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Sequential multiple ionization and fragmentation of SF₆ induced by an intense free electron laser pulse

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Abstract

We investigate the multiphoton ionization and the subsequent fragmentation of SF₆ molecules with intense x-ray-free electron laser pulses at different photon energies. We observe highly charged molecular and atomic ions which were absent in previous experiments with conventional x-ray sources. The observation of fully stripped fluorine ions suggests sequential multiphoton ionization processes with intermediate 1s electron excitation. We measure the average momentum and kinetic energy of each fragment, the comparison of which implies many-body fragmentation pathways of the molecular ions. The observed non-monotonic dependence of the kinetic energy on the charge states of fluorine indicates the multiphoton ionization of ‘isolated’ atomic neutral fluorine or fluorine ions resultant from bond cleavages and also implies the fragmentation of highly charged molecular ions that are produced at a later time during a single pulse.

(Some figures may appear in colour only in the online journal)

1. Introduction

Multiphoton ionization is an important process in the strong field interaction with atoms and molecules and has been intensively investigated with ultrafast table-top lasers [1–3]. Typically, optical lasers of near-visible wavelength ionize valence or inner valence electrons via a sequential or simultaneous absorption of multiple photons resulting in the population of ground or excited molecular ionic states. There has been much interest in investigating the fragmentation dynamics of small ionized molecules as prototypes [4–8], revealing the nature of the interaction and providing a basis to understand the breakups of more complex systems, such as large organic molecules [9]. Even for diatomic molecules, the dissociation channels can be complicated; for polyatomic molecules, the multibond cleavage associated with extra degrees of freedom adds an additional complexity to the dynamics and its investigation [8, 10]. Being an octahedral molecule, SF₆ has been chosen and intensively studied to understand the molecular fragmentation dynamics, especially many-body breakups of molecules [11–15]. With conventional ionizing sources, mostly the fragmentation of dications was studied: direct valence electron ionization via single-photon–two-electron processes using extreme ultraviolet or synchrotron light sources [12, 15, 16], and valence/inner valence ionization via inner valence/core ionization followed by the Auger decay using a high-energy ion/electron impact or synchrotron light sources [11, 17–19]. X-ray multiphoton ionization involving a core-shell ionization has been enabled only recently with the development of free electron lasers.
2. Experiment

The experimental system used to carry out this work was the high field physics chamber in the Atomic, Molecular and Optical Sciences hutch at the Linac Coherent Light Source at the SLAC National Laboratory. The ion time-of-flight (i-TOF) spectrometer used to collect the data presented in this work was oriented perpendicular to both the propagation and polarization directions of the x-ray beam [25]. The i-TOF spectrometer resided across from five-electron time-of-flight (e-TOF) spectrometers [23, 25, 26]. The target SF$_6$ molecules were delivered to the interaction region by means of a horizontally oriented supersonic jet, parallel to the beam polarization, via a 100 μm pulsed nozzle. Gas density of the SF$_6$ in the interaction region was estimated to be around 10$^{10}$ particles per cm$^3$. The photon energies of the FEL pulses were 800 and 1000 eV (±15 eV) and the pulse duration was 280 fs. The single pulse energies were 1.8 mJ at 800 eV and 2.0 mJ at 1000 eV, so that the fluences were roughly the same for the two-photon energies. The pulse energy was measured upstream of the beam transport and focusing optics [27] and was reduced by 65–85% at the interaction region due to the optics losses [27, 28]. The FEL beam was focused to an area of about 2 μm$^2$ by Kirkpatrick–Baez mirrors [29].

The i-TOF spectrometer was optimized for a high count rate mode of operation. It consisted of two acceleration regions, with the first one being the interaction region, and the third section being a drift tube (see figure 1). The voltages of the acceleration regions were chosen for a time-focusing setup. The second acceleration region was separated by a high-transmission grid from the drift tube to ensure uniform and constant electric fields without any lens effects. At the end of the interaction region away from the detector, a circular metal plate with a specially cutout opening (figure 1(c)) was used to allow electrons to fly through to the e-TOF entrances if the i-TOF spectrometer was not operating and the interaction region field was set to zero.

