# Impact of Ice Structure on Ultrafast Electron Dynamics in D₂O Clusters on Cu(111)

J. Stähler,[1] M. Mehlhorn,[2] U. Bovensiepen,[1] M. Meyer,[1] D. O. Kusmierek,[1] K. Morgenstern,[2] and M. Wolf[1]

[1]*Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin-Dahlem, Germany*\*
[2]*Leibniz Universität Hannover, Institut für Festkörperphysik, Appelstrasse 2, 30167 Hannover, Germany*
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The structure of D₂O clusters on a Cu(111) surface and the femtosecond dynamics of photoexcited excess electrons are investigated by low-temperature scanning tunneling microscopy and two-photon photoemission spectroscopy. Two types of amorphous ice clusters, porous and compact, which exhibit characteristic differences in electron dynamics, are identified. By titration with Xe we show that in both structures solvated electrons preferentially bind on the cluster surface.

Heterogeneous charge transfer (HET) across interfaces is a key process in various fields of physics, chemistry, and biology [1]. Besides the fundamental importance, HET is also technologically highly relevant for dye-sensitized solar cells, nanoscale electronic devices, as well as for electrochemistry [1,2]. However, the details of the interfacial electronic and molecular structure are often unknown, in particular, for complex interfaces of colloidal particles or solid-liquid interfaces. In contrast, surface science studies of molecular adlayers on single crystal surfaces allow for systematic investigations of the dynamics of HET across well defined interfaces [3]. A model system for HET is photoinjection of excess electrons in an adlayer of polar molecules—such as water—leading to the formation and localization of solvated electrons, which are localized and stabilized by the polar environment [4–7]. Thereby the transient confinement of the solvated electron's wave function results in a varying degree of overlap with metal states leading to a dynamically changing transfer rate [8]. Combining structural probes of the molecule-solid interface with time-resolved spectroscopy would therefore yield microscopic insights into the relation between structure and dynamics on an elementary level. This approach requires a structural probe on a molecular length scale in combination with a method that is sensitive to dynamics on the femtosecond time scale.

In this Letter we present a structural and electronic characterization of amorphous D₂O clusters deposited onto a Cu(111) single crystal surface employing low-temperature scanning tunneling microscopy (STM) combined with femtosecond time-resolved two-photon photoemission (2PPE) spectroscopy. We show that understanding of the cluster structure is crucial for excess electrons in water as the existence of pores in amorphous clusters leads to pronounced changes of the observed electron binding energy and its respective dynamical evolution. By titration experiments we reveal the binding-site of solvated electrons at the ice-metal interface.

Ice clusters are grown by expansion of D₂O vapor into ultrahigh vacuum onto the Cu(111) surface at 85 K. The D₂O coverage is normalized to the mass equivalent of one wetting bilayer (BL) of crystalline ice on the Cu(111) surface. We image the clusters with a low-temperature STM, which facilitates measurements at 5 K. The nondestructive imaging of water clusters is enabled by the sub-pA stability of the STM that avoids tip-induced modifications [9]. The binding energy and femtosecond dynamics of excess electrons in the ice clusters are investigated at 30 K by time-resolved 2PPE spectroscopy using a tunable femtosecond amplified laser system [10]. The pump (UV) and time-delayed probe (VIS) pulses (40 fs duration) excite and photodetach electrons, respectively [Fig. 1(d)]. Their kinetic energy $E_{kin}$ is measured by a time-of-flight spectrometer as a function of time delay with an energy resolution <20 meV. The spectra are plotted versus the intermediate state energy with respect to the Fermi level $E - E_F = E_{kin} + \Phi - h\nu_{VIS}$, $\Phi = E_{vac} - E_F$ is the sample work function [11].

