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# Charge separation mass spectrometry study of the chloroform molecule following valence and Cl 2p photoionization

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## Abstract

Chloroform ($HCCl_3$) molecule has been studied using time-of-flight mass spectrometry in the multi-coincidence mode and synchrotron radiation as the source of photons in the range from 34 to 230 eV, which encompasses the valence level and the Cl 2p edge. Photoionization branching ratios have been measured under efficient ion extraction. Photoelectron photoion coincidence techniques (PEPIPICO, and PEPIPIPICO) have been used in the elucidation of the fragmentation mechanisms of multiply charged molecular ions, formed following the absorption of energetic photons. Observations concerning the molecular fragmentation of the $HCCl_3^{2+}$ were attributed to the role of the fast dissociation leading to the release of H atom. It is shown that this unstable doubly charged parent molecule, fragments preferentially via the symmetric mechanism $m^{2+} \rightarrow m_1^+ + m_2^+ + m_3$ which is mostly driven by Coulomb forces and has the $Cl^+ + Cl^+ + m_3$ as its major outcome. The dissociation mechanisms for the trication $HCCl_3^{3+}$ have also been investigated and are seen to dissociate preferentially into singly charged fragments.

*Keywords:* Photoionization; Valence; Core excitation; $HCCl_3$; Multi-coincidence

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## 1. Introduction

Experimental studies of multiply charged atomic and molecular ions are of increasing interest in physics and chemistry. The absorption of a VUV photon by a molecule results in an efficient molecular fragmentation which presents many open theoretical questions that are in principle difficult to treat. Features such as the many-body character of the dissociation processes, the presence of possible repulsive excited states, as well as the correlation between the electrons during the molecular dissociation are part of the complex particularities involved in the molecular fragmentation.

VUV and soft X-ray range photons have enough energy to be absorbed by either valence or shallow core electrons opening the possibility of occurrence of several ionization channels due to the electronic relaxation which in turn, plays an important role in the molecular dissociation.

In recent years, substantial effort has been dedicated to the study of the dissociation dynamics of multiply charged molecules into charged fragments by the so called Coulomb explosion processes [1,2]. In the case of simple molecules the satisfactory application of a long-range Coulomb potential suggests that the kinetic energy of the charged fragments comes from the repulsive role of the ionic charged species. The study of the fragmentation processes in core-excited molecules is of great interest to many branches of science and technology including astrophysics, biophysics, environmental chemistry and molecular physics. Charge separation mass spectrometry (CSMS) is known as a powerful tool in the study of the dynamics of the fragmentation of from core-excited molecules [3,4]. The advent of CSMS provided the possibility of unambiguous identification of the fragmentation products and their dynamics of formation from the measurement of their absolute time-of-flights. These methods have been successfully applied to several molecular systems [5–8].

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The $CHCl_3$ molecule is highly symmetric in the ground state and belongs to the $C_{3v}$ symmetry point group. It presents most of its electron charge clouds concentrated on the three peripheral chlorine atoms because of their higher electronegativity as compared to the carbon and hydrogen atoms.

We have recently reported on the study of the dissociative photoionization of the chloroform molecule, excited in the valence region and in the vicinity of the Cl 2p edge using time of flight mass spectrometry in the single coincidence mode (PEPICO) [9], the deep core level ionization of this molecule was also studied around the Cl 1s edge [10] using ion yield spectroscopy. In addition, the dissociation dynamics of this molecule in the valence has also been recently investigated by threshold photoelectron photoion coincidence (TPEPICO) [11]. In the present work we extend the previous studies and report new results on the dissociative photoionization of the doubly and triply ionized $HCCl_3$ molecule following photo-excitation at the valence region and in the vicinity of the Cl 2p edge. To our knowledge no similar study has been reported in the literature for this molecule.

## 2. Experimental

A Wiley–McLaren type time-of-flight mass spectrometer [9,12] has been employed for mass/charge analysis of the ionic species. Electrons, accelerated in the opposite direction with respect to the positive ions, are recorded without energy analysis by two micro-channel plate detectors and provide the start signal to a time-to-digital converter (TDC). A 766 V/cm dc electric field is applied to the first ion acceleration stage. The ionized recoil fragments produced by the interaction of the sample with the light beam are accelerated by a two-stage electric field and detected by a pair of micro-channel plate detectors mounted in chevron configuration. Arrival of the ions gives rise to stop signals to the TDC, which allows simultaneous multi-hit capability with 1ns resolution. The time-of-flight spectrometer was designed to present negligible angular discrimination of the ejected ions with kinetic energy release up to 40 eV. We have used synchrotron radiation from the toroidal grating monochromator (TGM) beamline, which operates in the range from 12 to 310 eV at the Brazilian Synchrotron Light Laboratory (LNLS) [13]. This beamline provide a photon flux of approximately $10^{11}$ photons/s/100 mA/0.1%bandwidth and resolving power better than 2000. The sample was commercially obtained with purity better than 99.5%. No further purification was used except for degassing the liquid samples by multiple freeze–pump–thaw cycles before admitting the vapor into the chamber. The present coincidence experiments have been performed with the TOF drift tube linearly oriented relative to the plane of polarization of the synchrotron light. Two-dimensional spectra for double correlation between one electron and two positive ions, photo-electron photo-ion photo-ion coincidence (PEPIPICO or PE2PICO) and correlation between one electron and three positive fragments, photo-electron photo-ion photo-ion photo-ion coincidence (PEPIPIPICO or PE3PICO) have been recorded for chloroform molecule in the vicinity of Cl 2p edge.

