Dissociative Ionization of Molecular CF$_2$Br$_2$ under 800 and 400 nm Intense Femtosecond Laser Fields

Botong Liu $^1$, Zhipeng Li $^1$, Haitao Sun $^{1,2}$, Zhenrong Sun $^{1,2,*}$ and Yan Yang $^{1,*}$

1 State Key Laboratory of Precision Spectroscopy, School of Physics and Electronic Science, East China Normal University, Shanghai 200062, China; 52162099004@stu.ecnu.edu.cn (B.L.); zr.sun@phy.ecnu.edu.cn (Z.S.); htsun@phy.ecnu.edu.cn (H.S.)
2 Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan 030006, China
* Correspondence: zsun@phy.ecnu.edu.cn (Z.S.); yyang@lps.ecnu.edu.cn (Y.Y.)

Abstract: The interaction between the CF$_2$Br$_2$ molecule and 800/400 nm intense femtosecond laser fields is investigated by direct current (dc) sliced velocity mapping imaging implementation. By analyzing the kinetic energy release distribution and angular distribution of fragment ions, the dissociation channels along C-Br bond cleavage have been determined. The isotropic structure of the angular distribution for CF$_2$Br$_2^+$ ions is attributed to the coupling between the excited states. Additionally, a unique elimination channel of CF$_2$Br$_2^+$ → CF$_2$ + Br$_2^+$ has been observed and identified in the case of 400 nm laser field, in which the two C-Br bonds break asynchronously.

Keywords: dibromodifluoromethane (CF$_2$Br$_2$); femtosecond laser field; dissociative ionization (DI); excited states coupling

1. Introduction

The light-matter interaction process is one of the most fundamental physical process. Especially, with the development of laser technology, more and more new phenomena have been observed and investigated, such as multi-photon ionization (MPI) [1], above-threshold ionization (ATI) [2], tunneling ionization (TI) [3] and high-harmonic generation (HHG) [4]. In molecular system, the ionization mechanism can be calculated by Keldysh theory [5,6], where the Keldysh parameter $\gamma$ is proposed to distinguish the MPI and TI under different laser intensities and wavelengths. When $\gamma >> 1$, the electron(s) will be ejected by absorbing several photons. However, in the case of $\gamma << 1$, the potential barrier of the system will be distorted by the intense external electric field, and the electron(s) can escape the attraction from nuclei by tunneling the barrier or even over the barrier. After ionization, the dissociation would be observed, where some chemical bond(s) of the cation will be broken along the potential energy surface. It is well known that it takes hundreds of femtoseconds to break the molecular bond [7–9], thus the neutral molecule irradiated by femtosecond laser pulse will be firstly ionized, then the dissociation process occurs, which is called dissociative ionization (DI). During the low laser intensity (about $10^{12}$–$10^{13}$ W/cm$^2$), the ionization process depends strongly on the laser wavelengths [5]. After enough photons have been absorbed by molecules, which means the photon energies exceeds the threshold of ionization, the residual energy will be assigned to the kinetic energy and internal energy of fragments and electrons. When the laser intensity increases, the applied electric field strength is comparable to the internal coulomb attraction between nucleus and electron(s). In this case, the electron(s) can be easily stripped away and the charged molecular ions will further dissociate into fragments by the internal coulombic repulsive force, which is known as Coulomb explosion (CE) [10]. Differently from the resonant excitation with ultraviolet laser, the ionized molecule will be populated to numerous excited states due to the broad spectrum of the femtosecond pulses, and the dissociation dynamics can be observed along different chemical bonds simultaneously. Meanwhile, the coupling between excited states has influence on the dissociation dynamics [11].
Dibromodifluoromethane (CF$_2$Br$_2$) is widely used in fire retardant and refrigeration systems due to chemical inertness and nontoxicity, however, its photolysis in the stratosphere accelerates ozone layer destruction. For these reasons, the photodissociation of CF$_2$Br$_2$ has been widely studied under the ultraviolet laser irradiation in the past decades. Krajnovich et al. [12] have studied the photochemistry of CF$_2$Br$_2$ under 248 nm lasers field by the crossed laser-molecular beam technique [13]. Their results suggest that the molecular Br$_2$ elimination reaction, CF$_2$Br$_2$ → CF$_2$ + Br$_2$, cannot occur under their experiment condition. Park et al. [14] have studied the photodissociation dynamics of CF$_2$Br$_2$ using 2D ion image technique. The difference of parameter $\beta$ between channel (CF$_2$Br + Br ($^2\Pi_{3/2}$)) and (CF$_2$Br + Br ($^2\Pi_{1/2}$)) at 234 nm suggests that excited $A_1$ and $B_1$ states are strongly correlated by avoided curve crossing. However, the radical channel observed in 265 nm irradiation indicates the transition close to the curve crossing point is involved in the dissociation process. Das et al. [15] have studied the dissociation and ionization of CF$_2$Br$_2$ excited under 266, 355 and 532 nm laser fields by time-of-flight mass spectrometry. Their results demonstrate molecular dissociation followed by ionization and they observed that the primary dissociation leads to the formation of radical CF$_2$Br and atomic Br.

