



Dissociative photoionization of the tetramethyl silane molecule, $\text{Si}(\text{CH}_3)_4$, around the Si 1s edge

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ABSTRACT

Photoionization of the $\text{Si}[\text{CH}_3]_4$ molecule has been studied around the Si 1s edge, using time-of-flight mass spectrometry, photoelectron–photoion coincidence techniques (PEPICO, PE2PICO and PE3PICO) and synchrotron radiation. Partial ion yields have been recorded as a function of the photon energy. Strong fragmentation of the molecule is observed and singly charged species (H^+ , H_2^+ , C^+ , and CH_n^+) dominate the spectra, with the H^+ ion being the most abundant fragment. Although the contribution of stable doubly and triply charged species was not significant in the measured spectra, intense double and triple ionization of the molecule was demonstrated below and above the Si 1s edge, through PE2PICO and PE3PICO measurements.

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1. Introduction

Tetramethyl silane (TMS), $\text{Si}[\text{CH}_3]_4$, is a highly volatile compound with several important technological applications, for instance it is routinely employed as an etchant gas in microelectronics. TMS is also commonly used as a monomer for low temperature plasma technology, and is the most conspicuous compound used as an internal standard for calibrating chemical shift for ^1H , ^{13}C and ^{29}Si NMR spectroscopy. Moreover, from the chemical point of view, TMS is an important building block in organometallic chemistry.

Several studies have been dedicated to the photoabsorption and dissociation of the $\text{Si}[\text{CH}_3]_4$ molecule, both in the valence and in the inner-shell regions [1–13]. Morin et al. [1], combined photoelectron spectroscopy and photoion–photoion coincidence technique to study the core ionization of the TMS molecule around the Si 2p edge. Basner et al. [2] studied the electron impact ionization of the TMS molecule. Photoionization mass spectra were reported by Bozek et al. [3] near the Si 2p and 2s edges using a low-resolution quadrupole mass filter. Urquhart et al. [4] derived oscillator strengths for shallow core excitation of $\text{Si}[\text{Me}]_4$, among others molecules. More recently, Si containing compounds [14–16] have been studied following Si 2p and Si 1s core-level photoionization using photoelectron–photoion–photoion coincidence (PEPIPICO) and Auger electron–photoion–photoion (AEPIPICO) spectroscopy.

In contrast to the delocalized character of valence electrons, molecular deep core electrons are highly localized near the atom to which they primitively belonged. These atomic cores can be selectively excited using monochromatized synchrotron radiation,

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resulting in a fragmentation pattern which may be specific to that site, due to the localized character of the core electron.

In this paper, we have investigated the ionic fragmentation of the TMS molecule following Si 1s core photoexcitation and photoionization, using PEnPICO measurements and synchrotron radiation.

2. Experimental

During the sample manipulation, some cautions should be taken. The TMS is corrosive and an extremely flammable liquid and vapor. In the vapor phase, the TMS may cause flash fire. If swallowed, inhaled or absorbed through skin, may be harmful, causing severe irritation or burns to skin, eyes, and respiratory tract.

The experimental set up has been previously described [17–21]. Briefly, the experiment was performed at the Laboratório Nacional de Luz Síncrotron (LNLS), Campinas, São Paulo, Brazil. Light from the Soft X-ray Spectroscopy beamline (SXS) intersects the effusive gaseous sample inside a high vacuum chamber, with base pressure in the 10^{-8} Torr range. During the experiment the pressure is maintained below 10^{-5} Torr. The gas needle is kept at ground potential. The emergent light beam is recorded by a light sensitive diode.

The ionized moieties produced by the interaction of the molecule with the light beam are accelerated by a two-stage electric field and detected by a single detector comprising two micro-channel plates arranged in a chevron configuration, after being mass-to-charge analyzed by a time-of-flight spectrometer (TOFMS). They produce stop signals to a time-to-digital converter (TDC) started by the signal from one of the electrons accelerated in an opposite direction and recorded without energy analysis by another single detector comprising two micro-channel plates also arranged in a chevron configuration. The first stage of the electric field consists of a plate-grid system with the light beam passing in its middle and with a 708 V/cm DC electric field. The ejected electrons produced in the ionization region are focused by an electrostatic lens polarizing the electron grid with 800 V, designed to focus them at the center of the micro-channel plate detector. The sample was commercially obtained with high purity (99.5%) and was used without further purification. Conventional time-of-flight mass spectra were obtained using the photoelectron-photoion coincidence (PEnPICO) technique.

