

## The influence of the electronic structure of adsorbate–substrate complexes on photoisomerization ability

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## The influence of the electronic structure of adsorbate–substrate complexes on photoisomerization ability

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**Abstract.** We use time-resolved two-photon photoemission to study two molecular photoswitches at the Au(111) surface, namely azobenzene and its derivative tetra-*tert*-butyl-azobenzene (TBA). Electronic states located at the substrate–adsorbate interface are found to be a sensitive probe for the photoisomerization of TBA. In contrast to TBA, azobenzene loses its switching ability at the Au(111) surface. Besides the different adsorption geometries of both molecules, we partly attribute the quenching in the case of azobenzene to a shift of the highest occupied molecular orbital (HOMO) with respect to the gold d-bands, which renders the hole transfer involved in the photoisomerization mechanism of TBA inefficient.

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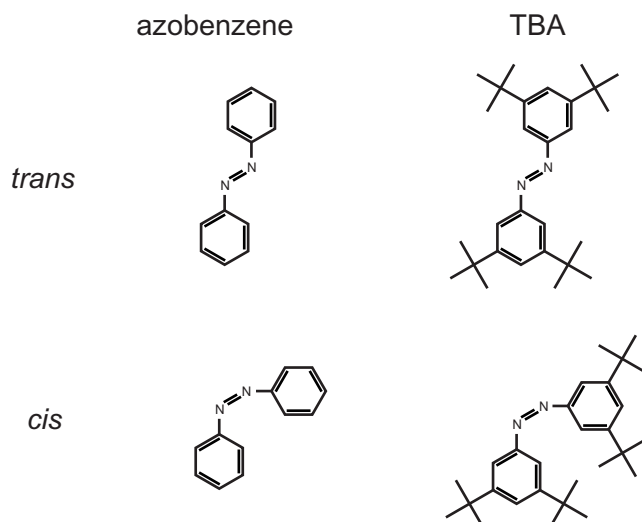
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## 1. Introduction

In order to overcome the principal limitations of today's computing, sensor and data storage technologies, present-day research focuses on the development of adequate devices on the scale of single molecules, i.e. a few nanometers [1–7]. This step is believed to solve problems arising from the simple down-scaling of existing systems (e.g. field effect transistors [8, 9]), such as increased heat development, and thus energy consumption and unwanted quantum effects such as tunneling through oxide barriers [10].

Single molecules performing structural or electronic changes upon external stimulation, i.e. molecular switches, are expected to play a role as building blocks for functional devices [11], in particular, photochromic switches such as azobenzene. While the switching properties of these systems have been studied in great detail in solution [12, 13], future technological applications are likely to require confinement of the functional molecular units to surfaces or interfaces. However, most molecular switches lose their photochromic capability when brought into direct contact with a metal surface [14–18]. This quenching is generally attributed to steric hindrance, an alternation of the molecule's potential energy surface (PES) (e.g. due to van der Waals or image charge interaction with a metal substrate) or the emergence of new decay channels for excited molecular electronic states. One prominent exception to this unfortunate tendency is tetra-*tert*-butyl-azobenzene (TBA; see figure 1) adsorbed on the Au(111) surface which keeps its photoisomerization capability—although driven by a substrate-mediated process (see below) [19–22] in contrast to the direct intramolecular electronic excitation responsible for the photoisomerization in the free molecule in solution.

In solution, azobenzene (see figure 1) undergoes an isomerization from its energetically stable, planar *trans*-form to the metastable *cis*-form upon illumination with ultraviolet (UV) light while the back-reaction can be stimulated with visible photons or thermally [12]. Along with the structural change toward the three-dimensional *cis*-form, the molecule obtains a dipole moment of 3.2 D [23]. Both pathways are stimulated by photoexcitation of an electron in the photochemically active diazo bridge ( $-N=N-$  group) which—by relaxation on the PES of a higher-lying electronic state—can overcome the ground-state potential barrier [24]. Adsorbed on the Au(111) surface, an isomerization can be induced by tunneling electrons in a scanning tunneling microscope (STM) junction [25], whereas the photoinduced reaction is found to be quenched [16]. Since the loss of the switching ability is caused by the interaction with the metal substrate, one concept is to electronically and geometrically decouple the switch. In general,



**Figure 1.** Azobenzene and its derivative TBA, each in their *trans* and *cis* configurations.

this can be achieved by thin insulating films [26] or bulky molecular spacer groups [27–29] attached to the photoswitch in order to lift the molecule from the surface. The latter approach was realized in TBA where four *tert*-butyl groups were attached to the phenyl rings of the azobenzene molecule (see figure 1).

Previous studies on TBA have shown that the molecule's photoisomerization ability is preserved on the Au(111) surface [21]. A reversible isomerization has been induced by light [16, 22] as well as in an STM junction by the applied electric field [30]. Similar to both azobenzene and TBA in solution, the *trans/cis* isomerization on the surface is bidirectional due to simultaneous photoinduced back-reactions, so that this system approaches saturation in a photostationary state (PSS). A complete reversal back to the pure *trans*-form is achieved thermally [20, 21].

