

# Femtosecond Time and Angle Resolved Photoemission Spectroscopy of Liquids

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**Abstract:** We report the first time and angle resolved photoemission spectroscopy of liquids using a time-of-flight photoelectron spectrometer and a sub MHz deep ultraviolet femtosecond laser.

**OCIS codes:** (300.6530) ultrafast spectroscopy; (320.2250) femtosecond phenomena

## 1. Introduction

Liquid surfaces have often been studied using non-linear spectroscopy such as sum frequency generation (SFG). Here we present a different approach using time and angle-resolved photoemission spectroscopy (TARPES). The method enables unprecedented direct access to ultrafast electronic dynamics, such as electron transfer reactions, near the liquid surface.

PES has been regarded as surface-sensitive, because an electron escape depth from bulk material is finite. However, the escape depth can be several nanometers, which is sufficiently large for aqueous solution to exhibit bulk properties owing to a large permittivity of liquid water. It is noted that photoemission angular anisotropy is anticipated only for molecular species on the liquid surface; photoemission from the bulk is isotropic due to considerable elastic scattering in the bulk. Thus, we employ TARPES for studying transient electronic states on the liquid surface.

Water has intriguing properties and dynamics due to strong hydrogen bonding, which are of great interest in various areas in science and technology. Liquid water is a wide-gap semiconductor, and an electron can be trapped in the band gap, being assisted by reorganization of hydrogen bonding network [1]. The electron binding energy (eBE) of this trapped state (a hydrated electron) in water is as large as 3.4 eV with respect to the vacuum level.

In addition to the trapped state in bulk water, it has been speculated that an electron can be trapped on the surface of water. A trapped electron on the surface of crystalline ice has been identified experimentally [2]. However, a surface-bound electron on liquid water is elusive [3]. A trapped state on the ice surface is long-lived, because there is insufficient internal energy in ice to enable reorganization of a “frozen” hydrogen-bonding network. An electron cannot penetrate into the confined lattice of crystalline ice. On the other hand, liquid water has thermal fluctuation, which enables ultrafast response of the hydrogen-bonding network and rapid penetration of the electron into the bulk. Thus, a surface electron state of liquid water, if any, is expected to be short-lived.

We create hydrated electrons by the charge transfer to solvent (CTTS) reaction from photo-excited solutes. Using hydrophobic solutes segregated on the water surface as an electron donor, charge transfer and generation of a hydrated electron primarily occur near the liquid surface, which is utilized in searching for a surface-bound electron.

## 2. Experimental Section

The schematic diagram of our experiment is shown in Fig. 1. We discharge a liquid laminar flow from a fused silica capillary with a 25  $\mu\text{m}$  inner diameter into a time-of flight (TOF) photoelectron spectrometer at a flow rate of 0.5 mL/min. A femtosecond 226 nm pump pulse (5.49 eV) electronically excites solutes in the liquid at ca. 1 mm downstream from the nozzle, where the liquid temperature is estimated to be 275 – 280 K. A femtosecond 260 nm probe pulse interrogates the non-stationary electronic state by photoemission. The cross-correlation of the pump and probe pulses is ca. 120 fs in this study. Photoelectrons emitted from the liquid surface are sampled into the TOF analyzer through a 0.5 mm $\phi$  skimmer located at 2 mm from the liquid surface. The electron flight path from the liquid surface to the detector is 1200 mm, which provides an energy resolution of ca. 50 meV. The 40 mm diameter of a microchannel plate detector provides a detection solid angle of  $10^{-3}$  steradians. A 100 kHz laser system [4] is

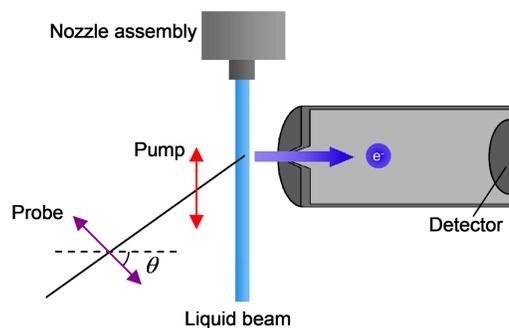


Fig. 1 Experimental setup

employed to compensate for the small detection solid angle. The linear polarization of the pump pulse is fixed perpendicular to the electron detection axis, and angle-resolved photoemission spectra are measured by rotating the linear polarization of the probe pulse from 0 to 90 degrees with respect to the electron detection axis. The time profile of the signal from the microchannel plate is recorded using a multichannel scaler.

