

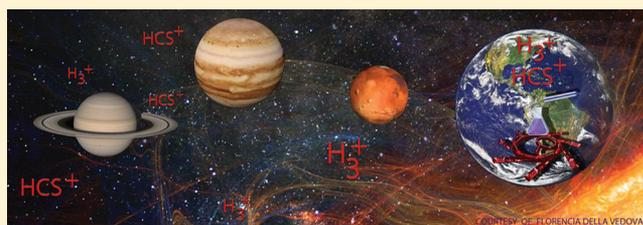
Interstellar H_3^+ and HCS^+ Ions Produced in the Dissociative Photoionization Process of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ in the Proximity of the Sulfur 2p, Carbon 1s, and Oxygen 1s Edges

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ABSTRACT: In this work we present a study of the dissociative photoionization of *S*-methyl thioacetate [$\text{CH}_3\text{C}(\text{O})\text{SCH}_3$] by using multicoincidence time-of-flight mass spectrometry and synchrotron radiation in the S 2p, C 1s, and O 1s edges. Total and partial ion yield spectra together with photoelectron–photoion coincidence (PEPICO) and photoelectron–photoion–photoion coincidence (PEPIPICO) spectra were measured. Fragmentation patterns deduced from PEPICO and PEPIPICO spectra at the various excitation energies show a moderate site-specific fragmentation. The dissociation dynamic for the main ion-pair production is discussed. Two-, three-, and four-body dissociation channels have been observed in the PEPIPICO spectra, and the dissociation mechanisms are proposed. The interstellar HCS^+ and H_3^+ ions can be observed during the synchrotron experiments reported in the present work.



INTRODUCTION

As part of a general project to study the shallow and core–shell electronic excitation and fragmentation dynamics in sulfenyl-carbonyl compounds with general formula $\text{XC}(\text{O})\text{SY}$, the species $\text{FC}(\text{O})\text{SCL}$, $\text{ClC}(\text{O})\text{SCL}$, $\text{CH}_3\text{C}(\text{O})\text{SH}$, $\text{CH}_3\text{OC}(\text{O})\text{SCL}$, $\text{FC}(\text{O})\text{SCH}_3$, and $\text{ClC}(\text{O})\text{SCH}_2\text{CH}_3$ have been studied by using multicoincidence techniques based on time-of-flight mass spectrometry and synchrotron radiation in the 12–1000 eV range as the photon source.^{1–7}

Total ion yield (TIY) and partial ion yield (PIY) spectra and multicoincidence spectra (photoelectron–photoion coincidence, PEPICO, and photoelectron–photoion–photoion coincidence, PEPIPICO) were measured around the S 2p, Cl 2p, C 1s, O 1s, and F 1s transitions of the sulfenylcarbonyl compounds mentioned before. Concerning the photofragmentation dynamics of both halogencarbonylsulfenyl chlorides, $\text{XC}(\text{O})\text{SCL}$ ($X = \text{F}, \text{Cl}$), 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. On the other hand, in a similar experimental study carried out for $\text{CH}_3\text{C}(\text{O})\text{SH}$, $\text{CH}_3\text{OC}(\text{O})\text{SCL}$, and $\text{FC}(\text{O})\text{SCH}_3$, a moderate site-specific fragmentation has been observed. Furthermore, the dissociation dynamic for the main ion-pair production has also been discussed. Thus, 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.^{1–7}

In the present work, we report a study of the photon impact excitation and ionization dissociation dynamics on another member of the carbonylsulfenyl family, namely, *S*-methyl thioacetate, $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$. Very recently, we have succeeded in analyzing the electronic structure and the ionic dissociation induced by photon absorption in the outermost valence region of the sulfenylcarbonyl compounds by using a combined experimental approach that includes HeI photoelectron spectroscopy and photoionization under the action of synchrotron radiation in the 12–21.5 eV region.^{8,9} In particular, for the title molecule, a significant feature is the observation of vibrationally resolved progressions in the valence synchrotron photoionization process, being associated with wavenumbers of 912, 671, 1288, 1690, and 1409 cm^{-1} for the bands at 12.82, 13.27, 15.66, 15.72, and 17.42 eV, respectively.¹⁰ Evaluation of the PE spectrum in concert with the synchrotron photoionization measurements and complemented by high-level ab initio calculations thus provides unusually detailed insights into the valence ionization processes of this molecule. In addition, the incidence of these low-energy photons causes the ionization of the molecule, and together with the molecular ion, a series of

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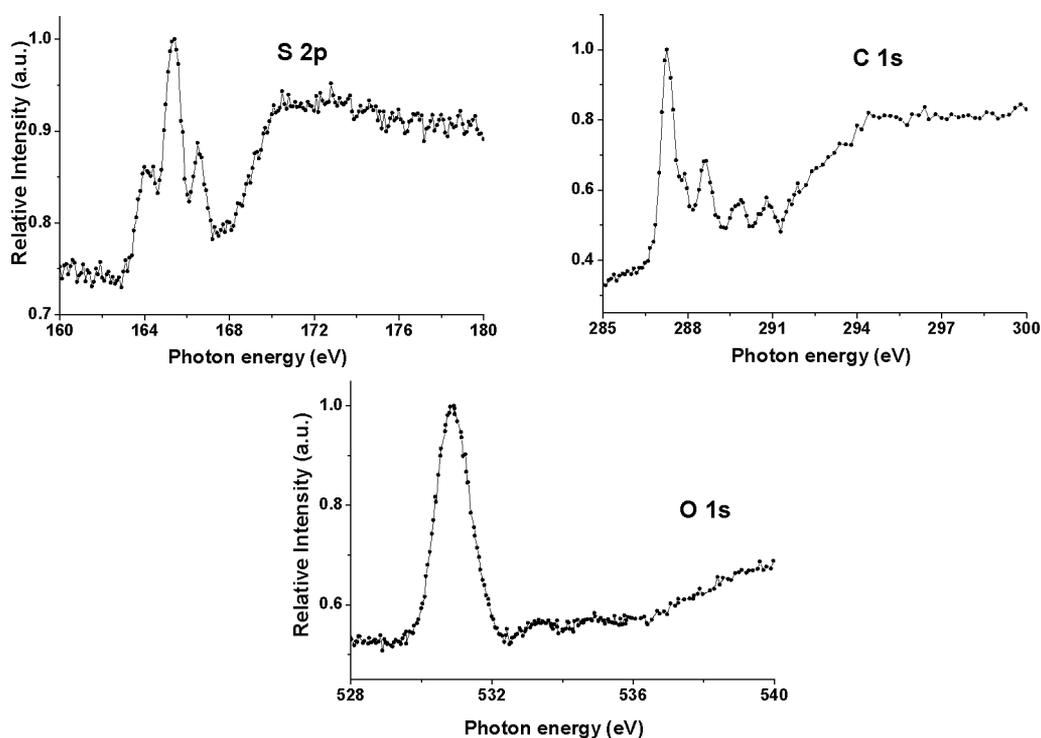


Figure 1. TTY spectra of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ measured in the 160–180 eV range (S 2p region), in the 285–300 eV range (C 1s region), and in the 528–540 eV range (O 1s region).

fragmentation channels are opened, mainly leading to the formation of CH_3CO^+ , OCS^+ , CO^+ , CH_3^+ , CH_3S^+ , and S^+ ions.

The main goal of the present study is to obtain evidence regarding the electronic transitions throughout the whole region of the S 2p, C 1s, and O 1s core edges as well as the ionic dissociation mechanisms following the electronic relaxation of the core excited *S*-methyl thioacetate. The methodology includes the use of multicoincidence time-of-flight mass spectroscopy (TOF-MS) techniques and tunable synchrotron radiation. Thus, fragmentation patterns deduced from PEPICO spectra at various excitation energies in the vacuum ultraviolet and soft X-ray regions were especially analyzed in order to establish the existence of site- and element-specific fragmentation effects.^{11,12} Also, ionic double coincidences were examined, and dissociation mechanisms were proposed to explain the shape and slope of observed PEPICO islands.

