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Evidence of Site-Specific Fragmentation on Thioacetic Acid, $CH_3C(O)SH$, Irradiated with Synchrotron Radiation around the S 2p and O 1s Regions

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Site-specific fragmentations following S 2p and O 1s photoexcitation of thioacetic acid, $CH_3C(O)SH$, have been studied by means of synchrotron radiation. Total ion yield (TIY) spectra were measured and multicoincidence techniques, which include photoelectron−photoion coincidence (PEPICO) and photoelectron−photoion−photoion coincidence (PEPIPICO) time-of-flight mass spectrometry, were applied. The equivalent-core approximation was employed in order to estimate ionization transition values, and the observed peaks were tentatively assigned. A site-specific fragmentation is moderately observed by comparing the mass spectra collected at resonant energies around the inner and shallow inner shell S 2p and O 1s ionization edges. Beside H^+ ion, the most abundant ions observed at the S 2p edge excitation were CH_3CO^+, SH^+, S^+, and CH_3^+. At the O 1s region the large CH_3CO^+ fragment was depressed, and small CH_x^+ ($x = 0, 1, 2, 3$), S^+, and SH^+ fragments were dominant. The dissociation dynamic for the main ion-pair production has been discussed. Two- and three-body dissociation channels have been observed in the PEPIPICO spectra, and the dissociation mechanisms were proposed.

Introduction

We have recently reported studies concerning shallow- and inner-core electrons in penta-atomic sulfenylcarbonyl XC(O)SY compounds FC(O)SCl[1] and ClC(O)SCl.[2] By using synchrotron radiation in the range of 100−1000 eV, total ion yield (TIY) and partial ion yield (PIY) 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 FC(O)SCl and ClC(O)SCl. 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 valence orbitals over the whole planar molecules. Concerning the photofragmentation dynamics of both halogencarbonylsulfenyl chlorides, XC(O)SCl (X = F, Cl), analyses of PEPIPICO spectra clearly allowed the identification of a two-body dissociation channel, which leads to XCO^+ 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 X^+ and OCS^+). Furthermore, a new three-body dissociation mechanism, which represents a *charge separation after an ion rearrangement* (CS-IR), was proposed in order to explain the process involving two double coincidences, namely, X^+/Cl^+ and CO^+/S^+.

As part of a general project faced to the study of the shallow- and core-shell electronic excitation and fragmentation dynamics of carbonylsulfenyl (XC(O)SY) compounds, the extension to another member of this family can be attractive. Thioacetic acid, $CH_3C(O)SH$, seems to be a good candidate to increase the molecular complexity, since the X and Y substituents (the methyl group and the hydrogen atom) are simple moieties.

Thioacetic acid was first obtained in 1854 by Kekule and represents the first known organic acid containing sulfur.[3,4] Currently this compound is widely used in chemical synthesis as a reagent for introduction of the thiol group into organic molecules, being the most common and versatile reagent for the free radical addition of thiol precursor to terminal alkenes and olefin.[5] Of close interest for the present study, the molecular structure of gaseous $CH_3C(O)SH$ in its electronic ground state has been early studied by Gordy. By using the electron diffraction technique, the heavy atoms geometrical parameters could be estimated.[6] Several studies of the vibrational spectra have been also carried out with the aim of seeking evidence of a possible thiol/thion tautomeric equilibrium.[7,8] Furthermore, Noe[9] has investigated the conformational equilibrium around the C−S bond in $CH_3C(O)SH$ by temperature dependence of the ^1H NMR spectrum. The syn conformation (C═O double bond in the synperiplanar orientation with respect to the S−H single bond) is preferred over the anti form (C═O double bond in the antiperiplanar orientation with respect to the S−H single bond), with a free energy difference of 1.9 kcal mol^{-1} between the two conformations. Recently, this equilibrium was also studied by using matrix infrared spectroscopy experiences.[10] The results indicate that the vapor of $CH_3C(O)SH$ at ambient temperature consists of a mixture of the syn and anti conformers, with the syn form predominating (ca. 85%). Additionally, broad-band UV−vis irradiation ($200 \leq \lambda \leq 800$ nm) of a $CH_3C(O)SH$/Ar mixture isolated as a matrix at 15 K leads to a conformational interconversion and to the formation of ketene ($H_2C{=}C{=}O$) and H_2S as the main photochemical decomposition products.

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The main objective of the present study is to obtain evidences regarding the electronic transitions throughout the whole region of the S 2p and O 1s ionization edges and ionic dissociation mechanisms following the electronic relaxation of core-excited $CH_3C(O)SH$. It includes the use of multicoincidence mass spectroscopy techniques and tunable synchrotron radiation. 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 $CH_3C(O)SH$.

Experimental Section

Synchrotron radiation was used at the Laboratório Nacional de Luz Síncrotron (LNLS), Campinas, São Paulo, Brazil.[11] Linearly polarized light monochromatized either by a toroidal grating monochromator (available at the TGM beam line in the range of 12−310 eV)[12] or by a spherical grating monochromator (available at the SGM beam line in the range of 200−1000 eV) intersects the effusive gaseous sample inside a high-vacuum chamber, with 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[13,14] measurements. This instrument was constructed at the Institute of Physics, Brasilia University, Brasilia, Brazil.[15] 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 sample of thioacetic acid, $CH_3C(O)SH$, was obtained from commercial sources (Aldrich, estimated purity 95%). The liquid sample was purified by repeated trap-to-trap distillation in vacuum. The purity of the compound in the vapor phase was checked by IR spectroscopy.