The interaction region was separated from the second acceleration segment by a plate shown in figure 1(b). A 1 mm × 10 mm slit in the centre oriented with its long side along the FEL polarization, serves as a very accurate x-ray focus alignment tool, and it also significantly suppresses the ion rate at the detector. Figure 2 shows the transmission curves due to the presence of this slit, obtained from the SIMION simulation. The suppression of the simultaneous detection of ion pairs originating from the two-body Coulomb explosion is particularly strong. As shown by the green curve in figure 2, only about 15% of all forward-going ions that hit the detector would have their backward-going ‘sibling’ ions go through the slit and also hit the detector. For comparison, a typical open COLTRIMS-like [30] spectrometer has this fraction close to 100%, not accounting for the multi-channel plate (MCP) single-ion detection efficiency, which would be comparable for both cases and is typically between 30 and 50%.

The i-TOF data were obtained by recording and analysing a complete MCP signal trace, using an ACQIRES [31] system,
in general, higher than that of molecular ions with the same electron. In general, the core electron BE increases for higher typical lifetime of a core hole state in light elements is a few All curves were generated assuming a typical 4 mm jet diameter at the interaction region.

for every FEL pulse. The resolution for the i-TOF was found to be better than 1 ns.

The very sharp TOF character of all the sulfur charge states (KE = 0) allowed for their separation and/or subtraction from the total ion TOF spectrum to reveal the spread of the fluorine ion TOFs, indicating their significant KE. This spread was used to extract the upper limit on the momentum (and thus KE) of different molecular and atomic ions.

### 3. Results

#### 3.1. Multiphoton ionization of SF₆

The dominant processes in the interaction of light atoms and molecules with intense FEL bunches at pulse durations much longer than the hole state lifetimes are sequential multiple photoionization-Auger-decay (PA) sequences [20, 21, 32–36]. At photon energies above the core-electron binding energy (BE), a core electron is ionized by photoabsorption. The typical lifetime of a core hole state in light elements is a few femtoseconds—the core hole will be filled in the following Auger decay resulting in the removal of a second outer electron. In general, the core electron BE increases for higher charge states with valence vacancies. Also, atomic BEs are, in general, higher than that of molecular ions with the same charge, i.e., the 1s electron BE of F⁺ is higher than the F 1s electron BE in SF⁺. Throughout this work, unless noted otherwise, ‘n+’ refers to vacancies in valence or inner valence shells. As long as the photon energy is above the core electron BE of the resultant ions, at high fluence of the FEL, the above PA process can repeat till the end of the x-ray pulse duration. These PA processes occur while the molecular ions dissociate [20]. The BE of the F 1s electron in SF₆ is 694 eV and the minimum 1s electron BE of F⁺ are 785, 825, 870, 908, 954 and 1103 eV, for n = 3, ... , 8 (integer n), respectively. The BEs of the 1s and the 2s electrons in atomic S are 2483 and 238 eV, respectively. The photon energies used in this work are above the BE of the 1s electron in F and all the F⁺ except F⁸⁺ and also above the BE of the 2s electron in S and Sⁿ⁺. Therefore, in this work, the dominant processes are the sequential PA steps at the fluorine 1s level and sulfur 2s level with the former having the higher photoionization cross section. These PAPA... sequences, concurrent with molecular dissociation, lead to highly charged atomic and molecular ions.

Figure 3 shows the i-TOF spectra taken at two different photon energies, at roughly the same fluence. We observe molecular ions SF⁺ (integer x = 1–5), SF²⁺ (x = 2–4), as well as abundant atomic ions F⁺ (integer n =1–9) and Sⁿ⁺ (n = 1–14). To the best of our knowledge, highly charged ions of F⁺ (n ≥ 3) and Sⁿ⁺ (n ≥ 3) are new products of ionization by the x-ray FEL pulse. The spectra at the two-photon energies are normalized to match the proton peak height. The spectrum at 800 eV shows more abundance of the lower charge atomic ions, especially the F⁵⁺ dissociating atomic peaks with a double peak structure. This is because at 800 eV, the dominant pathway to F⁶⁺, F⁷⁺ [1s(1s),ν⁴] → F⁶⁺ [1s(1s),ν⁴] → F⁵⁺ + F, via single-photon PA is energetically forbidden. Due to the photon energy jitter and minor processes that may occur, such as shake-off (one-photon–two-electron) processes, there is still a weak signal of higher charge states of F⁺ with n ≥ 6 at 800 eV.

