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Ionic fragmentation of the isoprene molecule in the VUV energy range (12 to 310 eV)



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ABSTRACT

Isoprene, C₅H₈, is a biogenic volatile compound emitted from plants and animals, playing an important role in atmospheric chemistry. In this work, we have studied the ionic fragmentation of the isoprene molecule induced by high energy photons (synchrotron radiation), both at the valence (12.0, 14.0, 16.0, 18.0, and 21.0 eV) and carbon 1s edge (270 and 310 eV, respectively, below and above edge) energies. The ionic fragments were mass-analyzed using a Wiley–McLaren time-of-flight spectrometer (TOF) and single (PEPICO) and double ionization coincidence (PEPIPICO) spectra were obtained. As expected, the fragmentation degree increases with increasing energy. Below and above the carbon 1s edge, the fragmentation patterns are quite similar, and basically the same fragments are observed as compared to the spectra following valence-shell ionization. Stable doubly-charged ions were not observed. A PEPIPICO spectrum has shown that the main dissociation route for doubly-ionized species corresponds to the [CH₃]⁺/[C₄H_{2–5}]⁺ ion pair. Intense fragmentation of the isoprene molecule has been observed following valence shell and core electron ionization. The observance of basically the same fragments when moving from valence to inner-shell suggests that basically the same fragmentation routes are present in both cases. All doubly (or multiply)-charged cations are unstable, at least on a microsecond scale.

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1. Introduction

Several biogenic volatile compounds may be obtained from essential oils derived from plants and animals. They are found to have several pharmaceutical, cosmetic and industrial applications. They may also be quite reactive towards atmospheric components and as such have been the focus of many studies in the UV range [1–3]. In our laboratory we have developed a systematic study of the excitation and fragmentation of these compounds when subjected to ionizing radiation (VUV and soft X-ray energy ranges). We have shown, for instance, that the degree of ionic fragmentation of monoterpenes such as carvone, C₁₀H₁₄O [4], limonene, C₁₀H₁₆ [5] and camphor, C₁₀H₁₆O [6], increases strongly with increasing photon energy. Excitation around the C 1s and O 1s edges also gives rises to unstable doubly-charged ionic species. Isoprene (2-methyl-,

3-butadiene—Fig. 1), to which we address our attention in the present paper, is the most abundant non-methane hydrocarbon compound found in the atmosphere, with an estimated emission of 250 to 503 Tg/year [7]. It plays therefore an important role in atmospheric chemistry, reacting with many oxidant species [8].

The isoprene molecule can also be considered as a building block for terpenes, a vast family of natural products. It is also used as a monomer in several industrial branches, with an annual world production around 1.3×10^6 t [9].

The electron impact spectrum of monoterpenes has been studied for a long time [10,11], with main focus on the formation of metastable ions and their subsequent dissociation routes [12], formation of doubly charged ions [13] and the fragmentation routes towards monoterpene cations [14]. A preliminary study concerning the dissociative photoionization of isoprene as induced by electrons and synchrotron radiation, was performed by de Souza et al. [15]. In a subsequent work, Liu et al. [16] presented an experimental and theoretical study related to the determination of the appearance energies for some isoprene ionic fragments in the valence region

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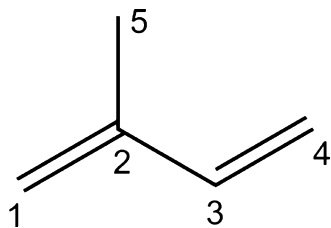


Fig. 1. Isoprene structure.

(8.5 to 18 eV). More recently, the valence shell electronic spectroscopy of isoprene was studied through theoretical calculations and by electron scattering, photoelectron, and absolute photoabsorption measurements [17].

In the present work, the ionic fragmentation of isoprene has been studied in an extended energy range, covering both valence-shell and carbon 1s photoionization processes. Within our knowledge, this is the first application of synchrotron radiation and photoelectron–ion (PEPICO) and photoelectron–ion–ion (PEPIPICO) techniques to the study of the photo induced fragmentation of the isoprene molecule.

