

Strong Selectivity in Symmetry forbidden vibronic transitions in Deep Core Ionic Photofragmentation of the SF₆ molecule



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ABSTRACT

Deep core photoionization of the sulfur hexafluoride molecule have been studied with X-ray photons at energies around the S K edge (from 2472 eV to 2489 eV), using time-of-flight multicoincidence technique with synchrotron radiation. Total and partial photoion yields for the fragments have been recorded as a function of the incident photon energy. The atomic fluorine ion, F⁺ is the most abundant species observed in the mass spectra at the energy range studied. The SF₆ molecule undergoes a complete break up with the formation of atomic doubly and triply charged S²⁺, S³⁺, and F²⁺ fragments. The intensity of absorption for the dipole-forbidden but vibronically allowed transition S K (1a_{1g} → 6a_{1g}) was calculated and it is shown that it play a relevant role in the fragmentation pattern.

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1. Introduction

The dynamic interaction concerning the electronic and nuclear degrees of freedom in molecules, the so-called vibronic coupling, becomes noticeable when the symmetry forbidden electronic transitions become opened due to the concomitant excitation of some asymmetric vibrations. Intensities can be relocated from symmetry allowed transitions via some specific normal modes, via the so-called promoting modes [1].

Sulfur hexafluoride is the most effective greenhouse gas, with a global warming potential 23900 times higher than that of CO₂ [2–5]. It is exceedingly long-lived, with a calculated atmospheric lifetime up to 3200 years, since is virtually inert in the troposphere and stratosphere [2–5]. SF₆ has an octahedral geometry (O_h point group), consisting of six fluorine atoms attached to a central sulfur atom. In the octahedral symmetry, only excited states of t_{1u} symmetry are permitted for dipole transitions from the a_{1g} state [1]. The observed feeble transitions in the S 1s edge photoabsorption spectrum of the SF₆ are explained as vibronically supported transitions to electronic states of same symmetry [1].

The SF₆ molecule has been focus of previous studies [5–8]. For instance, the lack in the observation of the parent SF₆⁺ ion has been

credited to a Jahn-Teller instability [5]. Near the S 2p edges, the complete fragmentation of the triply charged SF₆³⁺ was observed to take place in a sequential manner, where the first step is the loss of an F atom and formation of SF₅³⁺, followed by a violent ejection of two F⁺ ions. Slow separation of F atoms brings the residual SF₃⁺ to the stable S⁺ [6]. Absolute photoabsorption cross sections of KL-edge double core hole of SF₆ was measured by Reynaud *et al.* [7]. Molecular orbital calculations for SF₆ have been performed by Nakamatsu *et al.* [8] using the discrete variational X α method. The threshold photoelectron spectrum of SF₆ was determined and the electronic structure of the outermost electronic levels is well-known [9]. It should be also noted that in the foundational works on the PEnPICO techniques, independently reported by Eland and Frasinsky, the SF₆ was included within the studied species. These studies could serve as a first approximation for the analysis of the PEPICO spectra here determined [10–12].

The PEnPICO spectra used in conjunction with synchrotron radiation are recognized as outstanding technique for studying the ionic fragmentation and dissociation dynamic of molecular systems. The reader should refer to references [13–17] for the last contributions that appeared on the literature involving PEPnPICO studies on molecules of atmospheric interest.

In this work, we have carried out time-of-flight measurements of branching ratios for the production of ionic fragments of SF₆ by synchrotron radiation around the S 1s edge. In the next section, the experimental set-up is described. The theoretical approach is

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presented in section III. In Section IV the measured relative probabilities of the different fragmentation channels are discussed. In the last section concluding remarks are made.

2. Experiment

The results were obtained at the Brazilian synchrotron facility LNS, on the Soft X-ray Spectroscopy beamline (SXS), on the gas-phase end station dedicated to time-of-flight spectrometry [18–21]. Photons beams from 2472 eV to 2489 eV were obtained using two double crystal monochromators with spectral resolution $\Delta E = 0.8$ eV at $E = 4000$ eV, and beam size at the sample was estimated to be 2.0×3.0 mm².

The target SF₆ (99.8% purity from White Martins) was introduced in the experimental chamber as an effusive gas jet through a grounded needle, placed in the middle of the extraction zone. The target is singly and multiply ionized by energy selected X-ray light in the interaction region of intense uniform electric field (750 V/cm) which pulls the photoelectrons to a microchannel plate (MCP) detector and the positively charged photoions into the flight path of a Wiley–McLaren time-of-flight (TOF) mass spectrometer. The flight times of the fragments, timed from detection of one of the photoelectrons by a multi-stop time-to-digital converter are built up. The spectrometer collects uniformly ions with energies up to 30 eV.

Owing to the partial multi-hit time resolution, it was not possible to fully detect coincidences between fragments with TOF differences smaller than 20 ns in the PE2PICO spectra. But in order to take into account the F⁺ + F⁺ coincidences correctly, the procedure explained in ref. [18] was followed. In brief, we have used the shape of the PEPICO spectra to correct the PE2PICO spectra. The F⁺ + F⁺ coincidences were projected onto the t₁ (the time-of-flight of the first ion) and t₂ (the corresponding time-of-flight of the heavier ion) axes, summed, divided the corresponding area by two. The projected peak shapes were adjusted to fit the borders of the summed projections. After adjusting the peaks from the PEPICO spectra to the sum of the projections of the F⁺ + F⁺ coincidences, the normalized PEPICO counts were considered as the value for the coincidence analysis.

