Photo-single and photo-double ionization and fragmentation of isoxazole molecules

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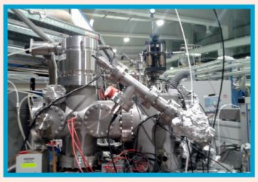
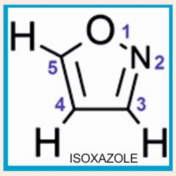
Abstract

The five-membered heterocyclic rings containing oxygen or nitrogen atoms are incorporated into a wide variety of structures that play a vital role in many biochemical processes. In particular, isoxazole molecule due to its unique ring structure that consists of one oxygen atom and one nitrogen atom at adjacent positions appears in many bioactive compounds and is utilized as the fundamental structure in the synthesis of new pharmaceutical medicines. The unique atomic composition and bond arrangement of isoxazole imply its specific electronic properties that cause exceptional dissociation mechanisms. The understanding of the role and possible control of electron dynamics in these reactions and chemical reactivity is itself a problem of fundamental importance. Therefore in the present communication, we present results on the photo-single and photo-double ionization and fragmentation of isoxazole molecule. The dissociative processes where only one electron is emitted are quite well known. However, double ionization is a unique mechanism producing the doubly charged parent ion after the emission of two correlated electrons. Both the single and doubly charged parent ions are very reactive entities that can dissociate into several ionic fragments. The current study aims to unravel the dissociation processes of the parent ions of isoxazole, leading to the formation of different ionic products in the photon energy range of 9–34 eV, using ion time-of-flight (TOF) spectrometry combined with the photoelectron-photoion coincidence (PEPICO) technique.

Experimental method

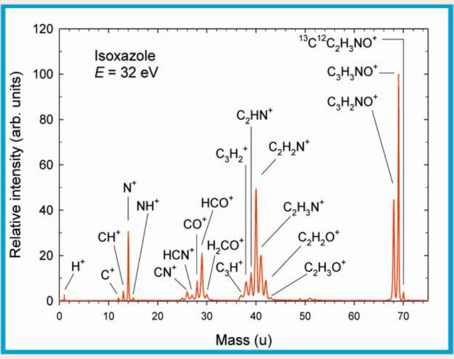




The measurements were carried out at the Circular Polarization (CiPo) beamline [1] of the Elettra synchrotron radiation storage ring in Trieste, Italy. The CiPo beamline supplies radiation from an electromagnetic elliptical undulator/wiggler and is equipped with a Normal Incidence Monochromator for low photon energies (5–35 eV). The used undulator mode produced linearly polarized radiation, which was dispersed in the energy range 9–35 eV by two different gratings: an aluminum holographic spherical grating with 1200 grooves mm−1 (Al-NIM) used to cover the 5-16 eV energy range and a gold holographic spherical grating with 2400 grooves mm−1 (Au-NIM) used to cover the 16-35 eV energy range. The photon energy was calibrated by observing the valence excitations in noble gases.

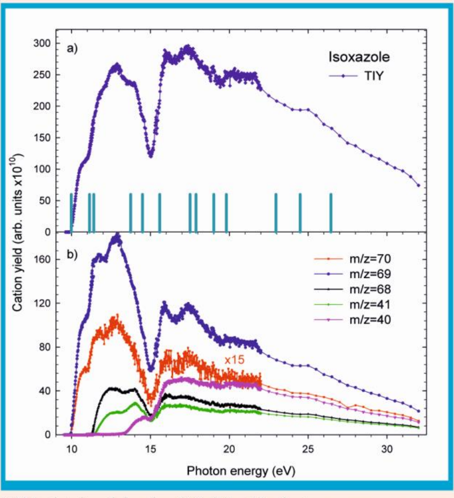
We used the experimental apparatus described by Kivimäki et al. [2]. It consists of a modified Wiley–McLaren time-of-flight spectrometer, which was originally used to detect photoelectron-photoion coincidences and subsequently also neutral-particle–photoion coincidences [3]. The setup in the modified configuration can also be used to measure PEPICO spectra. The TOF spectrometer (with a 203-mm long drift tube) was oriented parallel to the electric vector of the linearly polarized synchrotron light. In the interaction region, the monochromatic photon beam from the beamline crossed the effusive beam of the sample molecules emanating from a hypodermic needle [4]. When synchrotron light interacts with studied molecules, some of them are ionized and further dissociate into ionic and neutral fragments. Resulting positive ions were pushed toward the acceleration region and entered a drift tube, and were detected by a microchannel plate (MCP) detector. The flight times of the positive ions in the TOF spectrometer were used to determine the masses of the original fragments, and consequently to identify them. PEPICO method gives the coincidence maps plotted as the arrival time of the first ion and that of the second ion, with respect to the instance of detection of one of the photoelectrons. As the result, the pairs of correlated ions show up as areas with a higher density of points whereas the vertical and horizontal lines represent the points where uncorrelated ions occured.