EXPERIMENTAL SECTION

Synchrotron radiation was used at the Laboratório Nacional de Luz Síncrotron (LNLS), Barão Geraldo, Campinas, São Paulo, Brazil.^{13–15} Linearly polarized light monochromatized through a toroidal grating monochromator (available at the TGM beamline in the range 12–300 eV), with resolving power of $\Delta E/E < 400$, to excite the region of S 2p, and a spherical grating monochromator (available at the SGM beamline in the range 200–1000 eV) with $\Delta E/E < 200$, to excite the region of C 1s and O 1s, intersects the effusive gaseous sample inside a high vacuum chamber, with base pressure in the range 10^{-8} mbar.^{16–18} During the experiments the pressure was maintained below 2×10^{-6} mbar. The intensity of the emergent beam was recorded with 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 mass

spectrometer of the Wiley–McLaren type for both PEPICO and PEPICICO measurements. This instrument was constructed at the Institute of Physics, Brasília University, Brasília, Brazil.^{19–22} 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 multi-channel 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 *S*-methyl thioacetate [$\text{CH}_3\text{C}(\text{O})\text{SCH}_3$] was obtained from a commercial source (Aldrich, estimated purity better than 95%). The liquid was purified by repeated trap-to-trap condensations at reduced pressure in order to eliminate volatile impurities. The final purity of the compound in both the vapor and liquid phases was carefully checked by reference to the following spectra: IR (vapor), Raman (liquid), and ^{13}C NMR (liquid).^{23–25} No impurities have been detected using these techniques, and a purity higher than 98% should be expected for this reason.

RESULTS AND DISCUSSION

Total Ion Yield Spectra. TTY 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 the absorption spectroscopy.²⁶ The TTY spectra of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ measured near the S 2p, C 1s, and O 1s edges are shown in Figure 1. The tentative assignments of the principal bands observed in the TTY spectra measured in this work were made assisted by the computed

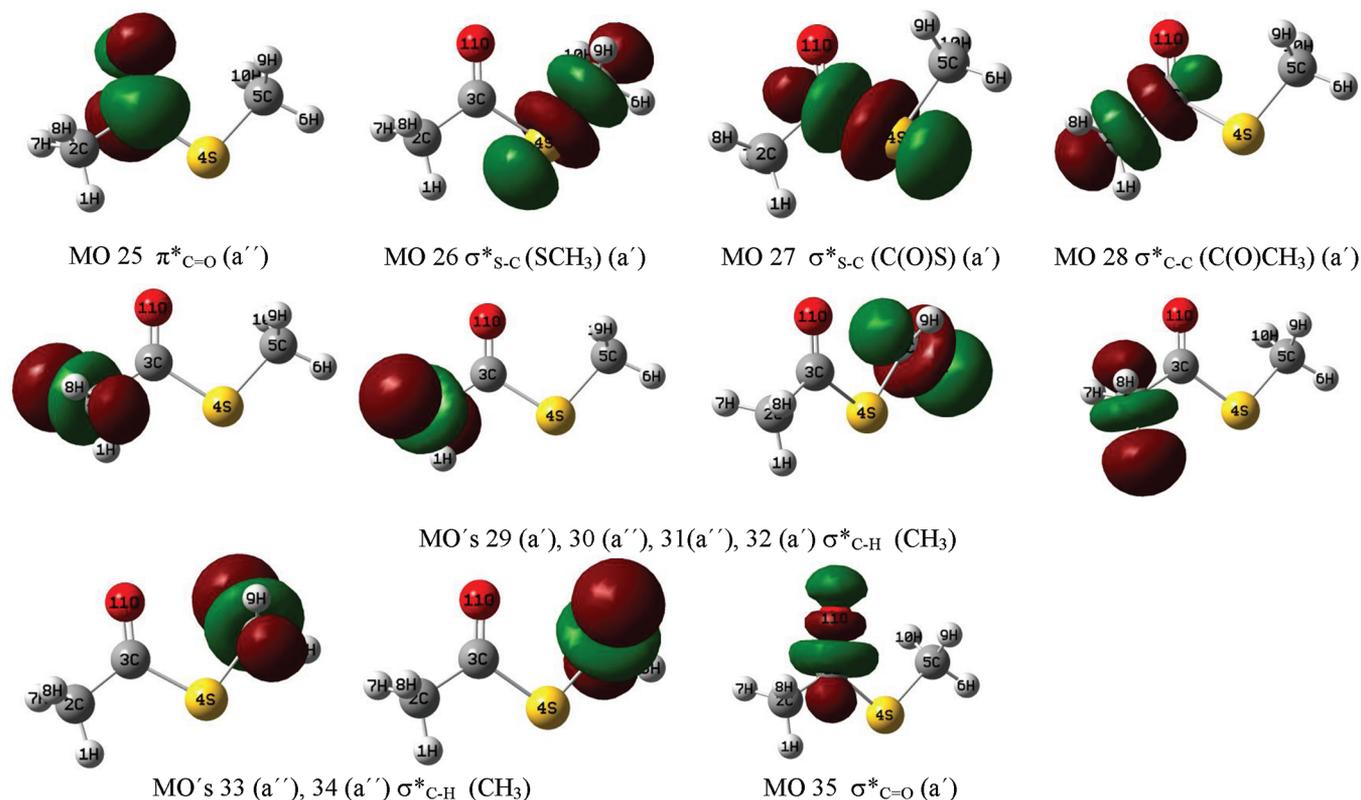


Figure 2. Characters of the eleven lower energy unoccupied molecular orbitals for $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ calculated at the B3LYP/6-311++G (d,p) level of approximation.

unoccupied orbitals and by comparison with relevant examples reported in the literature.

The *S*-methyl thioacetate molecule in the ground electronic state belongs to the C_s symmetry point group. Then, for further references, all canonical molecular orbitals of type a' are σ -orbitals lying in the molecular plane, while those of type a'' are π -orbitals. In the ground state, the 30 valence electrons are arranged in 15 double-occupied orbitals in the independent particle description. Quantum chemical calculations at the B3LYP/6-311++G(d,p) level of approximation using the Gaussian 03 program package²⁷ for neutral $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ in its ground state compute that the LUMO correspond to a $\pi^*_{\text{C}=\text{O}}$ (a') orbital with antibonding character. The next vacant orbitals correspond to the antibonding $\sigma^*_{\text{S}-\text{C}}$ (CH_3S) (a'), $\sigma^*_{\text{S}-\text{C}}$ [$\text{C}(\text{O})\text{S}$] (a'), and $\sigma^*_{\text{C}-\text{C}}$ [$\text{C}(\text{O})\text{CH}_3$] (a'). Six antibonding orbitals with similar energies attributed as $\sigma^*_{\text{C}-\text{H}}$ localized in the CH_3 groups and a $\sigma^*_{\text{C}=\text{O}}$ (a') complete the antibonding molecular orbital representation expected for $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ (see Figure 2).

Below the S 2p threshold, located at approximately 171.0 eV, the spectrum is dominated by a group of well-defined peaks centered at 164.0, 165.4, and 166.5 eV (Figure 1).

These resonant transitions observed in the TIY spectra were tentatively assigned to the electronic transitions involving the spin-orbit split of the 2p sulfur excited species ($2p_{1/2}$ and $2p_{3/2}$ levels) mainly to the most lower unoccupied π^* and σ^* antibonding orbitals.

A similar behavior was observed for other $-\text{SCO}-$ containing compounds previously studied.¹⁻⁷ A rather complex feature at resonant energies below the S 2p ionization edge seems to be systematic in the sulfonylcarbonyl compounds.