From the width of the time-of-flight peak distributions the average kinetic energy release (KER) of the fragmentation products of the core excited SF₆ were calculated using the standard relation [18]

$$\langle U \rangle = \left(\frac{qE\Delta t_{KER}}{2} \right)^2 \frac{1}{2m} \quad (1)$$

where q is the fragment charge state, E is the electric field in the interaction region, Δt_{KER} is the peak width (FWHM), and m is the mass of the fragment.

3. Theoretical approach

In the ground state electronic configuration of SF₆, the core molecular orbital is 1a_{1g}, which has an S 1s character [5]. The unoccupied 6a_{1g} and 6t_{1u} orbitals are antibonding (σ^*) in character. The first transitions in the S K-edge are of 1a_{1g} → 6a_{1g} and 1a_{1g} → 6t_{1u} types (see Fig. 1). For the second type, the transition is allowed by dipole selection rules, but in the 1a_{1g} → 6a_{1g} case, the transition is forbidden. This does not mean that the intensity of this transition is strictly zero since it can be feeded by the so called intensity borrowing mechanism. A simple analysis based on group theory shows that this transition can become allowed through vibronic coupling mechanism promoted by the normal modes of vibration belonging to t_{1u} and t_{2u} irreducible representation of O_h group. Accordingly, the transition moments and the oscillator strengths

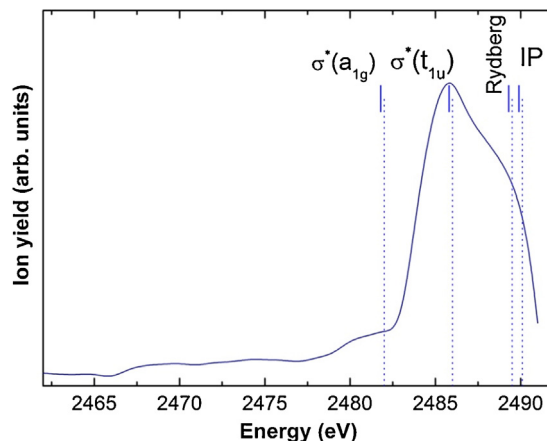


Fig. 1. Total ion yield of SF₆ positive fragments as a function of the photon energy in the near S 1s edge region. The vertical axis is in a log scale. The vertical lines indicate the positions of the transitions.

can be calculated by the direct vibronic coupling method [22–25]. The theoretical procedure used was discussed in details elsewhere [22]. Briefly, the expression considered for the optical oscillator strength is

$$f = \frac{2}{3} E g_k \left| \langle \chi_{kv} | M | \chi_{00} \rangle \right|^2 \quad (2)$$

where χ_{00} is the vibrational function of the electronic ground state and χ_{kv} is the v^{th} vibrational function of the k^{th} electronic state. E and g_k stand, respectively, for the transition energy and the degeneracy of the final state. In equation (2), only the lowest vibrational level of the electronic ground state is occupied at the moment the electronic transition takes place, assuming that the experiment is performed at low temperature. M is the transition moment involving ground and excited electronic states.

$$M = - \langle \psi_k(r_1, r_2, \dots, r_n; R) | \sum_i r_i | \psi_0(r_1, r_2, \dots, r_n; R) \rangle \quad (3)$$

Summing equation (2) over all vibrational states of the excited electronic state and expanding the squared dipole transition moment in power series of the normal coordinates of vibration motion lead to the expression

$$f = \frac{2}{3} E g_k \langle \chi_{00} | M^2(Q) | \chi_{00} \rangle \quad (4)$$

with

$$M^2(Q) = |M(0)|^2 + \sum_L \left(\sum_j a_j(Q_L)^j \right) \quad (5)$$

The transition moments are directly calculated along each one of the L normal modes, followed by fitting to a polynomial function of order j in Q_L , where a_j are fitting coefficients. Then, the integration of expression (4) becomes straightforward.

The first term in the right hand side of equation (5) represents the transition dipole moment calculated at the equilibrium geometry, the vertical transition. If the transition is dipole-allowed, this term results in the main contribution (a_{1g} → t_{1u}, for instance). On the other hand, if it is dipole-forbidden (a_{1g} → a_{1g}, for instance), the intensity comes entirely due to terms of the double summation (the summation is performed over all normal modes L of suitable symmetry).

The transition moments were calculated at inner-shell state-averaged multiconfigurational self consistent field [25]. The configurations in this MCSCF calculation includes the Hartree–Fock

Table I

Calculated oscillator strength for S 1s ($1a_{1g} \rightarrow 6a_{1g}$) transition (vibronic coupling) and S 1s ($1a_{1g} \rightarrow 6t_{1u}$) transition (vertical approximation).

S 1s ($1a_{1g} \rightarrow 6a_{1g}$)		
Symmetry	wavenumber(cm ⁻¹)	OOS
T _{2u}	335	6.40×10^{-9}
T _{1u}	602	2.38×10^{-4}
T _{1u}	955	7.80×10^{-4}
Total OOS		1.02×10^{-3}
S 1s ($1a_{1g} \rightarrow 6t_{1u}$)		
Total OOS		4.27×10^{-2}

(HF) configuration for the ground state and as many configuration as needed for a HF-like description of the core-hole excited state, one for $1a_{1g} \rightarrow 6a_{1g}$ and three for $1a_{1g} \rightarrow 6t_{1u}$. This method may also be considered as a state-averaged Hartree-Fock. Relativistic corrections, which are very important in S K-shell, are partially taken into account by the Douglas-Kroll method corrected to third order. All calculations have been done with aug-cc-pVTZ basis set for S and aug-cc-pVDZ for F.

