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BrCl$^+$ elimination from Coulomb explosion of 1,2-bromochloroethane induced by intense femtosecond laser fields†

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By using a dc-slice imaging technique, photodissociation of 1,2-C$_2$H$_4$BrCl was investigated at 800 nm looking for heteronuclear unimolecular ion elimination of BrCl$^+$ in an 80 fs laser field. The occurrence of fragment ion BrCl$^+$ in the mass spectrum verified the existence of a unimolecular decomposition channel of BrCl$^+$ in this experiment. The relative quantum yield of the BrCl$^+$ channel was measured to be 0.8%. By processing and analyzing the velocity and angular distributions obtained from the corresponding sliced images of BrCl$^+$ and its partner ion C$_2$H$_4^+$, we concluded that BrCl$^+$ came from Coulomb explosion of the 1,2-bromochloroethane dication 1,2-C$_2$H$_4$BrCl^{2+}. With the aid of quantum chemical calculations at the M06-2X/def2-TZVP level, the potential energy surface for BrCl$^+$ detachment from 1,2-C$_2$H$_4$BrCl^{2+} has been examined in detail. According to the *ab initio* calculations, two transition state structures tended to correlate with the reactant 1,2-C$_2$H$_4$BrCl^{2+} and the products BrCl$^+$ + C$_2$H$_4^+$. In this entire dissociation process, the C–Br and C–Cl bond lengths were observed to elongate asymmetrically, that is, the C–Br chemical bond broke firstly, and subsequently a new Br–Cl chemical bond started to emerge while the C–Cl bond continued to exist for a while. Hence, an asynchronous concerted elimination mechanism was favored for BrCl$^+$ detachment.

1. Introduction

The photodissociation of polyhalogenalkanes induced by intense laser fields has been extensively studied and is the subject of recent reviews.[1–14] Two major reactions are possible for dissociation of polyhalogenalkanes: the halogen atom release reaction channel and the halogen molecular elimination reaction channel. Thus far, most studies have been focused on the halogen atomic product channel, and the halogen molecular elimination channel as a research topic has received less attention in earlier papers.

Rather than breaking one carbon-halogen chemical bond, a halogen molecular detachment process involves cleavage of two carbon-halogen chemical bonds and formation of one halogen–halogen bond. Generally, two types of reaction mechanism (sequential and concerted) are associated with halogen molecular elimination from polyhaloalkanes. Sequential dissociation mechanism refers to that two halogen atoms detach from polyhaloalkanes in turn and then combine by a collisional process. A concerted reaction is defined as one for which breaking of the two carbon–halogen bond and formation of the one halogen–halogen bond occur

in a single kinetic step.[15–17] Asynchronous and synchronous mechanisms are included for concerted mechanism. In an asynchronous concerted reaction, the first carbon–halogen bond breaks and halogen–halogen bond is formed while the second carbon-halogen is still part of the molecule, the reaction ends when the second carbon-halogen chemical bond breaks; synchronous concerted mechanism refers to that the two carbon–halogen chemical bonds start to break at the same time and break at the same rate, and the cleavage processes are accompanied by the formation of a halogen–halogen bond.[9,12] Many authors have tried to explain the detachment mechanism of halogen molecular fragments from polyhalogenalkanes.[4–14] Lin and co-workers[4–7] investigated photodissocation of CH$_2$Br$_2$, C$_2$H$_4$Br$_2$, CH$_2$I$_2$, and CH$_2$BrI to molecular products of Br$_2$, I$_2$, and BrI by cavity ring-down absorption spectroscopy at 248 nm. Their theoretical calculations on potential energy surface of the poly-haloalkanes revealed that these halogen molecular dissocia-tion channels were anticipated to proceed *via* an asynchronous concerted mechanism. By using femtosecond pump-probe technique, Dantus and co-workers[8–12] identified the molecular detachment channel of YZ and X$_2$ from poly-haloalkanes CX$_2$YZ (X represents for Cl, H, or F, and Y, Z represent for Cl, Br, or I) under an ultraviolet laser field, and a ∼50 fs ultrafast process was observed for their elimination processes. They proposed that synchronous concerted

