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The double photoionization of propylene oxide

Abstract – A photoelectron-photoion-photoion coincidence technique, using an ion imaging detector and tunable synchrotron radiation in the 18.0 – 37.0 eV photon energy range, inducing the ejection of molecular valence electrons, has been applied to study the double ionization of the propylene oxide, a simple prototype chiral molecule. Energy thresholds for the formation of different ionic products, the related branching ratios, and the kinetic energy distribution of fragment ions are measured at different photon energies. The main recorded two body fragmentation channels yield $C_2H_4^+ + CH_2O^+$, and $C_2H_3^+ + CH_3^+$ product ions (66.70% and 18.70%, respectively). These new experimental data are relevant per se and are mandatory information for further experimental and theoretical investigations of oriented chiral molecules.

Keywords: double photoionization, molecular dications, synchrotron radiation, chiral molecule, propylene oxide, astrochemistry.

1. Introduction

The present paper represents an effort to unravel the physical chemistry of the elementary processes induced by the interaction of ionizing vacuum ultraviolet VUV photons with a simple chiral molecules, the propylene oxide, being the first chiral molecule detected by astronomers using highly sensitive radio telescopes in interstellar space [1]. It is well known that the left-right dissymmetry, both at macroscopic and micro-scopic scales, plays a fundamental role in life science. Investigation of molecular enantiomeric nature has therefore a strong impact in chemistry in various subareas such as, heterogeneous enantioselective catalysis, photochemical asymmetric synthesis, drug activity, enzymatic catalysis, and chiral surface science involving supramolecular assemblies [2, 3]. The interaction of polarized light with

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chiral systems has been extensively studied since Pasteur's pioneering experiments on optical activity leading to the enantiomer recognition [4]. Although techniques involving optical rotation and circular dichroism in photoabsorption with visible/UV light are routinely used as well established analytical methods, studies of chiral systems using ionizing photons are instead very limited to date (see Ref. [5] and references therein). Progresses in synchrotron radiation techniques allowed intense photon sources with high degree of both linearly and circularly polarized light of both helicities to be used in experiments like that one concerning the present paper. In particular, we intended to study the fragmentation dynamics following the double photoionization of propylene oxide whose importance from an astrochemical point of view has been already mentioned above. In fact, this chiral molecule has been detected in the gas phase in a cold extended molecular shell around the embedded, massive protostellar clusters in the Sagittarius B2 star-forming region, being a material representative of the earliest stage of solar system evolution in which a chiral molecule has been found [1]. To characterize the ionizing VUV interaction with such a molecule, we started by the use of a linearly polarized synchrotron radiation, as that one available at the «Circular Polarization (CiPo)» Beamline at the Elettra Synchrotron Facility of Trieste (Italy), to perform a double photoionization experiment using the same ARPES (Angle Resolved Photo-Emission Spectroscopy) apparatus successfully employed in previous studies, performed by our research team [6-10]. In such an experiment, the double photoionization of propylene oxide molecules in a racemic mixture, has been performed in order to measure: i) the threshold energy for the different ionic products formation; ii) the related branching ratios, and iii) the kinetic energy released (KER) distribution of fragment ions at different photon energies. This preliminary study is important to provide unavailable data on dication energetics and nuclear dissociation dynamics, this being mandatory information for further experimental and theoretical investigations of the interaction between chiral molecules and circularly polarized radiation. For such a reason, we are planning to switch in next future to use the circularly polarized light, as available at «CiPo» Beamline, using the two enantiomers of propylene oxide with the aim to investigate possible differences on the angular and energy distribution of fragment ions and ejected photoelectrons at different photon energies. (Figures 1-5 are adapted from Ref. 11).

2. Materials and Methods

The data reported and discussed in this paper were recorded in experiments performed at the ELETTRA Synchrotron Facility of Basovizza, Trieste (Italy). The ARPES end station was employed at the «Circular Polarization (CiPo)» beamline.

For the present experiment we used a 3D-ion-imaging TOF spectrometer that we have successfully applied recently to N_2O [12, 13], CO_2 [14, 15], C_6H_6 [16, 17], and C_2H_2 [18, 19] double photoionization experiments. In particular, this device consists in a time of flight (TOF) spectrometer equipped with an ion position sensitive

detector (stack of three micro-channel-plates with a multi-anode array arranged in 32 rows and 32 columns). It has been especially designed in order to properly measure the spatial momentum components of the dissociation ionic products [20]. The data were accumulated using the same method previously employed, and the analysis has been carried out by using the codes and computational procedure already well tested [12-19]. The energy selected synchrotron light beam operating in the 18-37 eV photon energy range crosses at right angle an effusive molecular beam of the neutral precursor molecule, and the ion products are detected in coincidence with photoelectrons coming out from the same double photoionization event under study.