However, the underlying photoisomerization mechanism for the surface-bound species is fundamentally different from that in the free molecule. Instead of an intramolecular transition between the frontier orbitals, a surface-mediated creation of a positive ion resonance (PIR) in the molecule drives the isomerization: upon illumination with photon energies above 2.0 eV, a hole is created in the gold d-bands which, on an ultrafast timescale, relaxes to their top and subsequently tunnels into the highest occupied molecular orbital (HOMO) of the adsorbed TBA [19]. In spite of the successful photoisomerization of the surface-bound TBA, the role of the *tert*-butyl groups has been identified to be different from what was originally assumed. Precise measurements of the molecular adsorption geometries using normal incidence x-ray standing wave and large-scale density functional theory (DFT) calculations show only insignificant adsorption height changes in the photochemically active diazo group in TBA compared to bare azobenzene/Au(111) since the *trans*-form is no longer planar [31, 32]. The changes in the PES that are induced by the altered geometry of the adsorbed species might have an effect on the switching behavior of the molecules.

In order to develop further functionalized molecular systems in direct contact with a (metal) surface, systematic studies should provide answers to the questions of why a vast majority

of molecular switches lose their functionality once adsorbed, and what the key parameters that influence this quenching are. With this paper we want to contribute to this effort by analyzing the similarities and differences in the electronic structure of two adsorbate/substrate complexes—one of which preserves the molecule's photoisomerization ability while the other does not. We will show that the HOMO of TBA lies closer to the d-band edge, which may allow a more efficient hole transfer compared to adsorbed azobenzene. Furthermore, we find delocalized states at the metal/molecule interfaces of both molecules. In the case of TBA, the energetic position of the interface state (IS) is sensitive to the switching state.

## 2. Experimental method

Employing two-photon photoemission (2PPE) allows us to study occupied as well as unoccupied electronic states in an energy window around the Fermi level  $E_F$  of the gold substrate, which contains the molecules' frontier orbitals that may be relevant to switching processes. Like conventional 'direct' photoemission, our technique is surface sensitive and in addition allows study of the charge carrier dynamics at interfaces on the femtosecond timescale [33–36]. Two laser pulses of equal or different photon energies that are lower than the work function  $\Phi$  of the sample excite electrons in a pump–probe process: the first laser pulse lifts an electron from an occupied state below the Fermi level to a real or virtual unoccupied intermediate state between Fermi energy and vacuum energy  $E_{\text{vac}}$ . Within the lifetime of this state the probe photon excites the electron into a final state of energy  $E_{\text{Final}} - E_F = E_{\text{kin}} + \Phi$  above the vacuum level whereupon the kinetic energy of the photoelectron  $E_{\text{kin}}$  is detected in a time-of-flight spectrometer.

2PPE spectra are displayed versus the final state energy since they may contain peaks originating from states of occupied or unoccupied nature. One can distinguish these cases and hence infer the energetic position of the respective states by investigating the shift of their final state energy as a function of photon energy. In the case of two-color 2PPE with a pump photon energy  $h\nu_2 = 2h\nu_1$  twice the probe photon energy, a peak originating from an unoccupied state will shift in the same way as the probe photon energy:  $\Delta E_{\text{Final}} = 1\Delta h\nu_1$ . In contrast, a peak associated with an occupied state exhibits three times this slope, i.e.  $\Delta E_{\text{Final}} = \Delta h\nu_2 + \Delta h\nu_1 = 3\Delta h\nu_1$ .

Introducing a delay between the pump and the probe pulse, the temporal evolution of an unoccupied state can be observed. For this, the pulse lengths are crucial and, in our experiments, are of the order of 50 fs (full-width at half-maximum of a single pulse duration). Angle-resolved 2PPE gives information about the dispersion of an electronic state with respect to the momentum parallel to the surface,  $k_{\parallel}$ .

$$k_{\parallel} = \sqrt{\frac{2m_e E_{\text{kin}}}{\hbar^2}} \sin \vartheta. \quad (1)$$

Here,  $\vartheta$  is the angle between the surface normal and the emission angle. In the approximation of quasi-free electrons of effective mass  $m_{\text{eff}}$ , the momentum-dependent energies  $E$  are fitted with a parabola around the band bottom  $E_0$ .

$$E(k_{\parallel}) = E_0 + \frac{\hbar^2 k_{\parallel}^2}{2m_{\text{eff}}}. \quad (2)$$

Femtosecond laser pulses are produced in a 300 kHz Ti:sapphire laser system, which serves an optical parametric amplifier delivering pulses of photon energies  $h\nu_1$  tunable over most of the visible spectrum. Part of this beam is converted into UV light of photon energy  $h\nu_2 = 2h\nu_1$  in a BBO crystal. Both beams are p-polarized when incident on the sample under an angle of  $45^\circ$  with respect to the surface normal (except in angle-resolved measurements).

Experiments were conducted in an ultrahigh vacuum chamber with a base pressure of  $1 \times 10^{-10}$  mbar. The Au(111) single crystal was mounted on a flow cryostat equipped with resistive sample heating, thus allowing temperature control from about 40 K (cooling with liquid helium) to above 800 K. For sample preparation and characterization the chamber is equipped with an ion gun (for sputtering), a quadrupole mass spectrometer, a Knudsen cell evaporator and a low-energy electron diffraction system.

After a routine cycle of  $\text{Ar}^+$  sputtering and annealing of the gold single crystal at 800 K, azobenzene or TBA molecules were evaporated from the Knudsen cell onto the clean surface. In order to obtain a defined coverage of 0.9 ML, the sample was heated to 410 K (TBA) or 295 K (azobenzene) in order to desorb the multilayer [22].