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process was observed for heteronuclear YZ elimination while asynchronous concerted process was detected for homonuclear X_2 ejection. Janssen and co-workers[13] studied the I_2 elimination from $C_2F_4I_2$ at 396 nm, and demonstrated that I_2 was ejected through an asynchronous concerted mechanism. They used the ion pair model to elucidate the I_2 formation. From the theoretical aspects, Bozzelli and co-workers[14] demonstrated that $C_2H_4Cl_2$ could give rise to Cl_2 by *ab initio* calculations.

Although there is a great amount of studies on the halogen molecular elimination reactions, these studies were performed under ultraviolet excitation in a relatively weak laser field, and halogen molecular elimination reactions induced by near-infrared (800 nm) intense femtosecond laser field have been rarely studied. When polyhaloalkanes interact with an intense femtosecond laser field, several electrons could be rapidly removed from polyhaloalkanes, resulting in departure of parent molecular ion into cationic fragments. This is the so-called Coulomb explosion (CE) processes. Liu and co-workers[18] observed molecular ions I_2^+ and ICl^+ under intense femtosecond laser irradiation, and they stated that their elimination processes were concerted elimination mechanism. However, whether asynchronous or synchronous elimination mechanism was not distinguished for I_2^+ and ICl^+ in this experiment. Our group have demonstrated that homonuclear Br_2^+ elimination from 1,2-dibromoethane under 800 nm femtosecond laser field was a synchronous concerted mechanism.[19] In this paper, photodissociation of 1,2-bromochloroethane was investigated in search of unimolecular ion elimination of heteronuclear $BrCl^+$ and its elimination mechanism *via* primary channel by dc-slice ion imaging technique at 800 nm under 80 fs laser field. The occurrence of $BrCl^+$ in mass spectrum verified the existence of unimolecular ion elimination channel of $BrCl^+$ in this experiment. The relative quantum yield of $BrCl^+$ was measured to be 0.8%. By analyzing the corresponding velocity and angular distributions of $BrCl^+$ and its partner ion $C_2H_4^+$, we concluded that $BrCl^+$ came from two-body CE of 1,2-$C_2H_4BrCl^{2+}$. With the aid of quantum chemical calculations at M06-2X/def2-TZVP level, the potential energy surface for $BrCl^+$ detachment from 1,2-$C_2H_4BrCl^{2+}$ have been examined in detail. According to our theoretical calculations, two transition state structures tended to correlate with the reactant 1,2-$C_2H_4BrCl^{2+}$ and the products $BrCl^+$ + $C_2H_4^+$, and an asynchronous concerted elimination mechanism was favored for $BrCl^+$ detachment.

2. Experimental section

The detailed description of our DC slice ion-imaging system was explained elsewhere.[19–21] Briefly, the experimental apparatus is mainly composed of a supersonic molecular beam system and a time-of-flight (TOF) mass spectrometer system. A pulsed valve was operated synchronously with the laser pulses to generate the pulsed molecular beam. The sample beam entered into the ionization region through a skimmer. Usually the sample mixture was prepared with 1,2-bromochloroethane (Sinopharm Chemical Reagent Co., Ltd, 98+%) seeded in He at

1 atm without further purification. The 800 nm linearly polarized laser pulses (80 fs, 1 kHz) were then focused onto the sample beam by a 40 cm focal-length lens and perpendicularly intersected the sample beam. The ions were accelerated and focused by ion lens to generate an image onto a 2D position sensitive detector. The detector was composed of a pair of microchannel plates (MCPs), a P47 phosphor screen (PS), an intensified charge coupled device (ICCD) camera (512 × 512 pixels) with time gate of 4 ns, which were mounted at the end of the drift tube. The output signals from PS could also be fed into a photomultiplier tube (PMT) to get TOF mass spectra. The laser intensities were calibrated according to the idea of Guo *et al.*,[22] and the calibrated intensities were 5.0×10^{13}–1.6 $\times 10^{14}$ W cm^{-2}. All the time delays were provided by a pulse generator (DG535).