## 3. Results and discussion

In this paper we report results of multi-fragmentation of the doubly and triply ionized $HCCl_3$ molecule in the realm of shallow core-excitation (Cl 2p) as follows:

$$HCCl_2{}^{2+} \rightarrow m_1{}^{+} + m_2{}^{+} + m_3$$

and

$$HCCl_2{}^{3+} \rightarrow m_1{}^{+} + m_2{}^{+} + m_3{}^{+} + m_4$$

or

$$HCCl_2{}^{3+} \rightarrow m_1{}^{2+} + m_2{}^{+} + m_3$$

Two-dimensional spectra for the correlation between one electron and two positive ions (PE2PICO) have been recorded in the form ($t_1$, $t_2$, *countsdouble*) where $t_{1,2}$ are the time of flights for the first or second ions and *countsdouble* is the number of double coincidence events. Coincidence events were taken into consideration only when *countsdouble* > 1. Similarly, the triple coincidence spectra (PE3PICO) which involve the correlation of one electron and three positive fragments have been compressed in the form ($t_1$, $t_2$, $t_3$, *countstriple*) where, *countstriple* is the number of triple coincidence events.

The double coincidence spectrum molecule recorded at 230 eV photon energy (above the Cl 2p resonance) for the $HCCl_3$ is shown in Fig. 1. The PE2PICO branching ratios for the observed pairs of ions are presented in Table 1. The same correction procedure adopted by Santos et al. [6] was used for events in which the two ions arrive within a time difference smaller than the multi-hit resolution of the present experiment (20 ns). An example of such event is the $Cl^+ + Cl^+$ pair in coincidence.

The double or triple photoionization events usually occur due to electron-electron correlation. For instance, the shake-off process (ionization of a single electron followed by the removal of another electron due to a change in the molecular field) requires an excess of energy above the ionization threshold so that the first ejected electron may leave the molecule fast enough to cause a sudden change in the field. The expected onset for direct double ionization of the $HCCl_3$ molecule is about 32 eV as predicted

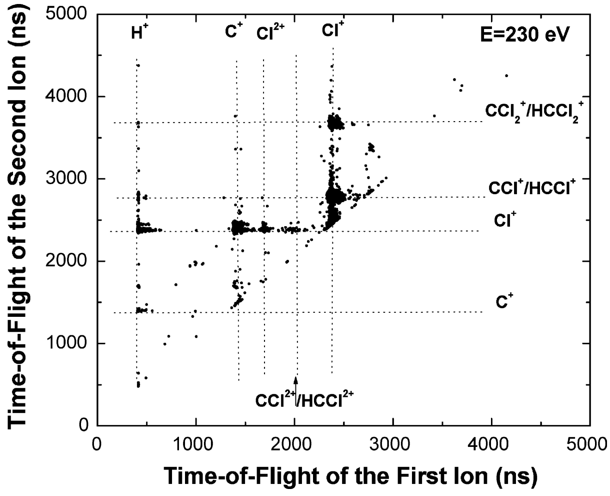

Fig. 1. PEPIPICO spectrum of $HCCl_3$ recorded at 230 eV photon energy.

Table 1
Corrected PEPIPICO branching ratios (%) as a function of the photon energy

