Photodissociation of CF$_3$Br at 193 nm: evidence for a distorted dissociation pathway

M.-A. Thelen, P. Felder *

Physikalisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

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Abstract

The photodissociation of CF$_3$Br at 193 nm has been studied by photofragment translational spectroscopy. The primary dissociation step leads to the formation of CF$_3$ radicals and Br atoms in the electronic ground state and in the spin-orbit excited state, with relative quantum yields $\phi({\text{Br}}) = 0.47 \pm 0.05$ and $\phi({\text{Br}*}) = 0.53 \pm 0.05$, respectively. At higher laser fluences the slowest and internally hottest CF$_3$ radicals undergo photoinduced secondary dissociation to CF$_2$ + F. The anisotropy parameters derived from measurements with a polarized photolysis laser are $\beta({\text{Br}}) = 1.8 \pm 0.2$ and $\beta({\text{Br}*}) = 0.7 \pm 0.3$. The experimental results are discussed in terms of a model that involves the initial excitation of two repulsive electronic states $^3Q_0$ and $^1Q_1$ via transitions polarized parallel and perpendicular to the C–Br bond, respectively. From the observed $\beta$ parameters it is concluded that in roughly two thirds of the molecules dissociation proceeds via a distorted geometry in which the molecular symmetry C$_3v$ is reduced to C$_1$ through the effect of e-type bending vibrations.

1. Introduction

The substituted methyl halide systems CX$_3$Y (X = H, F; Y = Br, I) have played the role of prototypical systems for studying the photodissociation dynamics of polyatomic molecules [1]. Photoexcitation in the first UV absorption band, the so-called A-band, leads exclusively to the fission of the C–Y bond according to:

$$\text{CX}_3\text{Y} + h\nu \rightarrow \text{CX}_3 + \text{Y}^*(^2P_{3/2}), \quad (1)$$

$$\text{CX}_3\text{Y} + h\nu \rightarrow \text{CX}_3 + \text{Y}^*(^2P_{1/2}). \quad (2)$$

In the case of the bromine compounds CH$_3$Br and CF$_3$Br, these reactions are environmentally relevant since the nascent bromine atoms can promote depletion of the stratospheric ozone layer [2,3]. CF$_3$Br (halon 1301) is widely used as a fire retardant and its yearly release rate is $3 \times 10^6$ kg. Its atmospheric lifetime is 72 years and the percentage contribution to ozone loss has been calculated to be 2.5% [2]. The main removal mechanism of CF$_3$Br is through ultraviolet photolysis.

The theoretical interest for CX$_3$Y compounds arises because of their C$_3v$ symmetry, which allows for an approximate treatment as linear pseudo-tritatomics [4], and because of the strong spin–orbit coupling in the heavy halogen atom Y, which gives rise to the well distinguishable reaction channels (1) and (2). The asymptotic product states are correlated with several potential energy surfaces (PES) of the electronically excited parent molecule, a situation in which interesting coupling phenomena between interacting PES are to be expected.

* Corresponding author. Fax: +41 1 3620139
The iodinated systems, in particular, have been the subject of numerous theoretical and experimental studies [5–13]. Their easily accessible A-band is centered around 260 nm and consists of three overlapping electronic transitions to dissociative excited states [14–16]. According to magnetic circular dichroism (MCD) measurements [17,18], the main contribution to the A-band absorption is due to the $^3Q_0 \rightarrow X$ transition, whereas two weaker components $^3Q_1 \rightarrow X$ and $^1Q_1 \rightarrow X$ are located in the low and high energy lobes, respectively. Although a given electronic state can be preferentially excited by a suitable choice of the photolysis wavelength, strong couplings between the excited PES generally lead to dissociation on more than one surface and hence give rise to the formation of both ground-state and spin-orbit excited iodine atoms [5,7,8,12]. Lao et al. [1] have demonstrated this so-called curve-crossing phenomenon in CH$_3$I by means of polarized emission spectroscopy. Shapiro [10] has developed a theoretical treatment of the multisurface dissociation of CH$_3$I and, more recently, Tadjeddine et al. [19] and Yabushita et al. [20] have calculated the coupling between the ground-state and low lying excited states by ab initio methods.