The propylene oxide molecular beams was prepared by effusion from a glass bottle containing a commercial sample (with a 99% nominal purity), and was supplied by a needle effusive beam source taking advantage of its high vapor pressure at a room temperature. A Normal Incidence Monochromator (NIM), equipped with two different holographic gratings, allowing to cover the 18-37 eV energy range by means of a Gold (2400 l/mm) and an Aluminum (1200 l/mm) coated grating has been used. Spurious effects, due to ionization by photons from higher orders of diffraction, are reduced by the use of the NIM geometry.

The resolution in the investigated photon energy range was about 1.5-2.0 meV. More details about the used experimental techniques have been detailed elsewhere [21-27].

3. Results and Discussion

In a recent double photoionization experiment of propylene oxide in a photon energy range of 18-37 eV [5] we found the following six two-body fragmentation channels accessible in the Coulomb explosion of the $(C_3H_6O^{2+})^*$ intermediate molecular dication with the measured relative abundances:



The measured threshold energy for the double ionization of propylene oxide was 28.3 ± 0.1 eV [6]. In this paper we present the KER distributions of product ions obtained as a function of the investigated photon energy for each reaction (1)-(6) above. Such KER distributions are reported in Figures 1-5. It was not possible to determine KER distributions related to product ions of reaction (6) because the

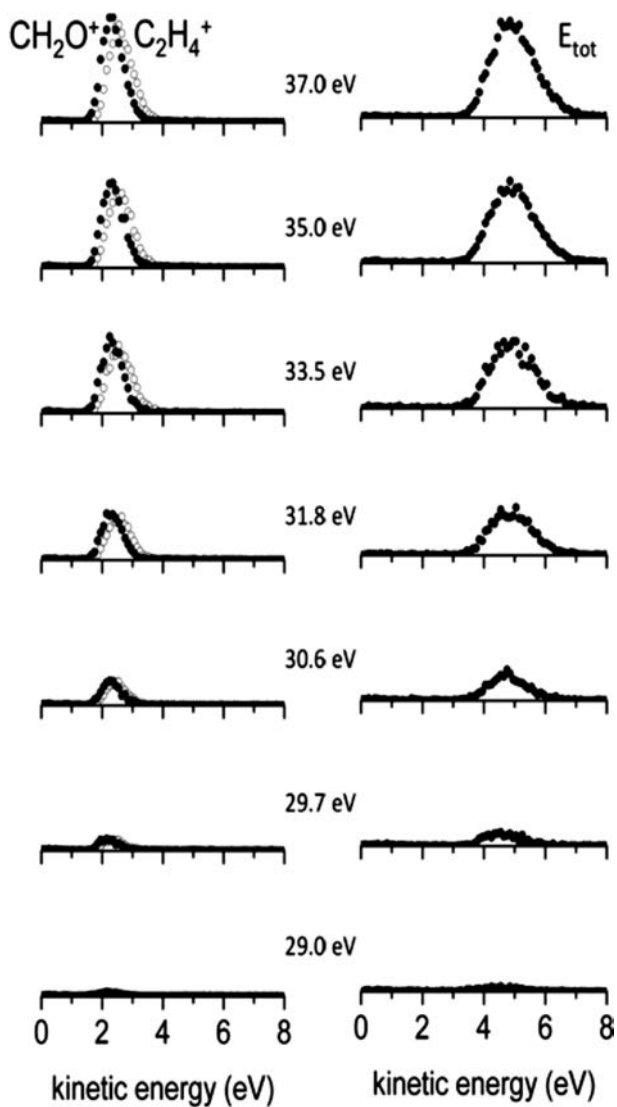


Fig. 1. The kinetic energy released (KER) distribution of the $\text{C}_2\text{H}_4^+ + \text{CH}_2\text{O}^+$ products for various investigated photon energies: in the left panel are reported the KER for each fragment ion, whereas in right panel the total KER distributions are shown.