Quantum chemical calculations for the neutral ground state and singly and doubly charged low-lying cationic states were performed using density functional theory (DFT) methods at the UB3LYP/6-31+G* level of approximation. The geometry optimizations were performed using standard gradient techniques by simultaneous relaxation of all geometrical parameters. The calculated vibrational properties correspond in all cases to potential energy minima for which no imaginary frequencies were found. Furthermore, the core-equivalent model[16,17] was implemented in order to estimate S 2p and O 1s core ionization energies, taking OCS as the reference compound.[18] This approximation has shown to give a good description for carbonyl compounds.[19] Shortly, the difference in core ionization energy between the sulfur in $CH_3C(O)SH$ and in OCS can be approximated by the change in energy of the following reaction:

$$CH_3C(O)SH + OCS^{*+} \rightarrow CH_3C(O)S^{*}H^{+} + OCS$$

where * indicates that a 2p electron is missing from the sulfur atom. In the core-equivalent approximation, the energy for the above reaction is equivalent as that for the reaction

$$CH_3C(O)SH + OCCl^{+} \rightarrow CH_3C(O)ClH^{+} + OCS$$

where core ionized $CH_3C(O)S^*H^+$ and OCS^{*+} are modeled as $CH_3C(O)ClH^+$ and $OCCl^+$, respectively (chloride assigned the mass of sulfur).[20] Finally, the S 2p binding energy for $CH_3C(O)SH$ is calculated as the energy change of the above reaction plus the experimental ionization energy of OCS (170.6 eV).[21] In a wholly equivalent fashion, the core ionization energy for the O 1s transition in $CH_3C(O)SH$ can be also estimated by using the experimental oxygen 1s binding energy in OCS and quantum chemical calculations on $CH_3C(F)SH^+$ and FCS^+ throughout the core-equivalent model (fluoride assigned the mass of oxygen). Core-equivalent related calculations were performed at the UB3LYP/6-311++G** level of approximation. All of the calculations were performed using the Gaussian98 programs system.[22]

Results and Discussions

Knowledge about the whole electronic structure of the molecule under study is desirable for a reliable analysis of experiences concerning inner-shell electrons, specially the first unoccupied valence orbitals that could be associated with electronic transitions. Electronic (UV−vis) and photoelectron spectra of $CH_3C(O)SH$ have been reported by Nagata et al.,[23] and the electronic transitions were assigned with the assistance of semiempirical calculations. Here, further quantum chemical calculations were performed for the electronic ground state as well as for low-lying singly and doubly charged cationic states of $CH_3C(O)SH$. Two orbitals very close in energy were found for the HOMO and NHOMO. They correspond to nominally lone pairs orbitals centered on the oxygen and sulfur atoms, respectively. Furthermore, in accordance with the experimental results, the $\pi^*_{C=O}$ orbital results to be the LUMO, with a calculated (B3LYP/6-31+G*) HOMO−LUMO energy difference of 6.5 eV which is larger than the experimentally reported value (5.13 eV).[23] The next vacant orbitals correspond to the antibonding σ^*_{S-H} and σ^*_{C-S}.

According to the UB3LYP/6-31+G* method, the low-lying singly and doubly charged states are located at 9.8 and 26.1 eV above the neutral ground state, respectively. Both charged $CH_3C(O)SH^+$ and $CH_3C(O)SH^{2+}$ forms are stable minima in the low-lying cationic potential energy surfaces, i.e., no imaginary frequencies were found in the calculations. The planar skeleton of the $CH_3C(O)SH$ molecule remains unchanged after simple ionization,[24,25] with a remarkable elongation of about 0.28 Å for the C−S single bond and the shortening of the other bonds lengths. Bond angles in $CH_3C(O)SH^+$ are quite similar to those calculated for the neutral species. A rather different structural behavior is found in the case of 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 especially in the main skeleton torsion. Thus, the CC−SH dihedral angle changes from an anti orientation (180°) to a nearly gauche orientation (93°). The acidic hydrogen S_4-H_5 bond becomes slightly longer as the positive charge of thioacetic acid increases. This behavior resembles our former studies on FC(O)SCl[1] and ClC(O)SCl.[2]

Total Ion Yield Spectra (TIY). 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 of the absorption spectroscopy.[26]

The TIY spectrum of $CH_3C(O)SH$ for the S 2p edge region is shown in Figure 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

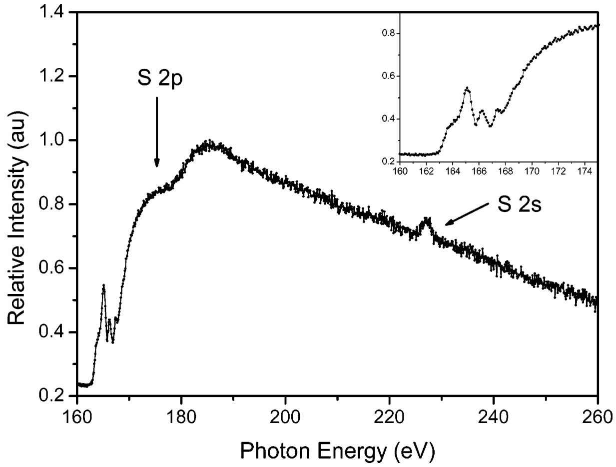

Figure 1. Total ion yield spectrum of $CH_3C(O)SH$ around the S 2p and S 2s regions. Enlargement of the TIY spectrum below the S 2p edge is shown on the top of the figure.