The brominated systems have been investigated less thoroughly. The main differences between brominated and iodinated species consist in a smaller spin-orbit coupling for Br, stronger C–Br bond and in a blue-shift of the A-band to approximately 200 nm in both CH$_3$Br [21] and CF$_3$Br [22]. Moreover, since the main transition $^3Q_0 \rightarrow X$ is formally spin-forbidden, the intensity of the A-band is reduced in the bromides due to smaller spin–orbit coupling. Van Veen et al. have investigated the photodissociation of CH$_3$Br at 193 nm and found no effective curve crossing between the $^3Q_0$ and $^1Q_1$ surfaces. However, Chandler et al. [23], who studied CH$_3$Br at 222 nm by applying a photofragment imaging technique, found that, while the images of Br$^*$ are fairly anisotropic and have the appearance of a $\cos^2 \theta$ angular distribution, the ground-state images are more isotropic and contain a distinct $\sin^2 \theta$ angular component. This finding was explained by curve crossing [23].

The fluorinated bromide CF$_3$Br has not yet been studied in such detail. Talukdar et al. [24] measured the quantum yield for the primary formation of bromine atoms in the photodissociation of CF$_3$Br at 193 and 222 nm and found it to be near unity at both wavelengths. Pence et al. [25] measured the relative quantum yield of spin–orbit excited Br$^*$ to be $\phi(\text{Br}^*) = 0.56 \pm 0.05$ at 193 nm, whereas Ebenstein et al. [26] reported a somewhat higher value $\phi(\text{Br}^*) = 0.66 \pm 0.07$.

In this paper, we report on an investigation of the photodissociation of CF$_3$Br at 193 nm by means of photofragment translational spectroscopy (PTS) [27–30]. This method permits determination of the translational and angular distributions of the photofragments and thereby provides direct information on the internal energy of the nascent fragments and on the orientation of the electronic transition moment in the parent molecule. In addition to an estimate of the branching ratio between the dissociation pathways (1) and (2), our measurements have allowed us to assess the importance of the interactions between various excited electronic states involved in the photodissociation.

2. Experimental

The molecular beam apparatus and experimental procedure have been described elsewhere [31]. The photolysis of CF$_3$Br at 193 nm was performed by means of an ArF excimer laser (Lambda Physik EMG 101 MSC) providing pulses with a fluence of 0.8 J/cm$^2$ at the intersection with the pulsed molecular beam. Time-of-flight (TOF) distributions of the neutral photofragments were measured with a quadrupole mass spectrometer located at a distance of 34.5 cm from the photolysis region. The angular distribution of the photofragments was determined from the TOF signals measured at a given laboratory (LAB) scattering angle $\Theta$ (angle between the molecular beam and the photofragment detection axis) as a function of the polarization angle $\epsilon$ (angle between the electric vector $E$ of the laser light and the detection axis). For that purpose, linearly polarized light with a polarization degree of 91% was produced by directing the laser beam through a pile of 10 quartz plates at Brewster's angle. The angle $\epsilon$ was varied by rotating the plane of polarization with a $\lambda/2$ plate. For brevity, the TOF distributions obtained with the polarized photolysis laser are...
henceforth addressed as “polarized TOF distributions”.

Some preliminary measurements were carried out with a mixture of 8% CF$_3$Br (Linde, purity 99.8 Vol%) seeded in helium at a stagnation pressure of 300 mbar, but for most of the experiments a 20% mixture of CF$_3$Br in He with a total pressure of 600 mbar was used. In spite of this rather high concentration and pressure, no significant formation of (CF$_3$Br)$_n$ clusters was observed. The molecular beam velocity distribution was measured by means of a slotted disc chopper [30]. Least-squares fits to the distribution function $f(v) \propto v^2 \exp\left(-\left(\frac{v - v_0}{a}\right)^2\right)$ [32] yielded average parameter values of $v_0 = 840$ m/s and $a = 65$ m/s for the 8% mixture and of $v_0 = 660$ m/s and $a = 44$ m/s for the 20% mixture. All the TOF spectra shown in this paper have been corrected for the flight time of the ions through the mass filter.

