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Dissociative Photoionization of sulfenylcarbonyl -C(O)S- compounds induced by synchrotron radiation

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Total ion yield spectra as well as photoinduced fragmetation around the S 2p,Cl 2p, C 1s, O 1s, and F 1s transitions of the carbonylsulfenyl compounds: FC(O)SCl,ClC(O)SCl, CH3C(O)SH and CH3OC(O)SCl, have been measured by using synchrotron radiation in the range of 100-1000 eV and multicoincidence techniques, which include photoelectron-photoion coincidence (PEPICO) and phtotoelectron-photoion-photoion coincidence (PEPIPICO) time-of-flight (TOF) mass spectrometry. Complex electronic processes were observed at resonant energies below the S 2p ionization edge, which appear to be characteristic for -SC(O)- containing compounds. The dissociation dynamic for the main ion-pair production is discussed. Dissociation channels were studied by evaluating the shape and slope of selected coincidence islands in the PEPIPICO spectra. Two- , three- and four-body processes, were proposed.

Keywords: Synchrotron; carbonylsulfenyl; photoionization.

En este trabajo se reportan los espectros de ionización y disociación fotoinducidas alrededor de las transiciones S 2p, 2p Cl, C 1s, O 1s, y F 1s de los compuestos carbonylsulfenyl: FC (O) SCL, CLC (O) SCL, CH3C (O) y SH CH3OC (O) SCL. Estos espectros se obtuvieron utilizando radiación sincrotrón en el intervalo de 100-1000 eV y las técnicas de multicoincidencia, que incluyen la coincidencia de fotoelectrones-fotoiones (PEPICO) y la coincidencia fotoelectrón-fotoión-fotoión (PEPIPICO) y espectrometría de masas por tiempo de vuelo (TOF). Se observaron procesos electrónicos muy complejos a energías de resonancia por debajo del límite de ionización S 2p, que parecen ser características de los compuestos que contienen -SC (O). En base a las observaciones se discute la dinámica de la disociación para la producción de los principales pares de iones. Los canales de disociación se estudiaron mediante la evaluación de la forma y la pendiente de las islas de coincidencias seleccionadas del espectro PEPIPICO. Se proponen procesos de dos, tres y cuatro cuerpos.

Descriptores: Sincrotón; carbonilsulfanilo; fotoionización.

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1. Introduction

Recently, we have started with the study of the shallow and core-shell electronic excitation and fragmentation dynamics of carbonylsulfenyl (XC(O)SY) compounds.

The 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. By using synchrotron radiation in the range of 100-1000 eV, total ion yield (TIY) spectra, as well as 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 the following carbonylsulfenyl (XC(O)SY) compounds: FC(O)SCl[2,3], ClC(O)SCl[4], $CH_3C(O)SH$[5] and $CH_3OC(O)SCl$[6].

Fragmentation patterns deduced from PEPICO spectra at various excitation energies in the VUV and soft X-ray regions were especially analyzed in order to establish the existence of a site-specific fragmentation effect. Also, ionic double coincidences were examined, and dissociation mechanisms were proposed to explain the shape and slope of observed PEPIPICO islands.

2. Experimental section

Synchrotron radiation at the Laboratório Nacional de Luz Síncrotron (LNLS), Campinas, Brazil, was used[7]. Linearly polarized light monochromatized either by a toroidal grating monochromator (available at the TGM beam line in the range 12-310 eV)[8] or by a spherical grating monochromator (available at the SGM beam line in the range 200-1000 eV)[9] 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 measurements[10] .This instrument was constructed at the Institute of Physics, Brasilia University, Brasilia, Brazil[11]. 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.

The samples of ClC(O)SCl, $CH_3C(O)SH$ and $CH_3OC(O)SCl$, were obtained from commercial sources (Aldrich, estimated purity 97%).The sample of FC(O)SCl, was prepared by the reaction between ClC(O)SCl and SbF3 in the presence of $SbCl_5$ as a catalyst[12]. The liquids samples were purified by repeated trap-to-trap distillation in vacuum. The purity of the compounds in both vapor and liquid phases were checked by IR and ^1H NMR spectroscopies, respectively.

