Electronic structure and ultrafast charge carrier dynamics at the interfaces between molecular switches and the Au(111) surface investigated with time-resolved photoemission

Elektronische Struktur und ultraschnelle Ladungsträgerdynamik an den Grenzflächen zwischen molekularen Schaltern und der Au(111)-Oberfläche untersucht mit zeitaufgelöster Photoelektronenspektroskopie

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“Why cannot we write the entire 24 volumes of the Encyclopedia Brittanica on the head of a pin?”

R. P. Feynman, *There's Plenty of Room at the Bottom* (1959)
1 Introduction

Although today, more than 50 years after Richard Feynman’s famous speech [1], it is in fact possible to store the content of a classical encyclopedia onto an area comparable to the size of a pin’s surface, his message remains as modern as ever. The size of microelectronics has come to a crucial point since further miniaturization using traditional technology is limited no longer by engineers’ abilities but by the laws of physics.

The limitations to the conventional electronic devices are evident: as the devices become smaller and smaller, more and more building blocks have to fit to less space. This results e.g. in increasing heat development. Also, with decreasing size, quantum effects come into play, for example electron tunneling through oxide layers in field-effect transistors (FETs) [2]. However, the development of faster computers is essential for scientific numerical methods, meteorological calculations, etc.

Nanoscience therefore currently aims at molecular devices, in which single functional molecules are supposed to replace conventional bulk techniques. Although this field of research has been active for decades, working applications are clearly exceptional. Concerning molecular electronics, different molecules have been synthesized which show promising properties. To mention only a few examples, a molecule with the characteristics of a rectifier was made (already in 1974) [3], conjugated polymers show properties of molecular wires [4, 5] and devices were fabricated which act as an optoelectronic gate [6]. Other developments are oriented even more toward technical applications, such as a carbon nanotube FET [7] or even an intramolecular transistor [8]. Another important field is data storage where today’s two-dimensional magnetic discs could in the future be replaced by optically addressable three-dimensional devices where information is stored in single molecule units [9, 10].

The advantages of molecular technology are striking: First of all, their size is significantly smaller than that of today’s devices. Since molecules can be synthesized in an almost arbitrary fashion, the properties of the involved building blocks can in principle be tuned so that the molecules could have a vast amount of different properties. Also, the speed of a molecular circuitry would be on timescales of the involved intramolecular processes.

But not only electronic devices have been investigated. A very intriguing field of research is the one of molecular machines [11, 12]. For example, “ATP synthase”, an enzyme, shows properties of a molecular rotational motor [11]. Probably one of the most spectacular molecular machines is a car consisting of a flat chassis which can be moved back and forth on four fullerene wheels [13].

A problem in this field is of course the fabrication of such microscopic structures. Single-molecule devices are obviously hard to assemble in a “top-down” fashion. This means that from the macroscopic level, the components are assembled, e.g. using lithography.
In nature, complex functional molecular units, such as the DNA for instance, are created in a self-assembling "bottom-up" way \cite{14,15}. Efforts are being made to imitate this concept, for example by bringing passivated molecular building blocks to a surface where they are activated and combine to a larger structure \cite{16}.

The above described progress over the past decades appears as a tremendous achievement (which it certainly is). But the construction of applicable devices is not the only task of the field since it is equally important to investigate and understand the mechanisms behind the functionalities. This is of course first done for smaller systems which may have less spectacular properties than the 'molecular car' but which may yield a fundamental understanding of their more basic function. An important category of such molecules are switches.

Molecular switches are required to have two or more at least meta-stable states between which can be switched by an external stimulus in a reversible fashion. The different states of course have different properties, such as the geometry, the absorption or fluorescence spectrum, magnetic properties, etc. As free molecules in solution, a number of switches are known and well studied: azobenzenes, spiropyans, fulgimides and diarylethenes are prominent examples \cite{17}.

Particular interest is placed on the switching mechanism of these molecules, i.e. the elementary processes involved in their functionality. An understanding of these fundamental processes might make it possible to deliberately design the functionality of molecular systems. This would be an important step toward a systematical development of molecular devices or their building blocks. The electronic structure plays a key role in this effort since, especially in the case of photo-switches like azobenzene, the change between the switching states is initiated by electronic excitations.

In future applications, those molecules would most likely be bound to some sort of rigid carrier structure, e.g. a matrix or a surface in order to be able to keep a specific molecule at a specific place, which is of course necessary for instance in an information storage device. Also, the need to attach a functionalized unit to an electrode may bring it into contact with a surface in the end.

In contact with each other, substrate and molecule will interact and form a new physical system, where the properties of the molecule are not necessarily conserved, particularly the switching behavior. For example, the surface poses a geometrical barrier which may result in steric hindrance of an isomerization, but the influence on the electronic structure is equally important. New excitation or decay channels might be accessible which involve charge transfer between substrate and adsorbate. Azobenzene and spiropyran\footnote{1,3,3-trimethyldindolo-6'-nitrobenzopyrrospiran} for instance, can be isomerized by light in solution \cite{18,19} but lose their photochromic properties on the Au(111) surface \cite{20,21}.
1 INTRODUCTION

Besides investigating the reason for this quenching, efforts are made to restore the functionality by geometrically or electronically decoupling the molecule from the surface. This can be done at the molecule, i.e. by attaching spacer groups as for the azobenzene derivative TBA\(^2\)\[22, 20\]. A different approach is the use of an isolating layer (e.g. NaCl) to decouple the adsorbate from the surface \[23\].

The studies of the electronic structure at the substrate-molecule interface are of great importance to the understanding of the switching mechanism at the surface (or its quenching). Not only can molecular orbitals or electronic states of the substrate (e.g. a surface state) be shifted in energy. An alteration of the potential energy surface (PES) along the reaction coordinate(s) or a change in the spatial charge distribution can significantly affect the functionality of the molecule.

In this work, the electronic structure of two molecular switches adsorbed at the Au(111) surface is investigated: TBA has been proved to preserve its photoisomerizability \[22, 20\] while spiropyran loses it. A thermally induced, irreversible ring-opening reaction toward the merocyanine form occurs instead, which is not observed in the free molecule \[21\]. While in the free molecule, the closed spiropyran form is the more stable isomer, the open merocyanine isomer is energetically favored. This phenomenon is referred to as 'stability inversion'.

Like its parent molecule azobenzene, TBA isomerizes from its \textit{trans} to the \textit{cis} form. The spiropyran molecule on the other hand isomerizes into the merocyanine form in a ring-opening reaction while the back-reaction which is observed in the free molecule closes the ring again. For both cases and in the free molecule, the photoisomerization is triggered by an intra-molecular electronic excitation upon which the molecules relax along the potential energy surface of the respective excited state where they can overcome the energy barrier separating the two isomers in the ground state.

TBA is the only molecule so far to photoisomerize reversibly in direct contact with a surface which constitutes a great interest in it and the driving mechanism of this process. It is believed that the intra-molecular electronic photoexcitation mechanism in the free molecule (HOMO\(^3\)-LUMO\(^4\) transition) is replaced by a substrate-mediated process, in which a positive ion resonance is created at the surface \[24\]. However, the lifetime of the adsorbed molecule’s LUMO exhibits a lifetime on the picosecond scale which is quite unusual and would point toward an excitation mechanism via this orbital. Since the respective experiment on the dynamics of this state was only of preliminary character, further measurements on TBA will be the first part of this thesis. Furthermore, the binding energy of TBA on Au(111) is determined by temperature programmed desorption (TPD) in the framework of a joint publication on the role of TBA’s spacer groups \[25\].

\(^2\)3,3’,5,5’-tetra-tert-butyl-azobenzene
\(^3\)Highest occupied molecular orbital
\(^4\)Lowest unoccupied molecular orbital
Spiropyran is the second molecule investigated in this work. Although it doesn’t photoisomerize on Au(111), this is an interesting system because of the observed stability inversion and considering that future experiments considering the electronic structure on modified spiropyran or on a different surface might restore its functionality which would perhaps require a comparison to the parent molecule or the molecule on an inert surface as a reference, respectively. Using scanning tunneling microscopy (STM), a ring-opening reaction on the Au(111) surface can be triggered by resonant electron tunneling into the LUMO of spiropyran creating a negative ion resonance. Electron transfer from the substrate into this molecular orbital via a light-induced excitation did however not succeed [21]. The latter might be due to reduced electronic coupling of the LUMO to the substrate since it is lying in the projected band gap of Au(111). For switching via resonant electron attachment to the LUMO in the STM junction on the other hand, this low electronic coupling does not play a role and additionally may prevent a fast decay of the attached electron into the substrate.

The electronic structure is investigated by time-resolved two-photon photoemission (2PPE) which gives access to occupied and unoccupied electronic states. In general, the electronic structure of a molecule’s isomers will be different. 2PPE is able to measure the ultrafast electron dynamics in a pump-probe scheme which is relevant for the understanding of elementary processes in the investigated system, such as the underlying mechanism of a photoswitching process. The dynamics of an electronic state can also give information on the potential energy landscape of a state that exhibits a steep change in energy which the system follows on an ultrafast timescale after the electronic excitation. Another advantage of 2PPE in comparison to e.g. STM or HREELS5 with respect to a photoisomerizable molecular switch, is that the method relies on exposure to light: For example, illumination (for switching) and measurement are performed at exactly the same spot. Also, for a photoswitching molecule, the probed situation in the sample (after electronic excitation by the pump photon) resembles the situation directly after the switching process is triggered.

In the first part of this thesis, the background of the employed experimental techniques (TPD and 2PPE) will be explained as well as a brief summary on image potential states, the electronic structure of the used substrate, Au(111), and background will be given on the investigated adsorbate molecules. In chapter 3 the femtosecond laser system and the ultra high vacuum chamber in the used setup will be described in detail as well as the adsorption properties of both molecules as determined by TPD.

Results of the experiments on both TBA and spiropyran will then be presented in chapters 4 and 5, respectively. A discussion of these results is given separately for both switches at the end of the respective chapter and a final summary is given in chapter 6.
2 PHYSICAL BACKGROUND

2 Physical background

In this chapter, background information is given on the physics behind the techniques used within this thesis as well as the substrate and the adsorbate molecules on which experiments were performed. In section 2.1 temperature programmed desorption and the so-called “complete analysis” is explained which will be used to determine the binding energy of TBA. The foundations for photoemission are elucidated in 2.2 where also angle and time resolved variants are discussed. Since they will play an important role in the discussion of the results later on, an overview of image potential states and the electronic properties of gold are given in sect. 2.3 and 2.4 respectively. Finally, in sect. 2.5 background on the two molecular switches TBA and spiropyran is given, such as their properties as a free molecule (in solution) and previous measurements on the Au(111) surface, e.g. with STM.

2.1 Temperature programmed desorption (TPD)

When working with adsorbate-covered surfaces, it is necessary to characterize the adsorbate in terms of thickness, binding energy, geometrical structure, etc. One way to obtain information is temperature programmed desorption\footnote{also referred to as ‘thermal desorption spectroscopy’ (TDS)}. It is a standard characterization method in surface science and requires only common equipment such as a temperature controller for sample heating and a quadrupole mass spectrometer (QMS) for detecting the desorbing species.

In TPD, the sample is heated with a constant heating rate (usually $\beta = 1 \text{Ks}^{-1}$). During this heating, the desorbing molecules are monitored mass-specifically by a QMS which gives a signal that is proportional to the partial pressure of the respective mass. The mass (or masses) which is (are) representing the adsorbate is (are) chosen from a mass spectrum, taken when the residual gas contains a sufficient amount of the target molecules (e.g. during dosing). In this case, the mass spectrum of the residual gas is called the molecule-specific ‘fragmentation pattern’. Usually, masses above $\sim 50$ amu are preferable as 'target molecule monitors' because in this region the usual contaminations (like water, nitrogen, oxygen, ...) have fewer contributions.

In appendix B the fragmentation patterns for the adsorbate molecules used within this work are shown.

The partial pressure measured by the QMS is proportional to the number of particles desorbing per unit time, i.e. the desorption rate. Denoting $\theta$ the adsorbate coverage, the desorption rate is its temporal derivative $\frac{d\theta}{dt}$.

Especially in order to obtain a defined coverage, e.g. one monolayer (ML), it does usually
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not suffice to control the number of adsorbed particles by the dosing time, for example because the dosing time is not such a well controllable quantity, which has a number of experimental reasons, such as the fact, that at least in our setup, the linear stage which carries the effusion cell, is moved by hand and the time this takes is not always equal. Also, the fluence in the molecular beam ejected from the dosing cell is sensitive to quantities like the effusion cell temperature or the pressure which experimentally can not be reproduced perfectly.

Instead, a defined coverage is sometimes achieved by annealing the sample to a particular temperature, that is when the monolayer has a significantly higher binding energy than the multilayer, as it is the case for TBA (see sect. 3.2.3).

TPD is also employed to measure the binding energy of the adsorbate molecule. For this purpose, several TPD are recorded for different initial coverages. In order to evaluate these data, a number of methods has been developed in the past [26]. In this work, the so-called "complete analysis" introduced by King [27, 28] is employed. It is explained in the following and schematically depicted in fig. 1.

The desorption rate \( r_{\text{des}} \) is described by a kinetic equation as proportional to an integer power of the coverage \( \theta \) [29].

\[
r_{\text{des}} = -\frac{d\theta}{dt} = k_0 \theta^n
\]

Therein, \( n \) is the desorption order and \( k_0 \) is the rate constant. Most desorption processes are described by orders zero, one and two. Zero-order desorption is indicated by a common rising edge of the desorption peak with increasing coverage followed by a sudden decrease in the signal. The signal maximum shifts to higher temperatures [30].

In eq. (1), the rate constant is assumed to be an Arrhenius term, which means that the rate constant depends exponentially on the binding energy \( E_B \) (divided by the temperature). The temporal derivative can be expressed in terms of the heating rate \( \beta \).

\[
k_0 = \nu \cdot \exp \left( -\frac{E_B(\theta)}{k_B T} \right)
\]

(2)

\[
\frac{d\theta}{dt} = \frac{d\theta}{dT} \frac{dT}{dt} = \beta \frac{d\theta}{dT}
\]

(3)

\( \nu \) denotes the attempt frequency\(^7\) \( E_B \) is the coverage dependent binding energy. Eq. (1) therefore becomes

\[
-\frac{d\theta}{dT} = \frac{\nu}{\beta} \theta^n \exp \left( -\frac{E_B(\theta)}{k_B T} \right).
\]

(4)

This equation is referred to as Polanyi-Wigner equation [30, 27]. \( k_B \) is the Boltzmann

\(^7\)The attempt frequency or 'pre-exponential factor' \( \nu \) is sometimes set to \( 10^{13} \text{ s}^{-1} \) for an approximation because this is the order of magnitude of lattice vibrations in the solid [29].
constant.

The evaluation method proposed by King is based only on the above equation, where it is usually written in its logarithmic form

\[ \ln I_{QMS} = \ln \frac{\nu}{\beta} + n \ln \theta - \frac{E_B(\theta)}{k_B T}. \]  (5)

Here, \( I_{QMS} \) is the QMS intensity normalized by an arbitrary unit. Assuming the usual value (see above) for the preexponential factor \( \nu \) and knowing the heating rate and coverage, the reaction order can also be determined from the axis intersection and most importantly (in this work), the desorption or binding energy of the adsorbate can be determined from the slope of this so-called Arrhenius plot. For convenience, \( \ln I_{QMS} \) is plotted versus the inverse temperature.

Since in general, the binding energy \( E_B \) may depend on the coverage, not all data points from all measured TPD spectra can be used in one single Arrhenius plot. In the “complete analysis”, a certain coverage \( \theta_0 \) is defined and from the integrated TPD curves, one can assign every spectrum (that has an initial coverage larger than \( \theta_0 \)) the temperature, at which this coverage is reached by desorption. This way, a single temperature is assigned to each TPD. From the TPD itself, the desorption rate (represented by \( I_{QMS} \)) at this temperature is taken and forms one data point \((T, I_{QMS})\). In this fashion, every TPD gives another data point, as long as the initial coverage is large enough (see. fig. 1). It is obvious from here that the accuracy of the evaluation depends critically on the number of recorded TPD curves.

The data points collected in the above described fashion can now be merged in an Arrhenius plot which yields the binding energy for the chosen coverage, \( E_B(\theta_0) \). It is of course useful to repeat this procedure for a number of \( \theta_0 \) so that (i) a better statistic is obtained for the final value and (ii) the coverage dependence of the binding energy can be observed at least qualitatively.

### 2.2 Photoelectron spectroscopy

The underlying process of all photoemission experiments is the photoelectric effect discovered by Hertz and Hallwachs in 1887 [32, 33]. Upon exposure to light, certain materials eject electrons whose kinetic energy was investigated in dependence on intensity and wavelength of the incident light. Most of all, it was surprising that the kinetic energy of those ‘photoelectrons’ was independent of the intensity of the light but directly proportional to its frequency. This phenomenon could not be explained in terms of classical physics. Einstein solved this mystery in 1905 [34] proposing a quantized nature of light in which every light particle (photon) carried an energy \( E_{\text{photon}} = h \nu \), where \( h \) is Planck’s constant and \( \nu \) is the light’s frequency. This energy quantum is absorbed by
2.2 Photoelectron spectroscopy

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Figure 1: Explanation of King’s method [31]. The TPD in a) are recorded for different initial coverages $\theta$. The shaded area is the chosen coverage $\theta_0$ which is analyzed here. b) shows the integrated TPD curves yielding the temperature-dependent coverage during the respective TPD. $\theta_0$ is marked as a dashed line. From the intersection of this line with the integrated TPD, the temperature is determined and the QMS signal at that temperature is used in the Arrhenius plot shown in c).

an electron in a photoemission process. In 1921 he was awarded the Nobel prize for his theory.

In this section, first the more common photoemission using ‘only’ one photon as well its extension into reciprocal space (angle-resolved photoemission) are introduced. Subsequently, two-photon photoemission and the respective pump-probe scheme are discussed in detail, since these techniques were used in this thesis.

2.2.1 One-photon photoemission

The phenomenon of photoemission has been exploited for decades to gain insight on the electronic structure of matter. Depending on the incident photon energy it is referred to as ultraviolet photoelectron spectroscopy (UPS) used to investigate valence electrons or as X-ray photoelectron spectroscopy (XPS) which probes the localized core level electrons. The ejected electrons are analyzed typically by a hemispherical or a time-of-flight analyzer which eventually deliver the relative number of electrons at a certain
kinetic energy composing the photoelectron spectrum \([35, 36, 29, 37]\).

An electronic state in the sample located at a binding energy \(E_B\) leads to a feature in the spectrum located at \(E_{\text{kin}}\). Knowing the photon energy \(h\nu\) and the sample’s work function \(\Phi\), one can deduce electronic states from the photoelectron spectrum by applying the conservation of energy:

\[
E_{\text{kin}} = E_B + h\nu - \Phi
\]  

(6)

In order to obtain precise information about the energetic structure of the sample, it is necessary to use monochromatic light in any photoemission experiment because the spectral width of the incident photons poses a limit to the resolution of the spectra. Lasers and synchrotrons are commonly used to conduct photoemission experiments.

Additionally, techniques have developed in which the electrons are measured with respect to their emission angle (angle-resolved photoelectron spectroscopy, ARPES), their spin polarization or with respect to the photons’ polarization.

One-photon photoemission is only capable of probing occupied states which is a major disadvantage when investigating the switching of molecules if unoccupied states like an adsorbate’s LUMO\(^8\) may participate in the processes of interest. A way to investigate unoccupied states is inverse photoemission (IPES), where monochromatic electrons are directed at the surface to resonantly populate an unoccupied state of the sample. From there, they decay and emit photons in the process. These photons can be detected yielding a photon spectrum from which information on the unoccupied states can be obtained. However, the energetic resolution and the count rate are not as good as in two-photon photoemission which will be discussed below. Another disadvantage of IPES is the exclusivity for unoccupied states and the inability to perform time-resolved measurements in order to determine the lifetime of electronically excited states \([38]\).

Figure 2 shows a schematic photoelectron spectrum and its origin in the electronic structure of the solid sample (in this case a metal). The spectrum is a direct representation of the density of states (DOS) in the solid. This is shown exemplary by an arbitrary localized initial state in figure 2. Having absorbed the photon energy, electrons from this state result in a peak in the photoelectron spectrum. The spectrum has a background that is highest at the secondary edge and then decreases toward higher energies: these ‘secondary electrons’ are the result of inelastic scattering events. A photoelectron must make its way through several layers of the solid to get to the surface. On the way, it is subject to a number of collisions, among them collisions with other electrons. The excited electron can now transfer energy to some of these electrons which are then also ejected forming the secondary electron background.

\(^8\)Lowest unoccupied molecular orbital
2.2 Photoelectron spectroscopy

The secondary edge is the result of the fact that electrons have to overcome the vacuum level in order to be ejected and is formed by the slowest ejected electrons. The Fermi edge in the spectrum is just the representation of the Fermi edge in the solid, that is the level up to which the electronic states are occupied. It is smeared out at $T > 0$ forming the characteristic shape of this high-energy edge.

From fig. 2 it is clear that the width of the photoelectron spectrum added by the work function is equal to the photon energy. Therefore, the work function $\Phi$ is easily accessible,

$$\Phi = h\nu - (E_{FE} - E_{SE}),$$

where $E_{FE}$ and $E_{SE}$ refer to the Fermi edge and the secondary edge, respectively.

2.2.2 Angle-resolved photoelectron spectroscopy (ARPES)

ARPES can be used to investigate the band structure of solids. The electron in its initial bound state in the solid has a momentum $\vec{k}_i$ and a binding energy $E_B$. Plotting the binding energy over a direction in reciprocal space gives the respective band structure\(^9\).

