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Anion and Cation-yield Spectroscopy of Core-excited SF₆

Maria Novella Piancastelli

Uppsala University, maria-novella.piancastelli@physics.uu.se

Wayne C. Stolte

University of Nevada, Las Vegas, wcstolte@lbl.gov

Renaud Guillemin

CNRS, Laboratoire de Chimie Physique-Matière et Rayonnement

A. Wolska

Polish Academy of Sciences

M. M. Sant'Anna

Lawrence Berkeley National Laboratory

See next page for additional authors

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Authors

Maria Novella Piancastelli, Wayne C. Stolte, Renaud Guillemin, A. Wolska, M. M. Sant'Anna, and Dennis W. Lindle

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Anion and cation-yield spectroscopy of core-excited SF₆

M. N. Piancastelli

*Department of Chemical Sciences and Technologies and INFM, University "Tor Vergata," Rome, Italy and
Department of Physics, Uppsala University, Uppsala, Sweden*

W. C. Stolte, R. Guillemin, and A. Wolska

Department of Chemistry, University of Nevada, Las Vegas, Nevada, 89154-4003

S.-W. Yu

*Department of Chemistry, University of Nevada, Las Vegas, Nevada, 89154-4003 and
Center for X-Ray Optics, Lawrence Berkeley National Lab, Berkeley, California 94720*

M. M. Sant'Anna

*Department de física, Pontifícia Universidade Católica do Rio de Janeiro, Caixa postal 38071,
Rio de Janeiro, Rio de Janeiro, 22452-970, Brazil*

D. W. Lindle

Department of Chemistry, University of Nevada, Las Vegas, Nevada, 89154-4003

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We report an extensive study on total and partial-ion-yield spectroscopy around both the S 2*p* and F 1*s* thresholds in SF₆. All positive and negative single-ion channels have been measured. Below the F 1*s* threshold we detect a large variation in relative intensity of the resonant structures according to the specific channel monitored, indicating selective fragmentation. Above threshold, at variance with previous cases described by us, we detect high-intensity structures related to shape resonances not only in the cation channels but also for the anions. We discuss the applicability and limits of a model we have developed for the analysis of shape resonances in anion yields as a function of molecular size. © 2005 American Institute of Physics. [DOI: 10.1063/1.1855314]

I. INTRODUCTION

Sulfur hexafluoride is a highly symmetric, stable system, which is very known because of its peculiar core-excitation properties. Namely, the absorption spectra of SF₆ around both the S 2*p* and the F 1*s* ionization thresholds show intense molecular resonances above and below both thresholds, while the Rydberg series are unusually weak. This system has been used as a showcase to describe the existence and properties of the continuum resonances known as shape resonances.¹ Such phenomena are connected to the existence of an effective potential barrier which forms an inner well and an outer well. The quasibound continuum states known as shape resonances are located in the inner well, while the Rydberg states are placed in the outer well, subsequently, they have poor coupling with valence states, and therefore low intensity in absorption and electron-decay measurements. A shape resonance can be described as continuum states supported by the potential barrier in which the emitted photoelectron is temporarily trapped, eventually tunneling through, and ejected into the continuum.² An alternative but equivalent description is electron excitation to virtual molecular orbitals pushed above the ionization threshold by the potential barrier.³ Both models give essentially the same picture. The scattering picture can be more useful when describing changes in electron angular momentum in the region of a shape resonance, while the molecular orbital picture can be more appropriate to describe the continuum resonances in terms of symmetry and selection rules.

Sulfur hexafluoride shows intense above-threshold reso-

nances with *t*_{2*g*} and *e*_g symmetry. Together with below-threshold resonances assigned as transitions to empty molecular orbitals, SF₆ has been the subject of a multitude of spectroscopic studies. Photoelectron cross-section measurements in the photon-energy region which includes the shape resonances above the S 2*p* threshold have shown multielectron character for the *e*_g resonance.⁴ In Ref. 5, high-resolution photoabsorption around both the S 2*p* and the F 1*s* thresholds are reported, together with a review of older photoabsorption data, while in Ref. 6 electron-impact experiments around the S 2*p* threshold are reviewed. Other types of experiments include angle-resolved ion-yield spectra,⁷ S 2*p* photoelectron angular distributions at the shape-resonance positions,⁸ and electron-ion coincidence experiments.^{9,10} In particular, state and site selectivity fragmentation, which will be dealt with in the present work, has been the subject of earlier electron-ion coincidence studies.^{8,11} Finally, a recent paper reports anion-yield results for both the valence and S 2*p* regions.¹²

