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Study of the Ionic Fragmentation of Shallow- and Core-Excited Fluorocarbonylsulfenyl Chloride, FC(O)SCl: Observation of a New Three-Body Dissociation Mechanism

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Total ion yield (TIY) and partial ion yield (PIY) spectra of fluorocarbonylsulfenyl chloride, FC(O)SCl, are reported by using tunable synchrotron radiation. These are the first data obtained for this type of (−C(O)S−)-containing compound. Multicoincidence techniques, which include photoelectron−photoion coincidence (PEPICO) and photoelectron−photoion−photoion-coincidence (PEPIPICO) time-of-flight mass spectrometry, are applied to the study of the fragmentation dynamics around the S 2p, Cl 2p, C 1s, O 1s, and F 1s ionization edges. Fragmentation patterns deduced from PEPICO spectra at the various excitation energies are essentially identical. The penta-atomic FC(O)SCl molecule with five different atoms is especially suitable for the analysis of decay mechanisms. Dissociation dynamic processes obtained from PEPIPICO spectra demonstrate the importance of both two- and three-body decay mechanisms, namely, deferred charge separation (DCS) and secondary decay (SD). Furthermore, to explain the behavior of two pairs of ions (F^+/Cl^+ and S^+/CO^+) appearing in coincidence, a decay mechanism consisting of a molecular ion rearrangement followed by a secondary decay (SD-IR) is proposed. To our knowledge, such a mechanism has not been reported.

Introduction

Simple thioester compounds of the type XC(O)SY, related to important biological macromolecules, especially to coenzyme A,[1] have been the subject of many theoretical and experimental investigations. The planar geometry around the −C(O)S− skeleton gives rise to syn and anti conformational structures. Thus, a comprehensive series of these molecules was analyzed by our group in La Plata[2,3] and others[4] to establish their conformational properties systematically. As a closely related antecedent of the present work, the study on the He(I) photoelectron spectroscopy (PES) of FC(O)SCl has recently been reported.[5] A wide electronic delocalization in the whole planar FC(O)SCl molecule, which leads to a strong energetic stabilization of the HOMO orbital (n''_S sulfur lone pair π nonbonded orbital), was deduced from these experimental and theoretical investigations.

However, no studies concerning inner shell spectroscopy have been reported for sulfenylcarbonyl compounds. With the beginning of the multicoincidence techniques, such as photoelectron−photoion coincidence (PEPICO) and photoelectron−photoion−photoion coincidence (PEPIPICO),[6] much more insight into dissociation dynamics and mechanisms of ion dissociation following excitations was feasable.

In the present work, the first study dealing with XC(O)SY molecules in the VUV and in the soft X-ray photon energy regions, which includes both spectroscopic and dynamical analysis of FC(O)SCl around the S 2p, Cl 2p, C 1s, O 1s, and F 1s ionization edges, is reported by using multicoincidence techniques and tunable synchrotron radiation.

Experimental Section

Synchrotron radiation at the Laboratório Nacional de Luz Síncrotron (LNLS), Campinas, São Paulo, Brazil, was used.[7] Thereby, linearly polarized light monochromatized either by a toroidal grating monochromator (available at the TGM beam line in the 12−310 eV range)[8] or by a spherical grating monochromator (available at the SGM beam line in the 200−1000 eV range)[9] intersected the effusive gaseous sample inside a high-vacuum chamber with a base pressure in the 10^{-8} Torr range. During the experiments, the pressure was maintained below 10^{-5} Torr. The gas needle was kept at the ground potential. The emergent beam was recorded by a light-sensitive diode. The ions produced by the interaction of the gaseous sample with the light beam were detected using a time-of-flight (TOF) mass spectrometer of the Wiley-Mac Laren type for both PEPICO and PEPIPICO measurements. This instrument was constructed at the Institute of Physics, Brasilia University, Brasilia, Brazil.[10] The axis of the TOF spectrometer was perpendicular to the photon beam and parallel to the plane of the storage ring. Electrons were accelerated to a multichannel plate (MCP) and recorded without energy analysis. The mass spectra (70 eV, electron-impact mode) were obtained with an AMD 604 instrument.

The sample of fluorocarbonylsulfenyl chloride, FC(O)SCl, was prepared by the reaction between ClC(O)SCl (Aldrich, 95%) and SbF_3 in the presence of $SbCl_5$ as a catalyst.[11] The liquid product was isolated by fractional distillation and subsequently purified several times by fractional condensation at reduced pressure in order to eliminate volatile impurities. The purity of the compound was checked by IR (vapor), Raman (liquid), and ^{19}F and ^{13}C NMR spectroscopy.[12]

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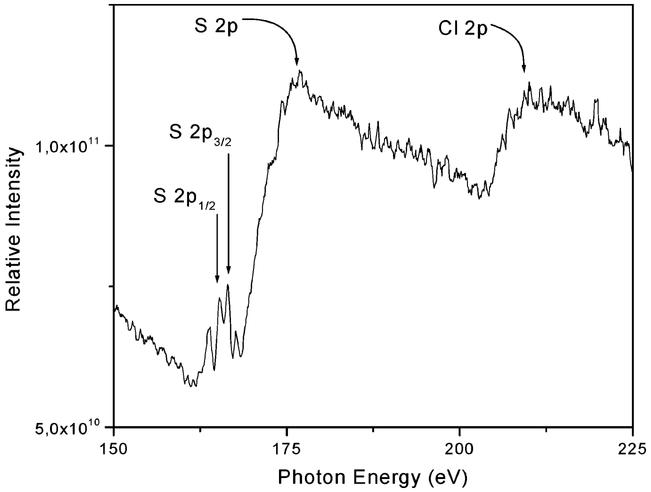

Figure 1. Total ion yield spectrum of FC(O)SCl in the S and Cl 2p regions.

Results and Discussions

Total and Partial Ion Yield Spectra. A “simple” small covalent penta-atomic compound with five different atoms has been selected for this study. Inner shell spectra of thioesters have not been reported so far. Theoretical calculations concerning the deeper electronic structure are also not available. This work is part of a more general project dealing with the thioester family including, for instance, ClC(O)SCl, $CH_3C(O)SH$, and $CH_3OC(O)SCl$.[13]

The total ion yield (TIY) spectrum of FC(O)SCl for the S and Cl 2p edge regions is shown in Figure 1. Below the S 2p threshold, at 176.1 eV, the spectrum is dominated by a group of four signals centered at 164.0, 165.3, 166.6, and 167.6 eV. The most intense features located at 165.3 and 166.6 eV should correspond to transitions involving the spin−orbit splitting of the 2p term of sulfur into $2p_{1/2}$ and $2p_{3/2}$ levels. In the case of the SH_2 molecule, this splitting was reported to be 1.201 eV.[14] The Cl 2p region of FC(O)SCl exhibits a simple feature without any fine structure, dominated by the ionization edge at 206 eV.

