He I Photoelectron Spectra and Valence Synchrotron Photoionization for XC(O)SCl (X = F, Cl) Compounds

Mariana Geronés,[‡] **Mauricio F. Erben,**[‡] **Rosana M. Romano,**[‡] **and Carlos O. Della Védova*,[‡,§]**

CEQUINOR (CONICET-UNLP), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C. C. 962, 1900 La Plata, República Argentina, and Laboratorio de Servicios a la Industria y al Sistema Científico, LaSeISiC, UNLP-CIC-CONICET, Camino Centenario e/ 505 y 508, 1903 Gonnet, República Argentina

Li Yao and Maofa Ge*

State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, Peoples Republic of China

Received: October 17, 2007; In Final Form: December 12, 2007

Small penta-atomic molecules like FC(O)SCl and ClC(O)SCl have been analyzed by using both photoelectron spectroscopy (PES) and results derived from the use of synchrotron radiation in the same energy range. For this second experiment total ion yield (TIY), photoelectron photoion coincidence (PEPICO), and partial ion yield (PIY) spectra have been recorded. This set of data together with results obtained by computational chemistry allow us to study electronic properties and the ionization channels of both species. Thus, whereas the photodissociation behavior of FC(O)SCl can be divided into three well-defined energy regions, the fragmentation dynamics of ClC(O)SCl seems to be more complex. Nevertheless, simultaneous evaluation of the PES and valence synchrotron photoionization studies helps to clarify the molecular ionization processes.

Introduction

Molecular photoionization and ionic photofragmentation processes are of fundamental importance and find applications in a large number of scientific contexts, including studies in astronomy, astrophysics, and radiation chemistry, physics, and biology.[1] Although for simple molecules quite detailed studies have been carried out by using many experimental techniques,[1–3] little is known for more complex molecules, even medium-size species. Covering this gap, relevant studies have been recently reported for simple biomolecules such as amino acids,[4–10] natural products,[11–13] and organic species.[14–19] Photoionization studies concerning the pentaatomic sulfenylcarbonyl −C(O)S− compounds FC(O)SCl[20,21] and ClC(O)SCl have been also reported recently by our group,[22] by using synchrotron radiation in the range 100–1000 eV, together with PEPICO and PEPI-PICO multicoincidence techniques. Increasing molecular complexity, other representative members of the family, thioacetic acid, CH₃C(O)SH,[23] and CH₃OC(O)SCl,[24] have been also analyzed.

Mainly due to experimental limitations, most of synchrotron-based studies on photodissociation dynamics are concerned with relatively high-energy photons. In effect, it is well-known that synchrotron beamlines operating in the vacuum ultraviolet range suffer from the problem of high-order harmonic contamination. On the other hand, photoelectron spectroscopy (PES) is a well suited technique for the direct measurement of the energy required to remove valence shell electrons from molecules and provide information on the bonding characteristics of orbitals.[25,26]

The recent development of a neon gas filter in the TGM line at the Brazilian Synchrotron National Laboratory (LNLS), which affords "pure" synchrotron radiation in the 12.0–21.5 eV range, allows us to expand the study of the photoionization process in the valence region. The complement between both PES and multicoincidence time-of-flight (TOF)-based techniques seems to be promising for a deeper understanding of the processes involving a photon absorption by a molecule followed an electronic excitation and eventually by a subsequent ionic dissociation. Here, continuing our work on −SC(O)− species, two simple five-atom FC(O)SCl and ClC(O)SCl molecules have been selected. Photoelectron (PES) for ClC(O)SCl and photoelectron photoion coincidence (PEPICO) spectra for the title molecules using synchrotron radiation in the valence region have been measured. Electronic properties and ionization channels have been studied by comparing experimental results and quantum chemically computed properties.

Relevant previous studies have been reported for both species selected here. The molecular structure of ClC(O)SCl has been experimentally reported by Shen and Hagen.[27] From a gas electron diffraction study, it is known that the ClC(O)SCl molecule 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. The observed features in the vibrational spectra [IR (gas) and Raman (liquid)] and quantum chemical calculations[28] support a planar structure for the molecule, with syn conformation. Recent matrix infrared spectroscopy experiences are in agreement with these former results. Thus, the predominance of the syn conformer in both gas and crystal phases have been reconfirmed.[29] Furthermore, the photochemistry of ClC(O)SCl isolated in solid Ar or N₂ matrixes at 15 K has been investigated and several photodis-

---

[‡] Universidad Nacional de La Plata.
[§] UNLP-CIC-CONICET.

Spectra and Photoionization for (F or Cl)C(O)SCl

J. Phys. Chem. A, Vol. 112, No. 11, 2008 **2229**

sociation channels were elucidated, including the finding of low amounts of *anti*-ClC(O)SCl after convenient irradiation times.[30] Recently, these mechanisms were further studied through the computed potential energy surface of the electronic excited states of ClC(O)SCl at the CASSCF and MR-CI methods with the cc-pVDZ basis set.[31]

Fluorocarbonylsulfenyl chloride, FC(O)SCl, was one of the first compounds investigated in this context. Gas electron diffraction,[32] vibrational analysis,[33] and ab initio calculations[34] demonstrate that this molecule exists as a mixture of two planar conformers with the syn form (C=O bond syn with respect to the S−Cl bond) being lower in energy than the anti conformation, with $\Delta G° = G°_{anti} - G°_{syn}$ values being 1.2(3) (gas electron diffraction) and 1.4 kcal mol^{-1} (infrared spectroscopy). The study of the He I photoelectron spectrum (PES) of FC(O)SCl has been recently reported.[35] A wide electronic delocalization in the whole planar FC(O)SCl molecule has been determined.