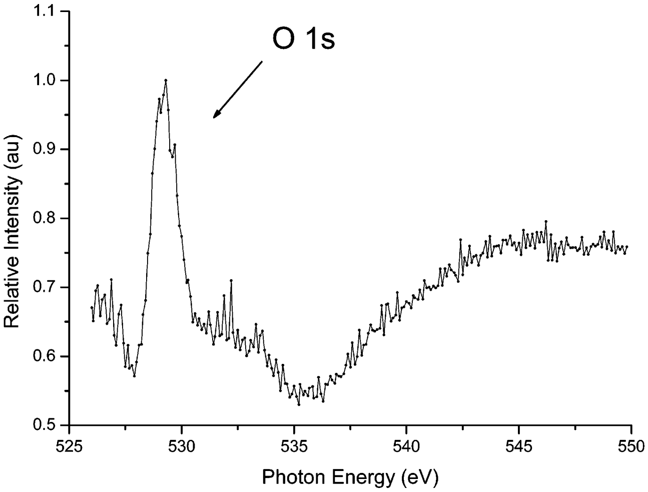

Figure 2. Total ion yield spectra of $CH_3C(O)SH$ in the O 1s region.

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 to be 1.201 eV.[27] 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 previously studied molecules FC(O)SCl[1] and ClC(O)SCl.[2] 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 (Figure 1).

Figure 2 displays the TIY spectrum around the O 1s region. 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. These results are in good agreement with the reported values obtained for FC(O)SCl[1] and ClC(O)SCl.[2] Furthermore, the proposed assignments, especially those corresponding to the inner shell transitions of the oxygen atom, are consistent with those reported for esters and carboxylic acids.[28]

The S 2p and O 1s ionization energies for $CH_3C(O)SH$ extracted from the TIY spectra were compared with those predictions based on the equivalent-core approximation taking OCS as the reference compound[18] for both ionization energies. The calculated (B3LYP/6-311++G**) S 2p and O 1s binding energies at 171.5 and 542.6 eV are in good agreement with the experimental values.

PEPICO Spectra. *Ionic Fragmentation Following Valence Shell Ionization.* In the electron impact mass spectrum of $CH_3C(O)SH$ the acylium ion CH_3CO^+ with an m/z ratio of 43 amu/q represents the most important product. CH_3^+ and $C(O)SH^+$ ions are also detected with relative intensities of 6% and 11%, respectively. Besides these contributions, the parent ion peak at $m/z = 76$ amu/q is observed as a relatively low-intensity signal (≈3%).[29] Furthermore, by using cyclotron resonance techniques, Caserio and Kim reported the formation of thioacylium ion CH_3CS^+ in the gas phase by reaction of CH_3CO^+ and a neutral $CH_3C(O)SH$ molecule.[30] Due to the effective overlap of π electrons involved in multiple bonds, carbonyl ions of the type $RC{=}O^+$ are anticipated to be stable because strong electronic resonance stabilization interactions ($RC{\equiv}O^+ \leftrightarrow RC^+{=}O$) can occur.

To shed some light on the fragmentation processes following valence shell ionizations induced by photons, PEPICO spectra were obtained at 12.0 and 155.0 eV by using synchrotron radiation. As was already mentioned, the HOMO and NHOMO in $CH_3C(O)SH$ are associated with ionization energies of 10.06 and 10.30 eV, respectively. A third band in the photoelectron spectrum appears at ca. 13.0 eV.[23] Thus, it is expected that fragments formed only from the ionization of single-charged species (those formed mainly by the ionization of electrons originally located at the sulfur and oxygen lone pair) contribute to the PEPICO spectra taken at 12.0 eV. This is also consistent with the calculated adiabatic ionization energy for the low-lying single-charged radical (9.8 eV, UB3LYP/6-31+G*). On the other hand, valence electron double-ionization events, even through direct double-ionization or autoionization processes, could play a decisive role in the ionic fragmentation of the species excited with 155.0 eV energy photons. The calculated (UB3LYP/6-31+G*) adiabatic ionization energy value for the double-charged cationic form reaches values of 26.06 eV. The 155.0 eV PEPICO spectrum should also provide a good reference with respect to the fragmentation pattern associated with the shallow- and inner-core electrons since this energy is even not enough to ionize shallow-core electrons (S 2p transitions appear above 160 eV). The PEPICO spectra at 12.0 and 155.0 eV measured in the range of 0−80 amu/q are presented in Figure 3.