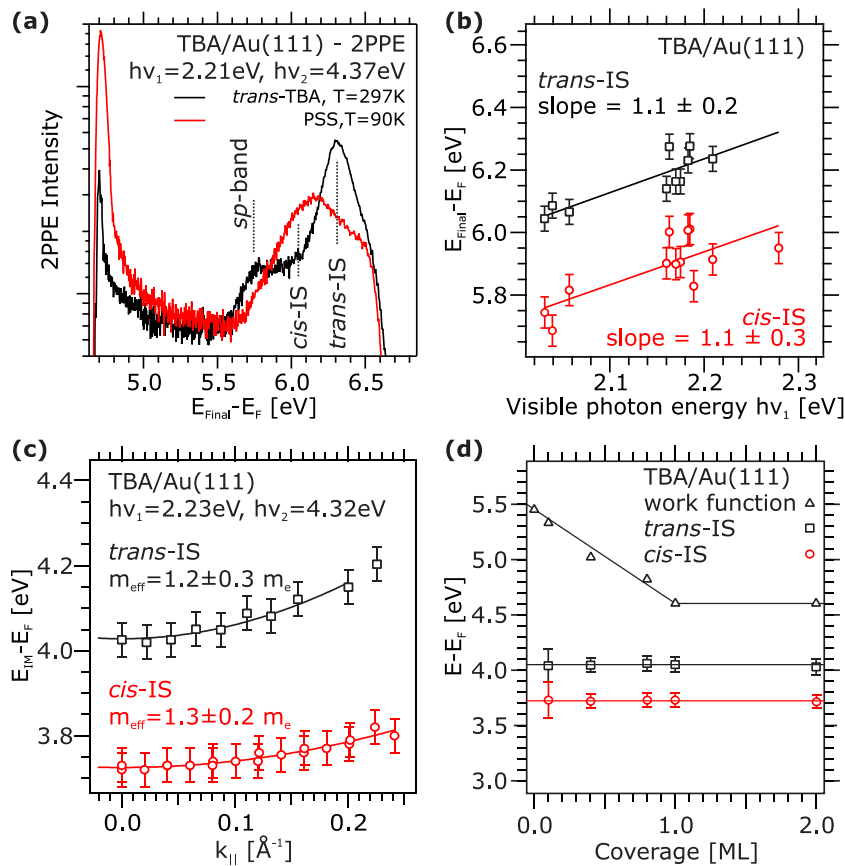
### 3. Results and discussion

#### 3.1. Tetra-tert-butyl-azobenzene (TBA)

Verification of a photoinduced isomerization reaction in 2PPE requires changes in the observed spectra, i.e. detectable changes in the electronic structure (occupied or unoccupied states) or the work function. In agreement with previously published 2PPE experiments in our group [19, 20, 22], we find that two-color 2PPE spectra (see figure 2(a)) show such changes when illuminating a sample consisting of TBA molecules in the planar *trans* configuration at a substrate temperature of 90 K: the most obvious change is the intensity loss of the prominent peak in the *trans*-TBA spectrum at 6.3 eV and the simultaneous intensity gain of a peak at lower energies. Since illumination leads to a PSS, the spectrum in the PSS shows the remaining intensity of the initial feature together with the new peak at lower energies. Consequently, we attribute the peak at higher energies to the more stable *trans*-TBA and the feature at lower final state energies to the *cis*-TBA. Note that the *trans* spectrum shown here was recorded at room temperature where the PSS lies almost entirely on the *trans* side due to the thermally activated back-reaction (so that the observed features can clearly be attributed to the *trans* isomer) [21]. Note that the position of the sp-band is temperature dependent [37]; therefore the corresponding feature is more pronounced in the *trans* spectrum.

Since the switching behavior of TBA, namely the optically induced and thermally activated reversible isomerization, has already been well analyzed [20, 21], in this paper we want to focus on the nature of the observed states which are associated with the two different isomers. Figure 2(b) shows the energetic shift of the two characteristic peaks as a function of the photon energy of the visible beam,  $h\nu_1$ . In both cases, a slope of one is found and thus both states can be assigned to unoccupied intermediate states probed by the visible light. The energies of these states are consequently determined from the final state energy found in the spectra by subtracting  $h\nu_1$ , which yields  $E_{\text{trans}} = 4.09 \pm 0.03$  eV and  $E_{\text{cis}} = 3.79 \pm 0.04$  eV.

In order to gain further insight into the nature of these states, we performed angle-resolved 2PPE experiments (AR-2PPE). Delocalization of an electronic state parallel to the surface plane manifests itself in a dispersion of the associated peak in an angle-resolved 2PPE measurement.



**Figure 2.** ISs of both TBA isomers probed and characterized using 2PPE. (a) Differences between a spectrum in the PSS and a pure *trans* sample recorded at room temperature. (b) Peak shift of both ISs with varying photon energy identifying them as unoccupied states. (c) Dispersion determined in AR-2PPE showing the effective mass of both IS. The peak positions are given in terms of the intermediate state energy  $E_{\text{IM}}$ . (d) Unlike image potential states (IPs), neither IS is pinned to the vacuum level.

In most cases it is a counter-indication for a molecular orbital since those states are usually localized at the molecule. Indeed, as becomes clear from figure 2(c), both isomer-specific states exhibit a dispersion with an effective mass  $m_{\text{eff}}$  which is only slightly higher than the mass of the free electron (to which this quantity is normalized), suggesting almost no lateral confinement of the electrons in these states.

