6. Summary and Conclusions

The present work focuses on the investigation of electron transfer and solvation processes at ice- and ammonia-metal interfaces by time-resolved 2PPE spectroscopy. The main goal of this study is to achieve comprehensive understanding of the underlying fundamental processes of charge injection, stabilization, and back relaxation of excess electrons in polar adlayers. For this purpose, various types of interfaces are systematically investigated and several new model calculations and analysis procedures developed. It is shown that the *elementary* steps of electron transfer and solvation dynamics are similar for all studied systems: Excess electrons are photoinjected from the metal substrate, Cu(111) or Ru(001), into the adlayer, D_2O or NH_3, via delocalized states in the conduction band of the adsorbate layer. Subsequently, the electrons localize at favorable sites, i.e. at local potential minima. The excess charge induces a reorientation of the surrounding polar molecules, which results in a stronger localization and energetic stabilization (solvation) of the interfacial electron. However, at the same time, the electrons decay back to the metal substrate, as it offers a continuum of unoccupied states. This electron transfer strongly depends on the degree of coupling of the excess electrons to the metal states. As the coupling strength is reduced upon solvation, due to enhanced screening of the excess charge by the solvent molecules, the electron transfer *competes* with the electron solvation: While the former leads to a population decrease of the solvated electron state, the latter reduces the decay probability and thus increases the electron lifetimes.

Despite the similarities of the fundamental steps of charge transfer and solvation, the investigated systems also exhibit pronounced differences in their interfacial electron dynamics. Depending on the coupling strength of the solvated electrons to the metal substrate, different regimes of heterogeneous electron transfer (HET) are identified: Substrate-dominated and barrier-determined, the strong and the weak coupling limit. Remarkably, *transitions* between these transfer regimes are observed in real time, which is enabled by the *dynamic* evolution of the electronic coupling degree of the solvated electrons to the metal substrate. These findings are facilitated by systematic variation of substrate, adsorbate, adsorbate structure and morphology, coverage, and sample temperature. The observed influences of these individual factors on the electron transfer and solvation dynamics are summarized in the following.

The comparison of the electron transfer and solvation dynamics at the amorphous D_2O/Cu(111) and D_2O/Ru(001) interfaces shows that electron hydration is governed by the formation of an interfacial potential barrier. Within the first 300 fs after photoinjection, the back transfer of excess electrons is considerably determined by the substrate's electronic surface band structure. In this *substrate-dominated* charge transfer regime, the electrons decay with time constants below 100 fs back to the respective substrate, due to their finite wave function overlap with the

metal. The coinciding ratio $\tau_0^{Cu}/\tau_0^{Ru} \approx \Delta k_{gap}^{Cu} / \Delta k_{gap}^{Ru}$ of decay times and band gap widths[112] of the two substrates suggests that the rate-limiting step of this back transfer of excess electrons is the width of the orientational band gap. In other words, electron decay is presumably mediated by elastic electron transfer. With ongoing solvation, the electrons are increasingly screened from the metal substrate by a reorientation of the surrounding polar molecules. This hydration is accompanied by the formation of a tunneling barrier, which reduces considerably the wave function overlap of the excess electrons with the respective metal. Tunneling through the interfacial barrier becomes the rate-limiting step for electron decay in this *barrier-determined* regime of electron transfer. The implementation of an empirical model description, which incorporates the transient degree of coupling of the hydrated electrons by energy-dependent transfer times $\tau(E)$ and which excellently reproduces the experimental results, shows that the actual stabilization rate for $D_2O/Ru(001)$ and $Cu(111)$ is similar for both substrates. Accordingly, the reaction of the water molecules to the excess charge is similar for both interfaces, i.e. the solvation shell remains unperturbed by the change of substrate.

The change of solvent from amorphous D_2O to amorphous NH_3 significantly influences the time-resolved photoelectron spectra. Both, the time-dependent peak shift of the ammoniated electron distribution and the population decay, change considerably at delay times $t \approx 300$ fs. At earlier delay times, the electrons stabilize with a rate of -0.8 eV/ps; at larger delays, the solvation is remarkably slowed down to -10 meV/ps. As shown by a rate equation model, the electron solvation occurs, after photoinjection through the ammonia conduction band, via two different isomers, e_s^I and e_s^{II}. The first one exhibits the faster stabilization dynamics and decays on fs-timescales. These faster dynamics – in comparison to the dynamics at ice-metal interfaces – are explained by the high number of dangling H-bonds in the ammonia layer.