| Ion pair | 34 eV | 195 eV | 201 eV | 230 eV |
|---|---|---|---|---|
| $H^+/C^+$ | 0.91 | 1.0 | 1.1 | 0.59 |
| $H^+/Cl^+$ | 4.8 | 5.4 | 5.1 | 2.6 |
| $H^+/CCl^+$ | 0.26 | 0.02 | 0.51 | 0.22 |
| $C^+/Cl^{2+}$ | 0.03 | 0.02 | 0.04 | 0.01 |
| $C^+/Cl^+$ | 4.0 | 8.1 | 8.2 | 4.1 |
| $CH^+/Cl^+$ | 4.9 | 9.1 | 9.7 | 4.4 |
| $Cl^+/Cl^+$ | 63.0 | 54.5 | 50.8 | 70.7 |
| $Cl^+/Cl_2{}^+$ | 0.03 | <0.01 | 0.14 | 0.01 |
| $Cl^+/CCl_2{}^{2+}$ | <0.01 | 0.06 | 0.12 | 0.04 |
| $Cl^+/HCCl_2{}^{2+}$ | <0.01 | 0.06 | 0.15 | 0.02 |
| $Cl^+/CCl^+$ | 6.6 | 14.6 | 9.6 | 6.5 |
| $Cl^+/HCCl^+$ | 9.8 | 2.4 | 10.2 | 7.6 |
| $Cl^+/HCCl_2{}^+$ | 1.9 | 4.1 | 2.3 | 1.7 |
| $Cl^+/CCl_2{}^+$ | 2.1 | <0.01 | 1.5 | 1.4 |
| $Cl^+/Cl_2{}^+$ | 0.03 | <0.01 | 0.14 | 0.01 |
| $(H)CCl^{2+}/Cl^+$ | <0.01 | 0.09 | 0.12 | 0.02 |
| $CCl^+/Cl_2{}^+$ | <0.01 | 0.04 | 0.05 | 0.01 |
| $HCCl^+/Cl_2{}^+$ | <0.01 | 0.21 | 0.10 | 0.02 |

by empirical rules [14]. Below the Cl 2p edge, double ionization of the $HCCl_3$ molecule is allowed only by the direct double ionization or autoionization processes. The branching ratios for the most intense dissociative double and triple photoionization channels of $HCCl_3$ are presented in Fig. 2 and Table 1. Some general observations about the PEPIPICO spectrum (Fig. 1) and the branching ratios (Fig. 2) are in order. First of all, it has been observed that the $Cl^+$ ion is a major outcome from the dissociation of the doubly and triply charged $HCCl_3$ molecule, and is the dominant peak in the coincidence spectra in the range studied in this work. This is in agreement with the results previously reported for the single ionization spectra for this molecule in the same energy range [9].

Doubly charged fragments, such as $Cl^{2+}$, $CCl^{2+}$, $HCCl^{2+}$, $HCCl_2{}^{2+}$ and $CCl_2{}^{2+}$ most likely originated from the unstable triply charged molecular ion $HCCl_3{}^{3+}$, following the mechanism $HCCl_2{}^{3+} \rightarrow m_1{}^{2+} + m_2{}^{+} + m_3$, have been observed in the PEPIPICO spectra, although with low intensity (<1%).

The $Cl^+ + Cl^+$ coincidence dominates the PEPIPICO spectra in the energy range studied here (50–70%) followed by the $Cl^+ + HCCl^+ + Cl$ and $Cl^+ + CCl^+ + H + Cl$ channels, with a small advantage for the $Cl^+ + HCCl^+$ coincidence channel (8–10%) in the valence and Cl 2p continuum. Near the Cl 2p, the release of neutral H increases and favors the $Cl^+ + CCl^+$ coincidence (~15%) in comparison with the $Cl^+ + CCl^+ + H$ (~2%) channel. As pointed out by Thiessen et al. [15], a strong change in the equilibrium geometry is expected to occur induced by the population of the $\sigma^*$ orbital, and the excitation of vibrational series associated to the C–H bond might be expected, hence leading to a more efficient neutral H release. The fast increase of the $H^+ + CCl^+$ channel near the Cl 2p edge is an additional indication that the excitation of orbitals corresponding to C–H bond is playing a role.

The $C^+ + Cl^+$ coincidence is another important outcome from the dissociation of the doubly charged $HCCl_3$ molecule, and