In the case of FC(O)SCl, the presence of various atoms nominally containing electron lone pairs leads to a PES spectrum dominated by in-plane (a′) and out-of-plane (a″) nonbonded electrons in the low-energy region. ($IE^{ver} = 10.7$ eV corresponds to the HOMO n''_S out-of-plane lone-pair sulfur orbital.) Furthermore, the planar structure of the molecule allows an effective interaction between the out-of-plane $\pi_{C=O}$ molecular orbital and the lone pair belonging to the fluorine atom. Their combination leads to both π^+_{FCO} and π^-_{FCO} molecular orbitals with vertical ionization values of 14.9 and 18.1 eV, respectively.[5] Such an interaction was previously proposed for the assignment of the experimentally observed PES of fluorocarbonyl-containing compounds.[15]

Below the threshold, the C 1s region shows a transition at 287.4 eV and a second intense signal at 293.4 eV. (See Figure 2.) These features may correspond to excitations to vacant π^{*+}_{FCO} and π^{*-}_{FCO} orbitals, respectively. The continuum region starts approximately at 303.6 eV.

The O 1s region (Figure 3) is dominated by an intense resonance at around 528.5 eV and by a second signal with lower intensity at 531.9 eV. Again, these signals could be related to the electronic excitation from the fundamental state to vacant π^{*+}_{FCO} and π^{*-}_{FCO} molecular orbitals, respectively. The experimental energy difference for these orbitals in the PES amounts to 3.2 eV. This is in agreement with the observed difference of about 3.5 eV in the O 1s region. The ionization energy (IE) is estimated to be 535.7 eV.

Finally, Figure 4 depicts the F 1s region, which exhibits two signals at 684.0 and 687.4 eV corresponding to similar transitions as observed in the O 1s region and being dominated by the π^{*+}_{FCO} and π^{*-}_{FCO} excitations. The ionization edge is located at 690.5 eV.

The proposed assignments, especially those transitions that correspond to the carbonyl group, are consistent with those reported for esters and carboxylic acids.[16,17]

The partial ion yield spectra (PIY) for selected ions formed after the excitation of the O 1s inner shell of FC(O)SCl are shown in Figure 5. It can be deduced from the Figure 5 that whereas total ion production is enlarged in the first resonance at 528.5 eV, only signals of ions related to the carbonyl group (i.e., $m/z = 12$, 16 and 28) increase their intensities at 531.9 eV. This behavior agrees with a transition associated with the π^{*+}_{FCO} empty orbital, as has been proposed from the TIY spectrum. Another feature observed in the O 1s PIY spectrum of FC(O)SCl is the presence of a weak signal at 530 eV, with

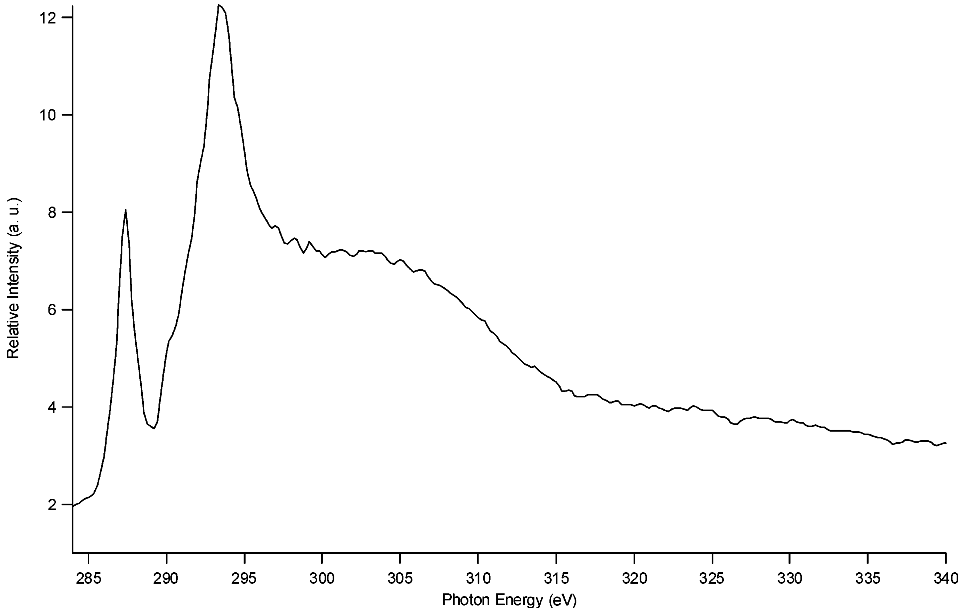

Figure 2. Total ion yield spectrum of FC(O)SCl in the C 1s region.

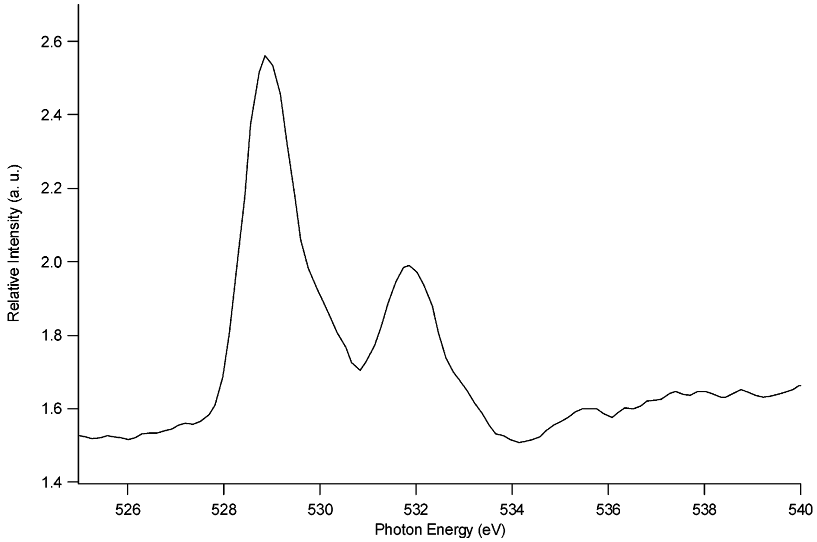

Figure 3. Total ion yield spectrum of FC(O)SCl in the O 1s region.

