Ionic Fragmentation on ClC(O)SCl. Evidence of a Highly Charged Molecular Ion and Confirmation of Unusual Dissociation Mechanisms for Halocarbonylsulfenyl Chlorides

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Total and partial ion yield spectra of chlorocarbonylsulfenyl chloride, ClC(O)SCl, are studied using tunable synchrotron radiation. Multicoincidence techniques, which include photoelectron−photoion coincidence (PEPICO) and photoelectron−photoion−photoion coincidence (PEPIPICO) time-of-flight mass spectrometry, were applied to study the fragmentation dynamics around the S 2p, Cl 2p, C 1s, and O 1s ionization edges. The search for site-specific fragmentation effects showed a definite enhancement of the Cl^+ signal at the Cl 2p resonance. However, fragmentation patterns of the PEPICO spectra at the various excitation energies are essentially identical. Evidence for the occurrence of the previously reported charge separation after an ion rearrangement dissociation mechanism was found. Highly charged species were observed in the multicoincidence spectra at K shell transitions, revealing the formation of a highly charged molecular ion.

Introduction

We have recently reported the foundational study concerning shallow- and inner-core electrons in sulfenylcarbonyl XC(O)SY compounds.[1] Several shallow- and inner-core electronic levels of FC(O)SCl were excited by using synchrotron radiation in the range 100−1000 eV. Total ion yield (TIY) and partial ion yield (PIY) spectra and multicoincidence spectra (photoelectron−photoion coincidence, PEPICO, and photoelectron−photoion−photoion coincidence, PEPIPICO) were measured around the S 2p, Cl 2p, C 1s, O 1s, and F 1s transitions of FC(O)SCl. The TIY spectra show 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 previously reported He(I) photoelectron spectrum.[2] The branching ratios for ion productions obtained from the PEPICO spectra exhibit only small changes with the incident photon energy, which was interpreted in terms of a "lose memory" effect or nonspecific fragmentation after an Auger decay, promoted by the delocalization of the valence orbitals over the whole planar molecule. The analysis of PEPIPICO spectra clearly allowed the identification of a two-body mechanism dissociation channel, which leads to FCO^+ and SCl^+ fragments. Also, three-body dissociation mechanisms were detected. They include a deferred charge separation (DCS) scheme (coincidence between CO^+ and SCl^+) and a secondary decay (SD) mechanism (double coincidence of Cl^+ and OCS^+). Furthermore, a new three-body dissociation mechanism, which represents a charge separation after an ion rearrangement (CS−IR), was proposed to explain the process involving two double coincidences, namely, F^+/Cl^+ and CO^+/S^+.

In view of the rich photodissociation processes following the shallow- and core-shell electronic excitation displayed by FC(O)SCl, the extension of the study to another member of the sulfenylcarbonyl family can be interesting. Looking for the same order of molecular complexity, that is, a molecule containing only five atoms, chlorocarbonylsulfenyl chloride, ClC(O)SCl, seems to be a good candidate for comparison of the results.

The molecular structure of ClC(O)SCl has been experimentally reported by Shen and Hagen.[3] From a gas electron diffraction study, it is known that the molecule ClC(O)SCl presents a planar structure with C_s symmetry and synperiplanar (syn) orientation of the C=O double bond with respect to the S−Cl single bond. These authors claimed that the presence of a second, less stable form with gauche orientation could not be excluded. The observed features in the vibrational spectra (IR (gas) and Raman (liquid)) support a planar structure for the molecule, with syn conformation.[4] Further quantum chemical calculations at the MP4/6-31G**//HF/6-31G** level of approximation confirm the syn form as the most stable one, and predict the antiperiplanar (anti) conformation as a stable high-energy form, with $\Delta E = E_{anti} - E_{syn} = 3.0$ kcal mol^{-1}.[5] A revision of the former GED data shows that a better result can be obtained when an anti instead of a gauche form is used in the refinement process (in a relative concentration around 1(3)%).[6] These results are in agreement with recent matrix infrared spectroscopy experiences, which reconfirmed the predominance of the syn conformer in both gas and crystal phases.[7] Furthermore, the photochemistry of ClC(O)SCl isolated in solid Ar or N_2 matrixes at 15 K has been investigated.[8] On the basis of evidence of the IR spectra of the matrixes, the products of irradiation with broad-band UV−vis light ($200 \leq \lambda \leq 800$ nm) were identified. ClC(O)SCl is subject to multichannel changes that include interconversion of the syn and anti rotamers, photodecomposition to give CO and SCl_2, formation of the hitherto unknown radical $ClC(O)S^\bullet$, and subsequent

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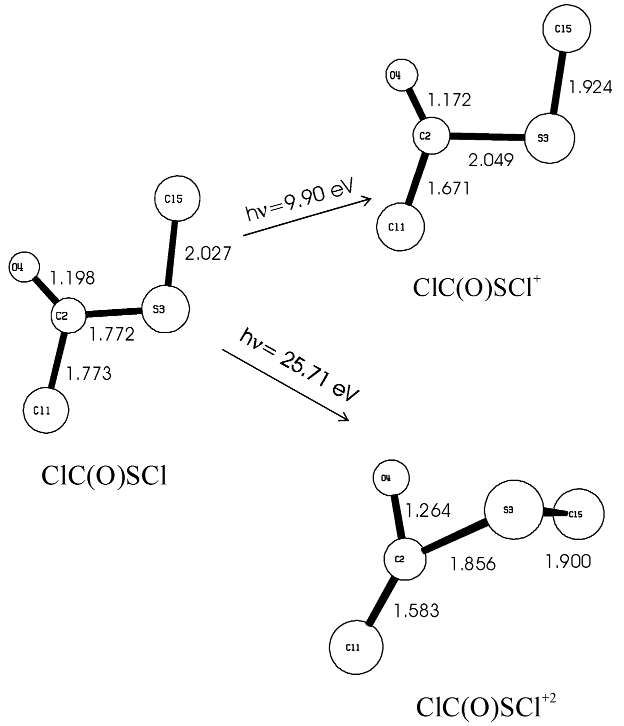
SCHEME 1: Ball and Stick Representation of ClC(O)SCl in Its Neutral Ground State (Left) and Singly (Top Right) and Doubly (Bottom Right) Charged Low-Lying Cationic States[a]



[a] Bond distances and adiabatic ionization energies were calculated at the UMP2/6-31+G* level of approximation.

decomposition of this radical to give either the ClCO$^\bullet$ radical or the OCS molecule.

In the present work a study including spectroscopic and photodissociation analysis of ClC(O)SCl around the S 2p, Cl 2p, C 1s, and O 1s ionization edges by using multicoincidence mass spectroscopy techniques and tunable synchrotron radiation is reported.

Experimental Section

Synchrotron radiation at the Laboratório Nacional de Luz Síncrotron (LNLS), Campinas, São Paulo, Brazil, was used.[9] Linearly polarized light monochromatized either by a toroidal grating monochromator (available at the TGM beam line in the range 12−310 eV)[10] or by a spherical grating monochromator (available at the SGM beam line in the range 200−1000 eV)[11] intersects the effusive gaseous sample inside a high-vacuum chamber, with a base pressure in the range of 10^{-8} mbar. During the experiments the pressure was maintained below 10^{-5} mbar. 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[12] measurements. This instrument was constructed at the Institute of Physics, Brasilia University, Brasilia, Brazil.[13] 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. This event starts the flight time determination process of the corresponding ion, which is consequently accelerated to another MCP. Thus, conventional mass spectra containing mainly contributions from single ionization processes are recorded. They might also contain some contributions of multiple ionizations where only the lightest ion fragment would be detected. It has been reported for the 1s level of the O in the H_2O molecule measured as PEPICO signals that the amount of aborted double ion fragmentation is smaller than 7%.[13] Therefore, a reasonable approximation at this level of accuracy could be carried out ignoring double ionization processes. Similarly, PEPIPICO spectra might contain contributions from triple ionization events where only the two lightest ions would be detected.

