

Ultrafast electron transfer and solvation dynamics in ice layers on Cu(111)

C. Gahl, U. Bovensiepen, C. Frischkorn, and M. Wolf

Fachbereich Physik, Freie Universität Berlin, 14195 Berlin-Dahlem, Germany
E-mail: wolf@physik.fu-berlin.de

Abstract. The dynamics of photoinjected electrons from copper into the conduction band of amorphous solid D₂O (H₂O) layers, the subsequent localization and energetic stabilization due to electron solvation in ice are investigated with time- and angle-resolved two-photon photoelectron spectroscopy.

The solvation dynamics of excess electrons in water have attracted special interest due to its fundamental importance for charge transfer and solvation processes in chemistry and biology and the apparent simplicity of the hydrated electron as a model solute [1-3]. Upon photoinjection in liquid water at room temperature an excess electron localizes and relaxes on a timescale of ~ 1 ps via several precursor states to the equilibrated solvated electron [3]. So far, most studies have focused on the solvation dynamics in the liquid phase, but very little is known about the initial stages of electron trapping in supercooled water and ice [4]. Photoinduced electron transfer into amorphous ice films leads to molecular rearrangements and crystallization [6]. Electrons in precursor states to solvated electrons in ice are known to enhance the dissociation of chlorofluorocarbons adsorbed on ice surfaces, a reaction which is of high relevance in the depletion of the ozone layer by released Cl atoms [5].

We have studied the dynamics of electron injection from a metal surface into ultrathin layers of amorphous ice and the subsequent localization, solvation and population decay using femtosecond time- and angle-resolved two-photon photoelectron (2PPE) spectroscopy. The inset in Fig. 1 illustrates the electron transfer, solvation and the 2PPE process in a schematic energy diagram: An UV pump pulse ($h\nu_1=3.92$ eV, 65 fs) excites electrons from the substrate into the conduction band (CB) of ice. The relaxation dynamics are monitored by a time-delayed probe pulse ($h\nu_2=1.96$ eV, 65 fs), which promotes the electron above the vacuum level, where its kinetic energy and momentum ($k_{||}$) is analyzed [7]. D₂O (H₂O) is adsorbed on a Cu(111) single crystal surface in ultra-high vacuum at 100 K. Under these conditions, water is known to form an amorphous solid [8], while scanning tunneling microscopy indicates layer by layer growth [9]. The ice coverage Θ is determined in bilayers (BL) of bulk ice by the integrated intensity of thermal desorption spectra.

Time-resolved 2PPE spectra of amorphous ice on Cu(111) are depicted in Fig. 1. At early time delays the spectra exhibit two features: A pronounced peak e_s at

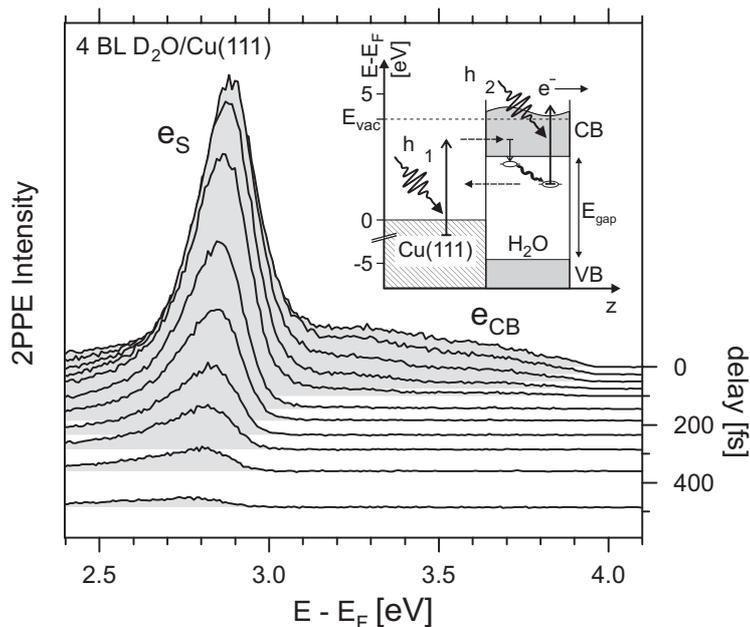


Fig. 1. Time-resolved 2PPE spectra of 4 BL D₂O/Cu(111) at normal emission; the inset represents the 2PPE process, the electronic structure of the ice layer on a Cu surface and the successive photoinjection, localization and solvation of electrons in the ice layer and their back transfer to the metal substrate.

