Photofragment alignment from the photodissociation of HCl and HBr

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Abstract

Slice imaging is used to measure the alignment of Br(3P 3/2) and Cl(3P 3/2) photofragments from the photodissociation of HBr and HCl, respectively, at 193 nm. In both cases the A'Pi state is predominantly optically excited, which correlates to \( m_J = \pm 3/2 \) for the halogen atom photofragments. However, both the Br and Cl photofragments are measured to populate mostly \( m_J = \pm 1/2 \), showing that for both HBr and HCl nonadiabatic transitions transfer more population to the a'Pi state (which correlates to \( m_J = \pm 1/2 \)) during dissociation than remains in the A'Pi state. The interference between these two pathways is also measured. © 2002 Published by Elsevier Science B.V.

1. Introduction

There have been significant experimental [1–13] and theoretical [14–18] investigations into the photodissociation of HCl and HBr molecules. These systems are suitable for probing nonadiabatic coupling between multiple dissociative states, and the interference effects that arise from the multiple dissociation pathways. These interference effects are manifested in the atomic angular momentum of the halogen atom photofragments. In addition, in some cases, such a photodissociation process can act as an intense source of highly aligned and oriented, monoenergetic, atomic photofragments, which can be used in scattering experiments.

Photofragment alignment has been treated theoretically, and decomposed into coherent and incoherent contributions from multiple dissociative states accessed by parallel and perpendicular transitions [19]. The similar \( a_q^{kl}(p) \) formalism is used here to describe photofragment alignment [20].

The photofragment alignment of halogen (\( 3P_{3/2} \)) atoms has been measured for Cl atoms, from the photodissociation of Cl2 [21–25], ICl [21],...
BrCl [26] and Br atoms, from the photodissociation of Br2 [24], using time-of-flight (TOF) [21,25], and imaging techniques [22–24]. In this Letter, we report the measurement of Cl$^2P_{3/2}$ and Br$^2P_{3/2}$ photofragment alignment from the photodissociation of HCl and HBr at 193 nm, using slice imaging [27].

Slice imaging measures directly the two-dimensional center slice of the three-dimensional photofragment velocity distribution (analogous to the result obtained using the inverse-Abel transform in conventional photofragment imaging [28,29]). For $J \leq 3/2$ (as for Cl and Br photofragments), the angular distribution of this slice can be expressed by the expansion:

$$I(\theta)^{FG} = 1 + \beta_2^{FG} P_2(\cos \theta) + \beta_4^{FG} P_4(\cos \theta),$$

(1)

where F and G denote the directions of the photolysis and probe polarization directions, respectively, with respect to the slicing plane (which is perpendicular to the time-of-flight axis), and $\theta$ is the angle about the photolysis polarization. Since the 193 nm photodissociation of HCl and HBr is of at least 95% perpendicular character, we analyze the angular distributions using the perpendicular alignment parameters only ($a_0^2(\perp)$ and $a_2^2(\perp)$ [20]). For particular (FG) polarization geometries (XX), (XZ), and (ZX), where the Z axis is parallel to the TOF axis, the $\beta_2^{FG}$ and $\beta_4^{FG}$ coefficients are expressed in terms of alignment parameters and the $\beta$ parameter by

$$\beta_2^{XZ} = \frac{\beta + (s_2/2) \left[ a_0^2(\perp) + \sqrt{6} a_2^2(\perp) \right]}{1 - (s_2/2) \left[ a_0^2(\perp) + \sqrt{6} a_2^2(\perp) \right]},$$

(2)

$$\beta_2^{ZX} = \frac{(s_2/3) \left[ 3a_0^2(\perp) + \sqrt{6} a_2^2(\perp) \right]}{1 - (s_2/3) \sqrt{6} a_2^2(\perp)},$$

(3)

$$\beta_2^{XY} = \frac{\beta + (s_2/7) \left[ 5a_0^2(\perp) - 4\sqrt{6} a_2^2(\perp) \right]}{1 - (s_2/5) \left[ a_0^2(\perp) - 2\sqrt{6} a_2^2(\perp) \right]},$$