As mentioned above, the dissociation dynamics of molecule CF$_2$Br$_2$ with the resonant excitation has been investigated extensively, however, the exploration under the intense femtosecond laser field is not yet reported in the literature. In this paper, we studied the dissociative ionization of CF$_2$Br$_2$ molecule by the time-of-flight (TOF) mass spectrometry and dc-sliced velocity map imaging (VMI) technique under 800 and 400 nm intense femtosecond laser fields. The dissociation channels of singly charged parent ions have been revealed. A unique elimination pathway in the 400 nm laser field has been observed. In addition, the relationship of excited states and angular distribution of fragment ions has also been discussed.

2. Experimental Methods

Our experiment was carried out with a home-build VMI apparatus with the same approach as described in our previous works [16,17]. Briefly, the CF$_2$Br$_2$ sample was seeded by argon gas and ejected into the source chamber. After adiabatic expansion of the supersonic molecular beam, the pressure inside the source chamber and the reaction chamber increased from 2.2 × 10$^{-7}$ and 4.0 × 10$^{-7}$ mbar to 2.2 × 10$^{-6}$ and 7.4 × 10$^{-6}$ mbar, respectively. Here we set the operating frequency of the pulse valve (general valve, Parker) to 100 Hz and the opening time to 170 us. The 800 nm (Spectra-Physics) and 400 nm (Generated from BBO I) laser pulses were focused into the reaction chamber and interact with sample molecules. The pulses duration in full width at half maximum (FWHM) for 800 nm and 400 nm were about 70 fs and 100 fs, respectively. The intensity of 800 nm laser pulses in the focal volume were estimated between 5 × 10$^{13}$ W/cm$^2$ and 2.5 × 10$^{14}$ W/cm$^2$ by calibration with the Ar$^{2+}$/Ar$^+$ yields ratio (See Supplementary Materials, Figure S1). The intensity of 400 nm laser pulses were estimated to be between 5 × 10$^{12}$ W/cm$^2$ and 4.0 × 10$^{13}$ W/cm$^2$. As the ions passed through the velocity mapping lens, they were stretched to meet the slice condition. Finally, the ion population was detected by a pair of microchannel plates coupled with a phosphor screen. The two-dimensional momentum images of each fragment correspond to the central slice of the corresponding three-dimensional momentum distribution and were collected by a charge coupled device camera (PI-MAXII, Princeton Instrument) with 5 ns time resolution. In our experimental condition, the laser pulse polarization vector was perpendicular to the flight axis.

The quantum chemical calculations were performed with the Gaussian 16 software to illustrate the dissociation and ionization processes [18]. Single point energies of the reaction products were calculated in Gaussian-4 theory (G4 theory) [19]. The potential energy surface (PES) was obtained by the equation of motion coupled cluster singles-and-doubles (EOM-CCSD) method with the correlation consistent polarized Valence Triple-zeta (cc-pVTZ) basis set [20,21]. The vibrational frequency was calculated at the B3LYP/6-31G* level [22] and relaxed force constant was obtained by the compliance software [23].
which can calculate the individual bond strength. The intrinsic reaction coordinate (IRC) calculation of transition state was calculated at the same level. The ionization energy of molecule CF$_2$Br$_2$ was calculated as 10.75 eV, which was in agreement with the previous experimental values 11.18 eV [24].

