1. Introduction

Homogeneous electron transfer (ET) from a molecular donor state to a distinct molecular acceptor state is the simplest conceivable reaction, as chemical bonds are neither formed nor broken. Such charge transfer reactions are of vital importance for a variety of different fields in physics, chemistry and biology: For example, photosynthesis [Was92, Mor00] and many other chemical reactions [Rot90, Tim90] are governed by electron transfer as a primary step. Also the *heterogeneous* electron transfer (HET) at molecule-solid interfaces has reached much interest in the past, as this process plays an important role in technologically highly relevant fields. For example, dye-sensitized solar cells (Grätzel Cells) convert light into electrical energy by photoexcitation of dye molecules adsorbed on semiconductor surfaces: The electron is transferred to the conduction band of the substrate so that the charge is separated at the interface. [ORe91] In addition, understanding of HET is highly important for the development of nanoscale electronic devices [Nit03], as any molecular electronic device has to be contacted to a conducting electrode. In the field of photochemistry at molecule-metal interfaces, excited substrate electrons can transfer to unoccupied orbitals of adsorbed molecules. Energy transfer to nuclear motions of the adsorbate can cause chemical reactions at the interface. [Zhu94, Gad95, Bon99, Wag05]

Different theoretical descriptions of charge transfer processes have been developed in the past. HET can be described to occur along the real space electron coordinate, where the charge transfer is mediated by the wave function overlap between donor and acceptor states. This picture is, for example, applied to describe the electron population decay of image potential states. [Ech04] Depending on the degree of coupling between the electronic levels, a tunneling barrier is assumed at the interface that determines the electron transfer rate. [Gad95] Another picture of charge transfer phenomena is given by the Marcus Theory. It was originally developed to describe *homogeneous* ET between two molecular levels in a solution. In this theory, charge transfer is rate-limited by nuclear motion of solvent molecules which arrange differently depending on the charge distribution of the solute. [Mar56, Mar57a, Mar57b] This approach to ET was also extended to the heterogeneous problem [Nit01, Zhu04] and is often applied to charge transfer phenomena at molecule-semiconductor interfaces, where charge transfer occurs to the conduction band of a wide band gap semiconductor. [Mil95] These two seemingly different explanations of HET, Marcus Theory and tunneling picture, are actually complementary, as charge transfer naturally involves both, a change of electron coordinate *and* nuclear rearrangement. Instead of discriminating between the two approaches, identification of the actual *rate-determining step,* i.e. coupling between the electronic levels or solvent rearrangement, is required. Thus, both pictures of charge transfer should be considered as a certain limit of a unifying concept, which involves both, electron and nuclear coordinate, as shown by Truhlar and

coworkers, who derived a theory for charge (proton) transfer taking into account both, real space and solvent coordinate. [Sch01]

Charge injection to a polar solvent environment leads to a reorganization of the solvent molecules, as their dipoles reorient to accommodate the excess charge. This so-called *solvation* leads to an energetic stabilization of the solute. Liquid water and ammonia are model solvents and known to solvate various species as, for example, salts (e.g. solvation of Na^+ and Cl^-) and alkalis (e.g. solvation of Na^+ and e^-). [Jun01, Hay02, Tho03] Observations connected with solvated electrons were first made in 1808: Addition of metal compounds turned liquid ammonia blue. [Dav08] 100 years later, this effect was attributed to the absorption of excess electrons in the solution that are surrounded by a cavity of NH_3 molecules. [Kra08] Later, in the 1960s, electron solvation was also observed in liquid water. [Har62] Since then, many studies have focused on the properties of *hydrated* and *ammoniated* electrons. Excess electrons in water play a key role in seemingly different fields ranging from DNA (*deoxyribonucleic acid*) damage due to dissociative electron attachment [Han03, Pan03] to enhanced dissociation of chlorofluorocarbons (CFCs) in atmospheric clouds, where solvated electrons in water-ice and ammonia particles[1] enhance the ozone layer depletion. [Lu99, Lu01] Electron capture and solvation in gas phase water and ammonia clusters has thus reached considerable attention in the past. [Bar99, Pai04, Ver05a, Tur05a, Coe06] However, gas phase cluster studies also aim at a deeper understanding of the solvated electron's properties in the liquid phase by extrapolation of cluster size-dependent measurements to the bulk liquid. [Her91] A controversially discussed issue in this field is the question, whether the solvated electrons bind at the surface or in the bulk of the clusters: Theory [Bar88, Tur05a] and experiment [Coe90, Ver05a, Coe06] identify a surface-to-bulk transition for different cluster size ranges. However, also the detailed formation process, microscopic structure of the solvation shell, and coupling to vibrational modes of the solvent are still debated for clusters and liquids. [Mig87, Tut91, Bal99, Erm02, Kam02, Her02, Sch04, Lin06, Shk06]