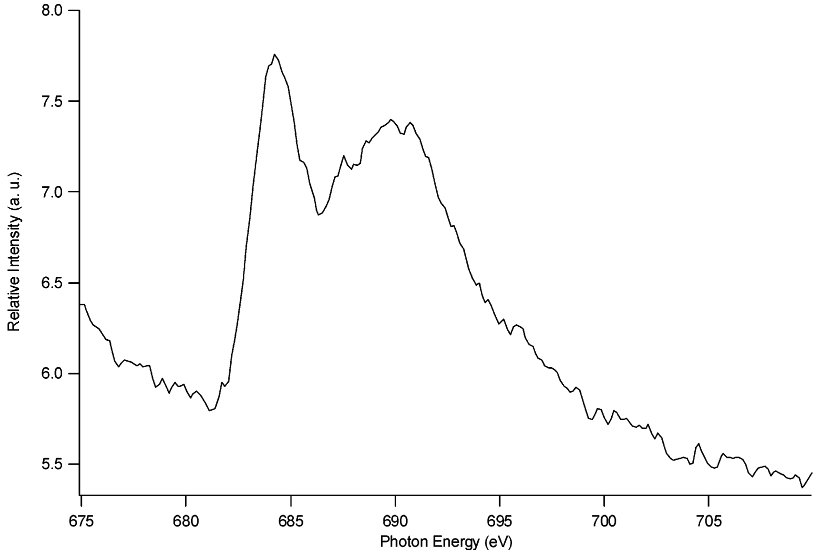

Figure 4. Total ion yield spectrum of FC(O)SCl in the F 1s region.

a major contribution of CO^+ ($m/z = 32$ amu) ions. This feature appears as a shoulder of the nonsymmetrical signal at 528.5 eV in the TIY spectra, and that transition may originate in the sum of 1s O to π^* and in Rydberg transitions.

PEPICO Spectra. Core- and shallow-shell excitations are highly localized on a specific atom of a molecule, and for this reason, nonstatistical fragmentations (i.e., site-specific or state-dependent fragmentations) can be anticipated. Evidence for atom-selective soft X-ray chemistry was formerly reported for acetone using a quadruple mass spectrometer. A strong resonance was observed in the C^+ and O^+ ion yield spectra for the excitation of C 1s to the π^* molecular orbital (MO) of the C═O group in acetone.[18] Differences in the relative yields of fragment ions were observed in simple molecules by exciting K-shell electrons.[19] Linked to the present work, the state-specific formation of the triply charged S^{3+} and OCS^{3+} ions has been reported in a study of the core-excited OCS molecule.[20] The theoretical connotation concerning these site-specific fragmentations is related to the timescale of such a process. In the case of a decay process of a core-excited species in the soft X-ray range, the short lifetime of the vacancy, occurring on a femtosecond time scale, is comparable either to the vibrational time or to the direct dissociation time along a repulsive surface. This process might not obey the classical Franck−Condon description. Questions arising beyond these phenomena are whether the memory effect induced on the short timescale is conserved at longer times and what the spacial extension of the fragmentation is.[21] Both the theoretical framework and experimental data regarding these phenomena are still scarce. Therefore, we have recorded several PEPICO spectra that include the most important shallow-core and core transitions of FC(O)SCl.

PEPICO spectra are generated when an ion arrives at the detector when the time window is open. It occurs when a photoelectron starts the process by reaching the electron detector switching on the time window. Conventional mass spectra containing mainly contributions of single ionization are thus provided. However, they may also include some contributions of multiple ionizations where only the lighter ion can been detected.

The PEPICO spectra of FC(O)SCl are shown in Figure 6 for the S and Cl 2p edges and in Figure 7 for the C, O, and F 1s excitations. Spectra have been recorded at the corresponding resonance transitions and at around 10 and 50 eV below and above of each transition, respectively. In this way, the main transition at this resonance energy can be determined.

Naturally occurring isotopomer fragments, mainly due to the presence of ^{35}Cl and ^{37}Cl, have been clearly observed because

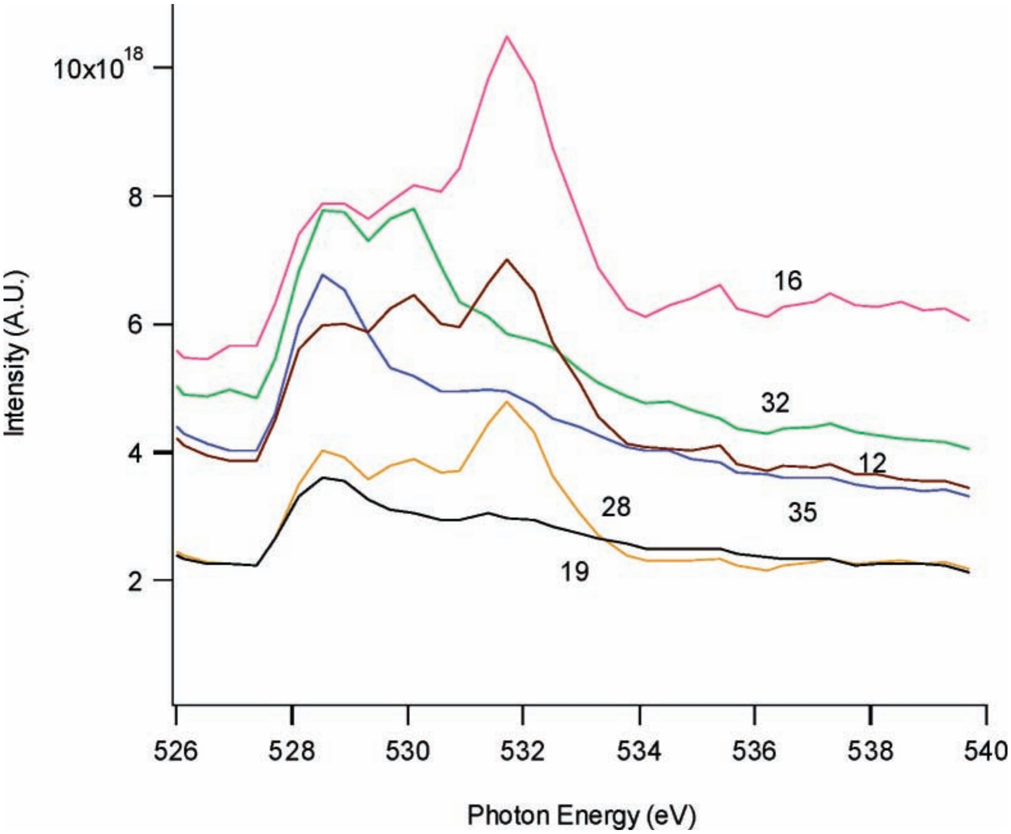

Figure 5. Partial ion yield spectrum of FC(O)SCl in the O 1s region.

