

## Surface Trapped Excess Electrons on Ice

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Local trapping of excess electrons at the surface of solid water systems has recently been observed in large water clusters and at the ice/vacuum interface. The existence of stable surface-bound states for the excess electron may have important implications in atmospheric chemistry, electrochemistry, and radiation physics. By means of first-principles molecular dynamics we find that excess electrons induce a structural reconstruction of the ice surface on a time scale of a fraction of a picosecond. The surface molecular rearrangement leads to an increase of the number of dangling OH bonds pointing towards the vacuum and to the appearance of an electrostatic barrier preventing the penetration of the electron in the bulk. Both factors imply a remarkable stability for the surface-bound excess electron, with respect to its decay into the bulk solvated state.

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Excess electrons (EEs) in water systems are a subject of widespread interest, with implications in biology, atmospheric science, astrophysics, and cluster science [1–6]. The dipole moment of the isolated water molecule is too small to bind an EE [7], but negatively charged states have been observed in the water dimer [6] and in many other larger water systems. Stabilization of the EE in larger systems is a consequence of cooperative molecular rearrangements [8]. Excess electrons in liquid bulk water are known to form a solvated complex characterized by a 4–6 Å electron pocket, surrounded by a solvation shell of six H<sub>2</sub>O molecules [9,10]. In water clusters, the location of the EE depends on the cluster size and structure [11,12]. For sizes smaller than a few tens of molecules, the EE resides outside the cluster, in a surface state, while for larger clusters it prefers a solvated state presumably similar to that found in bulk liquid water [5]. By varying the cluster formation pressure, however, Verlet *et al.* have recently found evidence for surface states even in large but cold clusters [11]. The observation of surface states was attributed to the fact that bulk solvation is kinetically hindered in cold clusters by the large energy barriers required to form the bulk solvation pocket [11]. Similar conclusions have been reached for the behavior of EEs at the surface of ice: while relaxation into a bulk solvated state is likely to be the ultimate fate of EEs initially attached to the ice surface, the kinetics of bulk solvation, at least below 150 K, is believed to be very slow (>1 ms) [3,13]. Based on the long lifetime of excess electrons at ice surfaces, it has been hypothesized that, in ice stratospheric clouds, excess electrons produced by cosmic rays, may catalyze some of the chemical reactions that lead to the formation of the radical halogen species responsible for the decomposition of ozone [2,3]. The relevance of this process to the depletion of the antarctic ozone is still under dispute [14–16]; but

its broader impact onto the rich electron-driven chemistry of condensed halogenated compounds is discussed, e.g., in [17].

Stabilization of the EE in a surface-bound state is likely to be associated with a structural reorganization of the surface molecular layers. Accurate theoretical studies in very small clusters, up to (H<sub>2</sub>O)<sub>12</sub>, indicate that the presence of the EE modifies substantially the molecular structure of the cluster with respect to the neutral case [12]. Attachment of an EE induces a reorganization of the cluster bonding topology such that one of the molecules exposes two dangling protons towards the EE. Such a structural reorganization increases the total dipole moment of the cluster and decreases the exchange repulsion between the EE and electrons in molecule [12]. Evidence for short-lived metastable surface trap states has been reported in a recent theoretical study of an EE at the surface of liquid water [18]. At the ice surface, the formation of “pre-solvated” surface states of the excess electron has been observed in experiments studying electron attachment to electronegative species [2,3]. Similarly, time-resolved spectroscopic studies on very thin ice films (up to four molecular layers) indicate that photoexcited electrons induce a local relaxation of the surface molecular structure with a characteristic time of less than 1 ps [19–21].

Generally speaking, attachment of an EE at the ice surface can be expected to be followed by one of the following processes. (a) Decay of the EE into a conduction band state of bulk ice. This mechanism is suggested by the observation that the conduction band of bulk ice lies below the vacuum level by about 1 eV [22]; however, it has not been reported in experiments so far. (b) Decay of the EE into a bulk solvated state. Kinetics hinders such process, as already noted, so we do not take it into account in this study. (c) The surface responds to the attachment with

some degree of molecular reorganization, which has not been identified yet. This appears to be the relevant process observed in experiments.

In this work we identify theoretically, based on state-of-the-art density functional theory (DFT) and molecular dynamics (MD) methods, the structural consequences of the attachment of an EE to the ice surface.