3. Results and discussions

3.1. Total ion yield spectra (TIY)

The TIY spectra were obtained by recording the count rates of the total ions while the photon energy is scanned. 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 is a powerful method to be used as a complement to absorption spectroscopy [13]. The TIY spectra of shallow-core levels S 2p and Cl 2p and inner-shell level O 1s, C 1s and F 1s of carbonylsulfenyl (XC(O)SY) compounds were obtained in the range 100-1000 eV.

The TIY spectrum of $CH_3C(O)SH$ for the S 2p edge region is shown in Fig. 1. Below the S 2p threshold, located at approximately 172 eV, the spectrum is dominated by a group of three signals centered at 165.1, 166.3, and 167.4 eV and a shoulder at 164.0 eV. Two of these signals (165.1 and 166.3 eV) may correspond to transitions involving the spin-orbit split of the 2p term in the $2p_{1/2}$and $2p_{3/2}$ levels in the excited species. In the case of the simplest sulfide, H_2S, this splitting was reported at 1.201 eV[14]. It should be noted, however, that in agreement with the 2J + 1 rule, an intensity ratio of 1:2 is expected for these transitions, which is not strictly observed in the present case. A similar behavior was observed for the others –SCO- containing compounds. A rather complex feature at resonant energies below the S 2p ionization edge seems to be systematic in -C(O)S- compounds. Superposed with the S 2p continuum a signal at 227 eV can be assigned to the S 2s edge (Fig. 1).

The TIY spectrum of $CH_3OC(O)SCl$ measured near the Cl 2p region is shown in the Fig. 2. The Cl 2p threshold is located at approximately 207.0 eV and below this photon energy two signals can be observed at 198.0 and 199.3 eV. The observed resonance transitions may be mainly assigned to transitions involving the spin-orbit split of the 2p term in the $2p_{1/2}$ and $2p_{3/2}$levels of the excited chlorine species.

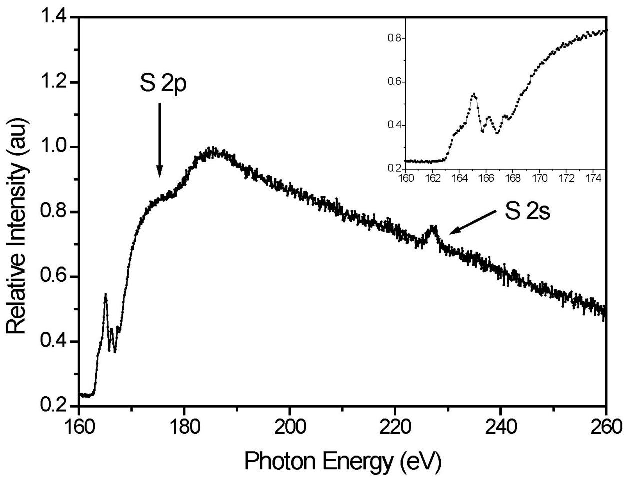

FIGURE 1. Total ion yield spectrum of $CH_3C(O)SH$ around the S 2p and S 2s regions. Enlargement of the TIY spectrum below the S 2p edge is shown on the top of the figure.

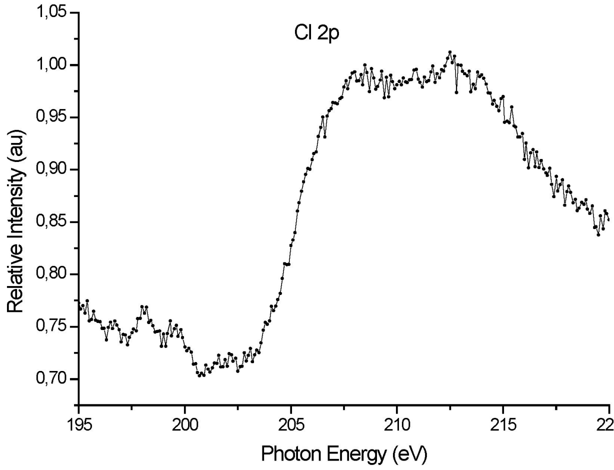

FIGURE 2. Total ion yield spectra of $CH_3OC(O)SCl$ in the Cl 2p region.

The TIY spectra around the O 1s region are dominated in all cases by an intense resonance and by a second signal with much smaller intensity. For example, the TIY spectrum of $CH_3C(O)SH$ for the O 1s edge region is shown in Fig. 3. The spectrum is dominated by an intense resonance at around 529.2 eV. A second broad band emerges as a low intensity signal at approximately 532.0 eV, while the ionization edge is observed at around 543 eV. These resonances involve electronic excitations to vacant $\pi^*_{C=O}$ and $\sigma^*_{C=O}$ orbitals, respectively.

