

## Ultrafast electron dynamics at alkali-ice interfaces probed with two-photon photoemission

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An excess charge in a polar environment, i.e. an electron or an ion, is known to form a charge-solvent complex [1]. This process involves a re-orientation of the molecules surrounding the charge, resulting in the screening of the extra charge and in the increase of its binding energy [2]. Electron and ion solvation is very common in nature and well studied. However, the microscopic steps involved are not fully understood, yet. Deeper insight into the dynamics of the process is of fundamental interest, as the ion solvation in condensed polar molecules is highly relevant in numerous fields such as, atmospheric heterogeneous chemistry [3]. Solvated electrons can also be very reactive species depending on their binding site and lifetime, as has been shown before [4]. The ability to control both of these properties is therefore highly interesting.

In this study we investigated the electron dynamics in ice water layers adsorbed on a Cu(111) single crystal with co-adsorbed sodium ions by means of time-resolved two-photon photoelectron spectroscopy. In amorphous ice multilayers these electrons are located in the bulk of the ice film [5] and the lifetime and the energetic stabilization rate of the excited electrons are known. After adsorption of sub-monolayer coverages of sodium the 3s electron of the parent Na atom is transferred into the water ice and decays back to the metal before spectroscopy is performed. The accumulation of positively charged sodium ions on top of the D<sub>2</sub>O film can be monitored by a decrease in the system workfunction, which is depending on the Na coverage. A new species of solvated electrons is observed in the presence of the alkali ions. By titration experiments with either Xenon atoms or by adsorption of an additional water overlayer, we can demonstrate that the binding site of these electrons is located at the ice/vacuum-interface. Furthermore the lifetime of the excited electrons in this state is in the order of several picoseconds, so more than one order of magnitude longer compared to solvated electrons in amorphous water ice. The energetic stabilization rate is with ~800 meV/ps almost three times higher than in the case without sodium. Possible scenarios for the origin of the alkali-induced state will be discussed.

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