At 1000 eV, pathways to higher charge states (n ≥ 6) are open. As shown in figure 3, we observed the high charge atomic states, up to the fully stripped fluoride atomic ion, F⁺⁺. It is energetically not allowed to produce F⁺⁺ via a single-photon–single-electron ionization—the photon energy for direct ionization of ground state F⁸⁺ is calculated to be 1103 eV (see footnote 7). We will discuss the possibility to remove the last core electron via a multi-photon process in section 4. As mentioned above, since both of the photon energies are far above the S 2s electron BE and far below the S 1s electron BE, the PAPA... sequences are dominantly 2s level photoionization followed by an Auger cascade. We observe Sⁿ⁺ ions up to n = 14 in both 800 and 1000 eV spectra, as shown in figure 3.

#### 3.2. Fragmentation of SF₆ subsequent to multiphoton ionization

In previous studies with conventional light sources [18, 19] or ion/electron impact [11, 17], mainly fragmentation patterns of SF₆ⁿ⁺ following the core/inner shell ionization and subsequent Auger decay have been investigated. It was found that the dications went through many-body cleavage, resulting in SF⁺⁺ (x = 1–5), SF²⁺⁺ (x = 1–4), neutral fluorine atoms, and singly or doubly charged fluoride and sulfur ions. The bond-breaking processes can be simultaneous (the charge separation and the breaking off of the neutral elements occur at the same time) or sequential (neutral elements are produced first followed by the charge separation), as shown below:

\[
SF_{6}^{2+} \rightarrow SF_{6}^{+} + F^+ + (v - 1)F
\]

\[
SF_{6}^{2+} \rightarrow SF_{6}^{x+} + vF
\]

(1) (deferred charge separation)

SF⁺⁺ → SF⁺⁺ + F⁺.
where $x + v = 6$ (integer $x$ and $v$). In some cases, F$_2$ is produced instead of F atoms [10]. Previous work also shows that, as the photon energy increases, in which case upper excited dicaticion states are reached, more doubly charged ions are produced than singly charged and more SF$_x^+$ or SF$_x^{2+}$ with smaller $x$ are produced, indicating more pronounced bond cleavage [15]. It is reasonable to consider that the first PA process by FEL which leads to highly excited dicationic states cleavage [15]. It is reasonable to consider that the first PA process by FEL which leads to highly excited dicationic states is likely to result in a similar fragmentation pattern. Further PA may occur on the dissociating fragments. To quantify the fragmentation pathways, convoluted with the multiple photoionization, we extracted the average momentum ($P_{av}$) and the kinetic energy ($KE_{av}$) of the fragment ions (see table 1).

As seen in the ion spectra (figure 3), the dominant observed atomic peak is F$^+$. The measured $KE_{av}$ is 11.9 ± 0.7 eV, which is consistent with 8.5–9.6 eV for S$^+$ + F$^+$ and SF$_x^{2+}$ + F$^+$ (x = 1–3) breakup pathways obtained in the previous work [11] using a photon source. The pathway of SF$_x^{2+}$ + F$^+$ typically produces F$^+$ with KE of less than 5 eV [11, 12]. The observation of F$^+$ ions with larger KE indicates production of smaller fragment ions with higher charges, which supports the general hypothesis that PA processes, involving the core electron ionization, lead to highly excited molecular states. Due to the geometry of SF$_6$, and since S–F bond angles change for different molecular charge states, when the molecules lose a neutral or ionized atomic fluorine in a simultaneous or sequential bond breaking, the residual molecular ion, SF$_x^{2+}$, may receive kicks in different directions. In addition, due to the relatively heavier mass, SF$_x^{2+}$ ions have smaller shares of the total KER compared to the fluorine atomic or dimer recoils. As a result, the final KE for all the SF$_x^{2+}$ (x = 1–5) and atomic sulfur ions is small with KE$_{av}$ of less than 1.5 eV; this is also indicated by the narrow spectral peaks shown in figure 3.

The KE for F$_2^{2+}$ is more than three times that for F$^+$ and the KE of higher charge states ($n \geq 2$) increases as the charge increases to $n = 5$, drops at $n = 6$, and increases more slowly thereafter. The KE of F$^+$ may indicate the origins of the ions and the pathways they go through, as will be discussed in the following.

![Figure 3](image)

**Figure 3.** i-TOF spectra for 800 (blue) and 1000 eV (red) x-ray beams. The rightmost part of the spectrum is shown on a logarithmic scale to amplify the molecular ion states. Double-sided arrows indicate the TOF distribution width of the fluorine charge states due to their significant KE (see table 1).