3.2. PEPICO Spectra

PEPICO spectra are generated when an ion arrives at the detector when the time window is open. It occurs when a

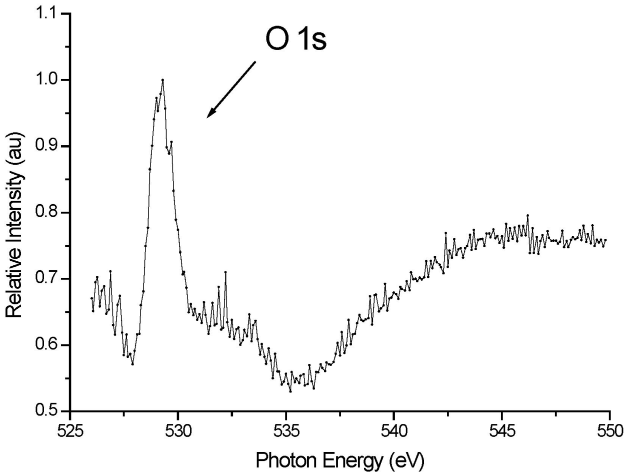

FIGURE 3. Total ion yield spectra of $CH_3C(O)SH$ in the O 1s region.

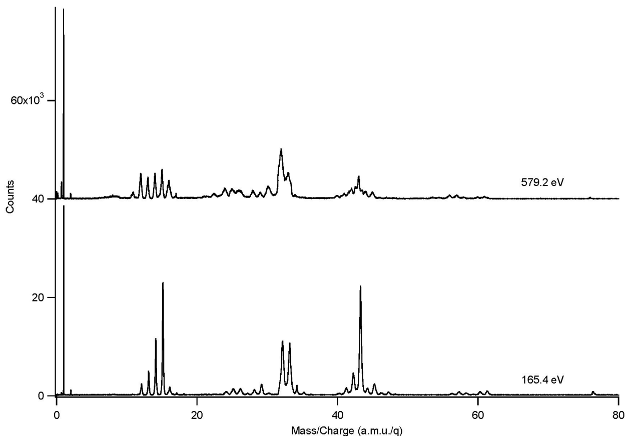

FIGURE 4. PEPICO spectra of $CH_3C(O)SH$ at resonant S 2p and O 1s edge absorptions.

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.

Several PEPICO spectra that include the most important S 2p, Cl 2p, C 1s, O 1s, F 1s transitions of carbonylsulfenyl (XC(O)SY) compounds have been recorded. In order to identify the role of resonant Auger processes in the fragmentation, spectra were not only measured at the resonant values (maxima of the absorptions) but also at photon energy values below (typically 10 eV) and above (typically 50 eV) each resonance. For all spectra, the intensity of each ionic fragment is obtained as the integrated area under the peak, fitting as a Gaussian function to the time of flight spectra. Fragmentation patterns deduced from PEPICO spectra at various excitation energies were especially analyzed in order to establish the existence of a site-specific fragmentation effect in the carbonylsulfenyl compounds.

Thus, in the case of $CH_3C(O)SH$, the site-specific fragmentation is moderately observed by comparing the mass spectra taken at resonant energies around the inner and shallow inner shell S 2p and O 1s ionization edges.

