Article

Dissociative Ionization of the CHBr₂Cl Molecule in 800 nm and 400 nm Femtosecond Laser Fields

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Abstract: The dissociative ionization of CHBr₂Cl molecules in femtosecond laser fields at 800 nm and 400 nm is investigated to enhance the comprehension of ultrafast dynamics phenomena. The kinetic energy distribution of the resulting ions following photo-dissociation is analyzed using time-of-flight mass spectrometry in combination with DC-sliced ion velocity map imaging. The findings from the experimental study indicate that the presence of low kinetic energy components is attributed to the dissociative ionization processes of CHBr₂Cl molecules. The complexity of individual dissociation pathways remains unaffected by the laser fields but is determined by factors such as bond energy, ionization energy of neutral groups, and charge distribution. In the case of 400 nm laser fields, distinct elimination channels enable CHBr₂Cl⁺ ions to circumvent the transition state, leading to the formation of BrCl⁺ and Br₂⁺ fragments.

Keywords: femtosecond laser field; dissociative ionization; elimination process

1. Introduction

The advancement of ultrafast laser technologies has transformed the laser into a potent instrument for investigating the rapid dissociation dynamics of molecules [1–5]. When a laser interacts with matter, ionization emerges as the predominant physical phenomenon. At sufficiently high laser intensities, molecules can undergo electron loss via multiphoton and above-threshold ionization (MPI/ATI), even when the energy of a single photon is lower than the ionization potential (IP). The interaction of the laser field with the molecular structure alters the potential barrier, thereby influencing the Coulomb potential between the molecular nucleus and the valence electron as the laser intensity escalates. The valence electron can surmount the barrier and transition to a continuum state through tunneling ionization (TI). As the laser intensity further rises, the energy barrier of the bound state can be completely suppressed below the energy level of the valence electron, facilitating the easy removal of the valence electron from the molecular system, a process known as over-the-barrier ionization (OTBI). Ionization is typically the initial step preceding dissociation processes, which may take hundreds of femtoseconds or even as much as a picosecond to occur. Consequently, ionization precedes the onset of dissociation in the femtosecond laser field, a phenomenon referred to as dissociative ionization (DI). In the presence of a femtosecond laser field with an intensity exceeding 10¹⁴ W/cm², multi-electron dissociative ionization can occur, leading to the rupture of chemical bonds within molecules due to the internal Coulomb repulsive energy of the multi-charged parent ions, a phenomenon termed Coulomb Explosion (CE) [6–9].

The photo-dissociation of halogenated hydrocarbons has been the subject of numerous investigations over the past few decades. Ibuki et al. measured the photo-absorption and fluorescence excitation spectra of CHBr₂Cl in the 106–200 nm region using synchrotron radiation. The CHCl radical was observed, and the lifetime of the excited state was first determined to be 7.01 ± 0.25 µs [10]. Zheng et al. have reported the transient resonance
Raman spectra for the photoproducts produced after the ultraviolet excitation of CHBr$_2$Cl in a cyclohexane solution. The transient resonance Raman spectrum observed following ultraviolet excitation was primarily attributable to the iso-CHBrCl–Br and iso-CHClBr–Br species, according to their findings [11]. Yang et al. have revealed the principal direct estimations of the transitional items in the multiphoton photo-dissociation response of CHBr$_2$Cl at 266 nm. The multiphoton photo-dissociation mechanism was confirmed based on these results [12]. Muthiah et al. have utilized cavity ring-down absorption spectroscopy (CRDS) to investigate the photo-dissociation of CHBr$_2$Cl at 248 nm. The photo-dissociation of CHBr$_2$Cl mainly produces Br$_2$ fragments, and the production of BrCl is limited by the high transition state energy barrier, which makes its experimental detection difficult [13].

While UV nanosecond laser fields are commonly used in halogenated hydrocarbon studies, limited attention has been given to ultraviolet femtosecond laser fields generated through second harmonic production of 800 nm laser fields. Halogenated hydrocarbons, characterized by easy dissociation in UV laser beams and low ionization energy, may ionize and fragment into smaller particles under weak UV femtosecond lasers. Hence, the examination of the dissociative ionization process of halogenated hydrocarbons under femtosecond laser fields at wavelengths of 800 and 400 nm, corresponding to single photon energies of 1.55 and 3.10 eV, respectively, has the potential to reveal the rapid dynamics of CHBr$_2$Cl molecules.

