polarized parallel to the C-Br bond. The potential-energy surfaces of CF$_3$Br can be inferred from those of CH$_3$Br. The structural similarity of the two molecules leads us to expect the molecules to have similar potential-energy surfaces pertinent to the A-band absorption in the UV region, except for slight differences in the oscillator strengths and in the energy levels of the individual states. The A-band absorption of CH$_3$Br was predicted by Mulliken$^8,9$ to stem from an $\sigma^* \rightarrow \pi$ type of electronic transition. In Mulliken’s notation, the three optically accessible states of CH$_3$Br are denoted $^1Q_1, ^3Q_0$, and $^3Q_1$, in descending order of energy. The $^1Q_1$ and $^3Q_1$ states are responsible for the electronic transitions aligned perpendicular to the C-Br bond and correlate with the channel for Br formation, whereas the $^3Q_0 \rightarrow X$ transition is polarized parallel to the bond and correlates with the Br* channel.$^{40}$ In the case of a molecule of $C_{3v}$ symmetry, in which large spin-orbit interactions are involved, the $^1Q_1$, $^3Q_0$, and $^3Q_1$ states correspond to the $3E$, $2A_1$, and $2E$ states, respectively.$^{41}$ The $^1Q_1$ and $^3Q_0$ states can cross to form a conical intersection. As a consequence, A-band excitation leads to Br production via three pathways ($^1Q_1$, $^3Q_0$, and a transition from $^3Q_0$ to $^1Q_1$), and to Br* production via two pathways ($^3Q_0$ and a transition from $^1Q_1$ to $^3Q_0$). All possible pathways are listed in Table I.

The relative fractions of the individual pathways can be determined from the relative quantum yields and recoil anisotropies using the following relationships:

$$\left[ \begin{array}{c} \beta_a \\ \beta_b \end{array} \right] = \begin{pmatrix} c_{a1} & c_{a2} \\ c_{b1} & c_{b2} \end{pmatrix} \begin{pmatrix} \beta_{1a}^{\text{eff}} \\ \beta_{1b}^{\text{eff}} \end{pmatrix},$$

### TABLE I. Possible pathways for Br and Br* production via the A-band dissociation.

<table>
<thead>
<tr>
<th>Product</th>
<th>Pathways</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>without curve-crossing</td>
</tr>
<tr>
<td>$^1Q_1$, $^3Q_1$</td>
<td>$^1Q_1 \rightarrow ^3Q_0$</td>
</tr>
<tr>
<td>Br*</td>
<td>$^3Q_0$</td>
</tr>
</tbody>
</table>

$\Phi_{Br} = \frac{N_{Br}}{N_{Br} + N_{Br*}} = \frac{1}{1 + \frac{N_{Br*}}{N_{Br}}}$

$$\Phi_{Br*} = 1 - \Phi_{Br},$$

where $N_X$ and $I_X$ ($X=Br$, Br*) are the number and signal intensity of X, respectively. The parameter $k$ is a factor related with the experimental setup and the relative REMPI intensities. A value of $k = 0.26$ was obtained for the experimental conditions used in this study. Therefore, the measured intensity ratio of 15.40 gives $N_{Br*}/N_{Br} = 4.00$, resulting in relative quantum yields of $\Phi_{Br} = 0.20 \pm 0.05$ and $\Phi_{Br*} = 0.80 \pm 0.05$ which favor Br*.
where $\beta$, $c$, $f$, and $\Phi$ represent the recoil anisotropy parameter, the fraction of the component stemming from either a parallel or perpendicular transition, the fraction of an individual pathway, and the relative quantum yield, respectively. Subscripts $a$ and $b$ denote Br and Br*, and 1 and 2 stand for the parallel and perpendicular transitions. X, Y, and Z indicate the $^1Q_1$, $^3Q_0$, and $^3Q_1$ states, respectively. The calculation as it stands is too complicated to be solved, and must therefore be simplified. The replacement of three H atoms with highly electronegative F atoms causes the UV spectrum of CF$_3$Br to be slightly blueshifted compared to that of CH$_3$Br.$^{15}$ Given that even in CH$_3$Br the contribution of the $^1Q_1$ state to the initial excitation is expected to be only minor at 234 nm, it is reasonable to assume that for CF$_3$Br the contribution of the $^1Q_1$ state can be neglected at this wavelength. This simplification gives $f_X = f_Y = 0$ which, along with the relative quantum yields of $\Phi_a = 0.20$ and $\Phi_b = 0.80$, leads to:

$$
\begin{pmatrix}
0.20 c_{a1} & 0.20 c_{a2} \\
0.80 c_{b1} & 0.80 c_{b2}
\end{pmatrix}
= 
\begin{pmatrix}
f_{X-Y} & f_X + f_Z \\
f_Y & f_{Y-X}
\end{pmatrix},
$$