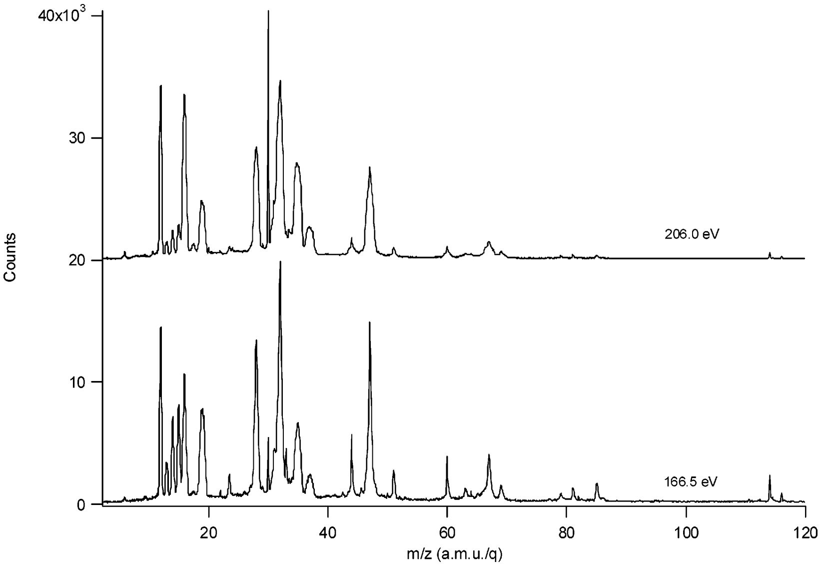

Figure 6. PEPICO-TOF mass spectra of FC(O)SCl recorded at selected photon energies around S and Cl 2p edges.

of the suitable mass resolution of the experiments. As an example of a typical mass spectrum, we will describe the one obtained at 166.5 eV (bottom of Figure 6), which corresponds to the S 2p transition region for FC(O)SCl. The most important peaks pertain to *m*/*z* ratios of 12, 14, 16, 19, 28, 32, 35, 44, 47, 60, 67, and 114 amu/q. The parent ion can be observed at 114 amu/q and shows the characteristic chlorine isotopic distribution. Intense peaks at 12, 16, 19, 32, and 35 amu/q are assigned to the singly charged main isotopes of C, O, F, S, and Cl atoms, respectively. Thus, FC(O)SCl exhibits important atomization even at a relatively low photon energy of 154 eV. Peaks at 28, 44, 47, 60, and 67 amu/q correspond to plausible fragments formed by logical single-molecular-bond rupture and are associated with singly charged ions CO^+, CS^+, FCO^+, SCO^+, and SCl^+, respectively. Doubly charged fragments, namely, SCO^{2+}, FCO^{2+}, and CO^{2+}, were also found and identified by their amu/q values as well as by characteristic narrow features. The pair of fragments S^{2+} and O^+ possess similar *m*/*z* ratios, being that the peaks are coincident at the present TOF mass resolution. To compare with the PEPICO spectra, we also recorded the electron impact (ionization energy of 70 eV) mass spectra. Thus, in the FC(O)SCl mass spectrum, the main fragment corresponds to an *m*/*z* ratio of 60 amu/q. Other fragments, such as $FC(O)^+$, SCl^+, and the molecular ion $FC(O)SCl^+$, show important contributions of 13, 7, and 16% with reference to the main peak, respectively. As expected, differ-

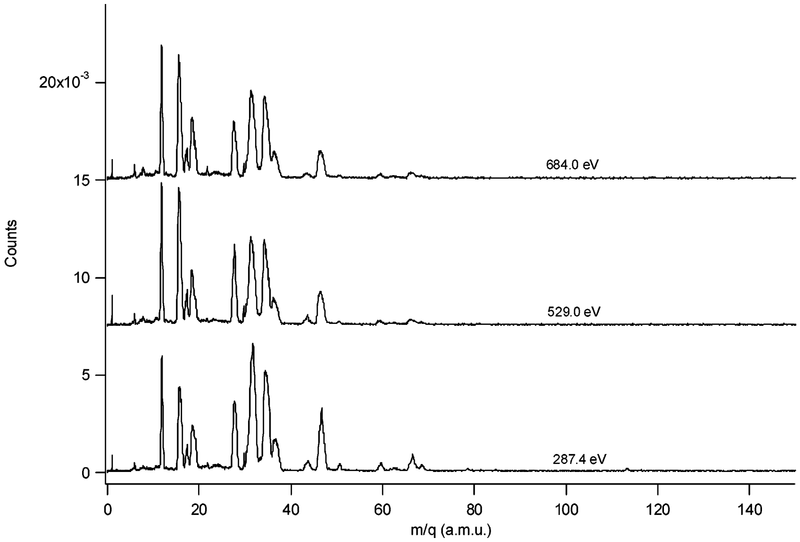

Figure 7. PEPICO-TOF mass spectra of FC(O)SCl recorded at selected photon energies around C, O, and F 1s edges.

TABLE 1: Branching Ratios at Different Energies for Fragment Ions Extracted from PEPICO Spectra for FC(O)SCl

		2p S			2p Cl		1s C				1s O					1s F			
m/z (amu/q)	ion	154 (eV)	164 (eV)	166.5 (eV)	190 (eV)	206 (eV)	284.2 (eV)	287.4 (eV)	310.4 (eV)	360.4 (eV)	519 (eV)	529 (eV)	532 (eV)	533 (eV)	582 (eV)	674 (eV)	684 (eV)	690 (eV)	740 (eV)
12	C^+	9.4	11.0	11.8	12.9	12.1	11.3	10.9	10.9	11.3	12.6	11.9	14.0	13.1	13.0	13.9	13.8	13.5	14.0
16	O^+/ S^{2+}	10.7	11.5	8.3	20.1	17.6	13.3	13.1	13.4	13.2	18.0	16.0	20.5	19.1	19.8	20.3	19.2	19.3	20.0
19	F^+	14.9	16.8	9.1	9.8	8.6	8.6	8.0	7.7	8.4	10.2	9.3	9.0	9.6	10.0	9.8	10.6	11.1	11.4
23.5	FCO^{2+}	2.2	2.3	1.2	1.4	1.0	1.2	1.3	1.1	1.1	1.1	1.3	1.2	1.3	1.4	1.3	1.3	1.4	1.4
28	CO^+	9.0	9.8	9.0	11.9	11.9	8.8	8.9	8.7	8.6	7.5	8.2	9.0	8.2	7.7	7.7	7.9	8.1	7.8
30	SCO^{2+}	1.0	1.2	1.0	5.1	3.7	1.1	0.5	0.6	0.6	0.7	0.6	0.6	0.7	0.6	0.6	0.5	0.5	0.5
32	S^+	11.0	12.0	13.2	18.1	20.1	20.3	19.9	19.8	19.8	16.9	17.7	15.1	16.1	15.9	15.9	15.7	15.5	15.4
35	Cl^+	7.3	6.4	7.0	10.1	13.6	18.0	16.4	17.3	17.6	15.9	15.7	13.7	14.5	14.5	14.4	14.2	14.1	14.0
47	FCO^+	7.8	6.5	7.5	7.8	9.5	8.1	7.1	7.9	6.9	5.7	5.7	5.2	5.4	5.1	4.8	4.6	4.5	4.3
60	SCO^+	1.2	1.0	0.8	0.5	0.5	0.5	1.0	0.9	0.9	0.7	0.9	0.8	0.8	0.8	0.7	0.8	0.8	0.6
67	SCl^+	1.9	1.3	1.8	1.3	1.4	0.9	1.9	1.6	1.6	1.1	1.6	1.2	1.2	1.2	1.1	1.3	1.2	1.1

ences in the photon and electron impact processes can be observed.[22] The effect of the single ionization of a series of XC(O)SY molecules has been studied using conventional electron impact mass spectra.[23] A diminution of both the enthalpy difference and the interconvertion barrier between the syn and anti forms was found when the single ion is formed.[23]

