Fragmentation of isoxazole molecules into neutral high-Rydberg fragments after core excitation and core ionization using soft x-ray synchrotron radiation

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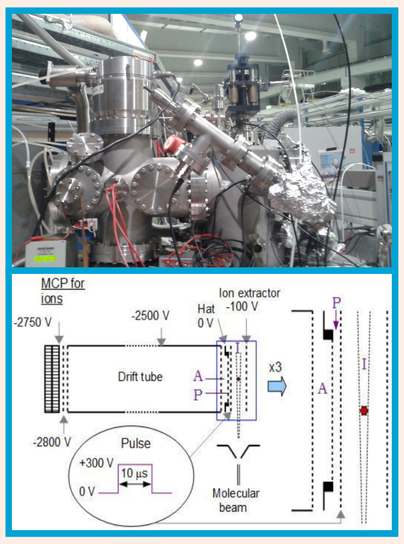
Abstract

Synchrotron radiation being the most effective light source gives rise to significant developments in spectroscopic techniques, which probe the electronic structure and decomposition mechanisms of molecules. In particular the near edge x-ray absorption fine structure spectroscopy (NEXAFS) provides detailed information about presence of specific bonds and interactions in molecules.

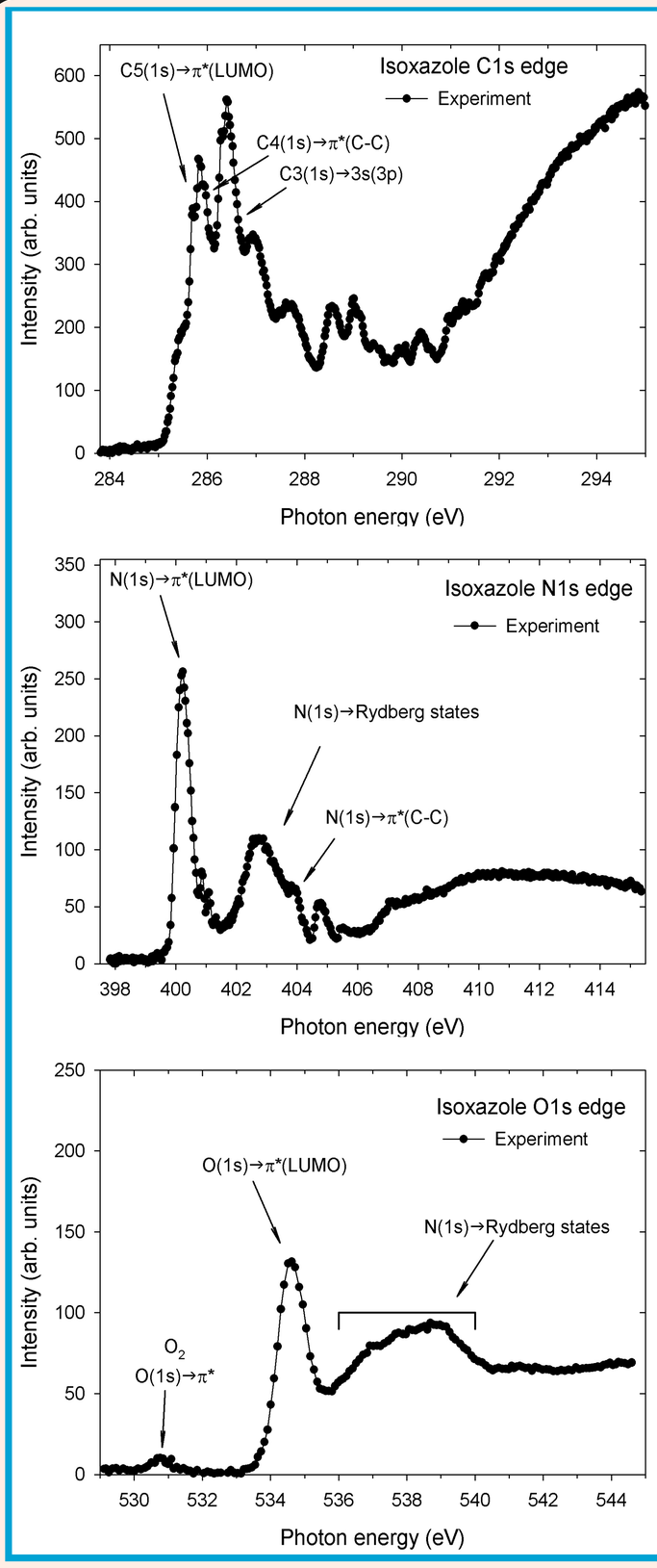
In the present work we have used the soft x-ray excitation combined with techniques of pulsed field ionization and ion time-of-flight (TOF) spectrometry to investigate the gas-phase C1s, N1s and O1s excitation spectra of isoxazole molecules as well as a new class of mechanism of the photon-induced fragmentation, namely photoelectron recapture into the high-Rydberg (HR) states. The NEXAFS spectra of isoxazole were measured using the total ion yield method.The neutral HR fragments formed after C1s, N1s and O1s inner-shell excitations/ionization and fragmentation have been detected and identified by the field ionization and measurements of the TOF mass spectra of the produced ions.