Though a comparison of electron and photon impact mass spectrum is not straightforward, similar results have been observed by comparing the 12.0 eV photon energy spectrum and the 70 eV electron impact spectra.[29] In effect, a strong signal at $m/z = 43$ amu/q, corresponding to the CH_3CO^+ ion, dominates the 12.0 eV PEPICO spectrum, whereas the parent ion and the CH_3^+ fragment are unambiguously observed at 76 amu/q and at 15 amu/q, respectively. The low-intensity signals at 32 and 33 amu/q indicate the presence of S^+ and SH^+ ions. Thus, the photofragmentation of $CH_3C(O)SH$ ionized at the outer valence orbitals is dominated by a rupture process involving the C−S single bond. The charge is held on the CH_3CO more likely than on the SH fragment.

In the 155.0 eV PEPICO spectrum, an increment in the intensity of the $m/z = 1$ amu/q peak corresponding to the H^+ ion becomes evident. The concentration of the CH_3CO^+ ion remains very abundant. Worthy to be mentioned, the intensity of the CH_3^+ ion is even higher than that of the CH_3CO^+, and

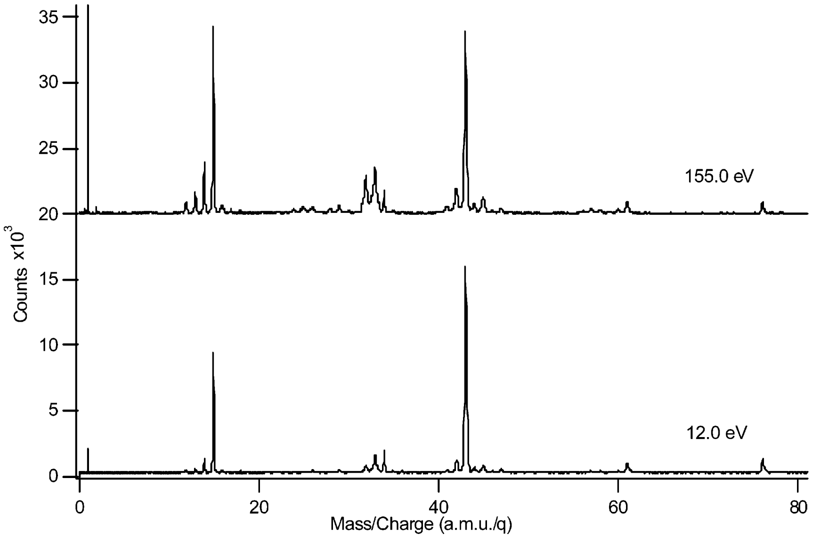

Figure 3. PEPICO spectra of $CH_3C(O)SH$ recorded at 12.0 and 155.0 eV photon energies.

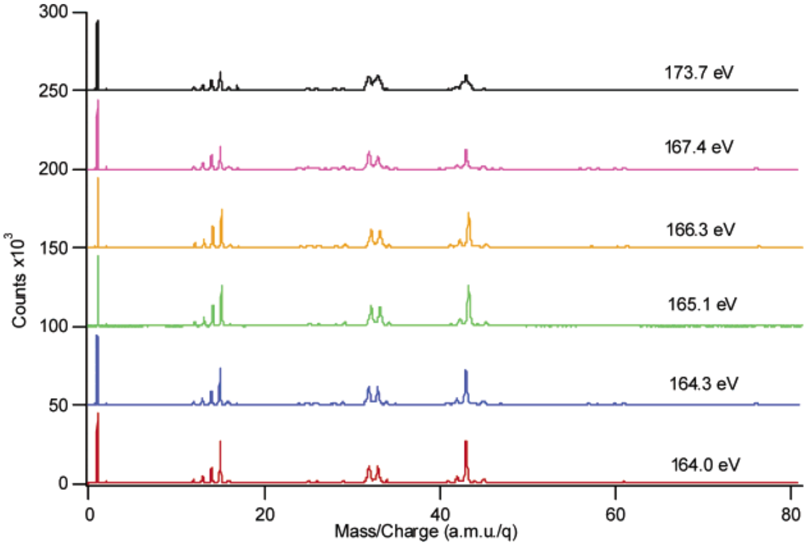

Figure 4. PEPICO spectra of $CH_3C(O)SH$ recorded around the S 2p edge.

the presence of the whole methyl series CH_x^+ ($x = 3$, 2, 1, and 0) can be detected in the PEPICO spectrum. The molecular ion can be still observed at this energy. As compared with the 12.0 eV PEPICO spectrum, an increment in the intensity derived from the ions S^+, SH^+, and $COSH^+$ can be also observed in the deep valence spectrum, evidencing a more complex fragmentation behavior than the 12.0 eV spectrum.