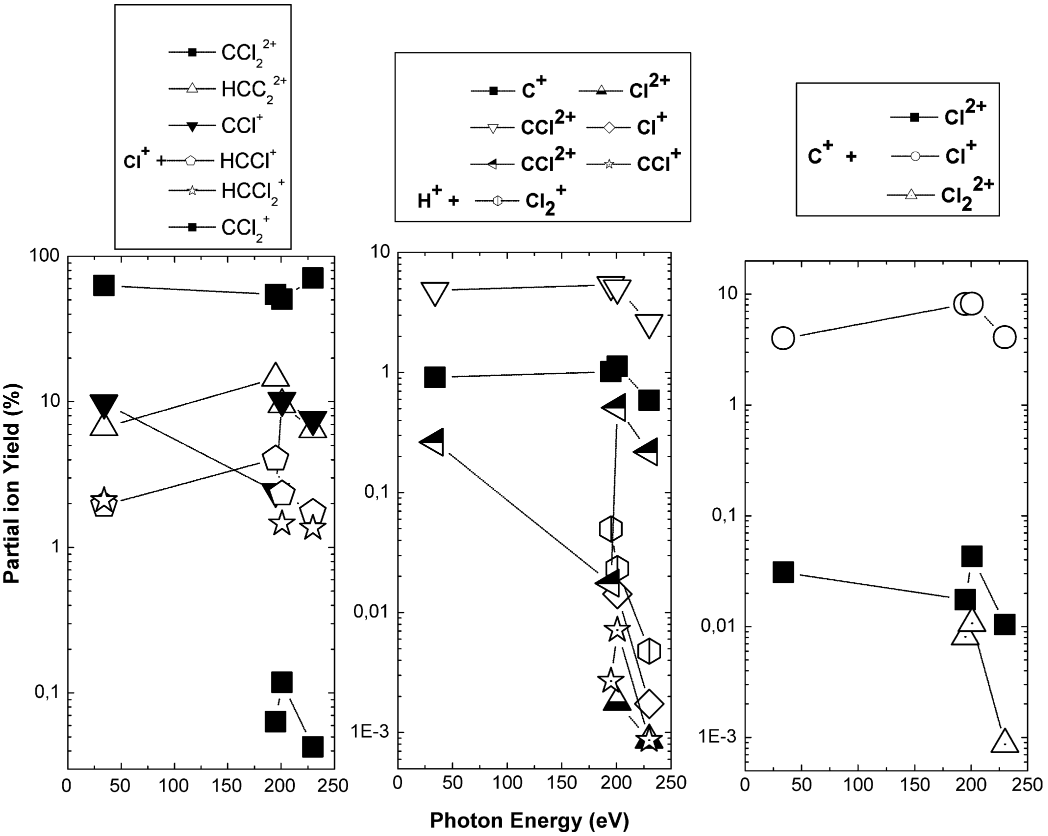

Fig. 2. PEPIPICO branching ratios for dissociative double and triple photoionization of $HCCl_3$ as a function of the incident photon energy.

points out to the complete atomization of the parent molecule. The intensity of this channel increases near the Cl 2p edge and decreases when the photon energy is higher than the Cl 2p ionization threshold. The $C^+ + Cl^{2+}$ intensity also presents a maximum at Cl 2p edge although its intensity is less than 0.1% in this energy range. The $C^+ + Cl_2{}^+$ coincidence, which corresponds to the atomization of the molecule followed by a fast rearrangement reaction, is also observed, albeit with very low intensity. The double coincidence involving the $CH^+$ fragment has also been detected, and the $CH^+ + Cl^+$ channel is found to contribute with almost 10% around the Cl 2p edge.

The contribution from triple ionization is mainly observable above the Cl 2p edge where the Auger process is energetically possible. Let us now turn our attention to the molecular fragmentation pathways. Eland [3,4] and Simon et al. [5] have discussed the possible fragmentation mechanisms for two- and three-body decay:

(1) Two-body dissociation

In the case of two-body dissociation, the momenta of the positively charged fragments are anti-correlated due to the momentum conservation law, and the coincidence peak in the $t_2 \times t_1$ plane would show a ‘cigar’ shape with slope $-1$.

The slopes for the two-body processes have been determined using a least-squares fit procedure. In fact the measured slopes for the two-body dissociations observed in this work, $H^+ + CCl_3{}^+$ and $Cl^+ + HCCl_2{}^+$, have been found very close to $-1$, within the uncertainties.

For the $CHCl^+ + Cl_2{}^+$ coincidence, the measured slopes in the vicinity of the Cl 2p edge were also found to be close to $-1$. However, this is obviously not a two-body dissociation since all the chlorine atoms are bonded to the central C atom. This result suggests that an instantaneous explosion is taking place in which the bonds holding two chlorine atoms are simultaneously broken, immediately upon the double ionization of the parent molecule and this is followed by a fast rearrangement $Cl^+ + Cl \rightarrow Cl_2{}^+$.

In the case of the $Cl^+ + HCCl_2{}^{2+}$ coincidence which is also a two-body dissociation process we would also expect a $-1$. However the statistics in our present experiment was not good enough to properly determine the slope for this channel.

(2) Three-body dissociation

In a three-body fragmentation process from a doubly charged molecule, the possible mechanisms are known as deferred charge separation (DCS), secondary decay (SD) and concerted dissociation (CD). In DCS, a neutral particle is ejected in the first step of the fragmentation process, and this is followed by the charge separation in the second step. If the energy release in the second step is much larger than the energy release in the first step, the expected slope would be $-1$, in analogy with the two-body fragmentation. In SD, the charge separation takes place in the first dissociation step, followed by ejection of a neutral particle from one of the charged fragments.