When an electron absorbs a photon of sufficient energy, it is ejected from the solid having a momentum $\vec{k}_f$. Due to symmetry reasons, $k_\parallel$, meaning the component of $\vec{k}_i$ parallel to the substrate’s surface, is conserved: $k_{\parallel,i} = k_{\parallel,f}$. Because of the work function, $k_\perp$ on the other hand changes when passing the surface: $k_{\perp,i} \neq k_{\perp,f}$. Hence, momentum is transferred to the crystal (see fig. 3).

\(^9\)Although $\vec{k}$ actually is the wave vector, it is referred to as momentum due to the relation $\vec{p} = \hbar \vec{k}$. 

---

\[\text{Figure 2: Schematic photoelectron spectrum. The spectrum shows two edges: the secondary edge at the low-energy side is the result of electrons no longer able to overcome the vacuum energy. The Fermi edge on the right represents the maximum kinetic energy obtainable by electrons from the ‘Fermi sea’ meaning occupied states below the Fermi level. The width of the spectrum yields the work function. The spectrum is set upon a background, which are the secondary electrons. The photon energy is indicated by the purple arrows.}\]
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2.2 Photoelectron spectroscopy

Figure 3: Momentum change during electron emission. $k_{\parallel}$ is conserved while $k_{\perp}$ is altered at the surface.

Photoelectron spectra can now be taken with respect to $k_{\parallel}$. This is simply done by rotating sample and/or analyzer or by using a position-sensitive analyzer [40]. The momentum of the photons can be neglected, hence the electronic excitation is 'vertical' (in a band structure diagram), which means the electron's energy is changed, its momentum is not. Therefore, the incidence angle of the light is not important in such an experiment, however this is not the case in experiments which employ the light's polarization.

Since $k_{\parallel}$ is not directly measurable, it has to be calculated from the angle of the ejected electrons with respect to the surface normal, $\vartheta$.

$$k_{\parallel} = \frac{\sqrt{2m_e E_{\text{kin}}}}{\hbar} \sin \vartheta$$

(8)

Here, $m_e$ is the rest mass of the electron, not the effective mass in the solid.

Displaying the peak position $E_{\text{kin}}$ as a function of $k_{\parallel}$ yields the dispersion of the respective state with an energetic offset of $h\nu - \Phi$. From the dispersion curve, the effective mass $m^*$ and the bottom binding energy $E_{B,0}$ can be calculated assuming a quasi-free electron, i.e. a parabolic dispersion. This assumption is not justified in case of localized states.

$$E_B = E_{B,0} + \frac{\hbar^2 k_{\parallel}^2}{2m^*}.$$  

(9)

This way, ARPES directly maps the band structure of a solid.

2.2.3 Two-photon photoemission (2PPE)

While the previous techniques employ only a single photon which ejects electrons directly from their initial state and out of the sample, pump-probe experiments can be performed yielding information on the temporal evolution of the system. Generally, a pump-probe experiment consists of an initial excitation of the investigated system triggered by a
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**Fundamental principle of 2PPE.** First, an electron is excited into an intermediate state from where it is ejected by the probing pulse, which may be delayed in time. Unlike in 1PPE (gray shaded area), unoccupied states between Fermi level and vacuum level can be observed in a photoelectron spectrum.

First stimulus (e.g. a laser beam or an electronic excitation) and followed by a probing process, in which information on the system is gained. Varying the time delay between excitation (pump) and probing, the temporal evolution of the system is obtained.

In 2PPE, the exciting process is a laser beam of a photon energy in the visible or ultraviolet regime while the probing is done by another photon of the same ("one-color 2PPE", 1C-2PPE) or another energy ("two-color 2PPE", 2C-2PPE) \[41, 42, 43, 44, 40, 22\]. Both photon energies need to be smaller than the work function of the sample, because otherwise direct photoemission becomes possible and since 1PPE is much more likely, the 2PPE signal will be very low compared to the direct photoemission signal in the spectrum. In order to obtain temporal information, the pump and probe events must occur at distinct times which makes continuous wave (cw) lasers unsuitable for this technique. On the contrary, the better the temporal resolution is supposed to be, the shorter the laser pulses used have to be. Since electron dynamics at metal surfaces occur in the femtosecond regime, pulses of few femtoseconds are necessary. Furthermore, a pulsed laser provides higher peak intensities which is necessary e.g. for the processes in the utilized non-linear crystals.

Unlike direct photoemission, which only gives access to occupied states, 2PPE makes it possible to probe both occupied and unoccupied states and, by analyzing the photon energy dependence of a state in the spectrum, both cases can be told apart. Generally, photoemission is very surface sensitive, having only a probing depth of only a few nanometers or less, depending on the electron energy. This high surface sensitivity is
the result of the low penetration depth of electrons which seems to be “universal” for metals [45].

Since the sample would charge electrically upon ejection of charge carriers, (i) the sample should not be insulating or only a thin insulating film can be deposited onto a conducting substrate and (ii) the sample must at least be grounded or held at some other constant potential (bias).

The ejected electrons’ kinetic energy is most simply connected to the initial binding energy \( E_B \) in the sample:

\[
E_{\text{kin}} = E_B + h\nu_1 + h\nu_2 - \Phi, \tag{10}
\]

where \( \Phi \) is the work function of the sample which usually lies in the order of magnitude of a few eV. Analogously to eq. (7), the work function can be directly read from the 2PPE spectrum.

\[
\Phi = h\nu_1 + h\nu_2 - (E_{\text{FE}} - E_{\text{SE}}) \tag{11}
\]

A spectral feature can have its origin in initial (occupied), intermediate (unoccupied) or final electronic states (above the vacuum level), respectively. From a single spectrum, this information can not be obtained. However, varying the photon energy in a one-color 2PPE experiment yields the nature of the observed state. This is best explained by fig. 5a where two 1C-2PPE experiments are ‘conducted’ for each case. The photon energy of one pulse in the ‘blue’ case is \( \Delta h\nu = h\nu_2 - h\nu_1 \) higher than in the ‘red’ case. In case (1) of an occupied state, the peak in the spectrum is then shifted by \( 2\Delta h\nu \), whereas in case (2) only one photon is needed to excite electrons from the considered state to above the vacuum level, therefore the peak shift is only \( \Delta h\nu \). Case (3) shows a final state which does not show a shift with varying photon energy. The electron is excited into a final state with the first and the second photon and at some point (depending on the state’s lifetime) will detach from this state above the vacuum level and be detected. For example, such a state can be an unoccupied molecular orbital as for TBA/Ag(111) [46].

The dispersion of bulk bands in solids perpendicular to the surface results in a photon energy dependent peak shift in photoemission which makes the assignment of such features in the spectrum difficult by the above described method. It only holds strictly for e.g. surface states or adsorbate-induced states.

Another ambiguity occurs in 2C-2PPE because of the two possible orders, in which the two excitations can happen (see fig. 5b). A pulse can either be the pump or the probe pulse, respectively. This ambiguity can be resolved by photon energy dependent measurements or time-resolved measurements.

The intermediate state in a 2PPE process can either be a real state, e.g. an adsorbate’s
LUMO, or a virtual state. Virtual states are introduced to explain an excitation with two photons. The lifetime of a virtual state is described by a delta function, i.e. the state has no lifetime. To make a two-photon process happen without a real intermediate state, the two photons must be temporally close enough to each other, that their pulse lengths overlap in time.

\[
E_B = 2\Delta hv \\
E_{\text{vac}} = 1\Delta hv + 0\Delta hv \\
E_F = 0 = E_{\text{vac}} - (hv_1 + hv_2)
\]

(1) occupied state
(2) unoccupied state
(3) final state

Varying the photon energy, 1C-2PPE can be employed to decide whether a state is occupied, unoccupied or final. b) The same peak position in a 2C-2PPE spectrum can arise from different states.

2.2.4 Time-resolved two-photon photoemission (TR-2PPE)

In TR-2PPE, a temporal delay is introduced between the pump and the probe pulse. Temporal information is then obtained by varying the delay and taking a spectrum every time. This way, the intensity of a feature in the 2PPE spectrum can be observed in the time domain and conclusions can be achieved concerning the dynamics of the system.

\[
\Delta t = \text{variable spatial detour} \\
\Delta t = \text{temporal delay}
\]

The delay is realized by a “delay stage” which is a linear motion stage driven by a step motor upon which a retro reflector is mounted, i.e. two mirrors between which is an
angle of 90°. When the stage is moved away from the light source by a length \( s \), the beam has to travel an additional way of \( 2s \) length. Therefore the pulse on this beam path is delayed by \( \Delta t = \frac{2s}{c} \) with respect to another beam path (\( c \) is the speed of light).

\[ \text{Figure 7: The origin of the temporal development of a state in a 2PPE spectrum. After the initial excitation, the population of the intermediate state decays with time constant } \tau \text{ and is probed after a time } \Delta t. \text{ The peak height is a measure for the population of the intermediate state. See text for further elaboration.} \]

Fig. 7 shows the processes involved in a time-resolved 2PPE experiment. A pump pulse (blue) populates an intermediate state. Due to the width \( t_1 \) of the pump pulse, the population increases in a time which corresponds to \( t_1 \), i.e. the shorter the pulse, the quicker is the intermediate state populated.

In the following we want to assume the simplest decay model: The excited electrons recombine with their respective holes in a one step process. The decay rate is proportional to the population \( \tilde{N}_{\text{IMS}} \),

\[ \frac{d\tilde{N}_{\text{IMS}}(t)}{dt} = -\Gamma \tilde{N}_{\text{IMS}}(t), \quad (12) \]

therefore the population decreases exponentially (here, the pulses are thought of as delta functions).

\[ \tilde{N}_{\text{IMS}}(t) = N_0 e^{-\Gamma t}, \quad \Gamma = \frac{1}{\tau} \quad (13) \]

\( N_0 \) is the initial population, \( \tau \) is the lifetime. The decay rate \( \Gamma \) will of course depend on the coupling of the two electronic states involved. In real physical systems the decay process can be more complicated, involving for example a two step decay process via a third state.
The decay starts as soon as the first excitation has taken place. However, it only becomes visible when the population is large enough, i.e. after most of the pulse has been absorbed. It then results in an asymmetry of the cross correlation Gaussian peak. After a time $\Delta t$, the probe pulse ejects the electrons from the intermediate state to above the vacuum level, where they manifest themselves in the 2PPE spectrum. The intensity of the peak in the spectrum is then proportional to the population of the intermediate state at the respective time delay. Therefore the cross-correlation (XC) curve is a representation of the population decay in this state.

Especially for low lifetimes, i.e. short living states, the pulse length is very important since the Gaussian shaped cross-correlation trace is much more dominant than the decay tail, i.e. the shorter the lifetime is compared to the auto-correlation width, the harder it is to determine the lifetime with a small error.

In order to model the time-dependence of the 2PPE intensity, the pulses have to be considered as well as a model for the population dynamics of the states involved. A detailed description of the theoretical concepts involved is given in [44, 47, 48]. Roughly summarized, the optical Bloch equations (which are a result of a quantum mechanical picture usually expressed in the density matrix formalism) express the behavior of the diagonal elements of the density matrix which represent the population of the states involved as well as the off-diagonal elements which describe coherence effects. Since in metals the coherence of the laser pulse is lost due the electron scattering already during absorption, the off-diagonal elements are neglected and only the diagonal elements play a role [47]. The diagonal elements then reduce to rate equations which deliver the population dynamics of a system of states.

In the following, 2PPE via a real intermediate state with lifetime $\tau$ is considered. Its population dynamics shall be denoted with $\tilde{N}_{\text{IMS}}(t)$\textsuperscript{10}. The specific functional dependence of this population would be given considering a set of electronic states which are coupled enough to the intermediate state and solving the optical Bloch equations for this system. However, an alternative way is to motivate rate equations which usually deliver one or two exponential decays.

To finally describe the development of the 2PPE spectrum, first, the real population is given by a convolution of the pump pulse $I_1(t)$ and $\tilde{N}_{\text{IMS}}(t)$.

$$N_{\text{IMS}}(t) = \left( I_1 * \tilde{N}_{\text{IMS}} \right)(t) = \int_{-\infty}^{\infty} I_1(x) \cdot \tilde{N}_{\text{IMS}}(t-x) dx$$

This populated intermediate state is now probed with a pulse described by $I_2(t)$. The measured data in the cross-correlation curve $XC(t)$ are consequently described by a

\textsuperscript{10}$\tilde{N}_{\text{IMS}}$ is the time-dependent population assuming a delta function shaped pump pulse, i.e. instantaneous population. $N_{\text{IMS}}$ on the other hand is the realistic population considering the actual pulse length.
convolution of the intermediate state’s population and the probe pulse intensity.

\[
XC(t) = (N_{\text{IMS}} \star I_2) (t) = \int_{-\infty}^{\infty} N_{\text{IMS}}(y) \cdot I_2(t - y) dy
\]  
\[
= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} I_1(x) \cdot N_{\text{IMS}}(y - x) \cdot I_2(t - y) dx dy
\]  

\(XC(t)\) can be used to fit the data obtained in a TR-2PPE experiment. To that end, functions have to be selected for the pulse shapes and the population. Usually, the pulse envelopes are described by either a Gaussian or a sech\(^2\) function.

\[
I_i(t) = \begin{cases} 
    I_{i0} \exp \left( -\frac{t^2}{t_i^2} \right) & \text{Gaussian} \\
    I_{i0} \text{sech}^2 \left( \frac{t}{t_i} \right) & \text{sech}^2
\end{cases}
\]  

Herein, \(t_i\) is a measure for the pulse length.

In summary, the cross correlation is

\[
XC(t) = \left[ (I_1 \star I_2) \star \tilde{N}_{\text{IMS}} \right] (t).
\]  

The convolution of the pulses can be expressed as (assuming Gaussian pulse shapes)

\[
(I_1 \star I_2) (t) = I_{10}^{(1)} I_{20}^{(2)} \frac{\sqrt{\pi}}{\sqrt{t_1^2 + t_2^2}} \exp \left( -\frac{t^2}{t_1^2 + t_2^2} \right).
\]  

Since \(t_1\) and \(t_2\) are not easily accessible, usually, the auto-correlation function \(AC(t)\) of a fictitious pulse \(\bar{I}\) with pulse length \(\bar{t}\) is used instead. This is justified by the assumption that shape and pulse lengths of the involved pulses are similar enough. At least for Gaussian pulse shapes this procedure is also mathematically correct since both (i) the convolution of two different pulses and (ii) the auto-correlation of one pulse result in another Gaussian whose pulse length and prefactor are fit parameters anyway.

\[
AC(t) = (\bar{I} \star \bar{I}) (t) = I_{\bar{t}0}^2 \begin{cases} 
    \sqrt{\frac{\pi}{2}} \bar{t} \exp \left( -\frac{\bar{t}^2}{4\bar{t}^2} \right) & \text{Gaussian} \\
    4 \frac{\bar{t}}{2} \cosh \frac{\bar{t}}{2} \sinh \frac{\bar{t}}{2} & \text{sech}^2
\end{cases}
\]  

In order to reproduce the data, this auto-correlation is now convoluted with the population function \(\tilde{N}_{\text{IMS}}(t)\) analogously to eq. (18).

\[
XC(t) = \left( AC \star \tilde{N}_{\text{IMS}} \right) (t)
\]  
\[
= \begin{cases} 
    A \int_{-\infty}^{\infty} e^{-\frac{x^2}{2\bar{t}^2}} \theta(t - x) \exp \left( -\frac{t-x}{\bar{t}} \right) dx & \text{Gaussian} \\
    A \int_{-\infty}^{\infty} \frac{\bar{t}}{2} \cosh \frac{\bar{t}}{2} \sinh \frac{\bar{t}}{2} \theta(t - x) \exp \left( -\frac{t-x}{\bar{t}} \right) dx & \text{sech}^2
\end{cases}
\]  

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2.3 Image potential states (IPS) 

Therein, \( A \) is a scaling factor, \( \tau \) is the lifetime of the intermediate state. The heaviside function \( \theta(t-x) \) is necessary since the decay process can only occur after the excitation. Eq. (21) or an analogous function containing a different \( \tilde{N}_{\text{IMS}} \) which depends on the decay process, can be used to fit the data. In case of a simple exponential decay of the transient population, the integral can be computed in terms of the complementary error function \( \text{Erfc}(z) = 1 - \text{Erf}(z) \). 

\[
XC(t) = A' \exp \left( \frac{t^2 - 2t\tau}{2\tau^2} \right) \text{Erfc} \left( \frac{t^2 - t\tau}{\sqrt{2t}\tau} \right) \quad \text{(Gaussian)} \quad (22)
\]

This formula is useful for fitting the actual spectra.

In case of a biexponential decay, \( \tilde{N}_{\text{IMS}} = A \exp \left( -\frac{t}{\tau_1} \right) + B \exp \left( -\frac{t}{\tau_2} \right) \), the cross-correlation curve becomes simply a sum of two terms similar to eq. (22).

In the case of a virtual intermediate state, the population function is usually described by a delta function, \( \tilde{N}_{\text{IMS}}(t) = N_0 \delta(t) \). With this, the XC trace can be employed to measure the pulse length of the pulses assuming a sech\(^2\) shape, at least the average pulse length \( \bar{t} \).

\[
XC_{\text{virtual}}(t) = N_0 \int_{-\infty}^{\infty} \frac{\bar{t}}{1} \cosh \frac{\bar{t}}{1} - \sinh \frac{\bar{t}}{1} \delta(t-x) dx \quad (23)
\]

\[
= N_0 \frac{\bar{t}}{1} \cosh \frac{\bar{t}}{1} - \sinh \frac{\bar{t}}{1} \quad (24)
\]

This is just the result obtained above for the auto-correlation function. This function can be fitted into the data and the parameter \( \bar{t} \) then gives a measure for the pulse duration.

2.3 Image potential states (IPS) 

In addition to the electronic structure of the bulk, the surface of metals gives rise to electronic states which are exclusively found at the surface, e.g. the metal/vacuum interface in case of the bare substrate. Besides surface states like the ones proposed by Shockley [49] or Tamm [50], image potential states (IPS) have proved to be an interesting feature of bare and adsorbate-covered metal surfaces since they are an ideal system to be studied using 2PPE and since they are considered a model system to study ultrafast electron dynamics [43, 51, 52, 53].

The origin of the IPS is explained by an electron located in front of the surface, i.e. in vacuum close to the metal (see fig. 8). Considering the metal as a conductive and continuous medium as in classical electrodynamics, electrostatics dictate that an electric field is formed which has the same shape as if there were no metal but a point charge

\[
\text{Erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^{z} e^{-t^2} dt
\]
with positive charge which is located inside the metal with the same distance to the surface as the electron. The electron is hence attracted by the image charge which is usually expressed in a Hydrogen-like potential, called ‘image potential’, $V_{\text{IP}}$, which depends on the distance $z$ between electron and surface [43].

$$V_{\text{IP}}(z) = E_{\text{vac}} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{4z}$$

Therein, $E_{\text{vac}}$ is the vacuum level, $e$ the elementary electron charge and $\epsilon_0$ the vacuum permittivity. This potential gives rise to a series of bound states with quantum number $n = 1, 2, 3, \ldots$ whose energy relative to the vacuum level is described by

$$E_n = -\frac{m_e}{32} \left(\frac{e^2}{4\pi\epsilon_0\hbar}\right)^2 \frac{1}{(a + n)^2},$$

where $m_e$ is the electron mass. The first value of this Rydberg-like series is $E_1 = -850\,\text{meV}$, if the quantum defect $a$ is assumed to be zero, which it is in case of the metal surface being considered a hard wall [43]. It is clear from eq. (26) that the energy of the IPS must lie higher than $E_{\text{vac}} - 850\,\text{meV}$. This is also supported by experimental data for a number of surfaces [54]. The first three IPS are displayed in fig. 8 in terms of their absolute squared wave function. With increasing $n$, the states’ energy converges to the vacuum level. Note that the position of the IPS is not fixed relative to the Fermi
level but to $E_{\text{vac}}$, i.e. they are 'pinned to the vacuum level'.

Since the image potential in eq. (25) is only dependent on $z$, the electron in an IPS can move freely parallel to the surface, therefore a dispersion with an effective mass $m^*$ in the order of the electron mass $m_e$ is expected.

In fig. 8 it becomes clear that the IPS are located outside of the metal (in the vacuum). The exact shape of their wave function, as well as the quantum defect $a$, are depending on the electronic structure of the substrate at the energy of the respective IPS, usually one considers the IPS lying inside a region with low density of states (DOS) along the direction of the surface normal [43].

As unoccupied states in front of the metal surface, they have a lifetime $\tau_n$, which scales proportional to $n^3$ [43] since higher lying IPS are located further away from the surface hence their electronic coupling to the substrate is decreased which makes a decay process slower.

Upon adsorption of atoms or molecules on the surface, the image potential states are shifted in energy (relative to the Fermi level) according to a change of the work function (upon adsorption) and their lifetime is usually increased due to the larger distance from the surface [55, 56]. Another possibility is that the IPS are quenched by an adsorbate, as e.g. in case of TBA/Au(111) [22].

### 2.4 Electronic structure of Au(111)

Gold is one of the noblest metals which means it has a very low reactivity. This is a good prerequisite for experiments with molecular switches since, ideally, the functionality of the photochromic molecules in solution is also wanted on the surface. The more the adsorbed molecules interact with the surface, the larger the influence of the substrate on their properties will be.