2. Experimental procedures

High photon energy mass spectra were obtained at the Brazilian Synchrotron Facility (LNLS), located at Campinas (SP), Brazil, using light from a toroidal grating monochromator (TGM) beam line [18]. The experimental set up has been previously described in detail [19]. Briefly, light from the TGM bending magnet beamline (12 to 310 eV) intersects the effusive vapor sample inside a high vacuum chamber, with base pressure in the 10^{-8} Torr range. The emergent beam is recorded by a light sensitive diode. During the experiment, the pressure was maintained below 5×10^{-6} Torr.

The ionic fragments were analyzed by a Wiley–McLaren type time-of-flight (TOF) mass spectrometer [20]. The ionized recoil fragments produced by the interaction of the gaseous sample with the light beam are accelerated by a two-stage electric field towards a drift tube and are afterwards detected by a pair of micro-channel plate detectors mounted in a chevron configuration. The incoming ions produce stop signals to a time-to-digital converter (TDC). Electrons, accelerated in the opposite direction with respect to the positive ions, are recorded without energy analysis and provide the start signal to the TDC. A 708 V/cm DC electric field is applied to the first ion acceleration stage. The time-of-flight spectrometer was designed in order to achieve 100% efficiency for ions with kinetic energies up to 30 eV. [19] The electrons produced in the ionization region are focused by an electrostatic lens and are detected by a pair of micro-channel plates. All electrons with kinetic energies up to 150 eV are detected without angular discrimination. For the valence region measurements (12 to 21 eV), a Neon filter was employed in order to eliminate contamination from higher order harmonics [21,22].

A commercial sample of isoprene, distilled some hours before the experiments (33–34 °C), was used. The liquid sample was subjected to repeated freeze–pump–thaw cycles before admission into the chamber in order to minimize contamination by atmospheric constituents. Due to its high vapor pressure, no heating procedure was necessary in order to introduce the sample in the collision chamber.

Conventional mass spectra were obtained using the correlation between a photoelectron and an ion generated at the same ionization event (PhotoElectron–Photolon Coincidence or PEPICO technique). In the PEPICO technique, following ionization of the sample, detection of an ejected electron gives rise to a start signal from which the times of arrival of the subsequent ions can be

measured. Doubly-charged cations are usually formed at high photon energies (above approximately 30 eV) and particularly at photon energies around core electron edges. These dications usually have an unstable and dissociative nature. They are characterized in our experiments through a double coincidence technique (PhotoElectron–Photolon–Photolon coincidence or PEPIPICO) [23].

Time-of-flight data (TOF) were converted into mass/charge (m/z) through Eq. (1), where A and B are parameters obtained by least square fitting, using as reference a 70 eV electron impact spectra [24].

$$\text{TOF} = B \times \sqrt{m/z} + A \quad (1)$$

The branching ratio for each fragment (BR) was calculated dividing the peak area (obtained by a Gaussian adjust) by the sum of the area of all peaks, excluding the area of known contaminants: m/z 16 (O^+ , from air oxygen and water), m/z 17 and 18 from water (OH^+ and H_2O^+ , respectively), m/z 28 and m/z 32 from air (respectively N_2^+ and O_2^+). Branching ratios for double coincidences (BRDC) were similarly calculated, after removing coincidences associated with only one count (those are taken as false coincidences).

In the absence of published data, we estimate the C 1s edge of isoprene to be very close to the C 1s edge of a similar molecule, 1,3-pentadiene (290 eV [25]). Spectra were obtained at 270 eV and 310 eV photon energies, corresponding respectively to below and above the C 1s edge of the isoprene molecule.

3. Results and discussion

3.1. Mass spectra as a function of the photon energy

Valence-shell time-of-flight mass spectra were obtained at 12.0, 14.0, 16.0, 18.0, 21.0 eV and the results are presented in Fig. 2. Mass spectra obtained below (270 eV) and above (310 eV) the carbon 1s edge have also been obtained and are shown in Fig. 3. The branching ratio (BR) values for the main fragments are presented in Table 1. In Fig. 4, the branching ratios (BR) for selected ions are presented as a function of the photon energy.

At the lowest photon energy available at the TGM beamline (12.0 eV) we may observe, according to Martins et al. [17], cationic contributions from two ionic states with π character (HOMO, $3a''$, $\text{IP}=8.842$ eV and from the SHOMO, $2a''$, $\text{IP}=10.834$ eV). An ionic state with σ character ($16a'$, $\text{IP}=11.846$ eV) also contributes. Individual contributions from each ionic state are not distinguishable with the present experimental set-up. From 13 to 14 eV, we expect an additional and large contribution from another orbital with a σ character ($14a'$).