Peaks in the time-of-flight mass spectra were assigned to appropriate fragment ions on the basis of their time-of-flight values. The limited mass resolution, due to high kinetic energy release of the fragments, did not allow for the full separation of peaks such as $\text{Si}(\text{CH}_n)_3^+$ and $\text{Si}(\text{CH}_n)_2^+$ (the overall time resolution, $\Delta T/T$, was found to be better than 0.2% for noble gases) The PEnPICO spectra were analyzed in terms of the relative integrated intensity of the peaks. The large width of the peaks is related to the kinetic energy release in the dissociation channels.

3. Results

3.1. PEnPICO spectra

The total ion yield spectrum of TMS, measured around the Si 1s edge is shown in Fig. 1A. A very good agreement is obtained with respect to previous measurements [4,8]. The Si 1s and Si 2p spectra are very similar. The observed resonances in TMS are attributed to Si ns excitations to a relatively delocalized σ_{SiC}^* orbital, and are due to core to unoccupied σ^* valence transitions [8–10]. A structure is also observed at 1853 eV, which was assigned to a shape resonance due to the methyl group [8–10].

In order to study the fragmentation processes following inner-shell excitation and ionization, mass spectra were obtained at

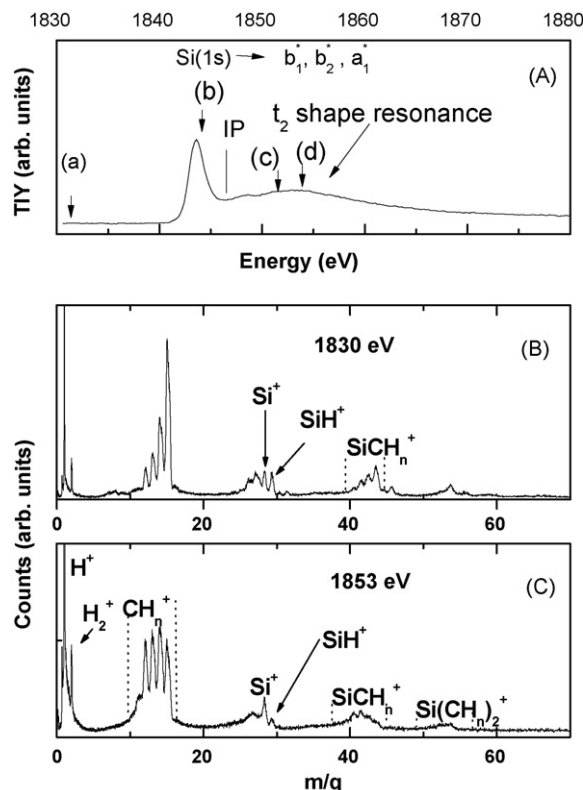


Fig. 1. (A) Total ion yield spectrum of TMS around the Si 1s region. The estimated ionization potential is 1845.9 eV [4,8]. The letters (a–d) indicate the photon energies where the mass spectra were measured. The assignments are those reported in [7]. (B) Time-of-flight mass spectra of TMS recorded at 1830 eV and (C) 1853 eV.

the following energies: 1830 eV, 1841 eV, 1852 eV and 1853 eV. Mass spectra measured in the 0–100 mass/charge range at energies below (1830 eV) and above (1853 eV) the Si 1s edge, are presented in Fig. 1B and C, respectively. The following singly charged fragments have been observed, in the photon energy range studied in this paper: H^+ , H_2^+ , C^+ , CH_n^+ ($n=1-3$), C_2H_n^+ , Si^+ , SiH_n^+ ($n=1-3$), $\text{Si}(\text{CH}_n)^+$, $\text{Si}(\text{CH}_n)_2^+$, and $\text{Si}(\text{CH}_n)_3^+$. A small H_3^+ peak could be seen only below the resonances, at 1830 eV. Some of the recorded peaks contain a mixture of ions with different Si isotopes ($^{29}\text{Si}^+$ with 4.7% and $^{30}\text{Si}^+$ with 3.0%). The contribution of doubly charged fragments may not be discarded. For instance, the fragment observed at $m/q=14$ is probably a mixture of CH_2^+ and $^{28}\text{Si}^{2+}$. Ordinarily, electronic relaxation precedes fragmentation in a deep core orbital of a molecule following an excitation or ionization. Although direct confirmation with the experimental capabilities used in this work is not possible, we suggest that single and double resonant and normal Auger processes are likely to contribute strongly in the Si 1s region. Following deep core excitation or ionization, a molecule is commonly left doubly or triply charged and this leads to a large degree of fragmentation. This is statement is based on the pioneering works by Carson and White [22,23] which demonstrated that after the creation of a K vacancy in atoms of the second- or higher-series of the Periodic Table, cascade Auger processes take place and highly charged molecular ion are produced. Besides Si^{2+} , no other stable doubly charged fragment was clearly observed in our mass spectra. At 1830 eV, however, CH_n^{2+} seems to be present. This may be seen as an indication that the doubly charged $\text{Si}(\text{CH}_3)_4^{2+}$ parent molecule fragments mainly via charge separation. Formation of many ion pairs associated to the loss of respective methyl groups from silicon atoms, such as $\text{Si}(\text{CH}_3)_n^+ + \text{CH}_3^+$ ($n=3-0$), have been observed even below the Si 2p edge [1]. Around the Si 1s

