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Multielectron dissociative ionization of SF_6 in an intense femtosecond laser field

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Abstract

The multielectron dissociative ionization of sulphur hexafluoride was investigated using 130 fs laser pulses at 810 nm wavelength. The pattern of the observed mass spectrum is explained based on the molecular structure symmetry and atomic ionization potentials. The kinetic energies of the atomic ions F^+ and F^{2+} are consistent with a Coulomb explosion at a single critical internuclear distance. High precision angular distributions of atomic ions are obtained and the geometric alignment is responsible to the observed anisotropic angle distribution of energetic atomic ions.

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Keywords: Femtosecond; MEDI; SF_6; Time-of-flight

1. Introduction

The molecules' response to an intense femtosecond laser field is a subject of attracting much more interest. The research is facilitated by the developments in laser technology and availability of tabletop femtosecond lasers. The multielectron dissociative ionization (MEDI) of diatomic and triatomic molecules has been carried out in recent years both experimentally [1–6] and theoretically [7–9] and reviewed [10,11]. For polyatomic molecules, benzene [12,13] and tetrahedral molecule CH_3I [14,15] were extensively studied for their simple highly symmetric structure. While the interaction of sulphur hexafluoride with femtosecond laser pulses was seldom studied [16]. Under the intense laser fields, the molecule ionization can be induced through multiphoton process (MPI) and/or field ionization (FI) mechanisms, depending on the laser intensity, laser frequency, and molecular ionization potential. Contribution from FI process is thought to be dominant where Keldysh parameter takes values $\gamma \ll 1$ [17]. If the laser field is strong enough (e.g. above 10^{14} W/cm^2), more than one electron can be stripped away from the molecule. The removal of several electrons from the molecule leads to the generation of multiple charged, often unstable, ions that undergo Coulomb explosion resulting in multiple charged atomic ions production. The kinetic energy of the fragment ions are substantially lower than that expected for prompt ionization/dissociation at the equilibrium bond length, R_e. Consequently, it has been deduced that the Coulomb explosion begins at a critical internuclear distance R_c larger than R_e. For small molecules, R_c is about twice as large as R_e. Sanderson et al. suggested that this relationship is also valid for SF_6 molecule [16]. The energetic atomic fragment ions usually exhibit anisotropic angular distribution due to the reorientation of the molecular axis and/or the dependence of the ionization rate on the angle between the laser polarization direction and the molecular axis. The understanding of these processes, known as MEDI, is of great significance for their fundamental importance and their close relation with processes such as coherent control, molecular alignment, high harmonic generation and etc.

In this paper, the multielectron dissociative ionization of sulphur hexafluoride was investigated by using a time-of-flight mass spectrometer (TOFMS) with the laser intensity up to 1.0×10^{16} W/cm^2. FI is thought to be the

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predominant molecule–radiation coupling mechanism at this laser intensity. Both linearly and circularly polarized light were used to shed light on the alignment mechanism. The kinetic energies and angular distributions of the fragment ions coming from the Coulomb explosion were measured and the possible explosion channels were discussed.

2. Experimental

The experimental setup has been described detailedly in our previous report [18]. A Ti:sapphire chirped pulse amplifier (CPA) laser system(TSA-10, Spectra-Physics Inc., USA), which delivers 810 nm, 130 fs pulses at a repetition rate of 10 Hz, was employed as the light source. The laser beam was focused by a lens with focal length 150 mm into the chamber of the TOFMS. To measure the angular distribution, a half-waveplate was inserted into the path of the laser beam to rotate the electric field vector with an angle interval of 4°. In the measurement, the polarization angle is defined as the angle between the axis of the TOFMS and the polarization vector of the laser beam.

The apparatus used here was a Wiley–McLaren-type time-of-flight mass spectrometer with a drift tube of 35 cm long [19]. The vacuum chamber can be pumped to an ultimate pressure of 10^{-5} Pa. A SF_6 gas sample was introduced into the chamber via a pulsed valve (Park Inc., USA) with a 0.2 mm orifice. When the gas sample was admitted, the chamber pressure was maintained to be at several 10^{-4} Pa to avoid the space-charge effect and pressure broadening of the ion peaks [20]. A microchannel plate assembly was used to detect the ions. The signals were recorded using ultrahigh speed data acquisition card (DP105, Acqiris Digitizers, Switzerland) with a maximum real-time sampling rate of 1 GHz and a load of 50 Ω. The measured signals were typically averaged over 256 laser pulses. The pulsed valve, the data acquisition card and the femtosecond laser pulses were timing scheduled by a DG535 digital delay and pulse generator (Stanford Research Systems, USA).

