Dissociative ionization and Coulomb explosion of ethyl bromide under a near-infrared intense femtosecond laser field

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The multi-photon dissociation and Coulomb explosion of ethyl bromide C₂H₅Br under near-infrared (800 nm) femtosecond laser field are experimentally investigated by a DC-sliced ion imaging technique. The sliced images of fragment ions C₂H₅⁺, Br⁺, CH₃Br⁺, H₂⁺ and C₂H₅Br⁺ are obtained, and their dissociative pathways are assigned by observing their corresponding kinetic energy release (KER) and angular distribution. It is shown that low-KER components of these fragment ions result from multi-photon dissociation of singly charged parent ion C₂H₅Br⁺, while high-KER components come from Coulomb explosion of doubly charged parent ion C₂H₅Br₂⁺. It is also shown that the precursor species [C₂H₅H⁺…Br⁺] has a longer lifetime than [C₂H₅Br⁺…H₂⁺] and [CH₃…C₂H₅Br⁺]. In addition, the probable H₂ and H₂⁺ elimination channels are theoretically simulated by Gaussian 09 software packages, and the results show that the former is an asynchronous process while the latter is a synchronous process.

I. Introduction

When atoms or molecules are exposed to a femtosecond laser field with laser intensities in the range of 10¹³–10¹⁵ W cm⁻², this intense femtosecond laser field will modify the potential energy surface (PES) of the electronic state in the atomic or molecular systems, and thus a variety of novel physical phenomena will occur, such as multi-photon ionization (MPI),¹–⁴ above threshold ionization (ATI),⁵–⁶ high-order harmonic generation (HHG),⁷–⁸ Coulomb explosion (CE),⁹–¹² and so forth. On the basis of these related phenomena, one can obtain the atomic or molecular dynamical processes. Alkyl bromide C₂H₅Br was usually taken as study example in the field of molecular dynamics under the intense laser field, and its photodissociation behaviors have been regarded as the reference for understanding photodissociation dynamics of polyatomic molecules.¹³–¹⁵ In the photodissociation process of alkyl bromide, the dominant dissociation channel is C–Br bond fission to form an alkyl cation and a ground or spin–orbit excited state bromine atom,¹⁶–²⁸ and such observation has an important significance on the photochemical study of atmospheric bromine. Zhang et al. have experimentally studied the photodissociation dynamics of C–Br bond fission in a series of alkyl bromide by ultraviolet (UV) laser excitation,¹⁹,²¹–²³ and shown that fragments Br⁺ (³Pₛ₂) and Br (³Pₛ₂) can be attributed to the perpendicular transition to the ¹Q₁ and ³Q₁ states and the parallel transition to the ³Q₀ state. In addition to C–Br bond cleavage, Xu et al. have demonstrated other photodissociation pathways of ethyl bromide cation C₂H₅Br⁺ based on 355 nm laser excitation,²⁴ and concluded that both C₂H₅Br⁺ → C₂H₅⁺ + H₂ + Br and C₂H₅Br⁺ → C₂H₅⁺ + HBr channels are produced through multi-center intermediates according to the anisotropy parameter. Gardiner et al. also confirmed above two dissociation channels by 266 and 355 nm laser excitations,²⁰ and theoretically simulated the lowest thermochemical threshold of accessible photofragmentation pathways from ethyl bromide cation C₂H₅Br⁺, involving C–C, C–Br and C–H bond fissions.

In these previous studies, fragmentation dynamics of ethyl bromide by C–Br, C–C or C–H bond cleavage were usually performed by UV laser excitation, while studying them by near-infrared (IR) laser field was seldom reported. In this work, we present an investigation on the photodissociation process of ethyl bromide C₂H₅Br by 800 nm intense femtosecond laser field based on a DC sliced ion imaging technique. These fragment ions H₂⁺, CH₃⁺, C₂H₅⁺, Br⁺, CH₃Br⁺ and C₂H₅Br⁺ by C–C, C–Br and C–H bond fissions are observed, and low-KER components of these fragment ions are attributed to multi-photon dissociation (MPD) of singly charged parent ion C₂H₅Br⁺ while high-KER components are assigned to Coulomb explosion (CE) of doubly charged parent ion C₂H₅Br₂⁺. Furthermore, elimination channels of H₂ and H₂⁺ in MPD and CE processes are also experimentally observed, and the theoretical simulations show that the former is an asynchronous concerned process while the latter is a synchronous concerned process.

