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Charge-transfer dynamics in azobenzene alkanethiolate self-assembled monolayers on gold

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ABSTRACT

We have studied the charge-transfer dynamics in azobenzene-functionalized alkanethiolate self-assembled monolayers. We compare the core-hole-clock technique, *i.e.*, resonant *vs.* non-resonant contributions in the azobenzene autoionization of the C1*s*-π^* core exciton, with the lifetime of a molecular resonance determined by two-photon photoemission spectroscopy using femtosecond laser pulses. Both techniques yield comparable charge-transfer times of 80 ± 20 fs for a linker consisting of three CH_2 groups and one oxygen unit. Thus the quenching of the excitation is about one order of magnitude faster than the time required for the *trans* to *cis* isomerization of the azobenzene photoswitch in solution.

1. Introduction

Photochromic molecules can serve as reproducible building blocks to optically manipulate and control surface and interface properties on the nanoscale [1,2]. This opens up interesting fields of application such as the operation of molecular actuators and motors, the development of switchable sensors, or the biasing of charge transport across organic devices [3,4]. Given the impressive examples in biology and the large variety of photochromic molecules in solution, a major challenge is to ensure that the molecular switch maintains its functionality when adsorbed on a surface. On the one hand excitations in the substrate can lead to a quenching of the photoexcited state [5]. Therefore the coupling between molecular switch and substrate excitations must be controlled by spacer groups. On the other hand, steric and excitonic interactions among the chromophores in the adsorbate layer can impede efficient switching [6]. The latter problem can be overcome by introducing large platforms or lateral spacers [5,7,8].

One of the best investigated molecular linker systems comprises the class of alkanethiols, which form self-assembled monolayers (SAMs) on gold substrates [9–12]. We employ SAMs to form well-ordered surface ensembles of azobenzene-functionalized molecules as well as to effectively decouple the photoswitch from the substrate. As sketched in Fig. 1 the azobenzene entity is coupled to the alkane chain *via* an oxygen bridge in para-position. The alkyl chain binds with the sulfur head group to the Au(111) surface and the molecules orient preferentially upright in the SAM with an angle of ~30° with respect to the surface normal [6]. Different rest groups (R = H, CN, CF_3) were used as markers for X-ray photoelectron and near-edge X-ray absorption spectroscopy (XPS and NEXAFS) studies [6,13,14]. In the following the molecules are referred to as R-Az*n*, where *n* denotes the number of CH_2 units of the alkyl linker.

In the present article azobenzene-functionalized SAMs on gold serve as a model platform to study the coupling between photoswitch and substrate. We compare two experimental methods, resonant photoemission and time-resolved two-photon photoemission, which both allow for determining the charge-transfer (CT) time of electrons excited to the lowest unoccupied molecular orbitals (LUMO + n) into the substrate. Independent of the alkyl spacer length ($n = 3,6,10$) the autoionization spectra of the azobenzene moiety are dominated by spectator and participator decay channels. Following the decay of the C1*s* to LUMO + 1,2 resonances the dominant participator-decay line shows a lower intensity for shorter chain length. Applying the core-hole clock we obtain for the CF_3-Az3 SAM a charge-transfer time of 73 ± 20 fs. The 2PPE spectra of H-Az3 show a negative ion resonance at $E - E_F = 3.6$ eV, which we attribute to a LUMO + n of the azobenzene chromophore. The resonance has a lifetime of 80 ± 20 fs in good agreement with the result from the core-hole-clock technique. While the charge-transfer time is compatible with a tunnel barrier of thickness $n = 4$ [15,16], it seems unaffected by the resonance position.

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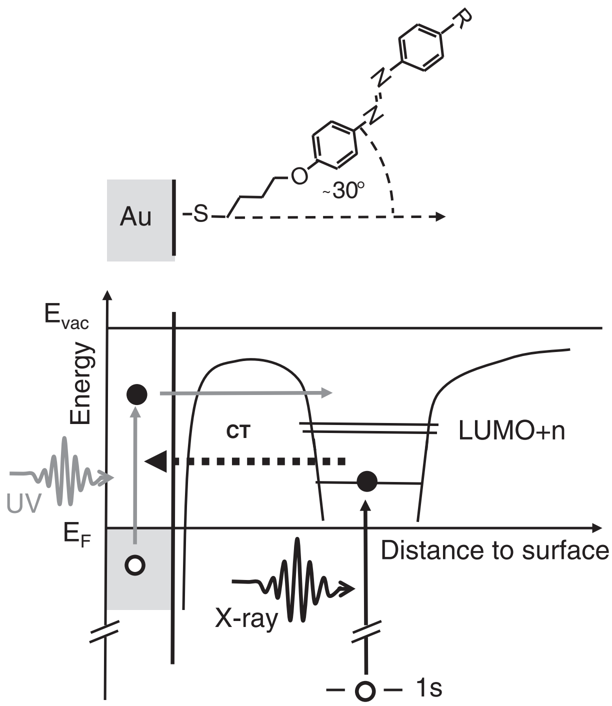

Fig. 1. Alkanethiols bind with the sulfur headgroup to the Au(111) surface and orient preferentially upright in a self-assembled monolayer (SAM). Thereby the alkyl chain shapes a tunnel barrier, which allows for decoupling the azobenzene endgroup from the Au metal. The unoccupied molecular orbital (LUMO + n) is populated either indirectly by electrons optically excited in the gold substrate employing ultraviolet (UV) laser pulses or by resonant intramolecular excitation of a *1s* core electron using X-rays. The charge-transfer (CT) time is determined by probing the excited state with a second laser pulse in a time-resolved photoemission experiment or by disentangling resonant autoionization from non-resonant Auger contributions in the core-hole decay.