For the $Cl^+ + HCCl^+ + Cl$ channel if we consider the secondary decay mechanism, the expected slope would be (neglecting the kinetic energy release in the second step):

$$\text{slope} = -\frac{m_{HCCl^+}}{m_{HCCl^+} + m_{Cl^+}} = -0.58$$

Considering the DCS mechanism, the expected slope would be $-1$. The measured slopes of the $Cl^+ + HCCl^+$ coincidence have ranged between $-0.67$ and $-0.78$. This difference is a clear indication that the kinetic energy cannot be neglected in the case of the neutral Cl release.

(3) Many-body decay

Four-body decay mechanism has also been proposed by Simon et al. [5]. As in the previous case, deferred charge separation (DCS), secondary decay (SD) and concerted dissociation (CD) processes may be observed. In addition, two other mechanisms have been proposed: secondary decay after a deferred charge separation (SDDCS) and secondary decay in competition (SDC).

The slopes of the projected coincident peaks onto the $t_1 - t_2$ plane as a function of the incident photon energy are presented in Fig. 3. The slopes have been determined by least squares fit, as well as by careful inspection of the contour diagrams. Due to the uncertainties in the time of flights, the least squares fit sometimes fail in providing a precise value for the slope. In the case of the $H^+/C^+$ coincidence, for instance, a positive value was found for the measured slope. This suggests that the kinetic energy released during the rupture of all three C–Cl bonds is probably considerable and may not be neglected. It was not possible to determine precisely the pathways leading to the $H^+ + C^+ + 3Cl$ and

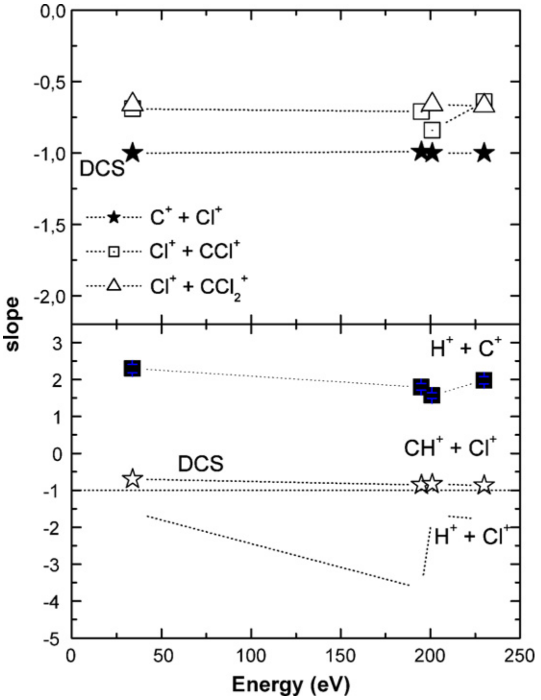

Fig. 3. Slopes of contour plots of some PE2PICO peaks as a function of photon energy. Dotted lines represent expecting values according the second decay mechanism.

$Cl^+ + Cl^+$ coincidence channels because of the previously mentioned instrumental limitations.

In the $C^+ + Cl^+$ coincidence case, the measured slopes are close to $-1$, thus suggesting the DCS mechanism. The deviations from unity may arise from the non-zero kinetic energy released during the neutrals dissociation, as previously pointed out. As suggested by Eland [3], many peak shapes are intermediate between the beforehand indications of the stepwise mechanisms and the concerted mechanism, implying that the hypotheses made in the formulation of the stepwise mechanisms may not be applicable in this case.

### 3.1. *Fate of the doubly charged molecular ion, $HCCl_3{}^{2+}$*

Important questions that arise from the investigation of multiply charged ions concerning their stability and lifetimes. If the bound minimum of a dication $AB^{2+}$ is lower in energy than the lowest atomic asymptotes, $A^+ + B^+$ and $A^{2+} + B$ then the cation $AB^{2+}$ would be stable.

The doubly charged molecular ion $HCCl_3{}^{2+}$ was found to be unstable on a microsecond time scale and consequently has not been observed in the PEPICO spectra [9]. The doubly charged parent molecule may fragment with charge separation, as follows:

$$m^{2+} \rightarrow m_1{}^+ + m_2{}^+ \qquad (1)$$

which is mainly driven by Coulomb forces, or via the asymmetric mechanism:

$$m^{2+} \rightarrow m_1{}^2 + m_2 \qquad (2)$$

which, on the other hand, is mainly driven by chemical forces. The processes summarized by Eq. (1) are the presented in Table 1 and those that follow Eq. (2) are listed below:

$$\begin{aligned} HCCl_3{}^{2+} \rightarrow\ & Cl^{2+} + HCCl_2 \\ & CCl^{2+} + H + 2Cl \\ & HCCl^{2+} + 2Cl \\ & CCl_2{}^{2+} + H + Cl \\ & HCCl_2{}^{2+} + Cl \end{aligned}$$