In this study, we investigated the dissociative ionization process of the CHBr$_2$Cl molecule under femtosecond laser fields with wavelengths of 800 nm and 400 nm. We analyzed the kinetic energy distribution of the photo-dissociation product ions. The results suggest that CHBr$_2$Cl molecules can undergo single ionization and dissociate into fragment ions with low kinetic energy. The ionization energy of the fragments influences the charge distribution of the parent ions, thereby affecting the emergence of the dissociation channel. Furthermore, a specific route observed under the 400 nm laser field allows the molecular ion to bypass the transition state, facilitating bond cleavage and the production of BrCl$^+$ and Br$_2$$^+$ ions.

2. Materials and Methods

The experimental setup utilized in the study is described in more detail in previous literature [14,15]. In brief, femtosecond laser pulses from Spectra-Physics were employed, featuring a central wavelength of 800 nm, a repetition rate of 1 kHz, and a pulse duration of 100 fs. These pulses were focused into the reaction chamber using a 400 mm lens. A pulsed valve from General Valve, Parker, operating at a repetition rate of 100 Hz and a duration of 130 µs, was utilized to introduce a gaseous sample of CHBr$_2$Cl seeded with argon (1:10) into the reaction chamber at a pressure of 5.0 $\times$ 10$^{-9}$ mbar. The interaction between the supersonic molecular beam and the femtosecond pulse occurred at the center of the ion lens’s repeller and extractor plates. Detection of the fragment ion cloud was achieved using micro-channel plates, a phosphor screen, and a mapping lens, with the resulting time-of-flight (TOF) mass spectra recorded by a photomultiplier tube (H7732-11, Hamamatsu, Shizuoka, Japan) connected to a digital oscilloscope (LeCroy Wave Pro). Momentum images were captured using a charge-coupled device camera (PI-MAXII, Princeton Instrument, Trenton, NJ, USA) with a time resolution of 5 ns. The laser’s polarization vector was oriented perpendicular to the ion flight direction. The intensity within the reaction region was calibrated by the Ar$^{2+}$/Ar$^+$ yield ratio [16]. A digital delay/pulse generator (DG645, Stanford Instrument, Sunnyvale, CA, USA) was employed for precise timing sequence control.

The dissociative ionization process was verified using Gaussian 16 software [17]. Optimization of fragment geometries and calculation of zero-point correction (ZPE) at the B3LYP level were performed with a 6-31G* basis set [18,19]. Single-point energies were computed using the CCSD(T) method with the cc-pVTZ basis set [20,21]. Vibrational frequencies were calculated to validate transition states, and the intrinsic reaction coordinate
3. Results

The time-of-flight (TOF) mass spectrum of the CHBr₂Cl molecule under femtosecond laser irradiation at 800 nm and 400 nm, with intensities of $1.0 \times 10^{14}$ and $4 \times 10^{13}$ W/cm², respectively, is depicted in Figure 1. The abundance of Br⁺ ions in each spectrum is standardized to one. The experimental results reveal the predominant formation of CH⁺, CHCl⁺, Br⁺, CHBr⁺, CHBrCl⁺, and CHBr₂⁺ ions. Notably, Figure 1a exclusively displays the ion CHBrCl₂⁺, potentially attributed to the elevated intensity of the 800 nm laser fields at $2.5 \times 10^{14}$ W/cm². The generation of fragment ions may be attributed to multi-electron dissociative ionization of the parent molecules. Figure 1b illustrates the parent ion CHBr₂Cl⁺ alongside the fragment ions BrCl⁺ and Br₂⁺, indicating the occurrence of distinct reaction pathways, which will be elaborated upon in subsequent sections.

![Figure 1](image-url)

Figure 1. The time-of-flight mass spectrum of the molecule CHBr₂Cl irradiated by (a) $1.0 \times 10^{14}$ W/cm², 800 nm, and (b) $4 \times 10^{13}$ W/cm², 400 nm laser fields, respectively.

In addition to identifying the ion species, interesting discoveries about ion yields can also be made by further exploration of time-of-flight mass spectra. It is generally believed that in the femtosecond laser action to the molecular system, when the laser
intensity is low, the main occurrence of multiphoton ionization produces low valence state molecular ions, and then dissociates to produce fragment ions, while the laser intensity enhancement will occur in the field ionization, then produce high valence molecular ions and then the Coulomb explosion. As depicted in Figure 2, at lower intensities in both 800 nm and 400 nm laser fields, the yields of product fragment ions are relatively low and comparable. However, as laser intensity escalates, discernible differences in yield growth emerge, particularly with the most rapid increases observed in Br and Cl ions. The ion yields resulting from dissociation pathways involving the C–Br bond are observed to be greater than those involving the C–Cl bond. This observation indicates that the dissociation process is not significantly influenced by the laser wavelength but is likely influenced by the energy of the molecular bond, which will be analyzed in detail in the next section.