3. Computational details

The $BrCl^+$ elimination channel on the singlet ground-state potential energy surface of 1,2-bromochloroethane dication 1,2-$C_2H_4BrCl^{2+}$ was characterized. M06-2X/def2-TZVP level of theory[23,24] has been used to calculate the geometries, the vibrational frequencies, and the energies of reactants (1,2-BCE^{2+} and S1), transition states (TS1 and TS2) and fragmentation products ($BrCl^+$ and $C_2H_4^+$). Here, the structure S1 represents the geometry of the intermediate in $BrCl^+$ elimination process. The calculated vibrational frequencies could be used to get zero-point vibrational corrections and to determine whether the structure was a transition state or a local minimum. The geometries of 1,2-BCE^{2+}, S1, $BrCl^+$, and $C_2H_4^+$ were ascertained when the number of negative frequencies were zero. However, the structures of TS1 and TS2 were confirmed with the number of imaginary frequency being one. All of the above calculated energies contained zero-point energy corrections. The intrinsic reaction coordinate (IRC) calculations at M06-2X/def2-TZVP level were done on TS1 and TS2 geometries to make sure that the transition states were connected to the specified reactants and products. The Gaussian 16 program[25] was employed for these mentioned quantum chemical calculations.
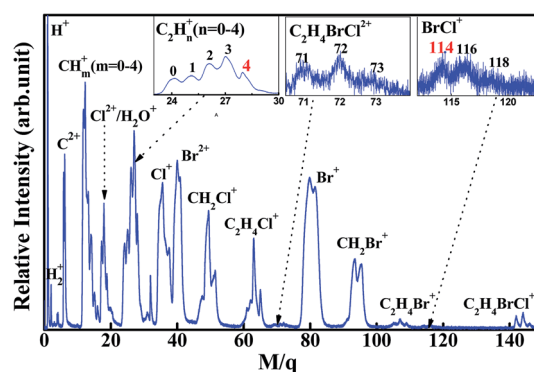

Fig. 1 Mass spectrum of 1,2-bromochloroethane induced by 80 fs laser pulses at 1.2×10^{14} W cm^{-2} intensity. The inset is the enlarged $BrCl^+$, $C_2H_4BrCl^{2+}$ and $C_2H_4^+$ spectrum.
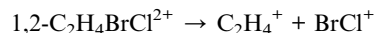
4. Results and discussions

Fig. 1 shows photoionization mass spectrum of 1,2-C_2H_4BrCl (1,2-BCE) induced by 80 fs laser pulse at 1.2×10^{14} W cm^{-2} intensity. Because of the existence of Br and Cl in 1,2-BCE, the Br- and Cl-containing ion signals exhibit intensity patterns. This can be well understood by the natural abundance of bromine (^{79}Br:^{81}Br = 1.02)[26] and chlorine (^{35}Cl:^{37}Cl = 3.08).[26] The fragment ions stemming from the single C–Br, C–Cl and C–C bond rupture, Cl^{2+}, Br^{2+}, Cl^+, Br^+, CH_2Cl^+, CH_2Br^+, $C_2H_4Cl^+$, and $C_2H_4Br^+$, are the major products in the spectrum. The generation of doubly-charged fragment ions C^{2+}, Cl^{2+} and Br^{2+} implies the presence of Coulomb explosion (CE). The ion BrCl$^+$ with m/q = 114, 116 and 118, resulting from breakage of C–Br and C–Cl bonds and formation of Br–Cl bond, can be clearly identified in the inset spectrum of Fig. 1, which indicates the occurrence of BrCl$^+$ unimolecular ion elimination in this experiment. As illustrated in this figure, a single C–Br and C–Cl bond-breaking channel leading to Br^+, Br^{2+} and Cl^+, Cl^{2+} are the major channel for dissociation of 1,2-BCE, and their corresponding relative quantum yields are measured to be 30% and 21% for Br^+, Br^{2+} and Cl^+, Cl^{2+} respectively. In contrast, the relative quantum yield of BrCl$^+$ is calculated to be 0.8%. These relative yields are calculated by the ratio of the corresponding ion signal to the total ion signals in TOF mass spectrum. This conclusion of 1,2-BCE is in agreement with the previous literature on polyhalogenalkanes that halogen product pathway is regarded as the primary fragmentation pathway for polyhaloalkanes.[1–12] The aim of the present work has been to explore the mechanism on unimolecular ion elimination of BrCl$^+$, so we would concentrate on BrCl$^+$ and its partner $C_2H_4^+$ in the sections below.