~ 2.9 eV above the Fermi level (E_F) and a broad continuum e_{CB} extending up to 3.9 eV, which is attributed to photoinjected electrons in the conduction band of ice. Within the laser pulse duration the electrons of e_{CB} relax towards the band bottom or transfer back to the metal by coupling to electron-hole pairs in the metal [6]. The energetic position of e_S shifts with -270 meV/ps accompanied by a pronounced decrease in intensity. Angle-resolved measurements of the wave vector dispersion (not shown) unveil the transition from an extended to a localized state within 100 fs.

To understand the stabilization of e_S a sequence of elementary steps is considered: The CB intraband relaxation is followed by localization of the electron within 100 fs at favorable sites like free OH groups or a locally distorted environment. In analogy to charge transfer reactions, localization of the electronic wave function is achieved in a Marcus-type picture [10] by a change in the molecular configuration like the transition from V_{CB} to V_S along a configuration coordinate q_1 (Fig. 2). In addition, the electron is stabilized further on the timescale of 1 ps as evidenced by the time-resolved energetic shift of e_S (Fig. 1). This increase in binding energy is accomplished by electron solvation, i.e. screening of the excess electron through rearrangements of the water dipoles. The electron is stabilized on the potential V_S along a coordinate q_2 , which is different from q_1 (Fig. 2). During all these steps,

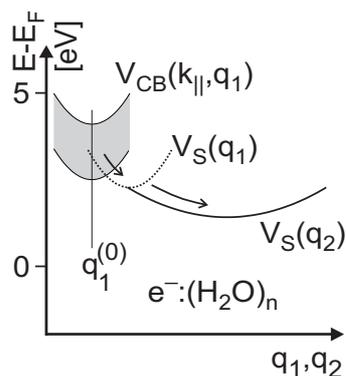


Fig. 2. Scheme of electron localization and solvation: Electron potentials of the conduction band V_{CB} and the solvated electron V_S along the configuration coordinates q_1, q_2 ; $q_1^{(0)}$ denotes the ground state configuration for the conduction band.

higher mobility of the solvent at the surface with respect to bulk. For thicker layers the solvated electron resides in the bulk, because further increase of the coverage does not influence the dynamics.

Recently, it was suggested that the solvation dynamics are considerably slower in solid than in liquid water due to a proportionality to the dielectric relaxation time of the medium in the thermodynamic equilibrium [5]. In contrast, we have recorded timescales comparable to the solvation dynamics in the liquid phase [1-3] and small anion clusters [11]. Adsorption of water at surfaces, which serve as templates for the solvent, allows to modify the solvent structure and facilitates systematic studies of the relation between structure and solvation dynamics in low dimensional systems.

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which follow the primary photoexcitation, back transfer to the metal substrate provides a more or less efficient relaxation channel. The crucial parameter is the wave function overlap of the respective initial and final states. Also electrons which formed a solvated electron complex $e^-(H_2O)_n$ finally transfer back to the substrate as seen from the decay of the signal e_s (Fig. 1).

Coverage dependent experiments result in two distinct regimes of solvation dynamics for coverages $\Theta \geq 3$ BL and $\Theta \leq 2$ BL. At low Θ a four times faster peak shift of e_s is found at delays < 300 fs compared to higher coverages. Considering the lower coordination of molecules at the surface, the fast solvation dynamics for $\Theta \leq 2$ BL are attributed to solvated electrons near the surface in the ice layer due to the