The TIY spectrum in the C 1s region (Figure 1) is dominated by an intense band at around 287.2 eV and other low-intensity bands could be observed. From this spectrum, the C 1s threshold is estimated to be 294.5 eV for the title molecule. Although three nonequivalent carbon atoms are present in $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$, we were not able to assign the spectra steaming from these different excitation sites. Possibly, the most intense signal observed in this energy range is associated with the excitation of the 1s C ($\text{C}=\text{O}$) toward the vacant π^* antibonding orbital, because the carbon atoms of saturated hydrocarbons show mainly Rydberg transitions, the intensities of which are in general 1 order of magnitude lower than excitations to the π^* antibonding orbital.²⁸ The features observed in the TIY spectrum are compatible with previous recently analyzed data obtained for the related molecule $\text{FC}(\text{O})\text{SCH}_3$.⁶

On the other hand, the TIY spectrum measured in the vicinity of the O 1s (Figure 1) is dominated by an intense resonance located at 530.9 eV, whereas the O 1s threshold is located at approximately 539.0 eV. A low-intensity signal is also observed at 533.5 eV. In this case, the O 1s $\rightarrow \pi^*$ (530.9 eV) transition dominates this region. As has been reported for other carbonyl compounds,²⁹ electronic excitations to vacant antibonding $\pi^*_{\text{C}=\text{O}}$ and $\sigma^*_{\text{C}=\text{O}}$ orbitals may be associated with the signals observed at 530.9 and 533.5 eV, respectively. In a similar way, for the analogous sulfonylcarbonyl compounds previously reported, the TIY spectra around the O 1s region are also dominated by an intense resonance and by a second signal with much smaller intensity than in the present case.¹⁻⁷

The S 2p, C 1s, and O 1s ionization energies for $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ extracted from the TIY spectra were compared with those predictions based on the equivalent-core approx-

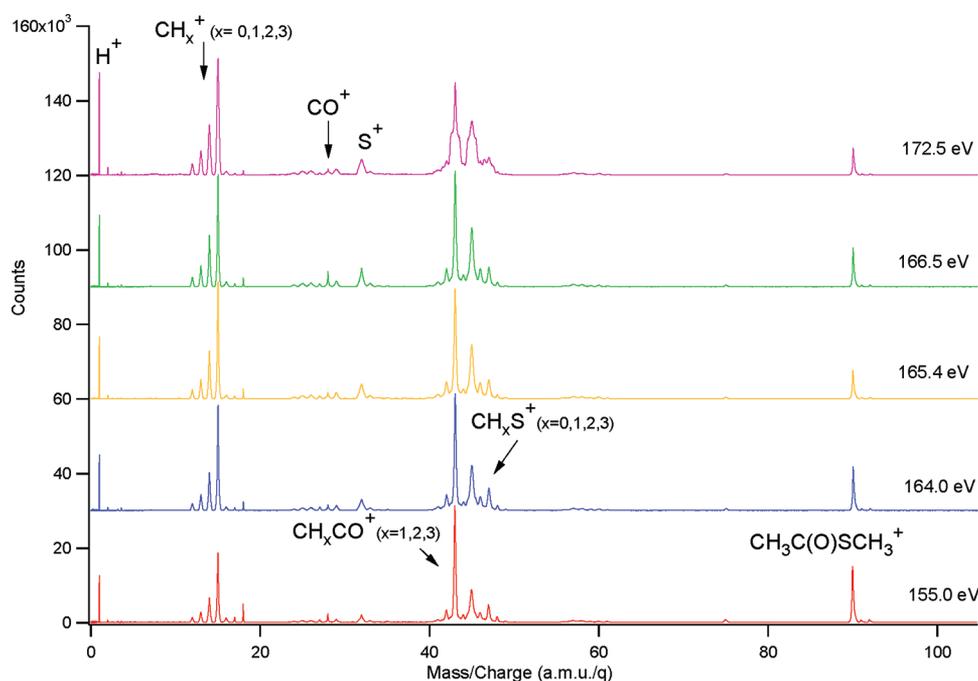


Figure 3. PEPICO spectra of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ recorded at selected irradiation energies around the S 2p edge together with a fragment assignment of the bands: off resonance at 155.0 eV; on resonances at 164.0, 165.4, and 166.5 eV; and above threshold at 172.5 eV.

Table 1. Branching Ratios (%) for Fragment Ions Extracted from $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ PEPICO Spectra Taken at Photon Energies around the S 2p, C 1s, and O 1s Edges

ion	photon energy (eV)								
	155.0	165.4	172.5	277.0	287.3	337.0	521.0	530.8	540.0
H^+	7.3	7.1	8.8	18.0	16.0	21.6	24.0	20.0	22.0
H_2^+	0.6	0.6	0.9	1.5	1.1	1.5	1.5	1.2	1.4
C^+	1.6	1.8	1.8	3.5	3.1	4.1	4.6	3.8	4.3
CH^+	3.0	3.8	3.8	5.6	5.4	6.4	6.3	5.6	6.1
CH_2^+	6.5	9.0	7.9	9.2	9.7	9.8	9.3	9.1	9.3
CH_3^+	14.0	19.0	17.1	14.0	14.0	12.0	11.0	13.0	12.0
O^+/S^{2+}	1.6	0.9	0.9	1.2	1.0	1.2	1.4	1.4	1.4
C_2^+	0.8	0.6	0.7	1.3	1.0	1.4	1.5	1.4	1.5
C_2H^+	1.0	1.1	1.1	1.6	1.5	1.8	1.8	1.9	1.8
C_2H_2^+	1.0	1.1	1.1	1.2	1.3	1.3	1.2	1.7	1.3
C_2H_3^+	0.7	0.6	0.4	0.4	0.6	0.4	0.4	0.7	0.5
$\text{CO}^+/\text{C}_2\text{H}_4^+$	1.2	1.1	1.0	1.4	1.1	1.3	1.3	1.1	1.3
$\text{HC}(\text{O})^+/\text{C}_2\text{H}_5^+$	0.6	0.7	0.7	1.5	1.4	1.5	1.4	1.3	1.4
S^+	2.5	3.9	3.6	5.9	4.6	5.6	6.0	5.0	5.6
SH^+	0.8	0.9	0.9	0.8	0.9	0.9	0.9	0.9	0.9
$\text{CHC}(\text{O})^+$	1.0	1.0	1.0	1.1	1.3	1.2	1.2	1.1	1.2
$\text{CH}_2\text{C}(\text{O})^+$	2.8	3.2	2.5	2.8	3.5	2.8	2.8	2.9	2.8
$\text{CH}_3\text{C}(\text{O})^+$	19.2	17.4	17.8	11.0	11.0	7.8	7.3	7.0	7.1
CS^+	1.7	1.6	1.7	1.3	1.7	1.6	1.6	1.6	1.5
HCS^+	11.3	12.4	14.6	10.0	12.0	10.2	9.6	11.0	10.0
CH_2S^+	2.5	2.9	2.4	1.9	2.5	1.7	1.6	2.3	1.7
CH_3S^+	4.0	3.6	3.8	2.2	2.4	1.6	1.4	2.2	1.5
CH_3SH^+	1.0			0.2	0.4	0.2	0.2	0.3	0.2
$\text{C}_2\text{H}_4\text{C}(\text{O})^+$				0.2	0.3	0.3	0.3	0.4	0.4
$\text{C}_2\text{H}_5\text{C}(\text{O})^+$	1.0	0.6	0.6	0.4	0.8	0.5	0.5	1.1	0.6
$(\text{CH}_3)_2\text{C}(\text{O})^+$				0.2	0.6	0.3	0.3	0.9	0.3
OCS^+				0.1	0.2	0.2	0.2	0.2	0.2
$\text{C}(\text{O})\text{SCH}_3^+$	0.7				0.1	0.05	0.07	0.09	0.08
$\text{CH}_3\text{C}(\text{O})\text{SCH}_3^+$	5.9	2.1	1.5	0.5	0.3	0.2	0.3	0.3	0.3

imation taking OCS as the reference compound for both ionization energies.^{30–33}

This approximation has been shown to give a good description for carbonyl compounds.^{34,35} Thus, the calculated

(UB3LYP/6-311++G**) S 2p, C 1s, and O 1s binding energies for $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ are 172.0, 297.0, and 543.1 eV, respectively.

PEPICO Spectra. Several PEPICO spectra obtained with photon energies that include the most important S 2p, C 1s, and O 1s transitions of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ have been recorded. In order to identify the role of resonant processes in the fragmentation, the spectra were also measured at photon energy values below (typically 10 eV) and above (typically 50 eV) the ionization edge.