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II. Experimental arrangement

Our experimental setup of DC sliced ion imaging system has been described in our earlier publications, and here the simple statement is given. The multi-stage ion lens installed in the main chamber has the similar geometry designed by Suits et al. According to ion trajectory simulation by Simon 8.0 software, the voltages applied on these electrodes are set to be \( U_{\text{repeller}} = 2000 \text{ V}, U_1 = 1768 \text{ V}, U_2 = 1661 \text{ V} \) and \( U_3 = 0 \text{ V} \), respectively. The ethyl bromide vapor seeded in helium gas at a backing pressure of 0.3 atm is expanded into the source chamber through a pulsed valve with a repetition rate of 100 Hz, and the supersonic molecular beam is skimmed before entering the reaction chamber. The femtosecond laser outputted from a regenerative amplification laser system has the center wavelength of 800 nm, pulse width of about 72 fs and repetition rate of 1 kHz, and the linearly polarized femtosecond laser pulse is focused into the reaction area by a lens with the focal length of 400 mm. The ethyl bromide is ionized and dissociated by the femtosecond laser field in the reaction chamber. These fragment ions are accelerated by multi-stage ion lens velocity apparatus and detected by a pair of 77 mm micro-channel plates (MCP) coupled to a P47 phosphor screen, and finally the sliced images of the fragment ions are recorded by an intensified charge-coupled device (ICCD) camera. To identify the fragment ion species, the time-of-flight (TOF) mass spectra are measured by a photomultiplier tube connected to a digital oscilloscope. In this experiment, all the timing sequence is controlled by Stanford Instrument Digital Delay/Pulse Generation (DG535).

III. Results and discussion

Fig. 1 shows three typical TOF mass spectra of ethyl bromide \( \text{C}_2\text{H}_5\text{Br} \) with the laser intensities of \( 1.8 \times 10^{13} \) (a), \( 4.9 \times 10^{13} \) (b) and \( 1.5 \times 10^{14} \text{ W cm}^{-2} \) (c). In this experiment, all the timing sequence is measured by a photomultiplier tube connected to a digital oscilloscope. In this experiment, all the timing sequence is controlled by Stanford Instrument Digital Delay/Pulse Generation (DG535).
Thus, these fragment ions with low KER in Fig. 2 should result from the MPD process of singly parent ion C$_2$H$_5$Br+$^+$, and these corresponding MPD channels can be assigned as follows:

C–Br bond cleavage:

\[
C_2H_5Br \rightarrow Br^+ + C_2H_5^+ + e^- \quad (1)
\]
\[
C_2H_5Br \rightarrow Br^+ + C_2H_5 + e^- \quad (2)
\]

C–C bond cleavage:

\[
C_2H_5Br \rightarrow CH_3 + CH_2Br^+ + e^- \quad (3)
\]
\[
C_2H_5Br \rightarrow CH_3^+ + CH_2Br + e^- \quad (4)
\]

C–H bond cleavage:

\[
C_2H_5Br \rightarrow H_2^+ + C_2H_3Br + e^- \quad (5)
\]
\[
C_2H_5Br \rightarrow H_2^+ + C_2H_3Br + e^- \quad (6)
\]

Under the intense femtosecond laser field, the ethyl bromide can also be ionized to the multi-charged parent ions, and then dissociates into fragment ions with high KER by Coulomb repulsive force. As well known, in the two-body CE model, the two fragment ions produced by the two-body CE process should have a relationship as follows:

\[
\frac{KER(X^+)}{KER(Y^+)} = \frac{M(Y^+)}{M(X^+)} \quad (7)
\]

where X and Y denote the two fragment ions, M is mass of fragment ions, and p and q are charge numbers of the ions. According to eqn (7), the two fragment ions Br$^+$ (1.29 eV) and C$_2$H$_5^+$ (3.55 eV) can be attributed to the CE channel as follows:

\[
C_2H_5Br \rightarrow Br^+ + C_2H_5^+ + 2e^- \quad (8)
\]