3. Results and disscussion

3.1. Molecular ions

A typical TOF mass spectrum of the SF_6 molecule, irradiated by a femtosecond laser beam with polarization vector along the direction of the TOFMS axis, is shown in Fig. 1.The extraction field used in this experiment is 200 V/cm. Our spectra have enhanced resolution compared with previous work of Sanderson et al. [16]. The energetic singly and doubly charged F ions are split into double peaks. This double peak structure indicates that they are coming from a Coulomb explosion of highly charged molecule ion. While all S ion peaks exhibit a single peak structure and the highest ionization stage reaches to five. The single peak structure of S ions indicates that the symmetric explosion channels are favored. Besides the atomic ions, abundant molecular ions were also observed in our mass spectrum. It should be noted that no molecule ions SF_6^+ were observed which is not common for using of the femtosecond laser. The absence of the parent molecule ion may be due to its rapid dissociation time of about 1 ps [21]. The H_2O^+, H^+ and C^+ ions are from the residua in the vacuum chamber.

The molecule SF_6 is highly symmetric structured with three linear F–S–F sharing the same sulphur atom. The axes

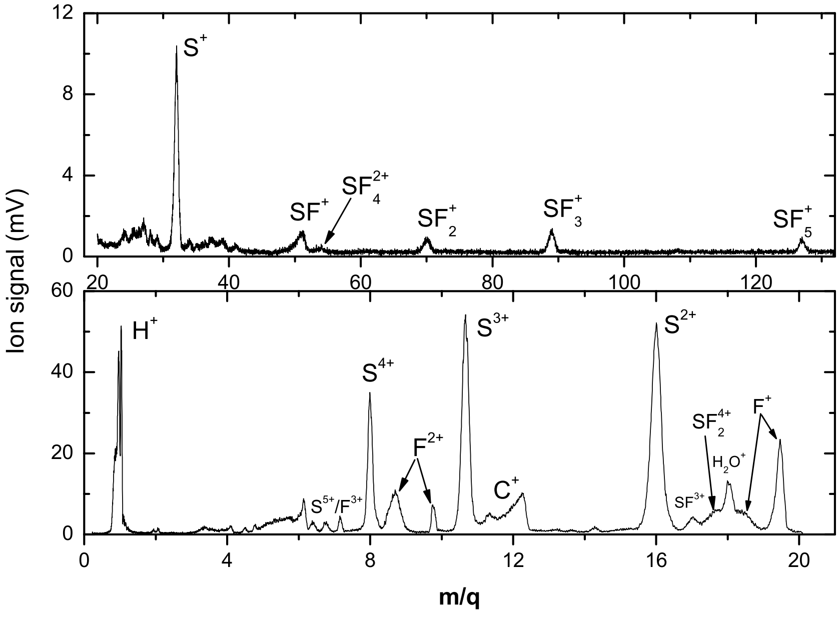


Fig. 1. Mass spectrum of the SF_6 molecule induced by 810 nm, 130 fs laser pulses at intensity of 1.0×10^{16} W/cm^2. The polarization was parallel to the TOFMS axis.

Table 1
Ionization potential of fluorine and sulphur

Specis	IP (eV)	Species	IP (eV)
S^+	10.36	F^+	17.42
S^{2+}	23.33		
S^{3+}	34.83	F^{2+}	34.97
S^{4+}	47.30		
S^{5+}	72.68	F^{3+}	62.71
S^{6+}	88.05	F^{4+}	87.14

of these three linear F–S–F are mutually perpendicular. For the SF_6 in an external laser field, the F atoms in the molecule can be classified into two groups: one group is the two F in linear F–S–F with its axis parallel to the laser polarization vector, the other group is the four F in two linear F–S–F with their axes orthogonal to the polarization vector. A reasonable assumption is that the F atoms in a group are of the same charge state for symmetry. So, the Coulomb explosion channel can be expressed as $SF_6 \rightarrow [SF_6]^{(2i+4j+k)+} \rightarrow 2F^{i+} + 4F^{j+} + S^{k+}$ and notated as (i, j, k). By treating each F–S–F as a triatomic molecule, we assume that the number i should be no less than j for the preferential ionization, also known as geometric alignment mechanism [22–24]. When discussing the possible explosion channels, another point to be considered is the ionization potential of the observed atomic ions. Table 1gives the zero-field ionization potentials for the sulphur atom and fluorine atom. The ions with higher ionization potential are harder to be ionized. So, the ions with higher ionization potential appear later when the laser intensity is changing from weak to strong [6]. This can establish a weak relationship between the number i, j, and k. For example, in a region where intensity is just high enough to produce F^+, S^+ is also produced.