![Figure 2](image_url)

**Figure 2.** The yield of product fragment ions varies with laser power at (a) 800 nm, and (b) 400 nm laser fields, respectively.

In addition to analyzing time-of-flight mass spectra, the investigation extends to the examination of kinetic energy release (KER) of fragment ions under varying laser conditions. Figure 3 displays the normalized velocity distribution of fragment ions along with the DC-sliced images. The red curve corresponds to data obtained using an 800 nm laser field, while the blue curve represents data acquired with a 400 nm laser field. The velocity distribution exhibits a multi-peaked structure for some of the fragments, indicating the existence of multiple reaction pathways. Typically, the low kinetic energy component of the fragments results from the dissociation of single-charged parent ions, whereas the high kinetic energy component is attributed to the Coulomb explosion process of multi-charged parent ions. Notably, it has been observed to reduce the yields of the heavy fragments CHCl+, CHBr+, CHBrCl+, and CHBr₂⁺ with high KER in the 400 nm laser filed. This reduction is linked to the limited laser intensity of up to 4 × 10¹³ W/cm² in 400 nm laser fields, rendering the Coulomb explosion effect negligible. The high kinetic energy component observed in the Br⁻ ion data in Figure 3(c') is proposed to stem from a sequential dissociation process rather than a Coulomb explosion, as no corresponding ion with a high kinetic energy component has been identified. Additionally, fragments of BrCl⁺ and Br₂⁺ ions have only been detected in Figure 3(g',h') when irradiated by 400 nm laser fields.
1.0 \times 10^{14} \text{ W/cm}^2@800 \text{ nm} \\
4 \times 10^{13} \text{ W/cm}^2@400 \text{ nm}

**Cl^+**

**CHCl^+**

**Br^+**

**CHBr^+**

Figure 3. Cont.
Figure 3. The normalized velocity distribution of the fragment ions, (a) Cl⁺, (b) CHCl⁺, (c) Br⁺, (d) CHBr⁺, (e) CHBrCl⁺, (f) CHBr₂⁺ in 800 nm laser fields and (a’) Cl⁺, (b’) CHCl⁺, (c’) Br⁺, (d’) CHBr⁺, (e’) CHBrCl⁺, (f’) CHBr₂⁺, (g’) BrCl⁺, and (h’) Br₂⁺ in 400 nm laser fields, respectively. The circle represents the experiment data, the green dashed lines represent the fitting peaks, and the red and blue solid lines represent the simulated distribution in 800 nm and 400 nm laser fields, respectively. The peak values of the correlating kinetic energy release (KER) are labeled in eV. The right inset shows the DC-sliced image of the corresponding fragment ions, and the double arrows show the direction of laser polarization.
4. Discussion

4.1. Dissociation of Single-Charged Parent Ion CHBr\(_2\)Cl\(^+\) in 800 and 400 nm Femtosecond Laser Fields

Given the 100 femtosecond (full width at half maximum) duration of our laser pulse, it is reasonable to expect that the CHBr\(_2\)Cl molecule will undergo ionization to form a molecular ion, followed by the subsequent fragmentation of the molecular ion as its bonds are broken. This section will concentrate on the dissociative ionization mechanisms, specifically the disintegration of the singly charged parent ion CHBr\(_2\)Cl\(^+\) under 800 and 400 nm femtosecond laser fields. The dissociative process results in the creation of two components: a neutral fragment and ions. Therefore, the potential pathways for fragment ion dissociation in both laser fields are delineated. It is important to note that the initial four pathways mentioned involve the cleavage of a single chemical bond. Channels (1) and (2) involve the rupture of a C–Cl bond, with the positive charge being attributed to either the CHBr\(_2^+\) or Cl\(^+\) fragment. Channels (3) and (4) entail the breaking of a C–Br bond, with the positive charge being assigned to either the CHClBr\(^+\) or Br\(^+\) fragment. The final two pathways mentioned involve dissociation across multiple chemical bonds. Channel (5) involves the cleavage of a C–Br bond and a C–Cl bond, assigning the positive charge to the CHBr\(^+\) fragment. Channel (6) involves the breaking of two C–Br bonds, with the positive charge being assigned to the CHCl\(^+\) fragment.

