Measurement of Br photofragment orientation and alignment from HBr photodissociation: Production of highly spin-polarized hydrogen atoms

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(Received 7 July 2004; accepted 27 July 2004)

The orientation and alignment of the $^2P_{3/2}$ and $^2P_{1/2}$ Br photofragments from the photodissociation of HBr is measured at 193 nm in terms of $a_q^{(k)}(p)$ parameters, using slice imaging. The $^1\Pi$ state is excited almost exclusively, and the measured $a_q^{(k)}(p)$ parameters and the spin-orbit branching ratio show that the dissociation proceeds predominantly via nonadiabatic transitions to the $^1\Sigma^+$ and $^3\Sigma^+$ states. Conservation of angular momentum shows that the electrons of the nascent H atom cofragments (recoiling parallel to the photolysis polarization) are highly spin polarized: about 100\% for the Br($^2P_{1/2}$) channel, and 86\% for the Br($^2P_{3/2}$) channel. A similar analysis is demonstrated for the photodissociation of HCl. © 2004 American Institute of Physics. [DOI: 10.1063/1.1794691]

I. INTRODUCTION

The measurement of photofragment angular momentum polarization, and the spatial decomposition of this polarization into coherent and incoherent contributions from multiple dissociative states, has intensified in recent years since the quantum mechanical treatment of Siebbeles et al.\textsuperscript{1–4} These contributions to the photofragment angular distributions can be expressed in terms of the $a_q^{(k)}(p)$ parameters,\textsuperscript{5} where $(p)$ denotes whether the contribution originates (coherently) from a dissociative transition that is parallel ($||$) or perpendicular ($\perp$), or (coherently) from the interference between parallel and perpendicular transitions ($||,\perp$). The measurement of each $a_q^{(k)}(p)$ parameter gives specific information about the dissociation process. Recently, for hydrogen halide photodissociation, Balint-Kurti et al.\textsuperscript{6} expressed $a_q^{(k)}(p)$ in terms of adiabatic and nonadiabatic-transfer probabilities, and in terms of phase shifts between asymptotic wave functions of dissociative states.\textsuperscript{6} Therefore, measurement of $a_q^{(k)}(p)$ allows the most complete understanding of the dissociation process, and detailed comparison with theory.

Polarized atoms and nuclei are used to study spin-dependent effects in atomic, molecular, nuclear, and surface collisions. The possibility of the production of highly polarized atoms from molecular photodissociation was suggested by van Brunt and Zare.\textsuperscript{7} The measurement of atomic photofragment polarization [such as the measurement of the complete set of $a_q^{(k)}(p)$ parameters] allows the identification of systems that yield highly polarized fragments. Strongly polarized atomic photofragments have been measured for O,\textsuperscript{8,9} S,\textsuperscript{10–12} Cl,\textsuperscript{13–16} Br,\textsuperscript{11,13} and H.\textsuperscript{12} The present study investigates the potential of HBr as a source of highly polarized H and Br photofragments.

Recently, the alignment parameters $a_q^{(2)}(\perp)$ and $a_q^{(2)}(\parallel)$ were measured for Br($^2P_{3/2}$) from the photodissociation of HBr at 193 nm using slice imaging,\textsuperscript{17,18} a variant of ion imaging,\textsuperscript{19} and velocity mapping.\textsuperscript{20} For HCl, it was shown that the H atom cofragments were strongly spin polarized, demonstrating that photodissociation can provide an intense source of spin-polarized hydrogen. The aim of this paper is to determine the Br($^2P_3/2$) and H cofragment polarization as well, and to include in the analysis the effects of the polarization parameters $a_q^{(k)}(p)$ with $k\leq3$ for the Br($^2P_{3/2}$) and Cl($^2P_{3/2}$) photofragments from the photodissociation of HBr and HCl at 193 nm. $a_q^{(k)}(p)$ can then be expressed in terms of dynamically significant variables such as nonadiabatic transition probabilities and asymptotic phase differences.\textsuperscript{8} From these expressions, we deduce the degree of polarization of the photofragments, and the nonadiabatic dissociation mechanisms.