The DC slice ion imaging technique can provide velocity distribution and angular distribution of fragment ions simultaneously. The images and the corresponding velocity distributions of BrCl$^+$ and $C_2H_4^+$ obtained from photodissociation of 1,2-BCE are shown in Fig. 2. It should be noted that the velocity distribution of BrCl$^+$ can be simulated by a single Gaussian function with velocity and kinetic energy release (KER) values peaked at 773 m s^{-1} and 0.35 eV, indicating that one dissociation channel is involved. Whereas for fragment ion $C_2H_4^+$, two curves are needed (the peak values of velocity and KER are 1014 m s^{-1}, 0.15 eV and 3183 m s^{-1}, 1.47 eV respectively), which means more than one pathway participate in the photodissociation process.

In our experiment, 1,2-BCE is the main component of the samples, although trace BrCl molecule might exist because of the decomposition of 1,2-BCE. If BrCl$^+$ stems from direct photoionization of BrCl in the sample, an isotropic distribution peaked at 0 eV should be detected in the image and velocity distribution of BrCl$^+$. Since no such distribution is observed, it is evident that BrCl$^+$ is from the dissociation of 1,2-BCE. We know that the motion of the two ions produced by a two-body CE channel follow the law of conservation of momentum. In other words, an inverse relationship exists between the energy ratio and the mass ratio of the two ions.[20,27,28] In this paper, the high-KER ratio of $C_2H_4^+$ and BrCl$^+$ is measured to be 4.20, and

the inverse mass ratio of BrCl$^+$ and $C_2H_4^+$ is calculated to be 4.07. These two values are quite close to each other, so we believe ^{79}Br^{35}Cl$^+$ and $C_2H_4^+$ come from two-body CE of 1,2-$C_2H_4BrCl^{2+}$

$$1,2\text{-}C_2H_4BrCl^{2+} \rightarrow C_2H_4^+ + BrCl^+$$

One can see another low-KER component of $C_2H_4^+$ (0.15 eV) in Fig. 2, and it is generally thought to arise from dissociative ionization of 1,2-BCE$^+$ by experimental analysis and theoretical calculations.[1,21,27,29] However, this dissociative ionization channel is our next work, so we won't elaborate here. From the viewpoint of momentum conservation, two ions generated by the same two-body CE channel must have the same angular distribution. Fig. 3 demonstrates that fragment ions ^{79}Br^{35}Cl$^+$ and $C_2H_4^+$ have a similar distribution, which is a good proof for our CE channel identification. Janssen et al.[13] have studied the concerted reaction of $C_2F_4I_2$ to I_2 and C_2F_4, and they used the ion pair model to elucidate the I_2 formation. On the basis of the 80 fs laser pulse we used and the isolated samples within our supersonic molecular beam, we tend to employ this argument to understand the BrCl$^+$ generation process in this experiment.