3. Results and Discussion

3.1. Time-of-Flight Mass Spectrum and DC-Sliced Images

Figure 1 shows the TOF mass spectra of molecule CF$_2$Br$_2$ irradiated by the 800 nm (a) and 400 nm (b) laser fields with intensities of $2.5 \times 10^{14}$ and $4.0 \times 10^{13}$ W/cm$^2$, respectively. Both in Figure 1 a,b, the ions C$^+$, F$^+$, CF$^+$, Ar$^+$ (carrier gas), CF$_2^+$, Br$^+$ and CF$_2$Br$^+$ can be observed distinctly. However, the signals of ion Br$_2^+$ and CF$_2$Br$_2^+$ are very weak and only appear in the 400 nm spectrum. The parent ion CF$_2$Br$_2^+$ in Figure 1b indicates that parent ions CF$_2$Br$_2^+$ are prone to dissociate into fragments in the 800 nm rather than 400 nm laser field. The ions Br$_2^+$ in Figure 1b indicates that a new reaction channel is involved in our experimental conditions (See Supplementary Materials, Figure S2), and the details will be discussed in the following section. On the other hand, the CF$_2$Br$^+$, Br$^+$, CF$_2^+$ and CF$^+$ ions yields are much higher in both cases. This suggest that the major dissociation processes originate from the cleavage of C-Br bond. To support this assumption, the relaxed force constants of the singly charged ion CF$_2$Br$_2^+$ have been calculated. In the compliance constants matrix, the higher is the value of diagonal element, the weaker is the corresponding chemical bond. Namely, the reciprocals of these diagonal elements, which are called relaxed force constants, can represent the bond strength (See Supplementary Materials, Table S1 and Figure S3a). The C-F bond in parent ion CF$_2$Br$_2^+$ is much stronger than C-Br bond. Therefore, it is reasonable that the cleavage of C-Br bond is dominant in the dissociation processes. In next section, we focus on the C-Br bond cleavage.

![Figure 1](image-url)

Figure 1. Time-of-flight (TOF) mass spectra of molecular CF$_2$Br$_2$ at $2.5 \times 10^{14}$ W/cm$^2$ in 800 nm laser field (a) and $4.0 \times 10^{13}$ W/cm$^2$ in 400 nm laser field (b), respectively. The inset shows the signal of Br$_2^+$ and CF$_2$Br$_2^+$ ions magnified thirty times.

In order to accurately assign the dissociation channels, the raw dc-sliced images were obtained, and the corresponding kinetic energy releases were also extracted. As shown in
Figure 2, the velocity distribution of fragment ions is similar to the mountain, and each peak represents the most probable velocity distribution of fragments from the dissociation process. We used Gaussian function to fit the distribution, and the peak values of the each fitted function were obtained. According to the Equation (1), the velocities were converted into kinetic energy ($E_k$) of fragments, which were labelled in units of eV, where $m$ and $V$ represent the mass and velocity of fragments.

$$E_k = \frac{1}{2}mV^2$$

3.2. The Dissociative Ionization of Molecule CF$_2$Br$_2$ in 800 nm Laser Fields

According to the Keldysh theory [5], we calculated the critical intensity of $9.0 \times 10^{13}$ W/cm$^2$ in the 800 nm laser field, where the MPI is favored over the TI in the range from $5.0 \times 10^{13}$ to $9.0 \times 10^{13}$ W/cm$^2$ in our experimental conditions. The preceding section has explained that DI is the dominant process for molecules under femtosecond laser pulses. Hence in our experimental conditions (70 fs FWHM), the multiphoton ionization occurs first, then the dis-
sociation process follows, namely multiphoton dissociative ionization (MPDI) [25,26]. Next, the estimated reaction channels and related the appearance energy (E_{AP}) are listed as Table 1, where E_{AP} denotes the required energy to switch on the channel [27]. The expression is shown in the following Equation (2), where \( \sum E_P \) and \( \sum E_R \) represent the sum of energy of the reaction products and reactants, respectively.