2. Experimental

The various R-Az*n* compounds were synthesized and purified as described elsewhere [13,17]. Their purity has been verified by ultrahigh-performance liquid chromatography. As substrates we used 200 nm thick gold films on mica (Georg Albert PVD), which exhibit large Au(111) terraces. SAMs were prepared by immersing the substrate into 10^{-4} molar ethanolic solution for 24 h. Afterwards the samples were copiously rinsed with pure ethanol, blown dry with argon, mounted on the sample holder and directly transferred into the ultrahigh-vacuum chambers (base pressure $\leq 2 \cdot 10^{-10}$mbar). The preparation procedure was routinely controlled by XPS [13,14].

We used two separate experimental setups for resonant and time-resolved photoemission. Both apparatuses were equipped with comparable load locks and sample holders for sample transfer and cooling. To reduce X-ray beam-damage experiments were performed at a sample temperature of ~120 K [18,19] and the X-ray exposure was minimized by scanning the sample and using a fast beam shutter.

Resonant photoemission experiments were performed at the undulator beamline U41 PGM-1 of the synchrotron facility BESSY II, Helmholtz-Zentrum Berlin. We used a hemispherical analyzer (Omicron, EA125) equipped with 5 channeltrons. The total energy resolution of the measurements was 0.2 eV as established by the width of the S2p XPS line and the Fermi level of the clean gold substrate. Measurements were performed in grazing incidence with an angle of 15° between X-ray beam and surface plane. The analyzer chamber is rotatable around the beam axis. In this way the polarization of the incoming X-ray beam was set parallel to the surface plane and the angle of electron detection normal to the surface. This measurement geometry optimizes the ratio between the autoionization signal and the photoemission background [20]. The photon energies and the binding energy scale are referenced to the binding energy of the Au 4*f* core level of 83.95 eV [21].

The laser system for 2PPE spectroscopy consists of two optical parametric amplifiers, both pumped by a Ti:Sapphire amplifier system running at a repetition rate of 300 kHz (Coherent, RegA). In this way independently tunable visible and ultraviolet (UV) light pulses are generated with a duration of ~50 fs and pulse energies of ~25 nJ and 3 nJ, respectively. A translation stage is used to adjust the delay of the visible pulse. Both beams impinge nearly collinearly on the sample in the horizontal plane, which forms an angle of 45° to the surface normal. Emission angle and kinetic energy of the photoemitted electrons are measured using a hemispherical electron analyzer (SPECS, Phoibos 100) equipped with a two-dimensional view-type detector.

3. Results and discussion

3.1. The core-hole clock

One means of studying the charge-transfertime between adsorbate and substrate is the so-called core-hole clock (see, *e.g.*, [22] and refs. therein). This method was pioneered by the groups of Dietrich Menzel in Munich and Nils Mårtensson in Uppsala initially investigating rare gas layers physisorbed on metal surfaces [23,24]. The method's keynote is illustrated in Fig. 2.

A core-to-valence excitation starts the core-hole clock, which stops on the time scale of the core-hole lifetime τ_Γ. If charge transfer between the excited valence level and the substrate occurs prior to the core-hole decay, one records an ordinary, *i.e.*, non-resonant Auger spectrum. In contrast, if the excited electron stays on the adsorbate it may either participate in the autoionization or additionally screen the core-hole decay. This results in either an enhancement of photoemission lines (participator decay) or a screening shift of the Auger decay spectrum to higher

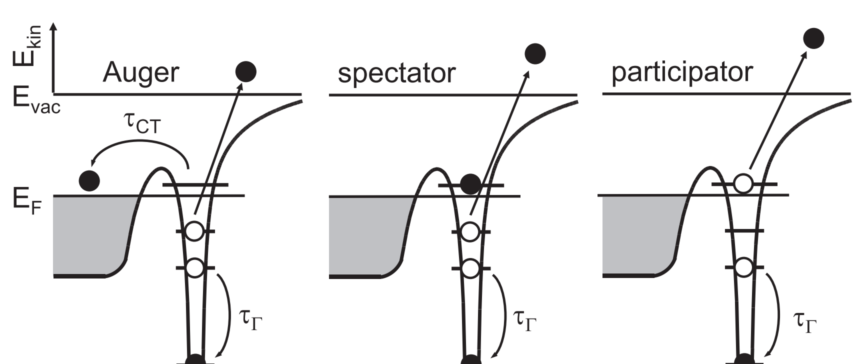

Fig. 2. Schematics of the core-hole decay. After resonant excitation of a coreexciton, the charge-transfer time τ_{CT} is deduced by reference to the core-hole lifetime τ_Γ comparing the intensities of non-resonant (Auger) and resonant (spectator, participator) decay channels: $\tau_{CT}/\tau_\Gamma = (I_{Auger} + I_{spectator} + I_{participator})/I_{Auger}$.