Experimental Section

Synchrotron radiation from the Brazilian Synchrotron Light Source (LNLS) was used.[36] Linearly polarized light monochromatized by a toroidal grating monochromator (available at the TGM beam line in the range 12−310 eV)[37] 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 5×10^{-6} mbar. The intensity of the emergent beam was recorded by a light-sensitive diode. The photon energy resolution, from 12.0 to 21.5 eV, is given by $E/\Delta E = 550$. 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 PEPICO measurements. This instrument was constructed at the Institute of Physics, Brasilia University, Brasilia, Brazil.[38] 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. High-purity vacuum ultraviolet photons were used, the problem of high-order harmonics contamination being suppressed by the innovative gas-phase harmonic filter recently installed at the TGM beam line at the LNLS.[39,40]

The PE spectrum of ClC(O)SCl was recorded on a double-chamber UPS-II machine that was built specifically to detect transient species at a resolution of about 30 meV, as indicated by the Ar^{+}(^{2}P$_{3/2}$) photoelectron band.[41−47] Experimental vertical ionization energies (I_v in eV) are calibrated by simultaneous addition of a small amount of argon and methyl iodide to the sample.

OVGF[48] calculations using the extended aug-ccpVTZ basis set and B3LYP/aug-cc-pVTZ optimized geometry of the syn conformers have been performed on the FC(O)SCl and ClC-(O)SCl ground state using the Gaussian 03 program package.[49] The energy of the dissociation of the FC(O)SCl^{+} and ClC(O)-SCl^{+} parent ions into possible fragments were calculated at the UB3LYP/6-311+G* level of approximation.

The sample of chlorocarbonylsulfenyl chloride, ClC(O)SCl, was obtained from commercial sources (Aldrich, 95%). FC-(O)SCl was prepared by the reaction between ClC(O)SCl (Aldrich, 95%) and SbF$_3$ in the presence of SbCl$_5$ as catalyst.[50,51] The liquid products were purified by fractional distillation and subsequently purified several times by fractional condensation at reduced pressure to eliminate volatile impurities. The final
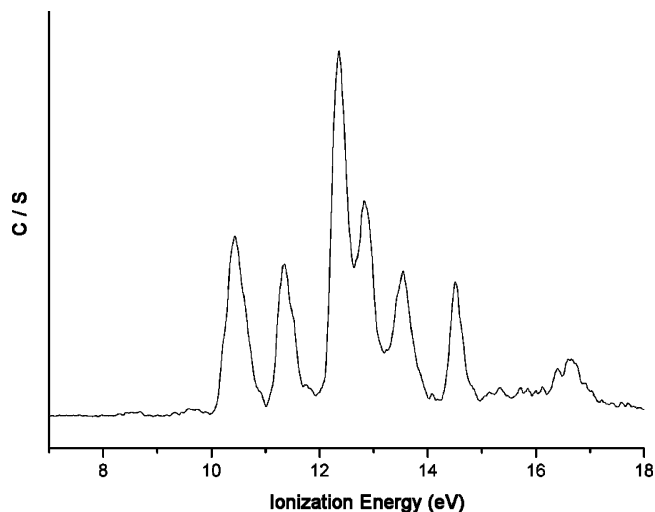

Figure 1. He I photoelectron spectrum of ClC(O)SCl.

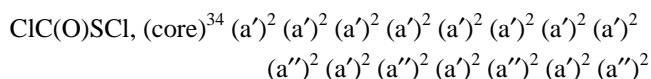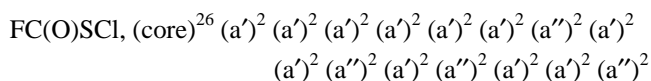**TABLE 1: Experimental and Calculated Ionization Energies (eV) and MO Characters for ClC(O)SCl**

PES	TIY	calcd^a	MO	symmetry	characters
10.36		10.10	(32)	a″	n$_\pi$S
11.32	12.1	10.90	(31)	a′	n$_\sigma$O
12.34	12.8	11.79	(30)	a″	n$_\pi$Cl$_{Cl(C=O)}$
	12.9	12.05	(29)	a′	n$_\sigma$Cl$_{Cl(C=O)}$
12.83	13.2	12.13	(28)	a″	n$_\pi$Cl$_{S-Cl}$
13.52	13.9	12.80	(27)	a′	n$_\sigma$Cl$_{S-Cl}$
	14.3				
14.51	14.7	14.08	(26)	a″	$\pi_{C=O}$
16.38	15.1	15.42	(25)	a′	σ_{S-Cl}
	15.5				
	16.2	15.97	(24)	a′	n$_\sigma$S
16.64	16.4	16.54	(23)		σ_{C-S}

^{a} Calculated values at the ROVGF/aug-cc-pVTZ level of approximation with B3LYP/aug-cc-pVTZ optimized geometries.

purity of the compounds in both vapor and liquid phases were carefully checked by IR (vapor), Raman (liquid), and ^{19}F and ^{13}C NMR spectroscopy.[28,33]

Results and Discussion

In the electronic ground state, both FC(O)SCl and ClC(O)-SCl belong to the C_s point group. In a molecular orbital representation of their most stable syn conformation, the leading electronic configurations are