4. Results and discussion

The total ion yield of the SF₆ molecule is shown in Figure 1. The spectrum of the SF₆ presents resonances around the sulfur 1s edge superposed to the background due to absorption by fluorine atoms as indicated in Fig. 1. The incident photon-energy calibration was accomplished by scanning the monochromator through the S 1s threshold region and monitoring the total photoion production. As the total ion production almost mimics the photoabsorption spectrum, by comparing peak structures in the total ion production to the photoabsorption results [7,26] the photon energy calibration is accomplished. From Fig. 1, a discrete absorption feature is observed at 2482 eV and assigned to a dipole-forbidden transition of the S 1s electron to the unoccupied antibonding $6a_{1g}$ valence MO and the S 1s $\rightarrow 6t_{1u}$ resonance at 2486 eV [26]. Core excitation to Rydberg orbitals are also identified at 2489.5 eV [7]. The rightmost vertical line (2490 eV) corresponds to the ionization potential, S 1s $\rightarrow \infty$ (IP) [7,26].

In order to corroborate the assignments for the first two peaks, theoretical calculations at IS-MCSCF level at the S K edge of SF₆ were performed. The S 1s ($1a_{1g} \rightarrow 6a_{1g}$) transition is formally forbidden but can become allowed by the vibronic coupling mechanism. This implies that the first term in the right-hand side of equation (5) vanishes and the contribution to the intensity of the transition results from the terms of the double sum of equation (5). The vibrational inducing modes are that belonging to t_{1u} and t_{2u} irreducible representation of O_h point group. The second transition, S 1s ($1a_{1g} \rightarrow 6t_{1u}$) is allowed, which means that the first term in the right-hand side of equation (5) gives the main contribution to the intensity. In Table I, we present the contribution of each mode to the intensity of the S 1s ($1a_{1g} \rightarrow 6a_{1g}$) transition. The t_{1u} mode with vibrational frequency of 955 cm⁻¹ presents the greater contribution to the oscillator strength. The oscillator strength for S 1s ($1a_{1g} \rightarrow 6t_{1u}$) transition is also included. As can be seen, the dipole-forbidden transition has an Optical Oscillator Strength (OOS), which is about an order of magnitude smaller than the allowed transition. This prediction agrees with the experimental results, as shown in Fig. 1. It is worth emphasizing that the intensity of the dipole forbidden transition although small, is not zero, and contributes to the fragmentation pattern, as shown in Fig. 2.

The calculated transition energies are 2495.9 eV and 2499.9 eV for S 1s ($1a_{1g} \rightarrow 6a_{1g}$) and S 1s ($1a_{1g} \rightarrow 6t_{1u}$) transitions respectively. The agreement with experimental values is within 0.6%. The main reasons for the small discrepancy are related to the absence of other relativistic and correlation energy corrections. The relative energy

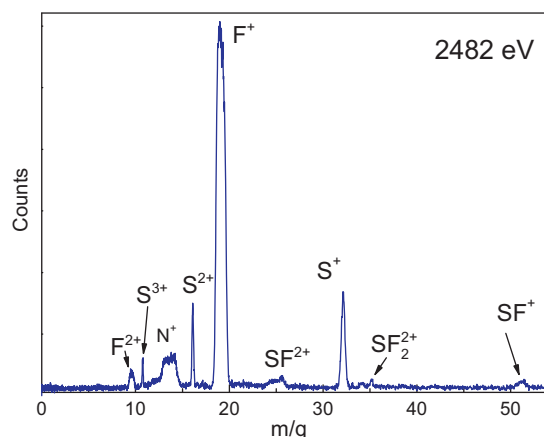


Fig. 2. PEPICO spectrum of the SF₆ molecule at 2482 eV.

shift among those transitions was calculated to amount 4 eV, which is in good agreement with the experimental spectrum, as shown in Figure 1 and presented also in Ferret *et al.* [26].

5. 1-PEPICO spectra

In order to study the fragmentation processes following inner-shell excitation and ionization, mass spectra were obtained at selected photon energies ranging from 2472 eV to 2489 eV, around the S 1s edge. For the sake of obtaining corrected mass spectra due only to single, double, and triple coincidences, the data analysis procedure described previously [18,21] was adopted to suppress false coincidences in the PEPICO spectra. Mass spectra measured at 2482 eV photon energy, on the $1a_{1g} \rightarrow 6a_{1g}$ resonance is presented in Fig. 2. The assignment of each peak in the time-of-flight mass spectra to its corresponding ion species is indicated in the figure. From Fig. 2 it can be seen that after the SF₆ molecule is core excited, its unity is damaged, directing the molecule to be effectively fragmented. Several electrons, responsible for the chemical bonds, are ejected, achieving virtually the complete breakup of the system. Exceptions are the small contributions of the triatomic SF₂²⁺, and the diatomic SF₂⁺, and SF₂⁺ molecular fragments. The mass spectra is dominated by atomic fragments, in all cases the F⁺ ion plays a very important role, being the dominant peak in the spectra with 70%. The F⁺ fragment is formed with large kinetic energy, as reflected in the peak broadness of ~37 ns. The doubly charged F₂²⁺ fragment observed at all photon energies also presents broad distributions (~37 ns), which is a signature of high kinetic energies. The heavier molecular fragments SF_n⁺ ($6 \geq n \geq 2$) were absent in the all photon energies. The lack of heavier molecular fragments can be attributed to the fast removal of the electrons from the molecule followed by Coulomb explosion producing the atomic ions with high kinetic energies. The heavier fragment observed in the mass spectrum is the doubly charged SF₂²⁺ ion. The presence of this doubly charged fragment were accounted to the fact that the S²⁺ ion exhibits a preference to combine with two F atoms in absence of sp hybridization [4].