\[
\begin{align*}
\text{CHBr}_2\text{Cl}^+ & \rightarrow \text{Cl}^+ + \text{CHBr}_2 \\
\text{CHBr}_2\text{Cl}^+ & \rightarrow \text{CHBr}_2^+ + \text{Cl} \\
\text{CHBr}_2\text{Cl}^+ & \rightarrow \text{Br}^+ + \text{CHBrCl} \\
\text{CHBr}_2\text{Cl}^+ & \rightarrow \text{CHBrCl}^+ + \text{Br} \\
\text{CHBr}_2\text{Cl}^+ & \rightarrow \text{CHBr}^+ + \text{Br}^+ \text{Cl} \\
\text{CHBr}_2\text{Cl}^+ & \rightarrow \text{CHCl}^+ + 2\text{Br}
\end{align*}
\]

For the problem in the previous section, we performed some calculations to explain. Initially, the geometry of the CHBr\(_2\)Cl molecule in its ground state was optimized. Subsequently, one electron was removed, and the structure was re-optimized to generate the ground-state CHBr\(_2\)Cl\(^+\) ions. The vibrational frequency was then determined. The compliance constant matrix was derived using a compliance program [22]. A chemical bond is deemed weaker if the diagonal element in the compliance constant matrix has a higher value. Consequently, the reciprocals of these diagonal elements, referred to as relaxed force constants, can serve as indicators of bond strength. As indicated in Table 1, the C–Cl bond in CHBr\(_2\)Cl\(^+\) is notably stronger than the C–Br bond. Thus, the primary dissociation reactions predominantly entail the cleavage of the C–Br bond.

**Table 1.** The compliance matrix element and relaxed force constant of the singly charged ion CHBr\(_2\)Cl\(^+\), calculated at the B3LYP/6-31G* level.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Compliance Matrix Diagonal Element</th>
<th>Relaxed Force Constant (mdyn/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H</td>
<td>0.18</td>
<td>5.56</td>
</tr>
<tr>
<td>C–Cl</td>
<td>0.28</td>
<td>3.57</td>
</tr>
<tr>
<td>C–Br(1)</td>
<td>0.71</td>
<td>1.41</td>
</tr>
<tr>
<td>C–Br(2)</td>
<td>0.71</td>
<td>1.41</td>
</tr>
</tbody>
</table>

In order to investigate the dissociation processes more effectively, the Gaussian 16 software package was employed to calculate all six channels. For simplification in the analysis, the ground state of the CHBr\(_2\)Cl molecule was designated as the zero-energy reference point. Consequently, the appearance energies of the dissociation channels were determined.
as the energy differences between the fragments and the CHBr$_2$Cl molecule. The energy values associated with the dissociation pathways are presented in Table 2, with detailed explanations of appearance energy and available energy provided in reference [4]. It is evident that all KER values of the fragment ions are lower than the calculated available energy, indicating that the fragment ions with low-KER components are likely products of the dissociation processes of the singly charged molecular ions CHBr$_2$Cl$^+$. The kinetic energy released by fragment ions, the appearance energy, and the available energy of the corresponding channel.

<table>
<thead>
<tr>
<th>Channel</th>
<th>$E_{\text{appear}}$ (eV)</th>
<th>KER (eV)</th>
<th>$E_{\text{avail}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>800 nm</td>
<td>400 nm</td>
<td>800 nm</td>
</tr>
<tr>
<td>(1)</td>
<td>17.58</td>
<td>0.27</td>
<td>0.05</td>
</tr>
<tr>
<td>(2)</td>
<td>11.32</td>
<td>0.11</td>
<td>0.08</td>
</tr>
<tr>
<td>(3)</td>
<td>15.67</td>
<td>0.26</td>
<td>0.18</td>
</tr>
<tr>
<td>(4)</td>
<td>10.77</td>
<td>0.17</td>
<td>0.05</td>
</tr>
<tr>
<td>(5)</td>
<td>15.24</td>
<td>0.21</td>
<td>0.12</td>
</tr>
<tr>
<td>(6)</td>
<td>14.74</td>
<td>0.25</td>
<td>0.14</td>
</tr>
</tbody>
</table>