FC(O)SCl, (core)^{26} (a′)^2 (a′)^2 (a′)^2 (a′)^2 (a′)^2 (a′)^2 (a″)^2 (a′)^2
(a′)^2 (a″)^2 (a′)^2 (a″)^2 (a′)^2 (a′)^2 (a″)^2

ClC(O)SCl, (core)^{34} (a′)^2 (a′)^2 (a′)^2 (a′)^2 (a′)^2 (a′)^2 (a′)^2 (a′)^2
(a″)^2 (a′)^2 (a″)^2 (a′)^2 (a″)^2 (a′)^2 (a″)^2

All canonical molecular orbitals of the type a′ are σ-orbitals (in-plane) and a″ are π-orbitals. In the ground state of both molecules, the 30 valence electrons are arranged in 15 double-occupied orbitals in the independent particle description. The photoelectron spectra as well as the dissociative photoionization and the photoion branching ratios of XC(O)SCl (X = F, Cl) are conveniently discussed with reference to this ground state electronic configuration.

Photoelectron Spectra. The He I PE spectrum of ClC(O)-SCl is depicted in Figure 1. The experimentally determined and theoretical ionization energies are listed in Table 1. Assignments were made with reference to the results of the OVGF/aug-cc-
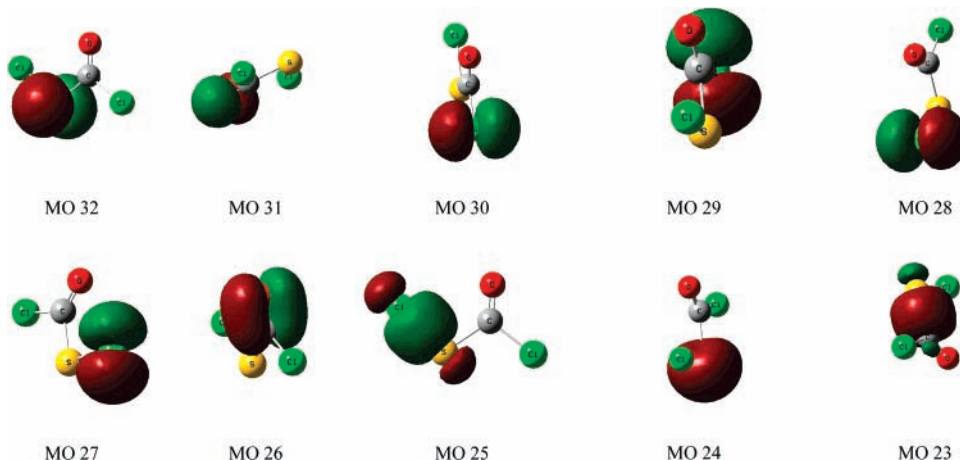
Figure 2. Schematic representation of the ten highest occupied molecular orbitals of ClC(O)SCl. The trend following Table 1 is from MO32 (n_πS) to MO23 (σ_{C-S}).

pVTZ calculations (optimized geometry for the syn conformer at the B3LYP/aug-cc-pVTZ level of approximation). In the low ionization region ($E < 14$ eV) there are five bands with no obvious vibrational structure. From the calculated orbital characters shown in Table 1 and Figure 2 it can be easily concluded that all five bands originate from the removal of nonbonded electrons on the sulfur, oxygen, or chlorine atom. Thus, the first ionization band appears in the spectrum of ClC(O)SCl at 10.36 eV and can be assigned with confidence to the ionization process from the HOMO, an out-of-plane n_πS orbital, which can be visualized as a lone pair nominally located on the sulfur atom. Vertical ionization values for $-$SC(O)$-$ related species, such as CH$_3$C(O)SH,[52] FC(O)SSCH$_3$,[53] and FC(O)-SCl,[35] are 10.0, 9.0, and 10.7 eV, respectively. The second ionization potential observed at 11.32 eV is assigned to the ionization process of an electron ejected from the n_σO orbital in the Koopman approximation. The following band in the PES of ClC(O)SCl at 12.34 eV is associated with ionization processes involving mainly the chlorine atom in the chlorocarbonyl group [$-$C(O)Cl]; calculated ionization values for n_π and n_σ orbitals are 11.79 and 12.05 eV, respectively. Similarly, the following two bands observed at 12.83 and 13.52 eV are assigned to the ionizations involving n_π and n_σ lone pair orbitals, respectively, mainly located at the chlorine atom in the S$-$Cl group. The 14.51 eV feature in the PES is related to an ionization process from the π orbital in the carbonyl double bond, the 16.38 eV to the σ_{S-Cl} bond, and the 16.64 eV to the σ_{C-S} orbital.

Photoionization Processes. For absorptions above the ionization thresholds, the quantum yield for molecular ionizations is quite likely tending to unity; i.e., for each photon absorbed, an ion is produced. 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 of the absorption spectroscopy.[54] Thus, an increase in the total ion production is expected every time the incident energy exceeds a particular ionization potential (PES conditions); the magnitude of the increment will depend upon the cross section of the particular ionic state. On the other hand, it is well-known that a valence ionic state even outside the ground state's Franck Condon region can be resonantly populated using tunable synchrotron radiation throughout a transition from the ground electronic state to a neutral state followed by a subsequent auto ionization process. Thus, comparable but not identical transition energies are expected by comparing PES and TIY spectra. Moreover, the yield of each of the different formed ions (partial

ion yield spectra) serves to infer information about dissociation channels related with particular ionic states.