Delocalized states near the vacuum level are reminiscent of image potential states (IPs) located at the vacuum interface [35, 38, 39], which appear as a result of the attractive interaction between an electron and its image charge within a metal. A characteristic property of IPs is that they are bound with respect to the vacuum level  $E_{\text{vac}}$  rather than the Fermi energy of the system ('pinning to  $E_{\text{vac}}$ '). Besides IPs, other delocalized states have been observed at metal/adsorbate interfaces: one example is buried ISs arising in thick layers of adsorbed rare gas (namely Ar) atoms due to a screened image potential of the metal [40, 41]. These states are pinned not to the vacuum level but to the conduction band minimum of bulk Ar and spatially



extend into several layers of Ar. In thin layers of organic adsorbates, a different type of ISs has been observed that are caused by a potential created at the metal/molecule interface and that are located between the substrate and the first molecular layer [42, 43]. Another adsorbate-induced effect on the electronic structure of an interface may be a partial hybridization of the Shockley surface state with molecular orbitals resulting in an energetic shift of the surface state above the Fermi level [44]. However, the shift in energy was less than 1 eV; therefore we do not believe that the electronic state near  $E_{\text{vac}}$  observed in our study is due to a shifted surface state.

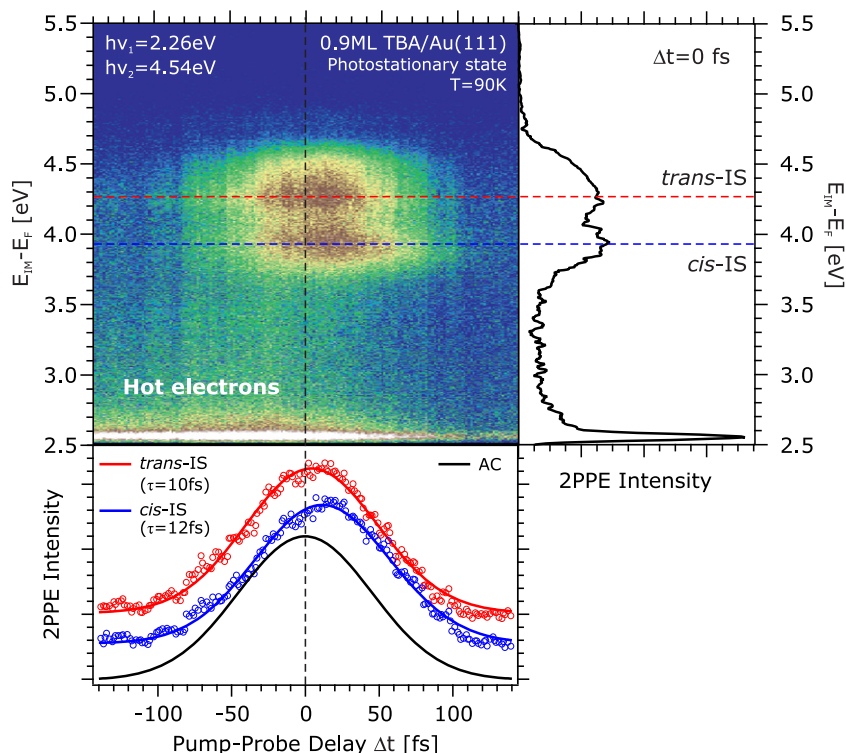
Since the deposition of TBA on the gold surface alters the work function significantly to lower values, the work function can be systematically varied (figure 2(d)). While the work function is decreased by about 0.9 eV upon the adsorption of a full monolayer, the energetic positions of both states remain constant, i.e. they are not pinned to the vacuum level. Furthermore, for low coverages the energy difference between the two states and the vacuum level significantly exceeds 850 meV, which is an upper theoretical limit for IPS binding energies [35].

Due to the delocalized character and considering the missing pinning to the vacuum level, it appears that the observed states originate neither from unoccupied molecular orbitals nor from the vacuum interface. Instead, we propose that they are localized at the metal/molecule interface due to the creation of an interface potential. However, on the other hand, it is known that, in the sub-monolayer regime, TBA adsorbs in molecular islands on the Au(111) surface [15, 16, 30] wherein the local work function will correspond to that measured in 2PPE for a full monolayer ( $\Phi_{\text{IML}} = 4.6$  eV). Since an IPS within the area of the molecular islands would not be pinned to the global, averaged work function (which is seen in 2PPE spectra) but to the local vacuum level, the binding energy of such a state would not vary along with the global work function. In this case the binding energies of the two characteristic states would be 0.55 and 0.88 eV with respect to the local vacuum level, respectively.

However, comparison to the closely related molecules azobenzene (see below) and tetra-*tert*-butyl-imine [43] on Au(111), where the ISs are found to be localized at the metal/adsorbate interface, suggests that this is also the case for TBA. Theoretical studies yielding the electron density distribution parallel and perpendicular to the surface would be desirable for a deeper understanding of the nature of these states.