3. Results and analysis

The TOF distributions of the Br atoms were measured with the mass filter setting $m/e = 79$. Very similar signals were also observed at the mass of the other isotope, $m/e = 81$. Figs. 1a and 1b show the unpolarized TOF distributions of Br obtained at the LAB angles $\Theta = 33^\circ$ and $60^\circ$, respectively. In both spectra the peak at shorter flight time reflects the formation of ground state atoms Br(2P$_{3/2}$) via reaction (1), whereas the signal at longer flight time is due to the spin–orbit excited atoms Br*(2P$_{1/2}$) produced in reaction (2). The TOF signal of the CF$_3$ radicals formed as the counterfragments of Br and Br* is displayed in Fig. 1c. This distribution was measured at $\Theta = 60^\circ$ and $m/e = 50$, corresponding to the daughter ion CF$_2^+$, since the signal of the parent ion at $m/e = 69$ is very weak as a consequence of cracking in the ionizer. While the TOF signals at $m/e = 79$ were found to be independent of the photolysis laser power, the relative intensity of the slower TOF peak at $m/e = 50$ is significantly reduced as the laser fluence is increased. This finding indicates that the slowest, and hence internally hottest, CF$_3$ fragments are depleted through the secondary photodissociation process

$$\text{CF}_3 + h\nu \rightarrow \text{CF}_2 + \text{F}. \quad (3)$$

To avoid the complications caused by this reaction and by the fragmentation in the ionizer, the initial analysis of the recoil distributions was based almost entirely on the TOF data of the Br atom measured at $m/e = 79$. However, as will be discussed further below, the data obtained at $m/e = 50$ were included in a second stage of the analysis in order to disentangle the overlapping signals of the two primary processes (1) and (2).

The photofragment angular distribution was determined from the polarization dependence of the TOF signal measured at $m/e = 79$. In the CM system of the parent molecule, the fragment angular distribution has the following form

$$w(\vartheta) \propto 1 + \beta P_2(\cos \vartheta), \quad (4)$$

where $P_2$ is the second order Legendre polynomial, $\vartheta$ is the angle between the $E$-vector and the recoil direction in the CM system and $\beta \in [-1, 2]$ is the anisotropy parameter [33]. Fig. 2a displays the TOF spectra measured with two mutually orthogonal laser polarization angles $\epsilon = -20^\circ$ and $-110^\circ$. With this choice of angles in the LAB frame, the $E$-vector is oriented parallel and perpendicular, respectively, to the direction of fragment detection in the CM frame. Note, however, that for a given angle $\epsilon$ the actual value of $\vartheta$ depends on the particular recoil velocity of the detected photofragment. The higher intensity of the TOF signal observed with $\epsilon = -20^\circ$ implies that the photofragments are ejected preferentially parallel to the direction of $E$. As shown in Fig. 2a, this effect is more pronounced for the TOF peak arising from ground-state Br. By integration of each TOF peak in a region of minimal peak overlap and by exploiting Eq. 4, the anisotropy parameters $\beta(1) = 1.8 \pm 0.2$ (Br channel) and $\beta(2) = 0.7 \pm 0.3$ (Br* channel) were obtained.

The total translational energy distribution $P(E_T)$ of the fragment pairs was determined from the data measured at $m/e = 79$ by means of a forward convolution procedure [5] and is displayed by the solid circles in Fig. 3. In the case at hand, the partial overlap of the signals due to the fragments produced in reactions (1) and (2) precludes a straightforward partitioning of $P(E_T)$ into the respective contributions $P(E_T^{(1)})$ and $P(E_T^{(2)})$. Therefore, additional experimental evidence was taken into account. On the one hand, since the recoil anisotropy of channel (1),
Fig. 1. Photodissociation of CF$_3$Br at 193 nm with unpolarized laser. TOF distributions of the Br fragments detected at m/e = 79 with (a) $\Theta = 33^\circ$ and (b) $\Theta = 60^\circ$; (c) TOF distribution of the CF$_3$ fragments detected at m/e = 50 with $\Theta = 60^\circ$. The fits (solid lines) were calculated from the total translational energy distribution $P(E_T)$ displayed with solid circles in Fig. 3. The dotted lines are the calculated signal contributions from dissociation channels (1) and (2), respectively.
Fig. 2. Photodissociation of CF$_3$Br at 193 nm with linearly polarized laser. (a) TOF signals of the Br atoms detected at $m/e = 79$ with $\Theta = 33^\circ$ and two mutually orthogonal polarizations. The "parallel" distribution was recorded with $\varepsilon = -20^\circ$, while the "perpendicular" distribution was recorded with $\varepsilon = -110^\circ$. The two distributions of (a) are shown again separately in (b) and (c) together with the respective best fits (solid lines), which were calculated with the $P(E_T)$ given in Fig. 3 and with the $\beta(k)$ values and relative quantum yields $\phi(k)$ listed in Table 1.
fl(1) = 1.8, is close to the upper limit of 2 whereas that of channel (2) is substantially lower, we conclude that channel (2) cannot contribute significantly to the first TOF peak. Stated differently, \( P(E_T^{(2)}) \) does not extend to low translational energies and thus overlaps with the slower component \( P(E_T^{(1)}) \). This conclusion is based on the power dependence of the TOF signal at \( m/e = 50 \), which shows a progressive depletion of the slower TOF peak as the laser fluence is increased. Most likely, this is due to the secondary photodissociation of CF\(_3\) according to reaction (3), although we cannot entirely rule out other photoinduced processes leading to a removal of CF\(_3\), such as multiphoton ionization. Regardless of the particular mechanism, the essential point is that preferential photoinduced depletion of the slower TOF peak can only occur if the corresponding CF\(_3\) fragments have an internal energy differing from that of the remaining CF\(_3\). However, if the slower TOF peak at \( m/e = 50 \) were entirely due to CF\(_3\) formed in coincidence with spin–orbit excited Br atoms, the internal energy of the CF\(_3\) radicals would not differ significantly from that of the radicals in the first TOF peak. There would then be no reason for a selective photodepletion. This argument is based on the following energy balance.

