On or Off?
Identifying isomerisation in molecular switches

P. M. Schmidt[1], R. Püttner[2], C. Kolczewski[1], K. Hermann[1], K. Horn[1], T. U. Kampen[1]
1 Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin
2 Freie Universität Berlin

The phenomenal rate of increase in the integration density on semiconductor microchips is driven by advances in optical lithography, that is, the process used for patterning in microelectronic device fabrication. Although the introduction of shorter-wavelength light sources and resolution enhancement techniques helps to maintain the current rate of device miniaturization, at some time in the near future this top-down approach can no longer attain the required feature sizes.

Among several alternative techniques for the future, promising results have been obtained by the use of molecular systems [1]. Here, the advantages are easy fabrication and the possibility to shape and fine-tune organic molecules into desired structures by organic synthesis. Molecules with an extended π-electron system are especially promising candidates. Intermolecular interactions of the π-systems favor a stacking of molecules with their aromatic planes parallel to each other. In such highly ordered thin films, overlap between π-orbitals takes place only in one direction leading to an anisotropy of optical and physical properties, i.e. charge carrier mobility or optical absorption [2, 3].

A further advantage of organic materials is that the smallest building block, the molecule itself, represents an entity with a certain functionalization. For example, a molecule with two different possible conformations incorporated into one-dimensional 'molecular wires' would ideally serve as a 'molecular switch' (Fig. 1) The simplest model switch of this sort is the stilbene molecule (1,2-diphenylethylene) for which the phenyl groups can be arranged in two conformations, on the same side or on opposite sides around the central C=C bridge, i.e. to cis- and trans-stilbene, respectively (Fig. 1). This isomerisation can be triggered by UV irradiation as already shown by experiment and explained theoretically for the gas phase and in solution [5, 6, 7, 8].

Our goal is to find a spectroscopic fingerprint for the two isomers on the surface corresponding to the 'on' or 'off' position of this molecular nano-switch (Fig. 1). For molecular switching to be useful in microelectronics the switching pathway has to work on surfaces, i.e. in a constrained situation. However, the bonding with the substrate surface must not hinder the switching process. This is possible for adsorbed stilbene since bonding to a surface via the central C=C double bond seems to be most favorable with the phenylrings allowed to rotate freely.

To identify changes in the molecule due to the adsorption on the surface, we have taken Near Edge X-Ray Absorption Fine Structure Spectroscopy (NEXAFS) spectra from the molecule in the gas phase (i.e. prior to adsorption) and in the adsorbed phase on the surface accompanied by theoretical calculations (Fig. 2.). NEXAFS is an element-specific and surface sensitive method. Using anglular-dependent measurements the geometry of the adsorbed molecules can be determined. Thus, σ*-orbitals of the molecular backbone and π*-orbitals can be probed selectively.

NEXAFS spectra of trans- and cis-stilbene in the gas phase (Fig. 3), show a prominent π*-resonance between 284 and 286 eV photon energy and several smaller σ*-resonances at higher photon energies [12]. The σ*-resonances are found to be quite comparable (with only minor differences) due to the isomers possessing the same backbone. The π*-resonance, on the other hand, shows significant differences. While the cis-isomer displays a single sharp peak, the π*-resonance of trans-stilbene is split. Theoretical studies obtained by transition potential calculations with corrections for the ionization potential and relativistic effects using the StoBe code [13] confirm all spectral features observed in the experiment. In particular, the also π*-resonances are very well reproduced by the calculations; this can be used to clearly identify both isomers. For higher photon energies the calculations predict stronger signal intensities than found in the experiment. This may be due to the use of stronger broadening in the calculated intensities above the ionization threshold.

Figure 4 shows NEXAFS spectra recorded for a monolayer of cis- and trans-stilbene. The intensity curves to the right refer to the π*-resonance for different photon incidence angles. The key features distinguishing between the isomers in the gas-phase spectra are also visible in the spectra of the adsorbed phase. The trans-isomer displays a split π*-resonance while that of the cis-isomer is sharp. Thus cis- and trans-stilbene adsorbed on Si(100) can be distinguished. The π*-resonance signal near 285 eV photon energy shows an asymmetric line shape which is different for the two isomers.