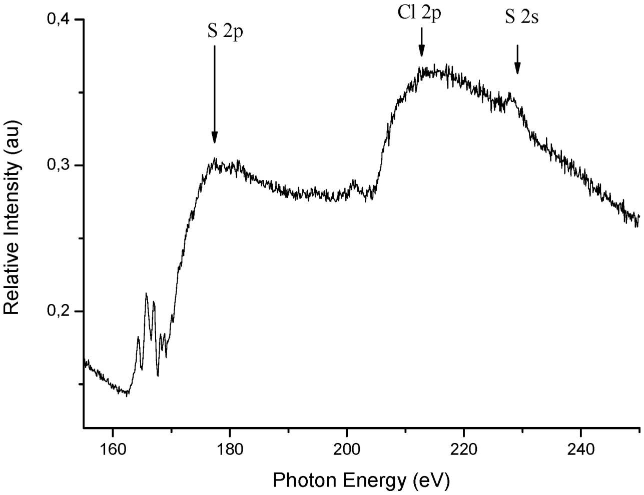


Figure 1. Total ion yield spectrum of ClC(O)SCl in the S 2p and 2s and Cl 2p regions.

The sample of chlorocarbonylsulfenyl chloride, ClC(O)SCl, was obtained from commercial sources (Aldrich, 95%). The liquid product was purified by fractional condensation at reduced pressure to eliminate volatile impurities. The purity of the compound was checked by IR (vapor), Raman (liquid), and ^{13}C NMR spectroscopy.[14]

Results and Discussion

For a truthful analysis of experiences concerning inner-shell electrons knowledge about the whole electronic structure of the molecule under study is desirable, especially the first unoccupied valence orbitals that could be associated with electronic transitions. The UV−vis spectrum of gaseous ClC(O)SCl shows two bands at 220 nm ($\epsilon_{293\,^\circ\mathrm{C}} = 4300$ L mol^{-1} cm^{-1}) and 300 nm ($\epsilon_{293\,^\circ\mathrm{C}} = 120$ L mol^{-1} cm^{-1}), which were tentatively assigned to $\pi \rightarrow \pi^*_{C=O}$ and $n_S \rightarrow \pi^*_{C=O}$ transitions, respectively.[15] The latter corresponds to the excitation of a single electron from the HOMO orbital, localized on the sulfur lone pair, to the LUMO $\pi^*_{C=O}$ orbital in the carbonyl chromophore. No further experimental studies were performed to confirm these assignments. Unfortunately, the photoelectron spectrum of ClC(O)SCl has not been measured so far. However, taking into consideration the similarity of chloro- and fluorocarbonylsulfenyl chloride, it is possible to anticipate some characteristics of the valence shell electronic structure of ClC(O)SCl: (1) The presence of various atoms nominally containing electron lone pairs should have an important contribution to the low-energy region in the He(I) PES. As assumed in the interpretation of the UV−vis spectrum of ClC(O)SCl, it is quite likely that the sulfur lone pair (n''_S) orbital is the HOMO. (2) The planarity of the molecule could allow the mixture of the orbitals with similar symmetry, leading to an electronic delocalization over the whole molecule.[16] This fact becomes important in the following discussion since the search for site-specific fragmentation is one of the aims of the present study. Thus, similarly

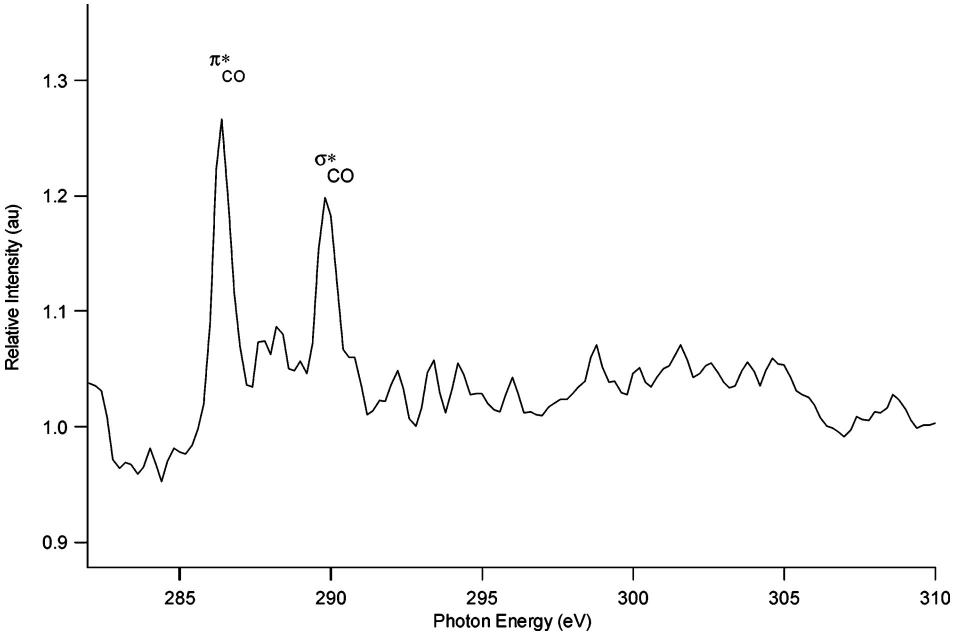


Figure 2. Total ion yield spectrum of ClC(O)SCl in the C 1s region.

to the PES of FC(O)SCl, the PES of ClC(O)SCl might be dominated by in-plane (a′) and out-of-plane (a″) nonbonded electrons, namely, lone pair orbitals, nominally localized in sulfur and chlorine atoms. Earlier ground-state quantum chemical calculations at semiempirical levels support these assumptions.[15] Further quantum chemical calculations were performed for the electronic ground state as well as for low-lying singly and doubly charged cationic states of ClC(O)SCl by using the Gaussian program suite.[17] According to the UMP2/6-31+G* method, the low-lying singly and doubly charged states are located at 9.90 and 25.71 eV, respectively, above the neutral ground state. Both charged $ClC(O)SCl^+$ and $ClC(O)SCl^{2+}$ forms are stable minima in the low-lying cationic potential energy surfaces; i.e., no imaginary frequencies were found. As for FC(O)SCl, the planarity of the ClC(O)SCl molecule remains unchanged after simple ionization.[2,18,19] The most important structural difference between the neutral and the doubly charged ionic species is that the ClC−SCl dihedral angle changes from 180° in syn ClC(O)SCl to 82.7° in $ClC(O)SCl^{2+}$ (almost in gauche orientation).

After a single ionization the C−S single bond experiences an important elongation of about 0.28 Å, while the other bond lengths decrease (Scheme 1). Bond angles in $ClC(O)SCl^+$ are similar to those in the neutral species, and a planar syn conformation is still the preferred form (Scheme 1). Quite different structural behavior is found for the low-lying doubly charged form. When this species is compared with the neutral form, huge differences are observed in bond distances, bond angles, and torsions. Thus, C−Cl and S−Cl single bonds are even shorter than those corresponding to the singly charged form, while the C−S bond in $ClC(O)SCl^{2+}$ is slightly longer than the same bond in the neutral form.