After dissociation, the energy available \( E_{\text{av}} \) to be partitioned among the photofragments is given by

\[
E_{\text{av}} = h \nu - D_0 = E_T + E_{\text{CF}_3} + E_{\text{Br}},
\]

where \( h \nu = 620 \text{ kJ/mol} \) is the photon energy at 193 nm and \( D_0 \) is the dissociation energy of the C–Br bond in CF\(_3\)Br, and where the small internal energy of the parent molecule in the supersonic beam has been neglected. \( E_{\text{av}} \) is distributed between the translational energy of the fragment pairs \( (E_T) \), the ro-vibrational energy of CF\(_3\) \( (E_{\text{CF}_3}) \) and the electronic energy of the Br atom \( (E_{\text{Br}}) \). Inserting \( D_0 = 287 \pm 7 \text{ kJ/mol} \) [34] into Eq. (5) we obtain \( E_{\text{av}} = 333 \text{ kJ/mol} \). The electronic energy is zero in case of Br\(^2\)P\(_{3/2}\), whereas \( E_{\text{Br}} = 44 \text{ kJ/mol} \) for Br*\(^2\)P\(_{1/2}\) [34]. Therefore, the maximum of the TOF signal attributed to the Br channel corresponds to a peak translational energy \( E_{\text{Tpeak}}^{(1)} = 195 \text{ kJ/mol} \) and hence to an internal energy \( E_{\text{CF}_3}^{(1)} = 138 \text{ kJ/mol} \), while in the case of the Br* channel, \( E_{\text{Tpeak}}^{(2)} = 145 \text{ kJ/mol} \) implies an internal energy \( E_{\text{CF}_3}^{(2)} = 144 \text{ kJ/mol} \). As already stated above, the CF\(_3\) radicals formed in channels (1) and (2) appear to have very similar internal energies. However, any signal in the slower TOF peak originating from the ground state channel (1) necessarily implies the formation of significantly hotter CF\(_3\) fragments. The depletion observed in this TOF peak is thus attributed to an enhanced absorption cross section of such hot CF\(_3\) radicals.

Based on these considerations, the partitioning of \( P(E_T) \) was refined by comparing the TOF data of the Br atoms at \( m/e = 79 \), which are not influenced by secondary photodissociation, with those at \( m/e = 50 \) and high laser fluence, where the hottest CF\(_3\) radicals have been photolyzed. This situation was modelled by removing the low kinetic energy part of each \( P(E_T) \) component displayed as hatched portions in Fig. 3. As shown by the solid line in Fig. 3c the truncated \( P(E_T) \) allowed to reproduce the TOF data at \( m/e = 50 \) and high fluence, whilst the complete \( P(E_T) \) reproduces the TOF signals at \( m/e = 79 \) (Figs. 1a and 1b) and also the spectrum at \( m/e = 50 \) obtained with reduced laser power (not shown).