The intensities of the π*-resonances upon changing the incidence angle of the monochromatized synchrotron light has been used to determine the orientation of the molecules with respect to the substrate surface. As shown in Figure 4 the intensity of π*-resonance of trans-stilbene increases with increasing incidence angle. From this qualitative behavior we can already conclude that this isomer is lying almost flat on the surface. The angular dependence of the π*-resonance of cis-stilbene, on the other hand, shows a different behavior. The intensity is high for normal incidence and decreases only slightly with increasing incidence angle. This angular dependence is also obtained in our theoretical studies on the most stable adsorption geometries of the isomers. The two structure models of this detailed analysis are shown in Figure 4, where both isomers are found to bond with the silicon dimer at the substrate surface via their central carbon double bond.

Our results demonstrate, that clear differences between the π*-resonance can serve as a fingerprint and permit a clear distinction between the cis- and trans-isomers, i.e. the 'on' or 'off' state of the molecular switch, which is essential for the detection and characterization of the isomerisation at the surface.

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[10] The program package StoBe is a modified version of the DFT-LCGTO program package DeMon, originally developed by A. St.-Amant and D. Salahub (University of Montreal), with extensions by K. Hermann and L.G.M. Pettersson.
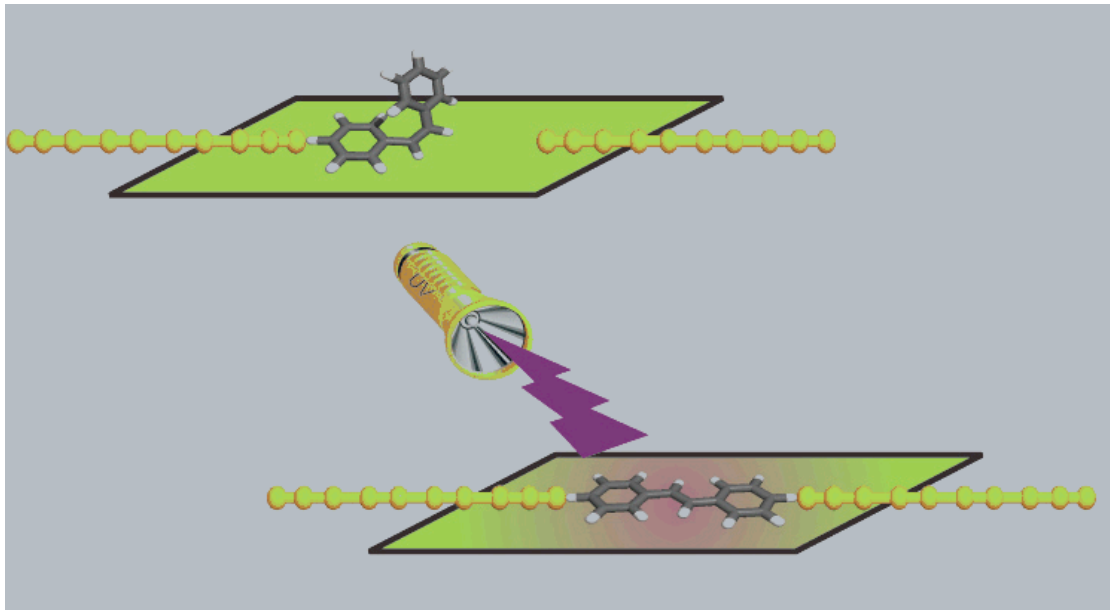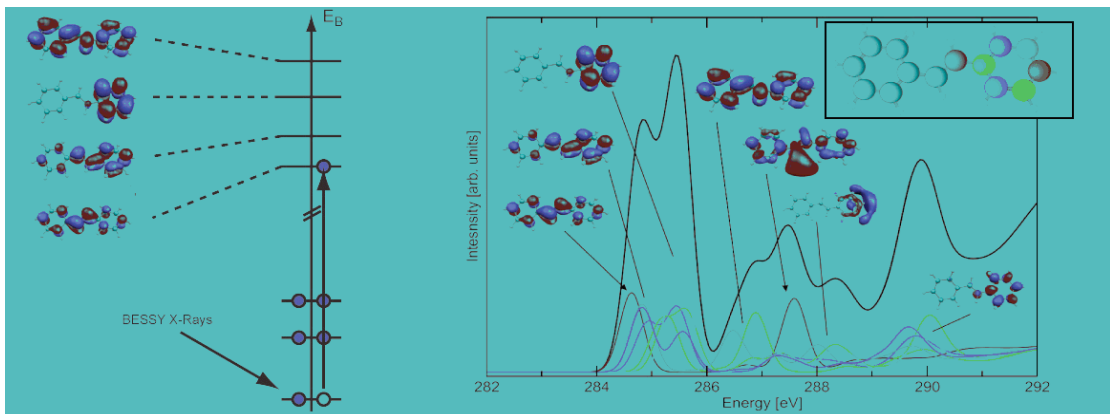
Fig. 1:
Basic concept of an optically activated molecular switch.