TIY Spectra. At high photon energies corresponding to shallow- and core-shell electronic levels the quantum yield for molecular ionization is quite likely tending to unity. Consequently, the detection of parent and fragment ions as a function of the incident photon energy (TIY) is a powerful method to be used as a complement to absorption spectroscopy.[20]

The TIY spectrum of ClC(O)SCl for the S and Cl 2p edge regions is shown in Figure 1. Below the S 2p threshold, at around 177.8 eV, the spectrum shows a rather complex feature, characterized by a group of five signals centered at 164.3, 165.7, 167.0, 168.3, and 168.8 eV. The most intense absorption of this region, located at 165.7 and 167.0 eV, should be originated from transitions involving the spin−orbit splitting of the 2p term of sulfur into $2p_{1/2}$ and $2p_{3/2}$ levels. It should be noted, however, that an intensity ratio of 2:1 is expected for transitions from the $2p_{3/2}$ and $2p_{1/2}$ levels to the same final orbital. Nevertheless, in this case both peaks show similar intensity, suggesting overlapping transitions. For the H_2S molecule, a similar transition splitting of 1.201 eV has been reported.[21]

The Cl 2p edge region of ClC(O)SCl exhibits a simple feature at 201.1 eV without any fine structure (Figure 1). However, a broad band dominates the region with a slow growth around the ionization edge. This makes it difficult to identify the Cl 2p ionization energy. The resolution of the Cl 2p transitions for both nonequivalent chlorine atoms is not feasible at the resolution used. The S 2s edge is clearly observed at 228.0 eV as a low-intensity signal superposed to the Cl 2p continuum.

Below the threshold, the C 1s region shows transitions at 286.4 and 290.0 eV (see Figure 2). These features may correspond to excitations to vacant π^*_{CO} and σ^*_{CO} orbitals, respectively. Unfortunately, it was not feasible to identify the C 1s ionization potential accurately.

The TIY in the O 1s region (Figure 3) is dominated by an intense resonance at around 528.2 eV and by a second signal with lower intensity at 532.1 eV. Again, these absorptions could be related to the electronic excitation from the fundamental state to π^*_{CO} and σ^*_{CO} vacant molecular orbitals, respectively, because similar values are observed for the π^*_{CO} and σ^*_{CO} orbital energy differences in both C and O 1s regions. In Figure 3 the electron total yield is also shown. From this spectrum, the O 1s IP is estimated to be 535.3 eV for the title molecule.

These results are in good agreement with the reported values obtained for FC(O)SCl. Furthermore, the proposed assignments, corresponding especially to the carbonyl group, are consistent with those reported for esters and carboxylic acids.[22,23]

PEPICO Spectra. Naturally occurring isotopomer fragments, mainly due to the presence of ^{35}Cl and ^{37}Cl isotopes, are clearly observed due to suitable mass resolution of the experiments. This fact facilitates the assignment of the ion fragments appearing in the coincidence spectra.

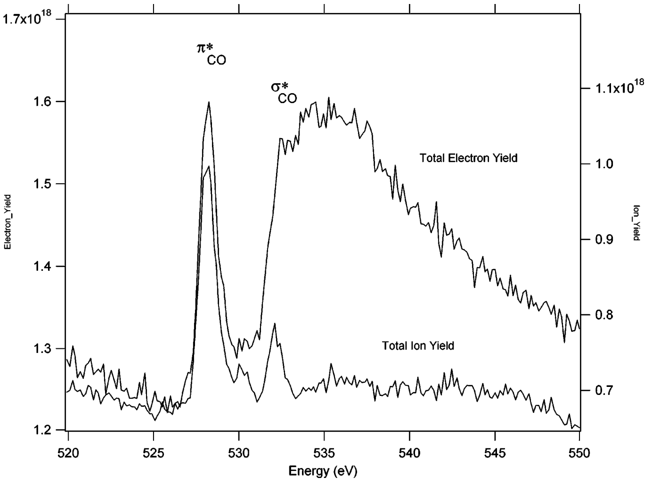


Figure 3. Total ion yield spectrum of ClC(O)SCl in the O 1s region.

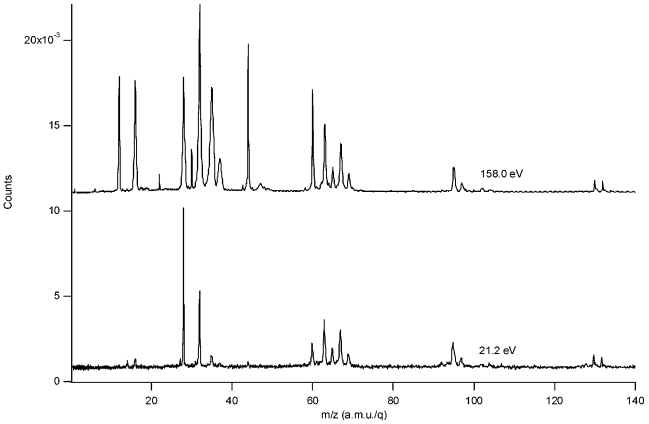


Figure 4. PEPICO spectra of ClC(O)SCl recorded at 21.2 and 158.0 eV photon energies.

Ionic Fragmentation Following Valence-Shell Ionization. To study fragmentation processes following valence-shell ionization, PEPICO spectra were obtained at 21.2 and 158.0 eV by using synchrotron radiation. The former corresponds to the resonant energy emitted by He(I) lamps, commonly utilized in photoelectron spectroscopy experiments. Thus, this spectrum may be useful for further spectroscopic studies on ClC(O)SCl. PEPICO spectra at 21.2 eV measured in the range 0−140 amu/q are presented in Figure 4. In agreement with quantum chemical calculations, fragments derived mainly from the single ionization of the outer orbitals (the calculated UMP2/6-31+G* adiabatic double ionization potential is 25.7 eV) are expected. Furthermore, valence electron double ionization events, through direct double ionization or autoionization processes, play a definite role in the ionic fragmentation of the molecule at 158.0 eV. On the other hand, the photon energy is not yet enough to ionize shallow-core electrons (S 2p transitions appear clearly above 160 eV). Consequently, the 158.0 eV PEPICO spectrum should also provide a good reference with respect to the fragmentation pattern associated with shallow- and inner-core electrons.

A strong signal at $m/z = 28$ amu/q, corresponding to the CO^+ ion, dominates the PEPICO spectra at 21.2 eV. The parent ion is unambiguously observed at 130 amu/q. A set of signals is observed at 63 (65) and 67 (69) amu/q, which correspond to fragments derived from a loss of SCl and ClCO neutral fragments from the parent ion, respectively. These processes give rise to the observed $ClCO^+$ ($^{37}ClCO^+$) and SCl^+ ($S^{37}Cl^+$) signals. The signal at 95 amu/q corresponds to a loss of a chlorine atom by the parent ion, generating either $ClC(O)S^+$ or $C(O)SCl^+$ ions. Signals corresponding to the S^+ and OCS^+ ions are observed at 32 and 60 amu/q. A very low intensity signal was observed at 35 amu/q. Thus, in the $ClC(O)SCl^+$ rupture processes involving both S−Cl and Cl−C single bonds ionic fragments with charge localization on either ClC(O)S or C(O)SCl fragments are originated, leaving a noncharged chlorine atom.

Ion signals corresponding to atomic C^+ and O^+ ions appear in the 21.2 eV PEPICO spectra at 12 and 16 amu/q as low-intensity bands. Such signals may be originated in ionization processes owing to photon energies coming from nonfiltered harmonic radiation components.