### 3. Results and Discussion

Figure 2 presents time- and angle-resolved photoemission spectra measured for aqueous 0.5 M DABCO (1,4-diazabicyclo[2,2,2]octane) solution. Each panel from (a) to (d) shows a photoelectron spectrum  $S(E, \theta)$  at different pump-probe time delays from 100 fs to 3 ps, respectively. Rapid change of the photoelectron spectrum appears predominantly in the low eBE region, where strong photoemission anisotropy is observed. The intensity is minimized when the probe laser polarization is perpendicular to the electron detection axis. For closer examination of the anisotropic photoemission component, we calculated the difference spectrum  $\Delta S_{\text{ani}}(E, \theta) = S(E, \theta) - S(E, 90)$  at each time delay, as shown in Fig. 2.  $\Delta S_{\text{ani}}(E, \theta)$  at 100 fs exhibits a Gaussian band shape centered at 2.2 eV, which is due to photoemission from the Rydberg state of hydrated DABCO. As time goes from 100 to 300 fs,  $\Delta S_{\text{ani}}(E, \theta)$  gradually diminishes and no anisotropic component is discernible at 3 ps. The eBE distribution peaked at 3.3 eV, seen in Fig. 2(d), is of a hydrated electron, although it is still weakly interacting with  $\text{DABCO}^+$  at this short time delay. Fig. 3(d) also indicates that photoemission from a hydrated electron is isotropic. We performed continuum multiple  $X\alpha$  scattering calculations and confirmed that this isotropic photoemission is due to elastic scattering of a photoelectron with a hydration shell. The result suggests that charge transfer from segregated DABCO on water surface occurs to the bulk side of water and not the liquid surface. TRPES using other solutes are also presented at the conference.

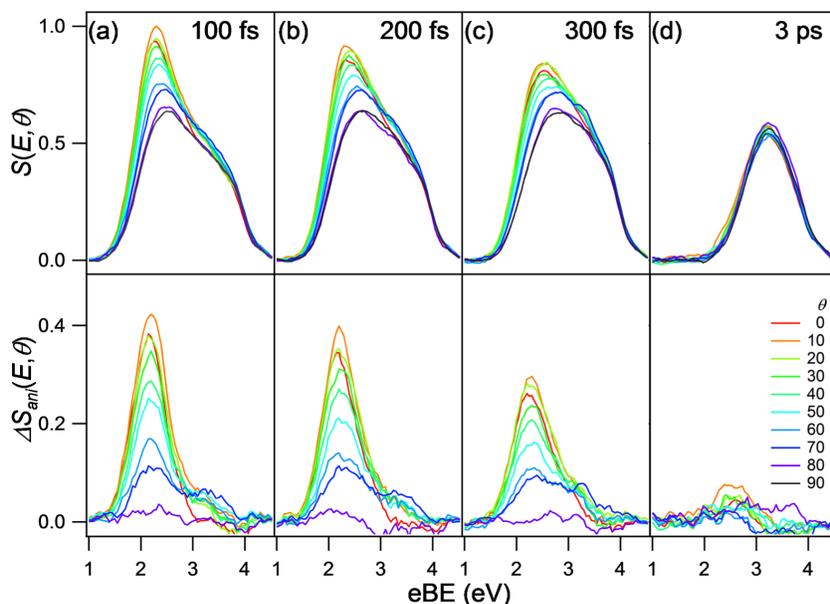


Fig. 2 Photoelectron spectra of aqueous 0.5M DABCO solution as a function of the polarization angle of the probe pulse  $\theta$  with respect to the electron detection axis. The spectra were observed at different pump-probe time delays of (a) 100 fs, (b) 200 fs, (c) 300 fs and (d) 3 ps.

### 4. References

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