Total ion yield spectra for FC(O)SCl and ClC(O)SCl in the valence photon energy range are shown in Figures 3 and 4, respectively. The spectrum of FC(O)SCl shows a well-defined band at 12.10 eV followed by an increase in the intensity of the ionic production with the photon energy, with a pronounced step near 13 eV. A group of well-defined bands superimpose this background. The position of the maxima of these bands coincides rather well with the ionization threshold observed in the PES.[35]

The first band in the TIY spectrum of FC(O)SCl at 12.10 eV agrees well with the ionization energy for the n'(O) in plane orbital. Above the step enhancement near 13 eV, a weak feature is defined at 13.26 eV, associated with the 12.9 eV ionization reported in the PES [n'(Cl)].[35] At higher photon energies, a group of three bands are clearly observed, a very well-defined peak at 13.84 and two others at 14.28 and 14.83 eV, which parallel the set of bands in the PES at 13.7 [n''(Cl)], 14.5 [n'-(S)], and 14.9 π^-(FCO) (πC=O) eV, respectively. Near 15.4 eV a diffuse and weak signal is defined, which coincides with the band assigned to the ionization of fluorine in-plane lone pair [n'(F)].

The TIY spectrum of ClC(O)SCl is quite similar (Table 1) to that of FC(O)SCl and shows a sharp peak at the same value of 12.10 eV, which can be associated with the same process as in FC(O)SCl. The band near 12.8 and the well-defined bands near 13.2, 13.9, and 14.3 eV of the TIY spectrum are related to photoelectron bands near 12.3, 12.8, and 13.5 eV in the PES of ClC(O)SCl. The 14.7 eV transition observed in the TIY spectrum is assigned to the ionization related with the $\pi_{C=O}$ orbital in a similar way as its counterpart in the PES spectrum about 14.5 eV.

A series of bands are well-defined in the TIY spectrum of ClC(O)SCl above 15 eV. These inner valence transitions are poorly resolved in the PES and are related with bonded electrons, such as σ_{S-Cl} and σ_{C-S} for the 15.5 and 16.4 eV signals of the TIY spectrum, respectively.

PEPICO and PIY Spectra. The quantum chemically estimated double ionization threshold at the UMP2/6-31+G* level of approximation for FC(O)SCl and ClC(O)SCl are computed at 27.2 and 25.7 eV, respectively.[20,22] Thus, no contribution of double ionization processes is expected in the range of energy used.

The PEPICO spectra obtained at selected photon energies together with a fragment assignment of the bands are shown in
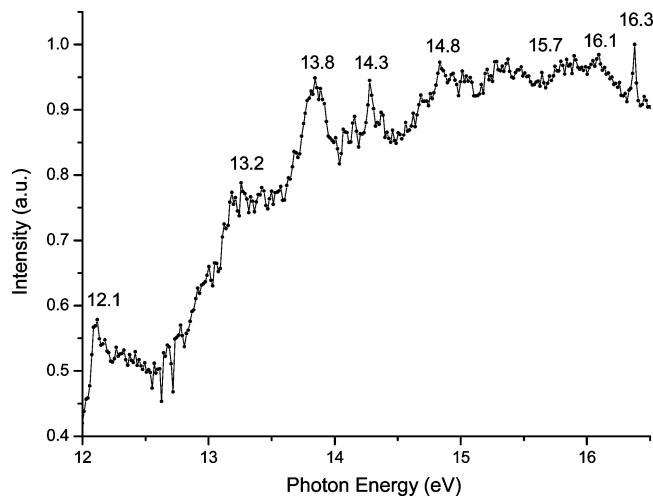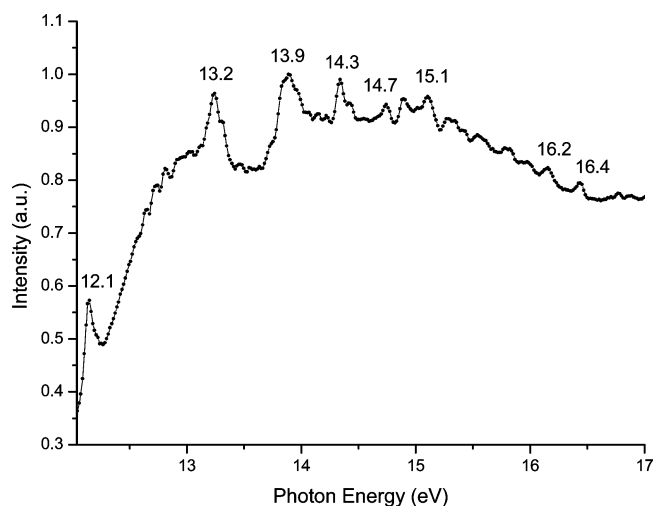
Figure 3. Total ion yield spectrum of FC(O)SCl.

Figure 4. Total ion yield spectrum of ClC(O)SCl.

Figure 5. Photoelectron photoion coincidence spectra of FC(O)SCl at selected irradiation energies.

Figure 6. Photoelectron photoion coincidence spectra of ClC(O)SCl at selected irradiation energies.

Figures 5 and 6 for FC(O)SCl and ClC(O)SCl, respectively. Naturally occurring isotopomer fragments, due to the presence of ^{35}Cl and ^{37}Cl isotopes are clearly observed. This splitting assists the assignment of the ion fragments appearing in the coincidence spectra.