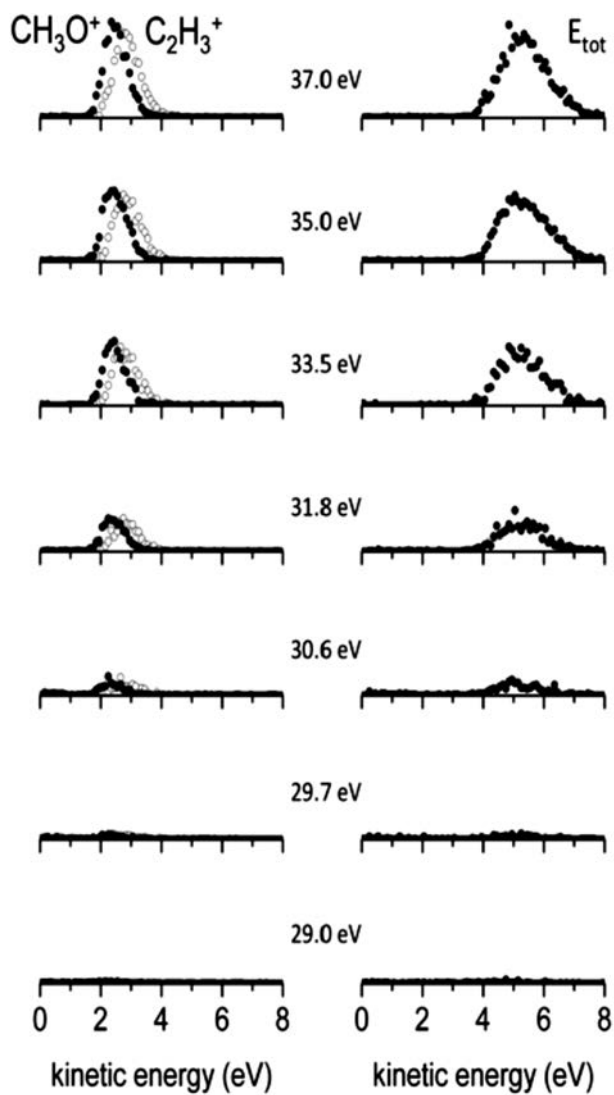


Fig. 2. The kinetic energy released (KER) distribution of the $\text{C}_2\text{H}_3^+ + \text{CH}_3\text{O}^+$ products for various investigated photon energies: in the left panel are reported the KER for each fragment ion, whereas in right panel the total KER distributions are shown.

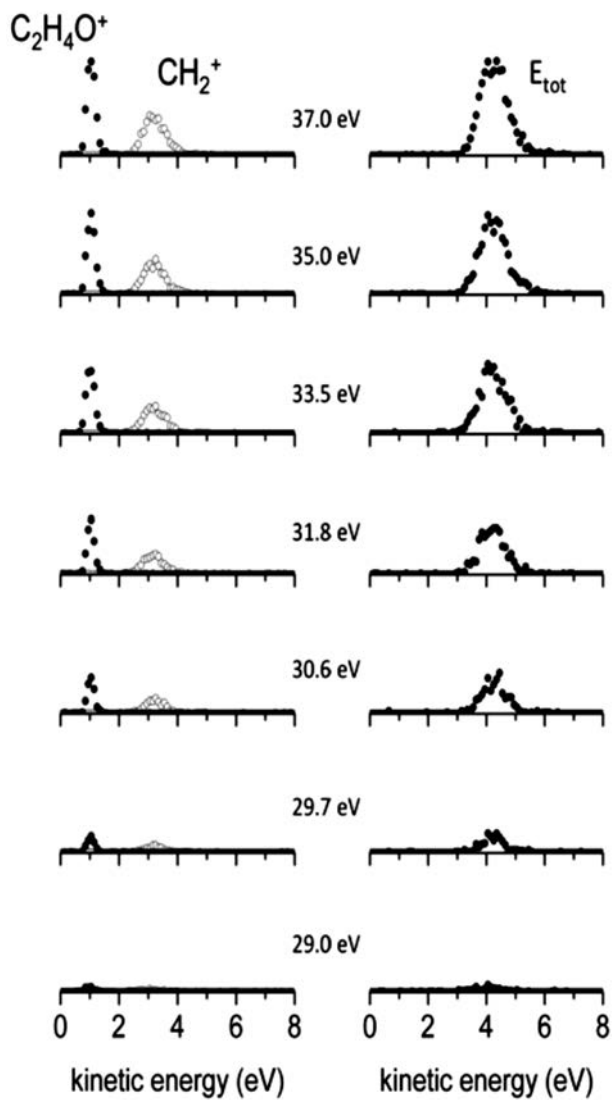


Fig. 3. The kinetic energy released (KER) distribution of the $\text{CH}_2^+ + \text{C}_2\text{H}_4\text{O}^+$ products for various investigated photon energies: in the left panel are reported the KER for CH_2^+ fragment ion, whereas in right panel the total KER distributions are shown.