Figures 1(a) and 1(b) present STM images of ice clusters on Cu(111). Deposition of D₂O at 85 K leads to three-dimensional clusters with a narrow size distribution as imaged by STM [Fig. 1(a)]. They exhibit neither long- nor short-range order and no defined shape in any direction (inset). In agreement with present understanding [12] we conclude that these clusters are amorphous. Annealing to 120 K for 2 s changes the appearance of the clusters [Fig. 1(b)]. Their size distribution broadens and less metal surface area is covered with ice clusters although no desorption of D₂O is encountered. We estimate the cluster height by measuring the apparent height $h$ of ice clusters before and after annealing as a function of tunneling voltage $U$. Figure 2(a) shows a typical result for $h(U)$ before annealing. Note that an extremely low current of 500 fA is employed in order to reduce electron induced and mechanical manipulation at $U > 250$ mV [13]. At nondestructive tunnelling conditions, $h$ is 0.3 nm [Fig. 2(b)]. Here, tunneling occurs through the ice band gap directly to the metal and $h$ underestimates the real height considerably. Up to the conduction band onset $h$ varies weakly with $U$. At $U > 2.7$ eV a pronounced increase of $h$ occurs
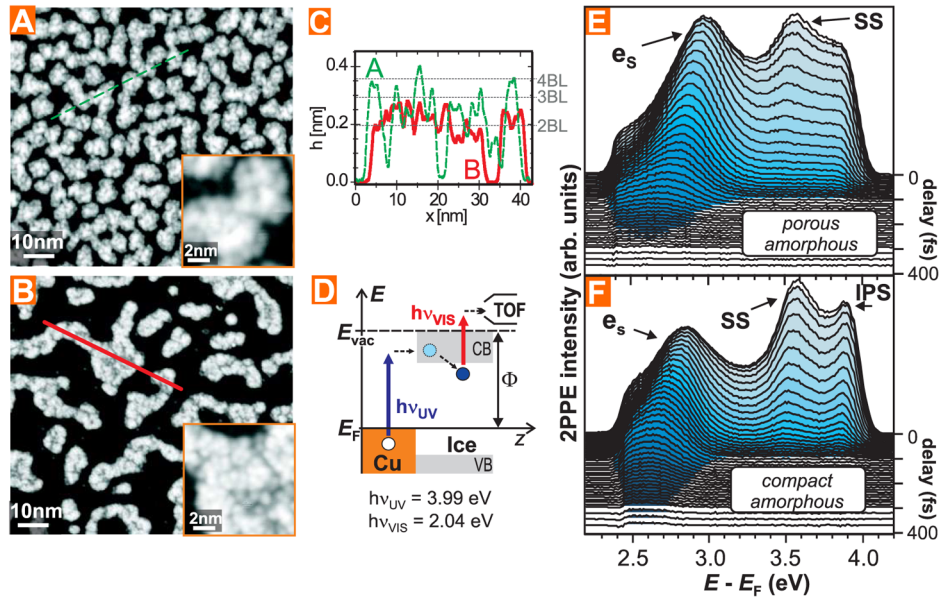
FIG. 1 (color online).  (a),(b): STM images of 1 BL (nominal coverage) amorphous $D_2O$/Cu(111) as deposited at 85 K (A; 0.2 V, 1 pA) and after annealing at 120 K (B; 0.1 V, 9 pA). As apparent from the high resolution images (insets) both structures are disordered, i.e., amorphous. The line scans (c) depict the apparent height $h$ in nm and the real height in BL before and after annealing. (e),(f): 2PPE spectra of 0.8 BL $D_2O$/Cu(111) at different pump-probe delays (right axis). Features at energies >3.3 eV result from the Cu(111) surface (SS) and image potential state (IPS). The peak in the spectra of porous ice (e) originates from solvated electrons ($e_s$) and its intensity decreases after transition to compact clusters (f). (d) In 2PPE a UV pulse excites metal electrons that are transferred to the ice conduction band (CB). A time-delayed VIS pulse probes the transient electron population.

[Fig. 2(c)]. The saturation at 3.5 eV yields the height of 1.1 nm [Fig. 2(d)]. At this voltage electrons tunnel into the ice conduction band and $h$ is close to the geometrical height. Normalization of $h$ to the respective ratio of apparent and real height facilitates the determination of the change in cluster height upon annealing. We find that the structural transition at 120 K is accompanied by a decrease in cluster height by 1 BL as depicted by the line scans in Fig. 1(c). The molecular resolution image [14] shows that water molecules are still disordered and therefore amorphous (inset). Comparison of the total volume of all imaged clusters before and after heating yields that the integrated cluster volume is reduced by 40(8)%. We conclude that the as-grown clusters [Fig. 1(a)] consist to a large extent of pores [15]. We will refer to these structures as *porous* amorphous and *compact* amorphous ice and show below that porous structure has considerable impact on the electron dynamics.