Mass spectrum



The normalized mass spectrum of the cations of isoxazole measured at the photon energy of 32 eV [5].

Ion yield curves



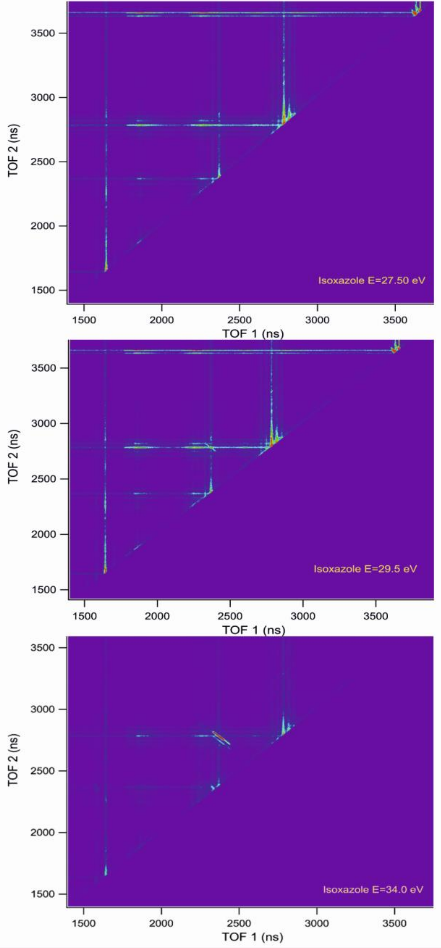
TIY obtained in the 9.8-32 eV photon energy range. The vertical bars show the energy positions of threshold photoelectron bands [6]. b) The yields of the most intense cations obtained in the 9.8-32 eV photon energy range [5].

Threshold energies

The obtained AEs (in eV) of the cations observed in the fragmentation of isoxazole molecule after absorption of VUV photons. [5] The present AEs are compared with the results from the threshold photoelectron (TPES) or photoelectron (PES) spectroscopies, and electron impact ionization spectrometry (EI).

M (u)	Cation	$AE^{Present\ work}$	$AE^{Other\ works}$
TIY		9.94; 9.96 (0.03)	9.949^a $9.976\ (0.003)^a$ $9.99\ (0.05)^b$
70	$^{13}C^{12}C_2H_3NO^+$	9.96 (0.04)	
69	$^{12}C_3H_3NO^+$	9.95 (0.04)	$9.93\ (0.05)^c$
68	$C_3H_2NO^+$	11.19 (0.05)	$11.24\ (0.05)^c$
42	$C_2H_2O^+$	12.97 (0.07)	$12.24\ (0.05)^c$
41	$C_2H_3N^+$	11.29 (0.07)	$11.80\ (0.05)^c$ $11.34\ (0.05)^d$
40	$C_2H_2N^+$	13.14 (0.07)	$13.34\ (0.05)^c$
39	C_2HN^+	13.90 (0.15)	
38	$C_3H_2^+$	17.40 (0.15)	
37	C_3H^+	17.25 (0.15)	
29	CHO^+	13.21 (0.10)	$13.62\ (0.05)^c$
28	CO^+	13.46 (0.15)	
25	C_2H^+	26.25 (0.50)	
15	NH^+	13.57 (0.10)	
14	N^+	14.09 (0.10)	
13	CH^+	19.24 (0.15)	
12	C^+	22.30 (0.50)	
1	H^+	22.40 (0.50)	

Coincidence maps



References

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