Femtosecond soft–X–Ray absorption spectroscopy of liquids with a water-window high-harmonic source

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We demonstrate femtosecond time–resolved soft–X–ray absorption spectroscopy of liquid samples by combining a sub–micrometer–thin flat liquid jet with a high–harmonic table–top source covering the entire water-window range (284 - 538 eV). Our work represents the first extension of table-top XAS to the oxygen edge of a chemical sample in the liquid phase. In the time domain, our measurements resolve the gradual appearance of absorption features below the carbon K-edge of ethanol and methanol during strong–field ionization, which trace the valence-shell ionization dynamics of the liquid alcohols with a temporal resolution of ~30 fs.

Table-top soft X-ray (SXR) sources driven by intense femtosecond lasers enabled time–resolved X–ray absorption spectroscopy (TRXAS) that has evolved into a powerful tool to investigate the structural and electronic dynamics of matter with element, site and orbital specificity. Pioneering transient–absorption experiments via HHG were performed using near–infrared (NIR) laser–based sources with a cut–off limited to the extreme ultraviolet (XUV) photon energy range [1]. Employing long-wavelength driving pulses allowed extending the high-order harmonic generation (HHG) cut-off and XAS measurements into water-window [2,3]. The water-window spectral range spanning between the carbon and oxygen K absorption edges (284 and 538 eV respectively) opens the possibility to perform TRXAS measurements in liquid samples and solutions and covers absorption edges of biologically-relevant elements of carbon, nitrogen and oxygen.

In this contribution we demonstrate the first time-resolved measurement of multi-photon induced dynamics in liquid alcohols using HHG-based setup [4]. These measurements required overcoming two bottlenecks: (i) extending the HHG cut-off in order to reach spectral range where liquids are sufficiently transparent [5]; (ii) implementing liquid sample system with sub-µm thickness. In contrast to gas-phase TRXAS measurements [2], liquid phase measurements provide access not only to the electronic structure of the individual molecule, but also to the inter-molecular interaction effects and allow studying bio-relevant molecular systems in their natural environment.

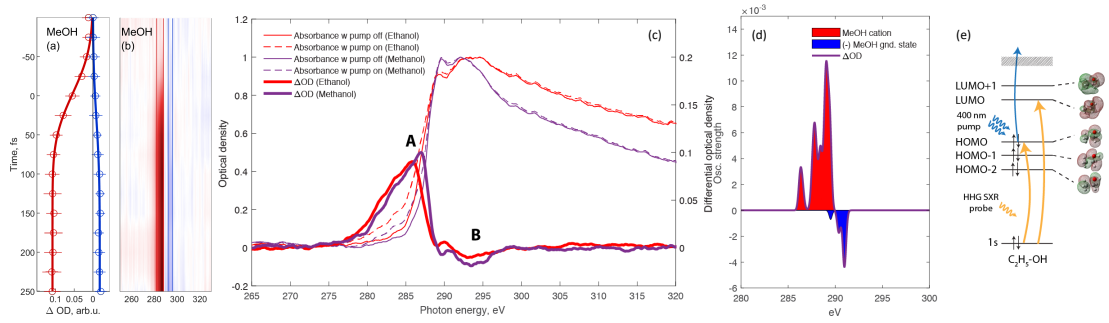

Figure 1. Time evolution of transient absorption spectra of methanol (a,b) pumped by 400 nm pulses. The lineouts (red and blue lines in (a)) correspond to the “A” and “B” spectral bands shown in (b) and were fitted using sigmoidal functions. (b) absorption spectrum and time-averaged spectral changes; (c) quantum chemistry calculations of a methanol dimer; the shaded red and

blue area plots indicate the methanol cation and ground states respectively. (e) scheme representation of pump and probe transition and the molecular orbitals of the ethanol molecule using the 6-31G** basis set.

Our recent measurements in aromatic heretocyclic hydrocarbons and solutions reveal dynamics iniduced via multi-photon excitation at carbon and nitrogen atomic edges simultaneously as illustrated in Figure 2. By performing measurements in liquid and gas phase, we are able to pinpoint differences in photoinduced dissociation dynamics in the liquid and gas phases.

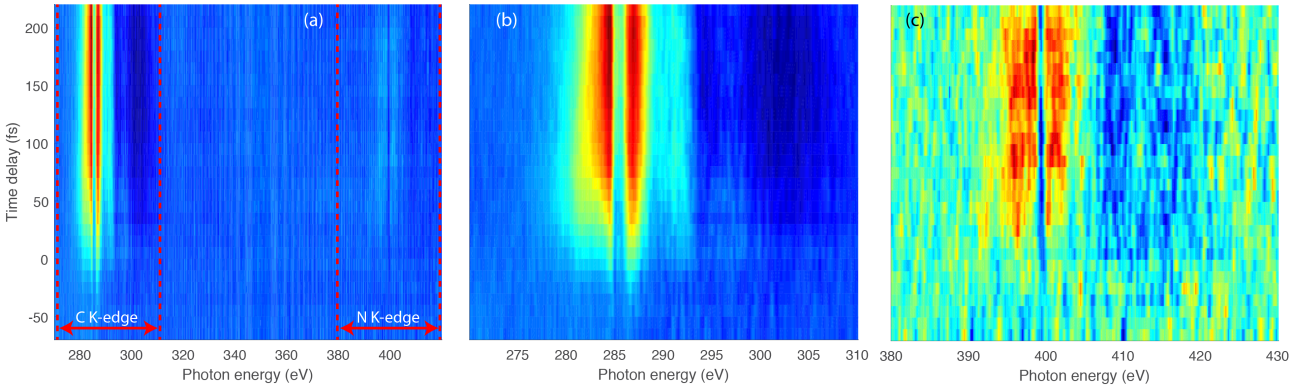

Figure 2. Time-resolved X-ray differential absorption spectra of pure pyridine excited via multi-photon ionization; (a) full spectrum covering nitrogen and carbonK-edges; (b) and (c) are cropped areas arround the carbon and nitrogen edges respectively

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