FC(O)SCl. The lowest energy delivered by the TGM beam line at the LNLS (12.0 eV) is higher than the first ionization potentials of both FC(O)SCl and ClC(O)SCl molecules. Therefore, the ionization processes can be already observed at the very first stage of the experiments. Thus, for FC(O)SCl irradiated with 12.0 eV photons, the molecular ion is clearly observed with the natural occurring isotopomeric ratio at m/z = 114 and 116 amu/q for the ^{35}Cl and ^{37}Cl isotopomers, respectively.

A second signal at m/z = 60 amu/q is also evident, denoting the presence of the OCS$^+$ ion. Whether the presence of OCS$^+$ is either due to an intrinsic process occurring in the molecule or is originated by decomposition or chemical byproducts formed in the synthesis is a question that shall be discussed. The very first chemical argument to explain that the OCS$^+$ signal derives from processes occurring in the FC(O)SCl molecule is that no evidence of the formation of ClF$^+$ is observed at 54 amu/q. To evaluate the second option, electronic properties and possible ionization processes of OCS have been analyzed in the valence region. The normal He I,[55] the threshold photoelectron,[56] and photoionization resonance[57] spectra for OCS have been reported and the ionic states well assigned. The OCS ionic

ground state X^{2}Π band extends from near 11.2 to about 12.0 eV. The following ionic state, Ã^{2}Π, located at about 15.1 eV is characterized by a very long and irregular band that extends over the B^{2}Σ$^+$ band. The second excited ionic state B^{2}Σ$^+$ is observed as the most intense photoelectron band near 16.0 eV. Moreover, it is well established that the OCS$^+$ first dissociation limits to yield S$^+$ (^{4}Su) + CO (X^{1}Σ$^+$) is observed in the region of 13.5 eV, in the Franck–Condon gap region between Ã and X.[58] Photoelectron photoion coincidence measurements have shown that for vibrational excited Ã^{2}Π states the predissociation is complete.[59,60] In competition with the predissociation, the autoionizing Rydberg levels are excited in the same gap.[61] The O(^{3}Pg) + CS$^+$ (X^{2}Σ$^+$) dissociation is reached at much higher energies, above 18 eV.

No clear evidence of this set of transitions is observed in the TIY spectra, with the exception of the sharp feature near 16.4 eV, which might in principle be assigned to the second excited ionic state B^{2}Σ$^+$ of OCS. As discussed, this transition corresponds to the most intense band in the PES of OCS. Therefore, a thorough analysis of the TIY spectra reveals that the amount of OCS that might either be originated as a decomposition product during the measurement or be derived as a byproduct of the chemical synthesis is not significant.

When the photon energy reaches a value near 13.3 eV, other ionization channels becomes accessible, as observed by the relative simultaneous diminution of the molecular ion intensity and the consequent formation of the FCO$^+$ ion as a new and dominant fragment besides the presence of minor quantities of

Figure 7. Partial ion yield spectrum for selected ions of FC(O)SCl in the valence photon energy range.

Figure 8. Theoretical energy profiles for FC(O)SCl.

Figure 9. Partial ion yield spectrum for selected ions of ClC(O)SCl in the valence photon energy range.

OCS^+ and S^+. Less intense signals located at 63 and 67 amu/q are assigned to the $COCl^+$ and SCl^+ fragments, respectively. At photon energy values near 13.8 and 16.4 eV, ionization channels for the production of CS^+ ($m/z = 44$ amu/q) and CO^+ ($m/z = 28$ amu/q) ions, respectively, from ionized states of FC-(O)SCl are formed.

More detailed information about the ion branched productions can be achieved form the partial ion yield spectra for selected ions showed in Figure 7. These spectra were normalized by the photon flux. It should be noted that the production of fragment ions may or may not exactly coincide with the ionization energy identified in the PES. Indeed, if the ionic state has a dissociation channel leading directly to the production of the observed fragment ions, identical values must be observed. However, for ionic XC(O)SCl molecules (X = F, Cl) the bound states produced in the low vibrational states within the Franck—Condon region will lead to the formation of the molecular ion. When the value of the photon energy is increased, higher vibrational states can be populated, which could then predissociate or dissociate, leading to the ionic fragments.

The first ionization potential of FC(O)SCl is reached at 10.7 eV. The high production of the molecular ion observed in the PIY spectrum below 12.5 eV seems to indicate that the low-lying (10.7 eV) and the first excited (12.1 eV) ionic states are mainly bounded and, after ionization, $FC(O)SCl^+$ is produced. The monotonic decrease of the PIY signal of the parent ion indicates that higher ionic states have dissociative character.

It becomes also apparent that at about 12.10 eV the OCS^+ fragment is predominantly formed. The possibility of a deeper study of the characteristics linked with the corresponding ionic state, formally created by removing an electron from the n′(O), is beyond our current results. As a first approximation, quantum chemical calculations were performed to estimate the energetic of the $OCS^+(X^2\Pi) + FCl$ dissociation channel. Moreover, in Figure 8, a schematic energy profile for the direct dissociation of C—S, S—Cl, and F—C bonds from the parent $FC(O)SCl^{\bullet+}$ species are shown. A qualitative agreement is observed between this diagram and the ion productions observed in the PEPICO spectra of FC(O)SCl. For example, FCO^+ is first observed in the 13.3 eV PEPICO spectrum and represents the most intense ion signal for higher photon energies. This ion is formed in the energetically most favored C—S bond rupture from $FC(O)SCl^{\bullet+}$. Dissociation channels leading to the formation of OCS^+ are also energetically favored, possibly by direct rearrangement process from the parent ion as well as by the subsequent dissociation of $FCOS^+$ or $COCl^+$ ions. The lack of halogen ion signals in

the PEPICO spectra can be related to the fact that dissociation pathways leading to the formation of atomic F^+ and Cl^+ ions are energetically disadvantaged.

