Chapter 5

Summary

The dynamics of heterogeneous electron transfer from photoexcited organic adsorbate molecules and single crystal surfaces were investigated by means of time-resolved two-photon photoemission spectroscopy. TR-2PPE enabled time resolved measurements on sub-monolayer coverages of molecules adsorbed on single crystal surfaces.

To achieve the necessary time resolution a novel laser setup was developed where two independently tunable NOPAs were operated at 150 kHz. The insufficient output-power of the commercial Ti:Sapphire laser system was compensated by using the same pump pulse for both NOPAs. The output of both NOPAs was frequency doubled to obtain the wavelengths desired for the TR-2PPE experiments. Crosscorrelation traces with 35 fs width were achieved in TR-2PPE experiments. The performance of the new laser setup was tested by time resolving the decay of transiently populated image potential states on the Cu(111) and Ag(111) surface. A novel TOF was constructed enabling angular resolved measurements. In connection with the new TOF apparatus the electronic devices and the software for data acquisition were updated.

The sample preparation required utilization of a special UHV chamber. This chamber allowed for switching between UHV conditions and inert gas atmosphere. Under inert gas conditions the samples were prepared by immersing into a solution that contained the adsorbate molecules. Together with a mobile UHV chamber for transportation this procedure minimized the contamination of the sample during the preparation procedure.

Cleanliness of the TiO_2 substrate was checked by means of UPS, XPS and LEED measurements. The contamination was monitored by measuring the C1s emission in XPS and the emission from impurity induced occupied band gap states in

UPS. The C1s emission was completely removed by cycles of Ar^+ ion bombardment and subsequent annealing. The C1s emission originating from the adsorbed molecules exhibited a pronounced chemical shift and electron emission from the HOMO and HOMO-1 state of the adsorbate molecules was clearly resolved in UPS.

The alignment of the HOMO and the first excited state of the adsorbed molecules with respect to the energy bands of TiO_2 and the work function of the samples was measured via UPS and 2PPE. The HOMO level of the perylene chromophores adsorbed on rutileTiO_2(110) was found to be located in the band gap of TiO_2 and the first excited state was located around 0.5 eV above the conduction band edge. The width of the HOMO and excited state spectra was found to be dominated by the Franck-Condon progression of the photoemission and electron injection process, respectively. From the shift of the work function of around 0.5 eV to lower energies upon adsorption of the molecules it was concluded that a dipole layer was formed presumably because of the interaction between the acid anchor group of the molecule and the surface Ti atoms.

The orientation of the adsorbed molecules with respect to the substrate surface was obtained from angular and polarization dependent 2PPE measurements. The carboxylic acid group was found to adsorb in an upright binding geometry whereas the phosphonic acid group resulted in a tilt angle of around 70° for a chromophore equipped with a long rigid spacer group.

Time resolved 2PPE measurements were carried out on two perylene chromophores equipped with long rigid spacer groups giving rise to slow electron injection dynamics. Both molecules exhibited a prominent fast time constant for electron injection when adsorbed in a sponge like colloidal film and measured via transient absorption spectroscopy. One of the molecules was investigated in an earlier measurement the other in a measurement carried out for this work. The short time constant was not present in the TR-2PPE measurements and was ascribed to the narrow pores in the colloidal film where ET occurs via a shortcut between the chromophore and an adjacent wall.

TR-2PPE measurements on perylene chromophores with short anchor/spacer groups adsorbed on TiO_2(110) exhibited additional slowly decaying components in the signal. These components were not observed in earlier transient absorption measurements where the rise of the perylene cation was measured. To elucidate the origin of these components the adsorbate molecule and the substrate were systematically varied.

The perylene chromophore was adsorbed onto the surface of Ag(110) to test wether the slowly decaying signal originated from the molecule or the substrate.

The excited state of perylene was identified with a lifetime of 15 fs. No long-lived component was observed with this sample. Additionally, a transiently populated intermediate state was observed which was assigned tentatively to an adsorbate induced image potential state delocalized in the adsorbate layer exhibiting a lifetime of 23 fs.

The influence of the TiO_2 substrate on the TR-2PPE signal was investigated further by adsorption of catechol onto the (110) surface. Catechol forms a charge transfer complex on the surface of TiO_2. Photoexcitation of this charge transfer complex results in a direct optical electron transfer from the catechol to the surface of TiO_2. The TR-2PPE signal is not influenced by a finite injection time in this case. The 2PPE spectrum was controlled by the Franck-Condon progression of the electron transfer process. The temporal evolution of the spectrum did not show any relaxation processes. This unusual behavior was attributed to the high effective mass of the conduction bands in TiO_2. The decay of the 2PPE signal was ascribed to the escape of electrons from the detection depth of the photoemission process. 2PPE time traces were fitted with a simple model accounting for the escape dynamics.

Under the assumption that the escape dynamics are a sequel to electron injection from perylene chromophores into TiO_2 with finite injection time the transient 2PPE signals of the perylene chromophore attached to TiO_2 via short anchor/spacer groups were fitted using an extension of the model used for the catechol system. Thereby it was possible to extract the injection times for these perylene derivatives from TR-2PPE measurements. The injection times were in good agreement with those obtained from transient absorption measurements.

This thesis shows that TR-2PPE is a suitable tool to investigate heterogenous ET from photoexcited chromophores to metal and semiconductor substrates. Firstly, the sensitivity is sufficient to investigate sub-monolayer coverages on single crystal surfaces. This is important when large molecules are to be investigated, in particular where transient absorption spectroscopy yields erroneous injection times. Furthermore, the binding geometry of the molecules with respect to the surface has been investigate here on single crystal surfaces. Secondly, TR-2PPE is capable of resolving electron dynamics in the surface region of the substrate, i.e. not only the injection dynamics can be investigated but also the transport of the electrons away from the surface region into the bulk.

TiO_2 turned out to be a substrate with some specialties. The energy distribution of injected electrons is conserved for a long time in the range of 200 fs due to the flat conduction bands at the conduction band edge. Thus the Franck-Condon progression of the electron injection process has been resolved. This is the first

measurement of the complete Marcus curve for heterogeneous electron transfer in the so called wide band limit. The surface structure of TiO_2(110) gives rise to an alignment of the adsorbed molecules in rows. This property may be utilized to selectively induce electronic as well as steric transitions in adsorbed molecules. Future investigations may address the distance dependence of the ET process by varying the length of the spacer group in the Pe'-rod molecule. Additionally, trough bond vs. trough space ET processes may be investigated by comparing the injection dynamics of a Pe'-rod molecule equipped with a phosphonic acid group with that of a Pe'-rod equipped with a carboxylic acid group, the latter is expected to form a bond that is directed normal to the (110) surface of TiO_2.