With this partitioning of the TOF signals, the relative quantum yield for the formation of spin–orbit
Table 1
Partitioning of reaction channels (1) and (2) into parallel (β_A = 2) and perpendicular (β_B = -1) contributions due to the initial photoexcitation of \(^3Q_0\) and \(^1Q_1\) states, respectively

<table>
<thead>
<tr>
<th>k</th>
<th>β(k)</th>
<th>φ(k)</th>
<th>(c^{(3Q_0)})</th>
<th>(c^{(1Q_1)})</th>
<th>(\langle E_T \rangle)</th>
<th>(\langle E_{CF_3}\rangle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃ + Br</td>
<td>1</td>
<td>1.8</td>
<td>0.47</td>
<td>0.44</td>
<td>0.03</td>
<td>188</td>
</tr>
<tr>
<td>CF₃ + Br*</td>
<td>2</td>
<td>0.7</td>
<td>0.53</td>
<td>0.30</td>
<td>0.23</td>
<td>142</td>
</tr>
</tbody>
</table>

\(^a\) Contribution coefficient of the \(^3Q_0\) state.
\(^b\) Contribution coefficient of the \(^1Q_1\) state.
\(^c\) Average total translational energy in kJ/mol.
\(^d\) Average internal energy of CF₃ in kJ/mol.

The partitioning of reaction channels (1) and (2) into parallel (β_A = 2) and perpendicular (β_B = -1) contributions due to the initial photoexcitation of \(^3Q_0\) and \(^1Q_1\) states, respectively.

The anisotropy parameters \(\beta(1) = 1.8\) and \(\beta(2) = 0.7\) obtained from direct integration of the polarized TOF spectra were confirmed by using these values together with the iteratively determined \(P(E_T)\) components and \(φ(Br^*)\) to simulate the shapes of the polarized TOF spectra by means of the forward convolution procedure. The calculated distributions for \(\epsilon = -20°\) and \(-110°\), shown as solid lines in Figs. 2b and 2c, are in good agreement with the experimental data.

4. Discussion

Our experimental results show that, in agreement with previous measurements of the absolute photodissociation quantum yield of Br atoms [24], the fission of the C–Br bond is the only significant photochemical decay process of CF₃Br at 193 nm. This leads to the formation of ground state and spin–orbit excited bromine atoms according to reactions (1) and (2), with the latter being slightly favored. The quantum yield of spin–orbit excited bromine, \(φ(Br^*) = 0.53±0.05\), derived somewhat indirectly from the partitioning of the pertinent TOF contributions (see previous section), is in good agreement with the value \(φ(Br^*) = 0.56±0.05\) measured by Pence et al. [25], but is slightly lower than \(φ(Br^*) = 0.66±0.07\) reported by Ebenstein et al. [26].

By comparison of the TOF signal shapes of the Br atoms with those of the CF₃ fragments obtained at various laser fluences, we found that part of the nascent CF₃ radicals undergo secondary photodissociation. As detailed in the preceding section, this process occurs preferentially among the slowest CF₃ radicals formed in coincidence with a ground-state Br atom. According to the energy balance (5), these radicals possess a remarkably high internal energy of 167 kJ/mol or greater. The strongly enhanced photon absorption cross section of the hot radicals indicates that cold CF₃ is nearly transparent at 193 nm but has an electronic transition at shorter wavelengths. This is in good agreement with the results of Larrieu et al. [35], who calculated the first 15 active spectroscopic states in absorption. For the vertical transition energy to the lowest lying excited state, evaluated with respect to the \(C_{3v}\) ground state of the CF₃ radical, they found a value of 7.66 eV, implying that in order to be accessible to photoexcitation at 193 nm the CF₃ radicals must have an internal energy greater than 120 kJ/mol. It is also noted that preferential secondary photodissociation of hot primary fragments has previously been observed for the CF₂Br radicals produced in the photolysis of CF₂Br₂ [36] and for the SOC1₂ fragments formed in the photodissociation of SOC1₂ [37].

The anisotropy parameters \(\beta(1) = 1.8±0.2\) and \(\beta(2) = 0.7±0.3\) imply that both dissociation channels originate mainly from electronic transitions polarized parallel to the C–Br bond. In order to discuss this finding, we briefly recall the behavior of other alkyl halides excited in the longest wavelength absorption band. As first discussed by Mulliken [14,16], this so-called A-band of the alkyl iodides and alkyl bromides arises from an electronic excitation of \(n→σ^*\) type. In the case of \(C_{3v}\) molecular symmetry, the excited electronic state is split up by the spin–orbit interaction into five components, three of which are accessible via electric dipole transitions from the
electronic ground state $\tilde{X}$. The spectral positions and relative intensities of these overlapping transitions have been established by magnetic circular dichroism (MCD) measurements in the A-band region [17,18].