Figure 3 shows time-resolved 2PPE data of TBA in the PSS in which a delay is introduced between pump and probe pulses. Both ISs are well separated in this measurement, which allows distinguishing of the excited state dynamics upon optical excitation (see the caption for a detailed description of the displayed plots). Both ISs lie well above the projected band gap of gold along the  $\Lambda$  line which extends up to 3 eV above  $E_{\text{F}}$  [45]. The energetic overlap of these states with metal bands and thus an elastic decay into the substrate might explain their low lifetime. However, the lower-lying *cis*-IS that is closer to the projected band gap exhibits a slightly higher lifetime and hence a weaker electronic coupling to unoccupied metal states, as demonstrated by a fit to the cross-correlation (XC) curves of both states (figure 3). The XC curves were fitted with a convolution of the Gaussian autocorrelation function and a single exponential decay. The lower coupling is also reflected in a longer time required for the population of the *cis*-IS where the XC curve is shifted by 10 fs to higher delays. In the light of earlier studies [19, 20, 22] of this system, we want to briefly comment on our findings. Previously, the two isomer-specific features observed in 2PPE spectra were assigned to the lowest unoccupied molecular orbitals (LUMOs) of the *trans* and *cis* isomers, respectively. With the extended analysis presented here and particularly the observed free-electron-like dispersion





**Figure 3.** Time-resolved 2PPE data for TBA in the PSS. The color code represents the 2PPE intensity, and on the right, an energy spectrum (versus the intermediate state binding energy  $E_{IM}$  relative to  $E_F$ ) at zero delay is displayed. At the bottom, horizontal cuts (XC curves) are shown for IS as well as the region around the Fermi edge where due to the absence of unoccupied states the XC is identical to the autocorrelation (AC), i.e. the convolution of both the pulses. *Trans*-IS and *cis*-IS are well separated and show no difference in lifetime, but the *cis*-IS XC trace is shifted to longer time delays. Positive delays indicate probing with visible photons, whereas for negative delays, UV photons probe the unoccupied states.

as well as the large discrepancy in energy when compared to scanning tunneling spectroscopy (STS) [30], we conclude that the observed states cannot be assigned to the LUMOs but to delocalized states at the metal/molecule interface.

So far we have concentrated on the two ISs. The electronic structure of the adsorbed molecule, i.e. the states corresponding to the molecular orbitals of the free molecule, shall be discussed in the following. Having ruled out that the aforementioned features arise from LUMOs and since such unoccupied states are also not observed in any other 2PPE spectra (e.g. using different photon energy combinations), we must rely on STS performed on both isomers yielding LUMO energies of 1.67 eV (*trans*) and 1.35 eV (*cis*) above the Fermi level, respectively [30].

In the regime of occupied states on the other hand, one-color 2PPE measurements reveal the position of the HOMO to be  $E_{HOMO} = -1.88 \pm 0.08$  eV with respect to the Fermi level [19, 46]. The energy of this particular orbital relative to the d-bands of gold is crucial for the

photoisomerization ability of TBA [19] since a hole transfer to the HOMO brings the molecule into an excited electronic state, which can subsequently lead to a switching event. The HOMO of the adsorbed TBA is believed to correspond to the bonding  $\pi$  orbital of the diazo group, according to DFT calculations [14] and core hole spectroscopy [47]. In a simple picture, the hole transfer to the HOMO, thus the removal of an electron, cleaves one  $\pi$  bond and thus weakens the rigidity of the diazo group.

### 3.2. Azobenzene/Au(111)

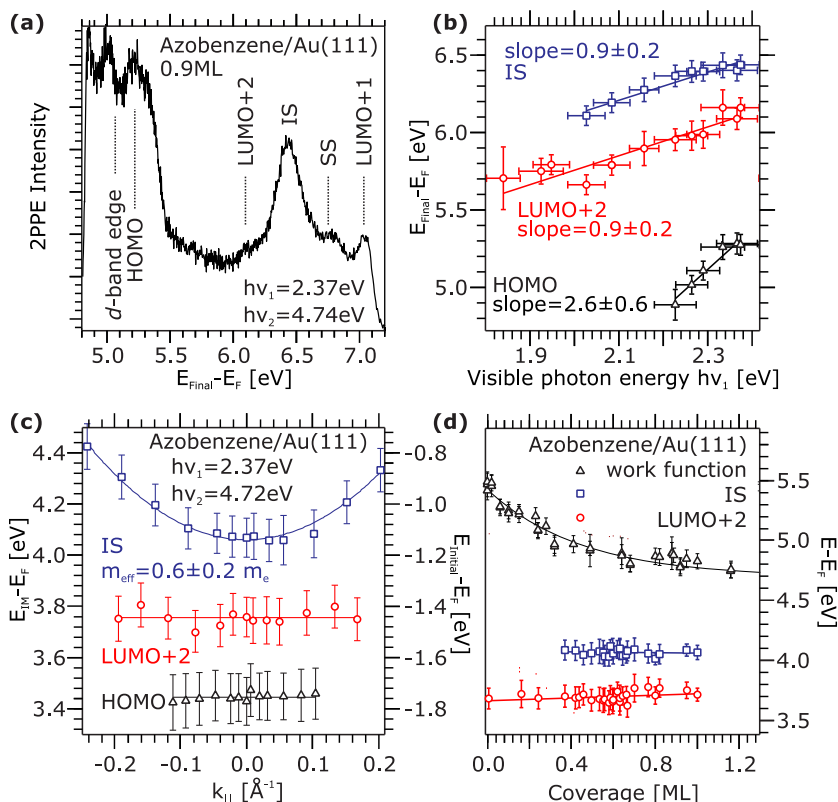
The idea of decoupling azobenzene with *tert*-butyl spacer legs came from the inability to switch azobenzene/Au(111) with light [16]. On the other hand, switching single *trans* azobenzene molecules on a Au(111) surface is feasible in an STM junction by applying negative bias voltages, i.e. by depopulating an occupied orbital roughly 1.5 eV below the Fermi level [25]. In principle, this depopulation should also be possible by photons. An important difference, however, is the attempt rate which correlates with the applied dose, i.e. the incident number of electrons or photons per molecule. While in the STM junction,  $10^{18}$  electrons are necessary to switch one molecule [25], the fluence in the illumination experiment, as reported, roughly translates into a dose of  $10^7$  photons per molecule. Although this comparison neglects some aspects, the difference of 11 orders of magnitude shows that it is much more difficult to switch a detectable portion of the molecules with light than by electron tunneling in an STM, as has been observed previously for a spiropyran derivative on the gold surface [18].

