Photodissociation of 2-Bromobutane at $\sim$265 nm by Ion-velocity Map Imaging Technique

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The photodissociation dynamics of 2-bromobutane has been investigated at 264.77 and 264.86 nm by ion-velocity map imaging technique coupled with resonance-enhanced multiphoton ionization. The speed and angular distributions have been derived from the velocity map images of Br and Br$^*$. The speed distributions of Br and Br$^*$ atoms in the photodissociation of 2-bromobutane at $\sim$265 nm can be fitted using only one Gaussian function indicating that bromine fragments were produced via direct dissociation of C−Br bond. The contributions of the excited $^3Q_0$, $^3Q_1$, and $^1Q_1$ states to the products (Br and Br$^*$) were discussed. It is found that the nonadiabatic $^1Q_1\leftrightarrow^3Q_0$ transition plays an important role for Br photofragment in the dissociation of 2-C$_4$H$_9$Br at $\sim$265 nm. Relative quantum yield of 0.621 for Br($^2P_{3/2}$) at $\sim$265 nm in the photodissociation of 2-bromobutane is derived.

By comparing the photodissociation of 2-C$_4$H$_9$Br at $\sim$265 nm and that at $\sim$234 nm, the anisotropy parameter $\beta$(Br) and $\beta$(Br$^*$), and relative quantum yield $\Phi$(Br) decrease with increasing wavelength, the probability of curve crossing between $^3Q_0$ and $^1Q_1$ decreases with increasing laser wavelength.

Key words: Ion-velocity imaging, Photodissociation, 2-Bromobutane

I. INTRODUCTION

The photodissociation of alkyl bromides in the A band has been extensively investigated in view of the ozone depletion potential of the halogen-containing radicals [1, 2]. The A band of methyl bromide (centered near 200 nm) arises from an $\sigma^*\leftrightarrow\pi$ transition localized on the C−Br bond, and this transition consists of overlapping transitions to three excited states $^3Q_1$, $^3Q_0$, and $^1Q_1$ in Mulliken’s notation [3], which are dipole allowed from a ground state of alkyl bromide. Due to the repulsive nature of the excited states, excitation in the A band could lead to the breaking of the C−Br bond, thereby forming an alkyl radical and the bromine atom in the ground state Br($^2P_{3/2}$) or in the excited state Br$^*$($^2P_{1/2}$). The $\sigma^*\leftrightarrow\pi$ transition is polarized parallel to C−Br bond. It is known that the $^3Q_0$ state, with the corresponding transition dipole moment aligned parallel to the C−Br bond, is correlated with the Br$^*$ product. The $^3Q_1$ and $^1Q_1$ states are correlated with the Br product [3], and the dipole moments are polarized perpendicular to the bond axis. Figure 1 shows the relations of the $^3Q_1$, $^3Q_0$, and $^1Q_1$ states [4].

In recent years, the time-sliced ion velocity imaging technique [5–7] combined with resonance-enhanced multiphoton ionization (REMPI) has been widely used to study the photodissociation of alkyl halides [8–22], such as CH$_3$Br [14], C$_2$H$_5$Br [15], iso-C$_3$H$_7$Br [16], n-C$_4$H$_9$Br [17], iso-C$_4$H$_9$Br [18], and tert-C$_4$H$_9$Br [18]. Following our recent study on the photolysis of 2-bromobutane at 233.62 and 233.95 nm ($\sim$234 nm) [23], the present work aims to study the photolysis of 2-bromobutane at 264.77 and 264.86 nm ($\sim$265 nm) using ion-velocity mapping imaging technique coupled with REMPI. With the aid of the speed and angular distribution of Br and Br$^*$ fragments measured from the map images at $\sim$265 nm, the photodissociation paths and the

FIG. 1 Schematic view of potential energy surfaces involved in 2-C$_4$H$_9$Br A band photodissociation [4].
contributions of the excited $^3Q_0$, $^3Q_1$, and $^1Q_1$ states to produce Br and Br$^*$ have been studied for 2-C$_4$H$_9$Br. By comparing the photodissociations of 2-C$_4$H$_9$Br at $\sim$265 and $\sim$234 nm, the dependence of the photolysis of 2-bromobutane on the excitation wavelength is investigated.