Table 1. The estimated reaction channels and the related energy.

| Channel | Reaction Path | \( ^* E_{AP} \) (eV) |
|---------|---------------|---------------------|
| 1       | CF\(_2\)Br\(_2\)+ih\(\nu\) → CF\(_2\)Br\(_2\)+ + e\(^-\) \rightarrow CF\(_2\)Br\(^+\) + Br + e\(^-\) , | 11.19 |
| 2       | CF\(_2\)Br\(_2\)+jh\(\nu\) → CF\(_2\)Br\(_2\)+ + e\(^-\) \rightarrow Br\(^+\) + CF\(_2\)Br + e\(^-\) , | 15.85 |
| 3       | CF\(_2\)Br\(_2\)+kh\(\nu\) → CF\(_2\)Br\(_2\)+ + e\(^-\) \rightarrow CF\(_2\)Br\(^+\) + 2Br + e\(^-\) , | 15.61 |

\(^*\) Calculated in G4 theory.

In the above channels, the i, j and k represent the photon number absorbed by the molecules, h\(\nu\) is the one photon energy (1.55 eV@800 nm). Once the E\(_{AP}\) were calculated, the number of photons absorbed has been determined. Hence, the number of photons i, j and k are 8, 11 and 11, respectively. On the other hand, the ion yields as a function of the laser intensity in the MPDI process meets the following Equation (3):

\[
E_{AP} = \sum E_P - \sum E_R
\]

\[
W_n \propto \sigma I^n
\]

where \( \sigma \) is the photoionization cross-section, \( I \) denotes the laser intensity and \( n \) represents the number of photon involved in the ionization process. In order to assess the consistency for the estimated reaction channels, the relationship between the ion yields and laser intensity was measured. In Figure 3, the slope of the curves obtained by fitting and shown in logarithmic coordinate matches the calculated photon number, which suggests that the estimated reaction pathways occur in a MPDI regime.

![Figure 3](image-url)

**Figure 3.** The schematic diagram of the ion yields as a function of the laser intensity in logarithmic coordinates, the red dashed line represents the critical intensity for multi-photon ionization (MPI) and tunnel ionization (TI).
After molecules absorb enough photons and overcome the ionization potential barrier, the residual amount of energy resulting from the difference between the photons energy and the energy required to activate the reaction channel is transferred to internal degrees of freedom and translational energy of the fragments. We shall abbreviate the residual amount of energy to $E_{AV}$ shown in Equation (4), and the total translational energy ($E_T$) of the fragments can be obtained according to the following Equation (5):

$$E_{AV} = n h \nu - E_{AP}$$  \hspace{1cm} (4) \hspace{1cm}

$$E_{T(AB)} = \frac{m_A + m_B}{m_B} E_{K(A)}$$  \hspace{1cm} (5) \hspace{1cm}

where $m_A$ and $m_B$ represent the mass of reaction products A and B, respectively. Because part of the $E_{AV}$ is released to the internal energy of fragments, the $E_T$ of fragments for each channel should be smaller than $E_{AV}$. Here, the recoil momentum of the ionized electron is neglected and only the ion and neutral partner are calculated. The $E_{K}$, $E_T$ and $E_{AV}$ for the three different reaction channels are listed in Table 2. The experimental results are in good agreement with the calculated results, which demonstrates the above estimated channels originate from the dissociative ionization of molecule CF$_2$Br$_2$.

Table 2. The energy list for above estimated channels.

| Channel | $E_K$ (eV) | $E_T$ (eV) | $E_{AV}$ (eV) |
|---------|-----------|-----------|-------------|
| (1)     | 0.01      | 0.03      | 1.21        |
| (2)     | 0.13      | 0.21      | 1.20        |
| (3)     | 0.11      | 0.14      | 1.44        |

The related dissociation channels of parent ions are shown in Figure 4 (red lines). The energy of the ground state of molecular CF$_2$Br$_2$ is defined as zero in order to simplify subsequent discussion. It is noted that the $E_{AP}$ of channel one is 11.19 eV; however, the $E_{AP}$ for channel two increases to 15.85 eV. The reason could be the difference in charge distribution after dissociation along the C-Br bond. Hence, we calculated the charge distribution between the above two channels.

Figure 4. Ab initio calculation of dissociation pathways of the singly charged CF$_2$Br$_2^+$ ions.