Several new signals appear in the mass spectrum obtained at 158.0 eV. The most important peaks belong to m/z ratios of 12 (C^+), 16 (O^+), 28 (CO^+), 32 (S^+), 35 (Cl^+), 44 (CS^+), 60 (OCS^+), 63 ($ClCO^+$), 67 (SCl^+), 95 ($ClC(O)S^+$ or $C(O)SCl^+$), and 130 ($ClC(O)SCl^+$) amu/q. Thus, ClC(O)SCl exhibits an important atomization even at relatively low photon energies, implying the occurrence of double ionization channels leading to atomic singly charged fragments. The observed peaks correspond to plausible fragments formed by logical simple molecular bond ruptures or rearrangement processes that are associated with singly charged ions. Doubly charged fragments, namely, CS^{2+} and OCS^{2+}, were also found and identified by their mass/charge ratio values (22 and 30 amu/q, respectively) as well as by their characteristic narrow features. The fragments S^{2+} and O^+ possess similar m/z ratios, the peaks being coincident at the present TOF mass resolution.

In the electron impact mass spectra at 70 eV ionization energy of ClC(O)SCl,[24] the main fragment corresponds to an m/z ratio of 60 amu/q (OCS^+). Atomic S^+ and Cl^+ ions show important relative abundance in the mass spectra, accounting for 35% and 32%, respectively. Other fragments, such as $ClCO^+$, SCl^+, $ClC(O)S^+$, or $C(O)SCl^+$, and the molecular ion $ClC(O)SCl^+$, show important contributions of 24%, 18%, 18%, and 11% with reference to the main peak, respectively. Though a comparison of electron and photon impact spectra is not straightforward, some similarities are observed when the 158.0 eV photon energy spectrum and the 70 eV electron impact spectra are compared. The effect of the single ionization of a series of XC(O)SY molecules has been studied using conventional electron impact mass spectra.[18] Both the enthalpy difference and the interconversion barrier between the syn and anti forms decrease when the singly charged ion is formed.

Inner- and Shallow-Core Excitations and Ionizations. Site-Specific Fragmentation. Differences in relative yields of fragment ions were observed in simple molecules by exciting K shell electrons.[25] 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.[26,27] 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.[28]

We recorded several PEPICO spectra that include the most important shallow and core transitions of ClC(O)SCl. To identify the role of resonant Auger processes in the fragmentation, spectra were not only measured at photon energy values equal to the resonant value (maximum of the peak) but also taken at photon energy values below (typically 10 eV) and above (typically 50 eV) each resonance.

Ionic Fragmentation Following S 2p and Cl 2p Shallow-Core Excitations and Ionizations. The PEPICO spectra around S and Cl 2p ionization edges of ClC(O)SCl are shown in Figure 5.

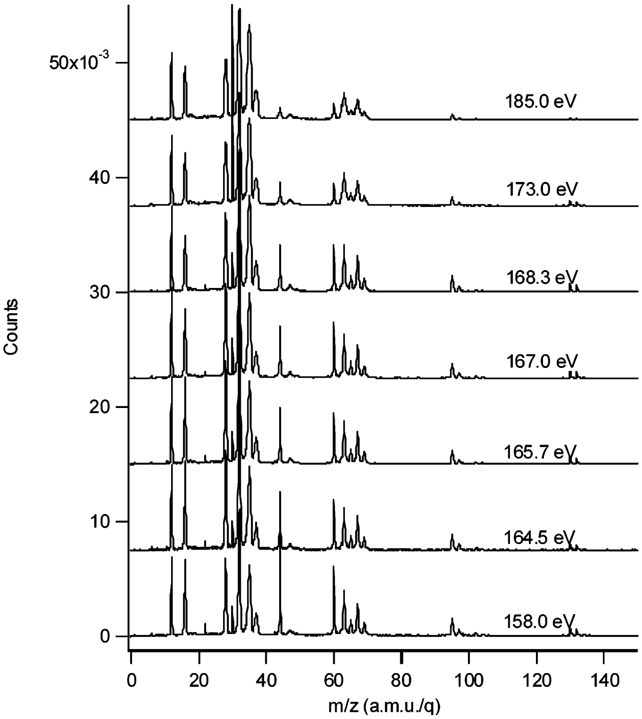


Figure 5. PEPICO spectra of ClC(O)SCl recorded at selected photon energies around the S 2p edge.

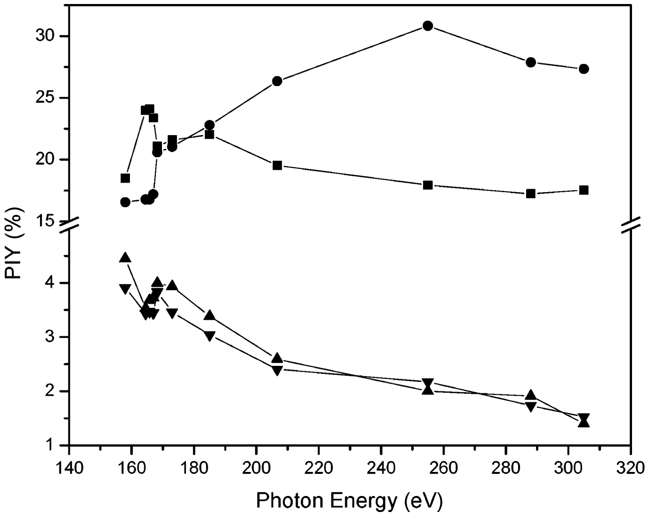


Figure 6. Partial ion yield spectra for selected ClC(O)SCl ions recorded at different photon energies around S 2p, Cl 2p, and C 1s edges: (■) $m/z = 32$ amu/q, S^+, (●) $m/z = 35$ amu/q, Cl^+; (▲) $m/z = 63$ amu/q, $ClCO^+$, (▼) $m/z = 67$ amu/q, SCl^+.

Table 1 collects the branching ratios extracted from PEPICO TOF mass spectra recorded at selected energies for this transition region. Similar to the valence-shell excitation spectra discussed above, the fragmentation patterns at the S and Cl 2p edges are dominated by signals appearing at 12, 16, 28, 32, and 35 m/z ratios, which possess relative abundances higher than 10%. A second group of less intense signals appears around $m/z = 60$ amu/q and comprises the OCS^+ (60 amu/q), $ClCO^+$ (63 amu/q), and SCl^+ (67 amu/q) fragments. The intensity of the $m/z = 44$ amu/q signal decreases with increasing photon energy. The molecular ion, $ClC(O)SCl^+$, is still observed as a low-intensity signal even at energies corresponding to the S 2p ionization edge, but has a negligible contribution above this region.

PIY spectra for the ions with $m/z = 32$, 35, 63, and 67 amu/q as obtained by integration of the PEPICO signals at selected energies are shown in Figure 6. The most intense peak in the PEPICO spectra around the S 2p ionization energy is observed at $m/z = 32$ amu/q, corresponding to the S^+ ion. Slight signal intensifications are observed at the resonant transition. Beyond this ionization edge, the feature corresponding to the Cl^+ ion becomes the dominant signal. Interesting to note, the intensities of the $ClCO^+$ and SCl^+ ion signals are almost the same and show a similar behavior with the variation of the photon energy. These ion signals may be generated by a two-body dissociation of the C$-$S single bond following a single ionization. Thus, the positive charge can remain either in the ClCO or in the SCl molecular fragments after the two-body dissociation.

In view of the position of the chlorine atoms in ClC(O)SCl, two possibilities exist for the appearance of the signal at the m/z M $-$ 35 fragment ion (130 $-$ 35 = 95), i.e., either the $ClC(O)S^+$ or the $C(O)SCl^+$ ion. The identification of these processes is not feasible using PEPICO spectroscopy. However, it is likely at this stage to clearly identify a second two-body photodissociation process involving a singly charged mechanism. In effect, the detection of either $ClC(O)S^+$ or $C(O)SCl^+$ fragments in the PEPICO spectra implies that the remaining chlorine atom *must be* a neutral particle. Along with this observation, doubly charged ionization processes are likely to be responsible for the production of Cl^+ ions. These features are in fine agreement with the results derived from the PEPICO spectra obtained at 21.2 eV where no Cl^+ ions were observed. Thus, double but not simple ionization processes originate dissociation channels involving Cl^+ ion production.