II. EXPERIMENTS

The experiments were performed in a home-built ion velocity imaging apparatus, details of which can be found elsewhere [24]. Briefly, sample gas seeded in He ($\sim$2.5%) at a stagnation pressure of $\sim$202 kPa was expanded through a pulsed nozzle (Series 9, General Valve) with an orifice diameter of 0.5 mm in a source chamber and skimmed to form a supersonically expanded molecular beam into a differentially pumped detection chamber. The operating pressures in the source and detection chambers were maintained at $\sim$133 and $\sim$26.7 $\mu$Pa, respectively. After passing through a 1 mm hole on the repeller plate, the molecular beam directed along the time-of-flight (TOF) axis was intersected at right angles by the laser beam in the detection zone. For all ion velocity imaging measurements, the electric vectors of both linearly polarized lasers were set perpendicular to the TOF axis and thus parallel to the front face of the microchannel plates (MCP’s) that form part of the ion detection system. The $\sim$265 nm laser is the output of a neodymium-doped yttrium aluminum garnet (Nd:YAG) (GCR-170, Spectra Physics) pumped dye laser (PrecisionScan, Sirah) and focused by an $f$=210 mm lens.

Br and Br$^*$ were probed at 264.77 and 264.86 nm (usually denoted $\sim$265 nm) via the $5p(4^2D_7/2)\leftarrow 4p^5(2^2P_{3/2})$ and $5p(2^2P_{3/2})\leftarrow 4p^5(2^2P_{1/2})$ transitions, respectively, using a (2+1) REMPI technology. Within a set of ion optics designed for the ion velocity imaging measurements, the Br$^+$ were accelerated by the focusing electric fields and projected onto a 40 mm-diameter Chevron-type dual MCP’s coupled to a P-47 phosphor screen (APD 3040FM, Burle Electro-Optics). A fast high-voltage switch (PVM-4210, DEI; typical duration $\sim$50 ns) was pulsed to gate the gain of the MCP’s for mass selection as well as the time slicing of the ion packet. The transient images from the phosphor screen were captured by a charge-coupled device (CCD) camera (Imager Compact QE 1376$\times$1024 pixels, LaVision) and transferred to a computer on an every shot basis for event counting [25] and data analysis. Timing of the pulsed nozzle, the laser, and the gate pulse applied on the MCP’s were controlled by a multichannel digital delay pulse generator (SRS, DG 535).

III. RESULTS

The raw images for Br and Br$^*$ produced by the photolysis of 2-bromobutane at 264.77 and 264.86 nm, respectively, are presented in Fig.2. The polarization axis of the photolysis laser is parallel to the detector. In Br and Br$^*$ images (see Fig.2), most of the intensity is at poles and very little intensity is along the equator.

The speed distribution of bromine, $P(v)$, as presented in Fig.3, can be obtained by integrating a three-dimensional speed distribution over all angles at each speed. The center-of-mass translational energy distribution $P(E)$ has been estimated from $P(v)$ as follows:

$$P(E) = P(v) \frac{dv}{dE}$$

The available energies for the photodissociation of 2-bromobutane can be calculated by the following re-
TABLE I Energy partitioning, anisotropy parameters $\beta$ in 2-C$_4$H$_9$Br+Br (Br$^*$) channel at $\sim$234 and $\sim$265 nm. Energies are in kJ/mol. The results at $\sim$234 nm are from Ref.[23].

<table>
<thead>
<tr>
<th>Wavelength/nm</th>
<th>Product</th>
<th>$h\nu$</th>
<th>$E_{avl}$</th>
<th>$\langle E_t \rangle$</th>
<th>$f_T$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>233.62</td>
<td>Br($^3P_{1/2}$)</td>
<td>512.1</td>
<td>212.1</td>
<td>83.2</td>
<td>0.39</td>
<td>1.55</td>
</tr>
<tr>
<td>233.95</td>
<td>Br($^3P_{1/2}$)</td>
<td>511.3</td>
<td>167.3</td>
<td>72.7</td>
<td>0.43</td>
<td>1.83</td>
</tr>
<tr>
<td>264.77</td>
<td>Br($^3P_{1/2}$)</td>
<td>451.7</td>
<td>151.7</td>
<td>54.0</td>
<td>0.36</td>
<td>0.65</td>
</tr>
<tr>
<td>264.86</td>
<td>Br$^*$($^3P_{1/2}$)</td>
<td>451.5</td>
<td>107.5</td>
<td>41.3</td>
<td>0.38</td>
<td>1.64</td>
</tr>
</tbody>
</table>