The PIY spectrum of CS^+ (Figure 7) shows a clear threshold at 13.6 eV, and irradiation of FC(O)SCl with photons of increasing energy ($E > 16$ eV) leads to the formation of the CO^+ ion. Signals at mass to charge ratios of 51 and 63 amu/q appear in the PEPICO spectra at photon energies above 14.0 eV. These peaks originated by the SF^+ and $COCl^+$ ions, respectively, may be fragments originated in rearrangement process.

ClC(O)SCl. For ClC(O)SCl, the PEPICO spectrum obtained near 12.1 eV close to the lowest proton energy available at the LNLS (12.0 eV) shows the presence of signals corresponding to the molecular ion (130 amu/q) and to $COSCl^+$ (95 amu/q), $COCl^+$ (63 amu/q), and OCS^+ (60 amu/q) fragments. Again, a major contribution of the OCS^+ ion is observed. As shown in Figure 6, an increment of the photon energy has a minor impact in the PEPICO spectra. At 13.2 eV, the ionization channel for the formation of SCl^+ (67 amu/q) is opened. A low intense band assigned to the Cl^+ fragment is also present, which increases its intensity at 13.9 eV.

One of the most intense ion signals present in the PEPICO spectra of ClC(O)SCl, at $m/z = 95$ amu/q, is due to the loss of a chlorine atom from the parent molecular ion ($M^+ - 35$). This ion can originate from the rupture of either the C—Cl or the S—Cl single bonds of ClC(O)SCl. Figure 9 shows the PIY for ClC(O)SCl.

Spectra and Photoionization for (F or Cl)C(O)SCl

J. Phys. Chem. A, Vol. 112, No. 11, 2008 **2233**

Figure 10. Theoretical energy profiles for ClC(O)SCl.

As mentioned before, quantum chemical calculations were performed to estimate the energetic of different pathways from ionic dissociation of the parent ion. A schematic representation is given in Figure 10. Concerning the C−S rupture, quantum chemical calculations predict the $ClCO^+ + SCl^\bullet$ channel favored against the $ClCO^\bullet + SCl^+$. This is in accordance with the observed behavior in the PEPICO spectra, where $ClCO^+$ appears at lower energies, but much higher energies are needed to form the SCl^+ ion. The extrution of the $Cl^\bullet$ atom from $ClC(O)SCl^+$ can produce both $COSCl^+$ and $ClCOS^+$ ions ($m/z = 95$), the latter being calculated to be energetically favored. Similar bond ruptures leading to the formation of charged chlorine atoms are thermodynamically disadvantaged, especially the $Cl^+ + COSCl^\bullet$ channel. Finally, similar to the behavior found for FC(O)SCl, the formation of the OCS^+ ion is expected to be present in photodissociation of valence excited ClC(O)SCl.

Conclusions

The simultaneous evaluation of the results from both PES and valence photoelectron ionization helps to clarify basic processes occurring when the ionization of a molecule from its ground electronic state occurs. The nature of both events can be well established by direct comparison of the two different processes. Moreover, such a combination would be necessary to give confidence to the interpretation of this kind of result. The preference of different dissociation channels with the incident radiation was explained in terms of the calculated relative stability of the possible ionic and neutral fragments.

The photodissociation behavior of FC(O)SCl can be rationalized by dividing the photon energy range (12.0−21.5 eV) in three regions clearly observed in the Figure 5, depending on the ions formed by the photonic impact. Thus, it is possible to identificate a low-energy region between 12.0 and 13.3 eV where only the OCS^+ and M^+ ions are formed, mainly associated with the ejection of electrons from the outermost orbitals. A second region comprises the 13.3−14.8 eV range, where the molecular ionization produces FCO^+ as the predominant species and other ionization channels are opened, originating, for instance, SCl^+, $COCl^+$, and S^+ ions. Finally, the more energetic region, at photon energies higher than 14.8 eV, is characterized by the formation of several ionic fragments, including those computed to be energetically less favored, like Cl^+ and SF^+ ions, the latter originated in a rearrangement process. The ionization of innermost valence electrons, including

bonding electrons, and the formation of excited ionic states should be responsible for the greater extent of the $FC(O)SCl^+$ fragmentation and the concomitant formation of such ions.

The fragmentation dynamic of ClC(O)SCl seems to be complex, as observed in Figure 6. In effect, the incidence of low-energy photons causes the ionization of the molecule and, together with the molecular ion, a series of fragmentation channels are opened, mainly leading to the formation of OCS^+, $COCl^+$, SCl^+, and $COSCl^+$ ions. The branching ratios for each of these channels change by increasing the photon energy. The formation of SCl_2^+, a rearrangement fragment, is also observed in concordance with the photochemically induced transformation of ClC(O)SCl isolated in a matrix.[30] Finally, the arguments for the formation of the OCS^+ rest in internal processes occurring both in FC(O)SCl and in ClC(O)SCl.

References and Notes

(1) Gallagher, J. W.; Brion, C. E.; Samson, J. A. R.; Langhoff, P. W. *J. Phys. Chem. Ref. Data* **1988**, *17*, 9−153.

(2) Feng, R.; Cooper, G.; Sakai, Y.; Brion, C. E. *Chem. Phys.* **2000**, *255*, 353−368.