As for the singly charged molecular ions, it is believed that they are from the rapid dissociation of the highly excited parent ions [25]. The appearance of doubly charged fragments SF_4^{2+} indicates that the parent ion has been doubly charged. Based on the above discussion on the possible explosion channel, we can guess the constitution of the highly charged molecule ions in our measured mass spectrum. They are listed below, $SF_4^{2+} = S^{2+} + 2F^+$, $SF^{3+} = S^{2+} + F^+$. All the observed highly charged molecular ions can be express in this form.

3.2. Atomic ions

The double-peak structure of energetic F ions is a hallmark of Coulomb explosion. The kinetic energy release (KER) in this process causes the ion signals to display peak splitting. The peak with a shorter flight-time arises from ions ejected along the axis of the TOFMS directly towards the detector and peak with a longer flight-time from ions ejected in the opposite direction. The kinetic energy of atomic ions resulting from the Coulomb explosion can be determined from the peak splitting in the mass spectrum according to [26]:

Table 2
Experimental measured kinetic energy (E_{exp}) at an intensity of 9×10^{15} W/cm^2 and calculated atomic ion kinetic energies (E_{the}) by solving the classical Newton equations at $R_c = 3.51$ Å

Ions	E_{exp} (eV)	Channels (i, j, k)	E_{the} (eV)
F^+	5.0	(1, 0, 1)	5.10
		(1, 0, 2)	9.20
		(1, 1, 1)	10.89
		(1, 1, 2)	14.99
		(1, 1, 3)	19.09
F^{2+}	43.5	(2, 1, 2)	36.13
		(2, 1, 3)	44.35
		(2, 2, 2)	43.64
		(2, 2, 3)	51.84
		(2, 2, 4)	60.04

$$E_{\text{kinetic energy}} = \frac{F^2 q^2\, \Delta t^2}{8m} \tag{1}$$

where F is the extraction field, q is the charge of the ion and Δt is the difference in the arrival times between the forward and backward ejected ions, m is the mass of the fragment ion. Typically the kinetic energies observed are consistent with Coulomb explosion occurred at a single critical internuclear distance for all channels, $R_c = C_m^{-1} R_e$, where C_m is a constant and R_e is the equilibrium internuclear distance of neutral molecule which is equal to 1.58 Åfor SF_6. The constant C_m has found to be 0.45 for molecules consisting of light atoms such as C, O, and N. Sanderson et al. suggested that it is also valid for SF_6 molecule [16]. Table 2 lists the experimental measured kinetic energies of F^+ and F^{2+} at a laser intensity of 9×10^{15} W/cm^2 and the theoretical ones. The theoretical values are calculated by solving the classical Newton equations starting at the critical internuclear distance R_c. When p–polarization (i.e. collinear with the TOFMS axis) was used, the energetic F ions we detected are those in linear F–S–F with its axis parallel to the TOFMS axis for the limited acceptance angle. For example, the acceptance angle for the F^+ ion having a kinetic energy of 5 eV is about 8° while for F^{2+} having 43.5 eV it is about 4°. So, the observed F^+ are from channels $(1, j, k)$, not from $(i, 1, k)$. By comparing the observed kinetic energies of fragment ions and the theoretical calculated ones, we can make some predications on the allowed MEDI channels. For F^+ ions, it is from the channel (1, 0, 1). While the F^{2+} may come from channels (2, 1, 3) and (2, 2, 2).