We clearly observe in Fig. 2 that fragmentation of the molecule increases with increasing photon energy. At 12.0 eV, the spectrum is dominated by the molecular ion $[\text{C}_5\text{H}_8]^+$ ($[\text{M}]^+ - m/z$ 68) and by the $[\text{C}_5\text{H}_7]^+$ ion ($[\text{M} - \text{H}]^+ - m/z$ 67). At this photon energy, peaks corresponding to the fragments $[\text{C}_3\text{H}_4]^+$ (m/z 40), $[\text{C}_3\text{H}_6]^+$ (m/z 42) and $[\text{C}_4\text{H}_5]^+$ (m/z 53) are broader and asymmetric, as compared with the molecular ion. A tail on the right hand side of some peaks (as observed in the inset on the top of Fig. 2), suggests that these are metastable fragments [26]. The ionic fragments observed at 12.0 eV agree with the results of Liu et al. [16], corroborating that these are indeed fragments with appearance energies (AE) below or equal to 12.0 eV.

The BR's for the $[\text{C}_4\text{H}_5]^+$ ($[\text{M} - \text{CH}_3]^+$) ion increase from 12.0 to 16.0 eV. At 16.0 eV, this fragment becomes the most abundant ion in the spectrum. The important contribution from this m/z 53 ion to the PEPICO spectra can be associated with the longest C(2)–C(5) bond length of the isoprene cation, which leads to an easier breaking into $[\text{C}_4\text{H}_5]^+ + [\text{CH}_3]$ fragments [16].

Table 1
Branching ratios (%) of isoprene molecule.

<i>m/z</i>	Fragment	Energies (eV)/Branching ratios (%)						
		12.0	14.0	16.0	18.0	21.0	270	310
1	[H] ⁺					0.2	2.1	5.0
2	[H ₂] ⁺						0.2	0.4
13	[CH] ⁺						0.4	1.1
14	[CH ₂] ⁺						0.8	2.0
15	[CH ₃] ⁺	–	–	–	–	–	2.7	4.4
26	[C ₂ H ₄] ⁺						2.3	3.0
27	[C ₂ H ₃] ⁺	–	–	1.0	3.4	4.6	8.1	9.1
37	[C ₃ H] ⁺						1.5	1.4
38	[C ₃ H ₂] ⁺						2.6	1.3
39	[C ₃ H ₃] ⁺	–	0.6	2.6	4.3	6.8	13.5	12.8
40	[C ₃ H ₄] ⁺	1.8	10.8	11.7	11.1	10.5	7.0	5.8
41	[C ₃ H ₅] ⁺	–	1.4	5.8	7.6	8.2	6.2	5.6
42	[C ₃ H ₆] ⁺	0.7	6.9	7.0	6.6	6.2	3.3	3.1
49	[C ₄ H] ⁺	1.3	0.3	0.4	1.1	4.5	0.2	0.4
50	[C ₄ H ₂] ⁺						1.8	1.9
51	[C ₄ H ₃] ⁺	0.4	0.7	0.2	0.7	2.2	2.6	2.3
52	[C ₄ H ₄] ⁺			0.8	1.2	1.3	1.5	0.8
53	[C ₄ H ₅] ⁺	6.4	23.2	28.7	24.7	22.5	13.9	14.3
65	[C ₅ H ₅] ⁺			1.1	1.5	0.8	1.3	1.4
66	[C ₅ H ₆] ⁺	0.8	0.8	1.4	1.3	1.0	1.0	1.2
67	[C ₅ H ₇] ⁺	40.5	34.6	23.1	20.8	17.4	11.9	6.8
68	[C ₅ H ₈] ⁺	46.3	17.5	12.9	12.7	11.9	11.1	9.9

Moving from 12.0 to 14.0 eV, a significant increase in the [C₃H₄]⁺ (*m/z* 40) BR can be seen. Besides, the [C₃H₃]⁺ (*m/z* 39) and [C₃H₅]⁺ (*m/z* 41) ions appear at 14.0 eV, in agreement with their measured appearance energies ([C₃H₃]⁺—13.48 eV, [C₃H₅]⁺—13.73 eV [16]).