(3) Masuoka, T.; Chung, Y.; Lee, E.-M.; Samson, J. A. R. *J. Chem. Phys.* **1998**, *109*, 2246−2253.

(4) Plekan, O.; Feyer, V.; Richter, R.; Coreno, M.; de Simone, M.; Prince, K. C. *Chem. Phys.* **2007**, *334*, 53−63.

(5) Plekan, O.; Feyer, V.; Richter, R.; Coreno, M.; de Simone, M. K.; Prince, C.; Carravetta, V. *J. Electron Spectrosc. Relat. Phenom.* **2007**, *155*, 47−53.

(6) Marinho, R. R. T.; Lago, A. F.; Homem, M. G. P.; Coutinho, L. H.; de Souza, G. G. B.; Naves de Brito, A. *Chem. Phys.* **2006**, *324*, 420−424.

(7) Kaznacheyev, A. O. K.; Jacobsen, C. *J. Phys. Chem. A* **2002**, *106*, 3153−3168.

(8) Gordon, M. L.; Cooper, G.; Morin, C.; Araki, T.; Turci, C. C.; Kaznatcheev, K.; Hitchcock, A. P. *J. Phys. Chem. A* **2003**, *107*, 6144−6159.

(9) Morita, M.; Mori, M.; Sunami, T.; Yoshida, H.; Hiraya, A. *Chem. Phys. Lett.* **2006**, *417*, 246−250.

(10) Cooper, G.; Gordon, M.; Tulumello, D.; Turci, C.; Kaznatcheev, K.; Hitchcock, A. P. *J. Electron Spectrosc. Related Phenom.* **2004**, *137−140*, 795−799.

(11) Nahon, L.; Garcia, G. A.; Harding, C. J.; Mikajlo, E.; Powis, I. *J. Chem. Phys.* **2006**, *125*, 114309.

(12) de Castilho, R. B.; Nunez, C. V.; Coutinho, L. H.; Lago, A. F.; Bernini, R. B.; de Souza, G. G. B. *J. Electron Spectrosc. Related Phenom.* **2007**, *155*, 77−80.

(13) Brophy, J. J. Maccoll, A. *Org. Mass Spectrom.* **1992**, *27*, 1042−1051.

(14) Ibuki, T.; Okada, K.; Gejo, T.; Saito, K. *J. Electron Spectrosc. Relat. Phenom.* **1999**, *101−103*, 149−154.

(15) Ibuki, T.; Okada, K.; Saito, K.; Gejo, T. *J. Electron Spectrosc. Relat. Phenom.* **2000**, *107*, 39−47.

(16) Okada, K.; Tanimoto, S.; Morita, T.; Saito, K.; Ibuki, T.; Gejo, T. *J. Phys. Chem. A* **2003**, *107*, 8444−8448.

(17) Nagaoka, S.-i.; Fujibuchi, T.; Ohshita, J.; Ishikawa, M.; Koyano, I. *Int. J. Mass Spectrom. Ion. Processes* **1997**, *171*, 95−103.

(18) Nagaoka, S.; Prumper, G.; Fukuzawa, H.; Hino, M.; Takemoto, M.; Tamenori, Y.; Harries, J.; Suzuki, I. H.; Takahashi, O.; Okada, K.; Tabayashi, K.; Liu, X.-J.; Lischke, T.; Ueda, K. *Phys. Rev. A* **2007**, *75*, 020502.

(19) Nagaoka, S.; Tamenori, Y.; Hino, M.; Kakiuchi, T.; Ohshita, J.; Okada, K.; Ibuki, T.; Suzuki, I. H. *Chem. Phys. Lett.* **2005**, *412*, 459−463.

(20) Erben, M. F.; Romano, R. M.; Della Védova, C. O. *J. Phys. Chem. A* **2004**, *108*, 3938−3946.

(21) Geronés, M.; Erben, M. F.; Romano, R. M.; Della Védova, C. O. *J. Electron Spectrosc. Relat. Phenom.* **2007**, *155*, 64−69.

(22) Erben, M. F.; Romano, R. M.; Della Védova, C. O. *J. Phys. Chem. A* **2005**, *109*, 304−313.

(23) Erben, M. F.; Geronés, M.; Romano, R. M.; Della Védova, C. O. *J. Phys. Chem. A* **2006**, *110*, 875−883.

(24) Erben, M. F.; Geronés, M.; Romano, R. M.; Della Védova, C. O. *J. Phys. Chem. A* **2007**, *111*, 8062−8071.

(25) Baker, A. D.; Brundle, C. R. In *Electron Spectroscopy: Theory and Applications*; Brundle, C. R., Baker, A. D., Eds.; Academic Press: 1977; Vol. 1, pp 1−73.

(26) Baker, A. D. *Acc. Chem. Res.* **1970**, *3*, 17−25.

(27) Shen, Q.; Krisak, R.; Hagen, K. *J. Mol. Struct.* **1995**, *346*, 13−19.

(28) Della Védova, C. O.; Cutín, E. H.; Varetti, E. L.; Aymonino, P. J. *Can. J. Spectrosc.* **1984**, *29*, 69−74.

(29) Romano, R. M.; Della Védova, C. O.; Downs, A. J.; Parson, S.; Smith, C. *New J. Chem.* **2003**, *27*, 514−519.

(30) Romano, R. M.; Della Védova, C. O.; Downs, A. J. *J. Phys. Chem. A* **2004**, *108*, 7179−7187.