\[ E_{avl} = h\nu - D_0 - E_{el} + E_{int}^p = \langle E_t \rangle + \langle E_{int} \rangle \]

where $E_{avl}$ denotes the available energies, $h\nu$ is the photon energy, $D_0$ is dissociation energy of the C–Br bond (300 kJ/mol [26]), $E_{el}$ represents the electronic energy level of the atomic halogen (0 kJ/mol for Br and 44 kJ/mol for Br$^*$), the internal energy of 2-bromobutane $E_{int}^p$ is estimated to be zero since the rotational and vibrational excitations are negligible in a supersonic molecular beam, $\langle E_t \rangle$ denotes the average translational energy of fragments, and $\langle E_{int} \rangle$ presents the average internal energy of C$_4$H$_9$ radical. $\beta$ can be obtained by the following equation:

\[ \langle E_t \rangle = \frac{1}{2} \left( m_{Br} + \frac{m_{Br}^2}{m_{C_4H_9}} \right) v_{Br}^2 \]

where $m$ represents mass, $v$ denotes velocity. The value of $v_{Br}$ is derived from the fitting functions of speed distribution. The ratio of $\langle E_t \rangle$ to $E_{avl}$ is defined as:

\[ f_T = \frac{\langle E_t \rangle}{E_{avl}} \]

The values of $\langle E_t \rangle$ and $f_T$ are listed in Table I.

The branching ratio, $N(\text{Br}^*)/N(\text{Br})$, can be expressed by the following equation:

\[ \frac{N(\text{Br}^*)}{N(\text{Br})} = \frac{S(\text{Br}^*)}{S(\text{Br})} \]

where $N(\text{Br})$ and $N(\text{Br}^*)$ denote the numbers of Br and Br$^*$ fragment, $S(\text{Br})$ and $S(\text{Br}^*)$ are the measured mass spectrum signal intensities of species Br$^+$ at 264.77 and 264.86 nm, respectively. $k$ represents the proportional constant, which is a proportional factor related with the experimental setup and the relative REMPI intensities [27]. It can be derived by performing a calibration experiment on photolysis of Br$_2$ under the same condition. The $k$ value at $\sim$265 nm is determined to be 0.64. The ratio of $N(\text{Br}^*)/N(\text{Br})$ is found to be 0.61 at $\sim$265 nm.

The relative quantum yields, $\Phi(\text{Br})$ and $\Phi(\text{Br}^*)$, can be obtained from the product ratio employing the following relations:

\[ \Phi(\text{Br}^*) = \frac{N(\text{Br}^*)}{N(\text{Br}) + N(\text{Br}^*)} \]

\[ \Phi(\text{Br}) = 1 - \Phi(\text{Br}^*) \]

At $\sim$265 nm, the relative quantum yields, $\Phi(\text{Br})$ and $\Phi(\text{Br}^*)$, are determined to be 0.62 and 0.387, respectively.

Theangular distributions of the bromine fragments, $P(\theta)$, were extracted by integrating a three-dimensional velocity distribution over an appropriate range of speed at each angle. Figure 4 shows $P(\theta)$ of Br and Br$^*$ fragments from the photolysis of 2-C$_4$H$_9$Br at 264.77 and 264.86 nm, respectively. The parameter $\theta$ denotes the angle between the laser polarization and the recoil axis of the bromine fragments (C–Br$^*$). The anisotropy parameter $\beta$ can be estimated by the angular distribution which has been fitted into the standard formula:

\[ P(\theta) \propto 1 + \beta P_2(\cos\theta) \]

where $P_2(\cos\theta)$ denotes the second-order Legendre polynomial. The $\beta$ values of Br and Br$^*$ images are listed in Table I.