Based on the analogy with the $^3\Pi_1$, $^3\Pi_0^-$, and $^1\Pi_1$ states of hydrogen bromide, the optically accessible states of CF$_3$Br are denoted in Mulliken's terminology as $^3\Omega_1$, $^1\Omega_0$ and $^1\Omega_1$, respectively. The transition $^3\Omega_0 \leftrightarrow \tilde{X}$ is polarized parallel to the C–Br bond, whereas the $^3\Omega_1 \leftrightarrow \tilde{X}$ and $^1\Omega_1 \leftrightarrow \tilde{X}$ transitions are perpendicularly polarized [15]. According to Mulliken's analysis, the $^3\Omega_0$ state is correlated with the photofragments CF$_3$ + Br*, while $^3\Omega_1$ and $^1\Omega_1$ are correlated with CF$_3$ + Br. This situation is depicted in Fig. 4a. Since the A-band of CF$_3$Br is centered near 210 nm [38], photoexcitation at 193 nm is not expected to involve the lowest lying state, $^3\Omega_1$, which we shall henceforth disregard, as was done in the case of CF$_3$I photolyzed at 248 nm [12,13].

In contrast to the correlations given in Fig. 4a, it is well established in the case of alkyl iodides that ground-state I atoms can also be formed with parallel polarization, that is, via initial excitation of the $^3\Omega_0$ state [1,6,12,7]. Within the framework of a pseudo-diatomic model, in which the CX$_3$ moiety is concentrated in a single effective atom, this finding implies a transition from the $^3\Omega_0$ to the $^1\Omega_1$ state, also denoted as curve crossing. The probability of curve crossing can be estimated qualitatively with the Landau-Zener model, which has been invoked to rationalize the $I^*/I$ branching ratios observed in numerous investigations [39]. However, as already pointed out by Butler and coworkers [40], the Landau–Zener model fails in the simplest of cases, the comparison between CH$_3$I and CD$_3$I. Based on multidimensional ab initio calculations of Morokuma and coworkers [20,41], it was suggested by Butler and coworkers that the process responsible for the apparent curve crossing in the pseudo-diatomic model is actually due to a distortion from the pseudo-linear geometry. In other words, either zero point motion along e-symmetry modes or excitation of vibrational bending modes leads to an effective symmetry reduction from C$_{3v}$ to C$_v$, which in turn induces a splitting of the doubly degenerate $^1\Omega_1$ electronic state. The situation under C$_v$ symmetry is displayed in Fig. 4b.

Recalling that under the influence of strong spin–orbit interaction the $^3\Omega_0$ and $^1\Omega_1$ states correspond to 2A$_1$ and 3E, respectively, where the numerical prefix is used to label the states of a given irreducible representation in order of increasing energy, the 2A$_1$ state becomes 3A' in C$_v$ symmetry. In contrast, 3E is split up into the pair of states 4A' and 2A''. The avoided crossing between 3A' and 4A' thus gives rise to a conical intersection.

Before proceeding to discuss our experimental results, a comment regarding the orientation of the electronic transition dipole moment is in order. As already pointed out, in C$_{3v}$ symmetry the transitions are either parallel or perpendicular to the symmetry axis, i.e. the C–Br bond direction. In C$_v$ symmetry, the transitions from the ground-state 1A' to the excited A' states are polarized within the symmetry
plane, whereas the transitions to the $A'$ states are polarized perpendicular to this plane. Moreover, since in the case at hand the $C_s$ symmetry is the result of merely a slight distortion from a geometry with $C_{3v}$ symmetry, the classification with respect to the latter group is expected to remain approximately valid. Therefore, the in-plane transitions of $A' \leftarrow A'$ type may be further differentiated with respect to the direction of the C–Br bond. Since the $3A'$ state results from a weak distortion of the $3Q_0 (2A_1)$ state, the $3A' \leftarrow 1A'$ in-plane transition is essentially parallel to the C–Br bond, whereas the $4A' \leftarrow 1A'$ in-plane transition is essentially perpendicular to the C–Br bond.