When the photon energy is increased, the intensity of the signals at $m/z = 44$ and 60 amu/q decreases. An increment in the $m/z = 30$ peak intensity was observed. These effects, i.e., the diminution of the OCS^+ peak intensity and the increment of the OCS^{2+} ion signal, can be rationalized because the cross-

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

	branching ratios at various m/z values (amu/q)												
photon energy (eV)	12	16	28	30	32	35	44	47	60	63	67	95	130
158.0	9.2	12.5	10.9	1.9	18.5	16.5	5.1	0.41	3.9	4.4	3.9	1.6	0.34
164.5	9.4	11.5	12.7	1.8	24.0	16.7	3.4	0.25	2.7	3.5	3.4	1.1	0.31
165.7	9.4	11.5	12.7	1.8	24.1	16.7	3.2	0.21	2.6	3.7	3.4	1.1	0.31
167.0	9.8	11.1	12.7	2.1	23.3	17.2	3.2	0.21	2.7	3.7	3.4	1.1	0.31
168.3	9.1	10.3	11.3	2.0	21.1	20.6	3.1	0.21	2.6	4.0	3.8	1.2	0.34
173.0	8.6	9.9	11.7	4.9	21.6	21.0	1.9	0.16	1.7	3.9	3.4	0.7	0.21
185.0	8.7	10.1	11.8	4.7	22.0	22.8	1.5	0.10	1.4	3.4	3.0	0.5	0.11
206.7	9.5	11.5	10.8	3.6	19.5	26.3	1.4	0.08	1.3	2.6	2.4	0.3	
255.0	9.3	11.3	9.7	2.0	17.9	30.8	1.2	0.08	1.6	2.0	2.2	0.2	
288.0	11.4	14.3	9.8	2.0	17.2	27.9	1.3		1.5	1.9	1.7	0.16	
305.0	12.3	15.5	9.3	2.3	17.5	27.3	1.1		1.3	1.4	1.5	0.18	

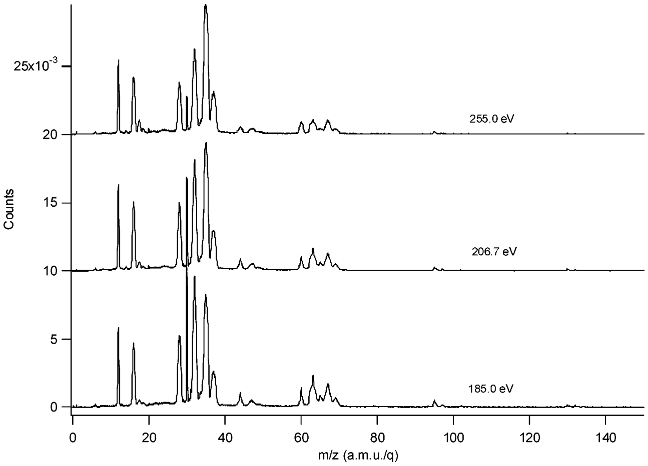


Figure 7. PEPICO spectra of ClC(O)SCl recorded at selected photon energies around Cl 2p edges.

section for the formation of multiply charged ions increases with the incident photon energy.

The molecular ion, M^+, and the $M - 35$ signals vanish when the photon energy reaches the chlorine 2p ionization value. Thus, at this high relative photon energy processes involving singly charged ions are less important than the doubly charged channels opened from a variety of events such as direct double ionization or Auger decays. When the photon energy increases from the S 2p to the Cl 2p regions, a broadening of the peaks is observed, especially of those taken at higher energies. The peak enlargement can be associated with a residual kinetic energy. This fact could be related to the formation of energetic fragments when the photon energy is increased. Another difference observed in the PEPICO spectrum obtained at the resonant 2p Cl photon energy is the enhancement of the Cl^+ ion signal, which accounts for ca. 26% of the relative abundance, becoming the main peak at the Cl 2p resonance (see Figure 7). This effect should be related to the importance of the resonant Auger decay mechanism in the Cl^+ ion production. According to the $Z + 1$ rule, both Cl 2p transitions should lead to dissociative excited states. The lack of resolution for the two Cl 2p transitions in the TIY spectra of ClC(O)SCl (Figure 1) precludes further studies tending to elucidate the nature of the σ^*_{S-Cl} and σ^*_{Cl-C} antibonding orbitals, which are likely to be involved in the detection of the increment of intensity for the Cl^+ signal ion around the Cl 2p region.

Ionic Fragmentation Following C 1s and O 1s Inner-Core Excitations and Ionizations. The PEPICO spectra of ClC(O)SCl around C and O 1s ionization edges are shown in Figure 8. Fragmentation patterns at the C and O K edges seem to be basically identical. The dominant signal ions in the PEPICO spectra were assigned to those generated by Cl^+, S^+, and C^+ ions. Signals around the $m/z = 60$ amu/q region nearly disappear, and the molecular ion cannot be observed. Signals are broad and poorly resolved, which makes the calculation of ion branching useless at these core−electron transitions. The presence of a broad new band is clearly observed at $m/z = 17.5$ amu/q, denoting the formation of the Cl^{2+} doubly charged atomic fragment. Thus, strong atomization processes occur at these high photon energies, which include the formation of multiply charged molecular ions. Moreover, the only nonatomic charged fragment present in the PEPICO spectra at high photon energies belongs to the CO^+ ion. This ion originates a medium-intensity signal at $m/z = 28$ amu/q, and it is even present in the O 1s edge region, indicating the strength of the carbonylic double bond.

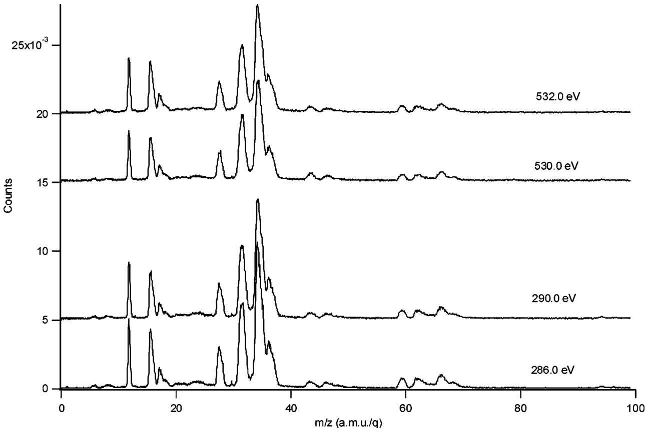


Figure 8. PEPICO spectra of ClC(O)SCl recorded at selected photon energies around C and O 1s edges.