Femtosecond time-resolved 2PPE spectra of ice clusters prepared under nominally identical conditions are given in Figs. 1(e) and 1(f). They exhibit contributions from ice clusters and bare Cu(111), which are easily distinguished, because the electronic structure of the Cu(111) surface is well known [16]. In both datasets, the peak at $E - E_F = 3.6$ eV results from the Cu(111) surface state (SS), 0.4 eV below $E_F$. In contrast, the feature $e_s$ represents electrons in the adsorbate which exhibit a finite lifetime. With increasing time delay the peak maximum shifts towards $E_F$; i.e., the binding energy increases. Based on our earlier studies [7,8,17] we assign this feature to the formation of solvated

electrons. Figure 1(d) schematically depicts the photo-induced transfer of metal electrons into delocalized states in the ice where the electrons localize at solvation sites and are stabilized by a rearrangement of neighboring polar molecules. The residence time of these excess electrons
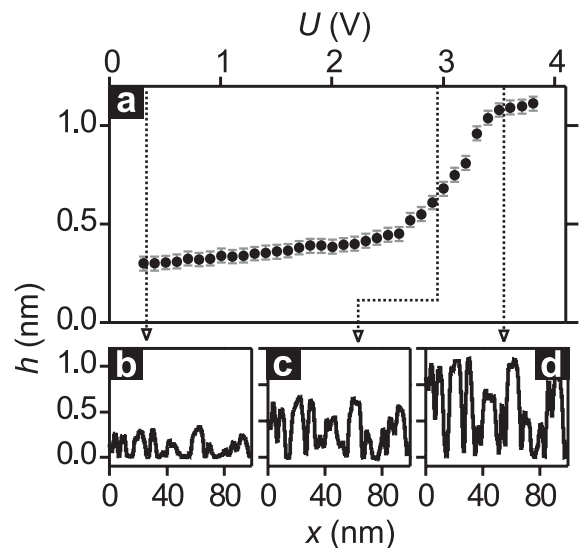


FIG. 2.  (a) Dependence of the apparent height of porous amorphous ice clusters on tunnelling voltage. (b)–(d) Line scans at the voltages indicated in (a) for tunneling through the band gap at 0.3 V (b), at the lower band edge of the conduction band at 2.9 V (c), and through the conduction band of the ice clusters at 3.5 V (d); $I = 500$ fA, 0.8 BL.

is limited by electron transfer back to the metal, which competes with the screening and stabilization of the hydrated electrons by solvent molecules that enables the finite lifetime of the hydrated electrons [8].

Figure 1(f) presents 2PPE data of compact amorphous ice clusters. Comparison with the results of porous clusters [Fig. 1(e)] shows that the spectral signature $e_s$ is also observed for compact clusters. However, at 0 fs the peak maximum occurs 140 meV lower in energy. Thus, solvated electrons are more strongly bound in the compact structure. The transient shift of the peak maxima as a function of time delay is given in Fig. 3 for both structures. Because of the slower solvation dynamics for compact clusters the peak maximum of $e_s$ reaches after 200 fs the same energy (2.6 eV) as in the porous ice; i.e., the hydrated electrons achieve an equivalent stage of solvation for both structures.

The transient population of $e_s$ is also affected by the structural transition. Figures 1(e) and 1(f) show that the formation probability of solvated electrons measured by the 2PPE intensity at $t = 0$ fs is lower for compact clusters. At later delays the population dynamics also differ as shown in the inset in Fig. 3. The transient hydrated electron population of porous and compact clusters are fitted with a single exponential decay (solid lines) convolved with the pulses' cross correlation envelope (dashed line). The decay time of porous $D_2O$ is 30% faster [$\tau = 36(5)$ fs] than for compact ice [$\tau = 50(5)$ fs]. This considerable impact of the ice cluster structure on the solvated electron's energetics, its formation probability, and lifetime demonstrates the sensitivity of the electron dynamics to the local environment.

To gain microscopic insight into this structural dependence of the dynamics identification of the actual binding site is 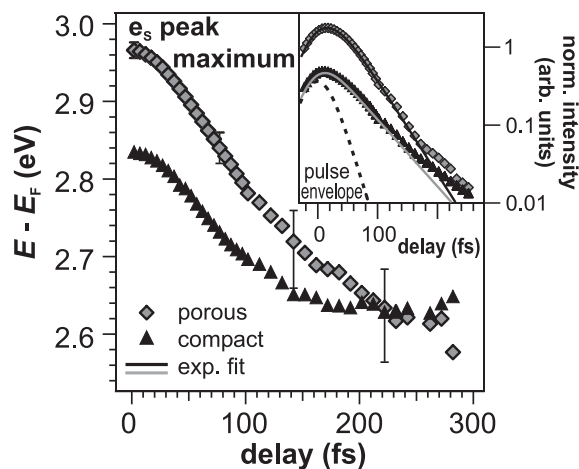required. Thus, we now address the question whether the hydrated electrons are localized on the surface or in the bulk of the ice clusters [18–20]. For this purpose we adsorb a xenon overlayer on the cluster-covered Cu(111) surface (Fig. 4, top) and obtain simultaneously 2PPE spectra. We assume that in the case of bulk solvation the hydrated electron does not interact with the xenon atoms, because it is surrounded and screened by water molecules. Only the net electric field of the solvation shell could polarize the Xe, which is a weak effect. However, for electron solvation on the surface of the ice clusters considerable changes in the photoelectron spectra are expected, since the localized charge would be directly affected by the presence of the Xe atoms due to (i) their polarizability and (ii) a confinement, "squeezing", of the solvated electron's wave function [21].