In a series of illumination experiments with our 2PPE setup, we attempted to switch adsorbed *trans* azobenzene by light at various photon energies<sup>2</sup> appropriate for both intramolecular and substrate-mediated switching processes. Since our technique allows simultaneous illumination and probing we can achieve much higher photon doses (up to  $10^{10}$  photons per molecule) compared to the above-mentioned illumination experiment [16]. However, we could not observe any changes in the 2PPE spectra which would indicate an isomerization. Note that upon illumination with 3.1 eV photons, the 2PPE spectrum of the adsorbate-covered surface evolves toward the spectrum of the bare Au(111) surface. The underlying process could not be clarified experimentally; however, due to the nature of the spectral changes (i.e. a strong increase of the work function and the recovery of the Shockley surface state) we do not believe that they occur because of an isomerization process. The original spectra can be restored upon annealing. We assume that this behavior is caused by laser-induced desorption and diffusion of neighboring molecules onto the then bare spot of the substrate at elevated temperatures.

In particular, in the light of studies showing that the diazo bridge in TBA is not significantly lifted compared to azobenzene [31], we wanted to gain further insight into the electronic structure of azobenzene in order to elucidate possible differences in the energetic positions of occupied and unoccupied electronic states of both TBA and azobenzene.

Since one major aspect of the photoisomerization mechanism of surface-bound TBA is the overlap between the HOMO and the gold d-bands, we are especially interested in the energetic position of the HOMO of azobenzene. Figure 4(a) shows a two-color 2PPE spectrum of azobenzene/Au(111). Four molecule-induced features are observed; one occupied and three unoccupied states can be assigned from photon energy-dependent measurements, as shown in

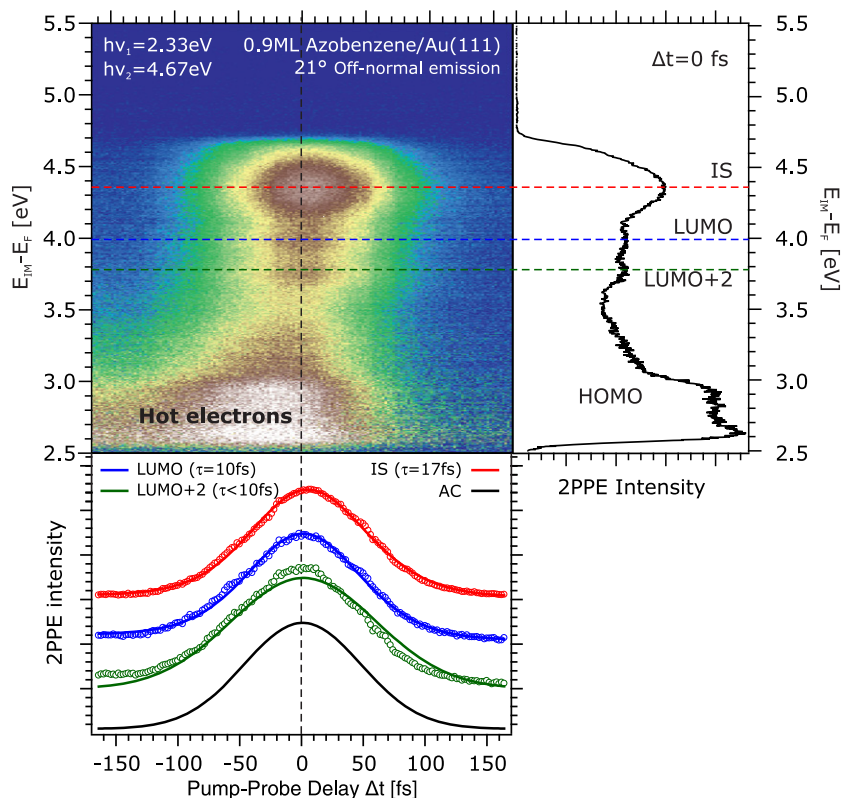
<sup>2</sup> Photon energies (photons per molecule): 2.23 eV ( $10^7$ ), 3.11 eV ( $10^{10}$ ), 3.88 eV ( $10^9$ ) and 4.30 eV ( $10^7$ ); illumination time: 30 min each.



**Figure 4.** Data from 2PPE measurements of azobenzene/Au(111). (a) A correlated two-color 2PPE spectrum showing an occupied and two unoccupied molecular states as well as an IS, the Shockley surface state and the d-band edge. (b) Photon energy dependence of the molecule-induced features (the LUMO+1 is seen only at high photon energies and is quantitatively evaluated from another series). (c) AR-2PPE shows a dispersing IS and two localized states. The HOMO is shown with respect to the initial state axis on the right, whereas the other two peak positions are given in terms of the intermediate state energy  $E_{\text{IM}}$ . (d) The energetic positions and work function for different azobenzene coverages. The IS is not pinned to the vacuum level.

figure 4(b). The HOMO position is determined to be  $E_{\text{HOMO}} = -1.77 \pm 0.04\text{ eV}$ ; thus it lies 0.1 eV higher than that of TBA.