In principle, distinguishing between processes (1) and (2) is not a simple task, due to the variety of dissociative multiple ionization channels, which contribute to different coincidence spectra at the same time. Using a calibration procedure suggested by Simon et al. [16], we have been able to determine reliable branching ratios for the dissociative double ionization process. In this procedure, we assume the contributions from higher ionization degrees such as quadruple ionization and so on are small, compared to the single and double ionization, which dominate in the energy range of the present study. Therefore, we also must correct single and double coincidence spectra accordingly, in order to account for "aborted" double and triple ionization events, respectively. The relative abundance of single, double and triple ionization to the total ionization rate can thus be determined. Let $D_{20}$ represent the rate of doubly charged ions (in the PEPICO spectra, represented by Eq. (2)), and $D_{11}$ the rate of dissociative double ionization (in the PEPIPICO spectra, represented by Eq. (1)). The total ion count rate for double ionization events will be given by

$$I_D = D_{20} f_i f_{e2} + D_{11} f_i^2 f_{e2} \qquad (3)$$

where $f_i$ is the ion detection efficiency, supposedly independent of the recoil ion charge state, and $f_{e2}$ is the efficiency for detection of at least one electron arising from a double ionization. The measured quantities are thus:

$$D_{20\ \mathrm{meas}} = D_{20} f_i f_{e2} \quad \text{and} \quad D_{11\ \mathrm{meas}} = D_{11} f_i^2 f_{e2} \qquad (4)$$

Branching ratios for the double ionization channels represented by Eqs. (1) and (2) can be written respectively as

$$\frac{D_{11}}{D_{20} + D_{11}} = \frac{D_{11\ \mathrm{meas}}}{D_{20\ \mathrm{meas}} f_i + D_{11\ \mathrm{meas}}} \qquad (5)$$

$$\frac{D_{20}}{D_{20} + D_{11}} = \frac{D_{20\ \mathrm{meas}}}{D_{20\ \mathrm{meas}} + D_{11\ \mathrm{meas}}/f_i} \qquad (6)$$

The ion and electron efficiencies have been measured following the procedures of Simon et al. [5]. In the present case, the determined ion detection efficiency was about 25%. From this analysis it results that at 195 eV photon energy, for instance, about 92% of the double ionization events in the $HCCl_3$ molecule follow the process $m^{2+} \rightarrow m_1{}^+ + m_2{}^+$. This result is roughly independent on the incident photon energy in the vicinity of the Cl 2p edge. It is interesting to compare the contrast to the case of the $SiF_4$ molecule [6], where the process $m^{2+} \rightarrow m_1{}^{2+} + m_2$ dominates the fragmentation of the doubly charged molecular ions. Fig. 4 illustrates the relative contributions of the double ionization channels of $HCCl_3$ molecule near the Cl 2p edge, compared

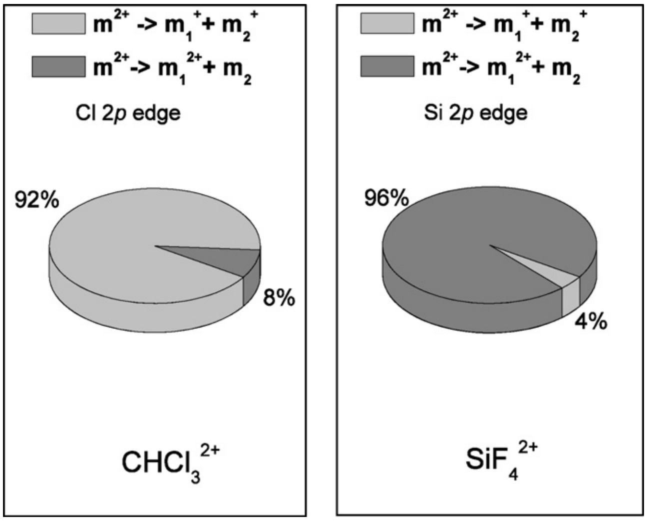

Fig. 4. Comparison between the contribution of the molecular fragmentation pathways $m^{2+} \rightarrow m_1{}^+ + m_2{}^+ + m_3$ and $m^{2+} \rightarrow m_1{}^{2+} + m_2$ for the double-ionized $HCCl_3$ and $SiF_4$ molecules in the vicinity of the Cl 2p and Si 2p edges, respectively.

to the corresponding channels for the $SiF_4$ molecule near the Si 2p edge [6].

### 3.2. Fragmentation of the $HCCl_3^{3+}$ trication

The onset for direct triple ionization of the $HCCl_3$ molecule is situated above 60 eV as estimated by empirical rules [14]. Because of the much higher instability of triply charged molecules, as a consequence of the strong Coulomb repulsion, they are usually not observed in the time scale of most spectrometric experiments. Triply charged molecular species are expected to dissociate mainly via charge separation.