Figure 3 shows the partial ion yield (%) of the SF₆ fragments as a function of the photon energy. Above the S 1s edge, one can observe the increasing in the production of S⁺, S²⁺, and S³⁺. Their widths, ~16 ns, ~9 ns, and ~7 ns, respectively, indicate that they are produced with very low kinetic energy. Below the S K edge, the presence of higher charged states occurs after the removal of an inner-shell electron (F 1s, S 2p, S 2s), where the residual ion decays via a non-radioactive decay.

From figure 3, a severe intensity change in the TOF spectra $1a_{1g} \rightarrow 6a_{1g}$ resonance is observed. This selective formation of the

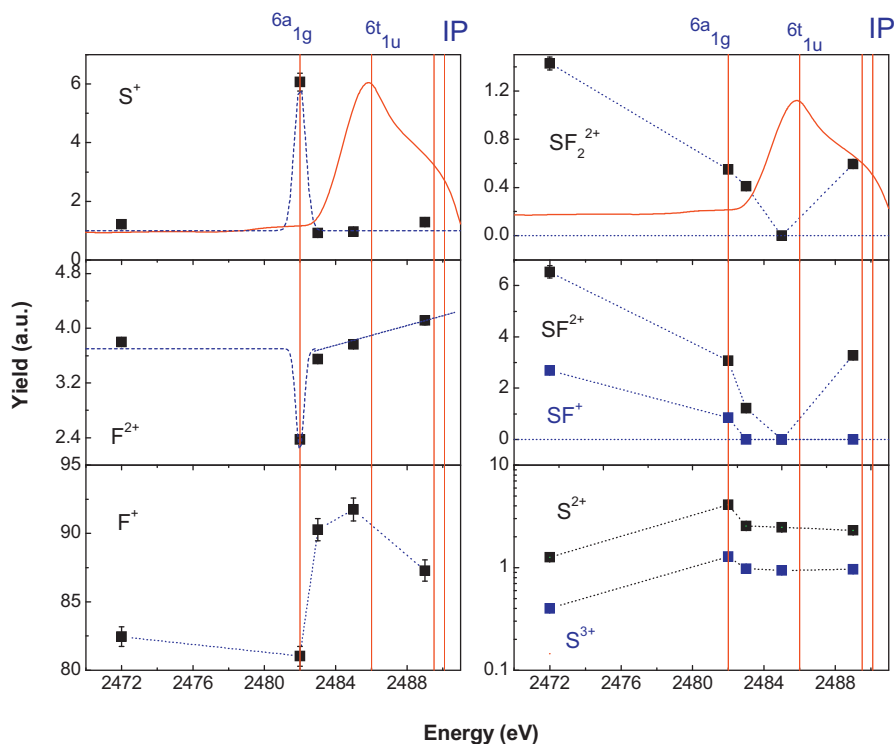


Fig. 3. Partial ion yield (%) of some SF_6 fragments as a function of the photon energy. For the sake of comparison, the total ion yield is also presented (full line). The vertical lines represent the following transitions: $1a_{1g} \rightarrow 6a_{1g}$ and $1a_{1g} \rightarrow 6t_{1u}$. Dotted lines are just to guide the eyes. The peak structures at the $6a_{1g}$ resonance in S^+ and F^{2+} yields just point out the strong variation in the ion yields of those fragments.

atomic sulfur ion $\text{S } 1a_{1g} \rightarrow 6a_{1g}$ resonance can be understood in terms of the fast breakup of the molecule. The excitation of the core electron to this LUMO gives rise to a repulsive potential curve (σ^* type) along the S-F coordinate. A fast fragmentation of the molecule takes place, leading to the production of neutral moieties and a core excited S atom. This later may de-excite by autoionization creating a large amount of S^+ , and a smaller amount S^{2+} ion through double autoionization. Notwithstanding, a severe change in the equilibrium geometry is anticipated to be brought forth by the population of the $6a_{1g}$ (σ^* type) molecular orbital. Thus, the induction of vibrational series associated to the S-F bond could be predictable.

The t_{1u} orbitals in SF_6 are positioned along the F-S-F axis. Consequently, one electron in $6t_{1u}$ experiences strong repulsive interaction with other t_{1u} orbitals lying on the fluorine atoms [1]. At the $\text{S } 1a_{1g} \rightarrow 6t_{1u}$ resonance, the excited SF_6^+ molecule will relax to the several energetically accessible continua ($\text{F } 1s$, $\text{S } 2p$, $\text{S } 2s$, and valence main-line and satellite final states of SF_6^+) [26]. Highly excited satellites produced by KLL-type transitions are the most important autoionization decay for this resonance. At this resonance, the relative intensities S containing fragments (S^+ , S^{2+} , SF_2^{2+} , SF^{2+} , and S^{3+}) decrease, while the corresponding F^+ and F^{2+} ion yields are favored. For a complete description of autoionization of the $\text{SF}_6 (1s^{-1}6t_{1u})$ state to SF_6^+ photoemissions channels, and subsequent S (LVV and LVV) Auger cascades to form SF_6^{n+} ($n = 2-5$) the reader is referred to ref. [26].