IV. DISCUSSION

As shown in Fig.3, for the photodissociation of 2-C$_4$H$_9$Br at $\sim$265 nm, all the speed distribution curves of Br and Br$^*$ can be fitted by a narrow single-peaked Gaussian curve except for the different center location. However, there is a little deviation between the measured signal and the Gaussian curve at $\sim$265 nm. This deviation may come from the noise in the experiment. Because of the weak absorption of 2-C$_4$H$_9$Br
at ∼265 nm, the pulse energy was increased to more than 0.6 mJ to obtain the images of Br and Br* in our experiment, which may lead to the strong noise. At ∼265 nm the speed distribution centers of Br and Br* are located at 749.5 and 655.3 m/s, respectively. It is well known that the appearance of single-peaked Gaussian curve often corresponds to the direct dissociation process via repulsive potential energy surface after absorption of one UV photon. The prompt dissociation can be explained reasonably by two models which have been proposed to present two radical limits [18, 28]. One is the rigid model which ignores vibrational excitation, the other is the soft model. For 2-C\textsubscript{4}H\textsubscript{8}Br, the rigid limit \( f_t \)=1, while the soft radical limit \( f_t \) is determined to be 0.31. In our experimental, for Br and Br* in the photodissociation of 2-C\textsubscript{4}H\textsubscript{8}Br at ∼265 nm, the values of \( \langle E_f \rangle / E_{av} \) are 0.36 and 0.38 (see Table I), respectively, which are much lower than the rigid limit and close to the soft radical limit.

The photolysis of 2-bromobutane at ∼234 nm has been investigated by ion-velocity map imaging technique coupled with RIMPI in our recent work [23]. At ∼234 nm the speed distributions of Br and Br* can be fitted with two Gaussian curves [23]. Moreover, the high-\( E_t \) Gaussian is related to the direct dissociation along the C–Br bond, and the low-\( E_t \) component to the dissociation from the repulsive mode with bending and C–Br stretching combination [23]. The high-\( E_t \) Gaussian of Br accounts for 66% of the sum of two Gaussian components [23]. In the present work, however, at ∼265 nm the speed distributions of Br and Br* can be fitted with only one Gaussian curve (high-\( E_t \) Gaussian) which are related to direct dissociation channels. It is found that the low-\( E_t \) component decreases with increasing wavelength. This situation is consistent with previous studies on the tert-C\textsubscript{4}H\textsubscript{8}Br [18]. For the photodissociation of tert-C\textsubscript{4}H\textsubscript{8}Br [18], when the wavelength increases from ∼234 nm to ∼265 nm, the relative contribution of low-\( E_t \) component in 2-C\textsubscript{4}H\textsubscript{8}+Br channel decreases from 0.25 to 0.18, the relative contribution of low-\( E_t \) component in 2-C\textsubscript{4}H\textsubscript{8}+Br* channel decreases from 0.19 to 0.15. In order to compare the photodissociation dynamics of 2-C\textsubscript{4}H\textsubscript{8}Br at different wavelengths, the corresponding results of the high-\( E_t \) components (values) for Br and Br* at ∼234 nm are also listed in Table I. From Table I, we could find that the total transitional energy and the available energy of the high-\( E_t \) component for Br and Br* decrease with increasing wavelength. It should be noted that in the following comparisons between ∼234 nm [23] and ∼265 nm (see Tables I and II), we only discuss the high-\( E_t \) components for Br and Br*.

The \( \beta \) values can be resolved into the relative contributions of the parallel and perpendicular components. The limit value of the parallel transition \( \beta_\parallel \) is equal to 2, while the limit value of the perpendicular transition \( \beta_\perp \) is equal to −1. The relative contributions of the parallel and perpendicular transitions can be calculated by the following equations:

\[
\beta = \chi_\parallel \beta_\parallel + \chi_\perp \beta_\perp \quad (9)
\]

\[
\chi_\parallel + \chi_\perp = 1 \quad (10)
\]

where \( \beta_\parallel = 2 \) and \( \beta_\perp = -1 \) denote the limit values for the pure parallel transition and the perpendicular transition, respectively. \( \chi_\parallel \) and \( \chi_\perp \) denote the fractions of parallel and perpendicular transition, respectively.