The PEPICO spectra taken at representative photon energies near the S 2p edge of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ are shown in Figure 3. In Table 1 the corresponding branching ratios are gathered for the main fragment ions. Furthermore, the PIY spectra were obtained in the 161–181 eV range (S 2p region) by recording the count rates of selected ions while the photon energy is scanned in steps of 0.2 eV (Figure 4). In these PIY spectra, each point corresponds to one time-of-flight spectrum measured at this defined photon energy. The intensity of each ionic fragment is determined through the TOF spectrum, by counting all ions in a specific time window and normalizing it

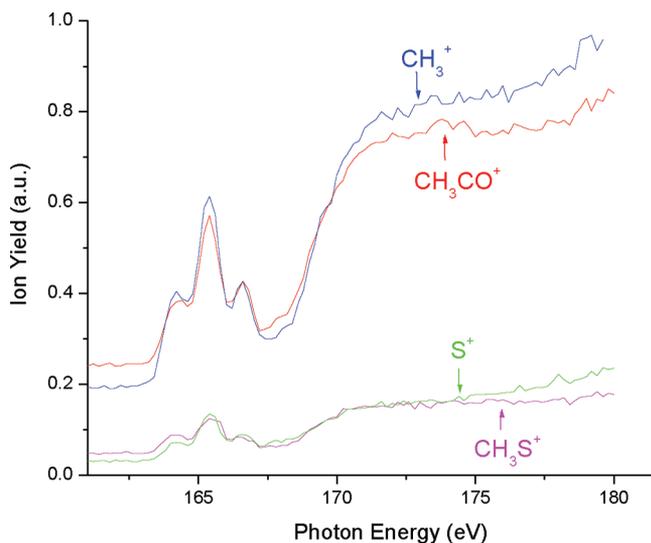


Figure 4. PIY spectra for the selected ions CH_3^+ , CH_3CO^+ , S^+ , and CH_3S^+ of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ acquired in the 161–181 eV range (S 2p region) by recording the count rates of selected ions while the photon energy is scanned in steps of 0.2 eV.

by the photon flux. These spectra were normalized by the photon flux. The PIY spectra for the main single charged ions simply mimic the TIY spectra around the S 2p region.

The calculated (UB3LYP/6-31+G*) adiabatic ionization energy value for the double-charged cationic form reaches a value of 25.1 eV. As observed in the TIY spectra, this energy is not yet enough to ionize the S 2p shallow-core electrons. 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. Thus, the coincidence spectrum excited with 155.0 eV photon energy should provide a good reference with respect at the sulfur 2p region. A strong signal at $m/z = 43$ amu/q, corresponding to the acetyl ion $\text{CH}_3\text{C}(\text{O})^+$, dominates the mass spectrum at 155.0 eV. The other peaks with appreciable intensities observed in that spectrum correspond to the CH_3^+ and HCS^+ ions, with

relative abundances of 14 and 11% respectively. The H^+ ion is also present with an intensity of 7%. The CH_x^+ ($x = 2, 1$, and 0), CH_xS^+ ($x = 3, 2$, and 0), and $\text{CH}_x\text{C}(\text{O})^+$ ($x = 2$ and 1) fragments are also observed with smaller relative intensity than the principal ions of that series CH_3^+ , HCS^+ , and CH_3CO^+ , respectively. The molecular ion can be observed at this energy with an intensity of 5%. Signals from the CO^+ ($m/z = 28$) and S^+ ($m/z = 32$) ions also appear in this spectrum, showing relative abundances on the order of 1 and 2.5%, respectively.

A weak band at $m/z = 75$ amu/q is also observed. This signal is assigned to the loss of a CH_3 group from the parent molecular ion ($M^+ - 15$). The resulting ion may originate from the rupture of either the C– CH_3 or the S– CH_3 single bond of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$. Thus, processes that involve excitations to the corresponding $\sigma_{\text{C-C}}^*$ and $\sigma_{\text{S-C}}^*$ antibonding orbitals, respectively, can be suggested.

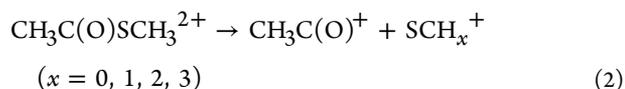
The diminution of the intensity of the single-charged molecular ion at increasing incident photon energies can be noticed, reaching values of 1.5% around the S 2p edge.

Higher photon energies also favor the formation of CH_3^+ being the most abundant ion at 165.4 eV (see Figure 4). Together with this enhancement a diminution in the signal intensity of $\text{CH}_3\text{C}(\text{O})^+$ can be observed. A small increment in the intensity of the $m/z = 45$ amu/q ion signal at increasing incident photon energies can also be noticed.

A signal for the atomic hydrogen ion appears in these spectra around the S 2p region having relative intensities between 7 and 9%. However, it may be feasible that this ion cannot be completely collected, since it is ejected in all directions with high energy values. Therefore, the branching ratio values for H^+ should be taken as tentative. This ion could be formed by ionization of both methyl groups of the molecule. A signal for the H_2^+ ion also appears in these spectra, having weak relative intensity (<1% approximately). This fragment is a typical signature of processes involving rearrangement reactions.³⁶

A group of signals also appears at $m/z = 24, 25, 26$, and 27 amu/q, having branching ratios of about 1%. They could originate from the ions C_2^+ , C_2H^+ , C_2H_2^+ , and C_2H_3^+ , respectively. In the previously reported $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ molecule, the PEPICO spectra also reveal the production of these last fragments. The presence of the C_2H_n^+ species was also revealed in the ionic fragmentation of acetone studied using monochromatic soft X-rays and the TOF mass spectrometer.³⁷

In addition, changes in the TOF spectral shape of the $m/z = 43$ peak at increasing incident photon energies can also be noticed (Figure 5). It is well-established that the analysis of ion peak shapes from a PEPICO spectrum provides information concerning fragment ion kinetic energies.³⁸ In the m/z spectra the width of a specific fragment is related to the kinetic energy release (U_0); at 172.5 eV we observed a double kinetic energy distribution (U_{01} and U_{02}) that could be rationalized in terms of an ionic generation from both singly and doubly charged molecular ion according to eqs 1 and 2:



Ions that originated in the process given by eq 1 should have a more narrow distribution of kinetic energies than those arising from eq 2. When the photon energy is increased, the second dissociation channel is enhanced and a broad peak is

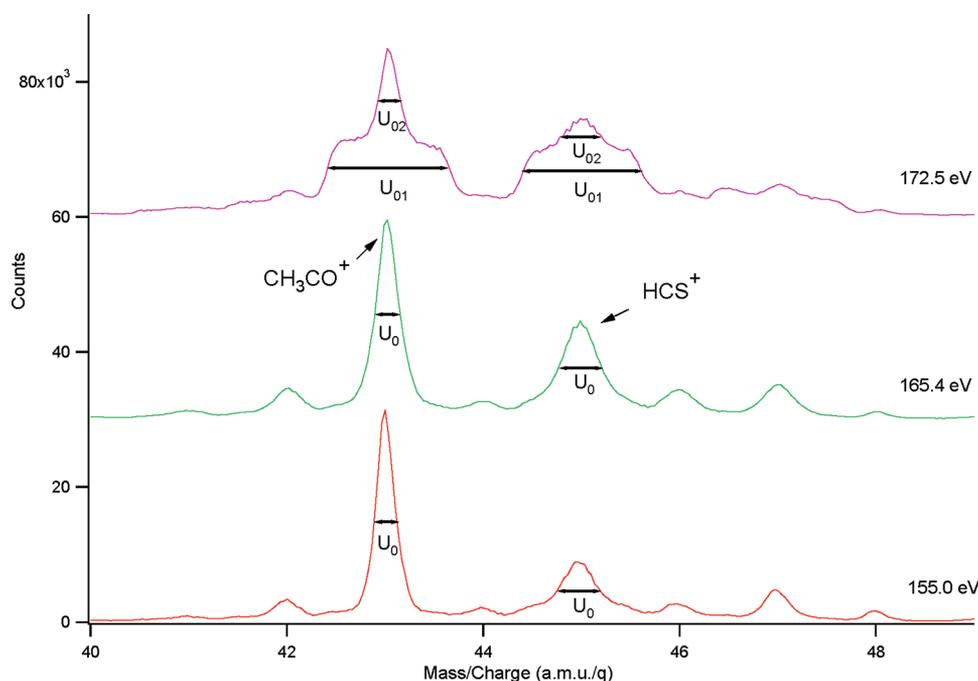


Figure 5. Part of the PEPICO spectra of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ acquired around the S 2p edge showing the enlargement of the peaks in the range of m/z 40–49 amu/ q : off resonance at 155.0 eV (bottom), on resonance at 164.0 eV (center), and above threshold at 172.5 eV (top). U_0 denotes the kinetic energy release; U_{01} and U_{02} correspond to the double kinetic energy distribution (see the text).