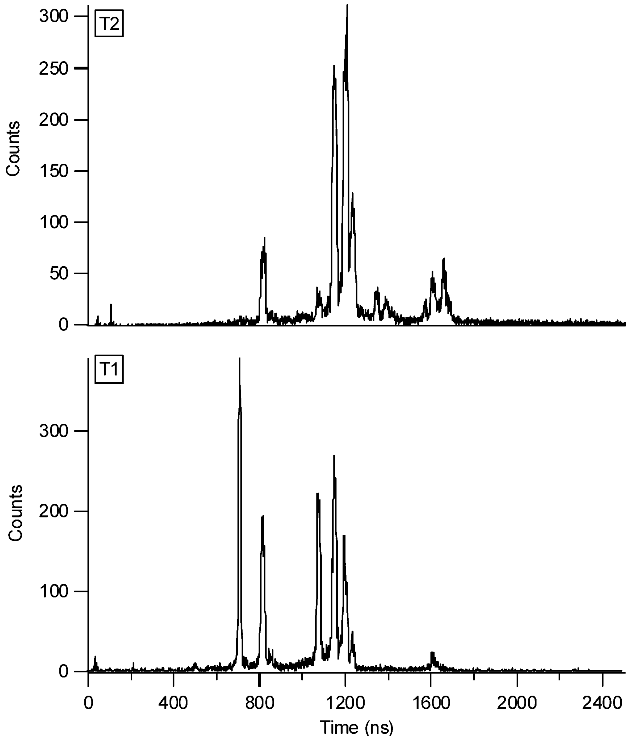


Figure 9. T1 and T2 PEPIPICO projection spectra of ClC(O)SCl recorded at the S 2p resonance (168.3 eV).

PEPIPICO Spectra. It is clear that PEPICO spectra are unable to distinguish between chlorine atoms arising from ionizations involving either Cl−C or S−Cl bond ruptures. Thus, to elucidate dissociation mechanisms in ClC(O)SCl, PEPIPICO spectra at different photon energies can be recorded. PEPIPICO spectra provide some information to elucidate this nonequivalent ionic contribution, especially in the presence of isotopic labeling, such as the natural 35/37 isotopic chlorine occurrences.

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 and O 1s) levels of ClC(O)SCl. Furthermore, projections of PEPIPICO spectra on the T1 and T2 axes were obtained by integrating the signal intensity over the times T2 and T1, respectively, for some selected photon energies. T1 and T2 PEPIPICO projection spectra of ClC(O)SCl, recorded at the main resonance energy of the S 2p transition, are depicted in Figure 9. The heaviest fragments observed in the T2 domain are $ClCO^+$ and SCl^+ that appear as low-intensity signals. Note that in the PEPIPICO spectra no signal is observed for the $(M - 35)^+$ fragment, reconfirming that the peak observed at 95 amu/*q* in the PEPICO spectra must be originated by a single ionization process. Furthermore, plausible two-body fragmentation channels producing both Cl^+ and $ClC(O)S^+$ ions and Cl^+ and $C(O)SCl^+$ ions can be discarded.

Whereas the main fragments in the T1 projection are those related to *m*/*z* values of 12, 16, 28, 32, and 35 amu/*q*, the T2 projection is dominated by ion signals corresponding to *m*/*z* ion ratios of 32 and 35 amu/*q*. Thus, the S^+ and Cl^+ can be formed in different processes where they are both the lightest and the heaviest fragments. The ion $m/z = 28$ (CO^+) gives rise to a high-intensity signal only in the T1 projection. This fact is in fine agreement with a previous finding of nonfragmentation in the C═O double bond. This chemically intuitive assumption is also corroborated by both the PEPICO and the PEPIPICO spectra, since no signal at $m/z = 114$ amu/*q* [$(M - 16)^+$] was detected. Note that the detection of CO^+ in the T2 domain would not have any physical meaning. Clearly, the S^+ and Cl^+ ions are heavier than 28 amu/*q*; therefore, detection of C^+ or O^+ (lighter ions than CO^+) in the T1 domain and CO^+ in the T2 domain is not expected.

However, the appearance of a signal corresponding to $m/z = 16$ amu/*q* in the T2 projection is significant. This fact could be related to the contribution of the O^+ ion formed in a multiple-body dissociation channel (in coincidence with C^+, the only detected fragment lighter than O^+), but it is likely that a contribution of a S^{2+} doubly charged ion—arising from dissociative triple ionizations—gives rise to this signal. The PEPIPICO spectra could contain contributions of multiple-body dissociative triple ionization, where only the two lighter ions can be detected.

Apart from some small increment in the fragmentation process with increasing photon energy, the projection spectra are similar for the whole range of photon energy.

Dissociation Mechanisms. Although the nature of the ions formed after excitation would be the subject 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, $ClC(O)SCl^{2+}$, can be assumed. From the experimental evidence, this ion is unstable on a microsecond time scale and was not observed in the coincidence spectra. Concerning the dynamics of molecular fragmentation of doubly charged species, Eland and Simon have discussed possible fragmentation mechanisms for two-, three-, and four-body decays.[29−31] For a pentaatomic molecule such as ClC(O)SCl, the interpretation of PEPIPICO spectra is pretty difficult. Furthermore, as expected from the PEPICO analyses, atomization processes make the spectra even more complex. As a selected example, the 2D PEPIPICO spectrum at 168.3 eV is presented in Figure 10.

Peaks corresponding to double coincidences involving the lightest masses, especially those related to $m/z = 12$ and 16 amu/*q*, show a high intensity, reflecting the importance of the atomization processes in the dissociation mechanism of ClC(O)SCl. However, their shapes cannot be described by a parallelogram, indicating that more than one specific dissociation decay gives rise to the coincidence. This fact means that the shape is originated from a superposition of parallelograms with different slopes. Furthermore, for coincidences involving an $m/z = 16$ amu/*q* value, the distinction between O^+ and S^{2+} ions is not always feasible. Similar problems were found in the analyses of some islands involving the Cl^+ ion. Islands with high intensity appear at times corresponding to the pair of ion coincidences CO^+/Cl^+ and S^+/Cl^+. The coincidence shapes are distorted parallelograms, without definite contours. Here, different dissociation decays involving the nonequivalent chlorine atoms and a second charged fragment (CO or S) give rise to the same coincidence with different mechanisms. Taking into consideration these limitations in the PEPIPICO analyses, in a first approximation the attention was focused on selected pairs of ions, for which a well-defined shape is observed (only one dissociation mechanism is involved).

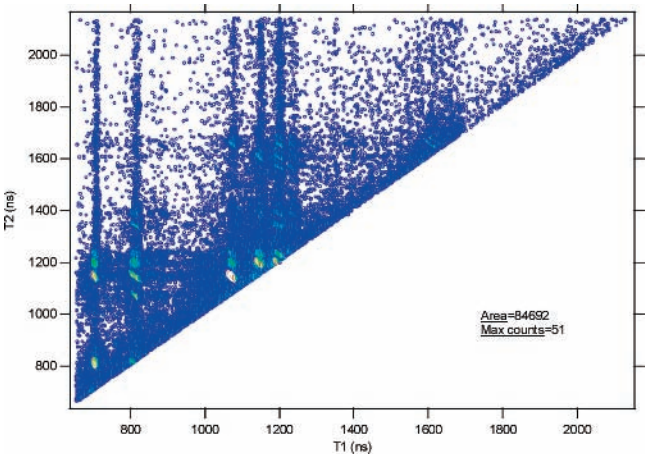


Figure 10. General overview of the PEPIPICO spectrum of ClC(O)SCl obtained at 168.3 eV photon energy.

Two-Body Fragmentations. From different channels expected for the dissociation of $ClC(O)SCl^{2+}$ following a two-body fragmentation, only process 1 is identified in the PEPIPICO spectra as a coincidence island with a characteristic cigar shape having a −1 slope. A low-intensity signal is observed for the T1 and T2 times corresponding to the $ClCO^+/SCl^+$ ion coincidence. The same behavior was found in the PEPIPICO spectra of FC(O)SCl, where the FCO^+ and SCl^+ ions were observed in coincidence following a two-body fragmentation mechanism.

$$ClC(O)SCl^{2+} \rightarrow ClCO^+ + SCl^+ \qquad (1)$$

Three- and Four-Body Fragmentations. A series of coincidences is observed in the PEPIPICO spectra between ions with T1 arrival times corresponding to ions having an *m*/*z* ratio in the range 28−35 amu/*q* (CO^+, S^+, and Cl^+) and those ions with an *m*/*z* ratio in the range 60−67 amu/*q* (OCS^+, $ClCO^+$, and SCl^+). The expected five double coincidences CO^+/SCl^+, $S^+/ClCO^+$, Cl^+/OCS^+, $Cl^+/ClCO^+$, and Cl^+/SCl^+ are observed as low-intensity islands showing a well-defined shape (Figure 11).