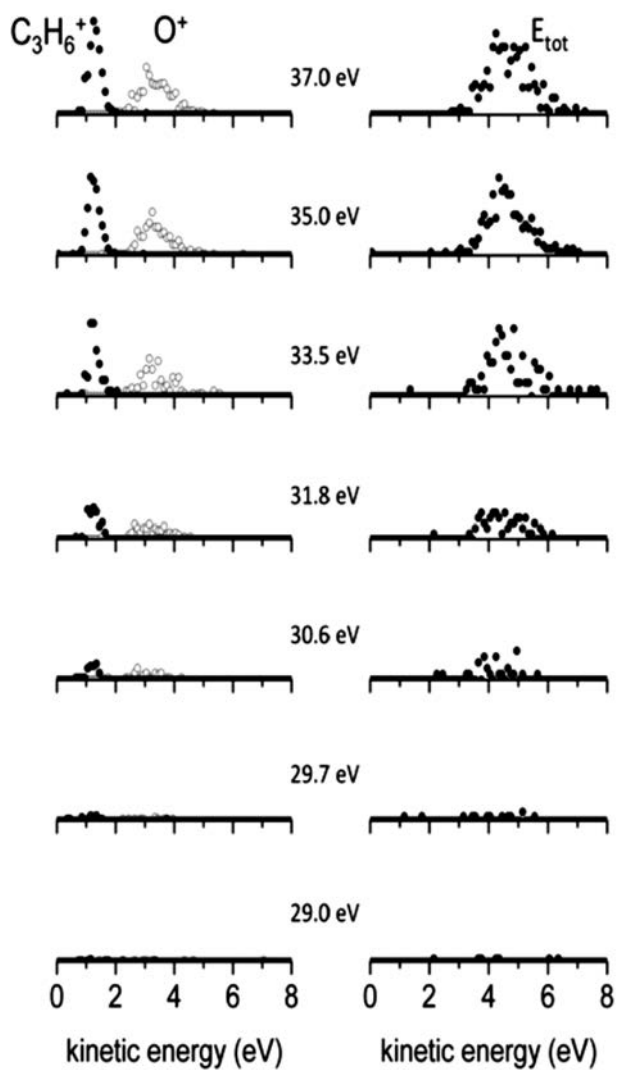


Fig. 4. The kinetic energy released (KER) distribution of the $O^+ + C_3H_6^+$ products for various investigated photon energies: in the left panel are reported the KER for each fragment ion, whereas in right panel the total KER distributions are shown.