One important aspect in triple ionization processes is the large amount of false coincidences that may contribute to the PEPIPIPICO spectrum, which represent as much as 30–40% in some cases. In order to reduce this contribution we usually reject the triple coincidences where at least one of the ions is not present in the single coincidence spectrum (PEPICO), and consequently does not represent a real fragment. As previously pointed out, the triple coincidence data is compressed in the form ($t_1, t_2, t_3$, *countstriple*), which results in complicated multidimensional ways visualizing the results. However it is possible to express the triple coincidence results in simpler ways. One way of simplify the visualization of a PE3PICO spectrum is by a two-dimensional graph. In this case, the coincidence spectrum involving one electron and three correlated charged fragments is projected onto one of three time axis. As an example, the PE3PICO spectrum of the $HCCl_3$ molecule (projected onto the $t_3$ axis) at 230 eV photon energy of the core excited is shown on the top of Fig. 5. Considering that the PE3PICO data are collected in a way that $t_3$ axis represents the slower (heavier) ion the in triple coincidence, hence such projected spectrum provides information on the other possible correlated fragments in a triple coincidence spectrum. For instance, the first peak in Fig. 5 (top) corresponds to the $Cl^+$ as the third correlated ion, and as expected is the most intense fragment at this energy. It is also in agreement with results for the single coincidence spectra for this molecule in the same energy range [9]. Therefore, one of the most likely pairs of ions to compose this triple coincidence with $Cl^+$ would be $H^+$ and $C^+$, originated from dissociation of the triply charged molecular ion $HCCl_3^{3+}$ where two Cl atoms leave as neutrals. Other possible combinations for this triple coincidence channel would be $C^+/Cl^{2+}/Cl^+$ and $H^+/Cl^{2+}/Cl^+$, both originated from a quadruple charged $HCCl_3^{4+}$, which are obviously less important at the energy range of this study. We would expect these channels to become more important with increasing energy. The same procedure is thus applied to the other peaks of the PE3PICO projected spectrum in order to characterize the possible dissociation channels resulting from the multiple ionization and dissociation processes. By having selected the possible fragment ion combinations from the PE3PICO projections, it is possible, for instance, to derive the relative intensity of each triple coincidence by selecting the time intervals for each fragment pair detected ($t_1$, $t_2$) and project them onto the corresponding $t_3$.

It should be pointed out that the peak corresponding to the $Cl^+$ only contains contribution from fragments that arrive at the detector in a time difference of at least 20 ns (the present time resolution). For this reason, in order to properly estimate the contribution from the coincidence $Cl^+ + Cl^+ + m_3{}^+$, where $m_3{}^+$ stands for the third correlated fragment, a similar correction as that applied to the $Cl^+ + Cl^+$ coincidence in the PEPIPICO spectra was also performed here. In case $m_3{}^+$ is also a singly charged chlorine ion, then the correction should be applied twice because the third chlorine atom may reach the detector in a time interval smaller than our electronics resolution.

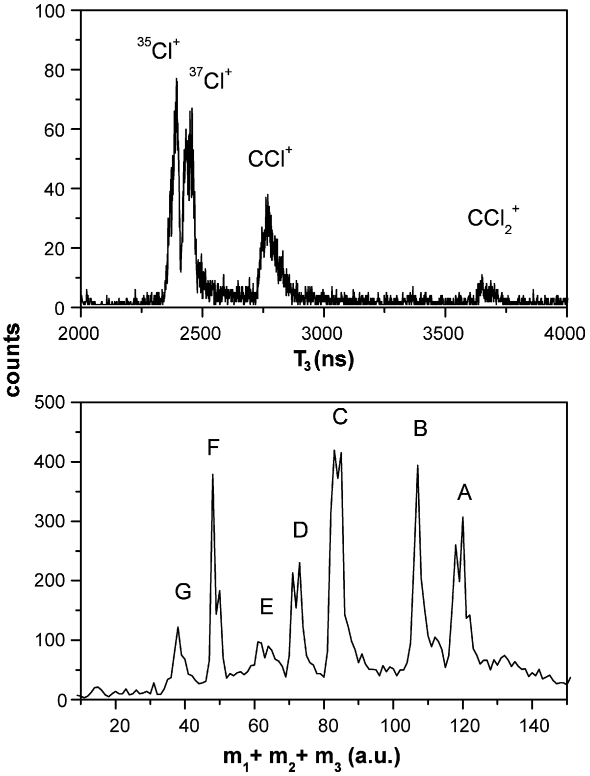

Fig. 5. Top: PEPIPIPICO spectrum of chloroform at 230 eV projected onto $t_3$ axis. Bottom: PEPIPIPICO triple-sum spectrum for $HCCl_3$ molecule plotted at 230 eV photon energy. The horizontal axis is presented in the form of a sum of mass ($m_1 + m_2 + m_3$) for presentational purposes.