The appearance energy from 1,2-$C_2H_4BrCl^{2+}$ to $C_2H_4^+$ and BrCl$^+$ is calculated to be 2.92 eV by Gaussian 09 software packages at M06-2X/def2-TZVP theoretical level. The KER values of $C_2H_4^+$ and BrCl$^+$ are 1.47 eV and 0.35 eV from Fig. 2, respectively. That is to say that at least 4.74 eV should be required in this dissociation process, and thus at least four photons are needed and a maximum of 1.46 eV available energy can be remained for this process in our experiment when the process proceeds under multiphoton conditions. The angular distributions of fragment ions BrCl$^+$ and $C_2H_4^+$ in Fig. 3 can be fitted by Legendre expansion:[30,31]

$$I(\theta) = 1 + \sum_L \beta_L P_L(\cos\theta) \quad (L = 2, 4, 6)$$

where, $I(\theta)$ is the angular distribution of fragment ion extracted from the images, θ refers to the angle between ejected ion and laser polarization direction, $P_L(\cos\theta)$ is the Legendre polynomial, and β_L represents the expansion coefficient. The leading expansion coefficient β_2 is an important parameter that reflects the lifetime of the precursor species state, and a smaller β_2 represents a longer lifetime of precursor species state.[30,31] In our experiment, the β_2 value of BrCl$^+$ and $C_2H_4^+$ is determined to be $\beta_2 = -0.28$. Therefore, a relatively long life-time can be inferred for the precursor ion $C_2H_4BrCl^{2+}$, and the observation of $C_2H_4BrCl^{2+}$ in our mass spectrum is consistent with this conjecture.

As we shall know, there are two mechanisms for halogen molecule detachment: stepwise and concerted mechanism.[15–17] In our experiment, the supersonic molecular beam has a very low temperature (with rotation temperature below ten Kelvin and vibration temperature a little more than ten Kelvin to tens of Kelvin). Therefore, the stepwise mechanism (collisional process of Br and Cl is involved) for the BrCl$^+$ formation can be ruled out. Moreover, Dantus et al. have addressed that the
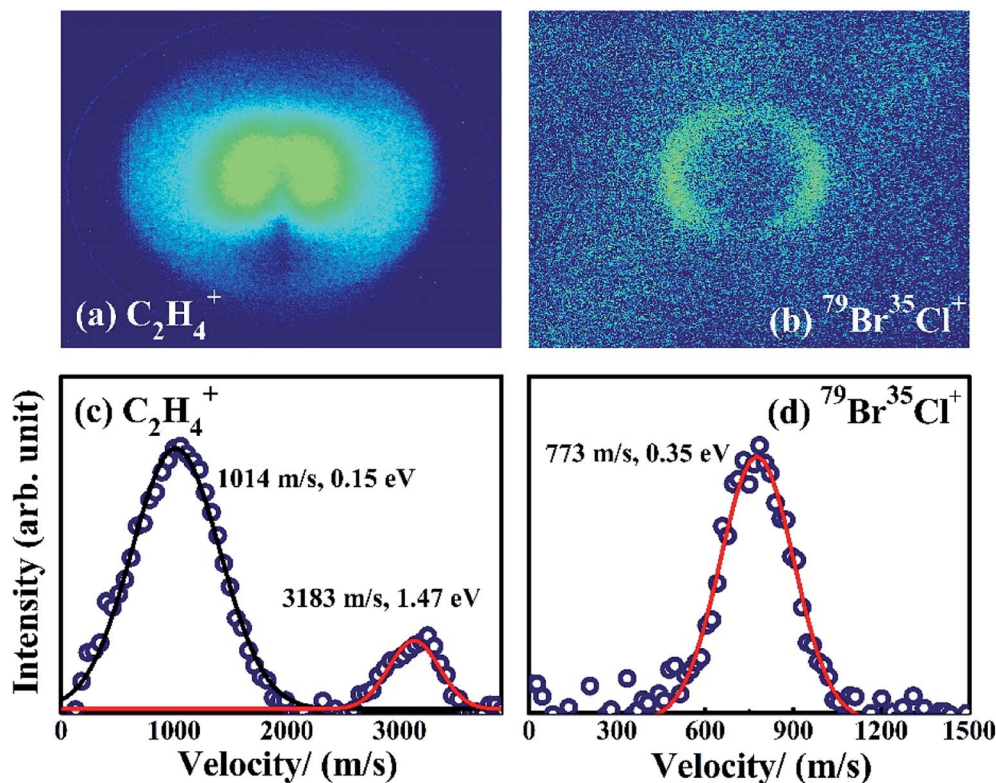
Fig. 2 Images and velocity distributions of $C_2H_4^+$ and $^{79}Br^{35}Cl^+$ at 1.2×10^{14} W cm^{-2} intensity. The navy circles (O) refer to experimental data, and the red (——) solid lines represent for the fitted curves for CE pathways.