Experimental method



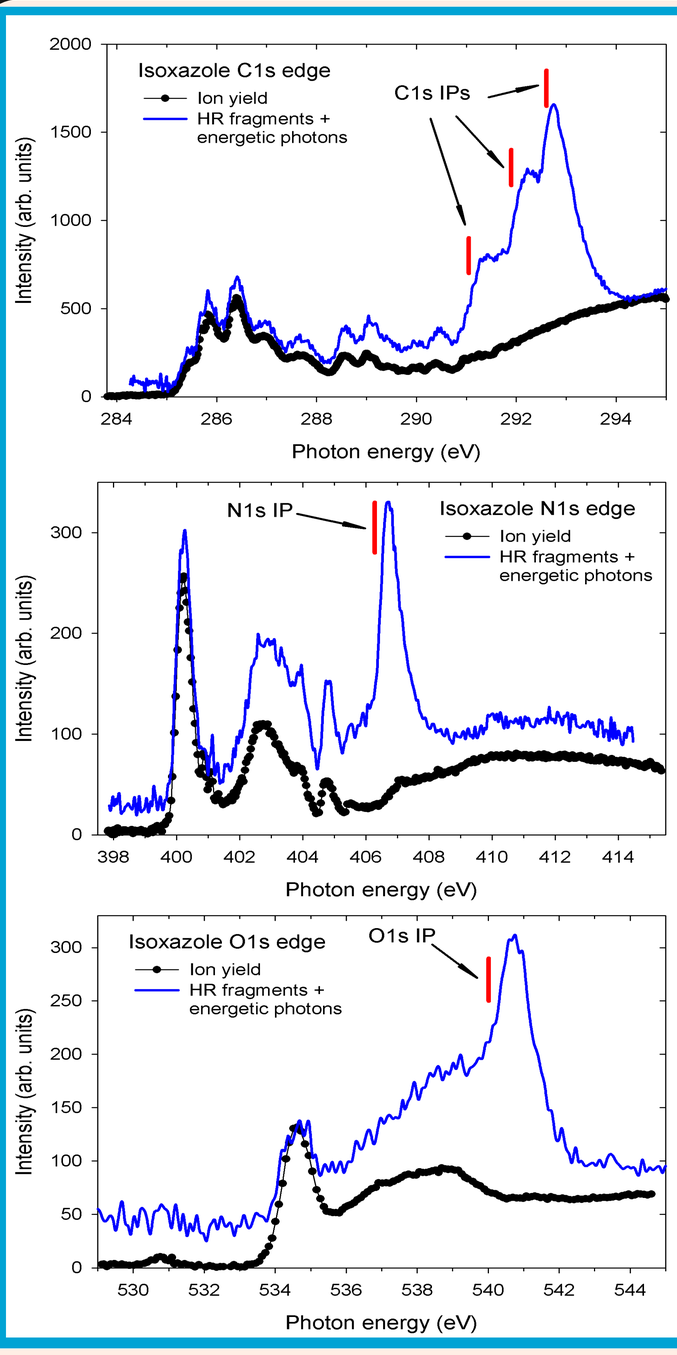
The experiments were carried out at the Gas Phase Photoemission beamline at the Elettra synchrotron radiation facility exploiting the TOF mass spectrometer that was modified for pulsed field ionization measurements [1, 2]. The experimental set-up also allows the measurements of the yields of neutral HR fragments, ions, and of the photoelectron-photoion coincidence spectra. In the interaction region (I), light interacts with studied molecules, some of which dissociate to ionic and neutral fragments. Neutral fragments can enter the source region (labeled P in Figure) of the TOF spectrometer, whereas positive ions created in the interaction region are pulled into the opposite direction. In the source region, neutral HR fragments can be ionized by a pulsed electric field. Each pulse represents a possible reference time when a positive ion is created and it can be used as a start signal for a TOF measurement. Resulting positive ions are pushed towards the acceleration region (A), enter a field-free drift tube and are detected by the MCP detector, which provides stop signals for the TOF measurement. The flight time of the positive ion in the TOF spectrometer can be used to determine the mass of the ion and consequently to identify the original neutral HR fragment. To measure the yield of neutral HR fragments (without mass resolution) the source region was kept at ground potential. Then,the ions originating from field ionization of neutral HR fragments in the acceleration region were collected. Such yields contain a contribution from neutral particles that move directly from the interaction region toward the MCP detector. These particles include soft x-ray and vacuum ultraviolet photons (wavelength < 150 nm), but also neutral fragments in metastable states and in such long-living Rydberg states for which field ionization is not possible. We have estimated that "background" contribution by measuring yield spectra in conditions where the collection of field-ionized fragments was blocked by a potential of +250 V in the drift tube. Total ion yields were measured using potentials that are appropriate for the collection of positive ions from the interaction region. All the yields have been normalized to the photon flux monitored simultaneously with a photodiode.