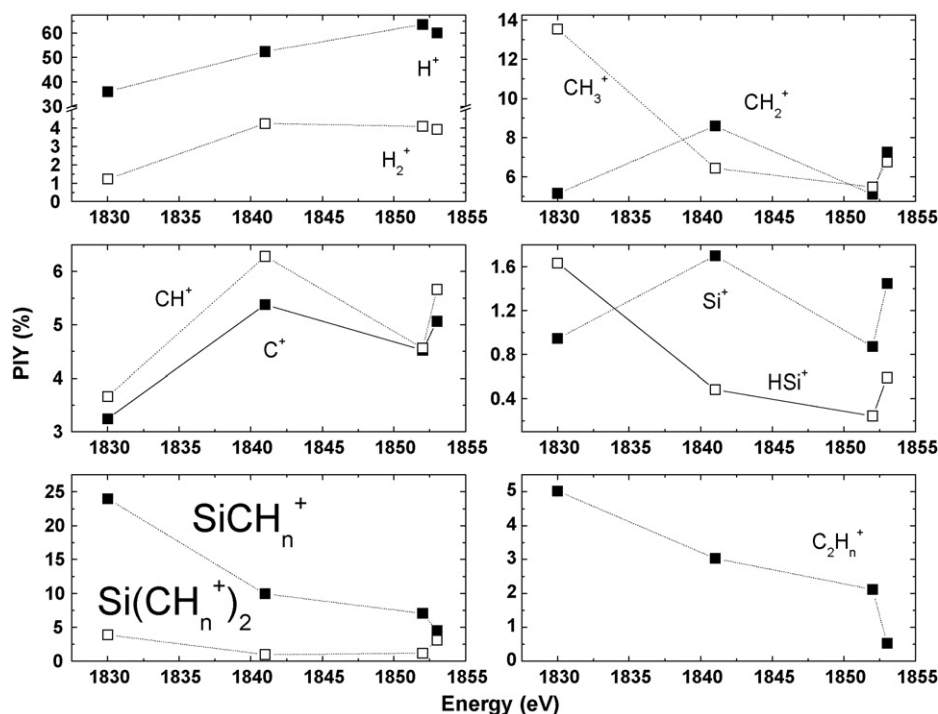


Fig. 2. PEPICO branching ratios as a function of photon energy near the Si 1s edge. The dotted lines are to guide the eye.

edge, the most intense peak in the spectra is associated with the H^+ cation (36% at 1830 eV, increasing up to 60% at 1853 eV), but additional atomic (C^+ and Si^+) as well as molecular ionic fragments are clearly observed. The relative intensity of CH_3^+ and $SiCH_n^+$ ($n = 1, 2, 3$) is inhibited around the Si 1s edge. This behavior has also been observed in the Si 1s fragmentation of $F_3SiCH_2CH_2Si(CH_3)_3$ vapor [16].