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. In contrast to valence electrons, which can be part of molecular orbitals and may be delocalized over the molecule, core- and shallow-shell electrons are highly localized on a specific atomic level of a molecule. Monochromatized synchrotron radiation can excite selectively inner shell electrons, and in case that the memory effect induced on the short time scale of the excitation is conserved at longer times required for the ionic dissociation, nonstatistical fragmentations, i.e., site-specific or state-dependent fragmentations, can be anticipated.[31,32] The insight on the nature of the site-specific fragmentation is of importance in understanding localization phenomena in chemical reactions.[33] Eberhardt et al.[31] reported evidences for the atom selection soft X-ray chemistry for acetone. Linked to the present work, the state-specific formation of the triply charged S^{3+} and OCS^{3+} ions has been reported in the study of the core-excited OCS molecule.[34]

Several PEPICO spectra that include the most important S 2p and O 1s transitions of $CH_3C(O)SH$ have been recorded in this work. To identify the role of resonant Auger processes in the fragmentation, spectra were not only measured at the resonant value (maximum of the absorptions) but also at photon energy values below (typically 10 eV) and above (typically 50 eV) each resonance.

Ionic Fragmentation Near the S 2p Shallow-Core Edge. The PEPICO spectra taken at photon energies around the S 2p edge are shown in Figure 4. In Table 1 the corresponding branching ratios are gathered for the main fragment ions. 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. Higher photon energies favor rupture processes increasing the intensity of this signal. However, it may be feasible that this ion cannot be completely collected, since it is ejected in all directions with high velocity. Therefore, the branching ratio values for H^+ should be taken as tentative. The next most important ions with relative intensities between 9% and 14% 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

TABLE 1: Branching Ratios (%) for Fragment Ions Extracted from PEPICO Spectra Taken at Photon Energies around the S 2p and O 1s Energies for $CH_3C(O)SH$[a]

photon energy (eV)	*m*/*z* (amu/*q*)																	
	1	12	13	14	15	16	24	25	26	28	29	30	32	33	43	44	60	61	76
164.0	19.0	1.7	2.8	5.7	12.7	1.9				1.0	1.5	0.5	9.7	9.2	14.6	1.2	0.7	0.9	0.5
164.3	20.3	1.8	2.7	5.6	11.7	2.1				1.1	1.5	0.6	10.5	9.3	13.0	1.1	0.7	0.8	0.5
165.1	17.2	1.9	3.1	6.6	11.6	1.9				1.3	1.9	0.6	10.5	9.8	13.1	1.1	0.7	0.8	0.5
166.3	18.2	2.0	3.3	7.0	11.6	1.8				1.4	1.8	0.6	10.0	10.0	12.1	1.1	0.6	0.8	0.5
167.4	24.5	2.0	3.3	6.3	9.2	2.1				1.4	1.5	0.7	11.5	9.9	9.2	1.1	0.5	0.7	0.4
173.7	23.4	1.7	2.8	5.4	9.1	2.0				1.4	1.4	0.9	11.4	14.5	10.8	0.9	0.4	0.5	0.2
519.0	19.7	5.0	3.8	4.2	4.8	4.2	3.1	2.9	3.0	2.3	1.4	3.4	13.4	7.8	4.3	1.2			
529.2	17.3	4.3	3.5	4.7	5.8	3.8	3.2	3.0	3.3	2.0	1.4	3.0	11.7	7.8	4.0	1.4			
579.2	20.3	5.0	3.7	4.2	5.1	4.4	3.3	3.1	3.3	2.1	1.4	3.6	13.2	7.7	4.0	1.2			

[a] Ions with branching ratios lower than 0.2% are not listed.

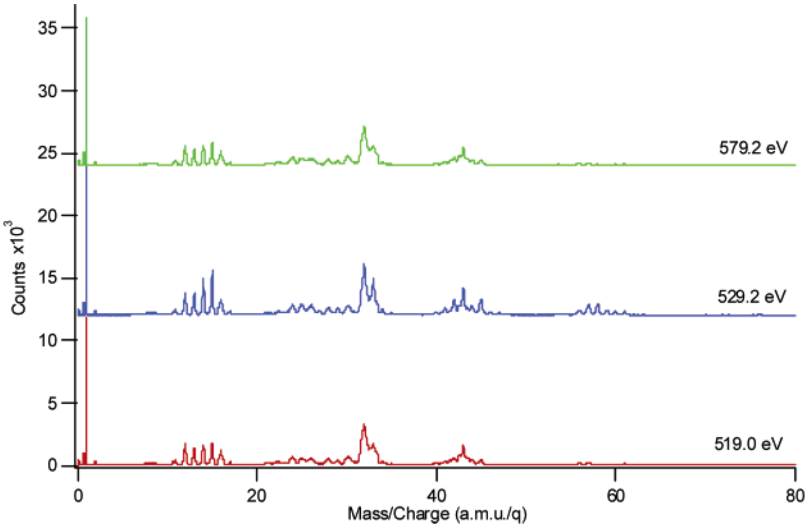

Figure 5. PEPICO spectra of $CH_3C(O)SH$ recorded around the O 1s edge.

incident photon energy is increased. Together with this diminution an enhancement in the signal intensity of other methyl fragments (CH_x^+, $x = 0, 1, 2$) can be observed. 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 diminution of the intensity of CH_3CO^+ at increasing incident photon energies can also be noticed. The molecular ion, $CH_3C(O)SH^+$, can be observed as a very low-intensity signal in all PEPICO spectra.

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.

Ionic Fragmentation Near the O 1s Core Edge. Figure 5 depicts the PEPICO spectra of $CH_3C(O)SH$ recorded at selected energies around the O 1s absorption edge. The corresponding branching ratios are listed in Table 1.