<table>
<thead>
<tr>
<th>Species</th>
<th>$P_{av}$ (au)</th>
<th>$KE_{av}$ (eV)</th>
<th>Abundance (arb. un.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF$_x^+$</td>
<td>$n = 1$</td>
<td>175 ± 5</td>
<td>11.9 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>$n = 2$</td>
<td>301 ± 30</td>
<td>35 ± 10</td>
</tr>
<tr>
<td></td>
<td>$n = 3$</td>
<td>313 ± 45</td>
<td>38 ± 12</td>
</tr>
<tr>
<td></td>
<td>$n = 4$</td>
<td>281 ± 100</td>
<td>31 ± 20</td>
</tr>
<tr>
<td></td>
<td>$n = 5$</td>
<td>455 ± 120</td>
<td>80 ± 40</td>
</tr>
<tr>
<td></td>
<td>$n = 6$</td>
<td>193 ± 80</td>
<td>15 ± 10</td>
</tr>
<tr>
<td></td>
<td>$n = 7$</td>
<td>246 ± 100</td>
<td>24 ± 15</td>
</tr>
<tr>
<td></td>
<td>$n = 8$</td>
<td>257 ± 60</td>
<td>26 ± 13</td>
</tr>
<tr>
<td></td>
<td>$n = 9$</td>
<td>348 ± 46</td>
<td>66 ± 15</td>
</tr>
</tbody>
</table>

**Table 1.** Measured average momentum ($P_{av}$), average kinetic energy ($KE_{av}$), and the corresponding abundances (1000 eV photon energy).

4. Discussion and interpretation

As mentioned above, we observe the fully stripped fluorine atomic ion F$^{2+}$ at 1000 eV, but at this photon energy, it is energetically not possible to remove the last 1s electron via a normal single photon ionization, which requires a minimum
photon energy of 1103 eV. Given the above x-ray beam/focus parameters, the absorption of the photons by the fluorine will happen every 15 fs or even less often, so that by the time it accumulates the charge of 8+, the ion will be well isolated from the parent and can be approximated to have atomic energy levels.

Considering the duration of the FEL pulse of 280 fs, a more likely scenario is a multi-photon process where a resonant photoexcitation of the electron is followed by a photoionization of the excited electron(s). There are two likely mechanisms for producing F$^{8+}$ at a photon energy of 1000 eV, as shown in figure 4. One of them (figure 4(a)) begins with F$^{7+}$ in the ground state. A 1s electron is ionized via direct photoionization. The remaining 1s electron is excited to the 3p orbital by absorbing a photon, followed by the photoionization producing fully stripped fluorine ions, i.e., a two-photon–one-electron process involving the resonant (980 eV (see footnote 7)) electron excitation. Considering a possible photon energy centroid error of $\sim$10 eV together with the FEL natural bandwidth and a jitter of $\pm$ 15 eV, the resonant 980 eV transition might be accessible. The other mechanism (figure 4(b)) starts with an excited state of F$^{7+}$ with one electron in the 1s shell and the other in the 2s shell. The core electron is photo excited (1003.3 eV (see footnote 7)) to the 4p orbital, followed by the direct single-photon double ionization or two sequential single-photon ionizations of the two electrons in the 2s and 4p orbital, i.e., a one- or two-electron–two-electron process. A PA sequence on the neutral F atom will eventually result in F$^{7+}$ in the excited state with one electron in the 2s state. A PA sequence on F$^{+}$ will result in F$^{7+}$ in the ground state. We will discuss next that the neutral F atom and the F$^{+}$ ion are dominant products of bond cleavage following the first PA process.

As presented in [11], where SF$_6$ was ionized via an ion impact, the intensity of the SF$_6^{x+}$ signal shows an ‘odd and even’ effect: SF$_6^{x+}$ ions with an even number of electrons are preferentially produced. In this work, this alternating pattern breaks down (see figure 3) due to the further multiple ionization of the resultant fragment ions from the first PA process.