The appearance energy in Table 2 indicates a noticeable disparity between channels (1) and (2), as well as between channels (3) and (4). This difference may be attributed to variations in charge distribution among the groups and discrepancies in ionization energy levels among the neutral groups. Gaussian 16 was utilized to examine the natural bond orbital (NBO) charge distribution of CHBr$_2$Cl$^+$ ions, as illustrated in Figure 4. The positive charge is distributed between the Cl atom and the CHBr$_2$ group, with charges of +0.228 and +0.772, respectively. In the event of the C–Cl bond breaking, either Cl or CHBr$_2$ will release the “extra electron” to form channel (1) or channel (2). The ionization energies of the fragments Cl and CHBr$_2$ are measured at 14.37 and 8.12 eV, respectively. This indicates that CHBr$_2$ is more inclined to release the “extra electron” to produce the CHBr$_2^+$ ion, resulting in channel (2) having a notably lower appearance energy than channel (1). A similar investigation was conducted on the dissociation channel of the C–Br bond. Br and CHBrCl exhibit charges of +0.477 and +0.523, respectively, with associated ionization energies of 13.09 and 8.19 eV. This analysis suggests that the ionization energy of fragments significantly impacts the appearance energy of the dissociation channel, thereby explaining the lower appearance energy of channel (4) in comparison to channel (3).

Figure 4. Natural bond orbital (NBO) charge distribution of CHBr$_2$Cl$^+$ ions.

4.2. The Special Dissociation Channels for CHBr$_2$Cl in 400 nm Laser Fields

The generation of BrCl$^+$ and Br$_2^+$ ions in 400 nm laser field, as depicted in Figure 1, indicates the presence of varied dissociation pathways. To delve deeper into these pathways, Gaussian 16 was employed for computational analysis. Figure 5 illustrates the elimination process, which can be divided into three sequential stages: firstly, the neutral parent...
molecule loses an electron to form the parent ion; secondly, the parent ion transitions via a conformation change to an immediate compound; and finally, the intermediate compound facilitates bond cleavage, resulting in the formation of distinct fragments.

![Diagram](image.png)

**Figure 5.** Ab initio calculated dissociation pathways of the singly charged CHBr₂Cl⁺ ions.

The detailed structural modifications observed throughout the entire reaction process are of particular interest. Initially, the molecule loses one electron, transitioning into an ionic state. Despite the loss of one electron, the length of the C–Br bond remains relatively constant, while the distance between the two Br atoms decreases from 3.2 to 2.8 Å. Additionally, the Br–C–Br bond angle decreases from 111.6° to 90.6°. This alteration is attributed to the electron of the CHBr₂Cl molecule’s highest occupied molecular orbital (HOMO), which is shared by both Br atoms. For channel (7), the elimination reaction progresses from the ground state of singly charged molecular ions to the transition state, where both C–Br bonds initially lengthen slightly. However, the separation between the Br atoms diminishes rapidly, along with the Br–C–Br bond angle. Subsequently, the transition state (TS_BrCl⁺) advances along the reaction pathway towards the metastable intermediate (IS_BrCl⁺). Throughout this progression, either the C–Br bond elongates until rupture or the Br–Br bond distance stabilizes. Ultimately, the C–Br bond breaks, resulting in the formation of Br₂⁺ and CHCl. For channel (8), the angle of the Br–C–Cl bond experiences a significant decrease. As the transition state (TS_BrCl⁺) is formed, there is a rapid reduction in the distance between the Br–Cl atoms, leading to stabilization, while the C–Cl bond elongates further to create a metastable intermediate (IS_BrCl⁺). Finally, the C–Br bond is cleaved to release the desired ions.

\[
\text{CHBr}_2\text{Cl}^+ \rightarrow \text{Br}_2^+ + \text{CHCl} \\
\text{CHBr}_2\text{Cl}^+ \rightarrow \text{BrCl}^+ + \text{CHBr}
\] (7) (8)

Channels (7) and (8) are uniquely favored in the 400 nm laser field due to the higher excitation efficiency of the transition state in comparison to the 800 nm laser field. This presents an opportunity for coherent control through the manipulation of laser field parameters, such as wavelength, to selectively stimulate particular dissociation channels.

**5. Conclusions**

The dissociative ionization of CHBr₂Cl molecules in 800 and 400 nm laser fields was investigated utilizing time-of-flight mass spectra and DC-sliced velocity ion imaging technology. In our experiments the dissociation processes are independent of the laser...
field intensities. They are rather influenced by the bond energy, neutral group ionization energy, and the charge distribution. In a 400 nm laser field, we find additional sequential dissociation channels that form BrCl+ and Br2+ fragment ions. Our findings demonstrate that by changing the wavelength of the laser fields, specific ultrafast photo-dissociation channels can be selectively triggered in molecular systems.

**Author Contributions:** B.L. completed the experimental work and draft, and Z.L. finished part of theoretical calculation. The original experiment idea was proposed and experiments were designed by B.L. and B.L. submitted the final manuscript for publication. All authors have read and agreed to the published version of the manuscript.

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