The peak position of $e_s$ as a function of Xe exposure for porous (diamonds) and compact amorphous ice clusters (triangles) on Cu(111) is depicted in Fig. 4. Upon titration, $e_s$ shifts for *both* types of amorphous clusters by more than 400 meV to higher energies [22]. As discussed above, we assign this pronounced effect to a direct interaction of the Xe atoms with the localized charge; i.e., the Xe atoms confine the hydrated electron's wave function and are polarized by the localized charge. Our titration experiment thus clearly shows that the solvated electrons are localized on the surface of both the porous and compact amorphous clusters. This emphasizes that the surface is considerably more favorable for electrons than bulk sites and structural
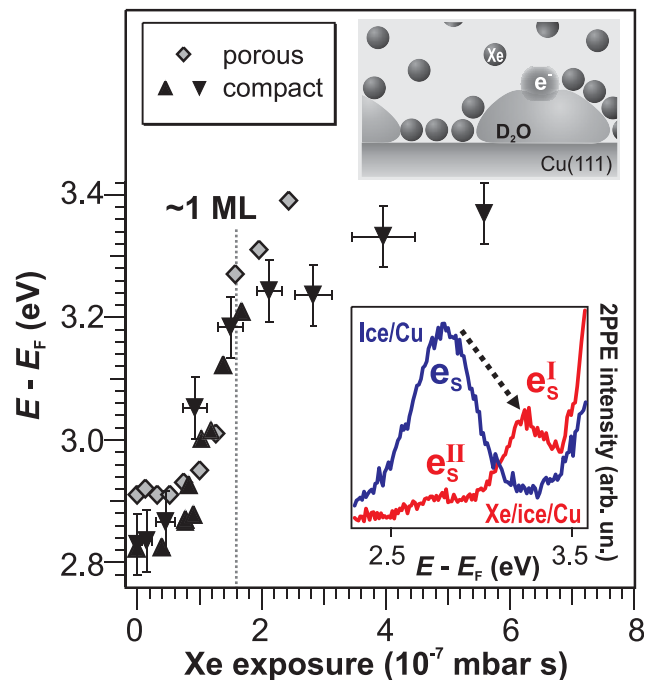


FIG. 3.    Transient shift of the peak maximum of $e_s$ in porous and compact amorphous clusters. Inset: Population decay of $e_s$. The population (symbols) is determined by integrating $E = 2.58$–$3.17$ eV. Fits (solid lines) consist of an exponential decay to positive delays convolved with the laser pulses' cross correlation envelope (dashed line) [8].



FIG. 4 (color online).    Energetic shift of $e_s$ as a function of Xe exposure ($\Delta t = 0$ fs). $1.6 \times 10^{-7}$ mbar s correspond to 1.0(5) ML (dashed line) calibrated on bare Cu(111). Inset (top): Schematic representation of the titration experiment. Inset (bottom): Spectra of compact clusters on Cu(111) before and after coadsorption of 2 ML Xe.

modifications in the bulk like pores are not sufficient to bind electrons. Considering the image potential in front of a metal surface this finding might appear counterintuitive. The image potential stabilizes electrons the better the closer they are to the metal and would therefore favor bulk solvation. However, the polar water molecules screen the hydrated electron from the environment including the metal substrate in agreement with the observed binding site at the ice-vacuum interface. The lower inset of Fig. 4 shows 2PPE spectra of compact amorphous ice clusters on Cu(111) before (black line) and after adsorption of 2 ML Xe. In addition to the shifted peak $e_s^{\mathrm{I}}$ we observe a second, weaker feature $e_s^{\mathrm{II}}$ at 2.8 eV. Apparently a minority of the solvated electrons, namely, isomer $e_s^{\mathrm{II}}$, remains unaffected by the Xe adsorption. They are attributed to sites that are not titrated with Xe. However, the pronounced shift of $e_s^{\mathrm{I}}$ evidences that surface solvation dominates.