Since all experiments which were conducted in this thesis used a Au(111) crystal as a substrate, the electronic structure of this surface is of great importance to this work. When investigating films in the monolayer regime with photoemission experiments, the substrate will have a large contribution to the spectra.

The band structure of gold is given in fig. 9 as calculated by Eckardt et al. [57] together with a scheme of the fcc Brillouin zone. The band structure along the Λ line (from $L$ to $\Gamma$) is highlighted. Since the photon energy in our experiment can not exceed the work function of the sample (see sect. 2.2.3), we can only access bands down to approximately 5 eV below the Fermi level. In this range, mainly the two d-bands $L_{4,5}^+$.

---

[43] Face-centered cubic. Gold has an fcc structure in real space and hence a body-centered cubic structure in reciprocal space.
and $L_6^+$ contribute to most 2PPE experiments [58, 59, 60]. They both have a dispersion along the Λ line, so the measured binding energy depends on the photon energy. In a photon energy dependent measurement, their peak shift can deviate from the one expected for a non-dispersive state. For example, instead of a peak shift with twice the photon energy, the slope can be less than two and non-integer (see e.g. fig. 44). At higher energies (closer to the Fermi level) is an sp-band which however does not show up in our spectra in a significant way.

Au(111) has a projected band gap from approximately $-0.8$ eV to $3$ eV relative to the Fermi level [60] which especially in the region around $E_F + 2$ eV also extends quite far from the center of the surface Brillouin zone (see fig. 10). This has an influence on the population and/or decay of adsorbate states from/to the substrate, i.e. the coupling to the surface is weaker in this energy region.

Another prominent feature of the Au(111) surface is the Shockley surface state, which lies at $-0.487$ eV [62] (below the Fermi level). Its dispersion is reported to be $m^* = 0.37 m_e$ [63] or $m^* = 0.28 m_e$ [64] and it shows a spin-splitting [65]. The binding energy of the surface state and of the sp-band is reported to shift toward the Fermi level with increasing temperature [66].

In our experiments, the work function plays a significant role (i) as a limit to the employable photon energies ($h\nu_{1,2} < \Phi$) and (ii) as switching may be indicated by a change...
of the work function. In the literature, it is reported to be between 5.31 eV [66] and 5.55 eV [67] for Au(111). In measurements within this thesis, the work function has been determined to be $\Phi = (5.46 \pm 0.05)$ eV.

On the bare Au(111), also an image potential state is observed which lies between $(0.60 \pm 0.05)$ eV [68] and $(0.42 \pm 0.16)$ eV [54] below the vacuum level having a dispersion of $m^* = (1.0 \pm 0.2) m_e$ [68].

### 2.5 Investigated molecular switches

The motivation for research on molecular switches was already elaborated in the introduction. There a molecular switch was characterized as a molecule with (usually) two stable or meta-stable states. They must be switchable controllably by an external stimulus, e.g. light. In the cases investigated in this work, these states are different isomers. Upon illumination, TBA performs a $trans$-$cis$ isomerization in solution as well as on the gold surface while spiropyran undergoes a ring-opening reaction which is reversible in the free molecule but not on Au(111). In solution, both conformational changes are triggered by an intramolecular electronic excitation upon which the system relaxes on the potential energy surface of the excited state and thereby overcomes the energy barrier of the ground state (see fig. 11b).

The molecules studied in this thesis are discussed in the following with regard to their isomerization behavior on the Au(111) surface. Note, that the adsorption behavior as determined by temperature programmed desorption (TPD) is elaborated in section 3.2.3.
and [3.2.4] respectively.

2.5 Investigated molecular switches

2.5.1 Tetra-tert-butyl-azobenzene (TBA)

![Absorption spectra and reaction coordinate](image)

Figure 11: a) Absorption spectra of both azobenzene isomers in solution (adapted from [18]). b) Excitation mechanism in free azobenzene with simplified potential energy curves (adapted from [22]). The more stable trans state is separated from the cis state by an energy barrier and is 0.6 eV more stable. Bi-directional photoswitching is possible due to the well separated absorption bands shown in a).

Azobenzene in solution is a photochromic molecule which performs a trans to cis isomerization upon exposure to light [18]. For the structure of the molecule, see fig. 11. It consists of two phenyl rings which are connected by a “diazo-group” (double-bonded $sp^2$-hybridized nitrogen atoms). The planar trans form has a vanishing dipole moment, whereas the three-dimensional cis form has a dipole moment of 3.2 D [69]. Absorption spectra for both isomers are given in fig. 11a, showing two well separated bands which undergo a significant intensity change during isomerization.

The switching mechanism involves two distinct pathways, rotation and inversion, through which the conformational change can take place. However, it is still not completely clear how the mechanism is working exactly. Electronically, the transitions $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, which correspond to the molecular excitations from the ground state $S_0$ to $S_1$ and $S_2$, respectively, play a role in the switching process [70].

The photoisomerization process is schematically depicted in fig. 11b in a simplified potential energy diagram. A transition to a higher lying electronic state (e.g. $S_2$) is induced by light. Thereafter, the system relaxes on the potential energy surface of this state and then decays onto the energy barrier of the ground state, from where the ground state can relax to the other isomer. Since the absorption bands for azobenzene are separated, azobenzene can be switched in both directions by light of the respective wavelength. Additionally, the energy barrier separating the isomers can be overcome by thermal activation as indicated by $kT$ in fig. 11b.
However, for future applications, a molecular switch at a surface is interesting and particular focus is put to the Au(111) surface. Since at this surface, pure azobenzene does not isomerize photo-induced \([20]\) but only by electron tunneling using STM \([71]\), tert-butyl “spacer legs” were added to the molecule in order to decouple it from the surface, especially the photochromic center near the nitrogen double-bond. Especially the azobenzene’s HOMO\(^{13}\) and LUMO\(^{14}\) are calculated to be localized mostly at the diazo-group \([69]\). The resulting compound (3,3’,5,5’-tetra-tert-butyl-azobenzene) is shown for both configurations in fig. \([12]\) It also shows switching behavior similar to pure azobenzene in solution \([58, 46]\) and it was expected that the geometrical distance brought between the diazo-group and the substrate decouples the photochromic center electronically, thus preserving the switching ability on the surface.

---

\(^{13}\)Highest occupied molecular orbital

\(^{14}\)Lowest unoccupied molecular orbital
now three-dimensional. Alemani et al. discovered that a switching process occurred which was caused by the electric field in the STM junction and concluded that the field had distorted the potential energy surface of the molecule yielding the isomerization \cite{72}. Scanning tunneling spectroscopy (STS) measurements of both isomers are shown in fig. 13e, where a peak was found at 1.35 eV in the cis and at 1.67 eV in the trans state, respectively \cite{72}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure14.png}
\caption{2PPE experiments on TBA/Au(111). a) In 1C-2PPE using UV light, a change in the spectrum is observed after irradiation (red curve) which can be reversed by annealing (bottom curve) \cite{74}. The labels in a) were changed since by now it is believed that the original assignment may not be correct. b) Electronic structure as determined in 2PPE. IS 1 is attributed to the cis state while IS 2 is attributed to the trans state \cite{22}.
\end{figure}

The electronic structure of both isomers of TBA/Au(111) was further investigated in our group \cite{22, 75, 76, 77, 58, 74} using 2PPE. The experiments yield three occupied and three unoccupied states, of which four are assigned to molecular orbitals and two to states located at the molecule/metal interface (IS) (see fig. 14b). Additionally, the photoisomerization process has been investigated thoroughly, e.g. in dependence on temperature and photon dose \cite{22}. TBA/Au(111) does not isomerize completely but the isomer ratio saturates in a temperature-dependent photo-stationary state (PSS).

The 2PPE spectra show three dominant changes during photoisomerization (see fig. 14b): The work function decreases as can be observed at the secondary edge, the intensity ratio of the two interface states changes and the secondary edge is largely elevated. The ratio of the interface states (IS) was used as a marker for the relative amount of switched molecules.

Using STM, photo-induced switching of TBA can also be detected, which was done in
comparison to pure azobenzene and an azobenzene derivative having only two spacer legs. Comstock et al. used ultraviolet light from a continuous wave laser diode of 375 nm wavelength to isomerize trans-TBA. The back-reaction could be induced for the same molecule using UV light again [20]. In the described experiment, TBA was the only molecule which was photoisomerizable. This is attributed to the greater height above the surface which it has compared to the other molecules and thus a higher degree of decoupling from the surface.

Further confirmation of the observed switching and information e.g. on the geometry have been obtained using other techniques, such as HREELS\textsuperscript{15} [78, 79], NEXAFS\textsuperscript{16} and theoretical calculations concerning the free molecule [69] as well as the role of the spacer groups for decoupling by comparison to azobenzene and the geometry on the surface (see fig. 16) [25].

Figure 15: Switching mechanism of TBA/Au(111). a) Simplified schematic of the potential energy surfaces of the ground state and an excited state (the positive ion resonance) with light-induced and thermal transitions [76]. b) Substrate-mediated hole transfer [24].

2PPE experiments also give information about the switching mechanism of TBA/Au(111), which differs from that of the free azobenzene molecule described above. There, an intramolecular electronic excitation triggers the isomerization. Such a mechanism occurs at a distinct photon energy, whereas surface-bound TBA does not show a resonance in the photon energy dependent isomerization cross-section at all. On the surface, further excitation mechanisms are possible, such as the creation of a negative ion resonance (NIR) which would mean an electron from the substrate were excited into e.g. the LUMO of the molecule where it would trigger the switching. However, because of an

\textsuperscript{15}High-resolution electron energy loss spectroscopy
\textsuperscript{16}Near-edge X-ray absorption fine structure
\textsuperscript{17}X-ray photoelectron spectroscopy
increase of the cross-section at around 2 eV, a NIR via the LUMO which lies at 1.7 eV is considered less likely than a positive ion resonance (PIR) as shown in fig. 15b. In the suggested process, a hole in the substrate’s d-bands is created (the upper edge of which coincides with the measured threshold at 2 eV), which decays toward the upper d-band edge. This decay is slowed down significantly at the d-band edge due to the lower density of states (DOS) between d-bands and Fermi level. It therefore becomes more likely that the hole tunnels into the TBA’s HOMO which lies close to the d-band edge. In fig. 15b, the excited state could be considered as the mentioned PIR, the potential energy surface of which has a minimum near the energy barrier of the ground state, thus causing isomerization of some of the excited molecules. Since the trans state is more favorable also on the surface, the complete thermal back-reaction is possible [22, 24, 74].

Calculations yielding the geometry of the adsorbed molecule [25] suggest a slightly distorted trans form, in which the diazo-group is closer to the surface than expected for an azobenzene molecule which is simply lifted from the surface by spacer groups (see fig. 16a). As expected for the cis form, one phenyl ring is tilted upright and also in this case, the nitrogen atoms are close to the substrate (see fig. 16b).

Figure 16: Perspective view of the trans (a) and cis (b) isomers of TBA on Au(111) [25].

2.5.2 Trimethyl-6-nitro-spiropyran

Spiropyran (1,3,3-trimethylindolino-6’-nitrobenzopyrylospiran, abbreviated SP) is a photochromic molecule in solution, which isomerizes to the merocyanine (MC) form upon exposure to UV light. This switched, open form is re-converted to the original SP form by visible light or thermal activation [19]. While SP is three-dimensional due to the $sp^3$ hybridized carbon atom between the indoline and nitrobenzopyran part (see fig. 17), MC is planar. The two isomers differ not only in their structure but also in their properties: SP is colorless while MC is colored, the dipole moment of the open form is about twice as large (11 D) as for the closed SP form [81]. The open MC form is a resonance of several rotamers [82], in which the angles $\alpha$, $\beta$ and $\gamma$ in fig. 17 differ. It also has a
2.5 Investigated molecular switches

Figure 17: Lewis formulas of spiropyran (SP) and one rotamer of merocyanine (MC). UV light can be used to switch to the open form while visible light and the thermal back-reaction are possible to switch back to the closed form. Also shown are two sub-groups of the molecule, the indoline group and the nitrobenzopyran group (adapted from [21]).

zwitterionic character due to the negative charge accumulated at the oxygen atom and the positive charge at the nitrogen atom.

In solution, the isomerization mechanism after UV excitation involves inter-system crossing from an excited singlet SP state to a triplet state, which has a steep potential energy surface declining toward MC. The back-reaction from MC to SP after excitation with light in the visible regime occurs via a singlet MC state. SP is more stable in solution and the potential energy barrier between the two isomers is overcome thermally at approximately $308 \, \text{K}$ [83]. The reaction pathway involves different rotamers of MC which represent local minima of the potential energy landscape [82].

Due to the photochromism, spiropyrans are interesting candidates for future technological developments in functionalized surfaces which may find applications in sensorics [84, 85] or data storage [86, 87, 88, 89]. In such an application, it is crucial to bring the photochromic molecules to a substrate surface in order to allow repeated addressing of a specific molecule. Therefore, the properties of SP must be investigated on such a surface and gold seems to be a good candidate because of its low reactivity. Au(111) is therefore expected to interact only weakly with the SP adsorbate, hence conserving its isomerization properties. As it turned out, this hope remains unfulfilled, however, like for azobenzene, slight tuning of the molecules, e.g. via side-groups may restore the switchability on the surface.

The system has been observed by Schulze using STM [21]. On the Au(111) surface, spiropyran adsorbs first in islands of unordered molecules (at liquid nitrogen temperatures [90, p. 57]). After annealing to 220 K, ordering effects take place inside the islands (see
2 PHYSICAL BACKGROUND

2.5 Investigated molecular switches

Figure 18: STM measurements of SP (a,b) forming ordered islands above 220 K and MC (c,d) which appears in chains of dimers after annealing to above 300 K, both at different magnification. For both isomers, scanning tunneling spectroscopy (STS) spectra are shown in (e) and (f) (adapted from [21]).

The islands seem to be quite weakly bound to the surface since the rows of molecules inside the islands do not seem to align along the herringbone structure of the gold surface. Scanning tunneling spectroscopy (STS) shows an unoccupied state at (2.4 ± 0.1) eV above the Fermi level which is assigned to the LUMO of SP. Also, the Shockley surface state (SS) is visible as a weak signal just below the Fermi level. After annealing to approximately 300 K, the adsorbate undergoes a drastic change by forming chains of MC dimers which show a preference for alignment along the herringbone reconstruction. In STS, two unoccupied states are observed which lie close to each other: they are assigned to the LUMO at (1.3 ± 0.1) eV and the LUMO+1 at (1.6 ± 0.1) eV above the Fermi level [21].

The assignment of the low and high temperature phases to SP and MC is not possible only by STM, therefore additional techniques were employed to identify a transition from SP to MC for increasing temperature. See ref. [91] for an overview.

High-resolution electron energy loss spectroscopy (HREELS) measurements performed by M. Koch et al. (FU Berlin) [90] give information on the geometry of the adsorbed molecule and provide further evidence for a conformational change from SP to MC. In HREELS, an unordered phase is observed after adsorption at liquid nitrogen temperatures. Above 210 K, an ordered phase emerges and a stretch vibration at 946 cm⁻¹ associated with the C-O bond of SP is observed. Since the C-O bond is broken during isomerization, this mode is an excellent marker. Consequently, it vanishes from the HREELS spectrum after annealing at the switching temperature of 323 K. Furthermore,
HREELS shows that the open MC form lies flat on the surface, while for SP, the indoline group stands upright and the nitrobenzopyran group with the nitro group attached to it lies parallel to the surface. The geometrical findings are confirmed in near-edge X-ray absorption fine structure (NEXAFS) measurements carried out by W. Kuch and coworkers [21, 91]. The activation energy for the thermal ring opening reaction is determined to be $(0.84 \pm 0.05) \text{eV}$ in HREELS measurements [90].

![SP/Au(111) MC/Au(111)](image)

**Figure 19:** Geometrical structure of both isomers on the Au(111) surface (adapted from [90]).

In solution, SP is the more stable isomer but this is not the case on Au(111). On the surface, a stability inversion makes the MC isomer the energetically favored one. This is attributed to the zwitterionic character of the open form which creates a strong bond to the metal via image charges. Another reason is the molecule's geometry. MC lies flat on the surface, hence the van der Waals interaction between the molecule's $\pi$ systems and the surface is enhanced as the 'contact area' is increased. Since the activation barrier for the ring opening reaction determined by HREELS is comparable to that of the free molecule, the activation barrier for the ring closing reaction must be elevated on the surface. This excludes that the stability inversion were a consequence of a weaker C-O bond on the surface [21].

**Isomerization on the Au(111) surface** Using the STM tip at a bias corresponding to the SP's LUMO energy of about $2.4 \text{eV}$ (as observed in STS), an isomerization of a single molecule is observed by Schulze [21]. This ring opening reaction can be performed either on the edge of or inside a molecular island. However, the yield of this process is nine orders of magnitude lower than the one for light-induced switching in solution.

In fig. 20 STM images before and after the isomerization are shown as well as STS spectra for both cases. The STS spectrum for SP breaks down at the LUMO peak which indicates the switching. The subsequent STS spectrum is assigned to MC.

The mechanism for this isomerization at the surface is fundamentally different from that of the free molecule isomerized by UV light. While the latter is an intramolecular electronic transition which leaves the molecule neutral, the STM-induced switching attaches an electron to the LUMO, thus via an anionic state of SP.
Figure 20: Tip-induced isomerization observed by STM and STS. a) shows the edge of a SP island where the green dot is the position of the tip in the switching experiment. b) shows the dI/dV curve recorded during switching. When the bias reaches the LUMO energy, the signal drops rapidly. In d) STS shows that the electronic structure is now similar to that recorded on a MC sample. c) is a STM measurement after the isomerization [21].

A photon-induced isomerization for both the ring opening and ring closing reaction was attempted by Schulze [21] and Koch [90] using monochromatic light sources of various wavelengths. In the end, no photoisomerization could be observed in either direction.

The fact that the tip-induced switching has a very low yield is most likely due to the fast decay of the electrons attached to the LUMO into the substrate. This would also explain the inability to photo-isomerize SP. The back-switching reaction is most likely hindered by the strong bond between the ionic atoms in the MC molecule and the metal surface.

Using STM, spiropyran was also investigated concerning its isomerization behavior on the Bi(110) surface [21]. In contrast to gold, this semi-metal has no d-bands which seems to reduce the bond strength especially of the zwitterionic merocyanine form to the substrate. Also, the density of states at Bi(110) is lower in the region around the Fermi level. The ring opening reaction of SP/Bi(110) could be induced by electron tunneling in the STM junction, by thermal activation around 350K and by light at a photon energy of 2.8 eV. Upon illumination, the isomer ratio of SP and MC approaches a saturation, thus a photo-stationary state. Although this suggests also a photo-induced ring-closing reaction, a complete back-switching to SP seems not to be feasible. A temperature assisted reaction pathway is suggested which does not seem to rely on a HOMO-LUMO transition but on a substrate-mediated charge transfer process.
3 Experimental details

All experiments in this work were conducted at the same setup. It consists of two major parts: the femtosecond laser system in which ultra short pulses can be created in various wavelengths is described in sect. 3.1 while the ultra high vacuum (UHV) chamber containing the sample, the electron spectrometer (TOF) and various auxiliary equipment is presented in sect. 3.2. There, the in situ preparation of the substrate and the adsorption properties of the molecules is also described. In sect. 3.3, a brief overview is given on the experimental procedure of TPD and finally, the data acquisition electronics are schematically elaborated in sect. 3.4.

3.1 Laser system and ultra short pulses

The crucial condition for a time-resolved measurement in the femtosecond regime is the availability of ultra short laser pulses. In our setup, we have access to a laser system which provides a large variety of photon energies with pulse lengths in the order of magnitude of 30 fs.

![Schematic overview over the laser system used in this work](image)

Figure 21: Schematic overview over the laser system used in this work [22]. See text for elaboration.

Fig. 21 shows a schematic drawing of the laser system. It roughly consists of a ‘pulse creation’ section (left side) and a ‘pulse manipulation’ section (right side) where light of the necessary wavelength is produced and guided to the experimental chambers.

The pulse creation section mainly consists of commercial elements by Coherent: A...
3.1 Laser system and ultra short pulses

Verdi V18 pump laser provides a maximum of 18 W beam power at 533 nm in a cw (continuous wave) mode. The beam is used to pump both of the following components. A MIRA 900B Seed oscillator containing a Ti:Sapphire resonator provides ultra short laser pulses at a tunable central wavelength of around 800 nm with a pulse length of 40 fs, a repetition rate of 80 MHz and a pulse energy of 2 nJ – 3 nJ. The pulses are stretched in a stretcher/compressor unit in order to reduce the peak power and keep the optics in the amplifier from breaking. They are then amplified in a regenerative amplifier RegA 9050. Thereafter, they have a higher pulse energy of 6 µJ at a repetition rate of 300 kHz. The pulses are then again compressed in the stretcher/compressor unit. This completes the pulse creation section.

In the pulse manipulation section, this powerful infrared beam can now be processed in different ways. First, it can be used directly in a measurement or can be frequency doubled once (ultraviolet light of 3 eV) or twice (6 eV). The 6 eV beam can be used to perform direct photoemission experiments on metals such as Au(111) (Work function Φ = 5.55 eV [67]) or Ag(111) (Φ = 4.56 eV [66]).

The fundamental IR beam can also be used in one of the three optical parametric amplifiers (OPAs) on the table (see fig. 21). In such a device, white light is created and brought to an overlap with the frequency doubled fundamental (i.e. 3 eV) in a nonlinear crystal. Depending on the temporal delay between the two beams, which is realized on a linear stage, the crystal emits photons whose energy corresponds to the frequency of that part of the white light, which temporally overlaps with the UV light. This way, an OPA can be tuned over a large spectral range continuously.