We now consider the reaction (1) which produces ground state Br atoms. The anisotropy parameter $\beta(1) = 1.8 \pm 0.2$ being very close to the upper limit of $+2$ unambiguously shows that for this channel the transition moment $\mu$ is parallel to the recoil direction, i.e. to the C–Br bond. The formation of Br atoms via a parallel electronic transition reflects a correlation of the type shown in Fig. 4b and therefore leads us to conclude that the dissociation process occurs almost exclusively through a distorted configuration of $C_s$ symmetry ($\alpha \neq 0$). The fact that $\beta(1)$ is slightly smaller than 2 might be due to the anisotropy loss caused by rotation of the photoexcited molecule prior to dissociation. More likely, it is due to a small contribution of a symmetric ($C_{3v}$) photodissociation pathway involving initial excitation of $3Q_0$ (3E) via a perpendicular transition followed by undistorted dissociation as depicted in Fig. 4a.

Next, we consider the reaction (2) which produces spin–orbit excited Br* atoms. The strongly reduced anisotropy parameter $\beta(2) = 0.7 \pm 0.3$ shows that, in contrast to reaction (1), the formation of Br* involves a substantial contribution from a perpendicular transition. Again based on the correlation diagrams of Fig. 4, the predominant pathway of the Br* reaction corresponds to a symmetric ($C_{3v}$) dissociation mode ($\alpha = 0$, excitation of $3Q_0 (2A_1)$ through a parallel transition) whereas the minor pathway corresponds to a distorted ($C_s$) dissociation mode ($\alpha \neq 0$, excitation of $2A'' (1Q_1)$ through a perpendicular transition).

The qualitative statements made above can be expressed in a quantitative form by partitioning the photofragment signals according to the method described in Ref. [12]. As already mentioned, based on the MCD measurements for CF$_3$I, CH$_3$I and CH$_3$Br [17,18] it was assumed that at shorter wavelengths only the $3Q_0$ and $1Q_1$ states play a role. The relative contribution coefficients $c_{ik}$ of “constituents” $i = A, B$ to the reaction channel $(k)$ are given by

$$
c_{\alpha k} = \phi(k) \left[ \beta(k) - \beta_B \right] / \left( \beta_A - \beta_B \right),
$$

$$
c_{\beta k} = \phi(k) \left[ \beta_A - \beta(k) \right] / \left( \beta_A - \beta_B \right),
$$

where $\beta(k)$ is the anisotropy parameter determined for the corresponding channel, $\phi(k)$ the relative yield of the channel, and where $i = A, B$ refer to the initial excitation of the $3Q_0$ and $1Q_1$ surfaces, respectively. The anisotropy parameters $\beta_A$ and $\beta_B$ describe the angular distribution that would be observed if only one electronic transition were involved in the photodissociation. Using the experimentally determined $\phi(k)$ and $\beta(k)$ values listed in Table 1 and the appropriate values $\beta_A = 2$ and $\beta_B = -1$, the contribution coefficients shown in Table 1 are obtained. From these results it is concluded that the contribution of $3Q_0$ and $1Q_1$ to the total dissociation signal is roughly 74% and 26%, respectively. Obviously, these values correspond to the relative intensities of the $3Q_0 \leftarrow X$ and $1Q_1 \leftarrow X$ transitions at a wavelength of 193 nm.

A further conclusion to be drawn from Table 1 regards the relative importance of the symmetric ($C_{3v}$) and the distorted ($C_s$) dissociation mode. Since, according to the correlation diagrams of Fig. 4, formation of Br* via $1Q_1$ and formation of Br via $3Q_0$ require a distorted configuration, we conclude from the pertinent contribution coefficients that the undistorted dissociation mode occurs merely in one third of the photoexcited molecules.