The atomic hydrogen ion is again the most abundant fragment, followed by S^+ and SH^+, respectively. The $m/z = 15$ amu/*q* (CH_3^+) signal intensity is always higher than the intensity of the signal at $m/z = 43$ amu/*q* (CH_3CO^+) for all spectra in the Figure 5. This behavior is opposite to that observed in the S 2p region (Figure 4). The group of CH_x^+ fragments ($x = 0, 1, 2, 3$) presents similar intensities (between 3% and 5% approximately), evidencing a different behavior than that observed in the S 2p region, where the intensity of the CH_3^+ ion is considerably higher than the intensities of the remainder ions of this group. 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. A new group of signals having branching ratios of about 3% appears at $m/z = 24$, 25, and 26 amu/*q*. They could be originated by the ions CC^+, HCC^+, and H_2CC^+, respectively. The formation of these fragments involves necessarily the rupture of the C=O double bond implying the diminution of the intensity of the CH_3CO^+ ion signal. It is remarkable that for FC(O)SCl and ClC(O)SCl, such a bond rupture was not observed, and the CO^+ ion signal showed a high intensity even when the samples were irradiated with photon energies corresponding to the O 1s edge. The $CH_3C(O)SH^+$ molecular ion cannot be observed at these high energies. The increment of the signal at $m/z = 30$ amu/*q*, corresponding probably to the OCS^{2+} ion, represents another noticeable difference of the PEPICO spectra obtained in the O 1s region. For the sake of comparison, the Figure 6 shows the PEPICO spectra of $CH_3C(O)SH$ obtained at resonant S 2p and O 1s energies.

PEPIPICO Spectra. Photoelectron−photoion−photoion coincidence (PEPIPICO) time-of-flight mass spectrometry was applied, and the spectra were measured at several photon energies around the S 2p edge and O 1s edge. Two-dimensional 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. Possible

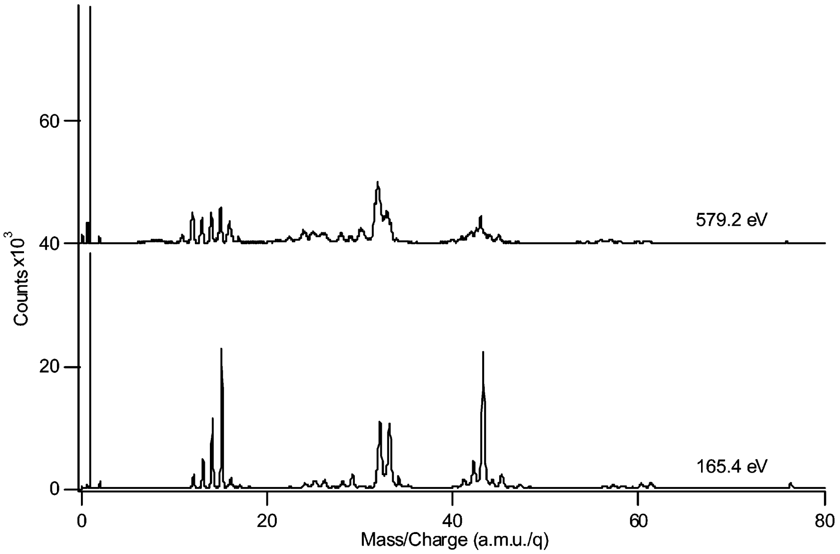

Figure 6. PEPICO spectra of $CH_3C(O)SH$ at resonant S 2p and O 1s edge absorptions.

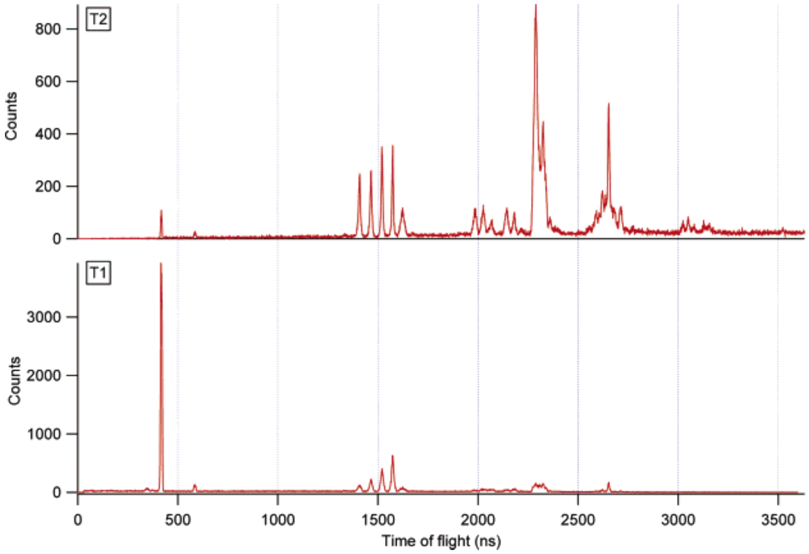

Figure 7. T1 and T2 projections of the PEPIPICO spectrum of $CH_3C(O)SH$ recorded at 165.1 eV on the S 2p resonance.

