

Ionic yield and dissociation pathways from soft X-ray double-ionization of alcohols

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Abstract

We present data from inner shell excitation and double-ionization of alcohols of interstellar interest, methanol and ethanol at energies around C 1s edge. The measurements were taken at the Brazilian Synchrotron Light Laboratory (LNLS), employing soft X-ray photons (100–310 eV) from a toroidal grating monochromator (TGM) beamline. The experimental set up consists of a high vacuum chamber with a time-of-flight mass spectrometer TOF-MS. Mass spectra were obtained using coincidence techniques. Mean kinetic energies, abundances and dissociation pathways for each ionic pair in coincidence have been obtained from the analysis of the corresponding peak shapes and slopes observed in photoelectron photoion photoion (PE2PICO) coincidence mass spectra. The main dissociation channels of double ionized methanol were associated to the ions pairs $H^+ + COH^+$, $H^+ + CO^+$, $H^+ + CH_2^+$ and $H^+ + CH^+$. In the case of double ionized ethanol, the main dissociation channels were associated to the ions pairs $CH_3^+ + COH^+$, $H^+ + COH^+$, $H^+ + CH_2^+$ and $H^+ + C_2H_2^+$. About 40% and 25% of the dissociation channels of doubly ionized methanol and ethanol, respectively, lead to the production of reactant COH^+ ion, important for the formation of other organic molecules.

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1. Introduction

Methyl alcohol or methanol (CH_3OH) and ethyl alcohol or ethanol (CH_3CH_2OH), the simplest alcohols, are some of the most detected molecules toward various astrophysical regions, including hot molecular cores (HMCs) associated with star-forming regions [1–6], dense molecular clouds [7–9] and in comets [10–13]. In these scenarios, the radiation field can promote several photophysical and photochemical processes onto molecules, including the photodissociation. The products of organic molecules dissociation (ex. reactive ions and radicals) can provide the formation of interstellar complex molecules like long carbon chain molecules.

In star-forming regions like Sgr B2, Orion KL and W51, the presence of widespread UV and X-ray fields could trigger the formation of photodissociation regions (PDRs) where many

molecules could be detected [14]. It is known that protostars are extreme efficient sources of X-rays [15]. The X-ray photons are capable of traversing large column densities of gas before being absorbed. The X-ray-dominated regions (XDRs) in the interface between the ionized gas and the self-shielded neutral layers could influence the selective heating of the molecular gas. The complexity of these regions possibly allows a combination of different scenarios and excitation mechanisms to coexist [16].

The photodissociation of methanol and ethanol has been studied experimentally and theoretically in the ultraviolet region and in the X-rays range [17–31]. Eland and Treves-Brown [24] showed that most of the ion-pair peak shapes could be interpreted in terms of simple sequential reaction mechanisms, although some processes remained unknown. The present work aims to examine the ionic yield and dissociation pathways from soft X-ray multi-ionization of both interstellar alcohols from 100 eV up to 310 eV, including the energies around the carbon K edge (~ 290 eV).

In Section 2, we present briefly the experimental setup. The results on multi-ionization followed by molecular dissociation

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are presented and discussed in Section 3. In Section 4, final remarks and conclusions are given.

2. Experimental details

The experiments were performed at the Brazilian Synchrotron Light Laboratory (LNLS) in Campinas, Sao Paulo, Brazil. Soft X-rays photons ($\sim 10^{12}$ photons/s) from a toroidal grating monochromator (TGM) beamline (100–310 eV), perpendicularly intersect the gas sample inside a high vacuum chamber [32,33]. The photon beam is linearly polarized, being the polarization direction parallel to the spectrometer axis. The gas needle was kept at ground potential. The needle position was optimized by measuring the signal-to-noise ratio in order to exclude the possibility that ionization of alcohol molecules on the needle surface could contribute to the signal. The emergent photon beam flux was recorded by a light sensitive diode. The sample was bought commercially from Sigma–Aldrich with purity greater than 99.5%. No further purification was performed other than degassing the liquid sample by multiple freeze–pump–thaw cycles before admitting the vapor into the chamber.

The ionized recoil fragments produced by the interaction with the photon beam were accelerated by a two-stage electric field and recorded in a detector using a set of two micro-channel plates detectors in a chevron configuration, after mass-to-charge (m/q) analysis by a time-of-flight mass spectrometer (297 mm long). They produced up to three stop signals to a time-to-digital converter (TDC), started by the signal from one of the electrons accelerated in the opposite direction and recorded without energy analysis by two micro-channel plate detectors. A schematic diagram of the time of flight spectrometer inside the experimental vacuum chamber is shown in Fig. 1.