In the present work, for 2-C\textsubscript{4}H\textsubscript{8}Br in the photodissociation at ∼265 nm, the anisotropy parameter \( \beta \) for Br and Br* is 0.65 and 1.64, respectively. As listed in Table II, the \( \chi_\parallel \) values for Br and Br* fragments are 0.55 and 0.88, and the \( \chi_\perp \) values are 0.45 and 0.12, respectively. It is obvious that all \( \chi_\parallel \) values are much bigger than that of \( \chi_\perp \). This indicates that the molecular is mainly excited to the \( ^3Q_0 \) state by parallel transitions. \( ^3Q_0 \) state is correlated with Br*, while \( ^1Q_1 \) or \( ^3Q_1 \) state is correlated with Br through perpendicular transition [18]. However, the resultant relative quantum yield \( \Phi(\text{Br}) \) suggests that Br is the main product. Therefore, we expect that in this situation the nonadiabatic \( ^1Q_1 \leftrightarrow ^3Q_0 \) transition plays an important role for Br photofragment in the dissociation of 2-C\textsubscript{4}H\textsubscript{8}Br, i.e., the most Br atoms are from the initial excitation to \( ^3Q_0 \) state followed by the curve crossing from \( ^3Q_0 \) to \( ^1Q_1 \) surface. The relative fractions of individual pathways to produce Br and Br* can be determined using the following relations [18, 26]:

\[
\left( \Phi_{\text{Br}} \chi_{\text{Br}||} \Phi_{\text{Br}} \chi_{\text{Br}||} \right) = \left( \begin{array}{c} f(\tilde{Q}_0 \leftarrow Q_1) + f(Q_1) + f(Q_1) f(3Q_0) \end{array} \right) \quad (11)
\]

where \( \chi_{\text{Br}||} \) and \( \chi_{\text{Br}||} \) represent the portion of Br and Br* which come from parallel transitions, \( \chi_{\text{Br}||} \) and \( \chi_{\text{Br}||} \).
χ_{Br^+⊥} represent the portion of Br and Br^+ which come from perpendicular transitions. Φ_{Br} and Φ_{Br^+} are relative quantum yields listed in Table II. The probabilities of the nonadiabatic transitions f(1Q_1←3Q_0) and f(3Q_0←1Q_1) were determined to be 0.342 and 0.045, respectively.

The relative quantum yields, anisotropy parameters β, the proportion of parallel and perpendicular transitions, and contribution of each state to the product at ~234 nm from Ref.[23] are also tabulated in Table II. From Table II, we found that β(Br) and β(Br^+) decreased with increasing wavelength. Furthermore, the proportion of parallel transitions χ∥ decreased with increasing wavelength, while the proportion of perpendicular transitions χ⊥ increased with increasing wavelength. This indicates that the probability of 3Q_0←X parallel transitions decreases, while the probability of 3Q_1←X perpendicular transitions increases with increasing wavelength. The energy of the 1Q_1 potential surface is even higher than that of the 3Q_0 potential surface, therefore, the probability of 1Q_1←X transitions will decrease. The relative quantum yields could also prove this phenomenon. Because there is a conical intersection between 1Q_1 and 3Q_0 states, the Br fragment in the A-band could be produced via three pathways (1Q_1, 3Q_1 and a nonadiabatic transition from 3Q_0 to 1Q_1), while there are only two pathways (3Q_0 and a nonadiabatic transition from 1Q_1 to 3Q_0) for Br^+ fragment. All the possible pathways and the relative fractions of the individual pathways are also listed in Table II. Because the energy of the photons at ~234 nm is larger than that of the photons at ~265 nm, the probability of the 2-bromobutane to be excited to the 3Q_0 and 1Q_0 states at ~234 nm is higher than that at ~265 nm, while the probability of 2-bromobutane to be excited to the 1Q_1 state at ~234 nm is lower than that at ~265 nm. This is in good agreement with our results. As listed in Table II, the probability of 3Q_0 ←X transition at ~234 nm is higher than that at ~265 nm, the total amount of Br and Br^+ fragments from the 3Q_0 state and from the transition of the 3Q_0 state to the 1Q_1 state (f(3Q_0)+f(1Q_1←3Q_0)) at ~234 nm (0.856) is larger than that at ~265 nm (0.730). This is also proven by the change of the anisotropy parameter listed in Table II.