II. THEORY

The spatial distribution of unpolarized photofragments about the linearly polarized photolysis direction light is given by the well-known expression.\textsuperscript{21}
where $\beta$ is the spatial anisotropy parameter, which, for prompt photodissociation of a diatomic molecule, ranges from $-1$ (for a pure perpendicular transition) to $+2$ (for a pure parallel transition), and $I_0$ is a constant. However, a more complicated expression is required for the description of the angular distribution of photofragments which have been detected in a fashion sensitive to angular momentum polarization of the fragments [such as resonantly enhanced multiphoton ionization or caser-induced fluorescence]. When the photolysis and probe polarization directions are parallel (for either linearly or circularly polarized light), and for $J \approx 3/2$, the photofragment angular distribution is given by:

$$I(\theta) = I_0[1 + \beta P_2(\cos \theta)],$$

(1)

where $I_0$, $\beta_2$, and $\beta_4$ are parameters that depend on $\beta$ and $a^{(k)}_q(p)$. The experiments reported in this paper deal with a single laser geometry, that with counterpropagating photolysis and probe lasers, which are both circularly polarized.

For the Br($^2P_{3/2}$) and Cl($^2P_{3/2}$) photofragments, $k$ is limited to $1$ (as $k \ll 2J$). In this case, $\beta_2 = 0$, and $I_0$ and $\beta_2$ expressed in terms of $\beta$, $a^{(1)}_0(\perp)$, and $\text{Re}[a^{(1)}_0(\perp, \perp)]$ by:\textsuperscript{22,23}

$$I_0 = 1 + \frac{s_1}{3} \left[ (1 - \beta/2) a^{(1)}_0(\perp) + \sqrt{2} \text{Re}[a^{(1)}_0(\perp, \perp)] \right],$$

(3)

$$\beta_2 = \frac{2s_1}{I_0} \left[ \frac{1}{3} (1 - \beta/2) a^{(1)}_0(\perp) - \frac{\sqrt{2}}{2} \text{Re}[a^{(1)}_0(\perp, \perp)] \right] - \beta/2,$$

(4)

where $s_1$ is the experimental sensitivity to the $k = 1$ parameters, which depends on the details of the detection transition (given in the Experimental section). The value of $\beta$ for both Br($^2P_{3/2}$) and Cl($^2P_{3/2}$) has been measured previously, therefore there are only two unknowns, $a^{(1)}_0(\perp)$ and $\text{Re}[a^{(1)}_0(\perp, \perp)]$. It is convenient to measure $I_0$ only as a relative quantity, such as the ratio of $I_0$ between the two polarization geometries $I_0[RL] / I_0[RR]$ (where the first $R$ indicates that the photolysis polarization is circularly polarized, and the second $R$ or $L$ indicates that the probe polarization is either right or left circularly polarized, respectively). This ratio is given by the ratio of Eq. (3), measured for the two geometries. Another equation can be generated by subtracted the $\beta_2$ values for these two geometries: $\Delta \beta_2 = \beta_2(\text{RL}) - \beta_2(\text{RR})$, using Eq. (4). These two equations can be solved for the two unknowns $a^{(1)}_0(\perp)$ and $\text{Re}[a^{(1)}_0(\perp, \perp)]$ in terms of the experimental observables $I_0[RL] / I_0[RR]$ and $\Delta \beta_2$.

For the Br($^2P_{3/2}$) and Cl($^2P_{3/2}$) photofragments, $k$ is limited to $3$, and now $I_0$, $\beta_2$, and $\beta_4$ are expressed in terms of $k = 2$ and $k = 3$ parameters as well. The complete inversion of all the $a^{(k)}_q(p)$ with $k \ll 3$ would require more detection geometries or detection transitions (beyond the one used here). However, in this particular case, the contribution of several parameters are negligible, so that approximations can be made to reduce the number of unknown parameters to be equal to the set of experimental observables.

The contributions from the $k = 2$ and $k = 3$ parameters will be significantly less than the $k = 1$ parameters, mainly because these parameters are reduced more by hyperfine depolarization (the $k = 1, 2$, and $3$ parameters are reduced by factors of 0.5, 0.27, and 0.02, respectively). Therefore, for a first approximation, the data for the ($^2P_{3/2}$) photofragments can be analyzed with the $k = 1$ parameters only, using Eqs. (3) and (4), as for the ($^2P_{1/2}$) photofragments. It will be interesting to compare this analysis to a more complete analysis including higher order $a^{(k)}_q(p)$ parameters.