In this paper we report an extensive study using total and partial ion-yield spectroscopy around both the S 2*p* and the F 1*s* thresholds. A peculiar feature of our experimental setup is the capability to detect not only positively charged species but also negatively charged ones. We have shown in a number of cases that anion-yield spectroscopy is a useful tool to deeply investigate the nature of above-threshold resonances.¹³⁻¹⁶ In SF₆, all the positive and negative single-ion channels have been measured. Below the S 2*p* edge the general appearance of the resonances is basically the same

for all of the measured partial-ion yields, but below the F 1s edge we detect a large variation in relative intensity of the resonant structures depending upon the specific ion channel measured. This implies selective fragmentation is occurring. Above threshold, at variance with previous cases described by us, we detect a high intensity for the spectral structures related to the shape resonances not only in the cation channels but also in the anion channels. We discuss the applicability and limits of the model we have previously developed in the analysis of shape-resonance-related features in anion yields as a function of molecular size, i.e., the possibility of delocalizing a triply positive charge amongst the various molecular fragments.

II. EXPERIMENT

Our measurements were performed on undulator beamlines (BL) 8.0.1.3 and 7.0.1.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory. The monochromator resolution on BL 8.0.1.3 around 200 eV was ≈ 60 meV when using an entrance slit width of 15 μm and an exit slit width of 20 μm . The same resolution was used on BL 7.0.1.2 with entrance and exit slit widths of 12 μm . We used an entrance slit width of 20 μm and an exit slit width of 30 μm on BL 8.0.1.3 around 700 eV, resulting in lifetime limited resolution. The experimental apparatus used in the present study has been previously described.¹⁷ Basically, the apparatus consists of an 180° magnetic mass spectrometer, providing a full width at half maximum corresponding to a fraction of a *u*ma, which is adequate to distinguish fragments with sequential number of hydrogen atoms, a lens system to focus the ions created in the interaction region onto the entrance slit of the mass spectrometer, and a gas cell containing an extraction field to move the ions created in the interaction region into the lens system. The target gas enters the open cell via an effusive jet of 2 mm in diameter. A channel electron multiplier is used at the exit slit of the spectrometer to detect the ions. Finally, a differential pumping system was used to isolate the target chamber vacuum (2×10^{-5} torr) from the beamline vacuum (1×10^{-9} torr). The SF₆ gas was commercially obtained from Air Gas (VLS1 grade, 99.999% purity) and used without further purification. Photon energies were calibrated at the S *L*_{2,3} edges and the F *K* edge using the S $2p_{3/2} \rightarrow 2t_{2g}$ resonance at 184.57 eV and the F $1s \rightarrow 6a_{1g}$ resonance at 689.0 eV, respectively.⁵ In order to obtain reasonable statistics, and verify reproducibility, all of the spectra presented in this paper are the sum of several recordings, which were separately normalized, especially the weaker dissociation channels as the doubly-charge ions and the anions for which up to ten spectra have been recorded and summed.

III. RESULTS AND DISCUSSION

When a core hole is induced in a molecule, dissociation is very likely to occur following or even during electronic relaxation. The main pathway to molecular fragmentation is the decay of the species with a core hole to a molecular ion with a single positive charge (mainly below threshold) or to a molecular ion with a double positive charge (mainly above