NEXAFS spectra



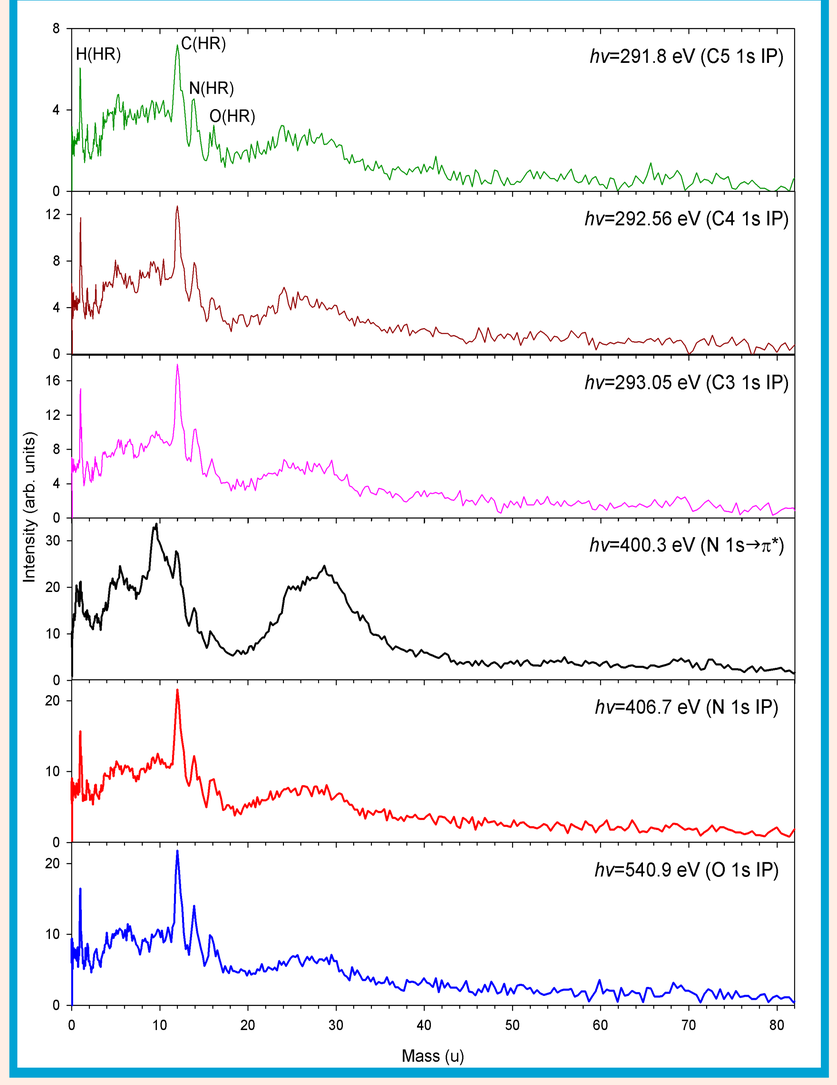
Experimental C 1s, N 1s and O 1s NEXAFS spectra of isoxazole. The most prominent transitions are also indicated.

Yields of neutral HR fragments



Figures compare the total ion yield (TIY) spectra of isoxazole measured near the K edges without field ionization with the total yield of HR fragments (and energetic photons) obtained after applying field ionization. Generally, the HR spectra resemble that of the TIY. However, near the ionization thresholds a strong peaks occur, not observed in the TIY spectra, that are attributed to the production of neutral fragments in the HR states. Here, they may be formed by recapture processes where photoelectrons are pushed back to be bound on the HR orbitals of the parent molecular ions after Auger decay [1,2].

TOF spectra of field-ionized fragments



Field ionization mass spectra of neutral HR fragments measured at the C 1s, N 1s and O 1s edges of the isoxazole molecule.

References

[1] A. Kivimäki, et al, J. Chem. Phys. 143 (2015) 114305.

[2] A. Kivimäki, et al, J. Phys. Chem. A 120 (2016) 4360-4367.

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