Having identified the binding-site of the excess electrons, the origin of the stronger binding and longer lifetime of the solvated electrons in compact clusters becomes apparent. It results from the higher density of $D_2O$ molecules underneath the electrons compared to the ones on top of the porous clusters: A better screening of the excess charge is facilitated. This effect dominates over the influence of the electron-metal distance, which is ~1 BL smaller in the case of compact clusters. A higher number of unbound hydrogens in the porous structure may lead to a more efficient stabilization; such a scenario is consistent with the observation of a faster peak shift in case of the porous clusters. Our study shows that the structural changes initiated by annealing ($\Delta T = 35$ K) critically determine the electron solvation and transfer dynamics at the interface.

In gas phase studies of water cluster anions the binding site of the hydrated electrons—surface vs bulk—is a long-standing issue [18,19,23]. Adsorbed clusters, as investigated here, are certainly perturbed by a metal substrate (Fig. 1). We find, however, that the excess charge is screened from the metal. Thus, it is meaningful to compare hydrated electrons in supported and gas phase clusters. We consider the number of molecules in a sphere with a diameter of the real height of the supported clusters as a lower limit of a corresponding gas phase cluster and obtain a cluster size >30 molecules. In this regime early gas phase studies reported bulk solvation [18,23] albeit theory favors surface solvation [19]. Only recent modifications on the cluster preparation resulted in observation of a new isomer attributed to surface solvation [18]. Thus it is remarkable that for our supported clusters surface solvation clearly dominates.

In conclusion we have identified porous and compact amorphous $D_2O$ clusters and find that energy and population dynamics of solvated electrons are sensitive to the porous or compact amorphous structure. By coadsorption of Xe we determine the ice-vacuum interface as the solvation site of electrons. Our results access the spatial and temporal dimension on microscopically relevant scales and prove the close relation of ultrafast dynamics and molecular structure in interfacial electron transfer processes.

*Electronic address: www.physik.fu-berlin.de/~femtoweb
[1] R. J. D. Miller et al., *Surface Electron-Transfer Processes* (VCH, New York, 1995).
[2] X.-Y. Zhu, J. Phys. Chem. B **108**, 8778 (2004).
[3] C. M. Wong et al., J. Phys. Chem. B **103**, 282 (1999).
[4] J. Zhao, B. Li, K. Onda, M. Feng, and H. Petek, Chem. Rev. **106**, 4402 (2006).
[5] A. D. Miller et al., Science **297**, 1163 (2002).
[6] B. Li, J. Zhao, K. Onda, K. D. Jordan, J. Yang, and H. Petek, Science **311**, 1436 (2006).
[7] C. Gahl, U. Bovensiepen, C. Frischkorn, and M. Wolf, Phys. Rev. Lett. **89**, 107402 (2002).
[8] J. Stähler, C. Gahl, U. Bovensiepen, and M. Wolf, J. Phys. Chem. B **110**, 9637 (2006).
[9] M. Mehlhorn, H. Gawronski, L. Nedelmann, A. Grujic, and K. Morgenstern, Rev. Sci. Instrum. **78**, 033905 (2007).
[10] M. Lisowski, P. A. Loukakos, U. Bovensiepen, J. Stähler, C. Gahl, and M. Wolf, Appl. Phys. A **78**, 165 (2004).
[11] Sample and spectrometer are electrically connected. The spectral signature of electrons from $E_F$ serves as reference energy. As $\Phi$ varies with the local $D_2O$ coverage, the measured value of 4.3 eV is an average within the laser spot. Thus, one cannot infer the vertical detachment energy of $e_s$.
[12] K. P. Stevenson, G. A. Kimmel, Z. Dohnalek, R. S. Smith, and B. D. Kay, Science **283**, 1505 (1999).
[13] K. Morgenstern and K.-H. Rieder, J. Chem. Phys. **116**, 5746 (2002).
[14] The white, round protrusions in the inset of Fig. 1(b) represent single water molecules.
[15] Porous ice clusters have been observed before, although under different preparation conditions [12].
[16] N. V. Smith, Phys. Rev. B **32**, 3549 (1985).
[17] U. Bovensiepen, Prog. Surf. Sci. **78**, 87 (2005).
[18] J. R. R. Verlet et al., Science **307**, 93 (2005).
[19] L. Turi, W.-S. Sheu, and P. J. Rossky, Science **309**, 914 (2005).
[20] F. Baletto, C. Cavazzoni, and S. Scandolo, Phys. Rev. Lett. **95**, 176801 (2005).
[21] M. Wolf, E. Knoesel, and T. Hertel, Phys. Rev. B **54**, R5295 (1996).
[22] The delayed onset of the peak shift is explained by preferential adsorption of Xe on Cu(111) patches before Xe adsorbs on ice clusters, as cross checked by thermal desorption of Xe on Cu(111) and closed ice surfaces.
[23] J. V. Coe et al., J. Chem. Phys. **92**, 3980 (1990).