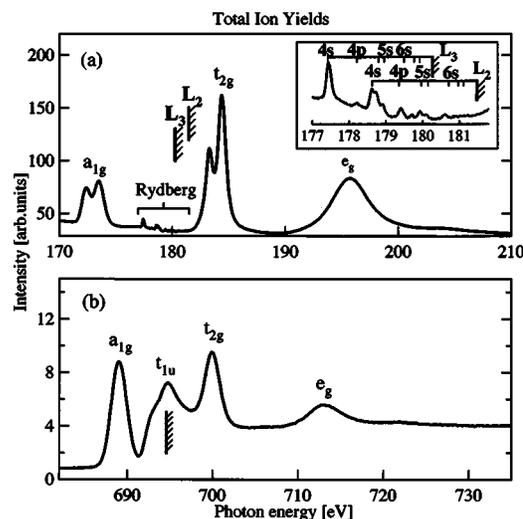


FIG. 1. (a) Total-ion yield in the region of the S $2p_{3/2}$ and the $2p_{1/2}$ ionization thresholds at 180.27 and 181.48 eV, respectively (Ref. 5). The inset shows details of the Rydberg excitation region. (b) Total-ion yield in the region of the F 1s ionization threshold at 694.6 eV (Ref. 6). Contributions from valence-shell ionization have not been subtracted.

threshold), which are often metastable and subsequently dissociate by breaking one or more chemical bonds. Observation of the resulting ions (molecular or atomic) is very informative of the nature of the excited or ionized state and of the dynamics of the photofragmentation process.

Sulfur hexafluoride has six equivalent S–F bonds in an octahedral geometry and belongs to the *O_h* point group. In this symmetry, the electronic configuration of the ground state ($^1A_{1g}$) may be written,^{6,18}

$$\underbrace{(1a_{1g}^2)}_{S\ 1s} \underbrace{(2a_{1g}^2)(1e_g^4)}_{F\ 1s} \underbrace{(3a_{1g}^2)(2t_{1u}^6)}_{S\ 2s} \underbrace{(2t_{1u}^6)}_{S\ 2p}$$

for the core electrons,

$$(4a_{1g}^2)(2e_g^4)(3t_{1u}^6)(5a_{1g}^2)(4t_{1u}^6)(1t_{2g}^6)(3e_g^4)(1t_{2u}^6)(5t_{1u}^6)(1t_{1g}^6),$$

for the inner- and outer-valence electrons, and for the four lowest-lying virtual orbitals,

$$(6a_{1g}^0 6t_{1u}^0 2t_{2g}^0 4e_g^0).$$

The $6a_{1g}$ and $6t_{1u}$ orbitals are empty valence states while $2t_{2g}$ and $4e_g$ are often associated with well-known shape resonances.⁴

Figure 1 shows total-ion yields measured in the energy regions of (a) the S $2p_{3/2}$ and the S $2p_{1/2}$ ionization thresholds, 170–210 eV, and (b) the F 1s ionization threshold, 682–735 eV. Below the S $2p$ ionization threshold, the double structure at 172.27 and 173.44 eV corresponds to transitions from the S $2p_{3/2}$ and $2p_{1/2}$ levels to the $6a_{1g}$ molecular orbital. The two intense resonances above threshold are assigned as shape resonances with t_{1g} and e_g symmetry. The first one is spin-orbit split and consists of two peaks at 183.40 and 184.57 eV, while the second broad one is centered at 196.2 eV.⁵ Below the F 1s ionization threshold, the peak at 689.0 eV corresponds to transitions from the F 1s levels to the $6a_{1g}$ molecular orbital. The two intense resonances above threshold at 699.9 and 713.2 eV are again assigned as shape resonances of t_{1g} and e_g symmetry, respec-