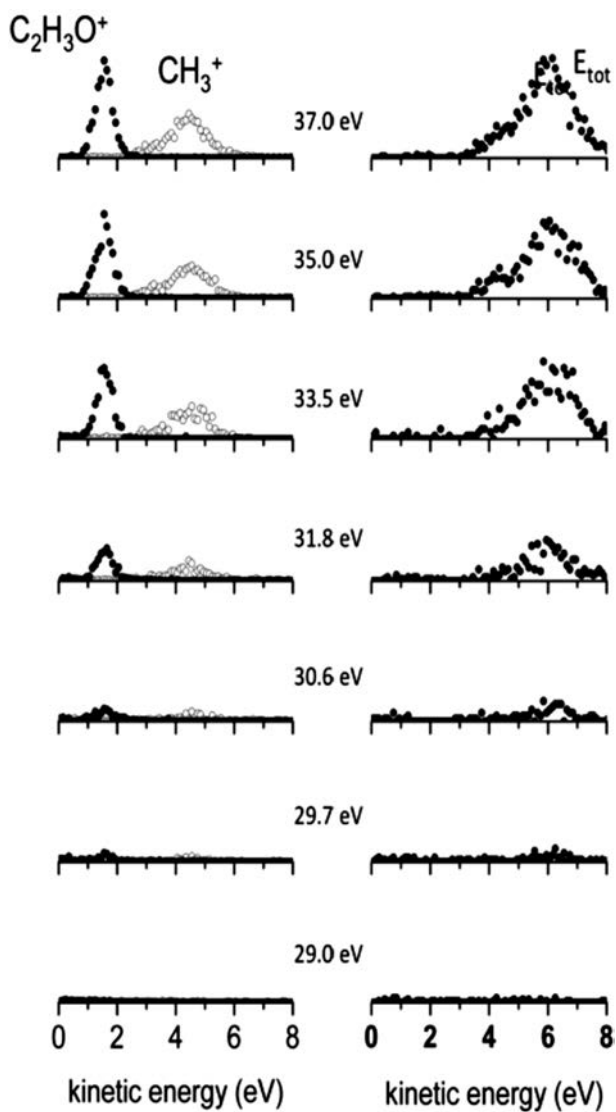


Fig. 5. The kinetic energy released (KER) distribution of the $\text{CH}_3^+ + \text{C}_2\text{H}_3\text{O}^+$ products for various investigated photon energies: in the left panel are reported the KER for each fragment ion, whereas in right panel the total KER distributions are shown.

very low intensity of recorded signals for $\text{OH}^+ + \text{C}_3\text{H}_5^+$ coincidences. All recorded KER distributions of Figures 1-5 do not change appreciably with the photon energy. In particular, they appear rather symmetric and can be easily fitted by a simple Gaussian function. It has to be noted that in such Figures the peaks position and relative shapes, for each analyzed dissociation channel, are practically the same for all investigated photon energies. This could be an indication that each fragmentation channel involves one specific region of the multidimensional potential energy surface, associated to the effective intramolecular interaction within the $(\text{C}_3\text{H}_6\text{O})^{2+}$ dication frame and responsible of the opening of the various two body fragmentation channels, at all investigated energies. Therefore, for all investigated fragmentation channels the excess of the used photon energy respect to the double ionization threshold energy should be released as electron recoil energy. The only exception is constituted by the recorded total KER distribution for the two $\text{CH}_3^+ + \text{C}_2\text{H}_3\text{O}^+$ product ions of reaction (3) shown in the right panel of Fig. 5 as a function of the investigated photon energy. It is evident that such total KER distributions are characterized by a bimodal behavior depending on the two possible microscopic mechanisms for the two body fragmentation of $(\text{C}_3\text{H}_6\text{O})^{2+}$ dication producing $\text{CH}_3^+ + \text{C}_2\text{H}_3\text{O}^+$. In fact, reaction (3) may occur by two different pathways: in one case (probably the most important one) a direct fragmentation of the $(\text{C}_3\text{H}_6\text{O})^{2+}$ dication into $\text{CH}_3^+ + \text{C}_2\text{H}_3\text{O}^+$ products can occur, while in a second case the Coulomb explosion of the $(\text{C}_3\text{H}_6\text{O})^{2+}$ dication takes place by means of a hydrogen migration from the methyl group of propylene oxide molecule to the end carbon atom bound with oxygen. Further experiments performed using isotopically labeled precursor molecules should clarify the relative importance of such different microscopic pathways for reaction (3).

Moreover, future experimental investigations recording the angular distributions of the final ions could be able to investigate in major detail the hypotheses discussed above concerning the microscopic two body dissociation mechanisms following the Coulomb explosion of the $(\text{C}_3\text{H}_6\text{O})^{2+}$ dication. These experiments are planned in next future at the Elettra Synchrotron Facility to measure the anisotropy parameter [28-30] in the angular distribution of dissociation ion products as a function of the photon energy, and possibly electron kinetic energy spectra as done in previous experiments [31-35].

4. Conclusions

In this paper, we presented a study of the double photoionization of a simple chiral molecule of astrochemical interest (the propylene oxide) promoted by direct ejection of two valence electrons. The study has been performed by using linearly polarized synchrotron radiation in order to identify the leading two-body dissociation channels and measure: i) the threshold energy for the different ionic products formation; ii) the related branching ratios, and iii) the KER distribution of fragment ions at different photon energies. This preliminary study is important to provide

unavailable data on $(\text{C}_3\text{H}_6\text{O})^{2+}$ molecular dication energetics, and nuclear dissociation dynamics, being mandatory information for further experimental and theoretical investigations of the interaction between chiral species and linearly or circularly polarized light. Besides, for all investigated fragmentation channels, the recorded KER distributions indicate that the excess of the used photon energy, respect to the double ionization threshold energy, should be released as electron recoil energy. The CH_3^+ formation by reaction (3) involves two different microscopic mechanisms in the Coulomb explosion fragmentation dynamics of the intermediate $(\text{C}_3\text{H}_6\text{O})^{2+}$ dication. This is confirmed by the observation of a bimodality in the total KER distribution for the $\text{CH}_3^+ + \text{C}_2\text{H}_5\text{O}^+$ product ions of reaction (3), as observed in previous experiments [5,11].

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