Utilizing the same method, the two fragment ions CH$_3^+$ (3.85 eV) and CH$_2$Br$^+$ (0.59 eV) by C–C bond cleavage are also attributed to the following CE channel:

\[
C_2H_5Br \rightarrow CH_3^+ + CH_2Br^+ + 2e^- \quad (9)
\]

Similarly, the two fragment ions H$_2$ (8.79 eV) and C$_2$H$_3$Br$^+$ (0.16 eV) by C–H bond cleavage can be assigned to such a CE channel:

\[
C_2H_5Br \rightarrow H_2^+ + C_2H_3Br^+ + 2e^- \quad (10)
\]

To further investigate the CE process of doubly charged parent ion C$_2$H$_3$Br$_2^+$, the angular distributions of these fragment ions from DC sliced images in Fig. 2 are extracted, and the calculated results are shown in Fig. 3. These experimental data are theoretically fitted by Legendre polynomial function,

\[
I(\theta) = 1 + \sum_L a_L P_L(\cos^2 \theta) \quad (L = 2, 4, 6) \quad (11)
\]

where $\theta$ is the ejection angle of fragment ions measured from the laser polarization direction, which represents the instantaneous spatial distribution at the moment of CE process, $a_L$ is the Legendre expansion coefficient, and the expectation value $\langle \cos^2 \theta \rangle$ is the characterization of fragmentation anisotropy. The values of $a_L$ and $\langle \cos^2 \theta \rangle$ are summarized in Table 1. It is
As shown in eqn (5), (6) and (10), the elimination of H\textsubscript{2} or H\textsubscript{2}' is the most complicated dissociative process that includes two C–H bond fissions and H–H bond formation. To understand how the fragment H\textsubscript{2} or H\textsubscript{2}' is produced from the parent ion C\textsubscript{2}H\textsubscript{2}Br+ or C\textsubscript{2}H\textsubscript{2}Br\textsuperscript{2+}, the probable photodissociation pathways are theoretically simulated by Gaussian 09 software packages.\textsuperscript{35} The geometry of parent ions, transition states (TS) and dissociative products are optimized at the MP2 level with a 6-311+G(d,p) basis set. Meanwhile, the energies of related fragment ions are further refined by CCSD/6-311++G (d,p) with MP2 level zero-point energy corrections (ZPE). Fig. 4 shows the structure evolution during the formation of H\textsubscript{2} from the singly charged parent ion C\textsubscript{2}H\textsubscript{2}Br+. The dissociation pathways of H\textsubscript{2} elimination from the same C atom and two C atoms are both calculated at the same theoretical level, and it is found that the energy barrier of H\textsubscript{2} elimination from two C atoms is much higher than from the same C atom, and so here only the H\textsubscript{2} elimination from the same C atom is presented. As shown in Fig. 4, the optimized geometry of parent ion C\textsubscript{2}H\textsubscript{2}Br\textsuperscript{+} is with C–H bond lengths of 1.10 Å, \( \angle \text{H–C–H} = 109^\circ \) and H–H distance of 1.78 Å. The elimination of H\textsubscript{2} starts with the C–H bond stretch to form TS. In the TS structure, two C–H bond lengths are elongated asymmetrically to 1.78 Å and 1.55 Å, \( \angle \text{H–C–H} \) is quickly decreased to 26°, and the distance between two H atoms is reduced to 0.79 Å, which is much shorter than that of parent ion C\textsubscript{2}H\textsubscript{2}Br+. After surpassing TS with energy of 2.30 eV, the singly charged parent ion C\textsubscript{2}H\textsubscript{2}Br\textsuperscript{+} dissociates into two parts C\textsubscript{2}H\textsubscript{2}Br\textsuperscript{+} and H\textsubscript{2}. The values of the three main parameters \( \angle \text{H–C–H} \), two C–H bond lengths and H–H distance along reaction coordinates are listed in Table 2. As can be seen, \( \angle \text{H–C–H} \) is decreased, H–H distance is shortened, and the two C–H bond lengths are asymmetrically elongated due to the uneven distribution of surface charges in the two H atoms, which indicate that the C\textsubscript{2}H\textsubscript{2}Br \( \rightarrow \) H\textsubscript{2} + C\textsubscript{2}H\textsubscript{2}Br\textsuperscript{+} elimination channel is an asynchronous concerned dissociation.