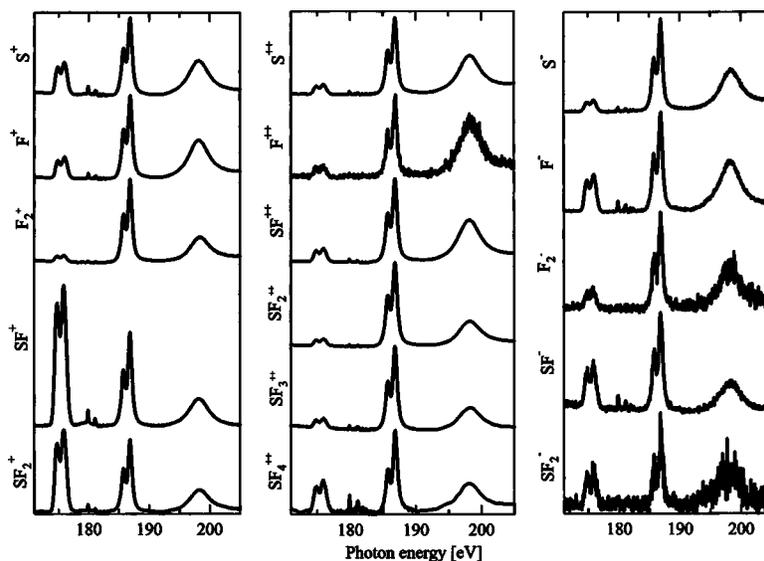


FIG. 2. Partial-ion yields in the region of the S $2p_{3/2}$ and $2p_{1/2}$ ionization thresholds. Contributions from valence-shell ionization has been subtracted. For clarity all of the ion yields have been normalized to the t_{2g} resonance.

tively. The main difference with respect to the S $L_{2,3}$ -edge spectrum is the presence of additional structure between these peaks; there is a peak at 694.7 eV with a shoulder at 692.9 eV and a small additional feature around 697 eV.⁵ This structure is related to excitation from the F $1s$ levels to the empty molecular orbital of t_{1u} symmetry. The analogous transition from the S $2p$ ($2t_{1u}^6$) core orbital to the $6t_{1u}$ empty orbital is dipole forbidden.

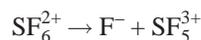
A. S $L_{2,3}$ edge

We obtained partial-ion yields in the energy region 165–215 eV, including the S $2p_{3/2}$ and the S $2p_{1/2}$ ionization thresholds at 180.27 and 181.48 eV,⁵ for the positively charged fragments SF_2^+ , S^+ , F_2^+ , F^+ , SF_4^{2+} , SF_3^{2+} , SF_2^{2+} , SF_2^+ , F_2^+ , and S^{2+} , and the negatively charged fragments F^- , S^- , F_2^- , SF^- , and SF_2^- . Heavier fragments such as the parent ion, SF_5^+ , SF_4^+ and SF_3^+ have a mass-to-charge ratio beyond the measurement range of our mass spectrometer. We show in Fig. 2 the yields for all detectable fragment ions.

The general appearances of the partial-yield curves are similar for all of the positively charged fragments and the total-ion yield, shown in Fig. 1. The most noticeable difference is the above-threshold resonances are more prominent relative to the below-threshold resonances in the doubly-charged fragment yields. This effect is well known and can be explained by the dominant decay pattern above threshold being normal-Auger decay producing doubly-charged cations. It is especially visible for spectral structures related to shape resonances, because the intensity of the Auger decay mimics the resonant increase in relative intensity of the photoelectron lines, and therefore the resonant enhancement is visible in fragment-ion yields, such as doubly-charged ions, reached after Auger emission. The low intensity of spectral structures related to the Rydberg series, which was previously observed in the photoabsorption measurements of Hudson *et al.*,⁵ is also evident in the total and partial-ion yields presented here. This low intensity is explained as

“borrowing” of intensity by resonances in the inner potential well (shape resonances) from resonances located in the outer well (Rydberg states). The similarity between all of the various ion-yield curves is due to the creation of an electron vacancy by primary excitation on the central atom, which leads to nonselective fragmentation patterns.

The yield of the anion fragments detected in this photon-energy region is particularly interesting. The most noticeable feature is the shape resonances have spectral intensities in the anion yields comparable to that of the cation yields. This is in contrast to a series of previous investigations^{13–16} where we discussed the possibility of using anion yields to assign above-threshold resonances directly via experiment. This argument was based on the fact that to produce an anion following the normal Auger decay of a core hole, which leads initially to a doubly-charged parent ion, a net concentration of triple positive charge on one fragment must be envisaged in a small molecule. In simple systems such as CO,¹³ N₂O,¹⁴ OCS,¹⁵ and NO (Ref. 16) this was found to be highly unlikely. However, while this argument is strong for diatomic or triatomic molecules, it does not necessarily hold for more complex systems, where the possibility for delocalization of positive charge exists. In the present case, the formation of F^- , S^- , F_2^- , SF^- , and SF_2^- following normal-Auger decay is relatively easy to imagine. For example, formation of F^- could stem from one of the following patterns, as well as many more not depicted here:



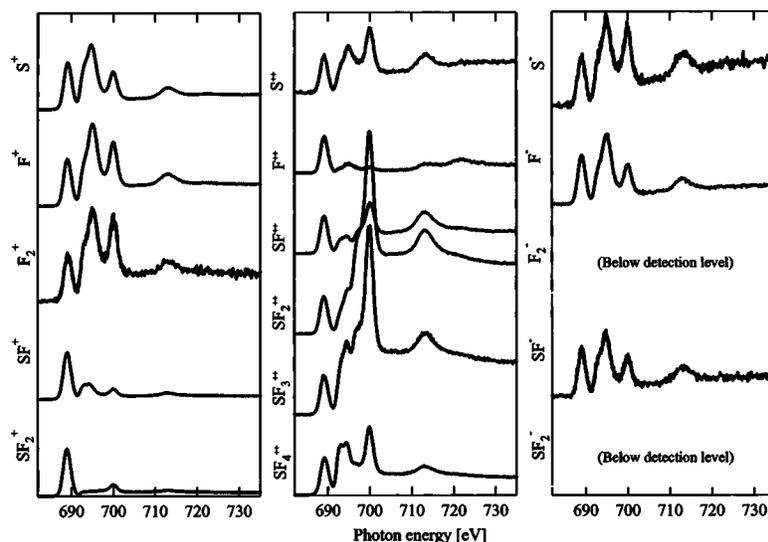
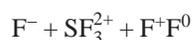
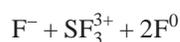


FIG. 3. Partial-ion yields in the region of the F 1s ionization threshold. Contributions due to valence-shell ionization have been subtracted.



In a recent paper,¹² negative ion yields have been reported in SF_6 in the photon-energy range 20–205 eV, indicating the S 2*p* edge, and a direct comparison with our results is possible. The quality of the data is comparable, because we had to relax our photon-energy resolution due to the fact that anions in general are generated from relatively weak channels. However, the authors interpret their data¹² using a unified description (autoionization or resonant-Auger decay) for both below- and above-threshold resonances. Our description of the phenomena is significantly different. We have demonstrated in several previous cases,^{13–16} anion spectroscopy is an important tool in assigning above-threshold resonances because it allows one to distinguish experimentally between multielectron excitations decaying through resonant-Auger pathways, and leading to singly positively charged species, and one-electron shape resonances, affecting only the outgoing photoelectron, leading to enhanced intensity in normal-Auger processes to doubly positively charged ions. This significant difference in decay modes manifests itself in anion spectroscopy of diatomic or triatomic molecules as negligible anion yields at the shape-resonance position, while the multielectron excitations above threshold are clearly visible in the anion yields. In the present case, it is most likely we see shape resonances in the anion yields not because they decay through autoionization but because the system under investigation is large enough to permit the dissipation of a triple positive charge over a series of fragments (see the example above concerning the formation of F^-). Furthermore, at variance with the interpretation of the authors of Ref. 12 who discuss partial localization of the shape resonances around a specific atom, we note that the absolute intensities

for S^- and F^- are comparable above both the S 2*p* and the F 1*s* thresholds, therefore those can hardly be connected to the localization of shape resonances around one particular atom.

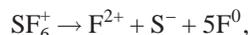
IV. F K EDGE

We have obtained partial-ion yields over the energy region 682–735 eV, which covers the F 1*s* ionization threshold at 696.4 eV.⁶ We show in Fig. 3 the yields for all detectable fragments: SF_2^+ , S^+ , F_2^+ , F^+ , SF_4^{2+} , SF_3^{2+} , SF_2^{2+} , SF^{2+} , F^{2+} , and S^{2+} , and the negatively charged fragments F^- , S^- , and SF^- . In this region both the F_2^- and SF_2^- fragment ions were below our detection limit ($\lesssim 1$ counts/s on the t_{1u} resonance).