The curve crossing probabilities can be calculated by the following equations.

\[ P_{up} = \frac{f(1Q_1←3Q_0)}{f(3Q_0)+f(1Q_1←3Q_0)} \]  \hspace{1cm} (12)

\[ P_{down} = \frac{f(3Q_0←1Q_1)}{f(3Q_0←1Q_1)+f(1Q_1)} \]  \hspace{1cm} (13)

\[ \geq \frac{f(3Q_0←1Q_1)}{f(3Q_0←1Q_1)+f(1Q_1)+f(3Q_1)} \]  \hspace{1cm} (14)

where \( P_{up} \) denotes the up-crossing probability from 3Q_0 to 1Q_1 state, \( P_{down} \) represents the down-crossing probability from 1Q_1 to 3Q_0 state, and \( f(X) \) is the fraction originated from the X state. For the photodissociation of 2-C_3H_7Br at ~234 nm, the values of \( P_{up} = 0.917 \) and \( P_{down} = 0.043 \) are estimated, the values of \( P_{up} = 0.507 \) and \( P_{down} = 0.139 \) are determined at ~265 nm. The curve-crossing phenomenon in the photodissociation of alkyl halide in the A band were generally described using the Landau-Zener model [29]. The curve-crossing probability of 1Q_1←3Q_0 transition is the same as that of 3Q_0←1Q_1 transition, if the Landau-Zener model is valid. However, in the present work, the probability of curve crossing from the 3Q_0 to 1Q_1 surface is much larger than that of the reverse process (see Table II). This disagreement with the limit of the Landau-Zener model may be due to the difference between the shapes of the two-dimensional potential surfaces of 3Q_0 and 1Q_0 states. The Landau-Zener model is valid for diatomic molecules, however, it does not apply to polyatomic molecules due to its one-dimensional potential-surface model. From the probability of the curve crossing listed in Table II, one could find that \( f(1Q_1←3Q_0)+f(3Q_0←1Q_1) = 0.790 \) at ~234 nm is higher than 0.387 at ~265 nm. This indicates that the curve-crossing probability between the 3Q_0 and 1Q_0 surfaces decreases with the photolysis wavelength. Fortunately, the results in the present work are consistent with the results in previous works about C_3H_5BrCl [21] and C_2H_5Br [22].

V. CONCLUSION

Based on the photodissociation investigation of 2-bromobutane at 264.77 and 264.86 nm by ion-velocity map imaging technique, the speed distributions of Br and Br^+ atoms can be fitted using only one Gaussian function indicating that bromine fragments in this study were produced via direct dissociation of C–Br bond. The contributions of the excited 3Q_0, 3Q_1, and 1Q_1 states to the products (Br and Br^+) were estimated at ~265 nm. The anisotropy parameter of Br^+ (β(Br^+)=1.64) is very larger than that of Br (β(Br)=0.65) and close to the limit value of the parallel transition (βp=2) related with Br^+ fragment, while the relative quantum yield of Br (Φ(Br)=0.621) is larger than that of Br (Φ(Br)=0.379). This indicates that the nonadiabatic 1Q_1←3Q_0 transition plays an important role for Br photofragment in the dissociation of 2-C_3H_7Br at ~265 nm. This phenomenon could also be proven by comparing the changes of β and Φ between ~265 and ~234 nm [23]. The β(Br), β(Br^+), and Φ(Br) decrease with increasing wavelength, while Φ(Br^+) increases with increasing wavelength. We also find that the probability of curve crossing decreases with increasing laser wavelength in the photolysis of 2-bromobutane. The results obtained in the present work are also very consistent with the results in previous works about C_3H_5BrCl [21] and C_2H_5Br [22].
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