We can express the ($^2P_{3/2}$) photofragment angular distributions in terms of the non-negligible (in this case) $k = 2$ and $k = 3$ $a^{(k)}_q(p)$ parameters:

$$I_0 = 1 + \frac{s_1}{3} \left[ (1 - \beta/2) a^{(1)}_0(\perp) + \sqrt{2} \text{Re}[a^{(1)}_0(\perp, \perp)] \right],$$

$$+ \frac{(1 - \beta/2) s_2}{15} \left[ a^{(2)}_1(\perp) - 2\sqrt{6} a^{(2)}_2(\perp) \right],$$

(5)

$$\beta_2 = \frac{1}{I_0} \left[ \frac{2s_1}{3} \left( (1 - \beta/2) a^{(1)}_0(\perp) - \frac{\sqrt{2}}{2} \text{Re}[a^{(1)}_0(\perp, \perp)] \right) \right.$$

$$+ \frac{4(1 - \beta/2) s_2}{21} \left( 4a^{(2)}_1(\perp) + \sqrt{6} a^{(2)}_2(\perp) \right) \left. \right] - \beta/2,$$

(6)

$$\beta_4 = \frac{1}{I_0} \left[ \frac{(1 - \beta/2) s_2}{35} \left( 6a^{(2)}_1(\perp) - 2\sqrt{6} a^{(2)}_2(\perp) \right) \right.$$ 

$$+ \frac{4s_3}{7} \left[ (1 - \beta/2) a^{(3)}_0(\perp) + \sqrt{3} \text{Re}[a^{(3)}_0(\perp, \perp)] \right].$$

(7)

The parameters $a^{(2)}_0(\perp)$ and $a^{(3)}_0(\perp)$ have been omitted from Eqs. (5)–(7) because their contribution to the experimental signals (for the experiments considered in this paper) can be neglected. The contribution of the $a^{(2)}_0(\parallel)$ parameter is weighted by $(1 + \beta)$; for both Cl and Br($^2P_{3/2}$) photofragments, $\beta = -1$, so that $(1 + \beta) = 0$ [the magnitude of the contribution of $a^{(2)}_0(\parallel)$ parameter is a few times smaller than the sensitivity of the experiment] and therefore $a^{(2)}_0(\parallel)$ can be neglected. The $a^{(3)}_0(\perp)$ parameter is proportional to $\sin \Delta \varphi A_\sigma$, where $\Delta \varphi A_\sigma$ is the asymptotic phase shift between the $A^1\Pi$ state and $a^3\Pi$ state ($\Omega = 0$ component). The phase shift was both measured\textsuperscript{11} and predicted\textsuperscript{24} to be approximately zero at this photodissociation wavelength; therefore, the contribution from the $a^{(3)}_0(\perp)$ parameter can also be neglected in this case. Furthermore, both $a^{(1)}_0(\perp)$ and $a^{(3)}_0(\perp)$ can be expressed in terms of nonadiabatic transition probabilities between the $A^1\Pi$ and $a^3\Pi$ states (see the Discussion section); these expressions allow, in this case, $a^{(3)}_0(\perp)$ to be related in terms of $a^{(1)}_0(\perp)$:
\begin{equation}
a_0^{(3)}(\perp) = \left[ \frac{4}{5} a_0^{(1)}(\perp) - \frac{2}{\sqrt{15}} \right].
\end{equation}

Using these approximations, we have reduced the number of unknown parameters to 3, the $a_0^{(1)}(\perp)$, Re$[a_1^{(1)}(\perp\perp)]$, and Re$[a_3^{(1)}(\perp\perp)]$. As with Eqs. (3) and (4) for the $^2P_{1/2}$ atoms, Eqs. (5)–(7) can be used to generate three new equations: $I_0[RL]/I_0[RR]$, $\Delta \beta_2$, and $\Delta \beta_4$. These three equations can be solved for the three unknowns.

