

# Chlorine 1s Excitation and Fragmentation of Polyatomic Molecules

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## INTRODUCTION

Deep core excitation of small molecules has been the subject of interest in recent years [1]. In the present work, we extend this study to the analysis of the fragmentation of large polyatomic molecules. The carbon tetrachloride, CCl<sub>4</sub>, halothane (CHClBr-CF<sub>3</sub>), ethrane (CHFCl-CF<sub>2</sub>-O-CHF<sub>2</sub>), and forane (CF<sub>3</sub>-CHCl-O-CHF<sub>2</sub>) molecules (Fig. 1) have been excited in the vicinity of the chlorine 1s (~2800 eV) edge, using high energy tunable synchrotron radiation. The associated ionic fragmentation has been studied using time-of-flight mass spectrometry in the PEPICO mode. In this technique, molecules are ionized by photons and the resulting electrons and positive ions are detected in coincidence. Total and partial ion yields have been recorded as a function of the photon energy. A similar study has been previously done, focussing on shallow core-level ionization [2].

The present experiments were performed using x-ray synchrotron radiation from beamline 9.3.1 at the Advanced Light Source (ALS), Berkeley, CA and a time-of-flight mass spectrometer. The samples were commercially obtained and used without further purification.

Carbon tetrachloride, CCl<sub>4</sub>, is a volatile compound with several important technological applications, being for instance used as an etchant agent in microelectronics. In addition, the CCl<sub>4</sub> molecule pollutes the atmosphere and has also been related to the so-called greenhouse effect. It possesses tetrahedral symmetry (T<sub>d</sub> point group).

The halothane, ethrane and isoflurane molecules have been known for many years to possess anesthetic properties, i. e., induce unconsciousness, analgesia, muscle relaxation, etc.

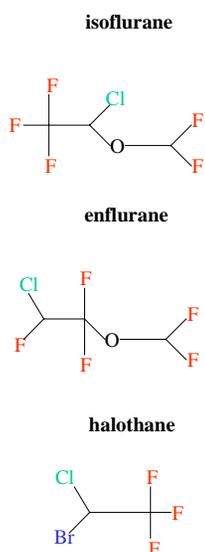


Fig. 1 – Structures of the anesthetics studied in this work.

## EXPERIMENT

The experiment was performed using x-ray synchrotron radiation from beamline 9.3.1 at the Advanced Light Source (ALS) in Berkeley, California. 9.3.1 is a bending magnet beamline covering 2-6 keV photon-energy range. This beamline provides a flux of  $10^{11}$  photons  $s^{-1}$  in a bandpass  $\leq 0.5$  eV [1].

Photon-energy calibration was achieved by scanning the monochromator through the Cl K-edge region while monitoring the total-ion yield. The photon-energy was determined with 0.2 eV accuracy.

The ionized recoil fragments produced by the light beam, under single collision conditions, were accelerated by a two-stage electric field and detected by two micro-channel plate detectors after being mass-to-charge analyzed using a 3,8 cm time-of-flight spectrometer. The ions produce stop signals to a time-to-amplitude converter (TAC) started by the signal generated by the electrons accelerated in a opposite direction and recorded without energy analysis. The first acceleration stage consists of a plate-grid system with a 2200 V/cm electric field. The gas inlet needle was kept at ground potential. The sample was commercially obtained with high purity. No further purification other than outgassing was used. The experimental chamber base pressure was in the  $10^{-9}$  Torr range. In order to diminish the contribution from false coincidences, the pressure during the measurements was kept below  $10^{-5}$  Torr.

We obtained conventional time-of-flight mass spectra from the correlation between one electron and a positive fragment (PEPICO) recorded in the form  $(t_1, counts)$  where  $t_1$  is the time-of-flight of the detected fragment, and *counts* the number of events of  $t_1$ .