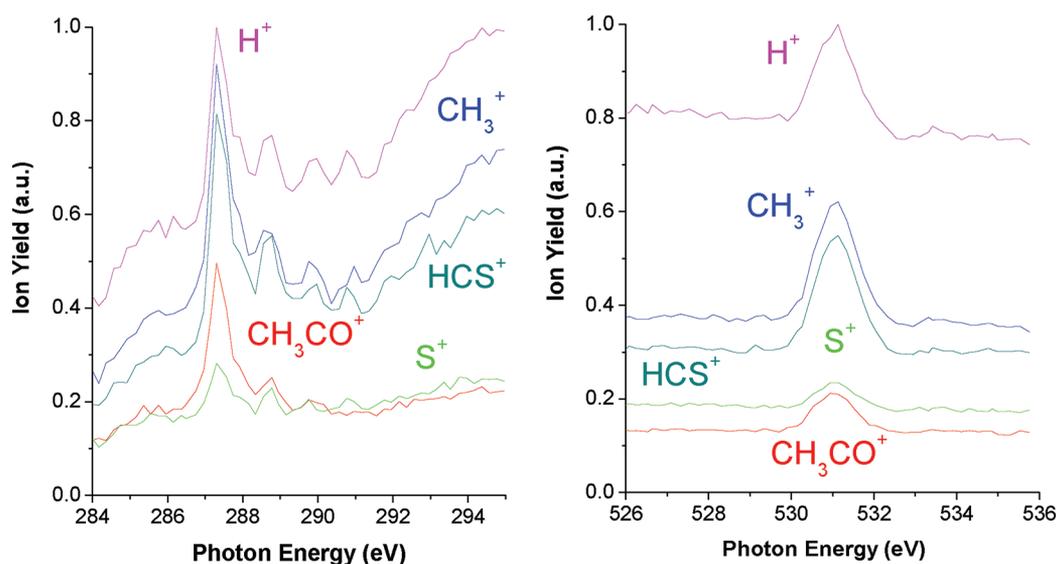


Figure 6. PIY spectra for the following ions H^+ , CH_3^+ , CH_3CO^+ , S^+ , and HCS^+ of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ in the 284–295 eV range (C 1s region) and 526–536 eV range (O 1s region).

observed for this ion. In effect, as will be explained later, the analysis of PEPICO spectra around the S 2p reveals the presence of some islands for the $\text{CH}_3\text{C}(\text{O})^+$ ions in coincidence with CH_xS^+ fragments, having the highest intensities at 172.5 eV. The same behavior was observed for the HCS^+ fragment.

The PIY spectra were obtained in the 284–295 eV range (C 1s region) by recording the count rates of selected ions while the photon energy is scanned in steps of 0.2 eV (Figure 6).

The most intense peak in the PIY spectra is observed at $m/z = 1$ (H^+) amu/ q , followed by the signals at 15 (CH_3^+) and 45 (HCS^+) amu/ q , respectively. The other strong signal in the PIY spectra corresponds to the CH_3CO^+ ion. The peak at 75 amu/ q ($\text{M}^+ - 15$) vanishes when the photon energy reaches these high

energies. Also in this case, the PIY spectra simply mimic the TIY spectra for the main single charged ions.

Partial ion yield spectra for selected $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ ions were also recorded around O 1s ionization edge (Figure 6). The fragmentation patterns at the C and O 1s edges seem to be basically identical. That is, the atomic hydrogen ion is again the most abundant fragment, and the next most abundant ions are CH_3^+ and HCS^+ , respectively.

A diminution in the intensity of the signal at $m/z = 43$ amu/ q [$\text{CH}_3\text{C}(\text{O})^+$], from 11% near the C 1s edge to 7% near the O 1s edge, can be observed. Near the S 2p edge, this fragment intensity is approximately 18%, the second most abundant ion. The molecular ion at $m/z = 90$ amu/ q can still be observed at

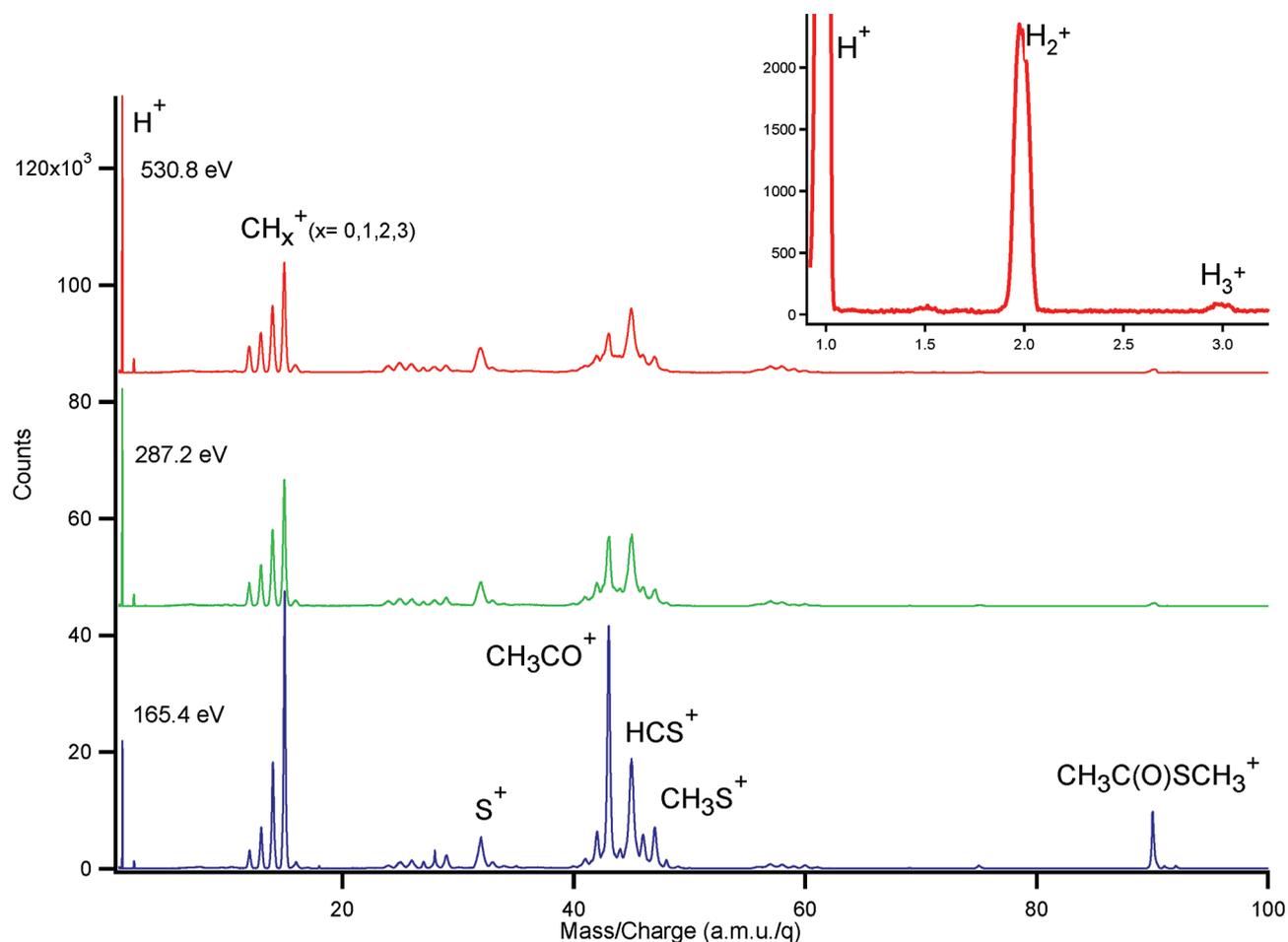


Figure 7. PEPICO of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ recorded at resonant S 2p (bottom), C 1s (middle), and O 1s (top) edge absorptions showing the assignments of the bands. The inset shows an enlargement of the mass/charge region of the PEPICO spectrum at 530.8 eV for the H_n^+ ($n = 1, 2, 3$) ions.

these high energies (C and O 1s regions) as a very low intensity signal (<0.5%).