III. EXPERIMENT

The apparatus has been described in detail elsewhere.\textsuperscript{14,25} Briefly, a 10 Hz pulsed molecular beam containing 5\% HBr or HCl in He is skimmed and collimated, and is intersected at right angles by two counterpropagating laser beams. The photolysis laser beam is generated by an ArF excimer laser (COMPEX, Lambda Physik); the linearly polarized Brewster reflection from a suprasil window is then circularly polarized with a quarter-wave plate, and is focused on the molecular beam ($f = 25\,\text{cm}$). The probe laser beam is generated by MOPO-SL (Spectra Physics 730DT10), and is also made circularly polarized using a quarter-wave plate. The Br($^2P_{3/2}$) and Br($^2P_{1/2}$) photofragments are ionized using the two-photon resonant transitions $5p(^2P_{1/2}) \rightarrow 4p(^2P_{3/2})$ at 250.41 nm and $5p(^2P_{1/2}) \rightarrow 4p(^2P_{1/2})$ at 263.12 nm, whereas the Cl($^2P_{3/2}$) and Cl($^2P_{1/2}$) photofragments are ionized at $4p(^2P_{1/2}) \rightarrow 3p(^2P_{3/2})$ at 234.62 nm and $4p(^2P_{1/2}) \rightarrow 3p(^2P_{1/2})$ at 236.51 nm, respectively.\textsuperscript{26–28}

For the ionsization of the $^3P_{3/2}$ photofragments, for right (upper sign) and left (lower sign) circularly polarized light, the $s_k$ are given by: $s_1 = + \sqrt{3/5}(1/2)$, $s_2 = + (5/4)(10/37)$, and $s_3 = \pm \sqrt{15/4}(1/5)$ (note that the long-time-limit hyperfine depolarization coefficients are included in these factors; 1/2 for $k = 1$, 10/37 for $k = 2$, and $1/5$ for $k = 3$).\textsuperscript{29} For the $^2P_{1/2}$ atoms, $s_1 = + \sqrt{3}(1/2)$ (which includes the depolarization coefficient of 1/2). Using the slice-imaging technique, 400 ns after the photofragment ionization, the extraction field is pulsed ON, and the Br$^+$ or Cl$^+$ 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 for slice-imaging velocity selection.\textsuperscript{14} Images appearing on the detector anode are recorded using a charged-coupled device camera (Cohu 4910, using EYESPY Software by k-Space Associates Inc.). Images are taken without Doppler scanning. Effects of Doppler selection are removed by normalizing the images with images taken with both photolysis and probe polarizations linear and perpendicular to the imaging plane.\textsuperscript{13}

IV. RESULTS

The Br($^2P_{3/2}$) and Br($^2P_{1/2}$) photofragment slice images are shown for the RR and RL polarization geometries in Fig. 1. The angular distributions (also shown in Fig. 1) are determined by integrating the signal within the full width at half maximum of the Br-photofragment slice-image radius as a function of $\theta$. The angular distributions are normalized with the corresponding ZZ angular distribution (for which both the photolysis and probe are linearly polarized parallel to the time-of-flight axis) and are then fit to Eq. (2).\textsuperscript{15} The slice images and angular distributions for Cl($^2P_{3/2}$) and Cl($^2P_{1/2}$) are shown elsewhere.\textsuperscript{12} The variations in $I_0$, $\beta_2$, and $\beta_4$ between the RL and RR geometries are given by $I_0[RL]/I_0[RR]$ and $\Delta \beta_2$, and $\Delta \beta_4$ are shown in Table I for both Br($^2P_{3/2}$) and Cl($^2P_{1/2}$).