The parent ion is virtually absent in the mass spectra. Small amounts of $Si(CH_n)_3^+$ can be observed (<1%). The $Si(CH_n)_2^+$ and $Si(CH_n)^+$ fragments are formed with much larger kinetic energy, as reflected in the corresponding peak broadness. Fragments associated with rearrangement reactions, such as H_2^+ ($m/q = 1$), SiH^+ ($m/q = 29$), SiH_2^+ ($m/q = 30$), and SiH_3^+ ($m/q = 31$), are clearly distinguished. SiH^+ and SiH_3^+ have also been observed by electron impact technique [2]. Compared to the low energy spectrum, a clear enhancement in the formation of the Si^+ is observed in the spectra obtained at the resonance (1841 eV) and above the ionization edge (1853 eV). The drastic change in shape observed simultaneously in the fragmentation around $m/q = 14$ may point out to an increase in the formation of the Si^{2+} ion accompanied by a higher degree of Si–CH₃ bond breaking events. Existence of the Si^+/CH_3^+ pair has already been demonstrated around the Si 2p edge [1].

PEPICO branching ratios as a function of photon energy are shown in Fig. 2 and are tabulated in Table 1. The H^+ fragment is the most abundant ion and its contribution increases at the Si 1s excitation and ionization regions. We do not discard possible discrimination effects against light and fast ions, such as H^+ , that could affect the partial ion yields. As can be seen from Figs. 1 and 2, the relative intensities of the CH_3^+ fragment decreases as the photon energy increases from 1830 to 1853 eV. These trends indicate that the ionic fragmentation processes producing CH_3^+ are inhibited following Si 1s excitation and ionization, in sharp contrast to the situation observed following Si 2p excitation and ionization [5]. The relative intensity of the HSi^+ fragment decreases at the Si 1s excitation and ionization regions. Around 1853 eV the rela-

tive intensities of the Si^+ , HSi^+ , $Si(CH_n)_2^+$, and $Si(CH_n)_3^+$ fragments, change drastically.

The asymmetric peak H^+ is a finger mark of metastable ions. This metastability is a characteristic of the surface potential of the parent ion, which dissociates by tunnelling through the surface potential barrier [24]. The lifetime of H^+ , which depends on the barrier height and width, can be estimated using the same argument used by Simon et al. [25] and Ponciano and Silveira [26]. We assume that the decay of the parent ion leading to CH_3^+ is a very fast process and that the CH_3^+ ion is slow to dissociate. In a metastable dissociation, the primary ion (CH_3^+) is firstly accelerated during a time τ in the interaction chamber. It then dissociates into the “daughter ion” that is also submitted to the extraction field. Assuming no collision during the flight, random and isotropic molecular dissociation, constant fragmentation probability per unit of time, the lifetime may be obtained from the expression

$$N_{CH_3}(t) = N_{CH_3}^0 e^{-t/\tau} \quad (1)$$

Table 1

Partial ion yield (PIY), given in percentages (%), of the PEPICO spectra fragments as a function of the photon energy

m/q	Ion	1830 eV	1841 eV	1852 eV	1853 eV
1	H^+	36.0	52.0	64.0	60.0
2	H_2^+	1.2	4.3	4.1	3.9
12	C^+	3.2	5.4	4.5	5.1
13	CH^+	3.7	6.3	4.6	5.7
14	CH_2^+	5.2	8.6	5.1	7.3
15	CH_3^+	14.0	6.5	5.5	6.8
27	$C_2H_n^+$	5.0	3.0	2.1	<1
28	Si^+	1.0	1.7	<1	1.4
29	SiH^+	1.6	<1	<1	<1
30	SiH_2^+	–	<1	–	–
31	SiH_3^+	–	<1	–	–
	$Si(CH_n)^+$	2.4	1.0	7.0	4.5
	$Si(CH_n)_2^+$	3.9	1.0	1.2	3.1
	$Si(CH_n)_3^+$	1.0	<1	<1	<1