mechanisms involved in the fragmentation of $CH_3C(O)SH^{2+}$ ion may be deduced from the shape of the PEPIPICO double-coincidence peaks.[35]

Projections of PEPIPICO spectra on the T1 and T2 axes were obtained by integrating the signal intensities over the time domains. T1 and T2 PEPIPICO projection spectra of $CH_3C(O)SH$ recorded at the main resonance energy of the S 2p transition are depicted in the Figure 7. The H^+ ion dominates the T1 domain followed in importance by the CH_x^+ ($x = 0, 1, 2, 3$) group of ions. Methyl ions also appear in the T2 domain. Since the CH_3^+ ion is observed with appreciable intensity in that projection, a double coincidence between the acidic hydrogen ion and the CH_3^+ ion arising from the acetyl group is expected and unambiguously determined. Other relative heavy fragments such as CO^+, S^+, SH^+, OCS^+, and CH_3CO^+ are originated in the same dissociative events together with the relative light ions H^+ or CH_x^+ ($x = 0, 1, 2, 3$).

In the case of a rather complex molecule such as $CH_3C(O)SH$, several islands are expected in the PEPIPICO spectra, and hence a complete interpretation of the spectra is not straightforward. As commented from the analysis of the triple-coincidence projection spectra, coincidences will be originated by arriving H^+ to the detector as the lightest ion. Eland[35] has pointed out that this kind of coincidence shows a highly nondiagonal feature, which makes difficult its study. Furthermore, as mentioned, the H^+ ion can be formed from both the methyl and the $-SH$ groups, making its assignment ambiguous in several cases. For islands involving m/z values of 16 amu/q, the distinction between O^+ and S^{2+} ions is not always feasible.

Taking into consideration these limitations of the PEPIPICO analyses, 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.

Two-Body Fragmentations. A coincidence between ions with m/z values of 43 amu/q (CH_3CO^+) and 33 amu/q (SH^+) is identified in the PEPIPICO spectra as an island with a cigar shape having a -1 slope (Figure 8). This features and the ion nature can be rationalized as originated by a two-body fragmentation process

$$CH_3C(O)SH^{2+} \rightarrow CH_3CO^+ + SH^+$$

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 in FC(O)SCl[1] and ClC(O)SCl[2] and emerge as a general route for double-charged XC(O)SY

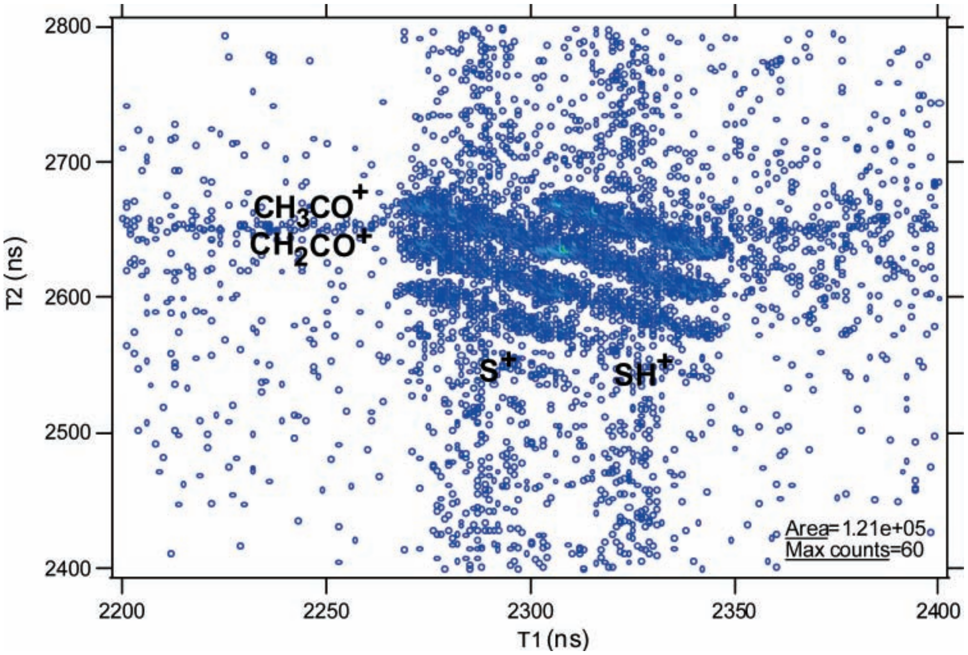

Figure 8. Enlargement of the PEPIPICO spectrum of $CH_3C(O)SH$ obtained at 165.1 eV photon energy in the ranges of m/z 32−33 and 42−43 amu/q for the T1 and T2 domains, respectively.