All of the sulphur peaks are centered about 0 eV indicating that symmetric channels of MEDI are predominant. For the nearly zero kinetic energy of the sulphur ions, they have an acceptance angle of almost 90°. This accounts for the isotropic distributions of S^{n+} ($n = 1$–4) ions which are shown in Fig. 2.The signal of S^{5+} is not presented because it is too weak. The angular distributions of F^+ and F^{2+} are depictured in Fig. 3. Both exhibit anisotropic distribution having a maximum along the laser polarization axis and a

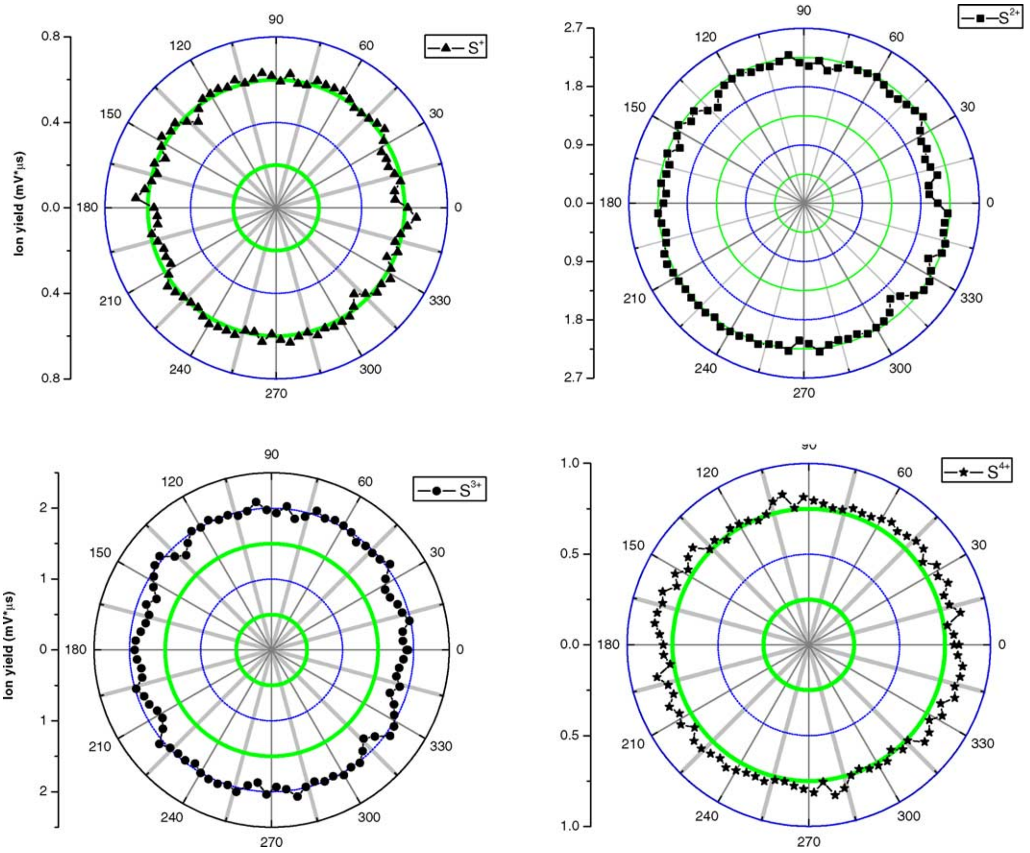
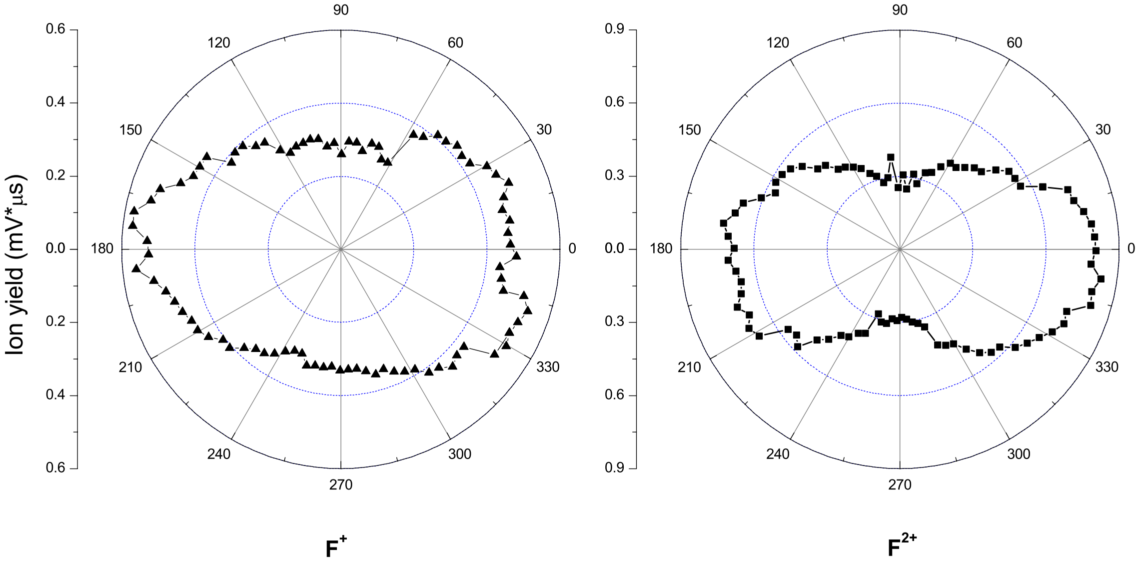