Figure 5 shows the natural bond orbital (NBO) charge distribution of ions CF$_2$Br$_2^+$ and the corresponding fragments. It is obvious that CF$_2$Br and Br share out nearly the same in the charge distribution of parent ion CF$_2$Br$_2^+$. Once the C-Br bond is broken, either CF$_2$Br or Br is likely to be ionic state. The ionization potential of CF$_2$Br and Br are 8.4 and 13.1 eV.
(G4 level), respectively, which indicates that CF$_2$Br more easily lose the electron to yield CF$_2$Br$^+$ ion. Therefore, the corresponding ionization energies of these neutral parts play a crucial role in the related dissociative ionization channels. Comparing with the channel one, the ions CF$_2$Br$_2^+$ need to break two C-Br bonds to yield the CF$_2^+$ ion according to the channel three. The relaxed force constants of the C-Br bond for CF$_2$Br$_2^+$ and CF$_2$Br$^+$ are 1.45 and 4.18 mdyn/Å, respectively (See Supplementary Materials, Table S1 and Figure S3b). The second C-Br bond strength is enhanced after losing one Br atom, which results in the E$_{AP}$ (15.61 eV) of channel three being much higher than that of channel one.

![Diagram](image.png)

**Figure 5.** Natural bond orbital (NBO) charge distribution of CF$_2$Br$_2^+$ ions and the charge assignment of the corresponding dissociation channel.

### 3.3. The Special Dissociation Channels for Singly Ion CF$_2$Br$_2^+$ in 400 nm Laser Fields

The elimination reaction only occurred in the 400 nm laser field. We have performed the related calculations to explore the dynamic process, and the results are shown in Figure 4 (blue lines). The elimination process can be separated into three stages. Briefly, the singly charged ions CF$_2$Br$_2^+$ overpasses the energy barrier of 1.7 eV to the transition state (TS$_1$), and then transfers quickly into the transition state TS$_2$. Finally, the TS$_2$ transforms spontaneously to the intermediate state (IS). The details of the structural changes are listed in Table 3. As shown in Table 3, the bond length for C-Br bonds is 1.96 Å for the molecule CF$_2$Br$_2$, and the distance of the two Br atoms is 3.24 Å. After losing one electron, the C-Br bond length hardly changes, but the distance of two Br atoms shortens to 2.86 Å and the bond angle of $\angle$Br-C-Br decreases from 112$^\circ$ to 92$^\circ$. The possible reason for this structure deformation is that the ionized electrons are mainly from non-bonding Highest Occupied Molecular Orbital (HOMO), where the electron cloud mostly distributes on the two bromine atoms. Then the ground state of singly charged molecular ions CF$_2$Br$_2^+$ becomes starting point for the elimination reaction. Both C-Br bonds length firstly increases from the 1.99 Å to the 2.57 Å. However, the distance of Br-Br decreases from 2.86 Å to 2.30 Å and the angle of $\angle$Br-C-Br decreases intensively from 92.0$^\circ$ to 53.2$^\circ$.

Next, the TS$_1$ releases an energy of 0.09 eV to the transition state TS$_2$. In this process, the structural changes are very gentle, and two C-Br bond lengths slowly increase to 2.62 Å. The distance of Br-Br and the bond angle $\angle$Br-C-Br remain almost unchanged. Finally, the TS$_2$ spontaneously evolves to the intermediate state IS. The C-Br(4) bond length shortens to 2.28 Å, while the other C-Br(5) bond elongates to 3.45 Å and the bond angle $\angle$Br-C-Br drops from 53.5$^\circ$ to 41.9$^\circ$. For the intermediate state IS, the distance of Br-Br equals the equilibrium internuclear distance of molecule Br$_2$. After the C-Br(5) bond cleavage, the molecular Br$_2$ and ion Br$_2^+$ are produced from the channels four and five, respectively. However, the molecular Br$_2$ is not observed in our experiment because of the impossibility to detect neutral particles by a VMI setup. Therefore, the channel...
four is confirmed by the appearance of the fragment ion CF$_2^+$ in the 400 nm laser field.