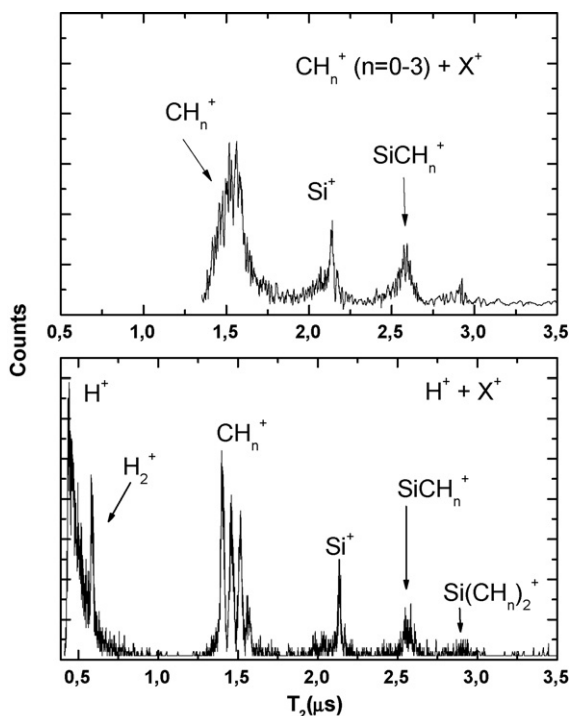


Fig. 3. Projection of PE2PICO spectrum at 1841 eV for coincidences where the ions CH_n^+ (top) and H^+ (bottom) are the present.

where τ is the CH_3^+ lifetime, $N_{\text{CH}_3}^0$ is the average number of metastable CH_3^+ ions at $t=0$. At 1830 eV, the value obtained by fitting Eq. (1) is $\tau=120 \pm 2$ ns. For higher energies, the lifetime does not depend on the photoion energy and is $\tau=72 \pm 2$ ns. The observed difference at 1830 eV can be attributed to a drastic change in the surface barrier.

3.2. Fragmentation of the $\text{Si}(\text{CH}_3)_4^{2+}$ dication

The photoelectron–photoion–photoion coincidence mass spectra (PE2PICO) of the TMS molecule around the Si 1s edge are complex, displaying peaks for numerous fragment ion pairs, produced from the unstable TMS dication. The H^+ ion is again the most abundant ion in the double ionization spectra of the TMS molecule. Fig. 3 shows the projections of PE2PICO spectrum onto the t_1 and t_2 axis as obtained at 1841 eV, for fragments detected in coincidence with H^+ (lower part) and in coincidence with CH_n^+ methyl fragments (upper part). We clearly see that when H^+ is the precursor, the CH_n^+ methyl fragments are observed as four well-resolved peaks. This is also a consequence of the fact that the light H^+ ion takes most of the available translational kinetic energy leaving little translational energy to their charged partners. On the other hand, when the CH_n^+ fragments are the precursors, the resolution of the mass spectrum decreases, due to the fact that the excess of kinetic energy is more evenly shared among the fragments.

A noticeable change in the fragmentation pattern concerns the relative intensities of the CH_n^+ fragments. Above the ionization edge, Auger decay leads to the creation of a second valence hole in the molecule, weakening the chemical bonds. We show in Fig. 4 that the relative contribution of the CH_3^+ ions to the double coincidence spectra decreases as one moves from 1830 eV to 1853 eV. This trend was also seen in the PEPICO spectra.

Fig. 5 shows coincidences between CH_n^+ with Si^+ at 1841 eV. It can be observed that the projections of CH_n^+ peaks are double-valued as a direct evidence of angular anisotropy, which reflects

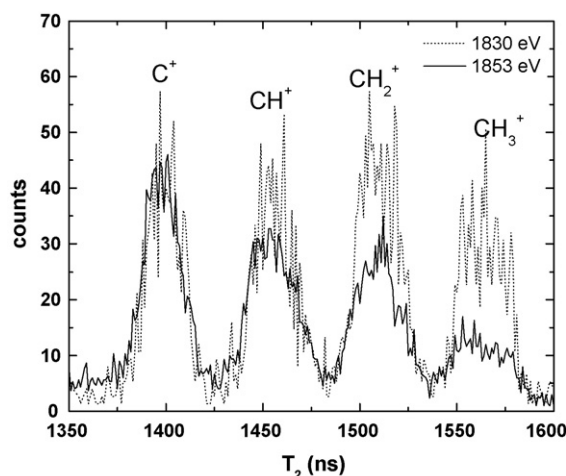


Fig. 4. Projections of PE2PICO onto t_2 axis for CH_n^+ fragments in coincidence with H^+ ion at 1830 and 1853 eV. The spectra have been normalized in order that both C^+ peaks present approximately the same intensity.