These equalities imply that at 234 nm Br* arises only from the curve-crossing between the $^1Q_1$ and $^3Q_0$ states following the initial parallel transition to the $^3Q_0$ state. Therefore, the value of $\beta = 1.83$ for Br* must represent a limiting value for the pertinent parallel transition to the $^3Q_0$ state. The translational anisotropy parameter $\beta$ is determined by the dissociation lifetime and the angle between the recoil axis and the transition-dipole moment,

$$
\beta = 2 P_2(\cos \chi)f(\omega, \tau),
$$

where $\omega \approx (\pi kT/2I)^{1/2}$ is the angular velocity of the parent molecule, $I$ is the moment of inertia, and $\chi$ is the angle between the recoil axis and the direction of the transition dipole for the final state.$^{42}$ For the pseudo-diatomic CF$_3$Br, the transition dipole moment for the $^3Q_0$ state is parallel to C-Br, i.e., $\chi = 0$. The limit of the anisotropy is thus determined only by the lifetime $\tau$. As a result, $\beta_{1 \text{eff}} = 1.83$ was chosen for the analysis. On the same account, $\beta_{2 \text{eff}} = -0.92$ was selected. The values determined for the relevant variables are listed in Table II. For comparison, the results at 193 nm were reanalyzed using $\beta_{1 \text{eff}} = 1.83$ and $\beta_{2 \text{eff}} = -0.92$. The contribution of the $^3Q_1$ state to the initial transition was ignored in the analysis at 193 nm, following the discussion in Ref. 32.

The results for 234 and 193 nm photolyses are illustrated in Fig. 5. Using the values given above, the curve-crossing probabilities can be extracted,

$$
P_{\text{up}} = \frac{f_{X-Y}}{f_{Y} + f_{X-Y}},
$$

FIG. 5. Schematic diagrams for the photodissociations of CF$_3$Br (a) at 234 nm (this work) and (b) at 193 nm (Ref. 31). Numbers in italic represent the components produced via the initial excitation to $^3Q_0$ surface. Numbers in parentheses indicate the components produced via the curve-crossing between the $^1Q_1$ and $^3Q_0$ states.
photodissociation of CF$_3$ Br at 193 nm posed for diatomic potentials, but can be used for the dissociation of molecules dissociating via the undistorted linear pathway. For example, when the molecule dissociates Br* with the limiting value of $\beta$ can be generated through the parallel transition to the $Q_0$ state. The lowering of the anisotropy parameter $\beta$ from the limiting value is due to the contribution of the initial transition to the $Q_1$ state, followed by dissociation through the distorted pathway. Supposing that curve-crossing in the linear pathway in $C_{3v}$ symmetry is invoked by the symmetry reduction, $f Y \rightarrow f X + f Z$. The fraction of the distorted pathway were thus estimated to be 11% at 234 and 68% at 193 nm, implying that the distorted pathway is more favorable at 193 nm than at 234 nm.

Although there is no a priori reason for the difference in fractions of the distorted pathways, insight into the reason for this difference can be drawn from the energy partitioning during the photodissociation process. At 234 nm, 81% (84%) of the available energy is transformed into the translational energy of the fragments for the Br (Br*) channel, i.e., 19% (16%) into the internal energy of the CF$_3$. In addition, it has been discovered that at 193 nm the average total translational energies are 188 and 142 kJ/mol for the Br and Br* channels, respectively, which indicates that 57% (49%) of the available energy is transformed into the translational motion of the fragments (see Table III).

The proportion of the translational energy to the available energy can be estimated by introducing the two radical limits of the impulsive model. According to the rigid model, almost all of the available energy should be partitioned into the translational energy, which is in contrast to the fractions observed at 234 and 193 nm. The rigid radical limit, which ignores vibrational excitation, is not valid for CF$_3$Br photodissociation studies on CF$_3$I and CD$_3$I, where it was suggested that the distortion away from the pseudo-diatomic ($C_{3v}$) geometry is responsible for the $I^*/I$ branching.  

### Table III. Energy partitioning in the photodissociation of CF$_3$Br at 234 nm (this work) and 193 nm (Ref. 31). Energies are in kJ/mol.