The polarization of the Br($^2P_{1/2}$) photofragments is described by the $a_0^{(1)}(\perp)$ and Re$[a_1^{(1)}(\perp\perp)]$ parameters only because $k \leq 2J$, and is limited to 1 in this case. The values for the variations in intensity and angular distributions [given by $I_0[RL]/I_0[RR]$ and $\Delta \beta_2$ described in the Theory and Re-

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
 & Br($^2P_{3/2}$) & Br($^2P_{1/2}$) & Cl($^2P_{3/2}$) & Cl($^2P_{1/2}$) \\
\hline
$\Delta \beta_2$ & 0.63 & 0.20 & 0.97 & 0.33 \\
$\Delta \beta_4$ & $-0.23$ & $-0.03$ & $-0.11$ & 0.02 \\
$I_0[RL]/I_0[RR]$ & 1.6 & 1.75 & 1.4 & 1.8 \\
\hline
\end{tabular}
\end{table}

FIG. 1. (a) Br($^2P_{3/2}$) and Br($^2P_{1/2}$) photofragments slice images following the photolysis of HBr at 193 nm. The photolysis laser is right (R) circularly polarized, and the counterpropagating probe laser is right (R) or left (L) circularly polarized. These distinct polarization geometries are denoted RR and RL, respectively. (b) The Br($^2P_{3/2}$) and Br($^2P_{1/2}$) photofragment angular distributions calculated from the images shown in (a) (and described in the text).
TABLE II. Calculated polarization parameters for Br and Cl(2P_J), using the experimental data from Table I and Eqs. (3)–(7). Measurements of $\beta$, $a_0^{(1)} \times (\perp)$, and $a_2^{(2)} (\perp)$ are given from Ref. 11. Error bars are 2\%.

<table>
<thead>
<tr>
<th>$\beta$</th>
<th>$Br(2P_{3/2})$</th>
<th>$Br(2P_{1/2})$</th>
<th>$Cl(2P_{3/2})$</th>
<th>$Cl(2P_{1/2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0^{(1)} (\perp)$</td>
<td>$-0.85 \pm 0.10$</td>
<td>$-0.21 \pm 0.10$</td>
<td>$-0.97 \pm 0.06$</td>
<td>$-0.87 \pm 0.06$</td>
</tr>
<tr>
<td>$a_0^{(1)} (\perp)$</td>
<td>$+0.30 \pm 0.07$</td>
<td>$+0.55 \pm 0.16$</td>
<td>$+0.39 \pm 0.08$</td>
<td>$+0.60 \pm 0.10$</td>
</tr>
<tr>
<td>$Re[a_0^{(2)} (</td>
<td></td>
<td>)]$</td>
<td>$+0.09 \pm 0.08$</td>
<td>$+0.46 \pm 0.16$</td>
</tr>
<tr>
<td>$a_0^{(1)} (\perp)$</td>
<td>$-0.7 \pm 0.2$</td>
<td>$\cdots$</td>
<td>$-0.5 \pm 0.2$</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$a_2^{(2)} (\perp)$</td>
<td>$-0.3 \pm 0.2$</td>
<td>$\cdots$</td>
<td>$-0.45 \pm 0.2$</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$Re[a_2^{(2)} (</td>
<td></td>
<td>)]$</td>
<td>$-0.22 \pm 0.14$</td>
<td>$\cdots$</td>
</tr>
</tbody>
</table>

It is worth noting that if the $\langle 2P_{3/2}\rangle$ data is ignored analyzing the k = 2 and k = 3 parameters, using Eqs. (3) and (4), then, for $Br(2P_{3/2})$ $a_0^{(1)} (\perp) = 0.38$ and $Re[a_2^{(2)} (||)] = -0.04$, and for $Cl(2P_{3/2})$ $a_0^{(1)} (\perp) = 0.42$ and $Re[a_2^{(2)} (||)] = -0.13$. These numbers deviate less than 10% of the physical range of the parameters from the more complete analysis using k = 2 and k = 3 parameters as well. Therefore, it seems that the k = 1 parameters can be measured fairly accurately to a first approximation by ignoring the higher-order parameters in this case. However, this approximation is unlikely to hold in cases where the higher-order parameters are not reduced by hyperfine depolarization, such as in $O(1D)$ and $S(1D)$.

