

Chapter 1

Introduction

The dynamics of electrons at surfaces and interfaces of solids are of considerable importance for many fields of study. Surfaces and interfaces are distinguished from bulk materials by a sudden change of some physical properties. For electrons, the determining factor is the change in the Coulomb potential. In most cases the change is not abrupt but leads to the formation of bound electronic states in the vicinity of the interface. In case where these states are unoccupied under equilibrium conditions one can initiate dynamics by adding an electron to such a state. Under certain conditions this will result in an electron transfer (ET) process from the normally unoccupied state localized at the surface to delocalized states in the bulk of the solid.

The simplest, but in no way simple, interface is the surface of a solid in vacuum. Even at such a surface bound electronic states exist under certain conditions without any rearrangement of the surface atoms. The self-induced Coulomb image potential results in image potential states at some metal surfaces located on the vacuum side of the surface. At many surfaces of binary compound solids, the abrupt loss of the nearest neighbor atom at the surface results in reorganization of the surface atoms extending up to several atomic distances into the solid (relaxation) and in the formation of new bonds between the surface atoms (reconstruction). Both processes in turn can lead to the formation of bound electronic states. The former are located on the solid side of the interface, the latter right at the interface. The obvious way of generating new electronic states at a surface is via anchoring molecules at the surface. This system is in some way a hybrid between an interface and a surface as the molecular side has no bulk properties but is clearly distinguishable from the solid, in contrast to surface states formed on reconstructed surfaces. The present work is dealing with the

dynamics of electrons at exactly such interfaces formed when organic molecules are chemically bound to the surface of a solid at sub-monolayer coverage. More precisely, the dynamics of the electron transfer process from the molecules to the solid is investigated upon photoexcitation of the molecules.

A more common approach than heterogeneous electron transfer, i.e. transfer between a single molecule and a solid, is its homogeneous counterpart, i.e. intermolecular ET. This is because light-induced homogeneous ET is the first step in several important processes in nature and technology, like photosynthesis and AgBr photography. Marcus established the theoretical description of homogeneous ET in 1956 [4] and was awarded the Nobel prize in 1992 *for his contributions to the theory of electron transfer reactions in chemical systems*. A brief overview of Marcus' ET theory is given in Sec. 2.1. In the homogeneous case ET is discussed in terms of a reactant and a product state, each with a distinct nuclear configuration. A key-parameter for the dynamics of the ET process is the change of the nuclear configuration of the reactant state into the nuclear configuration of the product state. In terms of transition state theory heterogeneous ET is distinguished by replacing the single molecular acceptor state against many electronic acceptor states in the solid.

The technical importance of heterogeneous ET was recently emphasized again when Grätzel published a dye-sensitized solar cell with an efficiency of 10% that is based on light-driven heterogeneous ET between organic dye-molecules and a semiconductor surface [5]. Another technical application of high importance may be found in the proposed field of molecular electronics.

Single electron devices are a promising possibility in progressing trend towards miniaturization of electronic devices. One way to realize such devices are carbon nano-tubes attached to metal contacts. With this method, single electron devices have been demonstrated recently [6]. Another approach is the use of organic molecules composed of different functional groups to realize the requirements of the specific device [7, 8]. Since modern synthetic techniques in chemistry enable us to manufacture very specific molecules, the main challenge seems to be how to assemble these molecules and how to connect the molecular device to the outside world electrically.

Although it is in principle possible to manipulate single molecules, i.e. with the tip of an STM, a more promising and by far more efficient way to solve this problem is the self-assembly of monolayers (SAMs). One mayor prerequisite for the formation of an SAM is the existence of an anchor group at the molecule that will form a (covalent) bond to the substrate. A prominent example is the SAM formed on a noble metal via a thiolate anchor group. Here, the alignment and

the electric contact are realized with one and the same bond. On such systems a lot of research has been done in recent years [9, 10, 11]. Whereas noble metals may be an appropriate choice for electric contacts in electronic devices, the combination of and hence the contact between molecular single electron devices with conventional semiconductor devices can be of great advantage.