orientation of the molecule due to selective excitation. The time difference between the two peaks of the same CH_n^+ fragment is 20 ns irrespective to the number of H atoms. On the other hand, the widths and relative intensities of the structures are not the same. For instance, in the case of CH_3^+ , the peak at higher flight times (peak a in Fig. 5), is 9.0 ± 1.5 ns wide (FWHM) while the peak b at lower flight times is 16.6 ± 1.5 ns wide. The overall CH_3^+ peak width is 40 ns and is broader than the corresponding CH_3^+ peak in the PEPICO spectrum at 1841 eV (34.2 ± 3.2 ns, FWHM), as would be anticipated derived from an increased electrostatic repulsion. Although asymmetric, the CH_3^+ peak in the PEPICO spectrum does not present the double peak structure as in the PE2PICO case. In the case of CH_2^+ , peak c is 16.6 ± 1.5 ns wide, peak d is 13.1 ± 1.2 ns wide, and the overall peak width is 48 ns. In the case of CH^+ , peak e is 18.9 ± 1.1 ns wide, peak f is 11.2 ± 0.5 ns wide and overall peak width is 39 ns. In the case of C^+ , the structure is not well defined and the overall peak width is 37 ns corresponding to a kinetic energy of 6.8 eV. The observed double peak structure might arise because of the well-defined symmetry of the excited orbital, where molecules with their axes parallel to the polarization vector of the incident photon, which coincides with the spectrometer axes, preferentially

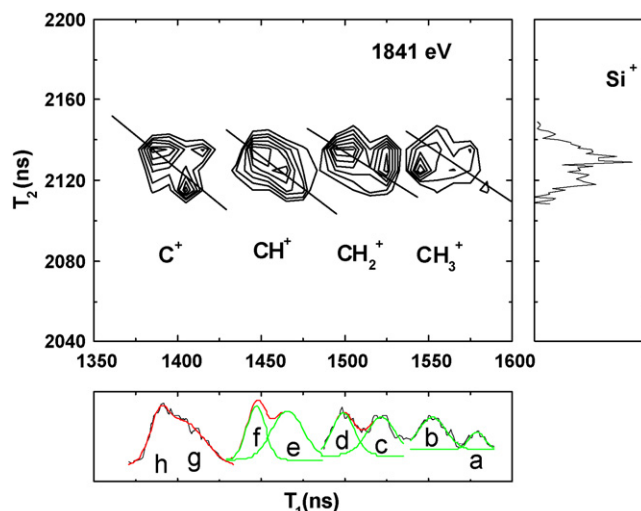


Fig. 5. CH_n^+ + Si^+ coincidences of TMS at 1841 eV. See text for details.

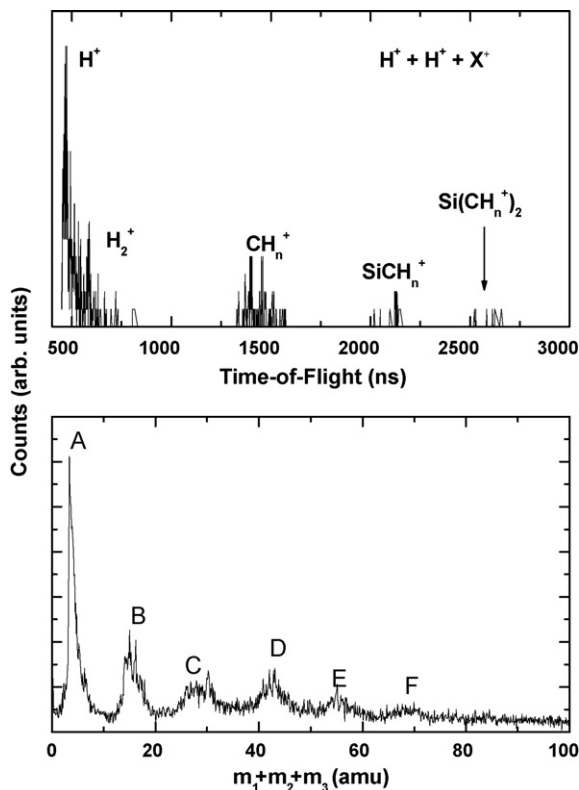


Fig. 6. Top: projection of PE3PICO (t_3 , *countstriple*) spectrum for $H^+ + H^+$ precursors ($H^+ + H^+ + X^+$) where X^+ means the third ion; bottom: PE3PICO triple-sum spectrum for TMS molecule. The horizontal axis is presented in the form of a sum of mass ($m_1 + m_2 + m_3$) for presentational purposes.

absorb the incident photons. Due to the fact that the fragmentation process is much faster than the molecular rotations, fragments may be ejected parallel to the spectrometer axes. The Si^+ peak is 21 ns wide (FWHM), corresponding to a kinetic energy of 0.9 eV irrespective to which CH_n^+ ion it coincides. The C^+/Si^+ has a slope of $21/37 = -0.57$ and the sum of kinetic energy of both fragments is 7.7 eV, where the C^+ fragment takes 88% of it.