The analysis of the PEPICO spectra of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ over the whole range of photon energies analyzed here reveals a preferential production of HCS^+ ions, while signals corresponding to ionic fragments CS^+ , CH_2S^+ , and CH_3S^+ appear as less intense bands. The thioformyl ion has been also constantly observed in the ionic fragmentation of other sulfur compounds having a methyl group attached to the sulfur atom as $\text{ClC}(\text{O})\text{SCH}_3$,¹⁰ CH_3SCN ,³⁹ and the last molecule analyzed, $\text{FC}(\text{O})\text{SCH}_3$.⁶

This behavior is opposite to that observed for the group of CH_x^+ ($x = 2, 1, \text{ and } 0$) and $\text{CH}_x\text{C}(\text{O})^+$ ($x = 2 \text{ and } 1$) fragments, where these ions are observed in the S 2p, C 1s, and O 1s regions, with smaller relative intensity than the principal ions of that series, CH_3^+ and $\text{CH}_3\text{C}(\text{O})^+$, respectively.

It should be noted that only a singly charged molecular ion can produce CH_3S^+ from ionized $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ by the rupture of the C–S bond involving the carbonyl carbon atom. Thus, a process involving excitations to the corresponding $\sigma_{\text{C-S}}^*[\text{C}(\text{O})\text{S}]$ antibonding orbital can be suggested. In effect, even the whole remaining group $\text{CH}_3\text{C}(\text{O})$ is lighter than SCH_3 and should be detected in the PEPICO spectra instead of CH_3S^+ . The prominent features observed by going from S 2p to the O 1s region are a clear increase in the peak intensity corresponding to the ion H^+ (from 7% near the S 2p edge to

22% near the O 1s edge) together with the diminution of the $\text{CH}_3\text{C}(\text{O})^+$ fragment, as we mentioned before, and the slightly decrease of the signal corresponding to the CH_3^+ ion (from 19% at 165.4 eV to 13% at 530.8 eV). In concert with the diminution of the methyl ion, an enhancement in the signal intensity of other methyl fragments CH_x^+ ($x = 2, 1, \text{ and } 0$) can also be noticed by going from S 2p to the O 1s region. Furthermore, a small increment in the peak intensities, corresponding to the atomic ion S^+ , is observed by going toward higher energies. This evidence can be related with the occurrence of a moderate site-specific fragmentation in $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$.

For the sake of comparison, Figure 7 shows the PEPICO spectra of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ obtained at resonant S 2p, C 1s, and O 1s energies.

In addition, it is important to mention that in the PEPICO spectra of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ taken over the whole range of photon energies analyzed here, peaks appearing at $m/z = 3$ amu/ q were observed with a very weak relative intensity (<0.1%) (see Figure 7). The formation of H_3^+ is quite remarkable since three C–H bonds of the CH_3 moiety have to be broken and three new H–H bonds have to be formed. The H_3^+ molecular ion consists of three protons bounded by two electrons in an equilateral triangle structure as initially shown theoretically by Coulson.⁴⁰ Protonated molecular hydrogen, H_3^+ , is the simplest polyatomic molecule. It is the most

Table 2. Relative Intensities for Double Coincidence Islands Derived from the PEPICO Spectra of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ as a Function of the Photon Energy

ion 1	ion 2	photon energy (eV)						
		155.0	165.4	172.5	287.2	337.0	530.8	540.0
H ⁺	C ⁺	4.7	4.7	2.9	6.7	7.1	7.7	9.0
H ⁺	CH ⁺	6.1	6.1	3.7	6.7	7.3	6.5	7.5
H ⁺	CH ₂ ⁺	7.6	6.8	4.4	6.2	6.4	5.4	6.3
H ⁺	CH ₃ ⁺	2.8	3.5	2.4	2.7	2.9	2.4	2.6
H ⁺	O ⁺				1.5	1.6	2.2	2.3
H ⁺	CC ⁺				2.2	2.3	2.6	2.8
H ⁺	CCH ⁺				1.9	1.9	2.1	2.1
H ⁺	CO ⁺				1.0	1.3	1.1	1.3
H ⁺	S ⁺	4.3	5.4	3.2	6.7	7.1	7.1	8.2
H ⁺	CH ₂ C(O) ⁺	1.7	1.8	1.6	1.9	1.8	1.4	1.8
H ⁺	CH ₃ C(O) ⁺		1.6	2.0	1.9	2.1	1.8	2.2
H ⁺	CS ⁺	4.2	2.8	2.2	2.5	2.5	2.3	2.5
H ⁺	HCS ⁺	10.4	7.2	6.5	6.7	7.0	5.9	6.8
H ⁺	CH ₂ S ⁺			1.0				
C ⁺	S ⁺					1.0		1.0
CH ⁺	CH ₂ ⁺	1.5	1.9	1.3	1.1	1.1	1.0	
CH ⁺	CH ₃ ⁺		1.7					
CH ⁺	S ⁺		1.5		1.7	2.0	1.8	1.8
CH ⁺	HCS ⁺	1.6	1.8	1.5	1.5	1.5	1.6	1.3
CH ₂ ⁺	CH ₃ ⁺	6.4	5.8	4.4	2.7	2.1	1.9	2.1
CH ₂ ⁺	S ⁺		3.3	1.7	2.9	3.0	2.7	2.7
CH ₂ ⁺	CH ₃ C(O) ⁺		1.5					
CH ₂ ⁺	HCS ⁺	4.9	5.0	4.1	3.8	3.4	3.2	3.3
CH ₃ ⁺	O ⁺	7.4		3.5				
CH ₃ ⁺	S ⁺		4.3	2.6	3.1	3.0	2.4	2.5
CH ₃ ⁺	CH ₂ C(O) ⁺		1.1					
CH ₃ ⁺	CH ₃ C(O) ⁺	3.5	5.4	10.2	3.7	3.3	2.2	2.5
CH ₃ ⁺	HCS ⁺	16.8	8.6	9.3	6.0	5.0	4.2	5.8
CH ₃ ⁺	CH ₂ S ⁺	1.3	1.1	1.0	1.0			
CH ₃ ⁺	CH ₃ S ⁺	2.2	1.5	2.1				
CH ₂ C(O) ⁺	HCS ⁺			1.0	1.6	1.3	1.4	1.4
CH ₃ C(O) ⁺	CS ⁺	4.0		1.1				
CH ₃ C(O) ⁺	HCS ⁺	7.3	3.9	11.8	4.9	4.3	2.9	3.5
CH ₃ C(O) ⁺	CH ₂ S ⁺			1.5				
CH ₃ C(O) ⁺	CH ₃ S ⁺			3.1	1.1			

abundantly produced interstellar molecule, next only to H₂, although its steady-state concentration is low because of its extremely high chemical reactivity. H₃⁺ is a strong acid (proton donor) and initiates chains of ion–molecule reactions in interstellar space, thus leading to formation of complex molecules. This ion is the dominant positively charged ion in molecular hydrogen plasmas and was first identified in 1911 by Thomson,⁴¹ using an early form of mass spectrometry. It was recently discovered both in molecular clouds and in the diffuse interstellar medium, and it provides a tool for characterizing Jupiter's atmosphere from afar.^{42,43} Fragmentation of dicationic methyl compounds of the type CH₃X [X = Cl, OH, SH, NH₂, and CH(O)], studied using the PEPICO triple coincidence technique at 30.4 nm, revealed the presence of H₃⁺ by two-body dissociation channels H₃⁺ + CX⁺.⁴⁴