Table 3. The bond lengths of the two C-Br bonds, the distance of the two Br atoms and bond angle of ∠Br-C-Br for the related channels.

|        | C-Br(4) | C-Br(5) | Br-Br * | ∠Br-C-Br |
|--------|---------|---------|---------|----------|
| CF$_2$Br$_2$ | 1.96    | 1.96    | 3.24    | 112.0    |
| CF$_2$Br$_2^+$ | 1.99    | 1.99    | 2.86    | 92.0     |
| TS$_1$  | 2.57    | 2.57    | 2.30    | 53.2     |
| TS$_2$  | 2.62    | 2.62    | 2.34    | 53.5     |
| IS      | 2.28    | 3.45    | 2.32    | 41.9     |

* The equilibrium internuclear distance of molecular Br$_2$ is 2.32 Å (G4 theory).

In addition, we argue that the hump for ions CF$_2^+$ (0.76 eV) originate from the multiphoton dissociative process as channel three in the 400 nm laser field (E$_T$ = 1.00 eV, E$_{AV}$ = 2.99 eV @400 nm). For ions CF$_2$Br$^+$ (0.75 eV) in the 400 nm laser field, it indicates a new reaction pathway different from channel reaction in the 800 nm case (See Figure 2c). Once passing through the transition state (E$_{AP}$ = 12.45 eV), the ions CF$_2$Br$^+$ can be produced due to the Br-Br bond cleavage. The E$_K$ of ions CF$_2$Br$^+$ in the 400 nm laser field is in accordance with the fact that the calculated values of channel six (E$_T$ = 1.97 eV, E$_{AV}$ = 3.05 eV @400 nm). Because of the much higher excitation efficiency to the transition state, channels four to six are the unique channels in the 400 nm laser field, which suggests that dissociative ionization processes are sensitive to laser wavelengths [28].

3.4. The Excited States and Angular Distribution of Fragment Ions

Besides the information about the kinetic energy for fragments, the angular distribution is another important factor to analyze the reaction channels. The angular distribution for fragment ions was obtained from the sliced images by integrating the signal over the pixel with the same kinetic energy at different angles in polar coordinate (See Figure 6). According to the above estimated channels, the precursor ions CF$_2$Br$_2^+$ should dissociate into the fragment ion CF$_2$Br$^+$ or Br$^+$, as shown in channels one or two. It is likely that similar angular distribution structure appears in both cases, however, there are remarkable differences on the angular distribution structure between fragment ion CF$_2$Br$^+$ and Br$^+$. The angular distribution of ion CF$_2$Br$^+$ is isotropic, instead, the angular distribution for Br$^+$ ion is anisotropic along laser polarization vector direction.
Figure 6. The angular distribution of Br$^+$ and CF$_2$Br$^+$ ions, in which the black double headed arrow represents the laser polarization direction.

To further explore the above reason, the potential energy surfaces (PESs) along the C-Br bond were calculated at the EOMCCSD/cc-pVTZ level. In Figure 7, the $G_0$, $S_0$ and $S_{1-3}$ represent the ground state and excited states of molecule CF$_2$Br$_2$ and ion CF$_2$Br$_2^+$, respectively. It is reasonable that the non-adiabatic excitation (the vertical excitation) dominates the ionization process in our experiment (70 fs FWHM). The equilibrium internuclear distance of the C-Br bond in the ground state of molecule CF$_2$Br$_2$ is 1.95 Å. Following to the Franck-Condon principle, the molecule CF$_2$Br$_2$ is excited to the high-lying excited states at this internuclear distance. Then the evolution of the vibrational wave packets undergoes on the corresponding PES of the excited states, and eventually dissociates into fragments with kinetic energies.