Fig. 2:
Calculated NEXAFS spectrum of trans-stilbene showing the contribution of each carbon to the overall spectrum. For some peaks the corresponding final states orbitals are shown.
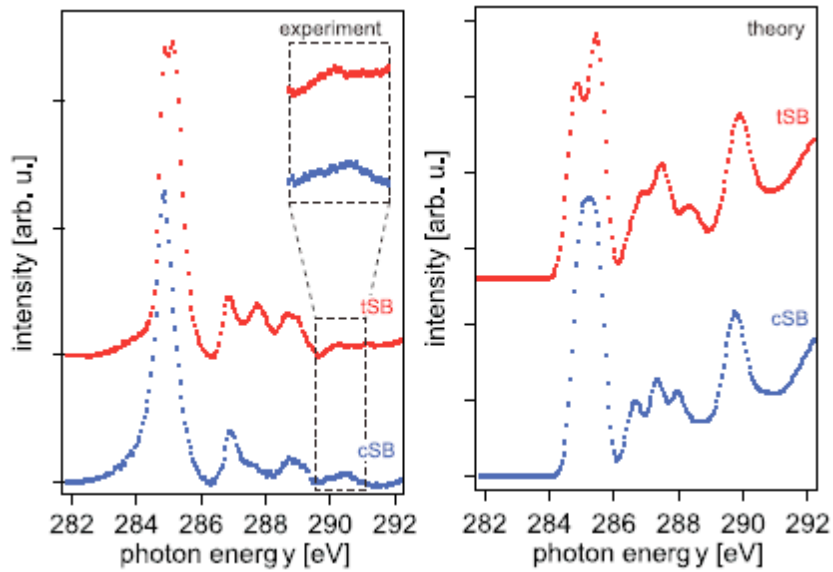
Fig. 3:
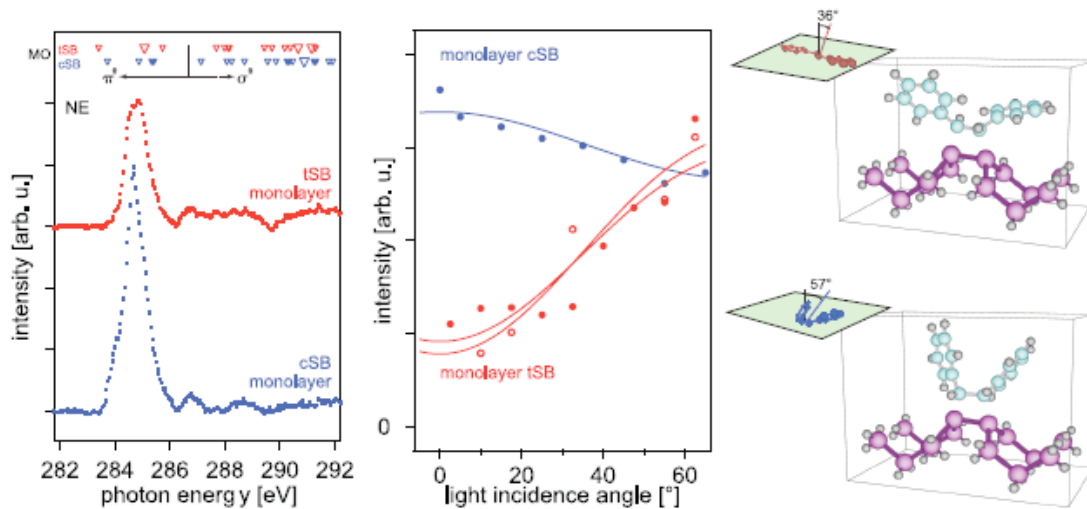Experimental and theoretical NEXAFS spectra of trans- and cis-stilbene in the gas phase.

Fig. 4:
Experimental NEXAFS spectra for trans- and cis-stilbene adsorbed on Si(100). The angular dependence of the π*-resonance is a consequence of the adsorption geometry of the respective isomer.