6. 2-Kinetic Energy Release (KER)

Figure 4 shows the kinetic energy release (FWHM) of selected photoions of the core-excited SF_6 molecule as a function of the photon energy. It can be seen from Fig. 4 that the hottest fragments F^{2+} (20–40 eV) and F^+ (2.5–8 eV), respectively. This is not surprising, since the fluorine ions are the lighter fragments in the mass spectra, notwithstanding, due to the momentum

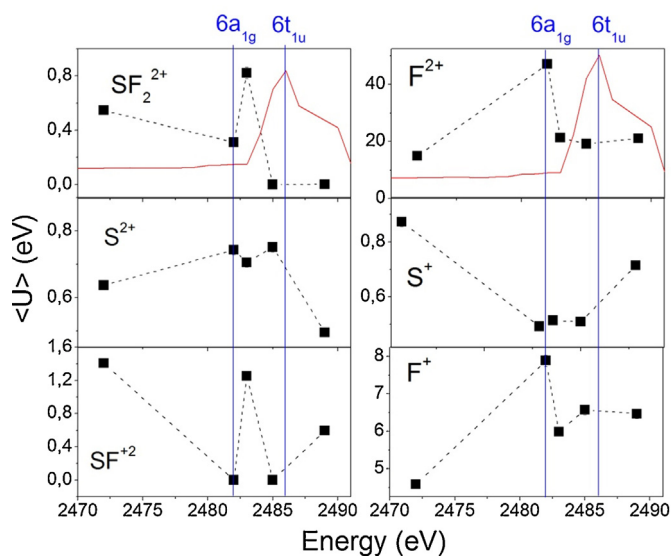


Fig. 4. Average kinetic energy release as a function of the incident photon energy of some photoions after photoexcitation of the SF_6 molecule near the S K edge. The vertical lines have been defined in Fig. 2. The full lines connecting the experimental data were drawn to guide the eyes.

conservation, they take most of the available KER. The KER of the F^+ and F^{2+} ions reveals maxima at the $1a_{1g} \rightarrow 6a_{1g}$ resonance. This behavior can be explained in terms of the repulsive nature of the $6a_{1g}$ orbital. A contrasting behavior is exhibited by the S^+ ion which shows a dip around the $\text{S } 1s \rightarrow 6a_{1g}$ and $\text{S } 1s \rightarrow 6t_{1u}$ resonances. The presence of the S^+ fragment corresponds to the fully atomization of the molecule. The values of S^+ KER cannot be directly interpreted univocally due to the lack of theoretical potential energy curves of the parent ion. In a simple picture of instantaneous dissociation into

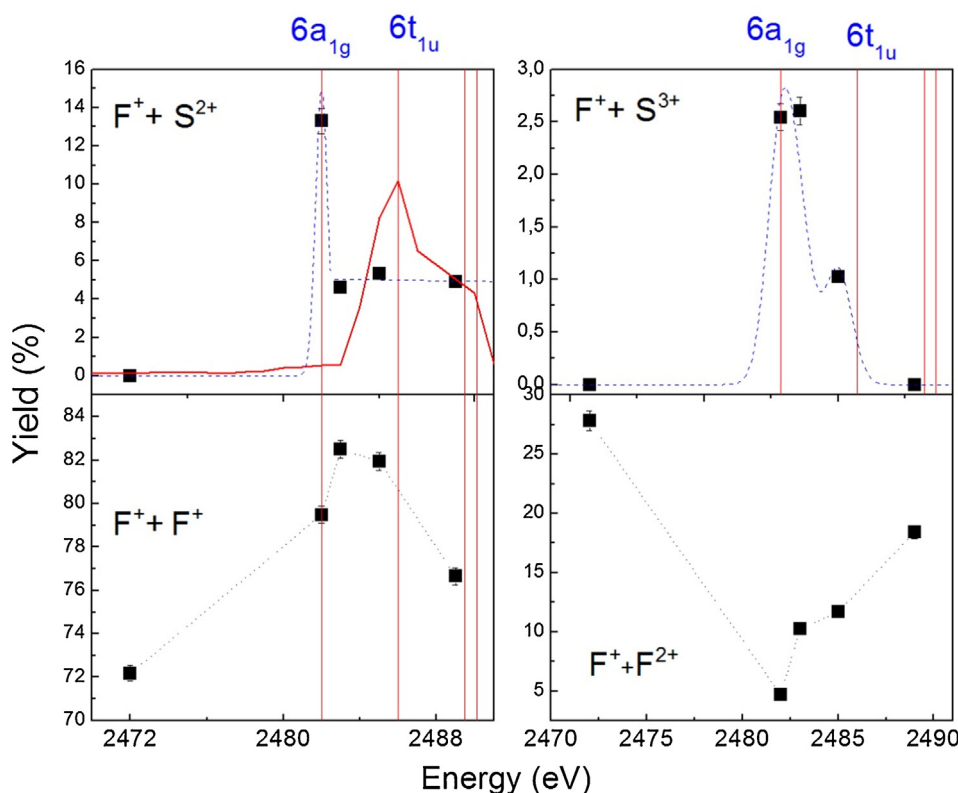


Fig. 5. Partial ion yield (in percentage) from the PE2PICO spectra of SF_6 fragments as a function of the photon energy. The vertical lines have been defined in Fig. 1. For the sake of comparison, the total ion yield is also presented (full red line). The lines connecting the experimental points were drawn to guide the eyes. The peak structures around the $6a_{1g}$ resonance in the $\text{F}^+ + \text{S}^+$ and $\text{F}^+ + \text{S}^{3+}$ yields just point out the strong variation in the ion yields of those fragments around the resonances.

several atomic fragments, the S^+ ions would be anticipated to hold very low kinetic energy due to its central position in the molecule.