Figure 7. Potential energy surfaces (PESs) of ground state of neutral molecule CF$_2$Br$_2$, parent ion CF$_2$Br$_2^+$ and the excited states of ion CF$_2$Br$_2^+$, which were calculated at the equation of motion coupled cluster singles-and-doubles (EOMCCSD)/cc-pVTZ level.
For channel one, the excitation of neutral molecule CF$_2$Br$_2$ can follow G$_0 \rightarrow$ S$_1$ or G$_0 \rightarrow$ S$_2$ transition by multiphoton absorption. Because the energy gap (0.4 eV) between the excited state S$_1$ and S$_2$ is less than one photon energy (1.55 eV@800 nm). Obviously, the excited state S$_2$ is a bound state, so the parent ions hardly dissociate along this potential energy surface and the related vibrational wave packet still oscillates in the potential well. Once the molecule is excited to the state S$_1$, it will dissociate on a short time scale, on the picosecond to sub-picosecond time scale [9]. Further, the rotation period for the precursor state parent ions estimates in tens of picoseconds [29]. Hence, the angular distribution of produced ions CF$_2$Br$^+$ is anisotropic. However, this intuitive assumption is inconsistent with our experiment results. Actually, a similar phenomenon has been observed in reference [11]; “the isotropic angular distribution of Cl$^+$ ions in channel (1,1) is attributed to the wave packet oscillation and strong coupling between the excited states in the range of 2.7–3.1Å. Some of these wave packets will be excited to the higher repulsive excited state by the laser field; in other words, the field excitation plays a crucial role in the dissociation of pathway (1,1)” . Here, we believe that the coupling between excited state S$_1$ and S$_2$ is strong enough to induce wave packet transition between the upper state and lower state when the bond length stretches from 2.0 Å to 2.2 Å (the black rectangle). Considering that the oscillation period of the wave packet is comparable with the rotation period of the precursor [CF$_2$Br$^+ \ldots$ Br], this means that the dissociation time for this channel is much longer than the time of fast dissociation process. Therefore, it is reasonable that the produced fragments are ejected isotopically.

For channel two, the most Br$^+$ ions are ejected along the laser polarization direction. Based on the above calculation, the neutral molecule firstly loses one electron and is excited to the fast dissociative state (e.g., excited state S$_3$). The dissociation time on strongly repulsive states is around tens of femtoseconds. As a result, the rotation of the precursor parent ions [Br$^+ \ldots$ CF$_2$Br] hardly affects the angular distribution for fragment ions. Therefore, the angular distribution of Br$^+$ ion is isotropic. In addition, the angular distribution is closely related to the electron density distribution and molecular structure [11]. We argue that the C-Br bond and the electron density distribution of the valence orbitals are likely to be parallel with the laser polarization direction, since in this case the ionization probability reaches the maximum. Then parent ions are excited to repulsive state S$_3$. Therefore, this results in a strong anisotropic angular distribution along the laser polarization direction.

4. Conclusions

In conclusion, the dissociative ionization of CF$_2$Br$_2$ in 800 and 400 nm femtosecond laser fields has been investigated by time-of-flight mass spectra and dc-sliced velocity mapping imaging technique. Because the C-F bond is much stronger than that C-Br bond, the main channel of reaction originates from the C-Br bond cleavage. With the aid of the quantum chemical calculations, the reaction pathways of dissociative ionization of CF$_2$Br$_2$ have been assigned. A unique elimination channel has been observed under 400 nm laser fields, and it indicates that reaction pathway is sensitive to laser wavelength. The distinct difference of the angular distribution for ion Br$^+$ and CF$_2$Br$^+$ suggests that the coupling between the excited states play crucial role in the dissociation dynamics.

Supplementary Materials: The following are available online at https://www.mdpi.com/2076-3417/11/4/1704/s1: Figure S1: The yield ratio of [Ar$^{2+}$]/[Ar$^+$] of our measurement comparing with the same ratio in literatures Ref [1]. The red solid square is the experimental results title, Figure S2: The time-of-flight mass spectra under different laser power, in the (a) 800 nm laser field; (b) 400 nm laser field, respectively, Figure S3: (a) the optimized structure of singly charged ion CF$_2$Br$^+$ at the B3LYP/6-31G$^*$ level and the related C-F and C-Br bonds strength calculated by the relax force constant (b) the optimized structure of singly charged ion CF$_2$Br$^+$ at the B3LYP/6-31G$^*$ level and the related C-F and C-Br bonds strength calculated by the relax force constant [2]. Table S1: The compliance matrix of singly charged ion CF$_2$Br$_2^+$ and CF$_2$Br$^+$, which is calculated by B3LYP level of theory using 6-31G$^*$ basis set.
Author Contributions: B.L. and Z.L. finished the experiment works and the draft. The theoretical calculations are supervised by H.S. Y.Y. proposed the original experiment idea and designed the experiments, and he revised the manuscript and submitted the paper. Z.S. is the funds holder which support our experiments, and participated the experiment design. All authors have read and agreed to the published version of the manuscript.

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