In our laser system, we can combine light from two OPAs and a non-collinear OPA (NOPA). The IR-OPA 9850 produces light in the infrared regime which can be frequency doubled by one or two β-barium-borate (BBO) crystal(s) reaching the visible and UV regime (see fig. 21 for more detail on the available photon energies). Its pulses are shorter than 30 fs having an energy of 500 nJ. The vis-OPA 9450 provides pulses of 150 nJ and about 60 fs length. Its wavelength can be tuned in the visible range and can be frequency doubled using a BBO to reach ultraviolet energies. In the custom built NOPA, the white light and the 3 eV beams are not collinear which results in shorter pulse lengths of less than 20 fs [92].

Fig. 22 shows the spectral ranges of the optical devices on our laser table. Despite a few small gaps, we can access light from the whole visible spectrum and large parts of the ultraviolet and infrared region. The laser fundamental of 1.5 eV and its higher harmonics can be used for fluence dependence measurements since they come with a lot of power which would be lost in the OPAs. It is also an advantage to have several tunable devices so that one can tune pump and probe beam separately, e.g. the pump beam can be taken from the IR-OPA while the probe beam can be taken from the frequency doubled vis-OPA path.

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18 Usually, the power is set to 16 W.
Figure 22: Available wavelengths in our laser system. With only few exceptions, a range from 0.8 eV in the infrared to 5.4 eV in the ultraviolet regime, tunable photon energies can be used. Additionally, high fluence beams are available for 1.5 eV, 3 eV and 6 eV.

Around the whole laser table, a tent of transparent plastic strips is placed. Inside the tent, air conditioning keeps the temperature constant and the humidity low to reduce thermal drift of the optics. The air condition also produces a slight overpressure inside the tent so that the amount of dust, which the optics on the table are exposed to, is minimized.

3.1.1 Pulse compression

Due to the Heisenberg uncertainty principle,

\[ \Delta t \Delta \nu \geq \frac{1}{2}, \quad (27) \]

a laser pulse with e.g. \( \Delta t = 40 \text{ fs} \) pulse length must have a spectral bandwidth \( \Delta h\nu \geq 0.05 \text{ eV} \). Because of this relatively large bandwidth, the chirp plays an important role. In most optics, the light experiences a positive group velocity dispersion (GVD) which makes light with larger wavelength travel faster through the materials. Therefore, the “red” part of the pulse is temporally ahead of the “blue” part. This effect causes the pulse to become stretched in time and therefore making the pulses longer which is of course an unwanted occurrence in a time-resolved experiment.

In order to compensate for this chirp (and consequently to make the pulses short again), a prism compressor is used to bring the different parts of the pulse back into temporal overlap at the desired position (e.g. at the sample or at an optical crystal). The prism compressor consists of two prisms whose bases are parallel and whose apexes point in opposite directions. After the beam passed both prisms, it is reflected at a mirror to pass through the prisms again in order to compensate for the lateral displacement of the
3.1 Laser system and ultra short pulses

different colors so that the exiting beam is collinear to the incoming one\(^{19}\) (see fig. 23). Before compression, a pulse usually has a positive chirp meaning that the lower wavelengths arrive first (positive GVD). The temporal compression originates in the second prism where the “red”\(^{20}\) photons have a longer way through the prism as the “blue” ones. When traveling through the glass, the photons experience a higher refractive index, \(n(\lambda)\), than in air, so their velocity is \(v = \frac{c}{n}\) (\(c\) is the speed of light in vacuum). The longer a photon has to travel through glass, the longer its optical pathway is. Because of the spatial dispersion from the first prism, “red” photons always have longer pathways than “blue” ones. This is why a prism compressor has a negative dispersion. By moving a prism along a line perpendicular to its base, the difference in the optical pathway can be changed which varies the relative temporal displacement of the different wavelengths. The prisms are cut in such a way, that the angle of minimal displacement corresponds to the Brewster angle of the central wavelength of the laser beam at which the losses due to reflection are minimized. This way, the angle adjustment is easiest and the photons of the central wavelength pass the prisms parallel to the base.

A more mathematical treatment of a prism compressor can be found in \([93, 92]\).

![Figure 23: a) A chirped pulse in space. The parts with higher wavelength are ahead of the others. b) Principle of a prism compressor. By passing the first prism, the different colors are separated which makes the parts with higher wavelengths having a longer optical pathway. By adjusting a prism (indicated by arrow), the temporal delay between the different colors can be changed thus bringing the pulses to a temporal overlap at the desired position.](image)

3.1.2 Beam path setup

Fig. 24 shows the beam paths used for a 2PPE experiment as done in this thesis. However, this is only one possible combination of the available beams, which are shown in fig. 21. In principle, any pair of beams can be used together. Because of rather practical considerations, this variant is often used and the idea of the setup can be transferred to any other combination.

\(^{19}\)In practice, the exiting beam is shifted a little down, otherwise one couldn’t pick it with a mirror to guide it into the desired direction.

\(^{20}\)For simplicity I will go on calling the less energetic photons “red” and the more energetic ones “blue”.

44
Figure 24: Typical setup of a beam path for a 2PPE experiment. In this case, the beam from an OPA is used as the pump beam ("vis") and its frequency doubled is used as the probe beam ("UV"). See text for elaboration.

The OPA output in the visible range is first sent through prism compressor 1 in order to bring the pulse to a temporal overlap at the site of the doubling BBO crystal because the generation of the second harmonic is a nonlinear process and therefore the intensity plays an important role. For the same reason, the beam is focused onto the BBO and defocused on either path behind it. A beam-splitter (shown in yellow) is used to separate the UV from the visible beam. One may think that a third prism compressor were necessary to focus the visible beam after the beam-splitter onto the sample but it turns out that this is not necessary, apparently the visible beam picks up a negligible chirp from the BBO to the sample.

The latter is reflected at a delay stage, which (controlled by a computer) moves very precisely in order to vary the path length of the visible path to bring both pulses to a temporal overlap at the sample (or give them the desired delay). Since 10 fs correspond to a way of 3 μm, the motion of the delay stage is done by a stepper motor driven commercial stage (Physik Instrumente).

Having been collimated, the UV beam passes a periscope which (i) flips its polarization and therefore brings it to the same polarization as the visible light since the BBO did the same and (ii) brings the beam to a higher level above the laser table for practical reasons. Both beams are p-polarized when they hit the sample. Another prism compressor 2 is then used to focus the UV beam temporally onto the sample. Lenses then focus the beams onto the sample position. The two beams enter the chamber under an angle of approximately 2°, i.e. quasi-collinear. This is necessary to avoid an additional temporal broadening.\footnote{Flipping here means rotating the polarization by 90°.\footnote{Imagine, the pump beam were hitting the sample under gracing incidence and the probe beam at normal incidence. The pump beam’s photons would then arrive at different times, depending on where}}
3.1 Laser system and ultra short pulses

Unlike in other 2PPE labs, the two beams are not superimposed by a beam-splitter again, but are brought together at a coated prism (see figure). In reality, the reunion of the beams happens in vertical direction, it is drawn differently here for simplicity.

The beams are usually set up every day from the beginning, i.e. from the regenerative amplifier on, because due to temporal drift and fluctuations in the laser system, the beams shift slightly. After having optimized the OPA and the beam’s way through compressors, crystals and pinholes, the spot positions on the sample have to be adjusted such that the beams are in spatial and temporal overlap. To that end, first, one beam is optimized (spatially by the last mirror and temporally by moving the prisms laterally) with respect to the 2PPE yield in the TOF spectrometer. Then the second beam is optimized temporally (by moving the prisms) and brought to spatial overlap by looking at the spots with a CCD camera (see fig. 24). The camera is positioned equivalently to the sample (by a mirror in front of the chamber window) so that overlap at the camera is equivalent to an overlap at the sample. When spatial overlap is achieved, temporal overlap has to be found: (i) After setting up new beam paths or major changes in the optical pathway, an oscilloscope and photo-diodes at RegA and the position of the CCD camera, respectively, are used to find the temporal delay between the two pulses (which then may be in the range of ns). (ii) However, usually it is sufficient to search “time-zero” by varying the delay at the delay stage and monitoring the 2PPE yield which shows a sharp maximum when the temporal overlap is found. Finally, both beams are optimized spatially with respect to the 2PPE intensity.

3.1.3 Properties of the laser pulses

The ultra short laser pulses play a central role in the experiment and their properties such as the optical spectrum, the spot shape, the spot size and of course the pulse length are crucial to the evaluation of the experiment. Therefore, it is an important part of the experiment to characterize the laser pulses.

First of all, the laser spectrum (see fig. 25) is important, e.g. for obtaining exact energetic positions of the states observed. These spectra are taken already during tuning of the OPA’s central wavelength. At the BBOs, the angle of incidence affects the output frequencies, so that the “frequency doubled” photons do not have exactly twice the energy of the incoming light. Therefore, after changing the angle of such a BBO crystal in the spot they hit. The probe pulse however would probe the system everywhere at the same time. Thus, the temporal resolution is limited to the time difference from one edge of the pump spot to the other one.

23When moving the prisms perpendicular to their base, the TOF signal shows a maximum in intensity which indicates short pulse durations at the sample because this 1C-2PPE process becomes more effective, the shorter the pulses are. In a 1C-2PPE event, two photons from the same pulse eject the photoelectron. Since generally, this happens via a virtual intermediate state with infinitesimally low lifetime, the chance of an emission process depends highly on the temporal delay between both photons.

24Charge-coupled device
(e.g. during optimization), the laser spectra have to be recorded again.

![Figure 25: Spectra of the laser pulses.](image)

*a) b*

**Figure 25:** Spectra of the laser pulses. *a*) shows the spectrum of the visible OPA output while *b*) is that of the frequency-doubled UV light. Note, that bandwidth is lost in UV, therefore the minimal pulse length is higher.

Another important characteristic is the pulse duration. In TR-2PPE experiments (see section 2.2.4), one easily has access to the cross-correlation ($I_{XC}$) of the two laser pulses, if one monitors the development of a part of the spectrum which is not influenced by a state of significant lifetime, i.e. a part which is dominated by a virtual intermediate state of infinitesimally small lifetime, such as the peak of a surface state in the spectrum as in fig. 26. The cross-correlation ($I_{XC}$) $I_{XC}(t)$ of two pulses $I_1, I_2(t)$ is in general defined as

$$I_{XC}(t) = \int_{-\infty}^{\infty} I_1(\tau) I_2(t-\tau) d\tau. \quad (28)$$

Assuming $I_1, I_2(t)$ to be Gaussian pulse envelopes,

$$I_i(t) = I_i^{(0)} \exp \left(-\frac{t^2}{t_i^2} \right), \quad (29)$$

this cross-correlation integral can be solved analytically and gives

$$I_{XC}(t) = \frac{\sqrt{\pi}}{\sqrt{\frac{1}{t_1^2} + \frac{1}{t_2^2}}} \exp \left(-\frac{t^2}{t_1^2 + t_2^2} \right). \quad (30)$$

The cross-correlation also has a Gaussian shape with a width of $t_{XC} = \sqrt{t_1^2 + t_2^2}$ and in case of equal pulse lengths, $t_{XC} = \sqrt{2} t_1$. The width of a Gaussian pulse corresponds
to its FWHM by

$$\text{FWHM}(\text{XC}) = 2\sqrt{\ln 2} \cdot t_{\text{XC}}. \quad (31)$$

So when the FWHM of the cross-correlation is known, the FWHM of the laser pulse can be approximated by

$$\text{FWHM}(\nu) \approx \frac{\text{FWHM}(\text{XC})}{\sqrt{2}}. \quad (32)$$

Assuming a \( \text{sech}^2 \) shaped pulse, \( \sqrt{2} \) is replaced by 1.543, however a Gaussian shape is more realistic even though it results in higher pulse lengths [40]. Fig. 26 shows an example of an experimental cross-correlation curve.

Figure 26: Cross-correlation curve in a TR-2PPE experiment. A Gaussian fit yields a FWHM of 123 fs which corresponds to a FWHM of the laser pulses of 87 fs (assuming equally long pump and probe pulses). In the inset, red lines mark the region of the energy spectrum from which the data for the cross-correlation curve have been taken, namely the surface state of Au(111).
3.2 UHV chamber and sample preparation

Figure 27: Schematic of the ultra high vacuum (UHV) chamber. It is organized in two levels (the upper one for sample preparation and the lower one for TOF measurements) [22].

Photoemission measurements (hence 2PPE as well) require ultra high vacuum (UHV) conditions, meaning a pressure in the range of $10^{-10}$ mbar, because (i) the mean free path of the ejected electrons is highly dependent on the pressure and (ii) the surface is continuously contaminated by residual gas particles and this effect is supported by relatively high pressure in the chamber.

The mean free path can be estimated assuming identical particles which in turn are thought of as 'hard balls'. In this simple picture, the mean free path $\lambda$ is [29]

$$\lambda = \frac{k_B T}{\sqrt{2} \sigma p}, \quad (33)$$

where $k_B$ is the Boltzmann constant, $T$ is the temperature, $p$ the pressure and $\sigma$ is the cross section of the scattering process. Assuming a cross section of $\sigma \approx 10^{-19} \text{ m}^2$ [94] for an electron-nitrogen collision, the need for vacuum conditions by the photoemitted

---

"Identical" in this context simply means 'of equal properties'. For these simple considerations, we are not considering quantum mechanical concepts of identity.
electrons becomes clear in table 1. In order to get the electrons to the detector, a pressure of $10^{-5}$ mbar would already suffice. At this pressure, the sample would however be contaminated by residual gas particles within less than a second.

Assuming a sticking coefficient of one, i.e. every particle hitting the surface is adsorbed, a Langmuir gives an estimate for the time $t_{\text{mono}}$, at which a full monolayer (ML) will cover the surface, depending on the pressure. One Langmuir is defined as $1 \text{L} = 1.3332 \cdot 10^{-6} \text{mbar} \cdot \text{s}$. Therefore, $t_{\text{mono}}$ is calculated by

$$t_{\text{mono}} \approx \frac{1.3332 \cdot 10^{-6} \text{mbar}}{p} \cdot \text{s}. \tag{34}$$

The importance of using UHV is illustrated by table 1, although this is just a lower limit for $t_{\text{mono}}$ since in reality, the sticking coefficient especially for noble metal surfaces will be lower than one.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Mean free path $\lambda$</th>
<th>Time for one monolayer $t_{\text{mono}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 bar</td>
<td>$2.9 \cdot 10^{-4}$ m = 290 nm</td>
<td>$1.33 \cdot 10^{-9}$ s = 1.33 ns</td>
</tr>
<tr>
<td>$10^{-2}$ mbar</td>
<td>$2.9 \cdot 10^{1}$ m = 29 m</td>
<td>$1.33 \cdot 10^{-1}$ s = 133 ms</td>
</tr>
<tr>
<td>$10^{-3}$ mbar</td>
<td>$2.9 \cdot 10^{0}$ m</td>
<td>$1.33 \cdot 10^{3}$ s = 22 min</td>
</tr>
<tr>
<td>$10^{-4}$ mbar</td>
<td>$2.9 \cdot 10^{0}$ m</td>
<td>$1.33 \cdot 10^{4}$ s = 3.7 hrs</td>
</tr>
</tbody>
</table>

Table 1: Mean free path of electrons in a rest gas of molecular nitrogen at room temperature and time to the formation of one monolayer of rest gas particles at the surface. For details, see text.

Our chamber operates at a base pressure of approximately $10^{-10}$ mbar, which is achieved by a large turbo molecular pump (Balzers TPU 520: 520 l/s) that is provided with a pre-vacuum from another (smaller, Pfeiffer TPU 071P) turbo pump and a four-stage membrane pump (Vacubrand MD4). In order to reach minimal pressures, a Titanium sublimation pump (Varian 922-0031) and an ion getter pump (Varian Vaclon Plus 75) can also be used. The sample transfer system and the effusion cell ("doser"), which are both separated by gate valves from the main chamber, are also pumped by turbo pumps. The rotational stage of the manipulator is differentially pumped by the pre-pump of the main chamber’s turbo pump. The pressure is monitored in the (ultra) high vacuum regime by a Varian ion gauge.

In order to reach pressure ranges this low, a “bake-out” of the system at approximately 130°C is necessary: when the chamber has been vented, vacuum-contaminating molecules stick to the chamber walls etc., especially water is a prominent unwanted adsorbate. The chamber is heated so that the contaminations desorb from the surfaces inside the chamber. Due to evaporation of our molecules, the chamber walls are continuously contaminated during experiments. Since a complete bake-out is an extensive event, the chamber can be heated by a small infrared lamp that can be turned on during nights or weekends to perform a ‘minor’ bake-out.
Since 2PPE measurements require very stable conditions, the whole chamber is attached to the laser table which is protected from oscillations by its large mass (high frequencies) and pneumatic dampers (low frequencies). Displacement or oscillation of the laser spots on the sample is thereby reduced. This is especially important when working with two laser beams that need to overlap in the spatial and the time domain, as is the case in time-resolved 2PPE.

Our UHV chamber is designed in two levels, the upper one for sample transfer and preparation and the lower one for photoemission measurements with a time-of-flight (TOF) spectrometer (see section 3.2.1). The laser beams necessary for 2PPE measurements are guided into the chamber (as explained in section 3.1.2) through a window made of MgF$_2$ which is a transparent material for both ultraviolet and visible light. Furthermore, it has an almost constant transmissivity over a wide range of the spectrum which is important when the absolute intensities of the used laser beams become relevant, for example in order to conduct a photon fluence dependent measurement.

For sample preparation, a home-built effusion cell is used which is mounted on a linear manipulation stage so that it can be completely retracted from the main chamber and be isolated by a gate valve. This is useful because (i) the molecules in the effusion cell can be exchanged quickly without the need to vent the main UHV chamber, which saves the extensive process of baking the chamber and (ii) the gate valve has the advantage that, when opened only for evaporation periods, the duration of the dosing is well defined and less contamination of the main chamber can occur, e.g. during heating the effusion cell.
As shown in fig. 29 our crystal substrates are mounted in a sample holder which allows an in situ sample transfer. The smaller, lower part with the crystal can be exchanged using a magnetically controlled transfer rod. Samples can be brought to a sample garage (“magazine”) which is separated from the main chamber by a gate valve or to a “load-lock”, where a sample can be brought into or out of the UHV chamber. This is advantageous in experiments, where samples are prepared outside the chamber (which was not the case in the presented thesis work).

The sample holder is mounted to a cryostat which is installed in a manipulator movable in all three spatial directions and which allows rotation along the cryostat axis. Temperature control from 77 K (for LN$_2$) to 800 K was established using a LakeShore 340 temperature controller which reads the sample temperature by means of a type K thermocouple. Resistive heating is realized by the Tantalum wires, which are also used to mount the crystal. The feedthroughs for heating are also used to apply a bias voltage to the sample for the 2PPE experiments or for grounding the sample during sputtering.
3 EXPERIMENTAL DETAILS

3.2 UHV chamber and sample preparation

3.2.1 Time-of-flight spectrometer (TOF)

The tool to investigate the emitted electrons in our 2PPE experiments is the home-built electron time-of-flight spectrometer (TOF) depicted in fig. 30. In combination with the corresponding electronics (see section 3.4) it determines the kinetic energy of the photoelectrons indirectly by measuring the time \( t \) it takes the electrons to pass the drift distance \( d \). From this information, the kinetic energy \( E_{\text{kin}} \) is determined by the fundamental relation

\[
E_{\text{kin}} = \frac{1}{2} m_e v^2 = \frac{1}{2} m_e \left( \frac{d}{t} \right)^2. \tag{35}
\]

\( v \) is the electron’s velocity, \( m_e \) is the electron mass.

The advantage of a TOF, compared to a hemispherical analyzer, which is also being utilized for 2PPE experiments in other groups [96, 97], is its ability to detect electrons of a wider energy range simultaneously whereas in a hemispherical analyzer, the pass energy has to be readjusted permanently to get a whole 2PPE spectrum of several electron volts width.

The spectrometer consists of a grounded cylindrical drift tube in the interior of which the electrons can propagate without being influenced by electromagnetic fields. This is nec-

\[\text{53}\]
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necessary because otherwise, the electron could be accelerated or decelerated which would alter the kinetic energy, or they could be deflected and brought to different trajectories. Electric fields are shielded by the metallic material of the tube itself, which constitutes a Faraday cage. Most of the electromagnetic fields are thereby avoided. In order to shield static magnetic fields, a μ-metal shielding surrounds the whole spectrometer\(^{27}\). The spectrometer is completely coated with graphite so that electric fields which result from inhomogeneities in the work function of the material are avoided \([52, 44, 48]\). The spectrometer therefore has a homogeneous work function of approximately \(\Phi_{\text{TOF}} = 4.3\,\text{eV}\) \([22]\).

The sample is brought into position a few millimeters in front of the TOF tip. The electrons enter the spectrometer through an aperture of \(\phi = 3\,\text{mm}\) \([58]\). The drift length is \(d = 210\,\text{mm}\); this value is determined by bringing spectra with different bias voltages to an overlap and is therefore more realistic then measuring the tube length because not only the geometrical length has to be considered but also the distance to the sample and effects from remaining electric fields (e.g. between tip and sample or near the mesh or multi-channel plates, MCPs) which alter the effective length of the spectrometer. The acceptance angle of the TOF is 6° \([22]\) which is relevant not only for angle-resolved measurements but also for normal emission experiments where not only the electrons with vanishing \(k_{\parallel}\) are observed but also those who, despite their off-normal emission, are within the angular acceptance.