concerted elimination of halogen molecules (X_2) from $RCHX_2$ is an ultrafast process about 50 fs.[8–12] Therefore, on the basis of the 80 fs laser pulse and the isolated samples within our supersonic molecular beam, we prefer to use the concerted mechanism to understand the generation process. In order to explain the formation of BrCl$^+$ from dication 1,2-BCE^{2+}, dissociation process calculations of 1,2-BCE^{2+} to BrCl$^+$ + $C_2H_4^+$ was conducted at M06-2X/def2-TZVP level.[23–25] The geometries of reactants (1,2-BCE^{2+} and S1), the transition states (TS1 and TS2), and products (BrCl$^+$ and $C_2H_4^+$) were fully optimized. The geometries of 1,2-BCE^{2+}, S1, BrCl$^+$, and $C_2H_4^+$ were ascertained when the number of negative frequencies were zero. However, the structures of TS1 and TS2 were confirmed with the number of imaginary frequency being one. The intrinsic reaction coordinate (IRC) calculations were done on TS1 and TS2 geometries to make sure that the transition states were connected to the specified reactants and products. The optimized structures involved in this unimolecular ion reaction process are shown in Fig. 4.

There are some noticeable differences in stable structure between ground-state 1,2-BCE and 1,2-BCE^{2+}: ∠BrCCCl of 180° and 25°, C–Br bond distance of 1.97 Å and 2.07 Å, and the C–Cl bond distance of 1.81 Å and 1.91 Å, respectively. Weitzel *et al.*'s and Mebel *et al.*[32,33] studied the structures of parent ions $C_2H_6^{2+}$ and $C_6H_{12}^{3+}$, and they reached a close conclusion for the markedly differences in molecular structure between neutral C_2H_6 and C_6H_{12} respectively. After 1,2-BCE^{2+} is formed, how is

the BrCl$^+$ ion brought out? Fig. 5 presents a complete reaction path from the stable structure 1,2-BCE^{2+} through two designed TSs toward the products $C_2H_4^+$ + BrCl$^+$. This reaction starts with the elongation of C–Br bond length of 2.07 Å in 1,2-BCE^{2+} to 2.72 Å in TS1 by surpassing an energy barrier of 0.26 eV. This leads to the S1 structure with the continued elongation of C–Br bond length to 4.11 Å, and the slightly shortening of the C–Cl
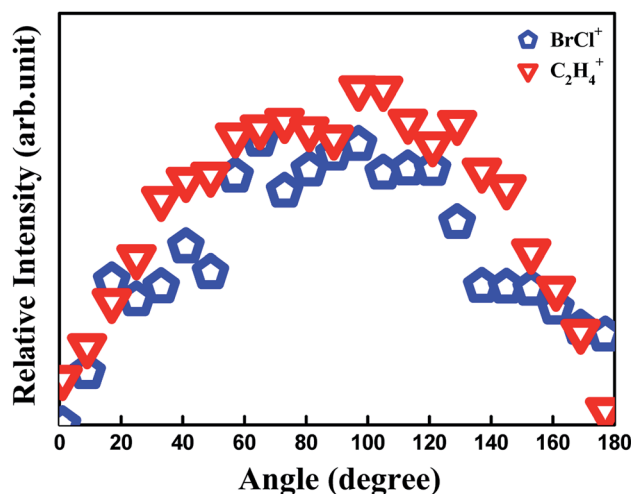