At the S 2p excitation edge, the intensity value of the atomic hydrogen ion represents the highest in all energy range. This ion could be formed by two processes, ionization of the methyl and of the thiol group. The next most important ions are CH_3CO^+, CH_3^+, SH^+, and S^+. The intensity of the signal at m/z = 15 amu/q, corresponding to the CH_3^+ ion, decreases slightly when the incident photon energy is increased. A small increment in the intensity of the m/z = 32 and 33 amu/q ion signals can be seen by going toward higher energies. The molecular ion, $CH_3C(O)SH^+$, can be observed as a very low-intensity signal in all PEPICO spectra measured at photon energies around the S 2p edge. Around the O 1s absorption edge, the atomic hydrogen ion is again the most abundant fragment. On the other hand, the intensity signal of the large CH_3CO^+fragment is depressed, whereas the small CH_x^+ (x = 0, 1, 2, 3) and S^+ fragments are dominant. Moreover, a group of new ions (CC^+, CCH^+, and CCH_2^+) appear in the PEPICO spectra measured at photon energies around the O 1s region. Analysis of the PEPIPICO spectrum reveals that these ions are actually formed from the doubly charged molecular ion implying a C=O double-bond rupture, promoted by the excitation of the O 1s inner shell electrons. It is remarkable that for FC(O)SCl and ClC(O)SCl, such a bond rupture was not observed, and the CO^+ ion signal shows a high intensity even when the samples were irradiated with photon energies corresponding to the O 1s edge. An increment in the m/z = 16 peak intensity, corresponding to the ions O^+ and/or S^{2+}, is observed by going from S 2p to the O 1s region. The $CH_3C(O)SH^+$ molecular ion cannot be observed at these high energies. Figure 4 shows the PEPICO spectra of $CH_3C(O)SH$ obtained at resonant S 2p and O 1s energies.

As a distinctive feature, out of the resonant energy values, PEPICO spectra show broad and less resolved peaks. The width of the peaks reflects directly the linear momentum carried by the fragments. For normal Auger decays, it is likely that final

2+ states correspond to strong repulsive states, favoring the atomization of the molecule, with the concomitant production of small fragments possessing high linear momenta.

The PEPICO spectra of $CH_3OC(O)SCl$ at resonant S 2p, Cl 2p and O 1s edge absorptions are shown in Fig. 5. In the Cl 2p region, apart from a moderate enhancement of the Cl^+ ion signal, the PEPICO spectra are very similar to those measured in the S 2p edge. Changes in the TOF spectral shape of the m/z = 44 peak can be noticed by going from the S 2p to the Cl 2p region. The production of two possible ions with the same value of mass/charge, CO_2^+ or CS^+ and different kinetic energy release, may be responsible for this observed change

An increase in the peak intensities corresponding to the ions H^+, C^+, O^+, or S^{2+}, together with the diminution in

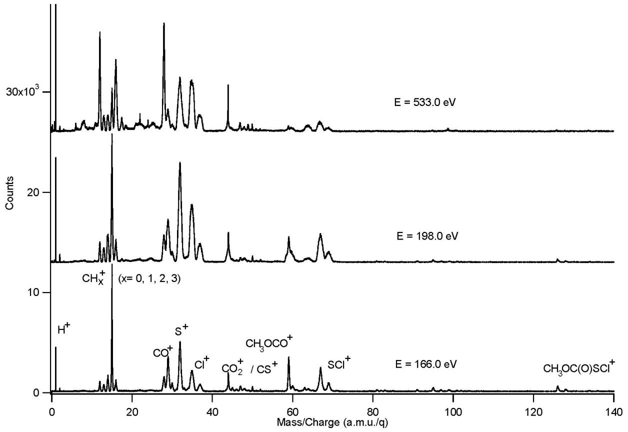

FIGURE 5. PEPICO spectra of $CH_3OC(O)SCl$ at resonant S 2p, Cl 2p and O 1s edge absorptions.

the intensity of the CH_3^+, HCO^+, H_2CO^+, S^+, CO_2^+, COS^+, SCl^+, and CH_3OCO^+ ion signals is observed by going from S 2p to the O 1s region. Thus, strong atomization processes occur at these high photon energies that include the formation of multiply charged molecular ions.

The TOF mass spectrum of $CH_3OC(O)SCl$ measured at the main transition below the 1s O ionization edge (533.0 eV) shows noticeable differences with the PEPICO spectra obtained in the other photon energy region near the 1s O edge. A clear increase in the intensity of the signals corresponding to the ions CO^+, O^+ or S^{2+} and C^+ results evident. It is noteworthy that all these fragments are related with the -OC(O)S- central moiety. The O 1s $\rightarrow \pi^*_{C=O}$excitation may give raise to the Resonant Auger processes that further results in the ejection of valence electrons from molecular orbitals involving the O-C and C-S single bonds. Thus, the preferred production of these ions can be understood.

For the ClC(O)SCl, 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. These results was interpreted in terms of a “lost memory” effect or non-specific fragmentation after an Auger decay, promoted by the delocalization of valence orbitals over the whole planar molecules.