The electrons pass a mesh at the end of the flight tube which keeps the electric field from the multi channel plates (MCPs) out of the drift space. Behind the drift tube are the MCPs which have a diameter of 40 mm and a thickness of 0.5 mm \([58]\). Between front and back of the MCPs, a high voltage of usually 2.7 kV is applied to accelerate the electrons onto the walls of the small capillary tubes which the MCPs consists of where they produce a cascade of secondary electrons upon impact that leads to a short decrease of the high voltage which is detected via a capacitor and a fast preamplifier (Ortec). The processing of this signal is described in section 3.4.

**Influence of the work function difference and correction by bias** In general, the work function of the sample will not be the same as the one of the analyzer (which is 4.3 eV due to the graphite coating). When sample and analyzer are electrically connected, e.g. via ground, the Fermi levels of the two systems will align. Because of the different work functions, however, the vacuum levels differ. If the work function \(\Phi\) of the sample is lower than that of the analyzer, \(\Phi < \Phi_{\text{TOF}}\), the slowest electrons can not reach it and the spectrum is cut accordingly at the secondary edge by an amount \(\Delta \Phi = \Phi_{\text{TOF}} - \Phi\) because due to the different vacuum energies, a potential barrier forms between sample and analyzer (see fig. 31). If \(\Phi > \Phi_{\text{TOF}}\), the secondary edge will be shifted to higher

\(^{27}\) and the LEED device which is situated in the opposite flange in the chamber
energies by the same amount. A bias voltage $U_{\text{bias}}$ can be applied to the sample to compensate this effect. Thereby, the Fermi level of the sample is lifted by $eU_{\text{bias}}$. Ideally, both deviations should compensate for one another: $\Delta \Phi = eU_{\text{bias}}$. However, one has to keep in mind, that due to a voltage between sample and analyzer (i.e. drift tube) an electric field emerges between sample and TOF which will of course influence the trajectory of the electrons.

![Diagram](image)

Figure 31: Influence of the different work functions of sample and analyzer. In the depicted case, $\Phi < \Phi_{\text{TOF}}$, a potential energy barrier forms which keeps slow electrons from reaching the analyzer. Here, the applied bias does not compensate this effect.

**Time measurement and rescaling of intensities** In eq. (35), $t$ denotes the time between the emission of the photoelectron from the sample and its impact at the MCPs. However, this quantity can not easily be measured: The arrival of the electron at the MCPs is detected by the voltage drop of the high voltage. But in order to determine $t$, one needs to know when the electron was emitted from the surface. This 'start time' can not be determined in a reasonable fashion. It is therefore obtained indirectly.

The start signal for the time measurement is taken from a photo diode which is positioned at the RegA output. There the beam is split and a small amount is guided to a photo diode which gives the start signal. The time difference between start and stop be $t'$. The time between start and stop is split into the time it takes the light to get to the sample, $t_0$, and the actual flight time $t$. Constant offsets due to a finite speed of the...
processing electronics etc. are also contained in $t_0$.

$$t = t' - t_0$$  

(36)

Assuming a laser beam path of 5 m length and an electron energy of 3 eV, it becomes clear that $t_0$ cannot be neglected: $t_0 = 17$ ns and $t = 204$ ns.

Eq. (35) can now be rewritten. In order to do so, one has to carefully distinguish between the different energies involved. What is denoted $E_{\text{kin}}$ above is the kinetic energy of the photoelectron with respect to the analyzer ($E_{\text{kin}}^{\text{TOF}}$ would be a more accurate notation), i.e. the energy with respect to the analyzer’s vacuum level. The goal of the measurement however is the electron’s energy with respect to the vacuum level of the sample, i.e. the final state energy $E_{\text{kin}}^S$. Those energies differ by the work function difference $\Delta \Phi$ and the applied bias.

$$E_{\text{kin}}^S = E_{\text{kin}}^{\text{TOF}} - \Delta \Phi + eU_{\text{bias}}$$  

(37)

$$E_{\text{kin}}^S = \frac{1}{2} m_e \left( \frac{d}{t' - t_0} \right)^2 - \Delta \Phi + eU_{\text{bias}}$$  

(38)

$t'$ is the measured quantity here. From a series of spectra ($I(E_{\text{kin}}^{\text{TOF}})$) taken at different bias voltages, the parameters $d$ and $t_0$ can be determined under the assumption that the spectra ($I(E_{\text{kin}}^S)$) are identical except for the energy shift. While the value for $d$ can be taken to be equal as long as no changes are made to the TOF, $t_0$ must be determined whenever the laser path is changed - usually, such a 'bias series' is taken once every day.

The data obtained from the TOF are intensities with respect to the time of flight $t$. Those information are later transformed into energy spectra. This is done by the above formula eq. (38). Since the measured signal intensity is the number $dN$ of events for a certain time frame (bin) $dt$ and the energy spectrum is supposed to contain the number of events $dN$ which occur in an energy frame $dE$, the signal has to be rescaled accordingly.

$$\frac{dN}{dE} = \frac{dN}{dt} \left| \frac{dt}{dE} \right| = \frac{dN}{dt} \cdot \frac{(t' - t_0)^3}{m_e d^2}$$  

(39)

Energy resolution The errors made in measurements of a time-of-flight spectrometer have been discussed in detail by Hotzel [98]. Important error sources are the imprecise positioning of the sample in front of the spectrometer tip, the acceptance angle which especially influences measurements of highly dispersive states, accelerations due to remaining electric fields between sample and TOF tip and the statistical errors from the length of the drift tube and the time measurement.

A good estimate to the resolution of the spectrometer is the width of the secondary edge from a clean surface since its broadening is only determined by errors in the measurement:
The vacuum energy is a sharp limit and has no intrinsic linewidth whatsoever. However, this is only true for a homogeneous and clean surface, where the work function does not fluctuate within the laser spot. The experimentally determined resolution of the spectrometer has been found to be in the range of $30$ to $60$ meV \cite{22}.

### 3.2.2 Preparation of the substrate

Measurements on surfaces require well-defined conditions. To reach this goal, the surface has to be as (chemically) clean and plane as possible mainly to obtain a well-defined electronic structure and a homogeneous work function as well as a minimization of step-edge or kink effects.

In order to obtain a clean surface, it has been sputtered with argon ions. The idea of sputtering is to remove atoms and molecules from the surface by simple momentum transfer from accelerated ions. Noble gas ions are chosen because they do neither bind chemically to substrate or chamber nor do they participate in the formation of new contaminants. Furthermore, they are easy to pump out of the chamber after the sputtering is complete.

Argon was injected from a gas bottle into the chamber by a dosing valve until a pressure of about $3 \cdot 10^{-6}$ mbar had established. In the sputter gun, argon atoms were ionized and the ions were accelerated by a voltage of $1.5$ keV (“hard sputtering”) in a sputter gun from which they hit the sample at an angle of $45^\circ$. During sputtering, the sample was grounded to divert the accumulating charge in the crystal. The ion current was measured by a multimeter to be around $I_S = 5 \mu$A. This ion bombardment was maintained under the above conditions for 5 minutes.

After sputtering, the surface is very rough due to inhomogeneities in the ion beam and the different scattering efficiency in the bombardment spot. To reestablish a plane surface, the sample has been heated for 30 min, which is known as “annealing”. Due to the additional thermal energy, atoms can overcome potential barriers that (in a cold state) force them into their position in the crystal. They become mobile and rearrange to occupy the energetically preferred arrangement, which is a plane surface because an atom situated at a surface rather than a bulk position is less strongly bound and therefore has a higher energy.

Since the annealing temperature should be as high as possible, only the melting temperature of the crystal poses a principal limitation, although other technical aspects like the maximum current bearable by the tantalum wires have to be considered. In our setup, the annealing temperature for the gold crystal was $T_{Au} = 800$ K.

Usually, this cycle of sputtering and annealing was performed once at the beginning of every day to maintain the good condition of the crystal which even in ultra high vacuum
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is exposed to contamination from the residual gas. However, after bringing the crystal into the vacuum after it has been under atmospheric conditions, the cycles of sputtering and annealing have to be repeated several times until the quality of the surface, which can be judged by the work function in 2PPE spectra, is sufficient. The work function $\Phi_{\text{Au}(111)}$ of a clean Au(111) surface is known to be between 5.31 eV and 5.55 eV from the literature \cite{66, 67}.

3.2.3 Adsorption of TBA

In order to obtain a defined coverage of TBA on the substrate, it has been evaporated from our effusion cell (see section 3.2). The properties of TBA have been discussed in detail in section 2.5.1. The focus in the following is supposed to be merely on the experimental details and the adsorption behavior of TBA known from other (past) studies.

A few grams of the TBA molecules which had been provided by Stefan Hecht and co-workers (Humboldt-Universität zu Berlin) were filled into the effusion cell. After the effusion cell had been attached to the main chamber again and had reached an appropriate pressure, the molecules could be heated by resistive heating of the whole pot. Convenient temperatures for dosing were reached at a molecule temperature of $T_{\text{doser}} = 380$ K. At this temperature, TBA sublimates to a sufficient amount and the molecules subsequently enter through the opened gate valve into the main chamber where the molecular beam first has to pass a cup (see fig. 27) which avoids adsorption onto the sample holder. During dosage, the substrate is held at $T_{\text{substrate}} = 410$ K in order to only adsorb a coverage of 0.9 ML which is the desired standard coverage because unlike in the whole monolayer, no high coverage phase exists, that would involve unordered adsorbate geometries. Alternatively, larger coverages were dosed onto the sample and by heating to 410 K, a coverage of 0.9 ML was reached by desorbing the multilayer. TBA was dosed for approximately 5 min. Note that the desired coverage of 0.9 ML is not achieved by the dosing time but by the substrate temperature. This way, the final coverage is independent of the exact dosing time, which is not easy to control due to the necessary motion of the effusion cell on the linear stage which is done by hand, and the exact temperature of the effusion cell, i.e. the amount of sublimating molecules per unit time.

The reason why a coverage of 0.9 ML has been chosen in previous studies of TBA can be explained best considering the temperature programmed desorption curves (see section 2.1) of TBA/Au(111) which are shown in fig. 32. They were recorded at the fragment mass of 190 amu (see appendix B). In this series, different dosing times were used to reach the different coverages. At low coverages, a single peak marked as $\alpha_3$ is visible at 525 K. With increasing dosing time, this peak becomes asymmetric and a second
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3.2 UHV chamber and sample preparation

Figure 32: Temperature programmed desorption curves of TBA/Au(111) shown for different TBA coverages. The sample was heated with a rate of $\beta = 1 \text{ K s}^{-1}$ and desorbing molecules were detected at a fragment mass of 190 amu. The temperature, at which the sample was held during evaporation, is indicated by the red line.

Peak ($\alpha_2$) at 400 K emerges as a shoulder while the height and width of the original $\alpha_3$ peak remains constant indicating saturation. With increasing coverage, the second peak $\alpha_2$ also remains unchanged while a zero-order desorption peak $\alpha_1$ appears clearly at around 310 K. The latter is assigned to the multilayer. $\alpha_2$ and $\alpha_3$ on the other hand are interpreted as two phases in the (sub-)monolayer regime: due to intermolecular interaction, the molecules in the closely packed high-coverage phase (which results in $\alpha_2$) are less strongly bound and therefore a shift to lower desorption temperatures is observed.

Dosing at $T_{\text{sample}} = 410$ K therefore means to neither let the high-coverage phase nor the multilayer form in the first place. This temperature was also maintained some time after the effusion cell had been retracted behind the gate valve in order to reduce adsorption of molecules remaining in the chamber when the substrate would cool down.

### 3.2.4 Adsorption of spiropyran

The preparation of a spiropyran covered surface is analogous to the preparation of TBA which is described in the previous section. 1,3,3-trimethylindolino-6′-nitrobenzopyrylospiran (henceforth referred to as “spiropyran”) powder is commercially available and was obtained from TCI Europe.
3.2 UHV chamber and sample preparation

The powder was evaporated from our effusion cell at temperatures between 360 K and 370 K. The temperature was held stable by the temperature controller. Dosing times varied depending on the desired coverage and the amount of molecules left in the effusion cell but the times were in the order of minutes, mostly even less. During dosing, the substrate temperature was kept constant at 120 K.

![Figure 33: TPD measurements of spiropyran on Au(111) for different coverages recorded at a fragment mass of 159 amu and a heating rate of $\beta = \frac{1}{5}$ K s. The red dashed line indicates the full monolayer. A number of features (a-f) are observable.](image)

The adsorbate-covered surface was characterized after every measurement by temperature-programmed desorption (TPD). Fig. 33 shows TPD curves for several initial coverages. These curves were measured at spiropyran’s fragment mass of 159 amu. The fragmentation pattern of spiropyran is given in appendix B. The here shown measurements consist of six features (labeled a) through f). a) through d) were observed by Koch [90] using the fragment mass at 77 amu. The highest coverage there was 2.9 ML.

Features a) through c) are assigned to the monolayer [90] which appears to consist of three different phases. Note that at around 323 K, the isomerization toward the open merocyanine (MC) form occurs at least in the sub-monolayer regime. It can be assumed that while f) and e) originate from the multilayer SP molecules, some of them (perhaps only in the second layer) isomerize at 323 K and then are more strongly bond. They desorb at higher temperatures than the SP molecules, forming feature d). In the monolayer regime, c) might resemble remaining SP molecules, whose isomerization was
quenched by molecules on top of them or because in a densely packed full monolayer, switching is sterically hindered. Eventually, after the remaining and more weakly bound SP molecules from the monolayer are desorbed, the remaining MC molecules desorb in features b) and a). Perhaps, two different binding energies for MC are realized because of the herringbone structure (MC on hcp and MC on fcc sites) or because the dimers have a different binding energy than single MC molecules.

The former interpretation is of course quite speculative. Further experiments would be in order to investigate especially the multilayer regime, which to the author’s knowledge has not been done so far.

It has been observed by HREELS\textsuperscript{29} that even after annealing at 700 K, fragments of MC remain on the surface \cite{90}. The fact, that the adsorbate in this case can not be completely removed by heating alone, as it were the case for TBA, makes it difficult to conduct experiments which involve different coverages, e.g. a detailed TPD series or coverage dependent 2PPE experiment. The ideal way would be to prepare a fresh layer for every coverage, which however would require a whole cycle of sputtering and annealing for every single data point, which takes almost an hour per cycle. Therefore, coverage dependent experiments with spiropyran were conducted in a different way, namely by dosing more molecules on top of the already existing layer. This will be elaborated in sections \textsection5.1 and \textsection5.3.

\textbf{3.3 Temperature programmed desorption (TPD)}

The underlying concepts for TPD have been explained in section \textsection2.1 so in this section, a quick overview over the experimental realization of the TPD measurements will be given.

The measurements were conducted in the same UHV chamber used for 2PPE experiments, which is described in section \textsection3.2.

For one TPD, the molecules were heated in the effusion cell and kept at a constant temperature, using the heater output of the \textit{LakeShore} temperature controller which provided thermal stability in the effusion cell. Once the molecules and the sample reached the desired temperatures, the gate valve to the effusion cell was opened, but in order to be able to get a defined dosing time, the effusion cell was not (manually) moved into the chamber by the linear motion stage.

As soon as the pressure has recovered from its increase during moving the manipulator, the TPD is started at a heating rate of $\beta = 1 \text{Ks}^{-1}$, unless otherwise stated. The heating is continued to the usual annealing temperature of the substrate, i.e. 800 K for Au(111).\footnote{29High-resolution electron energy loss spectroscopy}
The mass-specific QMS \(^{30}\) signal is recorded in the computer via an analog/digital converter (see sect. 3.4). The mass which stands representative for the whole molecule is determined by fragmentation patterns which are shown in appendix B for the two molecules used in this thesis.

For the determination of the initial coverage, the area under the TPD is determined by integration and compared to one TPD which is defined as a monolayer. It is therefore necessary to ensure most similar conditions at both measurements.

Additionally, a TPD is usually recorded at the end of every measurement day to characterize the adsorbate coverage.

### 3.4 Data acquisition

The time-of-flight (TOF) spectrometer delivers a voltage drop in the MCP \(^{31}\) high voltage whenever an electron arrives at the MCPs (see section 3.2.1). This signal is coupled out of the high voltage (HV) circuit by a capacitor and a preamplifier (see fig. 30 and the lower right part of fig. 34). In fig. 34, the brown box plugged into the HV connection of the back side of the MCPs at the TOF contains the capacitor and the preamplifier (Ortec VT120). From there on, the signal is rectified and brought to a defined amplitude in a constant fraction discriminator (CFD, Canberra CFD2126). It is then read out by a multi-event time digitizer card (FAST ComTec P7887) in the personal computer as the "stop" signal. The TOF signal is also monitored by an acoustic rate meter which makes the optimization of the count rate easier when standing at the laser table.

The corresponding “start” pulse is delivered by a photo-diode positioned after the RegA amplifier. Its signal is also processed in a CFD and read out by the computer. The multi-event time digitizer card captures the time difference between “start” and “stop” pulse by sorting the events into 8192 bins, each having a width of 0.25 ns. Every single event is saved in the computer and after having accumulated sufficient events, a time-of-flight spectrum emerges from the data.

The computer is equipped with a multifunctional data acquisition card from National Instruments (NI MIO-16E-1) and a LabView environment (also by NI). This card contains an analog/digital converter as well as a digital/analog converter and a direct digital input/output part (see fig. 34). In the A/D part, the signal (0-10 V) from the ion gauge controller (i.e. the pressure) is read as well as the QMS signal. At the D/A part, the mass of the QMS can be selected remotely from the computer and the bias voltage of the sample is adjusted. The digital interface is used to command the two laser shutters (pump and probe) and the shutter in front of the incoupling window of the chamber.

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\(^{30}\) Quadrupole mass spectrometer  
\(^{31}\) Multi-channel plates
Figure 34: Overview over the circuitry used in our experimental setup. The schematic shows the processing of the TOF signal as well as the wiring of large parts of the setup. See text for elaboration.
which is used to deflect the beam to the CCD camera (see fig. 24).

A GPIB\textsuperscript{32} card in the computer performs the communication with the temperature controller (LakeShore 340) which in turn steers the output of the power supply (Delta Elektronika SM35-45) heating the sample. The PID\textsuperscript{33} routine of the temperature controller allows very precise heating at defined rates and is able to hold the temperature within less than a Kelvin.

Additionally, the computer steers the delay stage for time-resolved measurements via a serial RS-232 interface and captures the images from the CCD camera via FireWire.

\textsuperscript{32}General Purpose Instrumentation Bus
\textsuperscript{33}proportional integral derivative
4 TBA adsorbed on Au(111)

Electronic structure and isomerization behavior of TBA\[^{34}\] have been extensively studied, particularly by Hagen [22]. In his PhD thesis he showed that this azobenzene derivative preserves its functionality on the Au(111) surface but the driving force in the photoisomerization is different than in solution. As TBA is the only reversibly photoisomerizable molecule in direct contact with a surface, this system and especially its elementary electronic excitation processes are of great interest [74].

As elaborated in sect. 2.5.1, the isomerization on the surface is triggered by a substrate-mediated process via creation of a positive ion resonance, wherein a hole is transferred from the substrate’s d-bands to the molecule’s HOMO\[^{35}\] [24]. This is different from the switching process in solution, where an intramolecular excitation (neutral molecule) from the HOMO to the LUMO\[^{36}\] is the driving force [70]. Although it is believed that the latter intramolecular mechanism is quenched on the surface, a measurement in [22] shows a lifetime of the LUMO after electron transfer from the substrate (negative ion resonance) on the timescale of picoseconds which would point toward a switching via this state.

In this chapter, first a series of temperature programmed desorption (TPD) measurements is presented in order to determine the binding energy of TBA/Au(111) for the limit of zero coverage as a contribution to a mostly theoretical publication on the role of TBA’s spacer groups [25]. Thereafter, the mentioned experimental results yielding the long lifetime of the LUMO are re-investigated using time-resolved two-photon photoemission.

4.1 Binding energy of TBA determined by TPD

In order to determine the binding energy of TBA on Au(111), temperature programmed desorption has been employed and evaluated using the “complete analysis” method by King. The method has already been described in detail in sect. 2.1.

Fig. 35a shows a number of TPDs in the sub-monolayer regime (colored) with their respective initial coverage. The absolute coverages have been determined using the shaded curve as a reference which defines 1.00 ML. A detailed discussion of the adsorption behavior is given in sect. 3.2.3 while here, focus shall be placed on the determination of the binding energy. In fig. 35b, the “complete analysis” by King is depicted briefly (see also sect. 2.1). From the integrated TPD curves, which represent the coverage at any given temperature during the desorption process, every curve is assigned the tempera-

\[^{34}\]3,3',5,5'-tetra-tert-butyl-azobenzene
\[^{35}\]Highest occupied molecular orbital
\[^{36}\]Lowest unoccupied molecular orbital
4.1 Binding energy of TBA determined by TPD

Figure 35: a) TPD curves of TBA/Au(111) for different TBA coverages. The initial coverage is marked on the left. The shaded TPD serves as the reference for the full monolayer. In the gray curve, the zero-order multilayer peak is also visible. b) King’s evaluation. The integrated TPD curves form the temperature-dependent coverage for each initial coverage. For a defined coverage (here $\approx 0.55\,\text{ML}$), the corresponding temperatures are determined from the integrated curves. These temperatures then are assigned to a QMS intensity in the respective TPD itself.

ture, at which a certain coverage is reached. These temperatures and their corresponding QMS$^{37}$ intensity in the TPD form one data point. Every curve thereby contributes one point in the Arrhenius plot which is why the total number of TPDs directly influences the precision of the obtained binding energy.