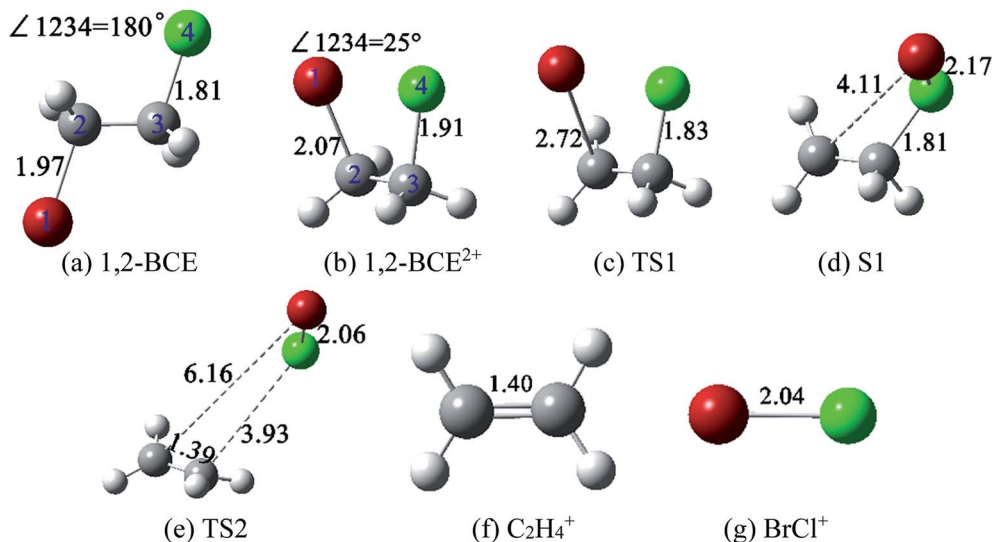**Fig. 3** Angular distributions for BrCl$^+$ and $C_2H_4^+$ at 1.2×10^{14} W cm^{-2} intensity.

Fig. 4 Structures of 1,2-BCE, 1,2-BCE^{2+}, TS1, S1, TS2, C$_2$H$_4^+$, and BrCl$^+$ ((a)–(g)) at M06-2X/def2-TZVP level. The unit of the decimals is in Å.

bond length at the same time. After that, the bond distances of C–Br and C–Cl in TS2 are asynchronously lengthened to 6.16 Å and 3.93 Å as compared with S1 where the bond distances of C–Br and C–Cl are 4.11 Å and 1.81 Å, respectively. The barrier calculated for this process from S1 to TS2 is 1.80 eV. In addition, the Br–Cl bond distance is shortened to 2.06 Å in TS2. After crossing the barrier TS2, the dication 1,2-BCE^{2+} decompose to BrCl$^+$ and C$_2$H$_4^+$ via CE process. Our computed results of IRC definitely demonstrate that TS1 and TS2 geometries are connected with their designated reactants and products.

Three reaction coordinates are chosen to describe this dissociation reaction: R_{CBr}, R_{CCl}, and R_{BrCl}. R_{CBr} and R_{CCl} are the C–Br and C–Cl bond lengths, respectively; R_{BrCl} is the distance between Br and Cl atoms. One can see in Table 1 that R_{CBr} and R_{CCl} increase asymmetrically, and R_{BrCl} decreases during the entire dissociation process. In other words, in this dissociation process, the C–Br and C–Cl bond are not broken synchronously, C–Br chemical bond break apart firstly, and subsequently a new Br–Cl chemical bond starts to emerge while C–Cl bond continues to exist for a while. According to these results, we can

deduce that 1,2-BCE^{2+} decomposes into BrCl$^+$ and C$_2$H$_4^+$ by an asynchronous concerted mechanism.