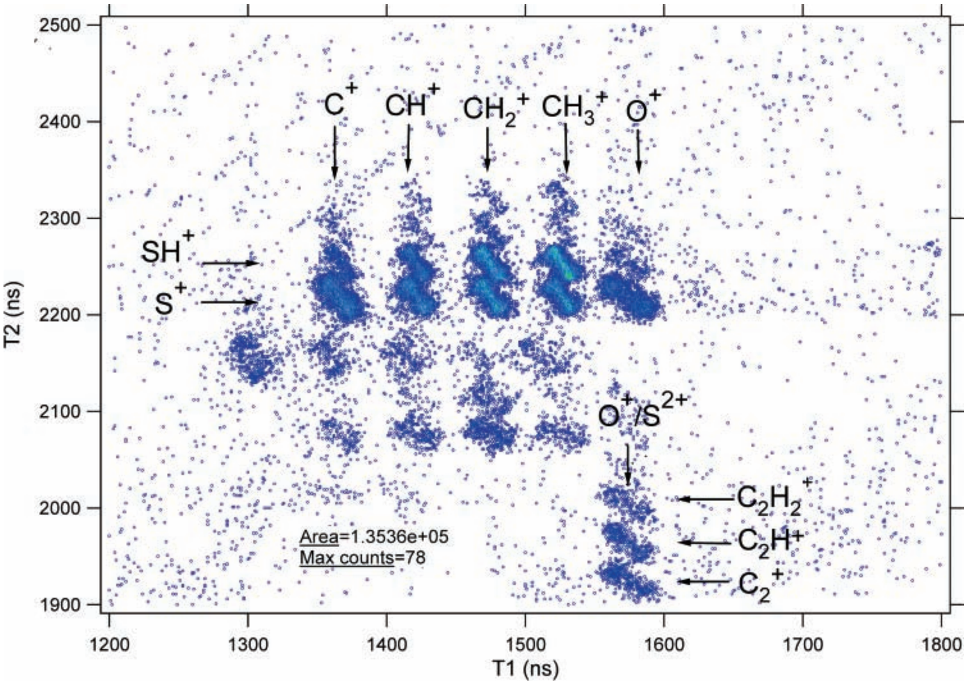

Figure 9. Enlargement of the PEPIPICO spectrum of $CH_3C(O)SH$ obtained at 529.2 eV photon energy in the ranges of m/z 12−16 and 24−34 amu/q in the T1 and T2 domains, respectively.

species excited at inner shell levels. 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.

A second two-body fragmentation mechanisms can be proposed for the coincidence observed for the ions with m/z = 15 amu/q (CH_3^+) and m/z = 61 amu/q ($C(O)SH^+$). The coincidence appears as a narrow diagonal peak with the expected slope value of −1.

$$CH_3C(O)SH^{2+} \rightarrow CH_3^{\ +} + C(O)SH^+$$

Three- and Four-Body Fragmentations. A coincidence of m/z = 15 amu/q (CH_3^+) with m/z = 33 amu/q (SH^+) is observed in the Figure 9 with an experimental slope of −1.9, in very close agreement with the value of −1.84 predicted for the sequential step with an initial charge separation or secondary decay (SD)[35] mechanism:

$$CH_3C(O)SH^{2+} \rightarrow CH_3^{\ +} + C(O)SH^+$$

$$C(O)SH^+ \rightarrow CO + SH^+$$

Coincidences between CH_x^+ (x = 0, 1, 2) and SH^+ show slight changes in the slope when the hydrogen loss increases. This fact might evidence that the mechanisms involved in the formation of CH_x^+ (x = 0, 1, 2) ions can be sequential via the

CH_3^+ ion formed in the very first step. Thus, four-body ion-pair processes[36] need to be invoked to explain the coincidence between CH_2^+ and SH^+ ions. Indeed 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.

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 Figure 9). 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 is more intense in the PEPIPICO spectra obtained around the O 1s energy region. As mentioned previously, ions with an m/z ratio of 24 (CC^+), 25 (CCH^+), and 26 (CCH_2^+) amu/q appear in the O 1s PEPICO spectrum at resonance values. Further analysis of a PEPIPICO spectrum obtained at 529.2 eV reveals the presence of low-intensity islands for these ions in coincidence with those arriving at times corresponding to ions with $m/z = 16$ amu/q (O^+, S^{2+}) and also with S^+ and SH^+ ions. The former coincidences are also shown in Figure 9. The occurrence of complex mechanisms should lead to the formation of these ions. Nevertheless, it is clear that the rupture of the C═O double bond takes place effectively in these dissociation events.

Conclusions

The inner shell S 2p and O 1s electronic regions of thioacetic acid ($CH_3C(O)SH$) have been studied by using tunable synchrotron radiation. Total ion yield (TIY) spectra were measured, and the equivalent-core approximation was employed in order to estimate ionization transition values. A rather complex behavior occurs at resonant energies below the S 2p ionization edge for −SC(O)− containing compounds. Electronic transitions to vacant orbitals, spin−orbit splitting of S 2p term on ionized species, and further processes such as autoionization or transitions involving Rydberg levels could be determined in this region.[18]

Time-of-flight PEPICO and PEPIPICO multicoincidence techniques were applied around both the S 2p and O 1s transition edges. 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. Beside the H^+ ion, at the S 2p excitation edge the main observed ions are CH_3CO^+, SH^+, S^+, and CH_3^+. On the other hand, at the O 1s region 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. This finding can be related with evidences for the occurrence of a site-specific fragmentation in $CH_3C(O)SH$, the first presented for carbonylsulfenyl molecules.

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- and three-body processes, the later via a secondary decay sequential dissociation mechanism, were proposed. 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.

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