Figure 36: a) Arrhenius plot for four exemplary coverages. b) Coverage dependence of the desorption energy as determined from the fits of the Arrhenius plots.

Such Arrhenius plots are shown in fig. 36b. From the fit, the binding energy $E_B$ is determined from the slope divided by the Boltzmann constant. With increasing coverage,

$^{37}$Quadrupole mass spectrometer
less and less data points are available since the initial coverage of the particular TPD must be larger than the chosen coverage for the evaluation.

From the Arrhenius plots, one obtains a number of binding energies for the respective coverage which are displayed in fig. 36b. The data show a decrease in the binding energy with increasing coverage. This is probably due to inter-molecular interaction which weakens the bond to the substrate (e.g. via dipole-dipole interaction). The decrease of the binding energy at higher coverages is also qualitatively observable in the original TPDs (fig. 35a), where desorption starts at lower temperatures for higher initial coverages.

In the limit of zero coverage (“single molecule desorption”), which is relevant for the comparison to theoretical calculations [25], the binding energy is found by a linear fit of the data up to $\theta = 0.35$ ML and the resulting axis intersection is

$$E_B = (1.69 \pm 0.15) \text{ eV}.$$  \hspace{1cm} (40)

Note, that only TPD curves in the regime $\theta < 0.9$ ML have been used for the evaluation because the binding energy of the high coverage phase differs from the one of the low coverage phase. In order to determine the binding energy of the high coverage phase, a model for $E_B(\theta)$ would be required to fit the TPDs, as has been done by Rockey et al. for the similar situation of benzene on Ag(111) [30].

### 4.2 Electron dynamics of TBA/Au(111)

The electronic structure of TBA/Au(111) has been extensively studied in our group [22, 75, 24, 76, 77, 58, 74]. Most of the work has been performed by Sebastian Hagen and is described in his PhD thesis [22]. However, only few measurements were performed using the combination of the tunable frequency-doubled OPA output in the UV range and the untunable 3 eV beam as the information of interest are mostly accessible using the OPA’s visible and the UV light instead. Unfortunately, the LUMO of TBA/Au(111) could not be observed without the 3 eV beam. Its energetic position has been determined using scanning tunneling spectroscopy (STS) to be 1.67 eV for the trans and 1.35 eV for cis isomer, respectively [72]. In order to verify this value, additional 2PPE measurements were performed by Hagen using the 3 eV beam and a feature was found at 1.7 eV which showed a surprisingly long lifetime of $(1.0 \pm 0.3)$ ps [22]. The LUMO of cis-TBA however could not be found in these 2PPE experiments.

Since the mentioned measurements were only of “preliminary” character, it was the first part of this thesis work to further investigate the LUMO feature observed in 2PPE.

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38 in terms of the light’s wavelength
39 Optical parametric amplifier, see sect. 3.1
Note, that the data presented in this section contain artefacts as illustrated in fig. 37 which were unfortunately discovered only after the experiments on this system were concluded. Due to a broadening of the uncorrelated 2PPE spectrum (black in fig. 37), compared to the UV only spectrum (blue), the routinely performed background subtraction, in which pump and probe spectra are subtracted, created two artefact peaks behind the Fermi edge of the 3 eV spectrum (yellow) and the d-band edge in the UV only spectrum (blue). Because the uncorrelated spectrum seems to be stretched in energy, those sharp edges have a slightly different position as in the respective one-color spectra. The broadening of the uncorrelated spectrum is indicated by a shift of the Fermi edge of the UV part by 165 meV. Normally, these features overlap perfectly so that in the correlated signal, no signal is visible in the respective region. As seen in the red spectrum, however, the signal in not zero at the respective position.

For comparison, a normal, artefact-free background subtraction example is shown in appendix C.

This problem did not occur in later measurements on spiropyran which are presented in sect. 5. In retrospect, we believe that the reason was a too small spot size of the 3 eV beam which led to a space charge effect in which the ejected photoelectrons interact electrostatically during the flight through the drift tube of the spectrometer. Due to this problem, the results shown here have to be considered with care, e.g. the energetic position of a peak might be shifted slightly.

Figure 37: Origin of the artefacts observed in 2PPE spectra of TBA. The correlated spectrum is determined from the uncorrelated one by subtracting the pump only and the probe only spectra. Due to a shift of the Fermi edge of 165 meV, artefacts are observed at the indicated positions.
photon energy: first on a sample in the trans configuration (at room temperature), then after the sample had been cooled with liquid nitrogen and illuminated until the photo-stationary state was reached. Since the features observed in this spectrum are well-known from Hagen et al., the assignment of the peaks is done without further elaboration. Despite the d-band edge of Au(111) at $-2.0 \text{ eV}$, four molecule-induced states are observed: the HOMO at $-1.8 \text{ eV}$, which could be slightly shifted during isomerization and the LUMO at $1.7 \text{ eV}$, which overlaps with a dominant artefact. The so-called “interface states” (IS) $^{[22]}$ of which one is assigned to each isomer are located at higher energies in the spectrum. Their energy is more definite since they are also observed in artefact-free visible/UV measurements. Another well-known property of the switching is the change of the work function toward lower values.

In the following, the focus is placed on the LUMO whose lifetime is of the most interest.

Fig. 38: Correlated 2C-2PPE spectra for both isomers of TBA/Au(111). The work function shift and the change of peak intensity of the so-called interface states (IS) indicate switching while the rest of the features are unaffected.

Fig. 39 shows a series of 2PPE spectra recorded at different UV photon energies. Since the LUMO is UV probed, it exhibits a shift to higher final state energies, which can hardly be quantified because of the overlap with the artefact. A fit using two Gaussians is shown, however, the artefact is most likely not correctly described by a Gaussian peak shape. Since the only alternative to a shift with the UV photon energy would be no shift (as the 3 eV energy is fixed), it can be said that a shift is observed and the peak is hence assigned to a UV probed unoccupied state. The peak could also originate from an occupied state at $-1.3 \text{ eV}$ but since no such peak was observed in other 2PPE measurements or in STS and since the position of $1.7 \text{ eV}$ fits very well to STS results.

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While STS shows two different energies for the respective LUMOs of the *trans* and *cis* isomers of TBA/Au(111) \[^{[72]}\], only one feature has been observed by Hagen \[^{[22]}\] using 2PPE and also in this work there seems to be no state at lower energies associated with *cis*-TBA. The switching experiment shown in fig. 38 shows no significant difference for *cis* and *trans* as far as the LUMO feature is concerned. The missing of the *cis*-LUMO is surprising, but could be explained by a strong decoupling from the substrate which would strongly reduce the peak in 2PPE due to the less efficient population. Note, that both LUMOs are located in the projected band gap of Au(111), as shown in sect. 2.4.

![Figure 39: Correlated 2C-2PPE spectra recorded using the 3 eV beam and different UV photon energies. The LUMO peak lies close to an artefact (indicated by fit using two Gaussian peaks) and shifts with the UV photon energy.](image)

In order to investigate the dynamics of the LUMO feature, time-resolved 2PPE measurements were carried out. The artefact peaks there expand to stripes which are constant over the whole delay range. Fig. 40a shows this effect at both artefact peaks which are marked ‘A’ and ‘B’. If these stripes represented a real physical phenomenon in the sample’s electron dynamics, it would mean (i) that two states would have a lifetime which is on the order of the laser’s repetition rate (see sect. 3.1, rate is 300 kHz, time between pulses 3.33 μs) or that (ii) each stripe were the result of two states probed by different photon energies whose final state energy coincided. Since both variants seem very unlikely and the latter can even be ruled out by varying the photon energy, these two peaks are definitely assigned to artefacts as described above.

In order to obtain a possibly better view on the time-resolved spectra, a different background subtraction method was employed: While in fig. 40a, separately recorded one-
color spectra were subtracted from the two-dimensional data array (as usual), fig. 40b was created by subtracting an average of ten 'cuts' of the false-color plot at the highest delays recorded at $+10$ ps (not shown in the plot) which is also a common method. Although this of course removes the stripes, at least the artefact peak 'A' at $\Delta t = 0$ has not vanished, which means that the process which creates the artefacts is enhanced when both pump and probe pulse overlap in time. This is an unfortunate result since otherwise, i.e. if the artefacts were constant in time, the artefacts would perhaps not influence the dynamics determined from these measurements but would only add a constant offset to any cross-correlation curve.

Figure 40: Different methods for background subtraction in TR-2PPE: a) Separately recorded pump and probe spectra are subtracted from the raw data. b) An average of ten spectra from the raw data at the very largest delays (in this case $+10$ ps) are subtracted.

A more detailed analysis of the time-resolved measurement (with a background subtraction as in fig. 40b) is shown in fig. 41. The false-color plot shows the correlated 2PPE intensity as a function of the delay of the laser pulses and the energy of the photoelectrons with respect to the Fermi level. It was recorded at a UV photon energy of 4.23 eV, so according to the experiment shown in fig. 39 the LUMO peak should still be observable as a shoulder of the 'B' artefact. Accordingly, the spectrum at time-zero shown in the right part of fig. 41 shows an asymmetry of peak 'B'. Positive delays in the figure correspond to the UV beam as probe, as indicated by the schematic above the false-color plot.

Below the false-color plot, the relevant cross-correlation (XC) curves are shown. The auto-correlation signal is obtained from the Fermi edge and yields a relatively large single pulse length of 96 fs, which in this case if not a problem since the lifetime on the picosecond timescale observed by Hagen is of interest.

The HOMO, as an occupied state, can not have a lifetime. The asymmetry of its XC curve is due to hot electrons, which are also visible in the false-color plot at lower energies.
probed by the UV beam. By comparison, the LUMO’s XC yields the same dynamics on the shown timescale. This is in agreement with the previous measurement where a bi-exponential decay for the LUMO feature is observed: a shorter decay is attributed to hot electrons and a longer one is observed as the state’s lifetime [22]. The artefact peak ’A’ also shows an asymmetry which could also result from a hot electron decay. Since this peak is located at higher energies, their lifetime would be expected to be smaller here.

In order to verify the observation of a picosecond-scale lifetime, the measurement shown in fig. 41 has been carried out up to a delay of 10 ps. The cross-correlation curve of the LUMO is again shown for the full delay range in fig. 42. Due to the low signal intensity at at larger delays (after the auto-correlation of the pulses), the noise in this region is more pronounced. However, despite the improvable statistics, one can not observe a significantly higher signal of the LUMO compared to the HOMO which definitely does not have picosecond-scale lifetime. Also, the two artefact peaks show the same behavior which indicates that the apparent slow decay is not of a physical nature.

4.3 Conclusion

TBA/Au(111) was investigated using temperature programmed desorption (TPD) with regard to its binding energy to the substrate, which was determined to be $E_B = (1.69 \pm 0.15)$ eV in the limit of single molecule desorption. This value is on the same order of magnitude as other organic molecules at noble metal surfaces such as azobenzene on Ag(111) [100] or benzene on various substrates [40, 101]. Furthermore, the binding energy shows a clear coverage dependence: with increasing coverage in the low coverage regime ($< 0.9$ ML), the binding energy becomes smaller which indicates a repulsive inter-molecular interaction.

The electron dynamics of the system were measured using time-resolved two-photon photoemission and particular focus was put on the trans-LUMO of TBA, for which a picosecond scale lifetime was observed previously [22]. The electron dynamics of the trans-LUMO show a relatively fast decay which is attributed to the superimposed signal of hot electrons in the spectrum. However, no picosecond lifetime was observed for the trans-LUMO.

Unlike in STS but consistently with previous 2PPE measurements, the cis-LUMO could not be observed. This is attributed to a very weak electronic coupling to the surface.

This would support the established interpretation of the photoisomerization mechanism as a process involving not the LUMO (in an intra-molecular process or a negative ion

\footnote{Considering the experimental values in the cited paper. Benzene shows binding energy values around 0.5 eV while azobenzene on Ag(111) has a binding energy of 1.1 eV corresponding to the fact that it consists of two benzene rings.}
Figure 41: Pump-probe experiment on cis-TBA/Au(111). At positive delays, the UV beam acts as probe as indicated by the schematic on top of the graphic. On the right, the correlated spectrum at $\Delta t = 0$ (temporal overlap) is shown and in the lower part, cross-correlation (XC) curves for three features are presented together with the auto-correlation (shaded gray) which was obtained from the Fermi edge at around $E_{\text{final}} = 7.3$ eV.
Figure 42: Cross-correlation curves from the measurement shown in fig. [41] for long pump-probe delays in the UV probed case. The LUMO shows no distinct behavior on the picosecond timescale.

resonance) but the HOMO of TBA (in a positive ion resonance), since a state with a low lifetime is unlikely to trigger the isomerization. The reduced lifetime of the LUMO is attributed to the electronic interaction with the metal substrate, although it is lying in the projected band gap along the $\Lambda$ line.

The experiments presented here must be considered with care due to artefacts in the spectra and it can not be ruled out that their presence has an influence on the observed cross-correlation curves. Since at present, no more artefacts are observed in our spectra, additional measurements in the near future should bring more certainty to this topic.
5 Spiropyran on Au(111)

In this chapter, 1,3,3-trimethylindolino-6'-nitrobenzopyrylospiran (from now on called ‘spiropyran’) is investigated. The light-driven ring-opening/ring-closing reactions in solution between the closed spiropyran (SP) and the open merocyanine (MC) form make it an interesting system also on the surface, although it has already been shown that on Au(111), no light-induced changes are observed [90] [21]. Nevertheless, since this is also true for bare azobenzene, the investigation of SP may lay the foundation for studies of modified spiropyran derivatives which in the end might show an isomerization behavior like in the case of the azobenzene derivative TBA.

After the geometrical structure of both isomers of spiropyran on Au(111) as well as its temperature-induced switching behavior has been investigated by HREELS[41] NEXAFS[42] and STM [91] as reported in section 2.5.2, the question, why the molecule’s photochromic properties are quenched on the gold surface, remains. As light-driven processes involve the electronic structure of the system, this electronic structure seems worth investigating more closely than this is possible in scanning tunneling spectroscopy (STS) [21]. Since the isomerization (ring-opening/ring-closing reaction) would mean a motion of the nuclei and therefore an excited state may require a lifetime long enough for the molecule to switch, the dynamics of the unoccupied electronic states of the system are also of interest.

In this chapter, 2PPE experiments on surface-bound spiropyran (SP) and merocyanine (MC) are reported. Unless otherwise stated, measurements were performed in the monolayer regime (see section 3.2.4) and for SP, the sample was annealed at 253 K to reach the ordered phase, as observed in STM. For isomerization to MC, the sample was usually heated to 323 K. All spectra were recorded at liquid nitrogen temperatures ($T_{\text{min}} = 88$ K).

First, the energetic positions of the observable states of SP are determined by photon energy dependent measurements, then the dispersion of these states and the ultrafast electron dynamics are monitored as well as the coverage dependence of these states with respect to their energetic position. Having then investigated the properties of SP, the temperature-induced transition to MC is observed and subsequently experiments on MC’s electronic properties are shown.

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[41] High-resolution electron energy loss spectroscopy
[42] Near-edge X-ray absorption fine structure
5.1 Electronic structure of spiropyran on Au(111)

Since the knowledge about the electronic structure of Spiropyran is fairly limited up to this point, the measurements described in this section were started at the highest possible photon energy in order to obtain an overview of the states observable in 2PPE. The photon energy was limited not by the OPA’s range but by the work function of the system. Therefore, the highest photon energies were close to 5 eV which was obtained from the OPA’s frequency-doubled output.

The 1C-2PPE spectrum taken with the highest photon energy of 4.89 eV is shown in fig. 43. It is part of a series of spectra, in which the photon energy was varied (“photon energy dependence”). The spectrum shows a very heightened secondary edge, which is due to hot electrons and (mainly) direct photoemission, as the photon energy is close to the work function in this measurement.

The enlarged part of the spectrum has been fitted with eight Gaussian peaks on an exponentially decaying secondary electron background. The blue curve shows the fit result. Note, that this fit is only to demonstrate how the features in this spectrum are composed, since they are quite weak. However all peaks included in the fit are also found in other spectra of this photon energy dependent series. The binding energy has also not been determined by such a fit, since the high number of parameters would make it unreliable. Instead, for each spectrum of the series, the peaks have been fitted in smallest possible groups, from which the binding energy has been calculated. The value shown in fig. 43 is the average of those.

The spectrum shows characteristic features of the Au(111) surface: the Shockley surface state (SS) has a binding energy of $E_B = -(0.43 \pm 0.02)$ eV with respect to the Fermi level. Two dominant features of the gold d-bands are found at $E_B = -(2.07 \pm 0.03)$ eV and $E_B = -(2.64 \pm 0.04)$ eV, in agreement with the literature [77, 63, 64]. The spectrum in fig. 43 also shows five molecule-induced states.

In order to determine the origin of a peak in the 2PPE spectrum, the photon energy dependence of the final state energy is considered (see fig. 44). A slope of one in this one-color experiment indicates an unoccupied state, a slope of two gives an occupied state. The information in fig. 44 now justifies the assignment of the surface state and the two d-band features made above. Strictly, the assignment of features to bulk bands judging from their shift with the photon energy is difficult due to their dispersion perpendicular to the surface. In this case however, the respective bands show only a weak dispersion (see sect. 2.4), which for the feature “d1” becomes visible in its slope being lower than two. Furthermore, the same features are visible in 2PPE spectra of the

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43 In the following, I will use SP synonymically for SP/Au(111) since all measurements were performed on this substrate.

44 Optical parametric amplifier, see sect. 3.1
5 SPIROPYRAN ON AU(111) 5.1 Electronic structure of spiropyran on Au(111)

Figure 43: 1C-2PPE spectrum of SP/Au(111). The largely elevated secondary edge shows that the photon energy is close to the work function (direct photoemission). The spectrum has been fitted with eight Gaussian peaks for demonstration (see text). The molecule induced states of SP were named with a letter indicating O (occupied) or U (unoccupied) and a number. At the blue Gaussian of a peak, the binding energy of the corresponding state with respect to the Fermi level is written.

Figure 44: Photon energy dependence of the 1C-2PPE (UV only) series. Except for SP-U1, all peaks in the spectrum (fig. 43) can be assigned to occupied or unoccupied states, respectively.
5.1 Electronic structure of spiropyran on Au(111)

bare Au(111) surface (data not shown here).

From the photon energy dependence, SP-U3 and SP-U2 are recognized as unoccupied states at $E_B = (4.24 \pm 0.06) \text{ eV}$ and $E_B = (3.83 \pm 0.02) \text{ eV}$ above the Fermi level, respectively. SP-U1 only appears in the two spectra with highest photon energy. Considering the error bars of these two data points, they cannot be assigned to an occupied or an unoccupied state. In fig. 43, the binding energies for these two possibilities are given. However, additional information is needed. Having a slope of two, the features marked SP-O1 and SP-O3 are attributed to occupied states at binding energies of $E_B = (−1.56 \pm 0.04) \text{ eV}$ and $E_B = (−2.85 \pm 0.03) \text{ eV}$, respectively.

Another photon energy dependence has been performed using 2C-2PPE with the visible output of the OPA and its frequency-doubled UV beam to get additional information on the system. Fig. 45 shows the spectrum with the highest photon energy in the respective series.

Again, the two unoccupied features SP-U3 and SP-U2 are observed and their energetic position is again proved by the photon energy dependence in fig. 46. The feature named SP-O2 shows a slope of three times the visible energy and is therefore assigned to an occupied state at $E_B = (−1.75 \pm 0.04) \text{ eV}$.

As in the 1C-2PPE experiment mentioned above, SP-U1’s slope cannot be determined since it only appears in two spectra of the series. In fig. 45, the energies for the two cases of an unoccupied state are given (visible probed or UV probed). The occupied case is not considered, since the two data points would yield a slope of 1.5. It has to be admitted that the assumption, the two features marked SP-U1 in the 1C and 2C experiments originated from the same state, has not yet been proved, however, considering the shape and position of the peak relative to the other two unoccupied ones and the fact that, interpreted as an unoccupied state, the binding energies of the different measurements have the highest consistency, SP-U1 is assigned to an unoccupied state at $E_B = (3.59 \pm 0.05) \text{ eV}$. Another property, that the features marked as SP-U1 have in common is their disappearance at UV photon energies below approximately 4.8 eV. See also the time-resolved measurement in appendix A.

The spectrum in fig. 45 also shows the surface state (SS) and its spin-off (SS’) which is shifted in energy but shows similar properties as the surface state itself [22].

With the combination of the not tunable 3 eV output of the OPA and the frequency-doubled OPA output in the UV range, another 2C-2PPE series has been performed. Fig. 47 shows the spectrum with the highest UV photon energy in which all features observed in this series appear. For clarity, they have been fitted to the spectrum in the same fashion as described above.

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45 The peak could also represent a final state, however, a slight shift was observed in the two available spectra.
5 SPIROPYRAN ON AU(111) 5.1 Electronic structure of spiropyran on Au(111)

Figure 45: Correlated 2C-2PPE spectrum of SP/Au(111). Here, the binning process is visualized by the solid line while the dots mark an unbinned spectrum. Besides the surfaces state (SS) and its spin-off (SS’), four molecule-induced states are observed. The binding energy with respect to the Fermi level is given for each peak.

Figure 46: Photon energy dependence in the 2C-2PPE experiment with visible and UV light, where the UV is frequency doubled from the visible. Except for SP-U1, all peaks can be assigned to occupied or unoccupied, respectively.
5.1 Electronic structure of spiropyran on Au(111)

Figure 47: Correlated 2C-2PPE spectrum of SP/Au(111) using the 3 eV beam. Five molecule-induced states can be observed. The spectrum has been fitted for demonstration (see text).