One approach to identify ion pairs from the same parent ion in a two-body breakup is to examine the momenta of the fragments, i.e., the momentum of each should be equal and opposite to the other, complying with the momentum conservation law. Figure 5 shows the measured $P_{av}$ of different ion species. The lack of a clear correlation between the momenta of different ion species indicates multibond cleavage of the molecular ions. Typically, the KE in the bond break with neutral elements (F or F$_2$) is much smaller than from charge separation [10, 11, 16]. Hence, the final measured KE is probably a result of the Coulomb explosion process. The measured KE$_{av}$ for SF$_2^{+}$ (0.83 $\pm$ 0.08, 1.4 $\pm$ 0.1 and 1.5 $\pm$ 0.2 eV, for $x = 3, 2, 1$) is consistent with what was measured in the previous work for determined pathways SF$_2^{+}$+F$^{+}$ (0.67, 1.2 and 1.8 eV for $x = 3, 2, 1$ [11]), indicating the likelihood that the dominant pathways to get to the SF$_2^{+}$ ions are through the SF$_2^{+}$+F$^{+}$ dissociation. For SF$_2^{+}$, the KE$_{av}$ measured in this work (0.4 $\pm$ 0.1, 0.9 $\pm$ 0.2 and 0.7 $\pm$ 0.2 eV for $n = 3, 2, 1$) are lower than what was obtained in the previous work for SF$_2^{+}$+F$^{+}$ (1.8, 2.3 and 3.6 eV for $x = 3, 2, 1$ [11]), implying the contribution from SF$_2^{+}$+F (or F$_2$), where the KE release is smaller than in charge separation. Therefore, the first PA dominantly produces neutral or singly charged fluorine fragments.

As mentioned previously, the measured value of the KE is the sum of the energies accumulated by the ions through all sequential breakups they experienced. The bond cleavage of dicationic SF$_6$ ions releases a significant amount of neutral F atoms or F$^{+}$ ions [10, 15]. We focus on the behaviour of a single fluorine ion and consider the rest of the fragments as one element (referred as SF$_{kernel}$) in an effective Coulomb repulsion scenario. In this simplified effective two-body/single-bond breakup, the further ionization either on the dissociating F/F$^{+}$ or SF$_{kernel}$ can occur at a short bond length, giving rise to a strong kick to fluorine fragments, in which case a monotonic increase of the KE of the fluorine ions for increasing charge states is expected; or, the further sequential ionization can occur at a long distance where the Coulomb repulsion is weak, in which case the ion KE is expected not to change from lower to higher charge states. As shown in figure 5 and table 1, we do not see either of the above two trends in the overall $P_{av}$ or KE$_{av}$ dependence on the charge state. The KE$_{av}$ of F$^{2+}$ is more than three times that of F$^{+}$. It then appears to increase for $n$ up to 5, then drop at $n = 6$, followed by a gradual increase for higher charge states. The deviation from a monotonic trend implies that certain dominant pathways are terminated before the ions reach high charge states.

* Private conversation with the instrument scientists at LCLS.
reason could be that for those pathways there is a ‘temporal’ barrier. As mentioned above, the first PA cycle dominantly produces neutral and singly charged fluorine fragments. Due to dissociation, these fragments become isolated, and the following ionizations occur at a large internuclear separation, which does not result in a dramatic increase of KE even when they get ionized to F\textsuperscript{9+}. The scenario is different for the residual ion, for example, SF\textsubscript{2}\textsuperscript{x+}, shown with high abundance in figure 3. The next PA cycle removes at least another two electrons resulting in SF\textsubscript{4}\textsuperscript{x+}, which undergoes a more violent Coulomb explosion resulting in fragments of higher KE. This explosion takes place at a later time during the x-ray pulse, thus the resulting fluorine fragments may not have time to get ionized to extremely high charge states. The contrast of these two pathways may explain the non-monotonic character of the KE dependence on the ion charge state.

For several charge states of fluorine there are low KE components as seen in figure 3, particularly for F\textsuperscript{n+}. These low KE ions possibly result from the further ionization of the F ions that are produced at the early stage of the multiple ionization and become ‘isolated’ quickly before losing more electrons and acquiring more kinetic energy.

5. Conclusion

This work presents the results of multiple ionization of SF\textsubscript{6} molecules via sequential photoabsorption followed by Auger decays inducing the molecular fragmentation. We observe the highly charged molecular and atomic S and F ions. The observed fully stripped fluorine ions are produced via a two-photon–one-electron process which involves the photoexcitation of core electrons. With the measurements of the \( P_{\text{av}} \) (and KE\textsubscript{av}) of the fragment ions, we provide quantitative constraints on dynamic pathways of many-body fragmentation following the multiphoton ionization. Our data indicate multibond cleavage of the molecular ions. We observe a non-monotonic dependence of the fluorine ion KE on the charge state. This indicates the multiple ionization of ‘isolated’ atoms or dimers resultant from the bond cleavage, while the highly charged molecular ions are produced at a later time during a single x-ray FEL pulse, giving rise to energetic atomic ions.

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