At this point it is instructive to consider the related molecules CH$_3$Br and CF$_3$I. For both of these molecules, the reaction channel forming ground-state halogen atoms does not show a high positive $\beta$ value, in contrast to the present findings with CF$_3$Br. The photodissociation of CH$_3$Br was investigated at 205 nm with the photofragment imaging technique by Chandler et al. [23], who found that the ground-state Br image appears nearly isotropic but has a distinct perpendicular contribution. The photolysis of CF$_3$I has been studied in this group...
with the PTS method by Felder at 248 and 308 nm [12,13]. As the absorption spectrum of CF$_3$Br is blue-shifted by about 60 nm compared to CF$_3$I, the present results should be compared with those of the CF$_3$I photodissociation at 248 nm. More specifically, it is assumed that in both investigations the analogous region in the absorption spectrum is sampled. Felder [12] measured the kinetic energy dependence of the recoil anisotropy. He found the averaged recoil anisotropy parameters $\beta(1^*) = 1.6$ and $\beta(1) = -0.2$ and calculated the contribution of the $^3Q_0$ and $^1Q_1$ states to the photodissociation signal to be 80% and 20%, respectively, when using the anisotropy parameters $\beta_A = 2, \beta_B = -1$. While these contribution coefficients are obviously rather close to the ones found here with CF$_3$Br, the relative importance of the symmetric and distorted dissociation modes is strikingly different. Using the values of Table 2 in Ref. [12], one finds that in CF$_3$I roughly 85% of the molecules dissociate via the symmetric (C$_{3v}$) pathway, in contrast to the fraction of 33% found here with CF$_3$Br. Viewed again from a different perspective: while photoexcitation of CF$_3$I at 248 nm and CF$_3$Br at 193 nm leads predominantly to the $^3Q_0$ state in both molecules, the importance of a geometry distortion from C$_{3v}$ symmetry is significantly higher in CF$_3$Br and thereby leads to a substantially larger yield of ground state atoms (47% versus 12% in CF$_3$I).

Kang et al. [42] have recently studied the photodissociation of n-butyl iodide at 277 nm. Since this molecule has a lower symmetry than C$_{3v}$, one might expect a behavior similar to that of a distorted CX$_3$Y molecule. Indeed, Kang et al. [42] found a relatively higher yield (~0.39) of ground state atoms and, moreover, they observed anisotropy parameters $\beta(1) = 1.6$ and $\beta(1^*) = 0.9$ that are fairly similar to those found with CF$_3$Br. One might thus conclude that in spite of the fact that the lowest $\sigma^* \rightarrow n$ electronic transition of the alkyl bromides and iodides is rather localized on the carbon halogen bond and that, therefore, the substituents do not appear to influence the overall appearance of the absorption spectra, they may nevertheless have substantial influence on the dynamics of photodissociation.

Returning to the CF$_3$Br molecule, we note in closing that the enhanced significance of the distorted photodissociation pathway, e.g. in comparison with CF$_3$I, can only be explained qualitatively at present. The reduced mass involved in the e-type bending motion is certainly smaller in CF$_3$Br and one therefore expects a larger zero-point vibrational amplitude. Accordingly, the wavepacket produced on the excited potential energy surface upon photoexcitation necessarily spans a larger range of distorted geometries than in the iodinated system. Moreover, the relative velocity at which the system traverses the conical intersection is expected to be different in CF$_3$Br and CF$_3$I. Therefore, a quantitative assessment of the photodissociation behavior of CF$_3$Br will require consideration of the involved potential energy surfaces. It would thus be highly desirable to carry out for CF$_3$Br ab initio calculations of the type performed for CH$_3$I by Morokuma et al. [41].

5. Conclusion

The main findings of the present investigation relate to the general photodissociation mechanism of CX$_3$Y (X = H or F; Y = Br or I) molecules excited in the first UV absorption band. As has long been known, the dissociation behavior of these molecules is complicated by the presence of several near-degenerate excited electronic states which give rise to overlapping electronic transitions and to non-adiabatic effects. The latter are known to be particularly pronounced in the neighborhood of the conical intersection between the $^3Q_0$ and $^1Q_1$ surfaces. Similar to CH$_3$I and CF$_3$I excited at 248 nm and CH$_3$Br excited at 205 nm, the photolysis of CF$_3$Br at 193 nm involves mainly the $^3Q_0 \rightarrow X$ transition with a smaller contribution of $^1Q_1 \rightarrow X$. However, the photodissociation of CF$_3$Br was found to differ significantly from that of the other CX$_3$Y systems in that it appears to proceed predominantly (i.e. with a probability of ~2/3) via distorted configurations in which the CF$_3$Br system assumes a bent structure. The symmetry reduction from C$_{3v}$ to C$_s$ leads to an avoided crossing of the excited $^3Q_0$ and $^1Q_1$ states and thereby reverses the correlation between the initially excited state and the spin–orbit state of the Br photofragment. This conclusion was obtained from the analysis of the polarization dependent TOF distributions, which showed that $\beta(\text{Br}) = 1.8$ is significantly larger than $\beta(\text{Br}^*) = 0.7$, thus indicating that...
ground-state Br atoms are formed almost exclusively via initial excitation of the $^3Q_0$ state, whereas in the case of spin–orbit excited Br\* atoms both the $^1Q_1$ and the $^3Q_0$ state contribute to their formation.

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