Figure 48: Photon energy dependence in the 2C-2PPE experiment using 3 eV and UV light. Only peaks with a slope of zero can be assigned non-ambiguously, since a slope of one might indicate a UV probed or an initial state (because $h\nu_1$ stays unchanged).
Besides the known gold features and hot electrons, two occupied and three unoccupied states induced by the adsorbate are observed in this spectrum, which have all been identified above. Unfortunately, in this series, the photon energy dependence (fig. 48) is not definite, since a state, whose slope is determined to be one, can either be an occupied state (the 3 eV are not tuned!) or a UV probed unoccupied state. However, the information obtained from this experiment confirm (as far as they can) the former results and give additional values for the determination of the binding energies of the involved states.

The states SP-U2 and SP-U3 can, however, be assigned to unoccupied states since they have a vanishing slope. From this experiment, they are assigned binding energies of $E_B = (3.89 \pm 0.02) \text{ eV}$ and $E_B = (4.22 \pm 0.07) \text{ eV}$, respectively. The energetic position of SP-U1 also fits to the argumentation above: $E_B = (3.63 \pm 0.06) \text{ eV}$.

![Figure 49: Dispersion of the surface state and the unoccupied states SP-U2 and SP-U3 as determined from angle-resolved 2PPE experiments. The data have been fitted with parabolas yielding the effective electron mass. The unoccupied states are shown at an intermediate state energy axis (left) while the surface state is displayed versus the initial state energy scale (right).](image)

**Dispersion of the unoccupied electronic states of SP/Au(111)** Angle-resolved measurements have been performed by rotating the sample in front of the analyzer by...
5.1 Electronic structure of spiropyran on Au(111) 5 SPIROPYRAN ON AU(111)

approximately ±20°. As explained in section 2.2.2, this yields the dispersion of the respective state. Of special interest are the unoccupied states near the vacuum level, since a strong dispersion can be a hint to identify them as an image potential state, although it would not be a prove for this hypothesis.

This measurement was performed using the 3 eV beam and the frequency-doubled OPA output in the UV range at 4.93 eV. Thus, the spectrum at normal emission is similar to the one in fig. 47. Since the unoccupied states and the surface state are lying quite close to another, SP-U2, SP-U3 and the surface state have been fitted together to obtain the angle-dependent binding energies shown in fig. 49.

The dispersion curves shown in fig. 49 were fitted using eq. (9). The fit yields the effective mass \( m^* \): for the surface state, one obtains \( m^* = (0.58 \pm 0.09) \, m_e \). This value is larger than the one determined in ARPES\(^{66}\)\(^{[64, 63]}\). Perhaps, the adsorbed molecules alter the surface state’s dispersion.

The unoccupied states SP-U2 and SP-U3 have effective masses of \( m^* = (0.47 \pm 0.09) \, m_e \) and \( m^* = (1.8 \pm 0.8) \, m_e \), respectively. Since image potential state have an effective mass of about one electron mass (see sect. 2.3), SP-U2 can be ruled out as such whereas SP-U3 could be one.

The angle-resolved measurements also showed that the states SP-U1 and SP-O2 show no dispersion, therefore seem to be localized at the molecule.

Electron dynamics at the SP/Au(111) interface Using the visible OPA output and its frequency-doubled, time-resolved 2PPE measurements have been performed on SP/Au(111). Fig. 50 shows such a measurement, in which the unoccupied states SP-U2 and SP-U3 are displayed in a false color plot. As indicated by the schematics above the plot, the right side of \( \Delta t = 0 \) (“time zero”) represents the UV pump / visible probe regime. Time zero has been determined from the fits of the two states, which includes a convolution of the two pulses and a single exponential decay of the state with a lifetime \( \tau \). This is represented by the gray-shaded auto-correlation curve in the lower part of the figure. Normally, one would use the region around the Fermi edge to determine time zero. However, in this case, in this region, no symmetrical cross-correlation curve is observed which might be due to (i) the influence of SP-U3 up to the Fermi edge or (ii) another state located between SP-U3 and the vacuum level.

From the cross-correlation curves, one can observe a shift of the maxima of SP-U2 and SP-U3 with respect to the auto-correlation curve. Also, the fit mentioned above yields lifetimes of \( \tau_{SP-U2} = 38 \, \text{fs} \) and \( \tau_{SP-U3} = 36 \, \text{fs} \). There are no errors stated for these values as the error given by the fitting routine is definitely to small, because (i) depending on the initial guesses, the values vary more than the given error and (ii) for other measurements

\(^{66}\)Angle-resolved photoelectron spectroscopy. \( m^* = 0.37 m_e \)\(^{[63]}\), \( m^* = 0.28 m_e \)\(^{[64]}\).
Figure 50: Time-resolved 2PPE experiment on SP/Au(111). The false color plot shows the correlated 2PPE intensity versus the final state energy and the time delay between pump and probe, $\Delta t$. Below the false color plot, the cross-correlation curves for the two states SP-U2 and SP-U3 are shown as data points with the solid line representing a fit (convolution of two pulses with a single exponential decay). The gray-shaded autocorrelation curve defines $\Delta t = 0$ and is obtained from the fits. Right to the false color plot is the correlated spectrum at $\Delta t = 0$ showing two clear peaks.
under the same conditions, the lifetimes also vary significantly. This may be due to bad data quality of the measurements or a dependence of the lifetime on other parameters such as the exact coverage.

The third unoccupied state SP-U1 is not observable in this measurement. In appendix A an experiment at higher photon energies is shown in which the lifetime of this state is determined to be \( \tau_{\text{SP-U1}} = 8 \) fs. Unfortunately, this value is not more precise than the ones discussed here.

Summing up, it can only be said with certainty that all three unoccupied states visible in 2PPE (SP-U1, SP-U2 and SP-U3) have a small lifetime of less than 50 fs and that the lifetime of SP-U2 is slightly larger than that of SP-U3 while SP-U1 seems to have the shortest lifetime of the three.

States with such a small lifetime seem unlikely to support an isomerization process occurring via an excitation into these states, since the motion of the nuclei occurs at timescales of picoseconds.

![Figure 51: Work function and energetic position of SP-U3 as a function of SP coverage. The blue arrow marks the 850 meV which in theory separate the image potential state from the vacuum level to which it is pinned. In two cases, two data points appear at the same temperature which is due to the necessary change of the photon energy because of the decreasing work function.](image)

**Coverage dependence** In order to see the emergence of the molecule-induced states, a coverage dependent series has been performed in which cycles of dosing for 15 s and heating to a temperature of 253 K, at which SP undergoes a transition to an ordered phase [90, 21], have been repeated and 2PPE spectra have been recorded between the
cycles. The total coverage was determined after the 2PPE measurements via temperature programmed desorption (TPD) and since the dosing times were identical in all cycles, the coverage of each cycle was calculated as the fraction of the final coverage according to the respective dosing time.

Although the emergence of molecule-induced states could not be observed, as expected, their energy could be monitored with increasing coverage. Fig. 51 shows a continuous decrease of the work function starting from 5.46 eV for the bare gold surface to approximately 5.1 eV for the full monolayer. There seems to be no saturation of the decrease even for approximately 2.5 ML.

Unlike the work function, the unoccupied state SP-U3 remains constant at an energy of $E_B = (4.20 \pm 0.03)$ eV above the Fermi level. The only coverage dependence for this state is that it is only observed for coverages larger than one half monolayer.

The coverage dependence of the binding energy for SP-U1 and SP-U2 is difficult to determine from the conducted experiments in which those peaks overlap and shift when the photon energy was changed because of the decreasing work function.

In section 2.3, it has been explained that image potential states (IPS) are pinned to the vacuum level, i.e. the $n = 1$ IPS is ideally located 850 meV below it. On the other hand, the $n = 1$ IPS for bare Au(111) is experimentally known to lie between $(0.60 \pm 0.05)$ eV [68] and $(0.42 \pm 0.16)$ eV [54]. At first sight, SP-U3 can not be assigned to an IPS since its energy is not pinned to the vacuum level.

This could however be explained by the growth of SP in ordered islands: The IPS would be pinned to the vacuum level of SP/Au(111) as inside an island. The work function measured in 2PPE on the other hand is the average of the work functions of the islands and the bare spots which are within the laser spots and would therefore decrease with increasing SP coverage while the work function inside the island would remain constant and therefore, the IPS would not be pinned to the average work function.

The argumentation above is only valid for growth in islands, which has been found for SP in the monolayer [21]. The growth in the multilayer has not been analyzed e.g. by STM so far (to the author’s knowledge).

Two cases can now be considered if one assumes SP-U3 to be an IPS. (i) The SP multilayer does not grow in islands. In this case, SP-U3 should be pinned to the vacuum level for coverages higher than 1 ML. (ii) SP forms ordered islands in the second (and maybe higher) layer. Then, the peak at the observed position should become less intense (and finally vanish) and another peak at a lower energy should emerge while the second layer is formed which would also not be pinned to the vacuum level.

SP-U3 is neither pinned to the vacuum level (at any coverage) nor does it lose intensity while another peak emerges. It can therefore be ruled out that it originates from an IPS.
It must be admitted, that the utilized procedure, in which more molecules were always deposited on top of the previously measured coverage, is not optimal. Ideally, one should have measured a prepared coverage, then the coverage should have been checked by TPD and a new sample should have been prepared after a whole sputtering/annealing cycle.

5.2 Thermally induced ring-opening reaction

It has been shown in a number of previous experiments that spiropyran on Au(111) undergoes a structural change at a temperature of around 320 K [90, 21, 91]. This change has been attributed to an isomerization (ring-opening reaction) toward the merocyanine form. See section 2.5.2 for more details.

In the following, the change of the electronic structure is investigated with 2PPE as the molecules undergo the ring-opening reaction. The measurements were performed with a combination of the visible OPA beam and its frequency-doubled. In order to observe the changes continuously, the SP sample was annealed at a certain temperature for 10 s and subsequently cooled down again for measurement. The annealing was done in steps of 10 K and later 5 K. The photon energy had to be changed twice in this experiment in order to avoid direct photoemission to come up as the work function decreases during switching. On the other hand, high photon energies are required to distinguish the states in the spectra.

Fig. 52a shows the change of the highest lying features near the vacuum level. Up to approximately 320 K, SP seems unaffected. Around the temperature of 323 K, which was used in this thesis and in [90] as the default 'switching temperature', the work function decreases significantly by around 0.5 eV very quickly. SP-U3 disappears at this point and MC-U3 appears. The latter state’s peak shifts to lower binding energies with increasing temperature, following the decrease of the work function in this area.

The peak representing SP-U2 in the spectrum starts moving to lower energies at the 'switching point' of 323 K. Again, the decrease in energy follows that of the work function. From the energetic position, one can not distinguish if SP-U2 and MC-U3 arise from the same state which undergoes a continuous transition or if SP-U2 disappears and at the same position, MC-U3 emerges as an exclusive feature of the switched form. Anyway, MC-U3 lies approximately 850 meV below the vacuum level and shifts with it which makes it seem to be an image potential state (IPS).

Parallel to the changes near the vacuum level, (i) the state SS’ disappears for MC and (ii) the Shockley surface state (SS) shifts to lower binding energies with increasing annealing.

47 The exact value depends on the coverage. See the coverage dependent measurements for SP and MC, respectively.
48 The notation for the MC states is not yet justified at this point, but already used for convenience.
49 As far as one can speak of “same” for two different isomers...
5  SPIROPYRAN ON AU(111)  5.2  Thermally induced ring-opening reaction

Figure 52: Temperature-induced changes in the electronic structure. a) Binding energy of the states near the vacuum level and work function depending on the annealing temperature. The measurements were performed at LN$_2$ temperatures. Changes occur at the 'switching temperature' of 323 K given in [90]. b) Sudden disappearance of SP-O1 during switching. Its intensity (measured relative to the intensity of the d-band feature II) decreases to the background level (secondary electrons) around 320 K.
temperature.

Except for the states mentioned above, all other features remain unchanged during switching, as has also been observed with a 3 eV/UV measurement which was performed in the same fashion as the here mentioned one using visible light. In the 3 eV spectra, the feature SP-O1 is observed for low temperatures. In fig. 52b, one can see the disappearance of this state at the 'switching point'. There, the intensity of the peak reduces to the level of the secondary electron background, so that this feature can be assigned to SP only. A shift of this peak to another energy is not observed. Perhaps this state represents a molecular orbital which is located at the C-O bond, which is broken in the isomerization process.

The annealing time of 10 s is relatively small compared to similar experiments on molecular switches. Possibly, the slow and for several features parallel change after the 'switching temperature' of 323 K is an effect of the small annealing times and not of a temperature dependence of the binding energy which extends beyond this point. Note, that the 'switching temperature' can not be seen as a sharp point, since because of the statistical distribution of thermal energy (Arrhenius-like expression), switching is possible at any temperature. However, the reaction's speed will of course depend highly on the temperature. The 'switching temperature' of 323 K is simply introduced as a reference point which was also used in previous experiments [90].

In the following section, the electronic structure of MC is investigated further to characterize the respective states in terms of electron dynamics, dispersion and coverage dependence.

5.3 Electronic structure of merocyanine on Au(111)

After the ring-opening reaction to the MC form on the surface, one must assume that the electronic structure of the molecules changes. For this, evidence was presented already in the previous section. The data given there are only based on switching experiments, in which the temperature was varied and the change in the spectra was analyzed. The spectral features appearing for the open form have however not been investigated closely, e.g. by means of photon energy dependent measurements, dispersion or electron dynamics. These measurements are presented in this section.

To identify the states observed before, a photon energy dependent series of correlated 2C-2PPE spectra was taken from MC. Again, the spectrum in fig. 53 stands representative for all the measurements in this series. In this spectrum, which was taken after heating the sample to the 'switching temperature' of 323 K, four features are visible, one at the secondary edge, which is attributed to MC-O1, an occupied state at $E_B = -1.77$ eV. This assignment will be justified later and does not become clear from this measurement.
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Figure 53: Correlated 2PPE spectrum of MC/Au(111) after heating to 323 K. The dots symbolize the unbinned spectrum. The high energy part of the spectrum has been fitted (red line) to obtain the three states involved.

Figure 54: Photon energy dependence for MC investigated with visible and frequency-doubled UV light. The surface state and MC-U3 can be assigned while for MC-U4, too few data points are available.
since the peak shifts to lower final state energies and hence below the vacuum level already after few changes in the photon energy.

MC-U3 can be assigned to an unoccupied state located at $E_B = (3.74 \pm 0.03)$ eV, thus 770 meV below the vacuum level, which means the state is UV pumped. The assignment is based on the photon energy dependent measurement, which can be seen in fig. 54 where the peak shows a slope of one. In the same way, the surface state (SS) is identified. MC-U4 can not be assigned by this photon energy dependent measurement since the peak only appears in two spectra. Its position becomes clear from the time-resolved measurements (see fig. 57).

In fig. 53 the three peaks have been fitted on top of an exponentially decaying secondary electron background, which is cut off by a Fermi function (fit components in blue).

In order to obtain more information, an analogous experiment has been performed using the OPA’s untunable 3 eV beam and the frequency-doubled visible output. Fig. 55 shows the spectrum of this series with the highest photon energy ($\hbar \nu_2 = 4.37$ eV).

Near the secondary edge, the d-band features at $E_B = -2.58$ eV and $E_B = -1.98$ eV are observed. They show a slope of one in the photon energy dependence which in this experiment is not unique since the 3 eV beam’s photon energy is not varied and hence, a slope of one can mean an occupied state or a UV probed unoccupied state. However, these features are well known and therefore assigned to the d-bands. The surface state also has a slope of one but is identified from the time-resolved measurements shown below.

MC-U2 is a very weak and broad feature, but after consideration of all spectra, it can be said with certainty that there is a peak. It is assigned to a UV probed unoccupied state in a time-resolved measurement later on (see fig. 58) and, in this case, has a binding energy of 1.8 eV above the Fermi level. This value would coincide with the LUMO+1 as seen in scanning tunneling spectroscopy (STS) [72] (see sect. 2.5.1).

At the edge of the gold d-bands, the feature labeled MC-O1/MC-U1 is found which could be assigned to either an occupied state located at $E_B = -(1.77 \pm 0.03)$ eV or a UV probed unoccupied state at $E_B = (1.34 \pm 0.03)$ eV. Unfortunately, it does not show up in the UV only spectra where it could be assigned definitely nor does it exhibit a lifetime in the time-resolved measurements. As an occupied state, it would have the same position as SP-O2 for SP/Au(111), could hence be a molecular orbital located in a part of the molecule which is only slightly affected by the isomerization, e.g. at the nitro-group. If attributed to an unoccupied state, it would energetically coincide with the LUMO found in STS at 1.3 eV above the Fermi level.

Overlapping with the surface state in the high energy part of the spectrum, MC-U3 is identified as a 3 eV-probed unoccupied state located at $E_B = (3.78 \pm 0.03)$ eV. It has
Figure 55: Correlated 2PPE spectrum of MC/Au(111) using the 3 eV beam and the frequency-doubled OPA output ($h\nu_2 = 4.37$ eV). Despite the usual gold features, three molecule-induced peaks are observed. The fitted peaks are displayed for clarity as blue Gaussian peak shapes.

Figure 56: Photon energy dependence for the 3 eV/UV measurement. Only MC-U3 can be assigned with certainty, the other features are either UV probed or occupied.
5.3 Electronic structure of merocyanine on Au(111)  

SPIROPYRAN ON Au(111)

a slope of zero in the photon energy dependence, as seen in fig. 56, hence its position is now proved by both the visible/UV and the 3 eV/UV measurements.

As the photon energy dependent measurements can not ultimately assign MC-U2 and MC-U4 to unoccupied states, their location shall be proved in the following by time-resolved measurements. The dynamics seen there as well as the subsequently discussed dispersion and coverage dependence may help clarify the nature of these molecule-induced states.

Electron dynamics at the MC/Au(111) interface  

Since the photon energy dependent experiments for MC/Au(111) could not determine the position of all visible peaks with certainty, time-resolved measurements can give additional information: when a peak exhibits a lifetime, its assignment is definite since it must be an unoccupied state and the lifetime shows which is the pump and which is the probe beam by the 'direction' of the lifetime (toward positive or negative delay).

Fig. 57 shows a time-resolved measurement using the OPA’s visible output ($h\nu_1 = 2.26$ eV) and its frequency-doubled beam ($h\nu_2 = 4.48$ eV). The state in the middle represents the Shockley surface state (SS), as indicated by its binding energy of $-0.43$ eV and its vanishing lifetime. In this measurement, the SS serves as a reference for time-zero and pulse length as the Fermi edge shows an asymmetric shape due to the width of MC-U4.

At a higher final state energy, MC-U4 can now be assigned to an unoccupied state at 4.28 eV considering the cross-correlation in the lower part of the figure. Although the lifetime is 5 fs, which is given in the fit using two pulses and a single exponential decay, is very short and probably within the error of the fit, as has been explained before (see section 5.1), there is a clear shift of the peak toward positive delays which indicates the unoccupied nature of this state.

MC-U3 has the highest intensity of all and shows a more pronounced shift to positive delays. The fitted lifetime of $\tau = 20$ fs is also higher than that of MC-U4 which makes the assignment to an unoccupied visible-probed state certain. From the false color plot, one might have the impression, that MC-U3 slightly shifts to lower energies with increasing positive delay. This impression is due to the overlap with the surface state peak which makes the 'left' part of the MC-U3 peak look higher-lying.

As discussed in section 5.1, the fitted values for the lifetimes are given without a fitting error since it appears too small. Instead, it shall only be stated that the lifetimes are certainly shorter than 50 fs and that MC-U4 has a shorter lifetime than MC-U3.

Another TR-2PPE experiment was performed using the 3 eV output of the OPA and the UV beam. Figure 58 shows that certainly two unoccupied states are observed,
Figure 57: TR-2PPE measurement of MC/Au(111) using visible and UV light. The false color plot is a zoom-in to the high energy region of the spectrum. Three states can be observed close to each other, two of which have a short lifetime to positive delays, i.e. they are visible-probed. The surface state between them gives the gray-shaded autocorrelation function in the lower part of the figure. The cross-correlation data points are shown as dots while the solid line indicates the respective fit.
Figure 58: TR-2PPE experiment using the 3 eV output of the OPA. UV probed states would have a lifetime toward positive delay, as indicated by the drawing above the plot. Except for the surface state (SS), three states are observable, although MC-U4 shall be considered with care here, as it manifests only in a slightly elevated Fermi edge with a short lifetime. MC-U2 shows an unusual cross-correlation (see text). The solid cross-correlation lines represent the fit through the data points (dots).
one of which is MC-U3 which has been investigated above. Its fitted lifetime in this measurement yields 27 fs, which is in agreement with the previously shown experiment.

Here, not the surface state serves as auto-correlation function, but it is deduced from the fits of the other peaks. This is because the surface state peak is superimposed by the peak of MC-U3, more than it was in the other measurement above.

MC-U4 is only faintly visible, but the cross-correlation taken around the position of the Fermi edge yields a short lifetime and, judging from the secondary electron background, the Fermi edge seems a bit elevated. However, these hints are not clear enough to draw reliable conclusions concerning MC-U4 from this experiment.

Fig. 58 shows a very interesting feature which is not observed in the visible/UV measurements. The peak labeled MC-U2 has been observed in fig. 55 before and its energetic position of 1.8 eV would coincide with the LUMO+1 seen in STS [72]. Its cross-correlation is shown on a logarithmic scale in solid blue in the figure. This curve shows (i) a lifetime on the order of 100 fs which is attributed to hot electrons and (ii) a second, very slow decay on the order of picoseconds. The curve has not been fitted with a biexponential decay model in order to obtain more exact values for these two lifetimes since the data quality of this particular measurement would make especially the longer lifetime questionable. Further measurements should be carried out to determine this lifetime. There, a much higher maximum pump-probe delay should be chosen.

