

Frustrated proton transfer in liquid water probed with time resolved VUV photoelectron spectroscopy

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Time resolved photoelectron spectroscopy of liquid water was used to measure the frustrated proton transfer in liquid water. A liquid microjet (24 μm diameter) was excited with 2 μm laser pump and probed with a 40 fs VUV (39 eV) probe pulse. The results point to the initial formation of an OH^- - H^+ dissociative pair, which then recombines to H_2O due to ultrafast energy dissipation.

A micro liquid jet capable of producing several millimeters of laminar flow [1] was used under high vacuum conditions (10^{-6} mbar). Using the high harmonic source and time preserving monochromator at the Artemis laser facility at the Rutherford Appleton labs[2], and a novel differentially pumped time of flight electron spectrometer, the valence bands of liquid water were measured from the HOMO ($1b_{1, \text{liquid}}$ binding energy 10.9 eV) to the $2a_1$ (binding energy of 32 eV). In contrast to previous VUV studies of water [3], the temporal duration of the VUV pulse (40 fs) was preserved by using the monochromator grating with the grooves parallel to the incident radiation [4]. Thus we were able to maintain sub-eV energy resolution and 40 fs pulse duration to observe in real-time the bond motion in liquid water for the first time.

The pure water sample (with 20 mM NaCl to suppress charging from the motion of the jet) was pumped by ~ 10 μJ pulses at a wavelength 2 μm . By carefully controlling the pump pulse power we avoided significant plasma formation on the jet surface and were able to maintain the valence band structure of liquid water in our photoelectron measurements. The 2 μm pump excites the combination stretch-bend mode of water and we estimate about 30% of the pump energy was absorbed by the jet.

Upon excitation, an immediate shift of the binding energies of the intermolecular H-bond sensitive $1b_1$ orbital occurs to higher values (towards the gas phase ones) within the cross-correlation. It then comes back to its initial value in about 70 fs. We interpret the shift as resulting from the initial dissociation of water in H^+ and OH^- species, as anticipated from proton transfer studies. The pathway for this proton transfer is the huge anharmonicity of the intramolecular OH bond potential in liquid water. The close proximity of water molecules distorts the potential along the O-O intermolecular axis. A local minima forms away from the parent oxygen accessible via the stretch/bend mode. At the same time, the elongated H^+ - OH^- bond leads to an increase of the dipole moment of the excited water molecule, which enhances its energy dissipation via efficient dipole-dipole coupling, quenching the vibrationally excited state within 70 fs.

In summary we report on the first direct observation of the correlated proton transfer and dipole-dipole coupling dynamics in liquid water on the fs time scale using ultrafast VUV photoelectron spectroscopy. This new development now opens the liquid phase valence and core levels to exploration in the femtosecond time domain.

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- [3] Link *et al.* Ultrafast electronic spectroscopy for chemical analysis near liquid water interface: concepts and applications *App. Phys. A* **96**, 117-135 (2009)
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