3.3. PEPIPICO Spectra

Two-dimensional PEPIPICO spectra were recorded at several photon energies corresponding to transitions involving L and K levels of carbonylsulfenyl (XC(O)SY) compounds in the range 100-1000 eV. 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 reflect mainly pairs of singly charged fragment ions originated from the fragmentation of the doubly charged parent molecule. In a first approximation it is assumed that a different electronic decay, especially throughout normal Auger decay, leads to a double-charged molecular ion. The analysis of the PEPIPICO spectra is useful for identifying several two-, three- and four-body dissociation mechanisms which especially follow Auger decay mechanisms[15,16]. Several islands are expected in the PEPIPICO spectra of these compounds, and hence a complete interpretation of the spectra is not straightforward. In a first approximation, the attention is paid on selected pairs of ions, for which both a good statistics and well-defined shape are observed.

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 carbonylsulfenyl (XC(O)SY) compounds. 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.

3.4. Two-body fragmentations

Two-body processes concerning the rupture of the C-S bond to form two single-charged species were observed as the main two-body dissociation channel and emerge as a general route for double-charged XC(O)SY species excited at inner shell levels. A coincidence between XCO^+ andSY^+ ions is identified in the PEPIPICO spectra as an island with a cigar shape having a -1 slope. This features and the ion nature can be

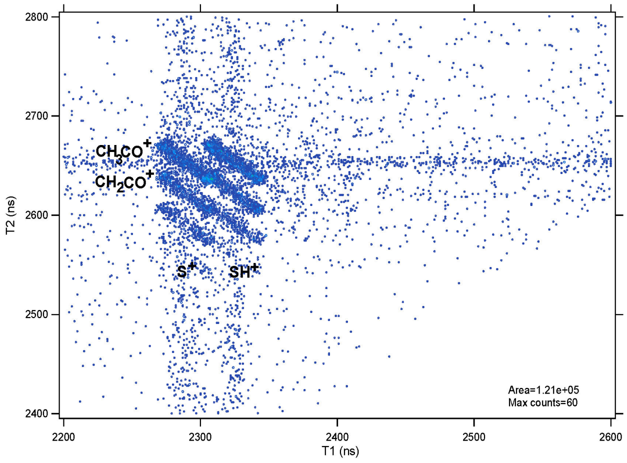

FIGURE 6. Enlargement of the PEPIPICO spectrum of $CH_3C(O)SH$ obtained at 165.1 eV photon energy in the ranges of m/z 32-33 and 42-43 amu/q for the T1 and T2 domains, respectively.

rationalized as originated by the following process:

$$XC(O)SY^{2+} \rightarrow XCO^{+} + SY^{+}$$

In the case of $CH_3C(O)SH$ a coincidence between CH_3CO^{+} and SH^{+} ions is observed in the Fig. 6 and the coincidence of the CH_2CO^{+} ion with the SH^{+} ion was also observed. The creation of CH_2CO^{+}can be sequential via the CH_3CO^{+} ion.

3.5. Three- and four-body fragmentations

For ClC(O)SCl, a coincidence between $CO^{+}$and $SCl^{+}$was observed with an experimental slope that is approximately -1 and can be explained by the following three-body ion pair process DCS:

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

$$OCSCl^{2+} \rightarrow CO^{+} + SCl^{+}$$

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

In the case of the $CH_3C(O)SH$ and $CH_3OC(O)SCl$ molecules the coincidences concerning the series of CH_x^{+} ions (x = 0, 1, 2) arise from four-body dissociation mechanisms by the loss of hydrogen atoms from the CH_3^{+} ion.

For example, in the case of $CH_3OC(O)SCl^{2+}$, a coincidence between CH_3^{+} and Cl^{+} fragments, shown on Fig. 7, is observed with an experimental slope of approximately –1 and can be explained by the following three-body ion pair process DCS (Deferred Charge Separation):

$$CH_3OC(O)SCl^{2+} \rightarrow CH_3Cl^{2+} + NP$$

$$CH_3Cl^{2+} \rightarrow CH_3^{+} + Cl^{+}$$

Coincidences between CH_x^{+} (x = 0, 1, 2) and Cl^{+} show slight changes in the slope when the hydrogen extrusion increases. Little differences are expected in the slope of double coincidences involving CH_x^{+} (x = 0, 1, 2) when compared with CH_3^{+} because of the low mass of the H^{+} ion. This fact might evidence that the mechanisms involved in the formation of CH_x^{+} (x = 0, 1, 2) ions can be sequential via the formation of CH_3^{+} ion in the very first step. Thus, four-body ion pair processes need to be invoked to explain the coincidence between CH_2^{+} and Cl^{+} ions.