Among the three unoccupied states in the spectrum, two originate from localized molecular orbitals at  $E_{\text{LUMO+1}} = 2.35 \pm 0.04\text{ eV}$  and  $E_{\text{LUMO+2}} = 3.76 \pm 0.03\text{ eV}$ . Note that the LUMO+2 is probed by visible photons, while the LUMO+1 is probed by UV photons, which makes the corresponding peak appear at higher final state energies in the spectrum. The quantitative evaluation of the LUMO+1 peak shift was done using the one-color 2PPE spectra of the very same series since in the two-color spectra this state cannot be populated at lower photon energies (data not shown). The LUMO is not observable in this spectrum since the corresponding peak overlaps the feature belonging to an IS. It can, however, be observed by rotating the sample and using the dispersion of the IS to shift it to higher energies (see figure 5). The LUMO was then determined to lie at  $E_{\text{LUMO}} = 1.68 \pm 0.04\text{ eV}$  and it is probed by UV photons.



**Figure 5.** Time-resolved 2PPE experiment on azobenzene/Au(111) with the sample rotated by  $21^\circ$  (corresponding to  $k_{\parallel} = 0.2 \text{ \AA}^{-1}$ ) with respect to the analyzer in order to shift the IS to higher final state energies so that the LUMO becomes apparent (see text). The false color plot shows the 2PPE intensity as a function of the intermediate state energy  $E_{\text{IM}}$  (assuming a visible probe beam) and pump-probe delay. The spectrum on the right (at zero delay) shows three features at high energies and the HOMO near the secondary edge. The XC curve for the IS and the LUMO+2 was fitted with a convolution of the laser pulse autocorrelation with a single exponential decay. The LUMO XC was fitted in the same way but with a decay toward negative delays that corresponded to probing by UV photons. The HOMO (which is superimposed on a hot electron background) is also seen in this plot.

A time-resolved measurement (see figure 5) shows that the LUMO of adsorbed azobenzene has a lifetime which is very short and thus unlikely to allow a relaxation of the molecule towards the *cis*-isomer. Indeed, the *trans*–*cis* reaction in the STM junction [25] is achieved *not* by the creation of a negative ion resonance but by depopulation of an occupied orbital. This is not the case for the back-reaction, which occurs via electron attachment to the molecule.

Besides the various molecular electronic states, we also find an unoccupied delocalized state at  $E_{\text{IS}} = 4.09 \pm 0.03 \text{ eV}$ , which has the same energy as the *trans*-IS in TBA. This is quite surprising since one would expect the bulky *tert*-butyl spacers to somehow alter the interface potentials of both metal/molecule and molecule/vacuum interfaces.

The effective mass, on the other hand, is quite different from the case of TBA. With  $m_{\text{eff}} = 0.6 \pm 0.2$  it is by a factor of two smaller than in the ISs of both TBA isomers. This might be explained by the structurally much smoother azobenzene layer, whereas in the TBA layer, the bulky spacers probably cause additional scattering. Another important difference that might influence the effective mass is the growth in the sub-monolayer regime, i.e. islands of TBA and chains of azobenzene [16].

Figure 4(d) shows that the binding energy of the IS with respect to the Fermi level is independent of the vacuum energy as the azobenzene coverage is increased. It can therefore be ruled out that this state is an IPS which would be pinned to the vacuum level (see section 3.1).

Time-resolved 2PPE (figure 5) shows that the lifetime of the IS is not significantly different from both ISs observed for TBA/Au(111). The short lifetime may be due to the localization of the IS at the metal/molecule interface, which probably leads to a large wave function overlap with metal states. Furthermore, the IS lies well above the projected band gap.

#### 4. The photoisomerization ability in both systems

Comparing the molecular frontier orbitals of the two molecules investigated in this study, we may contribute some insight into the understanding of the switching behavior of azobenzene derivatives at surfaces. The electronic structure is summarized in figure 6.

It is known from 2PPE investigations that a depopulation of the HOMO of TBA is part of the dominating pathway for photoisomerization at the Au(111) surface [19]. For azobenzene, on the other hand, a depopulation of the *trans*-HOMO leads to a switching event in an STM junction [25] but efficient photoswitching cannot be achieved, as shown in this paper. We also showed that the azobenzene HOMO lies 0.1 eV higher in energy than its counterpart in TBA. This shift reduces the overlap with the d-bands.

On the basis of these observations, we suggest that while in both molecules a PIR involving the HOMO might lead to switching, this PIR cannot be created equally effectively in the two systems because TBA, in contrast to azobenzene, has sufficient overlap with the upper d-bands to allow for efficient charge transfer (see figure 6). This would mean that the d-bands serve as a chromophore for the molecular switch TBA. More generally, this may suggest that in order to preserve the photoisomerization ability of an azobenzene derivative on a surface, it is necessary to provide a way for effective hole injection into the HOMO.