(4a)

$$\beta_4^{XY} = \frac{(6s_2/35) \left[ -3a_0^2(\perp) + \sqrt{6} a_2^2(\perp) \right]}{1 - (s_2/5) \left[ a_0^2(\perp) - 2\sqrt{6} a_2^2(\perp) \right]},$$

(4b)

where $s_2$ is the alignment sensitivity of the detection transition [30]. Note that both $\beta_3^{XZ}$ and $\beta_4^{XZ}$ are zero. Three of these four equations can be solved to yield the $\beta$, $a_0^2(\perp)$, and $a_2^2(\perp)$ parameters. Of the three equations, we choose the three $\beta_2^{FG}$ equations (Eqs. (2), (3), and (4a)), as the measurement of $k = 2$ moments should be less susceptible to experimental error than higher order moments (as is the $\beta_4^{XZ}$ parameter).

The approach used here to measure the Cl and Br photofragment alignment follows very closely the recent work of Rakitzis and Kitsopoulos on the photodissociation of Cl2 and Br2 [24]. The main difference here is that, due to the small relative mass of the H-atom co-fragment, the laboratory speeds of the Cl and Br atoms are very small and represent a challenge to our experimental technique. In addition, from a theoretical standpoint, due to large speed of the fragments during dissociation, we expect the nonadiabatic effects to be more significant than in the previous study [24]. We note that H($^2S_{1/2}$) atoms cannot possess angular momentum alignment (because $J < 1$), so the photofragment alignment is exhibited only in the halogen atom photofragments in the case of hydrogen halide photodissociation.

2. Experimental

The apparatus has been described in detail elsewhere [27,31]. Briefly, a 10 Hz pulsed molecular beam containing 5% HBr or HCl in He is skinned and collimated, and is intersected at right angles by two counter propagating laser beams. The 193 nm photolysis laser beam is generated by an ArF excimer laser (COMPEX, Lambda Physik), which is linearly polarized using a suprasil window placed at a Brewster’s angle to the laser propagation direction. The reflected beam, which is greater than 95% polarized, is used for photolysis, and the beam is focused onto the molecular beam ($f = 25$ cm) with typical laser powers of about 1 mJ/pulse. The probe laser beam is generated by MOPO-SL (Spectra Physics 730DT10). The Br- and Cl-atom photofragments are ionized using the two-photon resonant transition 5p($^2P_{1/2}$) $\leftrightarrow$ 4p($^2P_{1/2}$) at 250.454 nm and 4p($^2P_{1/2}$) $\leftrightarrow$ 3
$p^3(2P_{3/2})$ and 234.851 nm, respectively [32,33]. The value of $s_2$ for both $J_f = 1/2 \rightarrow J_i = 3/2$ transitions is calculated to be $-(5/4)(10/37)$ [30] (which includes a factor of 10/37 for the long-time-limit hyperfine depolarization coefficient [34]). Using the slice-imaging technique, 600 ns after the photofragment ionization, the extraction field is pulsed ON, and the Cl$^+$ or Br$^+$ ions are accelerated towards the ion-imaging detector. Ions of different mass separate in their time-of-flight during their field-free trajectory on route to the detector. The detector gain is pulsed ON for $\sim 20$ ns at the proper arrival time (at the center of the 200 ns broad ion packet) for slice-imaging velocity selection [31]. Images appearing on the detector anode are recorded using a CCD camera (Cohu 4910, using EyeSpy Software by k-Space Associates).

3. Results

The Cl and Br photofragment slice-images in various (FG) polarization geometries is shown in Fig. 1. The angular distribution is determined by integrating the signal within the FWHM of the Cl-photofragment slice-image radius as a function of $\theta$. The angular distributions for all six slice images (the (XX), (XZ), and (ZX) polarization geometries for both Cl and Br photofragments) are shown in Fig. 2. The angular distributions obtained from (FG) image analysis are normalized by the corresponding distributions obtained from (ZZ) images. The angular distributions of the ZZ images should depart from isotropic distributions only due to the presence of some systematic error. This normalization procedure corrects for systematic errors that do not depend on the laser polarizations, such as Doppler selectivity and detector inhomogeneity [24]. The normalized (FG) images are then fit to Eq. (2), and the $\beta_2^{FG}$ and $\beta_4^{FG}$ coefficients are tabulated in Table 1. Solving Eqs. (2), (3), and (4a) yields $\beta = -0.97 \pm 0.03$, $a_0^{(2)}(\perp) = -0.5 \pm 0.1$, and $a_2^{(2)}(\perp) = -0.45 \pm 0.1$ for the Cl photofragments, and $\beta = -0.88 \pm 0.05$, $a_0^{(2)}(\perp) = -0.7 \pm 0.2$, $a_2^{(2)}(\perp) = -0.6 \pm 0.1$ for the Br photofragments.
Table 1