Electron solvation occurs – besides in clusters or liquids – also in molecular adlayers adsorbed on metal or semiconductor surfaces. [Ge00, Bov03, Li06] The surface science approach yields several advantages compared with time-resolved studies of the liquids or gas phase clusters. First, studies under ultrahigh vacuum (UHV) conditions enable reliable and reproducible sample preparation due to systematic characterization. Second, the metal substrate acts as an electron source: While in studies of liquids or clusters excess electrons are generated by admixture of impurity atoms/ions or photoionization of the solvent molecules, the surface science approach enables electron injection from the substrate. This procedure allows investigation of the electron solvation dynamics without the presence of parent atoms or ions. However, the surface science approach has also an apparent disadvantage compared to gas phase studies or investigations of liquid water and ammonia: Electron solvation studies at molecule-metal interfaces are accompanied by a continuous electron decay to the continuum of unoccupied states of the metal. This back transfer to the substrate limits the lifetime of the interfacial electrons and thus hinders investigation of their complete equilibration dynamics. But this apparent draw-back of the surface

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[1] In the present work, the term "ice" always refers to the solid phase of H_2O or D_2O. The in literature frequently used expression "ammonia ice" is not applied to avoid misunderstanding.

science approach, the electron back transfer to the substrate, turns out to be a benefit: It was shown previously that excess electrons in ultrathin D_2O layers on metal surfaces subsequently change their degree of confinement after charge injection. [Gah02, Bov03] The coupling strength of the interfacial electron to metal states is reduced upon solvation, and the electron's decay probability decreases. Accordingly, the simultaneity of solvation and back transfer results in a *competition* of these two processes. The study of solvated electron dynamics at molecule-metal *interfaces* therefore enables the investigation of heterogeneous charge transfer as a function of coupling strength directly in the time domain. In other words, interfacial solvated electrons are – due to their transient degree of coupling to the metal substrate – model systems for heterogeneous charge transfer.

First investigations of the electron transfer and solvation dynamics at amorphous and crystalline ice layers on Cu(111) and Ru(001) were done in the context of Cornelius Gahl's dissertation [Gah04] and my diploma thesis [Stä04]. The present thesis continues the previous work on electron transfer and solvation processes and extends the study by a systematic investigation of various types of interfaces and in-depth analysis of the data. The competition of electron solvation in a molecular adlayer and ET back to the metal substrate is investigated by quantitative comparison of the electron dynamics for different substrates, different adsorbate structures, and different solvents.

Time-resolved two-photon photoelectron (2PPE) spectroscopy is a powerful tool to investigate electron dynamics at interfaces, as it probes the evolution of electron binding energies in excited states in real time. In this work, it is shown that the fundamental processes of charge injection, solvation, and back transfer are qualitatively similar for all investigated samples. The left panel of Fig. 1.01 illustrates the experiment schematically; the right panel shows the energy
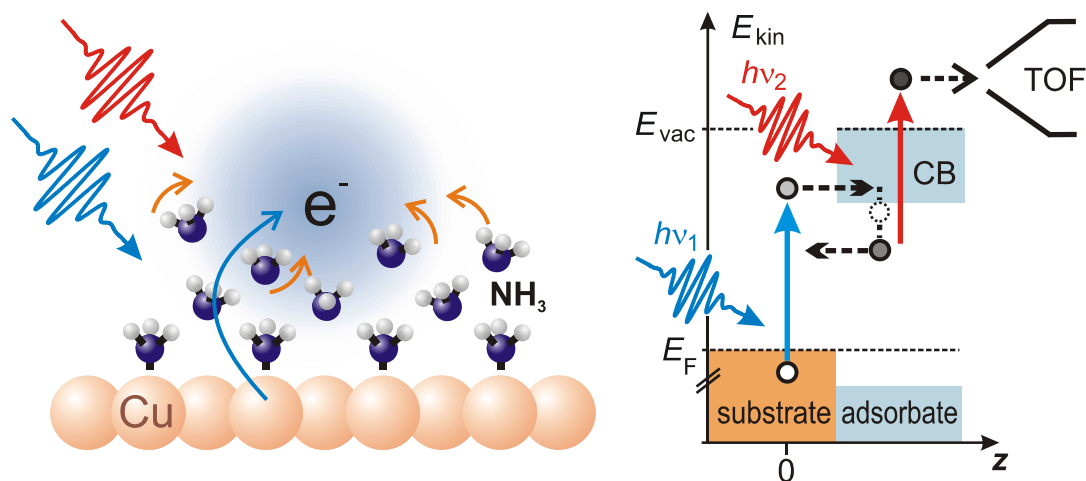