(1) Coincidence of $m/z = 28$ amu/*q* (CO^+) with $m/z = 67$ amu/*q* (SCl^+). The observed slope that is close to −1 can be explained by the following DCS mechanism:

$$ClC(O)SCl^{2+} \rightarrow Cl + OCSCl^{2+}\ (U_1) \qquad (2)$$

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

The same mechanism was found for the double coincidence between these ions in FC(O)SCl.

(2) Coincidence of $m/z = 32$ amu/*q* (S^+) and $m/z = 63$ amu/*q* ($ClCO^+$). The experimentally determined slope for this double coincidence is −1.2. Both SD and DCS schemes provide mechanisms that could cause the appearance of this pair of ions in coincidence. However, attempts to fit the observed value with SD mechanisms were unsuccessful (predicted slope −0.51).

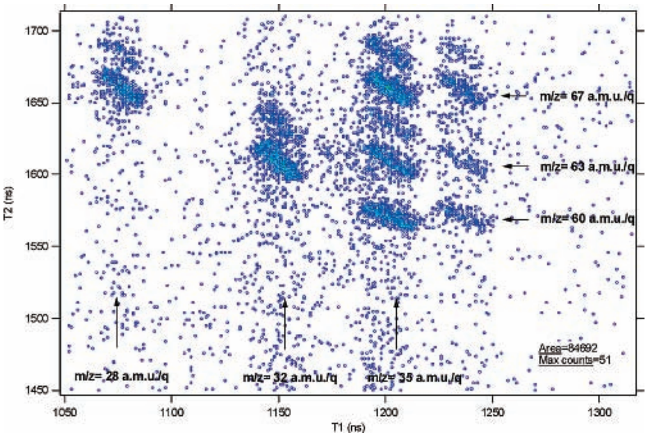


Figure 11. Enlargement of the PEPIPICO spectrum of ClC(O)SCl obtained at 168.3 eV photon energy in the ranges m/z 28−37 and 63−69 amu/q in the T1 and T2 domains, respectively.

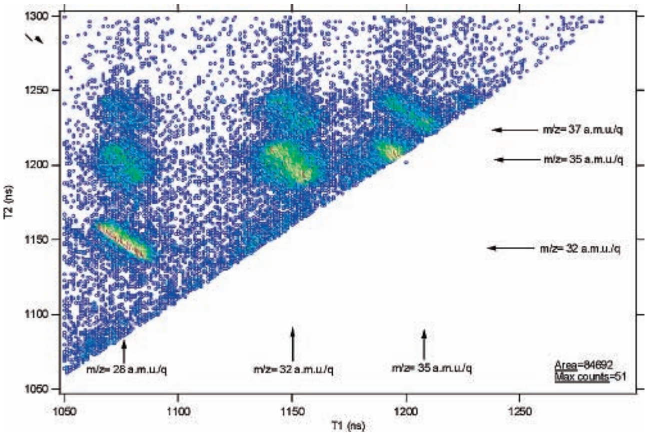


Figure 12. Enlargement of the PEPIPICO spectrum of ClC(O)SCl obtained at 168.3 eV photon energy around the $^{35}Cl^+/^{35}Cl^+$ double coincidence.

Similarly to that described above for the CO^+/SCl^+ double coincidence, the following DCS mechanism predicts a −1 slope:

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

$$ClC(O)S^{2+} \rightarrow ClCO^+ + S^+\ (U_2) \tag{5}$$

(3) Coincidence of $m/z = 35$ amu/q (Cl^+) and $m/z = 60$ amu/q (OCS^+). The experimental slope of −0.6 for this coincidence can be explained by a simple secondary decay with initial charge separation:

$$ClC(O)SCl^{2+} \rightarrow Cl^+ + OCSCl^+ \text{ or } ClC(O)S^+\ (U_1) \tag{6}$$

$$OCSCl^+ \text{ or } ClC(O)S^+ \rightarrow Cl + OCS^+\ (U_2) \tag{7}$$

where U is the energy release. Assuming that $U_1 \gg U_2$, a value of −0.62 can be deduced for the expected slope in the PEPIPICO spectra, in very good agreement with the experimental value. It is observed that the specific bond ruptures that originate the Cl^+ and OCS^+ ions in each step are not unambiguous. However, this coincidence appears in the FC(O)SCl PEPIPICO spectra following a similar SD mechanism. In this case, there are no doubts that the bond rupture exists: in the first step the S−Cl bond is broken. Accordingly, it is likely that $ClC(O)S^+$ rather than $OCSCl^+$ corresponds to the ion formed in the first step.

(4) Coincidence of $m/z = 35$ amu/q (Cl^+) and $m/z = 63$ amu/q ($ClCO^+$) and (5) Coincidence of $m/z = 35$ amu/q (Cl^+) and $m/z = 67$ amu/q (SCl^+). As can be seen in Figure 11, two clear islands are observed for the times corresponding to the arrival of the Cl^+ ion in coincidence with $ClCO^+$ and SCl^+ ions. Although with low intensity, islands produced by analogous coincidences involving ^{37}Cl-substituted ions are clearly observed. The $Cl^+/ClCO^+$ and Cl^+/SCl^+ coincidences appear as parallelograms with similar inclination, having a slope close to −1. Two SD mechanisms could explain the observation of these couples of ions in coincidence, but they are not capable of explaining the experimental slopes. The following concerted dissociation mechanisms can explain the observed ions in coincidence with a −1 slope:

$$ClC(O)SCl^{2+} \rightarrow Cl^+ + CO + SCl^+ \tag{8}$$

$$ClC(O)SCl^{2+} \rightarrow ClCO^+ + S + Cl^+ \tag{9}$$

In these “spectator neutral” instantaneous explosions, the two ionic fragments separate with equal and opposite initial momenta, while the neutral fragment receives no impulse.[29]

As was commented in the Introduction, a new dissociation mechanism recently reported for FC(O)SCl can be consistently described as CS−IR. Such a mechanism was necessarily invoked to explain the observation of double coincidence of F^+/Cl^+ and CO^+/S^+ ion couples with a −1 slope in the PEPIPICO spectra. One of the goals of the present work is to shed some light on the subject. According to the CS−IR mechanism, equivalent pairs of ions in ClC(O)SCl are CO^+/S^+ and Cl^+/Cl^+. The obvious disadvantage with respect to FC(O)SCl is that the ClC(O)SCl PEPIPICO spectra are cut onto the +1 slope, which prevents attempts to completely analyze the Cl^+/Cl^+ coincidence (in Figure 12 the “aborted” half-peak at $^{35}Cl^+/^{35}Cl^+$ times can be noted). However, the TOF resolution attained in the experiments allows resolving the natural occurrence of ^{37}Cl isotopes in PEPIPICO spectra. The study of the coincidence of two Cl^+ ions through the analysis of the $^{35}Cl^+/^{37}Cl^+$ double coincidence appearing as a full coincidence in the PEPIPICO spectra is feasible. It is worth emphasizing the full equivalence in both $^{35}Cl^+/^{35}Cl^+$ and $^{35}Cl^+/^{37}Cl^+$ coincidences. As expected from the natural occurrence of ^{37}Cl, the $^{35}Cl^+/^{37}Cl^+$ coincidence is observed in the PEPIPICO spectra as a low-intensity signal. However, the coincidence slope of −1.1 was calculated. Thus, to explain the manifestation of the Cl^+/Cl^+ double coincidence, the occurrence of a three-body fragmentation process represented by the following steps can be postulated:

$$ClC(O)SCl^{2+} \rightarrow Cl_2^{2+} + COS\ (U_1) \tag{10}$$

$$Cl_2^{2+} \rightarrow Cl^+ + Cl^+\ (U_2) \tag{11}$$

Thus, similarly to the mechanism reported for FC(O)SCl, in a first step, the doubly charged molecular ion experiences a rearrangement to yield a neutral COS molecule, whereas the doubly charged Cl_2^{2+} ion will be subsequently dissociated to give two Cl^+ ions (step 11). Coulombic forces dominate the last process, the U_1 term can be neglected, and the expected figure in the PEPIPICO spectra is a parallelogram of slope −1.