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Cl(2P_y/2)</th>
<th>Br(2P_y/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>φ_3^{FG}</td>
<td>φ_3^{FG}</td>
<td>φ_3^{FG}</td>
</tr>
<tr>
<td>(XY)</td>
<td>-0.98</td>
<td>+0.07</td>
</tr>
<tr>
<td>(XZ)</td>
<td>-0.97</td>
<td>+0.05</td>
</tr>
<tr>
<td>(ZX)</td>
<td>+0.33</td>
<td>+0.02</td>
</tr>
</tbody>
</table>

F and G denote the directions of the photolysis and probe laser polarizations, respectively. The Z^{lab} axis is parallel to the TOF direction, and the Y^{lab} axis is parallel to the probe propagation direction. For the φ_3^{FG} and φ_4^{FG}, σ = 0.05.

and \( a_0^{(2)}(\perp) = -0.3 \pm 0.2 \) for the Br photofragments. It should be noted that the error bars here are mostly covariant in nature: the sum of \( a_0^{(2)}(\perp) \) and \( a_0^{(2)}(\perp) \) is measured with a relatively small error bar of about 0.1; the uncertainty arises from how the sum is partitioned between the \( a_0^{(2)}(\perp) \) and \( a_0^{(2)}(\perp) \). Therefore, within the stated error ranges for these parameters, there is the additional constraint that the sum of the parameters is constant. For example, for the Br atoms (for which the sum of \( a_0^{(2)}(\perp) \) and \( a_0^{(2)}(\perp) \) is -1.0), pairs of values consistent with these constraints are \( a_0^{(2)}(\perp) = -0.5 \), and \( a_0^{(2)}(\perp) = -0.5 \), as well as \( a_0^{(2)}(\perp) = -0.7 \), and \( a_0^{(2)}(\perp) = -0.3 \). The limits of the values of the parameters are \(-0.8 \leq a_0^{(2)}(\perp) \leq +0.8\), and \(-0.566 \leq a_0^{(2)}(\perp) \leq +0.566\). In addition, the results obtained by solving Eqs. (2), (3), and (4a) are also consistent with the independent Eq. (4b).

4. Discussion

For both HCl and HBr, absorption at 193 nm occurs predominantly via the perpendicular \( \Lambda^1 \Pi_1 \leftarrow X^1 \Sigma^+ \) transition, whereas the perpendicular \( \Lambda^3 \Pi_1 \leftarrow X^1 \Sigma^+ \) and parallel \( \Lambda^3 \Pi_0 \leftarrow X^1 \Sigma^+ \) transitions participate by less than an order of magnitude. The β-parameter measurements for HCl and HBr (−0.97 and −0.88, respectively) show that the contribution from the parallel \( \Lambda^3 \Pi_0 \leftarrow X^1 \Sigma^+ \) transition is about 1% (±1%) and 4% (±2%), respectively.

Whereas β-parameter measurements probe only the Franck–Condon region of an excitation, the measurement of photofragment alignment additionally probes the asymptotic region of the dissociative states. The two lowest \( \Omega = 1 \) molecular states of HCl and HBr, the \( \Lambda^1 \Pi_1 \) and \( \Lambda^3 \Pi_1 \) states, which are accessed via a perpendicular transition, correlate asymptotically to the atomic states \( |m_X, m_H\rangle \) as:

\[
| \pm 1 \rangle_{\Lambda^1 \Pi_1} \xrightarrow{r \to \infty} \frac{3}{2}, \mp 1 \rangle,
\]