Table 1 collects the branching ratios extracted from each PEPICO mass spectrum for the 2p and 1s transition regions. When the spectra for each transition are compared, small changes are observed, and no significant differences in the branching ratios become evident. Moreover, no drastic changes are obvious when the branching ratios for different ionization edges are compared. The fragmentation patterns at the S and Cl 2p edges are dominated by the 12, 16, 19, and 32 *m/z* ratios. The main change related to the increasing photon energy from the S 2p to the Cl 2p excitation is that the 32 and 16 *m/z* ratios are increased. The fragmentation patterns at the C, O, and F K edges seem to be basically identical. That is, the yields (obtained by the peak areas) of dominant C^+, F^+, and Cl^+ ions were 12.5 ± 1.5, 9.5 ± 1.5, and 16 ± 2% in the C, O, and F K excitations, respectively. The intensity of the $m/z = 16$ signal is incremented by going from C to the O 1s region. It may be due to the production of not only O^+ but also S^{2+} ions. Assisted by the normal Auger decay process, the value of the double-ionization cross section increases with higher energies. Other main products were CO^+, FCO^+, and SCl^+ with yields of 7.5 ± 1.5, 8 ± 1.0, and 1.5 ± 0.5%, respectively, over the whole range of the photon energy.

PEPIPICO Spectra. In the PEPIPICO spectra, the times of flight (T1 and T2) of two ions arising from a dissociative double-ionization event are recorded coincidently. The arrival at the electron detector of an energy-unselected photoelectron gives rise to a starting signal from which the times of arrival of two subsequent ions can be measured absolutely. Thus, PEPIPICO spectra mainly reflect pairs of singly charged fragment ions originating from the fragmentation of the doubly charged parent molecule.

Two-dimensional PEPIPICO spectra for the correlation between one electron and two positive ions were recorded at several photon energies corresponding to transitions involving both L (S and Cl 2p) and K (C, O, and F 1s) levels of FC(O)SCl. These multicoincidence measurements enable the identification of the various ions produced in the same photoionization event. The correlation between ion signals is represented by 2D maps that plot the coincidence signal as a function of the time of flight of both the first and second ions (T1 and T2, respectively).

Furthermore, projections of PEPIPICO spectra on the T1 and T2 axes were obtained by integrating the signal intensity over times T2 and T1, respectively, for some selected photon energies. These spectra are nearly identical regardless of the specifically selected photon energy. In Figure 8, PEPIPICO T1 and T2 projection spectra of FC(O)SCl, recorded at the O 1s resonance transition, are depicted. The heaviest fragment is SCl^+ whereas the main fragments in the T1 and T2 domains are those related to *m/z* values of 12, 16, and 19 amu/q for the T1 projections and 32, 35, and 47 amu/q for the T2 projections. The ion $m/z = 28$ (basically CO^+) gives rise to a medium-intensity signal in both projections. The ion CO^+ can be produced by different dissociation channels where it is both

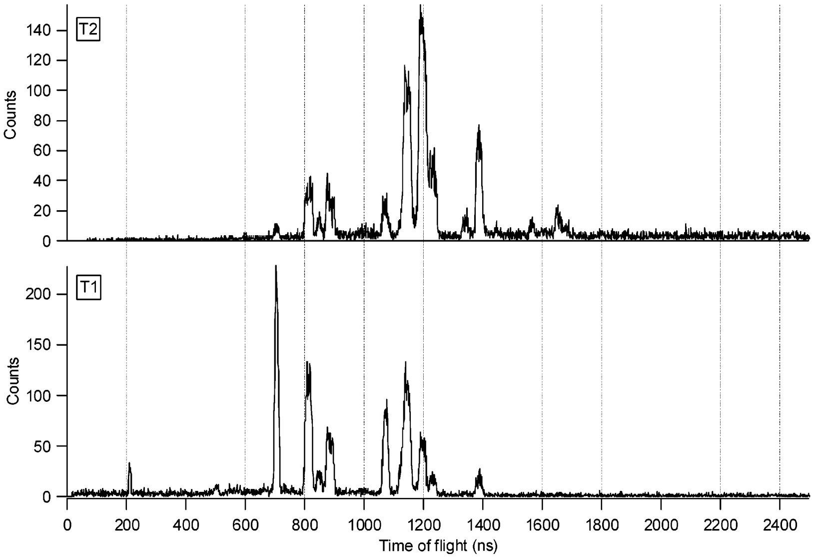

Figure 8. T1 and T2 projections of the PEPIPICO spectrum of FC(O)SCl recorded at 310.4 eV on the C 1s resonance.

the lighter and the weightier ion. Its important to note that in the T2 projection the intensity of the signal at $m/z = 16$ amu/q appears to be medium. This fact could be related to the contribution of the O^+ ion formed in some multiple-body dissociation channel and to some contribution of the S^{2+} doubly charged ion derived from dissociative triple ionizations. The PEPIPICO spectra contain the contribution of dissociative triple ionization, where only the two lighter ions can been detected. Apart from some small increment in the fragmentation process with increasing photon energy, the projection spectra are similar over the whole range of photon energy.

Although the nature of the ion formed after excitation would be a matter of a deeper experimental and theoretical study, to a first approximation different possible core excited decays (especially normal Auger decays) leading to a doubly charged molecular ion, $FC(O)SCl^{2+}$, can be supposed. Concerning the dynamics of molecular fragmentation, Eland[24] discussed the possible fragmentation mechanisms for two- and three-body decay. In the case of two-body dissociation, by neglecting the thermal velocity contribution before the dissociation, momenta of the positively charged fragments are anticorrelated because of the momentum conservation law. Under space-focusing conditions, in the first-order approximation, the coincidence peak in the 2D PEPIPICO spectra shows a "cigarlike" shape with slope of -1. The kinetic energy released in the dissociation is reflected by the length of the segment.

In a three-body fragmentation of a doubly charged molecule, the possible mechanisms are identified as deferred charge separation (DCS), secondary decay (SD), and concerted dissociation (CD). In the case of large timescales, the dissociation energies and the kinetic momentum conservation can be defined and applied to each dissociation step.