The photoionization and photodissociation of methanol with synchrotron radiation at C 1s photon energy was described elsewhere [32]. The authors have reported the conventional time-of-flight mass spectra (TOF-MS) obtained using the correlation between one photoelectron and a photoion coincidence (PEPICO) recorded at C 1s photon energy range. In Fig. 2a

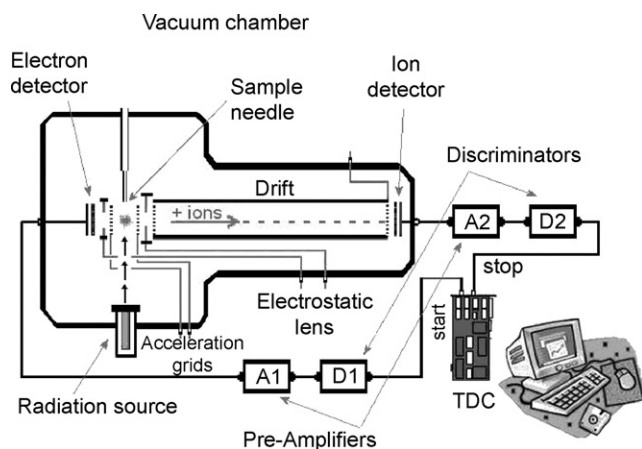
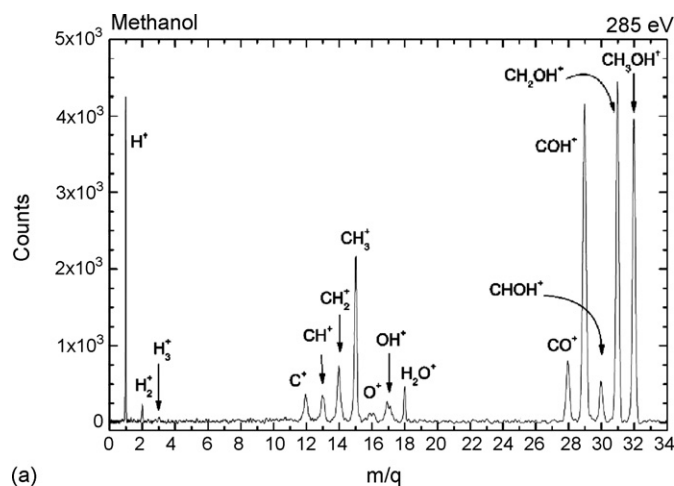
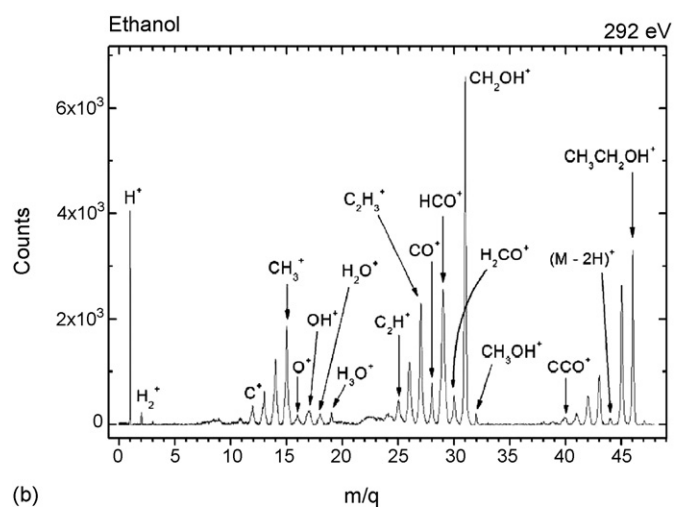


Fig. 1. Schematic diagram of the time of flight mass spectrometer inside the experimental vacuum chamber and the associated electronics.



(a)



(b)

Fig. 2. Time-of-flight mass spectra of (a) methanol recorded at 288.3 eV [31] and (b) ethanol recorded at 292 eV [34].

we can see an example of PEPICO spectra obtained from 288.3 eV photons [31]. The mostly produced ions are the COH^+ , CH_2OH^+ , and H^+ , followed by the parental ion and the methyl. The ethanol mass spectra recorded at 292 eV is present in Fig. 2b for comparison [34]. The mostly produced ions released by the dissociation of $\text{CH}_3\text{CH}_2\text{OH}^+$ were the CH_2OH^+ and H^+ . In both spectra the parental ion peaks of methanol and ethanol remain with high intensity showing a strong survival of both molecules on soft X-rays field.

Besides PEPICO spectra, other two kinds of coincidence mass spectra were obtained simultaneously, PE2PICO spectra (photoelectron photoion photoion coincidence) and PE3PICO spectra (photoelectron photoion photoion photoion coincidence). These spectra have ions coming from double and triple ionization processes, respectively, that arrive coincidentally with photoelectrons. Of all signals received by the detectors only about 10% come from PE2PICO and 1% from PE3PICO spectra, due to the limited detection efficiencies.

In Fig. 3a and b we present a double coincidence mass spectra (PE2PICO) of methanol recorded at 286–310 eV and ethanol recorded at 300 eV, respectively. Several ion pairs can be seen in

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