The energy path of H\textsubscript{2}' elimination channel from doubly charged parent ion C\textsubscript{2}H\textsubscript{2}Br\textsuperscript{2+} is shown in Fig. 5. It is noted that

![Fig. 3](image_url) Angular distributions of fragment ions C\textsubscript{2}H\textsubscript{2}+ (a), Br\textsuperscript{+} (b), CH\textsubscript{3}+ (c) and CH\textsubscript{3}Br\textsuperscript{+} (d). The open circles (○) are experimental data and the solid lines (——) are the simulated results by Legendre polynomial function.

![Fig. 4](image_url) The dissociation pathway for H\textsubscript{2} elimination from the singly charged parent ion C\textsubscript{2}H\textsubscript{2}Br+, and here the theoretical simulation is performed at MP2/6-311++G (d,p) level.

<table>
<thead>
<tr>
<th>Channels</th>
<th>Ions</th>
<th>( a_2 )</th>
<th>( a_4 )</th>
<th>( a_6 )</th>
<th>( \langle \cos^2 \theta \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7)</td>
<td>C\textsubscript{2}H\textsubscript{2}+</td>
<td>0.46</td>
<td>0.15</td>
<td>0.07</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>Br\textsuperscript{+}</td>
<td>0.46</td>
<td>0.15</td>
<td>0.06</td>
<td>0.35</td>
</tr>
<tr>
<td>(8)</td>
<td>CH\textsubscript{3}+</td>
<td>0.59</td>
<td>0.10</td>
<td>0.03</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{3}Br\textsuperscript{+}</td>
<td>0.61</td>
<td>0.04</td>
<td>−0.05</td>
<td>0.40</td>
</tr>
<tr>
<td>(9)</td>
<td>H\textsubscript{2}'</td>
<td>0.59</td>
<td>−0.01</td>
<td>0.05</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>C\textsubscript{2}H\textsubscript{2}Br\textsuperscript{+}</td>
<td>0.61</td>
<td>0.04</td>
<td>−0.02</td>
<td>0.39</td>
</tr>
</tbody>
</table>

noted that the two fragment ions that come from the same CE channel show the similar expectation value \( \langle \cos^2 \theta \rangle \) (i.e., fragmentation anisotropy), which can further confirm above photodissociation channel assignments in the CE process.