Neglecting the kinetic energy release corresponding to the neutral ejection step, the slope of the coincidence peak in the PEPIPICO spectrum can be used to understand the corresponding sequential information of the processes.[25]

Thus, in a DCS mechanism, a neutral particle is ejected in the first step of the fragmentation process. In the second step, it is followed by charge separation that is dominated by Coulombic repulsion. If the energy release in the second step is much larger than the energy release in the first step, then the expected figure is a parallelogram with a slope of -1. In an SD mechanism, charge separation takes place in the first dissociation step, followed by the ejection of a neutral particle from one of the charged fragments. The expected peak in the 2D PEPIPICO spectrum for the charged ions formed in the dissociation process is also a parallelogram whose orientation depends on the energy release and on the mass factor. Finally, in the CD mechanism, all bonds break up simultaneously, the momentum distribution is not unique, and the coincidence peak in the 2D PEPIPICO spectra possesses an ovoidlike shape, especially if the momenta of the fragments are not in the same plane.

The four-body decay has been discussed by Simon et al.[26] Two additional mechanisms were proposed: secondary decay after a deferred charge separation (SDDCS) and secondary decay in competition (SDC). The related peak shapes are parallelograms with slopes depending on the masses of the ejected fragments.

For the penta-atomic molecule FC(O)SCl with five different atoms, the interpretation of PEPIPICO spectra is rather complex. As expected from the PEPICO analyses, the molecule shows contributions of atomization processes, making the spectra even more complex. As a selected example, in Figure 9 the 2D PEPIPICO spectrum at 528.5 eV is presented.

Peaks corresponding to double coincidences involving the lightest masses, especially those related to $m/z = 12$ and 16 amu/q, show a high intensity, owing to the importance of the atomization processes in the dissociation mechanism of FC(O)SCl. However, there is evidence that their shapes cannot be described by a parallelogram, indicating that more than one specific dissociation decay gives rise to the coincidence. This means that the shape originates from a superposition of parallelograms with different slopes. Furthermore, for coincidences involving an $m/z = 16$ value, the discrimination between O^+ and S^{2+} ions is not feasible.

To a first approximation, this analysis focuses on five selected pairs of ions for which only one dissociation mechanism with a well-defined shape is observed. The selected islands for the pairs F^+/Cl^+ and CO^+/S^+ at 528.5 eV are shown in the PEPIPICO spectrum as contour plots in Figure 10.

Two-Body Fragmentations. The basic assumption for the following analysis is that the carbonyl bond will remain unchanged in a two-body fragmentation; that is, the contribution of the O^+ ion raising the signal observed at $m/z = 16$ amu/q can arise only from a three-body (or higher-number body)

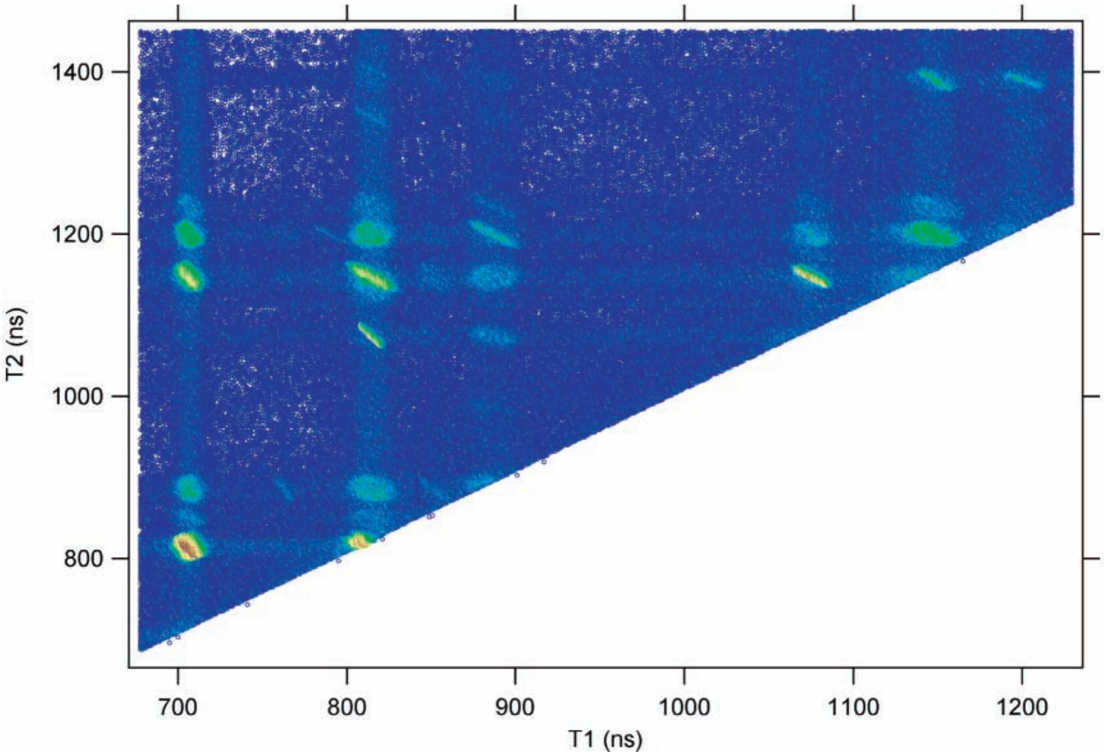

Figure 9. General overview of the PEPIPICO spectrum of FC(O)SCl obtained at 528.5-eV photon energy.

processes. This chemically intuitive assumption is corroborated by both the PEPICO and the PEPIPICO spectra because no signal at $m/z = 98$ amu/q ($FCSCl^+$) has been detected. From the different channels that may be expected for the $FC(O)SCl^{2+}$ dissociation following a two-body fragmentation, process 1 with a slope of -1 was obtained using a least-squares fitting procedure.

$$FC(O)SCl^{2+} \rightarrow FCO^+ + SCl^+ \qquad (1)$$

Three- and Four-Body Fragmentations.

(1) Coincidence of $m/z = 28$ with $m/z = 67$ amu/q:

The observed slope of -1.05 can be explained by the following DCS mechanism:

$$FC(O)SCl^{2+} \rightarrow F + OCSCl^{2+} \qquad U_1 \qquad (2)$$

$$OCSCl^{2+} \rightarrow CO^+ + SCl^+ \qquad U_2 \qquad (3)$$

(2) Coincidence of $m/z = 35$ with $m/z = 60$ amu/q:

The experimental slope of -0.78 for this coincidence can be explained by a simple secondary decay (SD) process with initial charge separation:

$$FC(O)SCl^{2+} \rightarrow FC(O)S^+ + Cl^+ \qquad U_1 \qquad (4)$$

$$FC(O)S^+ \rightarrow F + OCS^+ \qquad U_2 \qquad (5)$$

where U is the energy released. Assuming that $U_1 \gg U_2$, a value of -0.76 can be deduced for the expected slope in the PEPIPICO spectra, in very good agreement with the experimental value.