DFT has been demonstrated to be a reliable theoretical tool to describe excess electrons in liquid water and water clusters [4,23,24]. In our simulations, electronic states were expanded in a plane wave basis set with a cutoff of 80 Ry. Troullier-Martins pseudopotentials were used to describe valence electron-nuclei interactions. The Becke-Lee-Yang-Parr (BLYP) functional was adopted, as in most previous works on water systems. For reasons that will be illustrated later, we were required to introduce a self-interaction correction to the energy functional. This was done following the strategy of d’Avezac, Calandra, and Mauri [25]. The electronic states were evolved using the Car-Parrinello method, with a fictitious electronic mass of 200 a.u. Brillouin zone sampling was restricted to the  $\Gamma$  point. Forces on atoms were computed using the Hellman-Feynman theorem, and the velocity Verlet algorithm with a time step of 0.14 fs (6 a.u.) was used for the integration of the equations of motion.

We performed DFT-based molecular dynamics simulations of the ice surface at temperatures close to those reported in experiments, and to those found in polar stratospheric clouds (150–200 K). The thermodynamically stable phase of ice at these conditions is hexagonal (ice *Ih*), and its (0001) surface has been consistently observed in experiments [26,27]. Self-diffusion is negligible at these temperatures [28]. Our system consisted of 32 molecules arranged in four bilayers of 8 molecules each, with a full-

bilayer termination [Fig. 1(a)] [29]. The system was repeated periodically in three dimensions, with an in-plane hexagonal lattice spacing of 8.891 Å. Slabs were separated by a vacuum layer of 20 Å. Calculation details were very similar to those of previous work [30]. The proton distribution was disordered, but respected the Bernal-Fowler ice rules and had a vanishing total dipole moment, at least in the initial configuration. Each water molecule in the outermost layer was threefold coordinated and the slab contained, on each surface, two dangling H bonds pointing towards the vacuum region. During the molecular dynamic runs, one of the two surface bilayers was kept fixed in order to avoid spurious reconstruction effects and mimic the presence of an infinite bulk. We first considered the ideal *Ih*(0001) surface and relaxed its atomic coordinates with and without an EE. In both cases atomic relaxation was minimal. In the neutral surface calculation, we found that the lowest unoccupied level had a clear bulk character, while the lowest state with a substantial charge density in the vacuum region is found about 1.4 eV further above. This indicates that the conduction band of ice *Ih* lies below the vacuum level by at least 1.4 eV, in fair agreement with previous suggestions [22]. On the other hand, the calculation with the excess electron showed that its charge density was confined outside the surface, with exponential decay both into the vacuum and into the crystalline bulk (Fig. 2). This implies that a surface state exists on the ideal (0001) *Ih* ice surface, with an energy lower than the conduction band of bulk ice *Ih*. It is useful at this point to comment on the necessity to introduce a self-interaction correction (*SIC*) to the DFT energy functional. Because the EE state has little density overlap with any other electronic states of the system, it is clear that the electrostatic repulsion with itself, a spurious effect of the local density, or