The KER of the F^+ and F^{2+} fragments have roughly the same energy dependence, exhibiting a maximum at $\text{S } 1s \rightarrow 6a_{1g}$ transition.

7. 3-PE2PICO spectra

Ascribed to the single-particle essence of the photon-electron dipole operator, the ejection of two or more target electrons would not take place in the absence of the electron correlation and thus, the formation of double ionization events provides a sensitive probe of electron interactions in molecular targets [27]. The removal of a deep inner-shell electron in molecular targets is followed by a rearrangement of the valence electrons due to the downgraded shielding of the nucleus. The results of various multiple fragmentation processes in the core-excited SF_6 molecule, leading to a breakup of the molecule into many atomic fragments owing to the multiple ionization events is represented by



Two-dimensional spectra for the correlation between one of the electrons and two positive ions (PE2PICO) were recorded in the form $(t_1, t_2, \text{counts})$ where $t_{1,2}$ is the time-of-flight for the first or second ion and counts is the number of double coincidence events. As explained before, in the case of $\text{F}^+ + \text{F}^+$ events, the two ions may arrive within a time difference smaller than the multi-hit resolution, a correction procedure was applied.

As shown in figure 5, the $\text{F}^+ + \text{F}^+$ coincidence dominates with 72% – 82% the PE2PICO spectra. At 2472 eV, the $\text{F}^+ + \text{F}^{2+}$ coming from the triply charged SF_6^{3+} ion, is the second most intense coincidence ($\sim 30\%$), falling to $\sim 5\%$ at the $1a_{1g} \rightarrow 6a_{1g}$ resonance and

increasing again to $\sim 17\%$ at 2489 eV. The $\text{F}^+ + \text{S}^{2+}$ coincidence presents a strong selectivity at the $6a_{1g}$ transition, rising from virtually zero at 2472 eV up to 14% at the $6a_{1g}$ resonance, and falling again to 5% above it. The contributions from the quadruple ionization coming from the $\text{F}^+ + \text{S}^{3+}$ coincidence is nonzero only around the two resonances.

8. 4- Coulomb explosion versus one particle charge localization

Cations, which suffer the influence of the strong electrostatic Coulomb repulsion counterbalanced by the chemical bonding, prevent dissociation. Thus, molecular dications exhibits very shallow potential-energy wells. In the case of molecular dications AB^{2+} , there are two possible dissociative channels: the $\text{A}^{2+} + \text{B}$ channel, the so-called one particle charge localization, and the repulsive channel $\text{A}^+ + \text{B}^+$, the so-called Coulomb explosion channel [27,28]. Let $\text{IP}_n(\text{A})$ be the n th ionization potential of the atom A. The energy difference between the asymptotes of these two channels is $\text{IP}_2(\text{A}) - \text{IP}_1(\text{B})$ is the fundamental parameter that determines the branching ratio of the two dissociation channels. For estimating the relative contributions of the Coulomb and intermolecular forces in the fragmentation of the doubly charged SF_6 molecule, the method for data analysis described previously is followed [18].

Briefly, let D_{20} measure up to the events of cations (in the PEPICO spectra) portrayed by the sum of all non-symmetric dissociation $m^{2+} \rightarrow m_1^{2+} + m_2$ channels, and D_{11} the number of dissociative double ionization (in the PE2PICO spectra) depicted by the sum of all charge separation processes $m^{2+} \rightarrow m_1^+ + m_2^+$. The total number events for double ionization is given by

$$I_D = D_{20} f_{e2} + D_{11} f_i^2 f_{e2}, \quad (7)$$

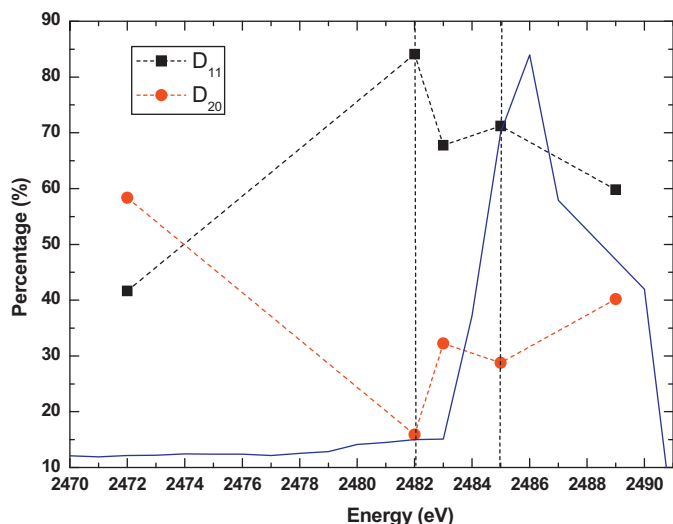


Fig. 6. Comparison between the contribution of the molecular fragmentation pathways D_{20} and D_{11} (see text for details) as a function of the photon energy. The full line represents the total ion yield as a function of the photon energy for comparison purposes.

