

Ultrafast Proton Transfer in Aqueous Urea Dimers Probed by X-ray Absorption Spectroscopy

Content

Photo-ionization of most systems induces coupled electronic and structural dynamics [1]. Distinguishing between the nuclear and electronic dynamics remains challenging. In this contribution we present femtosecond time-resolved X-ray absorption spectroscopy (trXAS) of aqueous urea ($\text{CH}_4\text{N}_2\text{O}$) solutions utilizing a high-harmonic-generation (HHG) source covering the carbon and nitrogen K-edges. We use this technique to investigate ultrafast proton-transfer dynamics in aqueous urea induced by ionization, as illustrated in Fig 1. The inherently broad HHG spectrum allows us to probe both K-edges simultaneously and is therefore ideal for trXAS [3]. Here, we demonstrate the remarkable properties of trXAS as an element and site-specific method in revealing coupled electronic and nuclear dynamics of matter including intermolecular proton transfer dynamics in a liquid environment. The inherent synchronization of laser-based experimental setup, where pump and probe pulses are derived from the same light source, allow for timing-jitter-free measurements. We utilize a sub- μm -thin flat jet to record artefact-free XAS in transmission mode [3,4]. Our experimental results show spectral features appearing after ~ 100 fs and increasing in absorbance up to around 700 fs before they reach a constant level. These bands are assigned to ionization-induced ultrafast proton transfer in urea dimers through comparison with calculations. The experimental findings are supported by nonadiabatic quantum-mechanical and molecular dynamics (QM/MM) calculations of several urea-dimer and urea-water geometries and can reproduce the main spectral features. They show that the shift of the absorption band highlighted by a black line in panels C and E traces the transfer of the charged proton, whereas the gradually increasing intensity traces the increasing amplitude of the valence hole at the carbon atom with site selectivity. Our results reveal an ultrafast proton transfer between urea molecules caused by valence ionization elucidating the electronic and nuclear dynamics driving proton transfer in a solvated biomolecule. They also reveal the remarkable capability of trXAS to distinguish electronic-structure rearrangements, manifested in the absorption strength, from the structural dynamics manifested in the resonance positions.

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