## RESULTS

**Anesthetics** → The PEPICO mass spectra of the halothane ( $CHClBr-CF_3$ ), ethrane ( $CHFCl-CF_2-O-CHF_2$ ), and Forane ( $CF_3-CHCl-O-CHF_2$ ) molecules are currently under analysis. In this report we focus our attention on the  $CCl_4$  data.

**$CCl_4$**  → The  $Cl^+$  fragment dominates the mass spectra, followed by the  $Cl^{2+}$  and the sum  $C^+ + Cl^{3+}$  (not resolved).

There is no evidence for stable  $CCl_4^+$  ion in the energy range studied in this work in accordance with earlier studies using electron impact technique. The  $CCl_4^+$  is not observed because the excitation of the carbon tetrachlorine molecule occurs into a repulse excited state of neutral  $CCl_4$  which dissociates into Cl and  $CCl_3$  that in turns, autoionizes giving rise to  $CCl_3^+$  ion [3].

The fragment ion branching ratios as a function of the photon energy are shown in Fig. 2. Generally speaking, the relative intensity of multiply-charged ions increases at the resonance, while the intensity of singly-charged ions is seen to decrease. The yields of  $CCl^+$  and  $CCl_2^+$  present a clear minimum at the resonance.

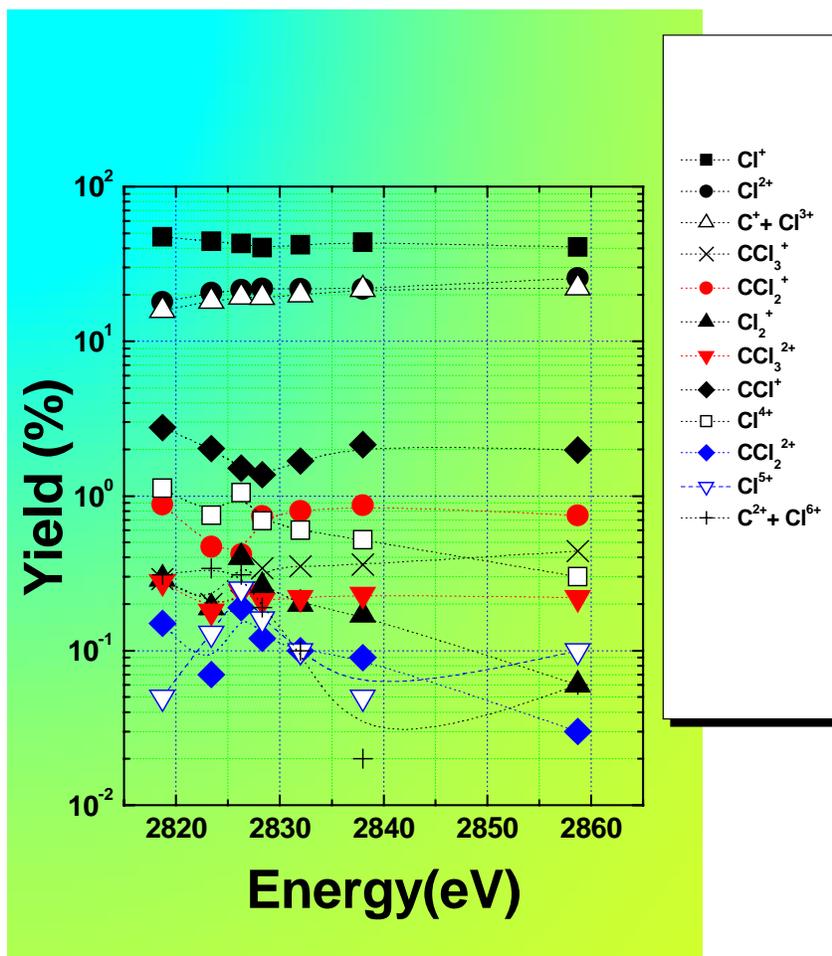


Fig. 2 – Percentual branching ratios of  $\text{CCl}_4$  fragments as a function of photon energy near the Cl K edge.

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