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>Product</th>
<th>$E_{mol}$</th>
<th>$\langle E_T \rangle$</th>
<th>$\langle E_{int} \rangle$</th>
<th>$f_T$</th>
<th>$f_{int}$</th>
<th>$f_{T,\text{predicted}}$</th>
<th>$f_{T,\text{ret}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>234 nm</td>
<td>Br</td>
<td>225</td>
<td>183</td>
<td>42</td>
<td>0.81</td>
<td>0.19</td>
<td>0.90</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>Br*</td>
<td>180</td>
<td>151</td>
<td>29</td>
<td>0.84</td>
<td>0.16</td>
<td>0.85</td>
<td>0.71</td>
</tr>
<tr>
<td>193 nm</td>
<td>Br</td>
<td>333</td>
<td>188</td>
<td>145</td>
<td>0.57</td>
<td>0.43</td>
<td>0.59</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>Br*</td>
<td>289</td>
<td>142</td>
<td>147</td>
<td>0.49</td>
<td>0.51</td>
<td>0.49</td>
<td>0.51</td>
</tr>
</tbody>
</table>

where $P_{up}$ and $P_{down}$ denote the up-crossing probability from $Q_1$ to $Q_0$ state and the down-crossing probability from $Q_0$ to $Q_1$ state, respectively. At 234 nm, only $P_{down}$ was obtained with the value of 0.13, whereas at 193 nm values of $P_{up}=0.88$ and $P_{down}=0.59$ were determined.

To explain the difference between the down-crossing probabilities at the two wavelengths, we introduce the Landau–Zener equation, where $P_{down}$ is the down-crossing probability through the curve-crossing point, and $\mu$ is the reduced mass of the two fragments. This model was proposed for diatomic potentials, but can be used for the dissociation of the pseudo-diatomic CF$_3$Br. According to the equation, the curve-crossing probability monotonically decreases with $v_c$. Since $v_c$ increases with the photon energy, this model predicts a lower curve-crossing probability at 193 nm than at 234 nm. In photodissociation studies on CF$_3$I at 248 and 304 nm, qualitative agreement was found between the model and the experimental findings ($P_{down}=0.035$ at 308 nm and 0.4 at 248 nm).  

In the case of CF$_3$Br, however, the model is not in agreement with the experimental findings. In addition, the model fails to explain the difference between the up- and down-crossing probabilities found in the photodissociation of CF$_3$Br at 193 nm (Table II). An additional discrepancy between this model and experiment was found in a study of the $I^*/I$ branching ratios resulting from the photodissociation of CH$_3$I and CD$_3$I, where it was suggested that a distortion away from the pseudo-diatomic ($C_{3v}$) geometry is responsible for the $I^*/I$ branching. We therefore propose that the symmetry reduction from $C_{3v}$ to $C_s$ during the photodissociation process should be considered for CF$_3$Br photodissociation. A reduction in the molecular symmetry of CF$_3$Br could be caused by zero-point motion along $e$-symmetry modes or the excitation of vibrational bending modes.
Photodissociation dynamics of \( \text{CF}_3\text{Br} \)

discontinuity when it is assumed that \( \text{CF}_3\text{Br} \) is of intrinsic \( C_{3v} \) symmetry, and that merely a slight distortion to \( C_1 \) symmetry is expected to be induced during the dissociation process.\(^{32}\) The recoil impulse along the C-Br axis is easily transformed into the umbrella vibrations of \( \text{CF}_3 \), as is observed in the photodissociation of \( \text{CH}_3\text{Br} \).\(^{3} \) On application of the soft radial limit of the impulsive model, which does account for vibrational excitation, it was estimated that \( \mu_{\text{Br-C}}/\mu_{\text{Br-CF}} = 28\% \) of the available energy is disposed into the fragments' translational energy. In this case, however, the estimated fraction is substantially lower than the observed values. Although neither model explicitly explains the energy partitioning, an implication can be deduced from the observed fractions. The fractions between the two limiting cases may arise from a situation in which the excited-state geometry deviates significantly from the ground-state geometry. Consideration of this geometrical change would lower the fraction predicted from the rigid radical limit of the impulsive model. The difference in fraction that is expected on inclusion of the geometrical change would be due mainly to the deviation from the pseudo-diatomic linear geometry, and to the subsequent excitation of the rotational modes in \( \text{CF}_3 \).\(^{3} \)

This hypothesis is supported by the fact that rotationally excited \( \text{CH}_3 \) has been observed in \( \text{CH}_3\text{I} \) photodissociation.\(^{3} \)