where $f_i = 0.29$ [18] is the ion detection efficiency, independent of the recoil ion m/q , and f_{e2} is the detection efficiency for detecting at least one electron emerging from a double ionization. The measured amounts are thus given by

$$D_{20meas} = D_{20} f_i f_{e2} \quad (8a)$$

and

$$D_{11meas} = D_{11} f_i^2 f_{e2} \quad (8b)$$

The branching ratios for both double ionization channels are given, respectively, as

$$\frac{D_{11}}{D_{11} + D_{20}} = \frac{D_{11meas}}{D_{11meas} + f_i D_{20meas}} \quad (9)$$

and

$$\frac{D_{20}}{D_{11} + D_{20}} = \frac{D_{20meas}}{\frac{D_{11meas}}{f_i} + D_{20meas}} \quad (10)$$

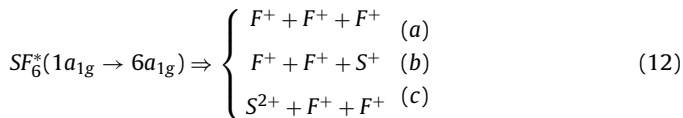
Figure 6 shows that, at the discrete absorption maximum at 2822 eV ($S\ 1s \rightarrow 6t_{1u}$) and above, there is a strong dominance of 60–85% of the symmetric ($A^+ + B^+$) dissociative double ionization from the coincidences presented in Fig. 5. This is in agreement with Carlson and White [29,30], whom early showed that after the creation of a K vacancy in atoms of the second -or higher- series of the Periodic Table, cascade Auger processes take place and highly charged molecular ion are naturally produced. Below the S 1s edge, a competition between the two channels is observed with a clear dominance of the asymmetric ($A^{2+} + B$) fragmentation (60%), due to the increasing contribution of the F^{2+} , and S^{2+} , SF^{2+} , and SF_2^{2+} dications which fall into the PEPICO spectra.

9. 5- PE3PICO

Due to the low counting statistics only the $S\ 1s \rightarrow 6a_{1g}$ forbidden transition is discussed. The excitation of the S 1s electrons by x-rays leaves the SF_6 molecule in a highly excited state. Subsequently, several electronic relaxation processes take place, and very unstable multiply charged ions are generated which breakup very fast into a manifold of cations. The reciprocal action involving the different processes which rule such highly energetic process is far from being fully understood. It is a defiance, both experimentally

and theoretically, to attain knowledge of which pathways dictates these processes. In relative large molecular systems, such as the SF_6 molecule, the available energy can be shared over many modes [31].

Figure 7 shows the PE3PICO projections of the SF_6 fragments after S 1s photoexcitation ($1s \rightarrow 6a_{1g}$). As can be seen from Fig. 7, when the SF_6 is multiply ionized, it primarily dissociates through Coulomb repulsion. Deep-shell excitation and ionization can thus lead to the production of a large variety of fragment ions following complex fragmentation pathways. The main coincidences are



From the S 1s hole (lifetime of about 1 fs) [31], it is reasonable to consider that the ultrafast electronic decay involves an initial Auger decay on the sulfur atom, with a subsequent charge redistribution. Several electronic decay processes are disposable, leading either to a multiply ionized ion before breakup, or to a charge distribution specific to the initial core hole site.

For the coincidences observed in Fig. 7, charge redistribution of the SF_6^{3+} molecule must occur faster than molecular fragmentation, and the breakup must be concerted, i.e., the fragments are ejected concomitantly in a Coulomb explosion, as opposed as in the case of the S^{3+} production channel, which falls into the PEPICO spectra. In the case of the fourfold ionized SF_6^{4+} molecule, the only route observed was the process (c) in (12).

10. 5-Mean ionization state

The character of the electronic correlation and structure of the molecule appears clearly in multiple ionization. The usual route to form multiply charged ions is via a multiple step process due to Auger decay. Mean ionization state is one of the main characteristics of plasmas. It is usually required for the modelling of thermodynamics, transport, and optical properties of plasmas. Figure 8 shows the average recoil ion charge q_{ave} of the SF_6 molecule ions around the SK edge, obtained by weighing the partial ion yields for q from the PEnPICO spectra as follows

$$q_{ave} = \frac{\sum_{q=1}^3 (q I^{q+} / f_{eq})}{\sum_{q=1}^3 (I^{q+} / f_{eq})} \quad (13)$$

where f_{eq} is the efficiency of detecting at least one electron from a q -fold ionization process, and I^{q+} represents the peak areas in the PEnPICO spectra, therefore including all the multiple coincidences. Figure 8 also shows the branching ratios for single, double, and triple ionization of the SF_6 molecule as a function of the photon energy.

The most prominent feature in Fig. 8 is the maximum in the average charge state due the relative increase of the double and triple ionization events at the S 1s $\rightarrow 6a_{1g}$ resonance. The ratio between triple and double ionization events does not depend on the photon energy in this energy range.