The general profile of the 18.0 eV spectrum is similar to the spectrum obtained at 16.0 eV, except for an increasing of the [C₂H₃]⁺ (*m/z* 27) ion BR. The BR of the [C₂H₃]⁺ ion is still more significant at 21.0 eV. A small amount of water (*m/z* 17—[OH]⁺ and *m/z* 18—[H₂O]⁺) can also be seen at 21.0 eV.

As expected, there is a higher degree of fragmentation in the vicinity of the carbon K edge (270 and 310 eV), as compared to the valence shell spectra. At these much higher energies, the *m/z* 39 and 27 ions are more prominent, while heavier fragments show proportionally lower intensities. [CH_x]⁺ ions, mainly [CH₃]⁺ (*m/z* 15), are clearly observed. The spectra obtained around the carbon K edge, (270 eV and 310 eV) show a similar fragmentation pattern, with the same ionic fragments and similar BRs. [C₄H₅]⁺ (*m/z* 53), formed by the elimination of the methyl radical ([CH₃]), is the dominant fragment around this edge, followed by the [C₃H₃]⁺ ion (*m/z* 39). Compared to the valence shell spectra, the mass spectra associated with core electron excitation and ionization show a relative increasing contribution from the lighter fragments. A decrease is observed in the BR for the [C₅H₇]⁺ ion (*m/z* 67), accompanied by a proportional increase in the BR's for lighter ions. The *m/z* 35 fragment, observed at 270 eV, probably corresponds to a Cl⁺ fragment originated from a CCl₄ contamination of the chamber [27].

[H]⁺ ions are clearly observed around the Carbon 1s edge, emphasizing the large increase in fragmentation of the molecule at high photon energies. Rearrangement ions like [H₂]⁺ are also observed in the same photon energy range, albeit with much lower intensity (branching ratios 0.2 and 0.4, respectively, at 270 and 310 eV). [H₂]⁺ ions have also been previously observed as a result of the core excitation of monoterpenes like carvone [4] and camphor [6].

Our results demonstrate a strong energy dependence of the intensity of the base (most intense) peak with photon energy. At low energies, [M]⁺ and [M—H]⁺ are dominant, corresponding to 86.6% of the total BR at 12.0 eV (dominated by [M]⁺ ion) and 52.1% at 14.0 eV (dominated by [M—H]⁺ ion). The ion corresponding to *m/z* 53 becomes the most intense peak in the spectra obtained from 16.0 eV to the carbon 1s edge photon energy. Contribution from the *m/z* 39 ion also increases with photon energy.

Except for the *m/z* 15 ion, basically the same ionic fragments are observed in the photoionization of the isoprene molecule, as the photon energy increases from 21.0 eV (valence shell) to 310 eV (C 1s edge).

An interesting behavior is observed with increasing photon energy, following removal of hydrogen atoms from the [C₄H₅]⁺ ion (*m/z* 53): at 12.0 eV, only species resulting from the successive loss of two hydrogen atoms are formed: [C₄H₃]⁺ (*m/z* 51) and [C₄H]⁺ (*m/z* 49). With increasing photon energy (14.0 to 21.0 eV), ionic species with an even number of hydrogen atoms, [C₄H₄]⁺ (*m/z* 52) and [C₄H₂]⁺ (*m/z* 50) can also be observed.

Similarly to our previous studies of the monoterpene limonene (C₁₀H₁₆) [5] and of the bicyclic terpene camphor (C₁₀H₁₆O) [6], no stable doubly-charged ion seems to be formed following photoionization of the isoprene molecule. In both cases, a similar fragmentation pattern was observed below and above the carbon 1s edge. As no stable doubly-charged ions were observed, we may assume that all dications have a very dissociative character, undergoing fast dissociation and consequently presenting a very short lifetime. In addition, a similar result was observed in the fragmentation study of the monoterpene carvone (C₁₀H₁₄O) [4], with the exception that a small contribution from the [H₂]⁺ and [C]⁺ ions was observed in the spectrum obtained above the carbon 1s edge.

3.2. Double ionization

According to the Tsai and Eland's empirical rule [28], the double ionization potential for the isoprene molecule should occur at approximately 33 eV. As mentioned before, no stable doubly-charged ion has been observed in our spectra. We assume consequently that the doubly ionized states have a dissociative character. The PEPIICO technique allows for the observation of pairs of ions coming out from the same ionization event. Although PEPIICO data were collected at 270 eV and 310 eV, the results were quite similar. Consequently, only the double coincidence mass spectrum (PEPIICO) obtained at 310 eV has been shown in Fig. 5.