So far, unimolecular ion elimination of BrCl$^+$ from CE of 1,2-BCE^{2+} is securely demonstrated in this experiment. Using femtosecond pump-probe technique, Dantus and co-workers[8–12] studied concerted elimination of CX$_2$YZ to halogen molecules YZ (X represents for Cl, H, or F, and Y, Z represent for Cl, Br, or I). They pointed out that these halogen molecular elimination reactions from CX$_2$YZ were ultrafast processes around 50 fs. On the basis of their conclusions and the 80 fs laser pulse we used, it is reasonable to assume that unimolecular ion elimination process of BrCl$^+$ from 1,2-BCE^{2+} proceeds during the presence of laser pulse. Hence, we can understand this whole process in this way: femtosecond lasers cause vertical ionization of 1,2-BCE into a repulsive region of the potential energy hyper surface of 1,2-BCE dication, followed by a relaxation of unstable 1,2-BCE dication (the previous step) to the local minimum of 1,2-BCE dication. As displayed in Fig. 4, the relaxation involves rotation of ∠BrCCCl and elongation of both C–Br and C–Cl bond.

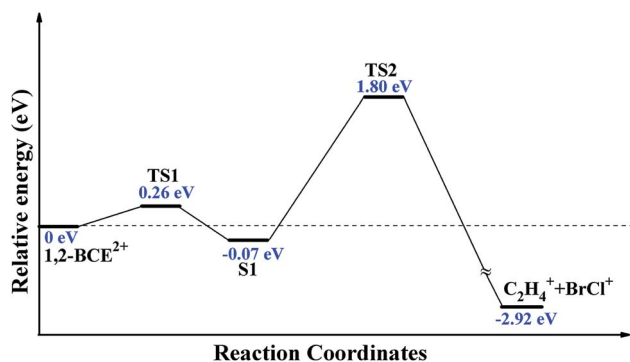Fig. 5 Dissociation of 1,2-BCE^{2+} to fragments C$_2$H$_4^+$ and BrCl$^+$ at M06-2X/def2-TZVP level of theory.

Table 1 Three reaction coordinates (R_{CBr}, R_{CCl}, and R_{BrCl}) along the dissociation path calculated at M06-2X/def2-TZVP theoretical level

R_{CBr} (Å)	R_{CCl} (Å)	R_{BrCl} (Å)
2.07	1.91	2.19 (BCE^{2+})
2.13	1.88	2.19
2.72	1.83	2.19 (TS1)
3.20	1.81	2.17
3.63	1.81	2.17
4.11	1.81	2.17 (S1)
4.82	2.04	2.18
5.29	2.78	2.09
5.65	3.24	2.07
6.16	3.93	2.06 (TS2)
6.87	4.99	2.06
7.10	5.32	2.06

Afterwards, fragmentation of 1,2-BCE^{2+} into C$_2$H$_4$$^+$ and BrCl$^+$ take place on ground PES of 1,2-BCE^{2+} with presence of the laser field. Eventually, the BrCl$^+$ is produced through an asynchronous concerted mechanism.

5. Conclusions

We have used dc-slice ion imaging technique to study unimolecular ion elimination of BrCl$^+$ from photodissociation of 1,2-BCE at 800 nm in an 80 fs laser field. The observation of fragment ion BrCl$^+$ in TOF spectrum confirmed the existence of unimolecular ion elimination channel of BrCl$^+$ in this experiment, and the relative quantum yield of BrCl$^+$ was measured to be 0.8%. Through analysis of the velocity and angular distributions of BrCl$^+$ and C$_2$H$_4$$^+$, BrCl$^+$ was demonstrated to stem from CE of 1,2-bromochloroethane diaction 1,2-BCE^{2+}. Theoretically, the pathway of 1,2-BCE^{2+} to BrCl$^+$ + C$_2$H$_4$$^+$ was simulated at M06-2X/def2-TZVP level. The calculation results showed that 1,2-C$_2$H$_4$BrCl^{2+} went over a small barrier of 0.26 eV to form S1 in which C–Br and C–Cl bond lengths were 4.11 Å and 1.81 Å respectively, and then S1 overcame a 1.80 eV barrier to dissociate into BrCl$^+$ + C$_2$H$_4$$^+$ through an asynchronous concerted elimination mechanism.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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