It is important to refer here to the presence of a coincidence between ions with m/z = 16 and m/z = 32 amu/q (see Fig. 7). There is no ambiguity about the ions; O^{+} (not S^{2+}) and S^{+}ions are involved. This implies again the rupture of the C=O double bond. This coincidence should be originated in fragmentation processes arising from at least triple charged molecule.

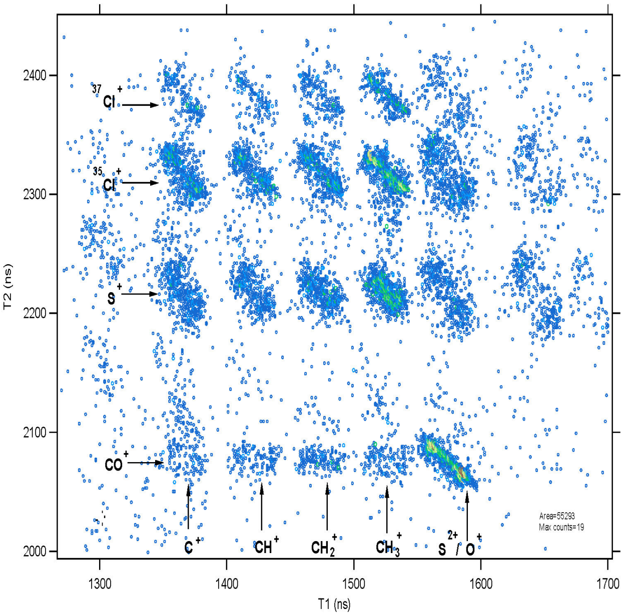

FIGURE 7. Enlargement of the PEPIPICO spectrum of $CH_3OC(O)SCl$ obtained at 533.0 eV photon energy in the ranges of m/z 12-16 and 28-37 amu/q in the T1 and T2 domains, respectively.

For a penta-atomic sulfenylcarbonyl compounds, FC(O)SCl, low-intensity signals involving coincidences between double and single charged cations were observed , such as C^{+}/Cl^{2+}, O^{+}/Cl^{2+}, Cl^{2+}/F^{+}, Cl^{2+}/CO^{+}, S^{+}/CO^{+}, and S^{2+}/FCO^{+}, are further evidences of the presence of multiple ionizations.

Thus, the coincidence between S^{2+} and CO^{+}, observed with an "egg" shape, with rounded edges, characteristic of nonsequential or concerted fragmentation processes, can be explained by the following concerted mechanism [17]:

$$FC(O)SCl^{n+} \rightarrow S^{2+} + CO^{+} + \text{ NP n } \geq 3$$

4. Conclusions

The TIY spectra of shallow-core levels and inner-shell level of carbonylsulfenyl (XC(O)SY) compounds were obtained in the range 100-1000 eV by using synchrotron radiation and coincidence detection techniques. Complex electronic processes occur at resonant energies below the S 2p ionization edge, which appear to be characteristic for -SC(O)- containing compounds. The observed features in the TIY spectra could be related with several phenomena such as electronic transitions to vacant orbitals with contributions of spin-orbit splitting of the S 2p terms of the ionized species, autoionization of transitions to Rydberg levels or a contribution of both of them. Thus, this family of compounds deserves further studies involving the use of electron spectroscopy based methods to cover these aspects.

Time-of-flight PEPICO and PEPIPICO multicoincidence techniques were applied around the different transition edges.

In the case of FC(O)SCl and ClC(O)SCl, it is expected that valence holes created in the Auger decay may delocalize over the whole planar molecules. In consonance with this fact, the fragmentation patterns are practically independent upon the atomic site of the core hole and non-specific fragmentation should be expected. When the size of the molecule increases, as in the related sulfenylcarbonyl species $CH_3C(O)SH$ and $CH_3OC(O)SCl$, different fragmentation patterns were obtained as the incident photon energy was varied.

The dissociation dynamic for the main ion-pair production has also been discussed. Dissociation channels were studied by evaluating the shape and slope of selected coincidence islands in the PEPIPICO spectra. Two- , three- and four-body processes, were proposed.

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