(5a)

\[
| \pm 1 \rangle_{\Lambda^3 \Pi_1} \xrightarrow{r \to \infty} \frac{1}{2}, \pm 1 \rangle.
\]

(5b)

Eqs. (5a) and (5b) show that the \( \Lambda^3 \Pi_1 \) state correlates to Br and Cl atoms with \( m_\nu = \pm 1/2 \) only, whereas the \( \Lambda^1 \Pi_1 \) state correlates to Br and Cl atoms that populate the \( m_\nu = \pm 3/2 \) states only (see Fig. 3). The \( m_\nu \) state distributions of the Cl and Br atoms can be calculated from the experimentally measured values of the \( a_0^{(2)}(\perp) \) by [20, 21]:

\[
p(J = 3/2, m_\nu = \pm 3/2) = \frac{1}{2} \left[ 1 + \frac{5}{4} a_0^{(2)}(\perp) \right],
\]

(6a)

\[
p(J = 3/2, m_\nu = \pm 1/2) = \frac{1}{2} \left[ 1 - \frac{5}{4} a_0^{(2)}(\perp) \right],
\]

(6b)

which yield \( p(J = 3/2, m_\nu = \pm 1/2) = 0.94 \pm 0.13 \) for the Br photofragments, and \( p(J = 3/2, m_\nu = \pm 1/2) = 0.81 \pm 0.06 \) for the Cl photofragments (note that \( m_\nu \) denotes that the quantization
axis is the recoil direction, v, and that Eqs. (6a) and (6b) sum to unity, as expected. In addition, the $a_0^{(2)}(\perp)$ and $a_2^{(2)}(\perp)$ parameters can be expressed in terms of the nonadiabatic transition probabilities [35]:
\begin{align}
 a_0^{(2)}(\perp) &= +\frac{4}{5}(1 - 2p), \\
 a_2^{(2)}(\perp) &= -\frac{4\sqrt{2}}{5}\sqrt{p(1 - 2p)} \cos \Delta \phi, \\
 p &= \frac{p_1}{1 - p_2},
\end{align}

where $p_1$ is the probability of nonadiabatic transition from the $A^1\Pi_1$ to the $a^3\Pi_1$ state, and $p_2$ is the probability of nonadiabatic transition from the $A^1\Pi_1$ to the $^3\Sigma_1$ that produces spin–orbit excited Cl$(^3P_{1/2})$ or Br$(^3P_{1/2})$, and $\Delta \phi$ is the phase difference between the asymptotic wavefunctions correlating to the $A^1\Pi_1$ and $a^3\Pi_1$ states.

As both HBr and HCl are optically excited predominantly to the $A^1\Pi_1$ state at 193 nm, we see that for both HBr and HCl a large degree of nonadiabatic transfer occurs to the $a^3\Pi_1$ state. The probability $p_2$ is not measured in this study, but has been measured elsewhere to be $p_2 = 0.41$ for HCl [6] and $p_2 = 0.15$ for HBr [5,8] photodissociation. Using these values of $p_2$, our values for $a_0^{(2)}(\perp)$, and Eq. (7a), we determine that the probability of nonadiabatic transition from the $A^1\Pi_1$ to the $a^3\Pi_1$ state is $p_1 = 0.48 \pm 0.04$ for HCl, and $p_1 = 0.80 \pm 0.11$ for HBr. Notice that the value for adiabatic dissociation via the $A^1\Pi_1$ state, given by $(1 - p_1 - p_2)$, is $0.11 \pm 0.04$ for HCl and $0.05 \pm 0.11$ for HBr. For the photodissociation of HF, which as for HCl the spin–orbit constant of the halogen is relatively weak, the value of $p_1$ is calculated to be about 0.35 at similar dissociation energies [35], showing qualitative agreement for similar systems.

Finally, the measured values of the $a_0^{(2)}(\perp)$ parameter are consistent with the values $p$ determined above, and a value of $\Delta \phi \approx 0$. A small phase shift is expected as the nonadiabatic transfer occurs at long range, where the two potential energy surfaces are nearly degenerate and are far below the total energy (the phase shift is proportional to the energy splitting of the dissociative states, relative to the excess total energy).

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