V. DISCUSSION

HBr is optically excited at 193 nm predominantly via the perpendicular transition $\Lambda^1\Pi \rightarrow X^1\Sigma^+$, and at this photodissociation wavelength the spatial anisotropy $\beta$ of the $Br(2P_{3/2})$ photofragments us close to the limiting value of $-1.11\rightarrow 33$. Here we use the value of $\beta=-0.88$ we have reported previously,\(^{11}\) which may indicate a small contribution of an $\Omega=0$ component to the excitation of about 4%. In contrast, the $a^3\Pi (\Omega=0\text{ component}) \rightarrow X^1\Sigma^+_0$ transition to the production of $Br(2P_{1/2})$ photofragments is about 25%. The phase difference between states $i$ and $j$ is denoted by $\Delta \varphi_{i,j}$. In terms of the phase shift between the $\alpha^3\Pi (\Omega=0\text{ component})$ state and the $1^3\Sigma^+_0$ state, $a^4_0(p)$ for the $\langle 2P_{1/2}\rangle$ atoms are given by

$$a_0^{(1)}(\perp) = \frac{1}{\sqrt{3}}.$$  

(9)

$$Re[a_2^{(2)} (||)] = \frac{2}{3\sqrt{3}} \sqrt{(1+\beta)(1-\beta/2)} \cos \Delta \varphi_{a0,3\Sigma}.$$  

(10)

We see from Fig. 1(a) that the measured values of the $a_0^{(1)} \times (\perp)$ and $Re[a_2^{(2)} (||)]$ parameters, for the $Br(2P_{1/2})$ photofragments, correspond, approximately, to the maximal physical range of these parameters. Therefore, the measured $a_0^{(1)}(\perp)$ is in agreement with Eq. (9), and the maximal value of $Re[a_2^{(2)} (||)]$ implies that $\cos \Delta \varphi_{a0,3\Sigma}$ is also approximately maximal.

The $\Omega$ components of the $\Lambda^1\Pi$ and $a^3\Pi$ states that participate in the dissociation, and yield $\langle 2P_{3/2}\rangle$ atoms, correlate asymptotically to the atomic states $|m_A,m_B\rangle$ as

$$|\pm 1\rangle_A \rightarrow \left| \frac{1}{2}, \pm \frac{3}{2}\right|.$$  

(11)

$$|\pm 1\rangle_a \rightarrow \left| \frac{1}{2}, \pm \frac{1}{2}\right|.$$  

(12)

$$|0\rangle_a \rightarrow \left| \frac{1}{2}, \pm \frac{1}{2}\right|.$$  

(13)

For the $\langle 2P_{3/2}\rangle$ atoms $a^4_0(p)$ are given by

FIG. 2. The measured $a^4_0(p)$ polarization parameters for the nascent $Br(2P_{3/2})$ and $Br(2P_{1/2})$ photofragments and the inferred nascent H-atom electron polarization $P_e$ from the photodissociation of HBr at 193 nm.
The electron polarization obtain 0.93

\[
\frac{p}{a_q} \approx 2
\]

state, only 6% dissociates adiabatically

Therefore, after excitation to the primary absorber, the recoil parallel to the photodissociation polarization direc-

\[\Delta \varphi_{A,a1} = 0.\]

The Re[\(a_1^{(1)}(\|,\perp)\)] parameter is small, and therefore we cannot separate the possibility that both the contributions from \(\Delta \varphi_{A,a0}\) and \(\Delta \varphi_{A,a1}\) are small [Eq. (15)], or that they are canceling each other.

The populations of the m states of the \(^5P_{3/2}\) photofrag-

\[p(J = 3/2, m_z = \pm 3/2) = \frac{1}{4} \left[1 + \frac{3}{\sqrt{15}} a_0^1(\perp) + \frac{5}{4} a_0^2(\perp) \pm \frac{\sqrt{15}}{2} a_0^3(\perp)\right].
\]

The electron polarization \(P_e\) of the nascent H atoms, also recoiling parallel to the photodissociation polarization direction, is given by the difference in population between the \(m = 1/2\) and \(m = 3/2\) states of the halogen \(^5P_{3/2}\) state:

\[P_e = -\frac{1}{4} \left[\frac{6}{\sqrt{15}} a_0^1(\perp) + \frac{5}{2} a_0^3(\perp) + 2 \sqrt{15} a_0^3(\perp)\right].
\]
28 NIST Atomic Spectra Database Levels Form, http://physics.nist.gov/cgi-bin/AtData/levels_form