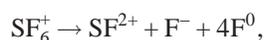
By comparing partial-ion yields, the main difference between the spectra is the relative intensity of the structures in the region 693–698 eV. These structures seem to be prominent in fragments which correspond to an extensive fragmentation process, such as S^+ , and much less evident in fragments which contain one or more S–F bonds. We can deduce that the promotion of an electron to empty molecular orbitals with t_{1u} symmetry easily induces multiple S–F bond rupture. This hint can be confirmed by considering the molecular orbitals: the empty orbitals with t_{1u} symmetry are the antibonding counterparts of filled orbitals with main S 3*p*–F 2*p* bonding character, thus a promotion of a core electron in one of these levels induces extended bond breaking and shortens the lifetime of SF_x^{n+} fragments. In some of the yields (e.g., SF_3^{2+}) the relative intensity of the structure in the 693–698 eV photon-energy region changes substantially compared to photoabsorption,⁵ allowing us to better resolve the three structures.

Above threshold, the shape resonances are again more prominent in the yields of doubly-charged cations, because doubly-charged fragments are more likely produced by normal-Auger decay, which is enhanced by the shape resonance. The only exception is the F^{2+} yield, where the shape-resonance structures are not very evident, but spectral fea-

tures at higher photon energies, around 722 and 727 eV are more pronounced at variance with the other ion-yield curves. Such features have been assigned as multielectron excitations,⁵ therefore F²⁺ seems to be produced more easily following the decay of a singly-charged species produced by resonant-Auger decay rather than by doubly-charged species produced by normal-Auger decay. Also, F²⁺ does not seem to stem from second-step Auger decay of F⁺, because the two yields do not mimic each other. Because the structures at 722 and 727 eV are also barely visible in the S⁻ yield, F²⁺ is possibly related to the formation of S⁻ through fragmentation processes such as



although this is likely to be a minor channel. The feature at 713.2 eV, assigned as a shape resonance of e_g symmetry, is relatively more intense in the F²⁺ yield than the other feature at 699.9 eV, assigned as a t_{1g} shape resonance⁵ compared to the other channels. There has been previous evidence^{4,10} of multielectron character for the e_g shape resonance, which we confirm because of the previously discussed evidence of F²⁺ production being related mainly to fragmentation of singly-charged species. The peculiar behavior of F²⁺ is confirmed by Auger electron-ion coincidence measurements, where it has not been detected around the S 2*p* or the F 1*s* edge,⁸ clearly indicating it does not stem from normal-Auger decay. Analogous considerations can be invoked in the comparison of the SF⁺ and the SF²⁺ fragments. Again, the relative intensity of the spectral feature connected to the shape resonance of e_g symmetry is higher in the doubly-charged fragment, and again the doubly-charged species cannot be simply related to the singly-charged one as stemming from second-step Auger process. Also in this case we can hypothesize a fragmentation process above threshold involving a singly-charged parent ion, such as



thus confirming once again the multielectron character of the resonance at 713.2 eV.

The yields of the anions F⁻, S⁻, and SF⁻ also are shown in Fig. 3. In general, the above-threshold features related to shape resonances are as pronounced in the anion yields as they are for the cation yields, confirming the explanation of the S 2*p*-edge data: in larger polyatomic systems there exist several fragmentation patterns for production of anions by dissociation of doubly positive charged species resulting from normal-Auger decay. In contrast, for smaller diatomic and triatomic systems, production of anions following the decay of a shape resonance is negligible.¹³⁻¹⁶ Studies are in progress on an intermediate case, SiF₄, to assess more clearly the relationship between anion production at shape resonances and molecular size.

V. CONCLUSION

The use of high-resolution partial-ion-yield spectroscopy in the photon-energy region around a core threshold is proven to be very effective in elucidating details of core excitation-deexcitation processes. In SF₆, significant differences in fragmentation patterns as a function of the intermediate core-excited state have been observed. In larger molecules such as SF₆, we conclude there are several ways to delocalize positive charge and create negative ions at shape resonances, at variance with our findings for smaller systems where this possibility is negligible. It is clear anion production at shape resonances must be a function of molecular size. Further studies are in progress to quantitatively refine this picture.

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