The branching ratios obtained for double coincidence (BRDC) events observed at 310 eV are presented in Table 2 (only BRDC values higher than 1% are displayed).

The PEPIICO results show that about 34% of the double ion coincidences involve the [H]⁺ ion, 31% the [CH_x]⁺ ions and 22% the [C₂H_x]⁺ ions. The main dissociation channel (17.4%) corresponds to

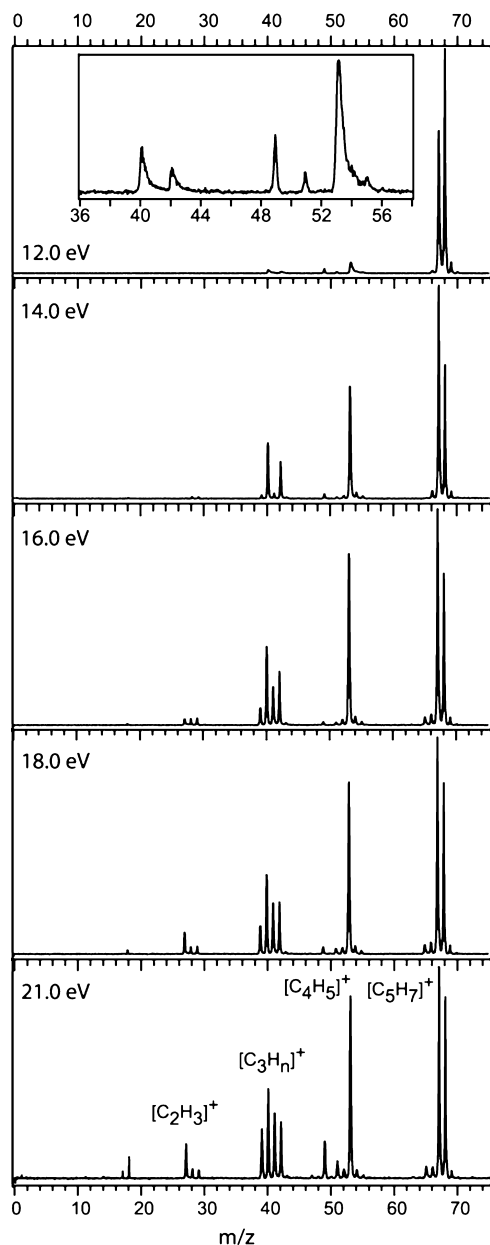


Fig. 2. Isoprene mass spectra obtained at 12.0 eV, 14.0 eV, 16.0 eV, 18.0 eV, and 21.0 eV photon energies. The inset on the top box is a zoom of the low m/z data for the 12.0 eV spectrum.

Table 2
Branching ratios for double coincidences (BRDC)—310 eV.

Ion 1	m/z	Ion 2	m/z	BRDC (%)
$[H]^+$	1	$[CH_{0-2}]^+$	12–14	6.6
$[H]^+$	1	$[C_2H_{1-3}]^+$	25–27	8.5
$[H]^+$	1	$[C_3H_{0-3}]^+$	36–39	14.1
$[H]^+$	1	$[C_4H_{2-3}]^+$	50–51	5.2
$[CH_2]^+$	14	$[C_2H_3]^+$	27	1.4
$[CH_2]^+$	14	$[C_4H_{2-3}]^+$	50–51	3.1
$[CH_3]^+$	15	$[C_2H_3]^+$	27	9.4
$[CH_3]^+$	15	$[C_4H_{2-5}]^+$	50–53	17.4
$[C_2H_{2-3}]^+$	26–27	$[C_3H_{5-8}]^+$	41–44	6.5

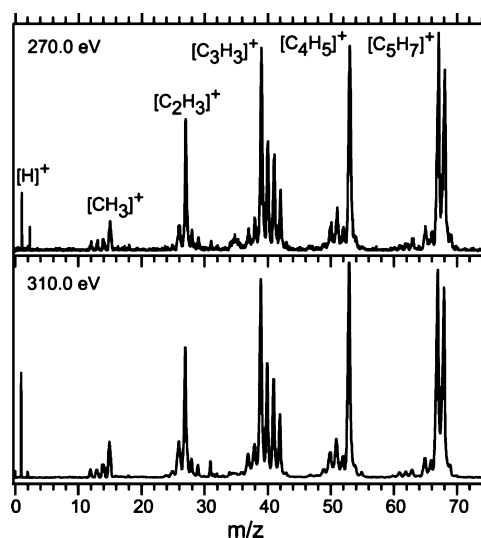


Fig. 3. Isoprene mass spectra obtained at 270 and 310 eV photon energies.