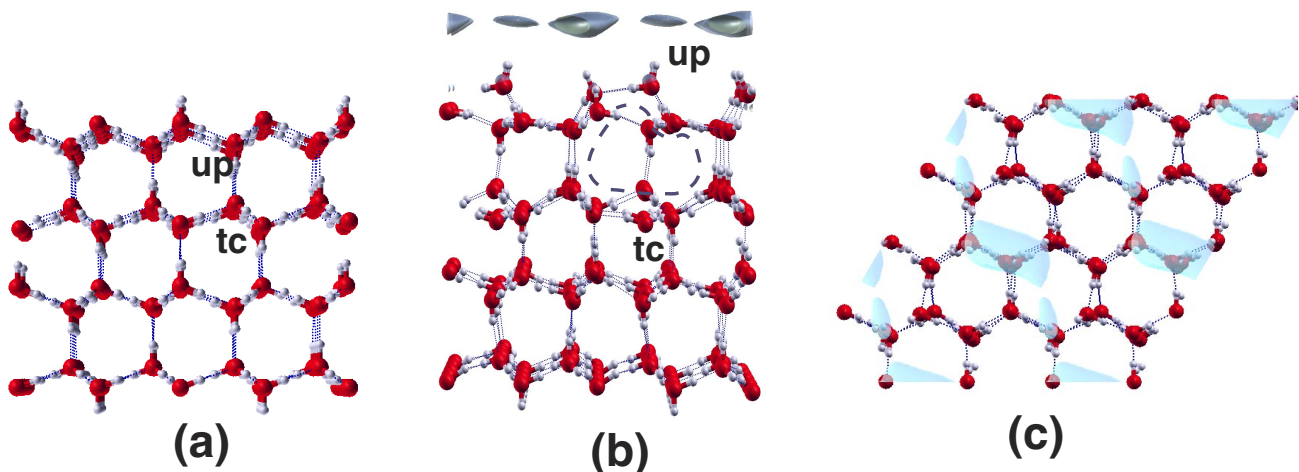


FIG. 1 (color online). (a) Unreconstructed configuration of the 32  $\text{H}_2\text{O}$  molecule surface cell. For clarity, the cell is repeated twice along surface plane. Dark atoms are oxygens, hydrogens are gray, and hydrogen bonds are shown by dotted lines. (b) Reconstructed surface with the excess electron. “Up” labels the molecule that has risen from the second monolayers while “tc” labels the threefold coordinated molecule in the second bilayer. The subsurface cavity is shown with a long-dashed line. (c) Same as (b), view along the surface normal. In (b) and (c) the excess electron charge density isosurface at 30% of its maximum value is also reported.

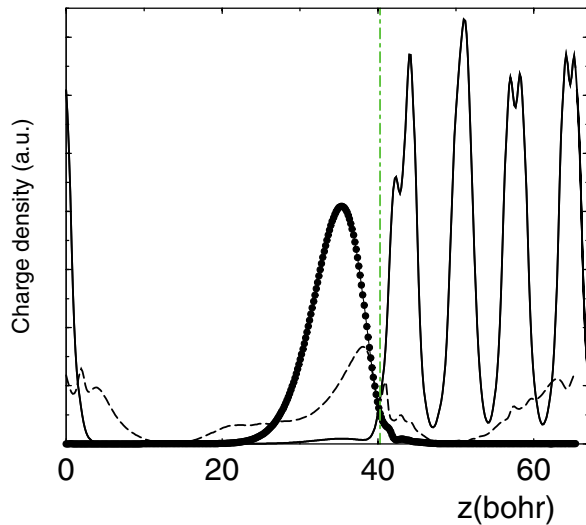


FIG. 2 (color online). Planar average of the excess electron charge density from a DFT calculation with *SIC* (full-dotted line) and without *SIC* (dashed line). As a reference, the planar average of the total charge density is also shown (solid line). The double peaks correspond to the bilayer ice structure and the dot-dashed line refers to the position of the outermost atom (hydrogen).

gradient-corrected approximations to DFT will be larger than the repulsion with any other state. We find that such self-repulsion can modify the shape and location of the EE substantially by, e.g., introducing spurious nodes and unphysical bumps in its charge density (Fig. 2). All these spurious effects disappear by introducing a self-interaction correction. We tested the reliability of this approach by evaluating the electron affinity of a single water molecule, which is experimentally known to be vanishing. The self-interaction-corrected value of the electron affinity was found to be slightly positive (a likely consequence of the finite size of the simulation box), while an uncorrected DFT-BLYP calculation mistakenly gave a stable charged anion with an electron affinity larger than 1 eV. All calculations reported in this work were thus performed with the self-interaction correction.

We now turn to the results of the molecular dynamics simulations. The ice surface with an EE was initially equilibrated at 150 K with a thermostat [31] for 0.25 ps. We then increased the temperature to  $T \sim 200$  K and continued the simulation in the microcanonical ensemble. After about 0.2 ps of simulation at 200 K the surface underwent a major restructuring event corresponding to the breaking of a hydrogen bond between a donor molecule  $(\text{H}_2\text{O})_{\text{up}}$ , see Fig. 1(b), of the second monolayer (first bilayer) and its acceptor counterpart in the second bilayer, which remains threefold coordinated,  $(\text{H}_2\text{O})_{\text{ic}}$ . Freed by its ties with the underlying lattice but still anchored through a donor and two acceptor bonds to two molecules of the first layer,  $(\text{H}_2\text{O})_{\text{up}}$  flew up towards the surface with a dangling H pointing downwards. After about 0.3 ps from the instant

when the first hydrogen bond broke, the dangling H replaced the H engaged in the second donor bond, which finally flipped as a dangling H towards the vacuum, as shown in Fig. 1(b). During the structural rearrangement, temperature was restored to 150 K by means of a thermostat for about 0.15 ps. The system was then allowed to evolve microcanonically at this temperature for 2 ps, during which no further changes took place. The atomic positions were finally relaxed and the reconstructed configuration was found to have an energy  $\sim 0.2$  eV lower than the relaxed ideal surface with the EE. For the total duration of the simulation the EE remained in a surface state peaked at about 3–4 Å from the topmost surface hydrogens; see Figs. 1(b) and 1(c).