The occurrence of the protonated molecular hydrogen with a low yield was also observed in the 70 eV mass spectra of various organic compounds of diverse types.⁴⁵ The production of H₃⁺ via the photodissociation of interstellar methyl compound organic molecules like methanol, methylamine, and acetonitrile was also studied at the LNLS by using photoelectron–photoion coincidence techniques employing soft X-ray photons.⁴⁶

PEPICO Spectra. Several two-dimensional PEPICO spectra for the correlation between one electron and two positive ions were recorded at several photon energies that include the most important S 2p, C 1s, and O 1s transitions of CH₃C(O)SCH₃. A multicoincidence measurement allows the identification of the various ions produced in the same photoionization event. The analysis of the PEPICO spectra is useful for identifying several two-, three-, and four-body dissociation events which especially follow Auger decay mechanisms.^{47,48}

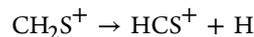
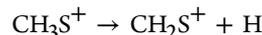
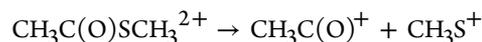
In the case of a rather complex molecule such as CH₃C(O)SCH₃, several islands are expected in the PEPICO spectra, and hence a complete interpretation of the spectra is not straightforward. As a first approximation, in the analysis of the PEPICO spectra the following two aspects were taken into account. Due to the inherent limited resolution used in the experiments, for islands concerning *m/z* values of 16 amu/*q*, the distinction between O⁺ and S²⁺ ions is not always feasible. In addition, the coincidences involving the CH_{*x*}⁺ (*x* = 3, 2, and 1) fragments with others ions can be formed from both methyl groups of the molecule, making its assignment ambiguous in some cases.

Furthermore, the peaks corresponding to double coincidences involving m/z values of 1, 12, and 32 amu/ q are present with a high intensity, reflecting the importance of the atomization processes in the dissociation mechanisms of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$. These processes may be originated by several multibody dissociation events that reduce to the same final pair of atomic ions, making the analysis of these coincidences ambiguous. Taking into consideration these facts, attention is paid to selected pairs of ions for which both good statistics and well-defined shapes are observed. The double coincidence branching ratio for double ion processes calculated from PEPIPICO spectra at several photon energies around S 2p, C 1s, and O 1s ionization edges is given in Table 2.

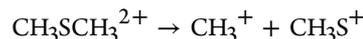
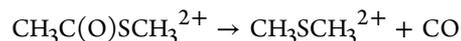
Two-body processes concerning the rupture of the S–C (carbonylic carbon atom) bond to form two single-charged species were observed as the main two-body dissociation channel in $\text{FC}(\text{O})\text{SCI}$,¹ $\text{ClC}(\text{O})\text{SCI}$,³ $\text{CH}_3\text{C}(\text{O})\text{SH}$,⁴ $\text{CH}_3\text{OC}(\text{O})\text{SCI}$,⁵ and $\text{FC}(\text{O})\text{SCH}_3$.⁶ This channel emerges as the general dissociation route for double-charged $\text{XC}(\text{O})\text{SY}$ species excited at inner shell levels. In this case, this fragmentation process leads to the formation of a coincidence between ions with m/z values of 43 amu/ q [$\text{CH}_3\text{C}(\text{O})^+$] and 47 amu/ q (CH_3S^+). Thus, this coincidence appears as a parallelogram-like shape with the expected slope value close to -1.0 (see Figure 8).

The coincidences of the CH_xS^+ ($x = 0, 1, 2$) ions with the $\text{CH}_3\text{C}(\text{O})^+$ ion were also observed, the intensity of the island with $x = 1$ (HCS^+) always being higher than the others, reaching values of ca. 3.9, 4.9, and 2.9% at the most important S 2p, C 1s, and O 1s transitions of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$, respectively. The islands involving the other ions corresponding to the series CH_xS^+ ($x = 0, 2, 3$) are observed as less intense signals in the PEPIPICO spectra. As mentioned before, the contribution of the $\text{CH}_3\text{C}(\text{O})^+/\text{HCS}^+$ coincidence to the double coincidence spectra is observed at S 2p absorption edge (172.5 eV) with larger relative intensity. In particular, the observed slope of

-0.98 for the coincidence between $\text{CH}_3\text{C}(\text{O})^+$ and HCS^+ ions (Figure 8) can be explained by the following four-body secondary decay involving the rupture of the S–C (carbonylic carbon atom) bond in a first step, followed by the loss of neutral hydrogen atoms:



A coincidence between CH_3^+ and CH_3S^+ , with a branching ratio of approximately 2% in the S 2p region and lower than 1% at the others photon energies, is observed with an experimental slope of -1 and can be explained by the following three-body ion pair process, DCS (differed charge separation):



Moreover, the analysis of PEPIPICO spectra reveals the presence of most strong-intensity islands for the CH_3^+ ions in coincidence with HCS^+ . This island was observed over the whole range of photon energies analyzed with a relative abundance higher than 4%, and four-body ion pair processes need to be invoked to explain the coincidence. Indeed, double coincidences involving CH_2^+ and CH^+ fragments with HCS^+ are also observed with a relative abundance between 3 and 5% and values of around 1.5%, respectively. A coincidence between the CH_3^+ ion with $\text{CH}_3\text{C}(\text{O})^+$ can be observed also over the whole range of studied photon energies and showed the highest intensity (10%) at the S 2p threshold. In this case, the fragmentation processes leading to the formation of the lighter fragments CH_3^+ must involve the rupture of the C–S bond of the SCH_3^+ group.

Several coincidences involving the H^+ ion as the lighter fragment such as H^+/CH_x^+ ($x = 0, 1, 2$), $\text{H}^+/\text{CH}_x\text{S}^+$ ($x = 0, 1, 2$), H^+/S^+ , and $\text{H}^+/\text{CH}_x\text{C}(\text{O})^+$ ($x = 0, 1, 2$) are clearly observed in the PEPIPICO spectra measured. Eland has pointed out that this kind of coincidence shows a highly nondiagonal feature, which makes its study difficult. Furthermore, as proposed recently by Montenegro et al., these kinds of processes can be characterized as “evaporation” (eliminating light H^0 neutral atoms) or “fission” (ejecting H^+ ions) or as the molecule breaking up into two or more charged species.⁴⁹

The contour plot obtained from the PEPIPICO spectrum at 530.8 eV for arrival times corresponding to H^+ and fragments with $m/z = 12\text{--}16$ is shown in Figure 9. The existence of two methyl groups in the molecule makes possible that the H^+/CH_3^+ coincidence can be observed in the PEPIPICO spectra, contrary to the observation in the other sulfonylcarbonyl compounds with only one methyl group, where this coincidence is absent, as expected. In addition, in the photofragmentation of $\text{ClC}(\text{O})\text{SCH}_2\text{CH}_3$ molecule with an alkyl chain CH_2CH_3 excited at inner-shell levels, only the progression of the double coincidence series of ions $\text{H}^+/\text{CH}_x\text{CH}_y^+$ ($x, y = 0\text{--}2$) was observed.⁷

The contribution of these islands increases approximately between 15 and 20%, when the C 1s and O 1s edges are reached. A group of coincidences between H^+ and O^+ or S^{2+} , CC^+ , and CCH^+ ions could be also observed around C 1s and O 1s edges having values between 1 and 3%.