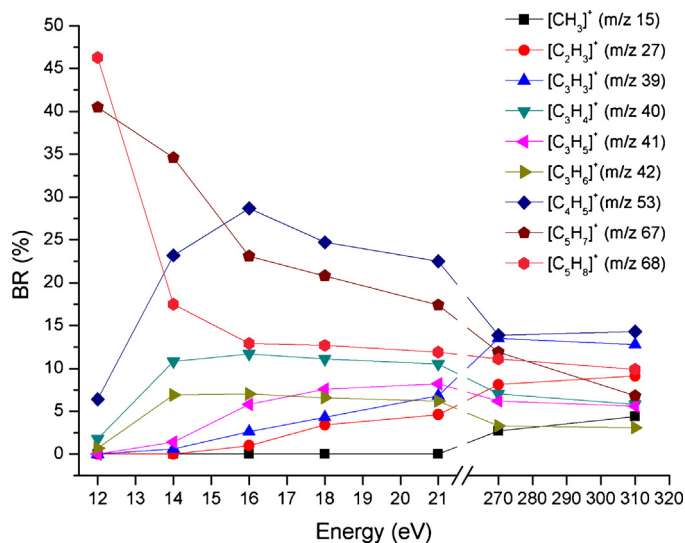


Fig. 4. Branching ratios (%) of selected fragments from isoprene as a function of the photon energy.

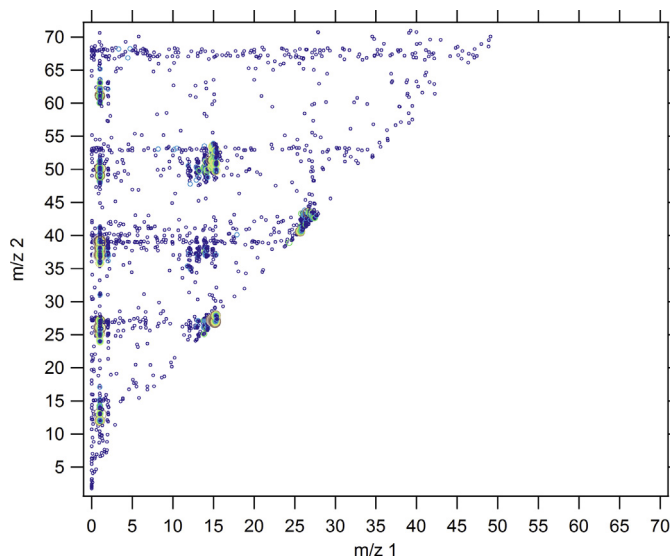


Fig. 5. PEPIPO spectra of isoprene obtained at 310 eV. The X axis corresponds to the m/z of the first fragment detected (lighter), while the Y axis corresponds to the second fragment (heavier).

the $[\text{CH}_3]^+ / [\text{C}_4\text{H}_2-5]^+$ ion pair, which can be related to the scission of the C(2)–C(5) bond, preserving the main chain of the molecule. As discussed in the PEPICO spectra, these results reinforce our suggestion that cleavage of the C(2)–C(5) bond is a usual dissociation pathway in this molecule.

4. Conclusions

Photoionization mass spectra have been obtained for the valence-shell and core excited isoprene molecule. Within our knowledge, the ionic fragmentation of this molecule, following ionization of core electrons has not been presented before.

A comparison between spectra obtained following valence and core-shell electron ionization shows that basically the same fragments are observed, although lighter fragments become much more prominent at higher photon energies.

Regarding core ionization, a similar fragmentation pattern, both at the PEPICO and PEPICICO spectra, is observed below (direct ionization) and above (strong participation of Auger processes) the C 1s edge, evidencing that basically the same decaying processes are taking place.

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