As known to all, when the short-lived precursor specie rotates as a whole in the space, its corresponding fragment ions will have stronger angular anisotropy. In Table 1, the leading expansion coefficient \( a_2 \) is an important anisotropy parameter, which characterizes the lifetime of the precursor specie state, and the precursor specie with the longer lifetime will induce the smaller \( a_2 \) value of the fragment ions.\textsuperscript{33–35} In our experiment, the \( a_2 \) value by C–Br bond fission is determined to be \( a_2 = 0.46 \), which is smaller than that by C–C bond fission (\( a_2 = 0.61 \)) as well as C–H bond fission (\( a_2 = 0.61 \)). That is to say, the precursor specie \( [\text{C}_2\text{H}_2\text{Br}^-...\text{H}_2]^- \) has the longer lifetime than \( [\text{C}_2\text{H}_2\text{Br}^-...\text{H}_2]^- \) and \( [\text{CH}_3...\text{CH}_2\text{Br}]^- \). This means that the precursor specie \( [\text{C}_2\text{H}_2\text{Br}^-...\text{Br}]^- \) is prepared in a deeper well of potential energy surface, and dissociates into the fragment ions C\textsubscript{2}H\textsubscript{2}+ and Br\textsuperscript{+} by Coulomb repulsive force following by the C–Br bond stretch.
the optimized geometry of C\textsubscript{2}H\textsubscript{5}Br\textsuperscript{2+} is quite different from the structure of C\textsubscript{2}H\textsubscript{5}Br\textsuperscript{+}. The two C–H bonds are stretched to 1.37 Å, which are increased by 0.27 Å comparing with C\textsubscript{2}H\textsubscript{5}Br\textsuperscript{+}. Meanwhile, the distance between two H atoms is much closer, only 0.87 Å, which is almost half of the stable structure of C\textsubscript{2}H\textsubscript{5}Br\textsuperscript{+}. Such an observation indicates that Coulomb repulsive force will greatly change the molecular structure when the two electrons are stripped off under the intense femtosecond laser field. The elimination of \textsuperscript{2}H\textsuperscript{+} also starts with the C–H bond stretch. In the TS structure, \(\angle \text{H–C–H}\) is decreased from 37\(^{\circ}\) to 26\(^{\circ}\), the two C–H bond lengths are symmetrically elongated to 1.61 Å, and H–H distance is reduced to 0.81 Å. After surpassing TS, the doubly charged parent ion C\textsubscript{2}H\textsubscript{5}Br\textsuperscript{2+} dissociates into the fragment ions \textsuperscript{2}H\textsuperscript{+} and C\textsubscript{2}H\textsubscript{5}Br\textsuperscript{+}. It is noticeable that the energy of TS is lower (0.03 eV) than that of the doubly charged parent ion C\textsubscript{2}H\textsubscript{5}Br\textsuperscript{2+}, and this phenomenon has been demonstrated in previous studies.\textsuperscript{37,38} That is to say, the doubly charged parent ion C\textsubscript{2}H\textsubscript{5}Br\textsuperscript{2+} is trapped in a very shallow quasi-bound well of the potential energy surface, and can produce a barrierless reaction process. This conclusion can also be confirmed by the experimental observation that no doubly charged parent ion C\textsubscript{2}H\textsubscript{5}Br\textsuperscript{2+} is observed in the full range of laser intensity. The values of the three main parameters \(\angle \text{H–C–H}\), two C–H bond lengths and H–H distance are listed in Table 3. It is noted that the two C–H bonds are simultaneously broken and H–H bond is simultaneously formed, which shows that \textsuperscript{2}H\textsuperscript{+} elimination from the doubly charged parent ion C\textsubscript{2}H\textsubscript{5}Br\textsuperscript{2+} is a synchronous concerned process.

IV. Conclusions

In summary, we have experimentally and theoretically studied the photodissociation process of ethyl bromide C\textsubscript{2}H\textsubscript{5}Br under the near-IR (800 nm) intense femtosecond laser field by the DC-slice imaging technique. These fragment ions C\textsubscript{2}H\textsubscript{5}\textsuperscript{+}, Br\textsuperscript{+}, CH\textsubscript{3}\textsuperscript{+}, CH\textsubscript{2}Br\textsuperscript{+}, H\textsuperscript{2+} and C\textsubscript{2}H\textsubscript{5}Br\textsuperscript{+} by C–C, C–Br and C–H bond fissions were measured and their corresponding KER and angular distributions were calculated. We confirmed that these fragment ions with low KER are attributed to the MPD process of singly charged parent ion C\textsubscript{2}H\textsubscript{5}Br\textsuperscript{+}, while those components with high KER result from doubly charged parent ion C\textsubscript{2}H\textsubscript{5}Br\textsuperscript{2+} via the CE process. The angular anisotropy of the fragment ions by the CE process suggested that the precursor specie [C\textsubscript{2}H\textsubscript{5}...Br\textsuperscript{+}] has a longer lifetime than [C\textsubscript{2}H\textsubscript{5}Br\textsuperscript{+}...H\textsuperscript{2+}] and [CH\textsubscript{3}...CH\textsubscript{2}Br\textsuperscript{+}]. Moreover, the elimination channels of H\textsubscript{2} and H\textsuperscript{2+} were observed, and \textit{ab initio} calculations showed that H\textsubscript{2} elimination is an asynchronous concerned reaction while H\textsuperscript{2+} elimination is a synchronous concerned reaction.

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