The electronic structure at the interface, i.e. the alignment of the molecular levels with respect to the Fermi level of the substrate, is of great importance for the properties of the contact. This determines how strong a molecular level mixes with substrate states and subsequently the dynamics of charge transfer through the interface. Time-resolved two-photon photoemission (TR-2PPE) is capable of addressing both, the position of occupied as well as unoccupied states and the temporal evolution of transiently populated states, where the time resolution is sufficient to resolve even charge redistribution processes on a time scale of a few femtoseconds. Under certain circumstances even the orientation of the addressed transition dipole moments and consequently the orientation of the molecule with respect to the substrate can be deduced.

The semiconductor TiO_2 appears at first sight not as the best choice for an electric contact because of its large bandgap. But for investigating the molecular part of the assembly and the injection process it provides some clear advantages. Firstly, the large bandgap minimizes substrate induced background signal when optical techniques in the visible spectral range are used, i.e. molecular transitions can be addressed separately. Secondly, the bonds in the lattice are strong enough so that anchor groups like acids can form bonds to Ti atoms on the surface without disentangling the Ti atom from the lattice. Thirdly, the special morphology of the stoichiometric surface, i.e. the prominent oxygen rows, forces under certain circumstances the molecules to align along these rows and not only with respect to the surface plane.

In this work the injection dynamics of electrons photoexcited from the ground state of an organic molecule into empty electronic states of the substrate and the subsequent escape dynamics from the near surface region of the substrate into the bulk are investigated via TR-2PPE. The remaining chapters are organized as follows. Chapter 2 gives an overview of the two main processes governing electron dynamics at interfaces, i. e. the electron transfer from the adsorbate to the substrate and the subsequent dynamics of hot electrons in metals and semiconductors with a focus on TR-2PPE. In addition, the alignment of molecular levels with respect to the band structure of the substrate is discussed. Furthermore, an introduction to TR-2PPE and ultrafast laser spectroscopy is given. The chapter ends with a description of the different molecular adsorbates and of the metal

and semiconductor substrates investigated in this work.

In chapter 3 the experimental prerequisites for the measurements carried out in this work are discussed. The ultrafast electron transfer times reported in this work required the development of a new laser setup consisting of two independently tunable non-collinear parametric amplifiers (NOPAs) that were driven at 150 kHz. The setup demanded that the same pump pulse was used for both NOPAs. Crosscorrelations of sub-30 fs were measured via TR-2PPE between a visible and an UV pulse. The preparation of the samples required a special procedure where different ultra-high vacuum chambers were used to minimize the contamination of the samples. The vacuum chambers and a newly designed time of flight spectrometer allowing for angle-resolved measurements are described in this chapter as well as the preparation procedure.

The results of the measurements are presented in chapter 4. First, the characterization of the different samples by means of stationary one- and two-photon photoelectron spectroscopy as well as other standard surface science techniques is discussed. In the following the TR-2PPE signals of the bare surface of TiO_2 are reported and the unusual fast disappearance of the 2PPE signal is discussed. For the first time the decay of a surface state on the rutile $\text{TiO}_2(110)$ surface was time resolved. In addition the electron dynamics at the surface of different noble metal surfaces are discussed. These results demonstrate the outstanding performance of the laser system. The injection times for perylene molecules attached via long rigid spacer/anchor groups to the (110) surface of rutile TiO_2 were measured and are compared here with earlier measurements performed in our group of the same molecules bound to colloidal TiO_2 films. The advantage of measuring injection times for such long molecules on single crystal surfaces is discussed. The goal to measure the fast injection times of molecules with short anchor groups gave rise to further investigations of the escape dynamics of electrons from the near surface region of TiO_2 . Based on measurements of a catechol: TiO_2 system a simple fit model is developed to extract the injection times from the TR-2PPE measurements of the perylene molecules with short anchor groups. The shape of the 2PPE energy spectra turned out to be dominated by the Franck-Condon progressions of the different processes participating in TR-2PPE.

Chapter 5 summarizes the results of this work.