In order to exclude the long lifetime to be an artefact or a result of background subtraction (as for TBA, see sect. 4.2), the data have been evaluated with great care: An artefact resulting from space change can be excluded as in this case, a broadening of the two-color spectrum should be observed, which is not the case.

The background subtraction for these kind of measurements is done by subtracting two separately recorded pump beam only and probe beam only spectra from every data point in the false-color plot, respectively. Considering a cross-correlation curve, the same value is subtracted for all data points included in it, i.e. for all delays. Background subtraction hence results in a constant offset of the cross-correlation curve. Therefore, it can be excluded that the slow decay is actually not a decay, but an elevated zero-level due to background subtraction, because on the negative delay side, the curve goes down further. Also, a close examination shows that in the region above +250 fs delay there is a decrease of the 2PPE signal with time.

In order to exclude an effect of some kind which is a result of the hot electrons, the cross-correlation trace for $E_{\text{final}} = 5.9$ eV is given in the figure as a dotted blue line. There, the short decay from the hot electrons is also visible but the elevated signal for higher delays is not observable.

After careful evaluation, MC-U2 is hence assigned to an unoccupied UV probed state at
1.8 eV above the Fermi level having a very long lifetime. However, further experiments are needed to determine the lifetime more closely.

The long lifetime of MC-U2 might be attributed to the projected band gap of Au(111), in which it is lying (see fig. 61 and sect. 2.4). Therefore, the electronic coupling to the substrate is reduced which also explains the weak signal in the 2PPE spectrum, since the population is ineffective due to the low density of states in the band gap.

Figure 59: Dispersion experiment on MC/Au(111). The correlated 2PPE spectra for several angles are shown in rainbow colors. The normal emission spectrum is enlarged (3x) to show the superposition of MC-U3 and the surface state (SS). The inset shows the binding energy depending on the momentum parallel to the surface and the results of a parabolic fit.

Angle-resolved measurements of MC-U3 yielding its dispersion In order to investigate the observed states further, an angle-dependent experiment has been conducted using the 3 eV and UV beam, respectively. The correlated 2C-2PPE spectra of this series are shown in fig. 59. One can see that with the changing angle of the sample (α), the intensity of the features decreases. The d-band feature visible in this spectrum as well as MC-O1/MC-U1 and MC-U2 show no observable shift with the angle change. The feature near the Fermi edge, consisting of surface state and MC-U3 however shifts to higher energies.

The normal emission spectrum is enlarged in the figure and a fit using two Gaussians is shown (red line) to match the peak form at the high energy end of the spectrum.
the surface state is known to have a significant dispersion (see sect. 2.4), the feature was fitted for all spectra, yielding the binding energy $E_B$ of both peaks for all the angles.

The inset in the figure shows the binding energy of MC-U3 relative to the Fermi level, which has been extracted from the fit for each of the spectra versus the parallel momentum which is calculated from the kinetic energy of the peak via eq. (8). Due to the SS which is superimposed onto MC-U3, the error bars are quite large but nevertheless a fit can be performed to obtain at least an estimate of the effective mass. The parabolic dispersion described by eq. (9) has been fitted to the data yielding a binding energy at zero momentum of $E_{B,0} = (3.74 \pm 0.02) \text{ eV}$ and an effective mass of $m^* = (2.6 \pm 2.1) m_e$.

The error for the effective mass is so high that no definite conclusions can be drawn from the measurement but it can be said that the state has a non-vanishing dispersion.

Unfortunately the highest lying state of the switched form MC-U4 is not observed in this series.

Figure 60: Work function and the binding energy of the two highest lying states of MC/Au(111) as a function of the coverage. The distance of 850 meV, which points toward an image potential state, is indicated by the blue line.

Coverage dependence As a final characterization of MC/Au(111) and especially the two unoccupied states near the vacuum level, a coverage dependent series has been performed, in which SP molecules were evaporated onto the sample, subsequently heated to the 'switching temperature' of 323 K [90] and cooled to liquid nitrogen temperatures for measurement. The next higher coverage was then prepared by simply evaporating
more SP molecules onto the partially covered surface and heating to the 'switching temperature' again.

Also, the question arises, whether the molecules in the multilayer regime switch at all and if they do, the 'switching temperature' is not necessarily the same as in the first monolayer, since the contact the substrate is of course reduced. Perhaps the stability inversion does not occur in the multilayer since it is mainly attributed to the interaction of the substrate and MC.

The measurement was done using visible light from the OPA and its frequency doubled. The photon energy had to be changed twice to compensate for the decreasing work function. The coverage was again determined doing a TPD after the experiment which yields the final coverage. Since the dosing procedure and especially the dosing time was exactly the same during the whole experiment, the coverage after each dosing cycle can be obtained from the total coverage.

Fig. 60 shows the change of the work function and the two states close to the vacuum level during this experiment. The work function decreases from 5.46 eV of bare Au(111) to around 4.7 eV for a full monolayer and saturates below 4.4 eV in the first multilayer regime. Hence, the work function is decreased by over 1 eV upon adsorption of MC which is most likely due to the zwitterionic nature of MC.

The state MC-U4 appears only in the sub-monolayer regime and is quenched in the multilayer. Its energetic position is also not dependent on the coverage but remains at $E_B = (4.16 \pm 0.03)$ eV. It can hence be excluded that MC-U4 originates from an image potential state.

The binding energy of MC-U3 is depending on the MC coverage and is present also in the multilayer. It is pinned to the vacuum level with an energetic difference of approximately 850 meV. This is an interesting fact since this state also shows a dispersion. The energetic position, the dispersion and the pinning to the vacuum level suggest that MC-U3 is an image potential state with $n = 1$.

5.4 Conclusion

The electronic structure of spiropyran on Au(111) in its closed (SP) and open (MC) form were investigated using two-photon photoemission. Although the photoisomerization of spiropyran is quenched on this surface, it is an interesting system to study since the knowledge of its electronic structure might contribute to the development of derivatives which are photochromic in the adsorbed state. However, in order to interpret the observed electron dynamics, further information is needed (e.g. calculations of the potential energy surfaces). Still, a number of conclusions can be derived and this work can be seen as a contribution to the research performed on spiropyran at Au(111) using
Figure 61: Overview over the electronic structure of SP/Au(111) in the SP and MC forms, respectively. The yellow shaded region in the center represents the bare Au(111) surface while the states marked in blue on the left and right side refer to the adsorbate covered surface for 1 ML. The results of STS are added in gray. Φ refers to the respective work function. The “?” between MC-O1 and MC-U1 indicates that the assignment of the respective peak is not clear.

Table 2: Summary of the electronic states found for SP/Au(111) and MC/Au(111). $E_B$ refers to the binding energy with respect to the Fermi level, $m^*$ is the effective mass, $E_{vac}$ is the vacuum level. The lifetimes $\tau$ are taken from the measurements shown above. See the respective sections for a comment on these values. An effective mass of “$\infty$” means no dispersion.
various other techniques \cite{91}.

For SP, three occupied and three unoccupied states are observed in 2PPE. In case of the open form, three unoccupied states are found and one which can not definitely be assigned. Furthermore, the work function has been closely monitored. Fig. 61 and tab. 2 give an overview over the findings in this work. The values for the binding energies given there are stated under consideration of all measurements that were evaluated and the corresponding errors therein.

In case of the closed SP form, three occupied states are observed. One of the states, SP-O2, matches energetically with MC-O1/MC-U1 (if assigned to an occupied state). Therefore, SP-O2 and MC-O1 are assumed to be in fact the same orbital which is not affected during isomerization, perhaps because it is located away from the photochromic center, e.g. at the nitro group. It is therefore considered henceforth as the SP’s HOMO-1 and the MC’s HOMO. Consequently, SP-O1 and SP-O3 are assigned to the HOMO and HOMO-2, respectively. Since they do not appear in the open form, one can assume that their spatial distribution extends to parts of the molecule which are changed by switching, e.g. at the C-O bond.

SP-U1 is the only unoccupied state which does not show dispersion and is assigned to the LUMO+1. This nomenclature pays tribute to the STS measurement and the there observed LUMO which was not seen in 2PPE. The other two unoccupied states have a dispersion.

SP-U2 shows a dispersion but lies 1.3 eV below the vacuum level. Because of the large energy difference to the vacuum level, it can not be assigned to an image potential state. The dispersion it shows on the other hand makes it unlikely that SP-U2 is a molecular orbital. It is therefore assigned to a state localized at the interface between substrate and adsorbate (“IS 1”).

SP-U3 lies only 0.9 eV below the vacuum level which would fit to an IPS but the coverage dependence of its energetic position (which is fixed) does not fit to such a state (see sect. 5.1). Since it also exhibits a dispersion, it is also assigned to the substrate/molecule interface as “IS 2”.

The interpretation for the MC states seems not so complex. MC-U3 has a dispersion, is pinned to the vacuum level of the system (to which due to the chain structure, the argumentation in section 5.1 does not apply anymore) and lies approximately 850 meV below it. These are strong hints that MC-U3 is the first image potential state.

However, the higher lying state MC-U4 is too low to be the second IPS (assuming a quantum defect $a$ in eq. \cite{26} of zero\footnote{The assumption that $a$ is close to zero is justified by the fact that MC-U3 lies 860 meV below the vacuum level which is almost the value obtained from eq. \cite{26} assuming $a = 0.$} and is not pinned to the vacuum level. It could
be a molecular orbital, LUMO+2, or a state located at the interface to the substrate, which in case of MC has a very different character compared to the SP case (due to stronger van der Waals interaction and the zwitterionic character of MC). As shown by the temperature series in fig. [52], MC-U4 is most likely not identical to SP-U3, although they lie quite close to each other.

The states MC-U1/MC-O1 and MC-U2 which are lying in the projected band gap match the position for LUMO and LUMO+1 found in STS [21]. Therefore, MC-U2 is assigned to the LUMO+1. MC-U1/MC-O1 has been assigned to the HOMO because of its energetic match to the SP HOMO-1 and because the respective peak shows no lifetime, however, if the feature is assigned to an unoccupied state, it would lie close to the LUMO as observed in STS. The feature can therefore interpreted as a signal from electrons resonantly pumped from the HOMO to the LUMO which are subsequently probed from there.

Unfortunately, the states in the projected band gap could not or only weakly be observed. This is attributed to the low density of states and thus the ineffective population by the pump beam. On the other hand, this would be an explanation for the extraordinarily large lifetime of the LUMO+1 in the open MC form. This would imply that this state has no faster decay channel than the one via the few gold states in the projected band gap.

A state with a long lifetime on the scale of picoseconds could in principle host an electron long enough to let the nuclei perform an isomerization. Since this is not the case, it seems that the LUMO+1’s potential energy landscape is such that it does not allow a ring closing reaction, probably due to the strong bond of MC to the metal substrate. On the other hand, the MC’s LUMO might fulfill this requirement but does not exhibit a measurable lifetime, perhaps due to fast decay channels from this orbital into the substrate.

The fact that the SP LUMO could not be observed in 2PPE might also be due to weak electronic coupling with the surface which would make electron transfer from the substrate (pumping in 2PPE) ineffective. Note, that SP can undergo a ring-opening reaction in the STM junction by electron attachment to the LUMO [21]. This shows that the potential energy surface of the molecule (in case of a negative ion resonance) supports the isomerization. The low electronic coupling to the substrate might therefore quench the photochromism of spiropyran on the surface since one can assume that a light-induced electron transfer from the substrate to the LUMO should also trigger a ring-opening reaction via a negative ion resonance.
6 Summary and outlook

In this work, two molecular switches, namely TBA$^{51}$ and spiropyran$^{52}$ in direct contact with the Au(111) surface have been investigated using two-photon photoemission (2PPE). Additionally, the binding energy of TBA to the substrate has been determined.

**TBA** Using temperature programmed desorption (TPD), the binding energy of TBA to the Au(111) surface has been determined to be $E_B = (1.69 \pm 0.15)$ eV. This value represents the “single molecule” case, as extrapolated from the coverage dependent binding energy in the limit of zero coverage. Furthermore, the binding energy decreases with increasing coverage indicating repulsive inter-molecular interaction.

The previously observed photoswitching of TBA/Au(111) has been confirmed. The focus however was put on the lowest unoccupied molecular orbitals (LUMOs) of the two isomers since this system has been investigated extensively in the past. The binding energy of the trans-LUMO was found to be 1.7 eV with respect to the Fermi level as previously found in scanning tunneling spectroscopy (STS) and 2PPE while the cis-LUMO could not be seen in the 2PPE spectra. Contrary to the mentioned past 2PPE experiments, in this work no picosecond lifetime of the trans-LUMO could be observed.

**Spiropyran** Both for closed spiropyran (SP) and its open merocyanine form (MC), the electronic structure has been determined by 2PPE and the ultrafast electron dynamics of the unoccupied states (i.e., their lifetimes) has been investigated in time-resolved 2PPE experiments. Particularly the change of the electronic structure during thermally induced ring-opening was monitored.

For SP, three unoccupied and three occupied states are observed. The occupied states are assigned to HOMO$^{53}$, HOMO-1 and HOMO-2, respectively. Unlike in STS, the LUMO could not be found at all in 2PPE which is attributed to weak electronic coupling with the substrate. However, the LUMO+1 is observed having a very short lifetime of around 10 fs as well as two dispersive states with a lifetime of less than 50 fs which are assigned to states at the substrate/molecule interface.

Upon heating to 323 K, the work function decreases by around 0.5 eV, depending on the exact coverage. Furthermore, changes in the electronic structure are found: while SP’s HOMO and HOMO-2 are no longer found after annealing, the SP HOMO-1 peak remains and is assigned to the MC HOMO. The structure of the unoccupied states is completely changed for the open molecule. Since the SP’s HOMO-1 is not affected

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$^{51}$3,3’,5,5’-tetra-tert-butylationobenzene  
$^{52}$1,3,3-trimethylindolino-6’-nitrobenzopyrylospiran  
$^{53}$Highest occupied molecular orbital
during the ring-opening reaction, one can assume that it is not located at the broken C-O bond.

The electronic structure of MC shows only one occupied state, the HOMO, which however might be resonantly excited via the LUMO in 2PPE. However, this peak does not exhibit a measurable lifetime. In full consistency with STS, the merocyanine’s LUMO+1 is found and shows a picosecond scale lifetime. Furthermore, the first image potential state (IPS) is observed (lifetime around 20 fs) as well as another unoccupied state which might be assigned to a molecular orbital (LUMO+2) or a state originating from the substrate/molecule interface (IS) as for spiropyran. This state shows a very short lifetime of less than 10 fs.

**Outlook**  The findings of this thesis show that the strength of electronic coupling between the adsorbed molecular switch and the substrate is crucial for the photochromic functionality. In order to trigger an isomerization also on the surface, an excited state must (i) have a long enough lifetime, (ii) its potential energy surface must allow such a reaction and (iii) an effective excitation mechanism must be accessible by light (either intra-molecular or substrate-mediated).

Two effects are competing with each other: on the one side, decoupling the molecule is necessary to avoid fast electronic decay into the substrate but on the other hand this decoupling reduces the efficiency of charge transfer which is necessary for photoisomerization. Tuning the coupling strength precisely by changing the molecule or the substrate is therefore important.

Further experiments with spiropyran derivatives (e.g. by attaching spacer legs) promise to be interesting as a fine tuning of the electronic coupling strength might restore photochromism on the surface. Another interesting approach is a change of the substrate. Schulze et al. used a Bi(110) semi-metal surface to reduce the electronic coupling to the substrate. For SP/Bi(110), they indeed observed photo-induced switching from the SP to the MC form.
A  Electron dynamics of the state SP-U1

In section 5.1, the electron dynamics of SP/Au(111) have been investigated. Of the three unoccupied states found, the dynamics of two was shown in fig. 50 yielding short living states SP-U2 and SP-U3. In the there shown and discussed measurement, SP-U1 is not visible.

Fig. 62 shows a measurement at higher photon energies, in which SP-U1 is visible along with the two other unoccupied states, although SP-U2 is very weak.

Figure 62: TR-2PPE measurement on SP/Au(111). The false color plot shows the correlated 2PPE intensity as a function of the final state energy and the pump-probe delay. Attached to it are the cross-correlation curves for the surface state (SS), SP-U1 and SP-U3. On the right, the 2PPE spectrum for $\Delta t = 0$ is shown.
In this measurement, the surface state is very dominant and serves as the gauge for time zero ($\Delta t = 0$). Its cross-correlation curve is shown in gray in the lower part of the figure.

The cross-correlation curves of SP-U3 and SP-U1 have been fitted with a convolution of the pulses and a single exponential decay with lifetime $\tau$ as well as another exponential decay to negative delays taking the hot electrons into account. For SP-U3, the lifetime of $\tau_{\text{SP-U3}} = 18\,\text{fs}$ is different from the value obtained in the other measurement shown in section 5.1. This issue was treated in the mentioned section. The cross-correlation curve fit for SP-U1 gives $\tau_{\text{SP-U1}} = 8\,\text{fs}$ in the visible-probed regime, however this value is not more reliable than those of the other unoccupied states. Furthermore, the curve shows a significant lifetime in the UV-probed regime which results from hot electrons which are well visible in the false color plot at low energies.
B Fragmentation patterns

The fragmentation patterns of the molecules in this thesis were recorded using the quadrupole mass spectrometer (QMS). Just like in a rest gas analysis (RGA), the QMS mass is varied while the QMS signal is monitored. The RGAs shown below were recorded during evaporation. A prominent peak in the RGA is usually chosen to monitor the molecule e.g. in temperature programmed desorption (TPD).

![Fragmentation pattern for TBA](image1)

Figure 63: Fragmentation pattern for TBA. The peak at 190 amu was chosen as a marker. This resembles a benzene ring with two tert-butyl legs. Those legs each have mass 57 amu which is also a prominent peak.

![Fragmentation pattern for spiropyran](image2)

Figure 64: Fragmentation pattern for spiropyran. Here, \( m = 159 \text{ amu} \) is chosen as marker. It resembles the 1,3,3-trimethylindolino fragment.
C  Background subtraction

In a 2PPE experiment, one can not measure the correlated signal (i.e. only processes induced by both beams together) directly, since it is always superimposed on the signal from one-color processes of the respective beams. These signals have to be subtracted in order to obtain the correlated spectrum.

Fig. 65 shows the uncorrelated spectrum in black which is the 'bare' spectrum obtained upon illumination with both beams (in temporal overlap). The yellow and blue spectra represent the 3 eV and UV only spectra, respectively. The red spectrum is the correlated one obtained by subtracting pump and probe spectra from the uncorrelated one.

From the overlap of UV and uncorrelated spectra around $E_{\text{final}} = 8 \text{ eV}$, one can see that in this region, which due to energy conservation, no 2C-2PPE processes can reach, the two spectra overlap perfectly and the resulting correlated signal is a flat line (which in this logarithmic plot is maybe not so obvious).

If the two beams are not in temporal overlap, the correlated signal should be a flat line, except for long-living states' peaks.

Figure 65: Background subtraction. The example is taken from a measurement on MC/Au(111) using the OPA's 3 eV beam and the frequency-doubled OPA output (UV). Note the logarithmic scale.
D  Acronyms

1C-2PPE  One-color two-photon photoemission
1PPE    Photoemission employing one photon (in contrast to 2PPE)
2C-2PPE  Two-color two-photon photoemission
2PPE    Two-photon photoemission
ARPES   Angle-resolved photoelectron spectroscopy
BBO    \(\beta\)-barium-borate (crystal)
CCD     Charge-coupled device
CFD     Constant fraction discriminator
cw      Continuous wave (laser)
DNA     Deoxyribonucleic acid
DOS     Density of states
fcc     Face-centered cubic
FET     Field-effect transistor
FWHM    Full width (at) half maximum
GPIB    General Purpose Instrumentation Bus
GVD     Group velocity dispersion
HOMO    Highest occupied molecular orbital
HREELS  High-resolution electron energy loss spectroscopy
HV      High voltage
IPES    Inverse photoelectron spectroscopy
IPS     Image potential state
IR      Infrared (light)
IS      Interface state
LUMO    Lowest unoccupied molecular orbital
MC      Merocyanine
MCP     Multi channel plate
**ACRONYMS**

**ML** Monolayer

**NEXAFS** Near-edge X-ray absorption fine structure

**NIR** Negative ion resonance

**NOPA** Noncollinear optical parametric amplifier

**OPA** Optical parametric amplifier

**PES** Potential energy surface

**PID** Proportional integral derivative

**PIR** Positive ion resonance

**PSS** Photostationary state

**QMS** Quadrupole mass spectrometer

**RegA** Regenerative amplifier

**RGA** Rest gas analysis

**SP** 1,3,3-trimethylindolino-6’-nitrobenzopyrylospiran or spiropyran

**SS** Surface state

**STM** Scanning tunneling microscopy

**STS** Scanning tunneling spectroscopy

**TBA** 3,3’,5,5’-tetra-tert-butyl-azobenzene

**TOF** Time-of-flight spectrometer

**TPD** Temperature programmed desorption

**TR-2PPE** Time-resolved two-photon photoemission

**UHV** Ultra-high vacuum

**UPS** Ultraviolet photoelectron spectroscopy

**UV** Ultraviolet (light)

**XC** Cross-correlation (curve)

**XPS** X-ray photoelectron spectroscopy
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Eidesstattliche Erklärung gemäß § 17 Abs. 7 DPO


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