Two coincidences are of special interest: (3) coincidence $m/z = 19$ with $m/z = 35$ amu/q and (4) coincidence $m/z = 28$ with $m/z = 32$ amu/q.

The experimentally measured slopes for these ions coincidences are -1.04 and -1.02 for (3) and (4), respectively. (See Figure 10.)

Obviously, it is not possible to fit the observed slope of coincidences (3) and (4) with the usual mechanisms.[25] However, it is known that rearrangements (processes in which at least one bond is broken and another is formed) are possible, especially in the case of large molecules, which possess several degrees of freedom. For example, F_2^+ recently was reported as a rearrangement product in the photoinoization of the SiF_4 molecule.[27] The following three-body mechanisms can explain the observed slopes:

$$FCOSCl^{2+} \rightarrow OCS + ClF^{+2} \qquad U_1 \qquad (6)$$

$$ClF^{+2} \rightarrow Cl^+ + F^+ \qquad U_2 \qquad (7)$$

Thus, in the first step, the doubly charged molecular ion suffers a rearrangement to yield a neutral COS molecule whereas the doubly charged FCl^{+2} ion will dissociate to give Cl^+ and F^+ (step 7). This last process is dominated by Coulombic forces; the U_1 term can be neglected, and the expected figure in the PEPIPICO spectra is a parallelogram of slope -1.

Similarly, for dissociation channel 4, we may explain the coincidence of S^+ and CO^+ ions by the following processes:

$$FC(O)SCl^{2+} \rightarrow OCS^{2+} + ClF \qquad U_1 \qquad (8)$$

$$OCS^{2+} \rightarrow S^+ + CO^+ \qquad U_2 \qquad (9)$$

Whereas the rearrangement is the same as before, the OCS fragment remains charged. The dominant energy release is evidently U_2, and if U_1 tends to approach zero, then this mechanism is experimentally identical to the simple scheme of two-body fragmentation, except, of course, for the different nature of the fragments involved in these processes.

Taking into account the preferred syn conformation for the FC(O)SCl molecule, it might be unlikely that such an arrangement to form ClF (or ClF^{+2}) and OCS^{2+} (or OCS) takes place because the F and Cl atoms are oriented in opposite directions.

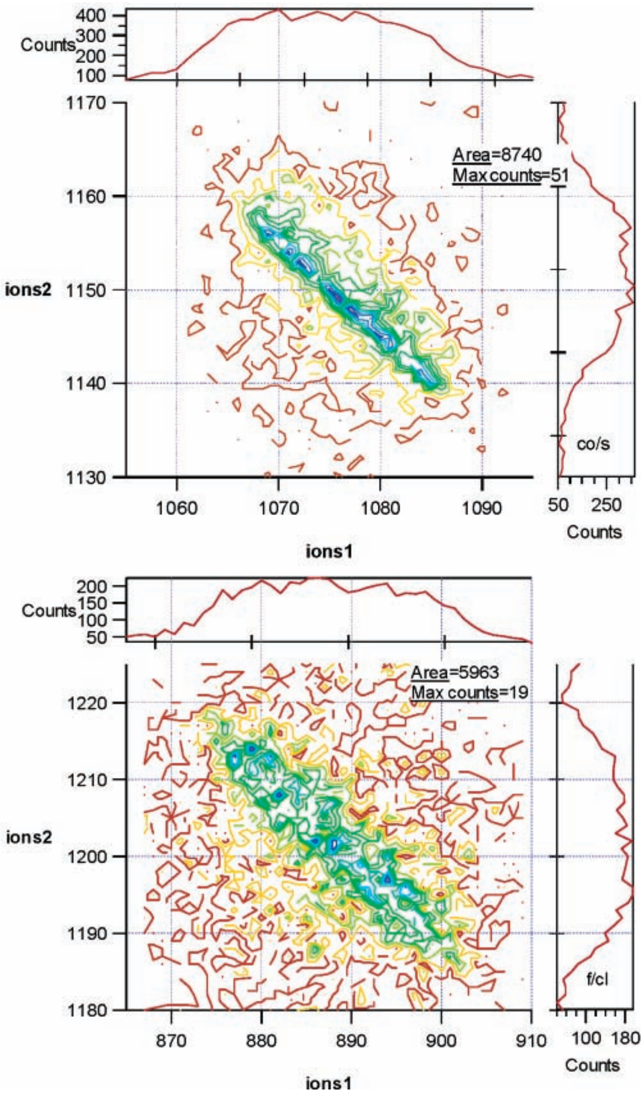

Figure 10. Contour plots derived from the PEPIPICO spectrum of FC(O)SCl at 528.5 eV for a selected pair of ions.

This raises the question about the structure and conformation of the FC(O)SCl^{+2} ion. Therefore, quantum chemical calculations were performed for the low-lying doubly charged cationic state of FC(O)SCl by using the Gaussian program suite.[28] According to the UMP2/6-31+G* method, this state is located 27.2 eV above the neutral ground state corresponding to a minimum on the potential energy surface (i.e., no imaginary frequencies were found). The most important difference between the neutral and the ionic species is that the FC−SCl dihedral angle changes from 180° in syn-FC(O)SCl to 80.5° in FC(O)-SCl^{+2} (almost in gauche orientation). This dramatic geometrical change would coincide with our proposed mechanisms. The geometry of the neutral species was reported to remain unchanged after simple ionization.[5,23]

Conclusions

The TIY spectra of shallow core levels S 2p and Cl 2p and inner-shell levels C 1s, O 1s, and F 1s of FC(O)SCl in the range of 100 to 1000 eV were obtained by using synchrotron radiation and coincidence detection techniques. These results, the first obtained for a sulfenylcarbonyl compound, are compatible with previous data obtained for related molecules,[29] such as carbonylic and sulfur-containing compounds.[16,17]

The main characteristic of the spectra is the presence of well-defined signals below the C 1s, O 1s, and F 1s ionization edges, which could be related to electronic transitions from the fundamental state to π^{-*}_{FCO} and π^{+*}_{FCO} vacant orbitals, in agreement with the reported PES spectra.[5]

The branching ratios of the ion production obtained from the PEPICO spectra exhibit only small changes with the incident photon energy. Similar behavior was observed by Ibuki et al. in $CH_3OC(O)CN$ upon O 1s and N 1s ionizations.[29] In a similar way, the valence electrons in FC(O)SCl are ionized via Auger decays after inner-shell electron excitations. Because of the planarity of the molecule, the nonbonding n_S, n_O, and even the $\pi_{C=O}$ HOMO orbitals are strongly delocalized over the entire molecule.[5] Thus, when these delocalized valence electrons are ionized via the Auger decay, the positively charged species would lose the memory of the atomic site excited initially.