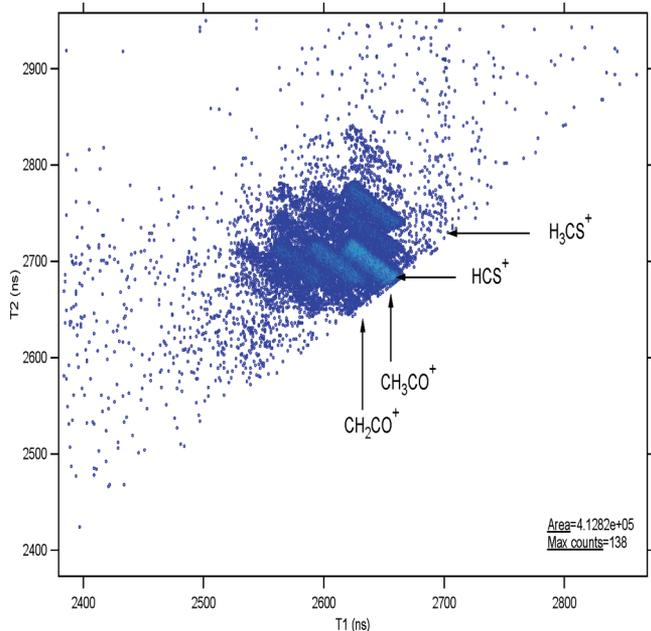


Figure 8. Enlargement of the PEPIPICO spectrum of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ obtained at 530.8 eV photon energy in the range of m/z 41–47 amu/ q in the T1 and T2 domains.

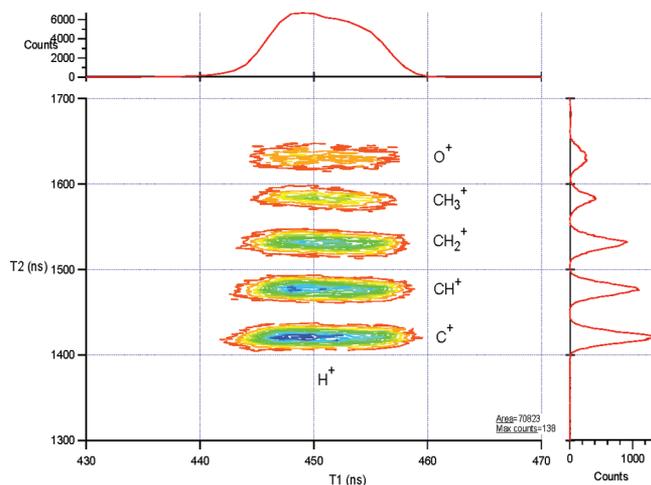


Figure 9. Contour plot derived from the PEPICO spectrum of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ obtained at 530.8 eV for the coincidence island between H^+ and CH_x^+ ($x = 0-3$) and O^+ ions.

An increase in the intensity of the islands involving the H^+ / C^+ and H^+/S^+ ions, together with a diminution of the intensity of the double coincidences involving molecular fragments such as $\text{CH}_3^+/\text{CH}_3\text{C}(\text{O})^+$, $\text{CH}_3^+/\text{HCS}^+$, and $\text{CH}_3\text{C}(\text{O})^+/\text{HCS}^+$, is observed by going from S 2p to the O 1s region.

The analysis of the PEPICO spectra of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ over the whole range of photon energies analyzed here reveals a preferred contribution of HCS^+ ions to the double coincidence, while signals corresponding to the other ions corresponding to the series CH_xS^+ ($x = 0, 2, 3$) appear as low-intensity islands. As we mentioned before, the high stability of the HCS^+ precludes subsequent dissociation of this ion.⁵⁰⁻⁵³ In the same way, an important contribution of the thioformyl ion was observed in the multicoincidence spectra of the molecule $\text{FC}(\text{O})\text{SCH}_3$ recently analyzed,⁶ confirming the high stability of this specie formed under synchrotron conditions. The high protonic affinity of the CS species is another way to understand this observation.

Indirect evidence of ultrafast fragmentation in S 2p excited $\text{CH}_3\text{C}(\text{O})\text{SH}$ was found from the analysis of the PEPICO spectra. Ultrafast dissociation of the core hole excited state also was considered for hydrogen bromide, silane, methyl bromide, hydrogen iodide, and methyl iodide, among others.⁵⁴⁻⁵⁶ When the hydrogen atom is formally replaced by a methyl group, the time scale for dissociation is lengthened, and autoionization competes more effectively with the dissociation processes so direct dissociation of the core hole state becomes less important.⁵⁷ Therefore, the presence of the thiol moiety (SH) in the $\text{CH}_3\text{C}(\text{O})\text{SH}$ molecule could favor the fast ejection of the acidic hydrogen atom bonded to the sulfur, and on the other hand, the presence of a heavier methyl group bonded to the sulfur atom in the $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ molecule should preclude the occurrence of a fast fragmentation following S 2p excitation. Accordingly, for the thioacetic acid, specific double coincidence islands are best explained as arising from dissociation of the doubly charged $\text{CH}_3\text{C}(\text{O})\text{S}^{2+}$ species rather than the parent $\text{CH}_3\text{C}(\text{O})\text{SH}^{2+}$ dication. In particular, for the thioacetic acid a coincidence of $m/z = 43$ amu/ q [$\text{CH}_3\text{C}(\text{O})^+$] with $m/z = 32$ amu/ q (S^+) is identified in the PEPICO spectra as an island with a cigar shape having a -1 slope and can be rationalized as originated by a two-body fragmentation process from the doubly charged $\text{CH}_3\text{C}(\text{O})\text{S}^{2+}$.

On the other hand, this coincidence was not observed in the PEPICO spectra for the $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ compound. In addition, when $\text{CH}_3\text{C}(\text{O})\text{SH}$ is irradiated with photons near the S 2p threshold, as much as 31% of the double coincidences involve the S^+ ion, and this contribution decreases to only 8% in the case of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ molecule.

CONCLUSIONS

The photofragmentation processes occurring under synchrotron radiation conditions are very interesting and varied. From the many species formed during the synchrotron experiments reported in the present work at least two call our attention, HCS^+ and H_3^+ . The first had also already observed using similar systems as the title compound.⁶ Its abundance not only under synchrotron conditions but also in the interstellar medium is attributable to the high proton affinity of the CS^+ species.⁵² H_3^+ also present and observed in our work is one of the most interesting small covalent species. It is used in the basic courses of chemistry to explain its equilateral triangle structure instead of a linear or bent form using basic molecular orbitals concepts. Its connection with its abundance in some parts of the universe is straightforward. Thus, it is well-known that H_3^+ has been detected in both Saturn and Jupiter auroral/polar regions.^{58,59} In contrast with the first remarked HCS^+ , H_3^+ presents a high acidity. Its proton donor ability serves to initiate ion–molecule reactions in the interstellar medium. In this medium its formation is clearly dependent on both abundant H_2 and H_2^+ species.⁶⁰ Our chemical intuition, rather important for neutral molecules, decreases by going to excited and ionic states. A roaming atoms and radicals mechanism can contribute to understand the remarkable formation of H_3^+ derived from a double charged species containing two methyl groups.⁶¹ In this context and also taking into account that a detailed computational investigation will be desirable, the formation of H_3^+ from $\text{CH}_3\text{C}(\text{O})\text{SCH}_3^{2+}$ can be originated by hydrogen atoms from only one or two methyl groups. The first option might be more plausible since the evolution of a H_2 complexed with a $\text{CHC}(\text{O})\text{SCH}_3^{2+}$ species followed by the subsequent development of H_3^+ and $\text{CC}(\text{O})\text{SCH}_3^+$ would be a plausible formation pathway. A roaming H^+ would be more unlikely and could be seen as a dissociative Coulombic explosion of the charged fragments. On the other side of the molecule, HCS^+ formation would be another statistically important process. However, the formation of H_3^+ from this side of the title molecule would be also possible as found in the related $\text{FC}(\text{O})\text{SCH}_3$ species possessing only one thiomethyl group. Contribution of roaming H atoms from both methyl groups could be equally possible and cannot be discarded on the basis of our current experimental evidence.

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, C 1s, and O 1s ionization edges. The prominent features observed by going from the S 2p to the O 1s region are a clear increase of the H^+ ion and a diminution of the $\text{CH}_3\text{C}(\text{O})^+$ fragment. In addition, the double coincidences branching ratio for double ion processes calculated from PEPICO spectra of $\text{CH}_3\text{C}(\text{O})\text{SCH}_3$ over the whole range of photon energies analyzed here reveals also some changes by going from the S 2p to the O 1s region.

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Notes

The authors declare no competing financial interest.

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