The higher value of \( f_T \) observed at 234 nm is indicative of a more impulsive photodissociation accompanied by less excitation of the vibrational modes. It has been shown in an \textit{ab initio} and trajectory study of the A-band photodissociation of \( \text{CH}_3\text{I} \) that the \( ^1Q_1 \) surface has a small bending-force constant, which is considered to induce the symmetry reduction outside the conical intersection.\(^{21} \) It was also discovered that the \( ^3Q_0 \) surface retains a large bending-force constant even outside the conical intersection, leading to the damping of the vibrational motion of \( \text{CH}_3 \). Consequently, the transition from the \( ^3Q_0 \) to \( ^1Q_1 \) surface conserves the vibration that is initially excited after photodissociation commences, whereas the transition from the \( ^1Q_1 \) to \( ^3Q_0 \) surface reduces this vibrational excitation. As the contribution of the \( ^1Q_1 \leftarrow ^3Q_0 \) transition becomes larger, less translational excitation of the fragments is expected, which is in good agreement with the observations at 234 and 193 nm. In addition, the \( ^1Q_1 \) surface is asymmetric along the bending angle prior to the conical intersection. This allows the molecule to dissociate along a pathway that deviates from the linear path along the C-Br axis.\(^{21} \) Therefore, the bending torque induced by the initial excitation to the \( ^1Q_1 \) surface may enhance the symmetry reduction, causing rotational and vibrational excitation. On the other hand, the \( ^3Q_0 \) surface is symmetric along the bending angle, forming a linear pathway. Therefore, assuming that this argument can be applied to the case of \( \text{CF}_3\text{Br} \), it can be suggested that both the larger \( ^1Q_1 \leftarrow ^3Q_0 \) transition probability and the contribution of the \( ^1Q_1 \) surface to the initial excitation are responsible for the smaller \( f_T \) (hence the larger \( f_{\text{in}} \)) observed at 193 nm. This dynamical picture coincides well with the difference between the fractions of the distorted pathway observed at 234 and 193 nm.

Another implication of the calculation presented above is that the \( ^1Q_1 \leftarrow ^3Q_0 \) and the \( ^3Q_0 \leftarrow ^1Q_1 \) and transitions occur across the seam.\(^{21} \) Since the pathways before and after the conical intersection are different in the two cases, the \textit{up-} and \textit{down-}crossing probabilities of the transitions differ from each other. In the case of \( \text{CH}_3\text{I} \) photodissociation, it has been observed that \( \Phi_{\text{up}} = 0.9 \) for the trajectory starting on the \( ^3Q_0 \) surface, and that \( \Phi_{\text{down}} = 0.03 \) for the trajectory starting on the \( ^1Q_1 \) surface.\(^{21} \) These results strongly support the idea that the discrepancy between \( P_{\text{up}} \) and \( P_{\text{down}} \) found in the \( \text{CF}_3\text{Br} \) photodissociation originates from the difference in shape between the surfaces before and after the conical intersection.

**V. SUMMARY**

In this work, the photodissociation dynamics of \( \text{CF}_3\text{Br} \) has been investigated utilizing a photofragment ion-imaging technique coupled with a REMPI scheme. Based on the recoil anisotropies and relative quantum yields, the relative contributions of the parallel and perpendicular transitions to the generation of bromine fragments have been extracted for the Br and Br* channels. The findings of this work reveal that a nonadiabatic transition between the \( ^3Q_0 \) and \( ^1Q_1 \) states is responsible for the reduction in the anisotropy for Br. In accordance with past work on the photodissociation of \( \text{CH}_3\text{I} \), it is suggested that the symmetry reduction from \( C_{3v} \) to \( C_1 \) during the photodissociation invokes a nonadiabatic coupling between the states, distorting the original one-dimensional linear pathway. This result is predicted by treating \( \text{CF}_3\text{Br} \) as a pseudo-diatomic molecule. The observation of a significant difference between the experimental fraction of translational energy and the fractions calculated for the two radical limits of the impulsive model also provides strong evidence that a substantial geometrical change occurs in the photodissociation process. The asymmetry of the \( ^1Q_1 \) surface along the bending angle is presumed to induce a torque, leading to the formation of a distorted pathway. In addition, the smaller contribution from a distorted pathway, and hence the smaller contribution of the \( ^1Q_1 \) state to the initial excitation, also leads to a more impulsive dissociation of \( \text{CF}_3\text{Br} \). Moreover, as the contribution of the \( ^1Q_1 \leftarrow ^3Q_0 \) transition decreases and hence the contribution of the \( ^3Q_0 \) surface increases, vibrational damping outside the conical intersection leads to less vibrational excitation of the fragments. In order to better describe the phenomenon of symmetry reduction during photodissociation and its influence on the corresponding photodissociation dynamics, we are currently investigating the photodissociation of other molecules of \( C_{3v} \) symmetry at various photodissociation wavelengths.

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