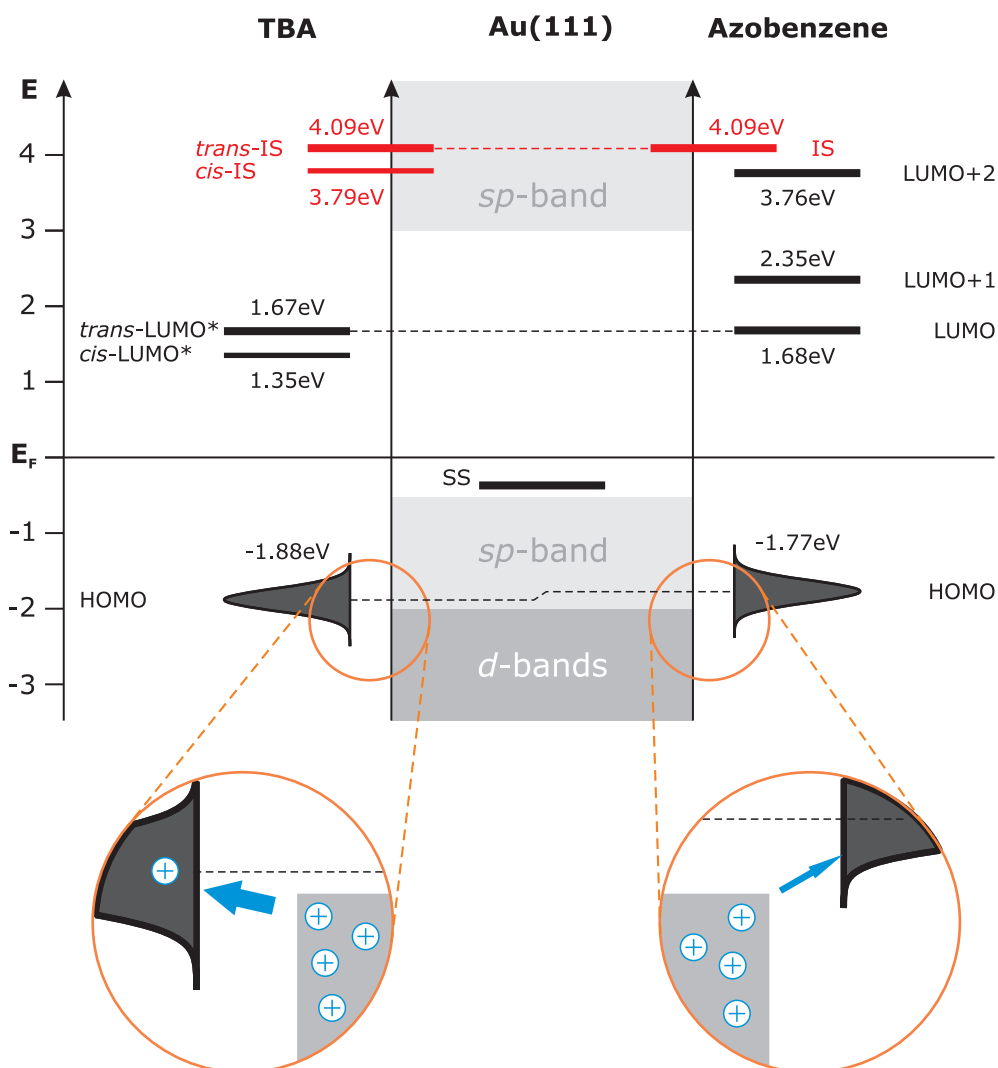
Besides the overlap of the HOMO and the d-bands, the adsorption geometry plays an important role in the photoisomerization ability [31, 48]. For example, it has been shown that the distance of the diazo group to the surface is not significantly increased by the *tert*-butyl spacer groups. This means that in contrast to azobenzene, surface-bound *trans*-TBA is not in a planar geometry but tilted, which might enable the molecule to isomerize more efficiently.

#### 5. Summary

Having investigated the electronic structure of both the azobenzene molecule and its photoswitchable derivative TBA on the Au(111) surface with 2PPE, we find differences as well as similarities.

The *trans* isomers of both molecules give rise to an IS at the same energy (4.09 eV relative to  $E_{\text{F}}$ ) and with the same ultrashort lifetime, whereas the effective mass is reduced in the





**Figure 6.** Occupied and unoccupied electronic states of TBA and azobenzene adsorbed on Au(111). The overlap of the HOMOs of both molecules with the  $d$ -band edge differs due to an energy shift of 0.1 eV in azobenzene compared to TBA. \*The *trans*- and *cis*-LUMO positions are determined with STS [30].

azobenzene case by a factor of two. A lower-lying IS is seen after photoisomerization of TBA molecules leading to the *cis*-form.

While no unoccupied molecular state for TBA could be detected with our method, three of them are seen in azobenzene. Comparing to tunneling spectroscopy results of TBA, the *trans*-LUMOs of both molecules lie at the same energetic position (1.67 eV). The HOMO position with respect to the Au  $d$ -bands, which is important for the photoinduced switching mechanism in TBA, is shifted by 0.1 eV to higher energies in azobenzene, which reduces the overlap with the  $d$ -bands. No photoinduced isomerization was observed in adsorbed azobenzene.

Of course one has to keep in mind that the electronic structure of the adsorbate/substrate complex, e.g. possible electronic excitation and decay channels, is not the only factor influencing the photoisomerization ability. Steric hindrance arising from interaction with the

substrate or neighboring molecules, the altered geometry due to the spacer groups and attractive forces between molecules and substrate (e.g. via dispersive forces) have to be considered as well.

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