The analysis of the PEPIPICO spectra is useful in identifying several molecular dissociation mechanisms followed by Auger decays. Thus, two-body mechanism dissociation channels, which lead to FCO^+ and SCl^+ fragments, were found. Three-body mechanisms have been also detected. They include a DCS scheme (coincidence between CO^+ and SCl^+) and an SD mechanism (double coincidence of Cl^+ and OCS^+). Furthermore, the existence of processes leading to atomization can be identified by the appearance of species such as carbon, oxygen, and fluorine. Multibody dissociation dynamics should be involved in these processes. It is worthy of mentioning that a new three-body dissociation mechanism, defined as secondary decay after an ion rearrangement (SD-IR), is proposed to explain the process involving two double coincidences, namely, F^+/Cl^+ and CO^+/S^+.

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References and Notes

(1) Stryer, L. *Biochemistry*; W. H. Freeman: New York, 1995.

(2) (a) Gobatto, K. I.; Della Védova, C. O.; Mack, H.-G.; Oberhammer, H. *Inorg. Chem*. **1996**, *35*, 6152. (b) Erben, M. F.; Della Védova, C. O.; Romano, R. M.; Boese, R.; Oberhammer, H.; Willner, H.; Sala, O. *Inorg. Chem*. **2002**, *41*, 1064. (c) Romano, R. M.; Della Védova, C. O.; Downs, A. J.; Greene, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 5794.

(3) (a) Mack, H.-G.; Oberhammer, H.; Della Védova, C. O. *J. Phys. Chem.* **1991**, *95*, 4238. (b) Romano, R. M.; Vedova Della, C. O.; Boese, R.; Hildebrandt, P. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2551.

(4) (a) Hocking, W. H.; Winnewisser, G. *Z. Naturforsch., A* **1976**, *31*, 422. (b) Shen, Q.; Hagen, K. *J. Mol. Struct*. **1985**, *128*, 41. (c) Willner, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39*, 314.

(5) Erben, M. F.; Della Védova, C. O. *Inorg. Chem*. **2002**, *41*, 3740.

(6) Eland, J. H. D.; Wort, F. S.; Royds, R. N. *J. Electron Spectrosc. Relat. Phenom.* **1986**, *41*, 297.

(7) Lira, A. C.; Rodrigues, A. R. D.; Rosa, A.; Gonçalves da Silva, C. E. T.; Pardine, C.; Scorzato, C.; Wisnivesky, D.; Rafael, F.; Franco, G. S.; Tosin, G.; Lin, L.; Jahnel, L.; Ferreira, M. J.; Tavares, P. F.; Farias, R. H. A.; Neuenschwander, R. T.; *Proc. EPAC*, Stockholm, 1998, and references therein.

(8) de Fonseca, P. T.; Pacheco, J. G.; Samogin, E.; de Castro, A. R. B. *Rev. Sci. Instrum.* **1992**, *63* 1256.

(9) de Castro, A. R. B. Conceptual *Project of a Soft X-ray Beamline for High-Resolution Spectroscopy*; LNLS Technical Memo CT-09/91; 1991.

(10) Naves de Brito, A.; Feifel, R.; Mocellin, A.; Machado, A. B.; Sundin, S.; Hjelte, I.; Sorensen, S. L.; Björneholm, O. *Chem. Phys. Lett.* **1999**, *309*, 377.

(11) Haas, A.; Reinke, H. *Angew. Chem*. **1967**, *79*, 687.

(12) Della Védova, C. O.; Cutín, E. H.; Jubert, A. H.; Varetti, E. L.; Aymonino, P. J. *Can. J. Spectrosc.* **1984**, *29*, 130.

(13) Erben, M. F., Romano, R. M.; Della Védova, C. O. *Beam Line Project D05A-TGM-1504*; LNLS; 2003.

(14) Svensson, S.; Naves de Brito, A.; Keane, M. P.; Correia, N.; Karlsson, L. *Phys. Rev. A* **1991**, *43*, 6441.

(15) (a) Klapstein, D. *J. Electron Spectrosc. Relat. Phenom.* **1987**, *42*, 149. (b) Klapstein, D.; O'Brien, R. T. *Can. J. Chem.* **1987**, *65*, 683.

(16) Ishii, I.; Hitchcook, A. P. *J. Electron Spectrosc. Relat. Phenom.* **1988**, *46*, 55.

(17) Robin, M. B.; Ishii, I.; McLaren R.; Hitchcock, A. P. *J. Electron Spectrosc. Relat. Phenom.* **1988**, *47*, 53.

(18) Eberhardt, W.; Sham, T. K.; Carr, R.; Krummacher, S.; Strongin, M.; Weng S. L.; Wesner, D. *Phys. Rev. Lett.* **1983**, *50*, 1038.

(19) (a) Murphy R.; Eberhardt, W. *J. Chem. Phys.* **1988**, *89*, 4054. (b) Müller-Dethlefs, K.; Sander, M.; Leslie, M.; Chewter, L. A.; Schlag, E. W. *J. Phys. Chem.* **1984**, *88*, 6098. (c) Suzuki I. H.; Saito, N. *Int. J. Mass Spectrom. Ion Processes* **1997**, *163*, 229. (d) Thomas, M. K.; Hatherly, P. A.; Codling, K.; Stankiewicz, M.; Rius, J.; Karawajczyk A.; Roper. M. *J. Phys. B: At. Mol. Opt. Phys.* **1998**, *31*, 3407.

(20) Erman, P.; Karawajczyk, A.; Rachlew, E.; Stankiewicz M.; Franzen. K. Y. *J. Chem. Phys.* **1997**, *107*, 10827.

(21) Morin, P.; Simon, M.; Miron, C.; Leclercq, N.; Hansen, D. L. *J. Electron Spectrosc. Relat. Phenom*. **1998**, *93*, 49.

(22) The harmonic components of the selected photon energy are not filtered in the TGM beam line at the LNLS. Thus, the comparison of electron and photon impact spectra is not straightforward. However, measurements performed using argon gas show that the contribution of harmonics is not appreciable. Furthermore, recent experiences in related molecules such as $CH_3C(O)SH$ and $CH_3OC(O)SCl$ show no important atomization processes.

(23) Della Védova, C. O.; Furlong, J. J. P.; Mack, H.-G. *J. Mol. Struct.* **1994**, *317*, 165.

(24) Eland, J. H. D. *Mol. Phys.* **1987**, *61*, 725.

(25) Eland, J. H. D. *Acc. Chem. Res.* **1989**, *22*, 281.

(26) Simon, M.; Lebrun, T.; Martins, R.; de Souza, G. G. B.; Nenner, I.; Lavolee, M.; Morin, P. *J. Phys. Chem.* **1993**, *97*, 5228.

(27) Santos, A. C. F.; Lucas, C. A.; de Souza, G. G. B. *J. Electron Spectrosc. Relat. Phenom*. **2001**, *114−116*, 115.

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(29) Ibuki, T.; Okada, K.; Saito, K.; Gejo, T. *J. Electron Spectrosc. Relat. Phenom*. **2000**, *107*, 39.