For reference, a separate microcanonical simulation without the EE was started from the atomic positions taken from the previous run at 200 K, before the reconstruction event. Without the EE, the temperature spontaneously equilibrated to about 150 K and the system did not show any sign of reconstruction in the 2 ps of the run. We also calculated the energy of the reconstructed surface by removing the EE, and found it to be about 0.8 eV higher than the unreconstructed surface. We therefore conclude that the structural rearrangement is due to the presence of the EE in a surface state.

As a consequence of the EE-induced structural rearrangement and, in particular, of the reversal of the molecular dipole of  $(\text{H}_2\text{O})_{\text{up}}$ , a net dipole moment appears in the slab along the surface normal. This is consistent with theoretical studies on small charged water clusters, where the EE is found to stabilize structures with high dipole moments and clustered dangling H atoms pointing towards the EE [12]. As shown in Fig. 3, the surface dipole is prevalently confined in the first bilayer, with a smaller contribution in the second bilayer. The sign of the dipole moment is such that it lowers the position of the vacuum level with respect to the bulk energy levels. We quantified such an effect by calculating the change in the work function of the neutral surface in the ideal and in the reconstructed configurations. We found that the reconstruction induces a reduction of the work function of the neutral surface of about 2.5–3 eV. This confirms that the EE energy level lies substantially below the conduction band of bulk ice. As a consequence, its decay into a bulk solvated state must necessarily involve a concerted rearrangement of the subsurface molecules which is likely to be severely hindered at low temperatures. We also found that the reconstructed surface displays, within the first two bilayers, a subsurface cavity with radius  $\sim 3$  Å. At variance with the solvation cavity of the EE in liquid bulk water [10], here no dangling OH appears to be pointing towards the center of the cavity, which is instead mostly surrounded by oxygen atoms. Therefore, this subsurface cavity acts as an additional electrostatic barrier against the decay of the EE into the bulk. Recent experiments suggest that the

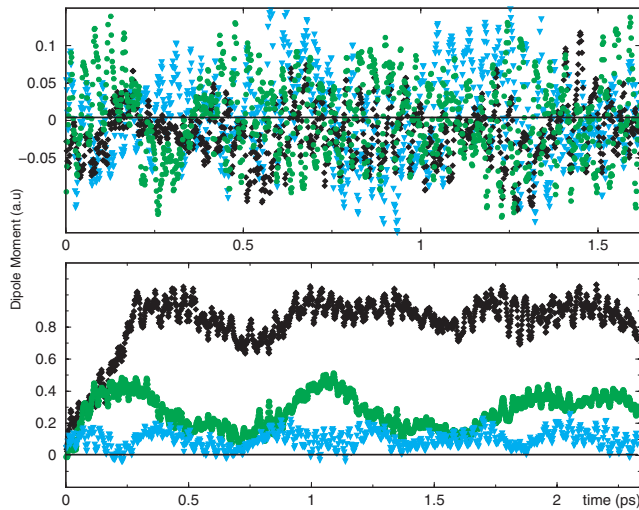


FIG. 3 (color online). Time evolution of the component of the dipole moments along the surface normal of each bilayer are shown for neutral (top) and charged (bottom) calculations [light gray for the third, gray for the second, and black symbols for the first (outermost) bilayer]. The reconstruction process takes place in the first 0.3 ps of the simulation with the excess electron (bottom), while the dipole moments in the neutral case remain close to their initial values (top).

number of free OH groups at the ice surface could be larger than those considered in this work [32]. This would provide an additional mechanism for the stabilization of the surface-bound EE and therefore would strengthen our conclusions.

In summary, we find that the structural rearrangement induced by an EE at the ice surface traps the EE in a very stable surface state and hinders its decay into the bulk through the buildup of a subsurface electrostatic barrier. Such a mechanism explains the remarkable stability of large cluster isomers with EE in surface states, observed recently by Neumark *et al.* [11] and provides a microscopical picture of the surface sites relevant for the heterogeneous chemistry on atmospheric ice particles [2,3].

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