An additional 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 ($t_1 + t_2 + t_3$). Therefore, it represents 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 [17], hence this procedure can be used to identify the masses of the fragment ions involved in the triple coincidence. This procedure has been previously applied with success by Simon et al. [18] to the investigation of the core-excited s-tetrazine molecule.

Fig. 5 (bottom) shows the triple-sum spectrum of the triply ionized $HCCl_3$ molecule at 230 eV photon energy, where 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 sake of presentation.

Considering the chlorine isotope contribution and 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 chloroform trication can be extracted.

The peak labeled as A most likely corresponds to the parent molecule which dissociates into three singly charged fragments:

$$\mathrm{HCCl_3}^{3+} \rightarrow \mathrm{Cl^+ + Cl^+ + CCl^+ + H}$$

$$\rightarrow \mathrm{Cl^+ + Cl^+ + HCCl^+}$$

The peak labeled as B represents the sum of three singly charged chlorine ions originating from the following fragmentation pathways:

$$\mathrm{HCCl_3}^{3+} \rightarrow \mathrm{Cl^+ + Cl^+ + Cl^+ + CH\ or\ (H + C)}$$

This intense triple coincidence channel is the signature of the preferential cleavage of the C–Cl bond from the multiply charged chloroform molecule.

The peak labeled as *C* corresponds to the $\mathrm{HCCl_3}^{3+}$ dissociation into the following three singly charged fragments and neutrals:

$$\mathrm{HCCl_3}^{3+} \rightarrow \mathrm{HC^+ + Cl^+ + Cl^+ + Cl}$$

$$\rightarrow \mathrm{C^+ + Cl^+ + Cl^+ + H + Cl}$$

The less intense peak labeled as D originates from the triple coincidence between the fragments $\mathrm{H^+ + Cl^+ + Cl^+}$. The low intensity peak labeled as E originates from the quadruple ionized $\mathrm{HCCl_3}$ molecule leading to the coincidence between $\mathrm{C^+ + Cl^{2+} + Cl^+}$ ions plus neutrals. Peak F represents the coincidence $\mathrm{H^+ + C^+ + Cl^+}$.

By the analysis of the feature labeled as G we came up with the following possibilities: the center of this peak locate at a time of flight sum corresponding to a mass/charge of about 37. By considering that in principle a triple coincidence event is only recorded if three correlated stop signals are detected then the first possibility would be the triplet of ions $\mathrm{H^+ + Cl^{2+} + Cl^{2+}}$. This would represent a dissociative process in which the precursor is a quintuple charged ion. Although it may be energetically possible, we would expect a low probability of occurrence of this channel with such intensity in the energy range of this study. The other possibility would be considering the peak labeled as G in Fig. 5 as a spurious coincidence. The explanation for this latter assumption is to consider a reflection of the signal of the $\mathrm{H^+}$ detected in time $t_1$ caused by the electronics, originating a second signal just after the first which would be counted as a second event $t_2$ leading to the false coincidence $\mathrm{H^+ + H^+ + Cl^{2+}}$. This would generate a peak in the same location as G in Fig. 5 (bottom). The background seen under most of the peaks in this figure is due to uncorrelated events.

As a final observation, the triple-sum spectra seems to be independent on the photon energy near the Cl 2p edge for this molecule, because no significant changes have been observed in the triple coincidence spectra at the energies 195 eV (below Cl 2p resonance), 201 eV (on resonance) or 230 eV (above resonance) studied in this work.

## 4. Summary and conclusions

CSMS studies are reported for the $\mathrm{HCCl_3}$ molecule using time of flight mass spectrometry in the multicoincidence mode and synchrotron radiation as photons source in the valence and soft X-ray range. Branching ratios, based on the PEPIPICO spectra have been measured along the valence and in the vicinity of the Cl 2p edge. Observations in the PEPIPICO spectra pointing out the active role of the extremely fast fragmentation of the $\mathrm{HCCl_3}$ molecule have been discussed. The doubly and triply charged molecular ions ($\mathrm{HCCl_3}^{2+}$ and $\mathrm{HCCl_3}^{3+}$) are known to be highly unstable in the microsecond time scale and have not been observed in the mass spectra for this molecule. Such species dissociate efficiently via different mechanisms. In the present work, we have shown that the fragmentation process in which two fragments share the excess of charge is the dominant decay mechanism from the double ionization of the $\mathrm{HCCl_3}$ molecule. From all the pathways coming from the double ionization of the core excited $\mathrm{HCCl_3}$ molecule, the $\mathrm{Cl^+ + Cl^+}$ coincidence is the most important and contributes roughly with 50%. The triply ionized $\mathrm{HCCl_3}$ molecule shows tendency to dissociate predominantly into three singly charged fragments plus neutrals in the energy range of this study.

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