A very definite island is observed for the coincidence between m/z values of 28 and 32 amu/q, and the plot contour for this double coincidence is presented in Figure 13. A −1 orientation of the parallelogram is clearly observed. The coincidence of S^+ and CO^+ ions can be explained by the following processes:

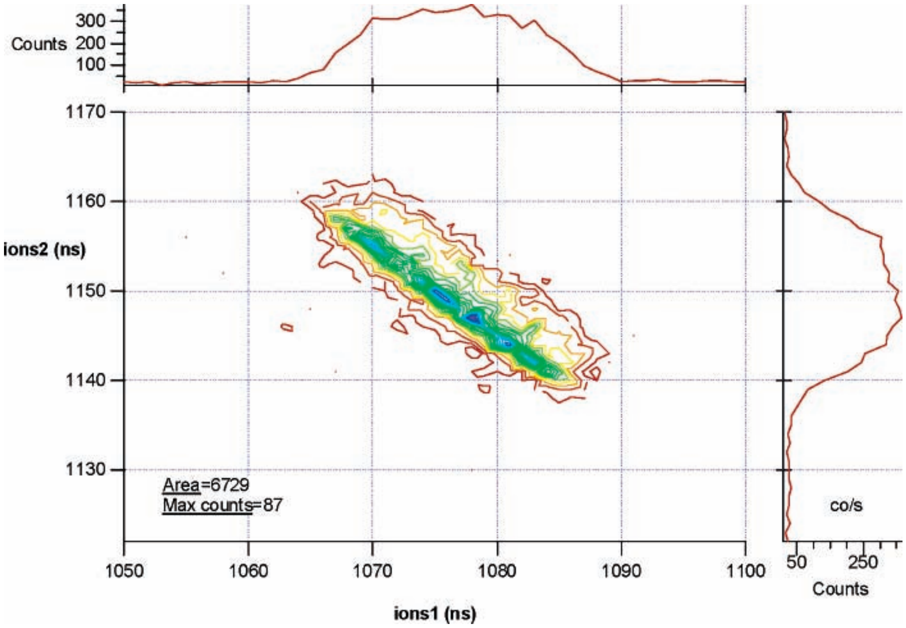


Figure 13. Contour plot derived from the PEPIPICO spectrum of ClC(O)SCl obtained at 168.3 eV for the CO^+/S^+ double coincidence.

$$ClC(O)SCl^{2+} \rightarrow OCS^{2+} + Cl_2\ (U_1) \tag{12}$$

$$OCS^{2+} \rightarrow S^+ + CO^+\ (U_2) \tag{13}$$

Whereas the rearrangement is the same as before, the OCS fragment remains doubly charged. The dominant energy release is evidently U_2, and if U_1 tends to zero, this mechanism is experimentally identical to the simple scheme of two-body fragmentation experimentally reported in OCS.[32,33]

The calculated change in the ClC−SCl dihedral angle from 180° in syn ClC(O)SCl to 83° in $ClC(O)SCl^{2+}$ (almost gauche orientation) seems to support the ion rearrangement. It is known that, when a core-excited state has a stable geometry which is different from that of the neutral ground state, differences in the electronic decay and dissociation dynamics are expected.[34,35]

Highly Charged Molecular Ion. A close examination of PEPIPICO spectra reveals an intense and sharp coincidence at the time-of-flight corresponding to m/z ratios of 16 amu/q for the T1 x-axis and 28 amu/q for the T2 y-axis. Because the latter signal is univocally assigned to the CO^+ ion, it is evident that the coincidence must involve the doubly charged S^{2+} species as the first arriving ion. The high intensity displayed for this double coincidence signal reveals the importance of processes involving a highly charged molecular ion. The high degree of atomization found in both FC(O)SCl and ClC(O)SCl molecules constitutes indirect evidence that reinforces the occurrence of a highly charged ion.

As commented above, the presence of a medium-intensity signal at times corresponding to m/z ratio values of 17.5 amu/q in the K level PEPICO spectra reveals the occurrence of the doubly charged Cl^{2+} ion. Detection of this ion in coincidence with another heavy ion in the PEPIPICO spectra gives rise to double coincidence islands. The manifestation of low-intensity signals involving Cl^{2+}/S^+ and Cl^{2+}/Cl^+ indicates the presence of triply charged ionizations at this high photon energy.

Conclusions

The TIY spectra of shallow-core levels S 2p and Cl 2p and inner-shell levels C 1s and O 1s of ClC(O)SCl in the range 100−1000 eV are obtained by using synchrotron radiation and coincidence detection techniques.

Apart from the intensification of the Cl^+ signal observed at the Cl 2p resonance, branching ratios of the ion production obtained from the PEPICO spectra exhibit only small changes with the incident photon energy. The related FC(O)SCl molecule shows a similar lack of site-specific fragmentation even for excitation at the S 2p, Cl 2p, C 1s, O 1s, and F 1s edges. A similar behavior has been observed by Ibuki et al. in $CH_3OC(O)CN$ upon O 1s and N 1s ionizations.[36] These results can be rationalized supposing that valence electrons in ClC(O)SCl are ionized via Auger decays after inner-shell electron excitations. Due to the planarity of the molecule, the nonbonding n_S, n_O, n_{Cl}, and even the $\pi_{C=O}$ orbitals are strongly delocalized over the entire molecule. Thus, when these delocalized valence electrons are ionized via the Auger decay, the positively charged species lose the memory of the atomic site excited initially.

The analysis of PEPIPICO spectra give results useful to identify several molecular dissociation mechanisms followed by Auger decays. Thus, two-body mechanism dissociation channels, which lead to $ClCO^+$ and SCl^+ fragments, are found. Furthermore, from PEPICO spectra, evidence about two-body dissociation channels of singly charged ClC(O)SCl involving the rupture of a C−S single bond is found.

Three-body mechanisms are also detected. They include DCS schemes (coincidences between CO^+ and SCl^+, and between $ClCO^+$ and S^+), an SD mechanism (double coincidences of Cl^+ and OCS^+), and a CD scheme (Cl^+/SCl^+ and $ClCO^+/Cl^+$). Worthy to be mentioned, evidence is found for the occurrence of the previously proposed three-body dissociation mechanism recognized as CS−IR. This three-body dissociation mechanism is used to explain the double coincidence between the CO^+ and S^+ ions and between the two Cl^+ ions with a slope of −1. Furthermore, the existence of processes leading to atomization can be identified by the observation of atomic species such as carbon and oxygen. Multibody dissociation dynamics should be involved in these processes. In the same direction, the presence of doubly charged Cl^{2+} ions is observed in the K shell excitation PEPICO spectra. Moreover, a triply charged molecular ion should be useful to explain the appearance of S^{2+} and CO^+ ions in coincidence in the PEPIPICO spectra.

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