Besides these differences of electron solvation in amorphous ice and ammonia adlayers, also similarities are found. Coverage-dependent measurements of the electron population dynamics in $NH_3/Cu(111)$ reveal that the transfer of isomer e_s^{II} electrons occurs by tunneling through an interfacial potential barrier. Its transfer time increases exponentially with increasing layer thickness. In addition, Xe overlayer experiments show that both, isomer e_s^I and e_s^{II}, are localized at the NH_3-vacuum interface. The tunneling barrier, which screens e_s^{II} from the substrate, is thus determined by the layer thickness. Therefore, electron transfer at the $NH_3/Cu(111)$ interface is *barrier-determined* for delays larger than 300 fs, as it was the case for the amorphous ice-metal interfaces. The transfer dynamics of isomer e_s^I for $NH_3/Cu(111)$, however, remain unaffected by an increase of the layer thickness. Apparently, no barrier separates the excess charge from the substrate. The finding that the transfer time of e_s^I is not affected by layer thickness variations, although the electrons' degree of wave function overlap with the metal changes, suggests that charge transfer is *substrate-dominated* at delays <300 fs. In other words, the width of the substrate's band gap is – as in the case of ice – presumably the rate-limiting step for HET.

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[112] Surface electronic band structure as a function of parallel momentum. Band gap widths are taken at the respective energy of the solvated electrons.

It is shown that temperature-dependent experiments are a reliable probe for the degree of coupling of a *not yet fully equilibrated* interfacial electron to metal states. In the strong coupling limit, the electron transfer is solely determined by the coupling matrix elements between solvated electrons and metal states. In the case of weak electronic coupling, thermal fluctuations of the solvent molecules contribute to the electron transfer. Due to enhanced screening of the excess charge, thermally assisted tunneling becomes the rate-limiting step for charge transfer. Temperature-dependent experiments reveal that the electron transfer and solvation in the substrate-dominated regime ($t < 300$ fs) is for both solvents, D_2O and NH_3, independent of temperature. Thus, it is concluded that the charge transfer in these early stages of solvation is in the *strong coupling* limit. However, the long lifetime and coverage-dependent coupling of isomer e_S^{II} in the case of $NH_3/Cu(111)$ enables observation of the transition to the *weak coupling* limit: The charge transfer rates for a 12 ML thick amorphous ammonia film exhibit a Arrhenius-like temperature dependence, revealing that the HET is mediated by thermally activated fluctuations of the solvent. Activation barriers of 45 meV and 55 meV are found for delay times > 3ps and 13-50 ps, respectively. Accordingly, the nuclear barrier, which has to be overcome for ET, increases with ongoing solvation. In addition, the transfer rate at $T = 0$ K is extrapolated, which is a measure for the coupling matrix element of ammoniated electrons in the respective state of solvation. However, for thinner NH_3 adlayers, such pronounced temperature-dependence is absent. The electronic coupling of the ammoniated excess electron is – despite the interfacial tunneling barrier – so strong that resonant tunneling through this barrier remains the rate-limiting step. Electron transfer mediated by thermally activated solvent rearrangement is considerably less probable: The electron has decayed before a significant change of solvent conformation occurs. This remarkable finding of a layer thickness-driven transition between the strong and the weak coupling limit has impact on future applications: The observed adjustability of the coupling degree of a localized charge at the adsorbate-vacuum interface might be useful to influence the electron supply for electron-driven chemical reactions at the solvent-vacuum interface: The tunable lifetime of the interfacial electrons could serve as an "internal clock" for such reactions.

Besides the variation of substrate, temperature, and layer thickness, also the dependence of the electron transfer and solvation dynamics on the adsorbate structure and morphology is investigated. In collaboration with K. Morgenstern and M. Mehlhorn, who perform state-of-the-art, high-resolution, low-temperature scanning tunneling microscopy, five different structures of D_2O clusters on $Cu(111)$ are identified and the corresponding electron dynamics investigated. Upon the transition from highly porous to compact amorphous ice clusters, the femtosecond electron transfer and solvation dynamics considerably slow down. However, further structural changes of the clusters, i.e. the transition to well-ordered facetted and pyramidal clusters hardly affect the interfacial electron dynamics. Successful application of the empirical model calculation developed for the ice layers, in combination with Xe overlayer experiments, reveal that the electrons bind on the edges of the supported ice *clusters*. As the electrons solvate in the bulk of closed ice *layers*, a surface-to-bulk transition of hydrated electrons is observed. This transition is a controversially discussed issue for gas phase water anion clusters. For the supported clusters investigated in this work, this transition occurs in a cluster size range, where theory only predicts

surface-bound solvated electrons for gas phase water anion clusters. [Bar88, Tur05a] However, experiments on gas phase clusters find a surface-to-bulk transition in the same cluster size range as the present work. [Coe90, Ver05a, Coe06]