As one can see from Fig. 8, around the S 1s ionization edge, electronic relaxation mechanisms lead mostly to singly charged ions. The resonant Auger decays are first-order relaxation processes where the S 1s excited electron can behave as a spectator or as a participator in the transition process. To first order, in most cases it gives rise to singly charged species. Below the $1a_{1g} \rightarrow 6a_{1g}$ transition (Fig. 8), the fragments come preferentially from the F 1s core-level

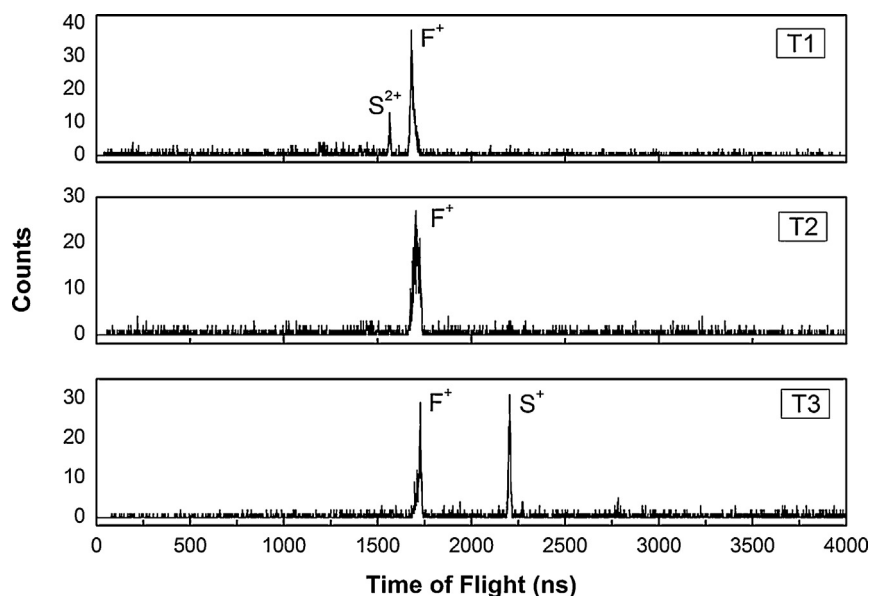


Fig. 7. Projections onto T_1 , T_2 , and T_3 , where T_i $i=1-3$ is the time of flight of the first, second, and third detected ion, respectively, of the SF_6 fragments at 2482 eV.

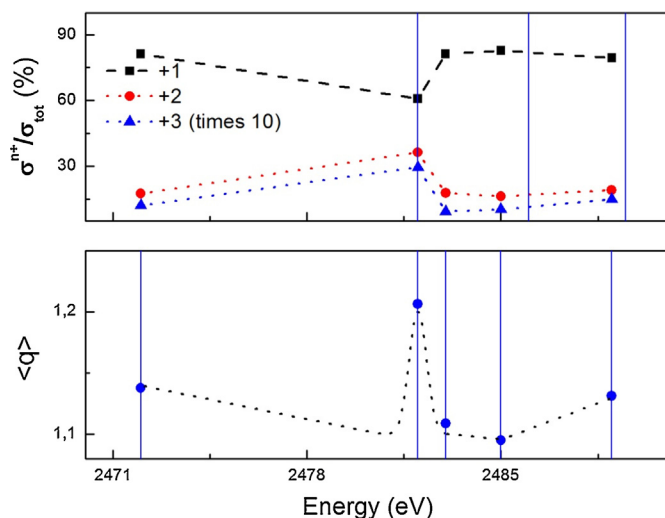


Fig. 8. A) Branching ratios of single, double and triple ionization events of SF_6 molecule as a function of the photon energy. B) Average charge state of SF_6 fragments as a function of the photon energy.

ionization. When the $1a_{1g}$ electron is excited to the $6a_{1g}$ state, the resulting vacancy cannot be promptly filled by another electron due to the fact that fluorescence yield is inhibited (long lifetimes) since the OOS is weak, favoring thus the Auger decay which provides an alternative mechanism by which the molecule can dispose of the excess of energy. The excitation to the $6a_{1g}$ state leaves the system in a highly unstable state that relaxes preferentially by Auger decay. After this deep-core excitation, relaxation processes often occur in a cascade involving multiple Auger decays, several electrons are emitted sequentially, and highly charged ions are produced [31]. At the $1a_{1g} \rightarrow 1t_u$ resonance, with a lifetime of about 1 fs [32], the excited neutral state $1s^{-1}6t_{1u}$ will decay, leaving the initially excited $6t_{1u}$ electron as a spectator (KLV) or involve it as a participant (KLV^{*}) in the decay [26], leading the molecule preferentially to a singly ionized state, as can be observed in Fig. 8.

11. –Conclusions

Strong selectivity in symmetry forbidden vibronic transitions, which come to light owing to the coupling between electronic and nuclear motions, in deep core ionic photofragmentation of the SF_6 molecule is reported for X-ray photons with energies around the S K edge (2472 eV to 2489 eV), using time-of-flight multicoincidence techniques with synchrotron radiation. Total and partial photoion yields for the fragmentation products have been recorded as a function of the incident photon energy. The atomic fluorine ion, F^+ , dominates the mass spectra in the energy range studied. It is shown that the SF_6 molecule undergoes a complete break up with the formation of atomic doubly and triply charged S^{2+} , S^{3+} , and F^{2+} fragments. The present data indicates that core excitation or ionization of the SF_6 molecule, leaves the target in a highly unstable state that decays mainly through Auger decay. In addition, after S 1s ionization, relaxation processes occurs in a cascade involving multiple Auger decays, where several electrons are emitted sequentially, and highly charged ions are produced. Furthermore, the intensity of absorption for the dipole-forbidden transition S K ($1a_{1g} \rightarrow 6a_{1g}$) was calculated for the first time. This transition is shown to play a part in the fragmentation pattern.

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