Fig. 1.01: *2PPE Experiment of Electron Transfer and Solvation Phenomena.* Left: Electrons are injected from the substrate into the ammonia adlayer and localize at favorable sites. The surrounding molecules reorient and stabilize the excess charge. Right: Energy scheme of the process. Metal electrons are excited by ultraviolet light ($h\nu_1$) and injected via the conduction band (CB). Subsequently, they gain binding energy through the stabilization of the solvent molecules. Concurrently, the electrons decay back to the substrate. The dynamic evolution of electron energy and population is probed by a second, visible laser pulse ($h\nu_2$). The kinetic energy of the photoelectrons is detected by a time of flight (TOF) spectrometer.

diagram of the course of events. By excitation of metal electrons from below the Fermi Level E_F with a femtosecond ultraviolet (UV) laser pulse, electrons are injected into the adlayer via the conduction band (CB). After localization at favorable sites near the CB bottom, the solvent molecules reorient to accommodate the excess charge, resulting in an energetic stabilization and screening of the electron. At the same time, electrons decay back to the metal substrate, which offers a continuum of unoccupied states. The resulting dynamic evolution of electron binding energy and population is probed by a second, time-delayed visible (VIS) laser pulse that excites the solvated electrons above the vacuum level E_{vac} of the system. Their kinetic energy is analyzed by a time of flight (TOF) spectrometer.

However, although the fundamental processes of electron transfer and solvation are similar for all investigated systems, their specific characteristics change depending on the solvent (NH_3 or D_2O), substrate (Cu(111) or Ru(001)), adsorbate structure (amorphous or crystalline), adsorption type (clusters or layers), and layer thickness. Systematic investigation of these interfaces and development of several new model calculations and analysis procedures allow for the observation of transitions between different regimes of charge transfer. For example, right after photoinjection into amorphous adlayers, excess electrons exhibit still considerable wave function overlap with the metal substrate. Thus, the transfer rate is determined by the substrate's surface electronic band structure. However, with ongoing solvation, a barrier evolves at the interface, which increasingly screens the excess electrons from the metal: Under these conditions tunneling becomes the rate-limiting step. For NH_3/Cu(111), even the transition to the weak coupling limit is observed: The rate of HET is determined by thermally activated nuclear motion of the solvent molecules. Furthermore, it is shown that the degree of coupling of solvated electrons to the metal can be tuned by varying the ammonia layer thickness.

Outline of the Thesis: The present work focuses on the electron transfer and solvation dynamics at the D_2O/Cu(111), D_2O/Ru(001), and NH_3/Cu(111) interfaces. The succeeding chapter outlines the physics background of electron transfer and solvation phenomena and introduces the properties of the adsorbates and substrates investigated. First, the different theories of charge transfer, tunneling picture, Marcus Theory, and Truhlar Concept are discussed. An overview of electron solvation in ice and ammonia is given in section 2.2. The previous work on D_2O-metal interfaces [Gah04, Stä04] is summarized in section 2.3, including a discussion of the remaining open questions. Subsequently, the third chapter introduces the employed experimental technique, time-resolved 2PPE spectroscopy, and describes the experimental setup. After discussing sample preparation and characterization (section 3.3) an overview of the 2PPE data analysis is given.

The results on the electron solvation and transfer dynamics are presented in two separate chapters for the ice- and ammonia-metal interfaces (chapter 4 and 5, respectively). First, the influence of the substrate and the adsorbate structure on the dynamics at *amorphous* ice-metal interfaces are analyzed, where the hydrated electrons are considerably coupled to the underlying substrate (section 4.1). Then, the change of electron dynamics upon crystallization is discussed. The very efficiently trapped electrons in *crystalline* ice adlayers allow for investigation of their solvation dynamics over 17 orders of magnitude in time (from femtoseconds to minutes, section

4.2). A comparable change of electron dynamics is observed for the $NH_3/Cu(111)$ interface upon crystallization of the adlayer. However, even in amorphous ammonia (section 5.1), the electron transfer and solvation dynamics are considerably slowed down compared with the dynamics at amorphous ice-metal interfaces. In addition, significant coverage and temperature dependences of electron transfer and solvation are observed. The similarities and differences between amorphous NH_3 and D_2O are discussed in paragraph 5.1.4. Subsequently, it is shown that the efficient trapping ("freezing") of excited ("hot") electrons, which enables observation of electron dynamics up to minutes, is also observed in crystalline ammonia adlayers. In chapter 6, all results are summarized to draw a consistent picture for electron transfer and solvation dynamics at polar molecule-metal interfaces.