(31) Lin, L.; Ding, W.-J.; Fang, W.-H.; Liu, R.-Z. *J. Phys. Chem. A* **2006**, *110*, 8744−8749.

(32) Mack, H.-G.; Oberhammer, H.; Della Védova, C. O. *J. Phys. Chem.* **1991**, *95*, 4238−4241.

(33) Della Védova, C. O.; Jubert, A.; Piro, O. E.; Varetti, E. L.; Aymonino, P. J. *J. Fluorine Chem.* **1982**, *21*, 90.

(34) Jubert, A. H.; Della Védova, C. O.; Aymonino, P. J. *Croat. Chem. Acta* **1987**, *60*, 207−213.

(35) Erben, M. F.; Della Védova, C. O. *Inorg. Chem.* **2002**, *41*, 3740−3748.

(36) 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. *European Particle Accelerator Conference*, *EPAC*; Estocolmo: 1998.

(37) de Fonseca, P. T.; Pacheco, J. G.; Samogin, E.; de Castro, A. R. B. *Rev. Sci. Instrum.* **1992**, *63*, 1256−1259.

(38) Naves de Brito, A.; Feifel, R.; Mocellin, A.; Machado, A. B.; Sundin, S.; Hjelte, I.; Sorensen, S. L.; Bjorneholm, O. *Chem. Phys. Lett.* **1999**, *309*, 377−385.

(39) Cavasso Filho, R. L.; Homem, M. G. P.; Landers, R.; Naves de Brito, A. *J. Electron Spectrosc. Relat. Phenom.* **2005**, *144−147*, 1125−1127.

(40) Cavasso Filho, R. L.; Lago, A. F.; Homem, M. G. P.; Pilling, S.; Naves de Brito, A. *J. Electron Spectrosc. Related Phenom.* **2007**, *156−158*, 168−171.

(41) Zeng, X. Q.; Ge, M.; Sun, Z.; Bian, J.; Wang, D. *J. Mol. Struct.* **2007**, *840*, 59−65.

(42) Zeng, X. Q.; Yao, L.; Wang, W. G.; Liu, F. Y.; Sun, Q.; Ge, M. F.; Sun, Z.; Zhang, J. P.; Wang, D. X. *Spectrochim. Acta A* **2006**, *64*, 949−955.

(43) Yao, L.; Zeng, X. Q.; Ge, M. F.; Wang, W. G.; Sun, Z.; Du, L.; Wang, D. X. *Eur. J. Inorg. Chem.* **2006**, 2469−2475.

(44) Zeng, X. Q.; Liu, F. Y.; Sun, Q.; Ge, M. F.; Zhang, J. P.; Ai, X. C.; Meng, L. P.; Zheng, S. J.; Wang, D. X. *Inorg. Chem.* **2004**, *43*, 4799−4801.

(45) Wang, W.; Yao, L.; Zeng, X.; Ge, M.; Sun, Z.; Wang, D.; Ding, Y. *J. Chem. Phys.* **2006**, *125*, 234303−234306.

(46) Li, Y. M.; Zeng, X. Q.; Sun, Q.; Li, H. Y.; Ge, M. F.; Wang, D. X. *Spectrochim. Acta A* **2007**, *66*, 1261−1266.

(47) Wang, W. G.; Ge, M. F.; Yao, L.; Zeng, X. Q.; Sun, Z.; Wang, D. X. *Chem. Phys. Chem.* **2006**, *7*, 1382 − 1387.

(48) Cederbaum, L. S.; Domcke, W. *Adv. Chem. Phys.* **1977**, *36*, 205−344.

(49) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian03*, revision B.04 ed.; Gaussian, Inc.: Pittsburgh, PA, 2003.

(50) Haas, A.; Reinke, H. *Angew. Chem.* **1967**, *79*, 687−688.

(51) Haas, A.; Reinke, H. *Chem. Ber.* **1969**, *102*, 2718−2727.

(52) Nagata, S.; Yamabe, T.; Fukui, K. *J. Phys. Chem.* **1975**, *79*, 2335−2340.

(53) Erben, M. F.; Della Védova, C. O. *Helv. Chim. Acta* **2003**, *86*, 2379−2395.

(54) Nenner, I.; Beswick, J. A. In *Handbook on Synchrotron Radiation*; Marr, G. V., Ed.; Elsevier Science Publishers: Amsterdam, 1987; Vol. 2, pp 355−462.

(55) Frost, D. C.; Lee, S. T.; McDowell, C. A. *J. Chem. Phys.* **1973**, *59*, 5484−5493.

(56) Delwiche, J.; Hubin-Franskin, M.-J.; Guyon, P.-M.; Nenner, I. *J. Chem. Phys.* **1981**, *74*, 4219−4227.

(57) Frey, R.; Gotchev, B.; Peatman, W. B.; Pollak, H.; Schlag, E. W. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *26*, 137−147.

(58) Eland, J. H. D.; Berkowitz, J. *J. Chem. Phys.* **1979**, *70*, 5151−5156.

(59) Brehm, B.; Frey, R.; Kustler, A.; Eland, J. H. D. *Int. J. Mass Spectrom. Ion Phys.* **1974**, *13*, 251−260.

(60) Judge, D. L.; Lee, L. C. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *17*, 329−333.

(61) Tanaka, Y.; Jursa, A. S.; LeBlanc, F. J. *J. Chem. Phys.* **1960**, *32*, 1205−1214.