3.3. Fragmentation of the $Si(CH_3)_4^{3+}$ trication

Due to the strong Coulomb repulsion, triply charged molecules are usually unstable and fragmentates. As a consequence, they are not usually observed in the time scale of most spectrometric experiments. Triply charged molecular species are expected to dissociate mainly via charge separation. In our experiment, the triple coincidence data is compressed in the form (t_1, t_2, t_3 , *countstriple*), which results in complicated multi-dimensional ways, difficult to visualize. However, it is possible to express the triple coincidence results in simpler ways. For instance, a way to visualize and extract information from a triple coincidence process is via the triple-sum spectrum, which corresponds to the sum of the three time components of the PE3PICO spectrum in the form ($t_1 + t_2 + t_3$). It represents therefore the abundances of the triply charged apparent precursors, but, because of secondary dissociations, in which neutral fragments are released, the observed ion triplets are not necessarily the primary precursors. Considering that the time of flight of an ion is directly related to its mass/charge ratio, this procedure can be used to identify the masses of the fragment ions involved in a triple coincidence.

The triple-sum spectrum of the triply ionized molecule $Si(CH_3)_4^{3+}$, around the Si 1 edge is shown in Fig. 6, along with

the projection of PE3PICO onto t_3 axis for a given t_1-t_2 window. No major changes have been observed in the PE3PICO spectra taken at different energies. Thus, in order to improve the statistics, spectra taken at different photon energies were summed up. The sum ($t_1 + t_2 + t_3$) has been converted into the corresponding sum of ion masses ($m_1 + m_2 + m_3$) for the sake of presentation, since the time of flight of an ion is directly related to square root of its mass. Considering the natural broadening of the peaks due to kinetic energy release in the dissociation processes, it was not possible to clearly distinguish fragments containing hydrogen for this molecule. Following the analysis of this triple-sum spectrum additional information on the dissociation of the TMS trication can be extracted.

In Fig. 6, Peak A most likely corresponds to the coincidences $H^+ + H^+ + H^+$ and $H^+ + H^+ + H_2^+$. Peak B is associated to $H^+ + H^+ + CH_n^+$ ($n=0$ or 1) and $H^+ + H^+ + Si^{2+}$, corresponding to a triple and quadruple ionization, respectively. Peak C corresponds to the TMS^{3+} dissociation into the following three singly charged fragments and neutrals: $H^+ + H^+ + Si^+$, $H^+ + H_2^+ + Si^+$. The less intense peak labeled as D originates from the triple coincidence between the fragments $H^+ + Si^+ + CH_n^+$. The low intensity peak E originates from the triply ionized TMS molecule leading to the coincidence between $C^+ + Si^+ + CH_n^+$ ions plus neutrals. Peak F represents the coincidence $C^+ + Si^+ + [CH_n]_2^+$. Broad structures are observed, indicating a high energy release.

4. Conclusions

Synchrotron radiation and time-of-flight mass spectrometry have been employed in the investigation of mass spectra for the $Si(CH_3)_4$, a compound with a wide range of significant technological applications, around the Si 1s edge. The fragmentation pattern of the TMS molecule is seen to change strongly at the shape resonance centered around 1853 eV.

The asymmetry of the H^+ peak was attributed to the slow dissociation of the CH_3^+ ion. By fitting an exponential decay, the decay constants were determined as a function of the photon energy.

Over the whole energy range of the PE3PICO spectra studied in this paper, an eminent contribution of H^+ fragments was observed. This observation is in accordance with the photofragmentation pattern described previously for TMS [4–10] and also for the related species $(CH_3)_3SiI$ excited at inner shell levels [27]. Indeed, the dynamic of fragmentation of charged hydrocarbon species is strongly dominated by the rupture of C–H bonds [28]. As proposed recently, the processes that take place in such molecules can be characterized as “evaporation”, i.e., eliminating light H neutral atoms, or “fission”, i.e., ejecting H^+ ions, or the molecule can breaking up into two or more charged species [29].

Although the contribution of stable doubly and triply charged species was not significant in the measured spectra, intense double and triple ionization of the molecule was demonstrated below and above the Si 1s edge, through PE2PICO and PE3PICO measurements.

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