Fig. 2. Angular distributions of the atomic ions S^{n+} ($n = 1$–4) observed in the MEDI of SF_6 at a laser intensity of 9×10^{15} W/cm^2.



F^+ F^{2+}

Fig. 3. Angular distribution of the atomic ion F^+ (left) and F^{2+} (right) at a laser intensity of 9×10^{15} W/cm^2.

minimum perpendicular to it. This anisotropic angular distribution can be attributed to two effects: dynamic alignment or geometric alignment. Since the ionization rate is primarily determined by the parallel field component, different strengths of the fragment signals for parallel and circular polarization measure the degree of alignment [23]. Both linearly and circularly polarized light were used to determine which alignment mechanism is predominant in our experiment. The mass spectra obtained with circularly polarized light at intensity of 9×10^{15} W/cm^2 (upper trace) and with p-polarization light at intensity of 4.6×10^{15} W/cm^2 (lower trace) were shown in Fig. 4. The ratio of F^+ ion yield obtained at circular polarization versus p-polarization is about 2.0. This value is about 3.2, 3.4 for F^{2+} and S^+, respectively.

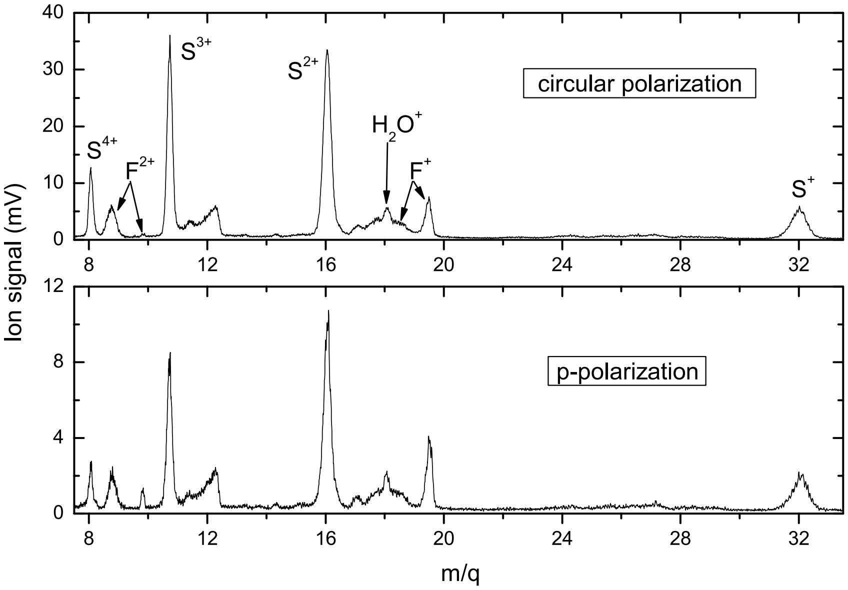


Fig. 4. Part of the TOF mass spectra of SF_6, (above) circular polarization, intensity of 9×10^{15} W/cm^2, (below) p-polarization, intensity of 4.6×10^{15} W/cm^2.

The suppression of the signal at the circularly polarized light case indicating that dynamic alignment is predominant and moreover, the larger degree of this suppression, the higher degree of dynamic alignment [23]. This is contrary to our experimental result. So, we concluded that the geometric alignment is dominated in our experiment.

4. Conclusions

The MEDI of sulphur hexafluoride in an intense femtosecond laser field was experimentally investigated by using a TOFMS. The Coulomb explosion seems to occur at a single, critical, internuclear distance. All the S ions exhibit isotropic angular distribution while the F ions are anisotropic, peaking along the laser polarization. By comparing the circular polarization and p-polarization case, we concluded that the geometric alignment is responsible for the anisotropic angular distribution of the energetic F ions.

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