The transition from amorphous to crystalline ice layers is accompanied by dramatic changes of the electron dynamics as shown previously in the context of C. Gahl's dissertation [Gah04] and my diploma thesis [Stä04]. The lifetime of excess electrons in the adlayers increases from a few hundred femtoseconds to several minutes. However, the present work reveals the *formation* dynamics of these ultralong-living, trapped electrons: By high-statistic fs-time-resolved 2PPE measurements and new background subtraction procedures, the electron injection via the $n = 1$ image potential state is observed in real time. The stabilization dynamics on the timescales of minutes are thus completed by the dynamics at femtosecond and intermediate delay times. In other words, electron dynamics occurring over a range of *17 orders of magnitude in time* are observed, manifesting the *freezing* of *hot electrons* at molecule-metal interfaces. An empirical model is developed that is based on a stretched exponential approach, which is well-known for protein-folding in polar environments. The significant temperature dependence of the trapped electron stabilization shows that solvation occurs thermally activated via conformational substates, which represent different solvent conformations separated by energy barriers. The empirical model describes the dynamics of the solvent-solute complex as the relaxation of an over-damped harmonic oscillator with a temperature-dependent friction coefficient. It excellently reproduces the time- and temperature-dependent peak shift, yielding a mean activation barrier of 96 meV for the transition between conformational substates. Collaboration with A. Rubio and M. Bockstedte, who perform sophisticated *ab initio* density functional theory calculations, allows identification of possible candidates of conformational substates. Orientational defects at the surface of the ice layer serve as solvation sites, and stabilization proceeds by flip rotations of neighboring molecules.

Qualitatively similar results are achieved for crystalline ammonia adlayers on Cu(111): Ultralong-living, trapped electrons are found, which are still increasingly stabilized on the timescale of minutes and which exhibit a temperature-dependent peak shift. However, these dynamics are – in comparison to the ones at ice-metal interfaces – less pronounced. The stretched exponential model derived for crystalline ice (including the temperature-dependent friction coefficient) is also applied to the NH_3/Cu(111) data. It suggests that stronger friction in the more rigid structure of the ice adlayer and less stretching of the "internal clock" of the system are the origin of the weaker effect of ammonia adlayers.

In summary, the investigation of a variety of different, but related interfaces allows for detailed understanding of the fundamental processes of electron transfer and solvation. Transitions between different regimes of charge transfer are observed, collective and – in favorable cases – microscopic mechanisms identified, and concerted influence on the coupling degree was achieved. The present thesis thus yields comprehensive insight into electron transfer and solvation dynamics at polar molecule-metal interfaces and enables understanding of the underlying elementary processes. It can be concluded that the ice- and ammonia-metal interfaces

investigated in this work present a multifaceted range of properties and have proven to be model systems for electron transfer and solvation.

Outlook: Resulting from the detailed investigation of electron transfer and solvation processes at the $D_2O/Ru(001)$, $D_2O/Cu(111)$, and $NH_3/Cu(111)$, several interesting questions arise. For example, the origin of the transition from isomer e_S^I to e_S^{II} at the amorphous $NH_3/Cu(111)$ interface should be revealed. It occurs with a mean time constant of 180 fs, followed by solvation and transfer dynamics on ps-timescales. Apparently, an ammonia-specific response of the solvent network occurs, which leads to a rapid change of electron screening. To understand the detailed origin of this transition, further studies of different isotopes of hydrogen and nitrogen might be helpful to decide between the three different scenarios proposed in this thesis: (i) Proton tunneling along hydrogen bonds towards the excess electrons occurs in NH_3 clusters on comparable timescales as the $e_S^I \rightarrow e_S^{II}$ transition. However, this process is known to occur even faster in ice. The absence of two isomers of solvated electrons at ice-metal interfaces suggests that a stronger localization of the excess electrons in ammonia leads to a higher gradient of the electric field and thus to a larger driving force for the proton transfer reaction. (ii) The *umbrella mode*, i.e. the tunneling of nitrogen atoms from one side of the hydrogen triangle to the other, has a cycle duration of 40 fs and is an ammonia-specific feature. Reorientation of NH_3 molecules, mediated by this mode, could lead to an enhanced screening of the excess charge. (iii) As the hydrogen-bonded network of ammonia is less rigid than the one of ice (weaker and fewer H-bonds), the transition from e_S^I to e_S^{II} could also be mediated by the breakage of hydrogen bonds, which subsequently reorient towards the excess charge.

Application of the stretched exponential model to the ultraslow dynamics of trapped electrons in crystalline ammonia predicted stabilization dynamics on ultrafast timescales. Confirmation of this peak shift by high-statistic measurements of the femto- and picosecond dynamics could corroborate the conclusions drawn from the comparison of the model calculation results of both crystalline solvents.

In addition, also the investigation of salt, alkali, or halide solvation in ice or ammonia adlayers appears promising: Many studies on hydrated and ammoniated electrons in liquids and clusters are performed using such species as an electron source. Investigation of doped ice or ammonia adlayers at well-characterized interfaces could yield insight into the impact of the parent ion or atom on the electron solvation dynamics. Furthermore, the metal-nonmetal transition of highly doped liquid ammonia, which was introduced in 2.4.1, also presents an interesting object of research.

Finally, electron-induced chemical reactions at the adsorbate-vacuum interface, mediated by localized solvated electrons, are highly fascinating. Promising candidates for such investigations are, for example, chlorofluorocarbons, which are known to dissociate upon electron attachment in atmospheric clouds.