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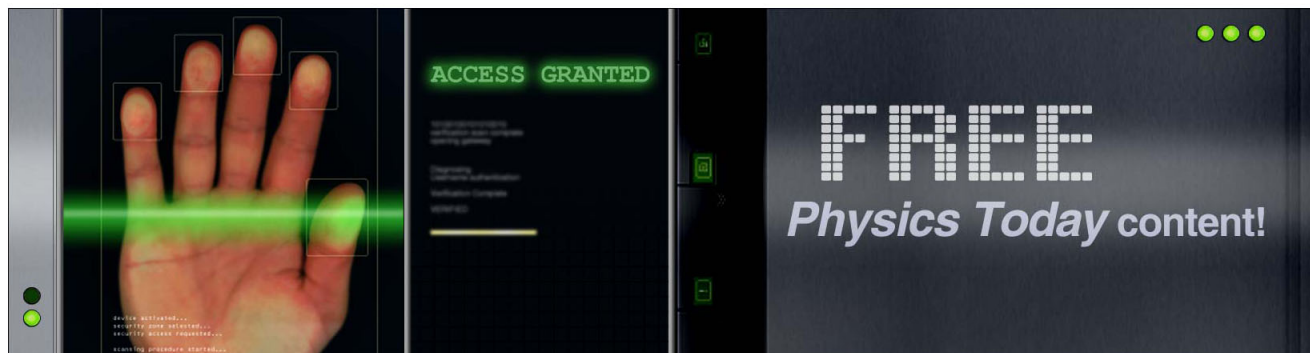
Photoswitching of azobenzene multilayers on a layered semiconductor

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In situ photoelectron spectroscopy is used to study the adsorption and photoisomerization of azobenzene multilayers on the layered semiconductor HfS_2 at liquid nitrogen temperatures. The measured valence band spectra indicate weak molecule–substrate coupling and provide evidence for reversible switching of azobenzene multilayers by light with different wavelengths. The photoswitching manifests itself in spectral shifts due to changes in the electrical surface conductance and in modifications of the electronic structure consistent with the results of outer valence Green's function calculations. The photoemission results appear to establish azobenzene as an optoelectrical molecular switch. © *2010 American Institute of Physics*. [doi:10.1063/1.3479502]

There is considerable interest in attaching molecular switches to solid surfaces because this bottom-up approach may lead to the development of innovative, intrinsically nanometer-scale devices based on switching the molecules' structural or electronic properties.[1–4] A "drosophila" of this scheme is azobenzene [Fig. 1(a)], which—in the gas phase, in solution, or in polymer films—can be reversibly transformed between the almost planar *trans* and the three-dimensional *cis* isomer by light with wavelengths of ~360 nm (*trans* to *cis*) and ~420 nm (*cis* to *trans*).[5–7] Yet, this photoinduced transition is not purely structural. It goes along with a significant change of the dipole moment and, potentially, of the electrical conductivity, as the conductance of the *cis* form is predicted to be almost two orders of magnitude lower than that of the *trans* form.[8] An intriguing perspective therefore is that surface-attached azobenzene could constitute an ultrasmall light-controlled *electrical* switch.

However, to fix a simple, stable, and efficient molecular switch to a solid surface is notoriously difficult because one has to find an optimum molecule–substrate coupling. If the coupling is too weak, the switch will not be localized at the surface. If the coupling is too strong, the switching efficiency will be strongly suppressed as compared to the one achieved in nonsolid environments.[9–13] To solve this problem, elaborate strategies have been introduced in which the switching units are spatially separated from the substrate and from each other.[14] Here, however, we are interested in the simplest approach: molecular switches lying flat on a surface.

In search for an ideal substrate for highly efficient photoisomerization of adsorbed monomolecular switches we study azobenzene on the layered semiconductor HfS_2 [Fig. 1(b)]. This compound should provide weak adsorbate–substrate bonding due to its inert surface as well as weak electronic coupling due to its band gap of 2.85–3.6 eV.[15] Employing ultraviolet photoelectron spectroscopy we demonstrate that it is indeed possible to photoswitch azobenzene multilayers on HfS_2. Our results particularly provide evidence for reversible light-induced changes in the surface conductance and thus appear to establish azobenzene as an electrical switch.

For the experiments HfS_2 single crystals were grown by chemical vapor transport using iodine as transport agent. The crystals were slightly *n*-doped. They were cleaved *in situ* and their work function was determined to be 5.12 eV. During preparation and measurements the samples were held at a temperature below 120 K. To avoid sample contamination, azobenzene (Sigma–Aldrich) was deposited *in situ* in the photoemission chamber, with a typical deposition cycle taking 1–4 min and a deposition time of 1 min corresponding to (0.16 ± 0.05) L. From azobenzene adsorption on the iso/structural metallic compound $TiTe_2$ under identical growth conditions, the film growth rate could be estimated to (1.7 ± 0.8) Å/min (using the attenuation of the substrate photoemission signal at the Fermi level). Photoemission measurements were done in normal emission geometry with a He discharge lamp ($h\nu = 21.22$ eV) and a hemispherical electron analyzer (Specs Phoibos 150). The total energy resolution was 42 meV. *Trans*-to-*cis* photoisomerization was induced by ultraviolet light with a wavelength of 365 nm and a maximum power density of 3.5 W/cm^2 (Hönle Power Pen). For the reverse switching white light emitted from a halogen lamp was used. The photoemission spectra were taken under permanent illumination unless noted otherwise. A Tougaard background[16] was subtracted from all spectra shown in this work. Valence band edges were determined by extrapolating the leading edges to the baseline. For comparison, theoretical
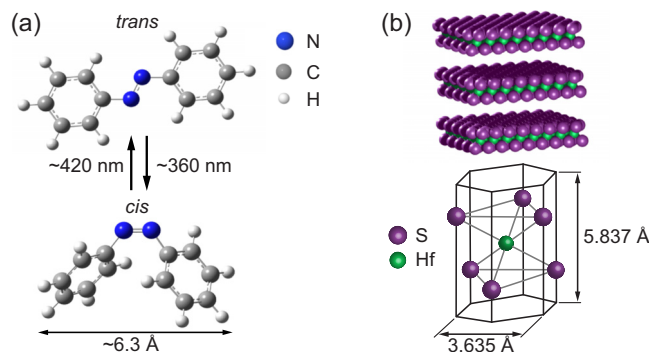

FIG. 1. (Color online) Schematic structures of the adsorbate and substrate: (a) Azobenzene in the planar *trans* and three-dimensional *cis* conformation. (b) Layer structure (with distance between layers enlarged) and unit cell of HfS_2.

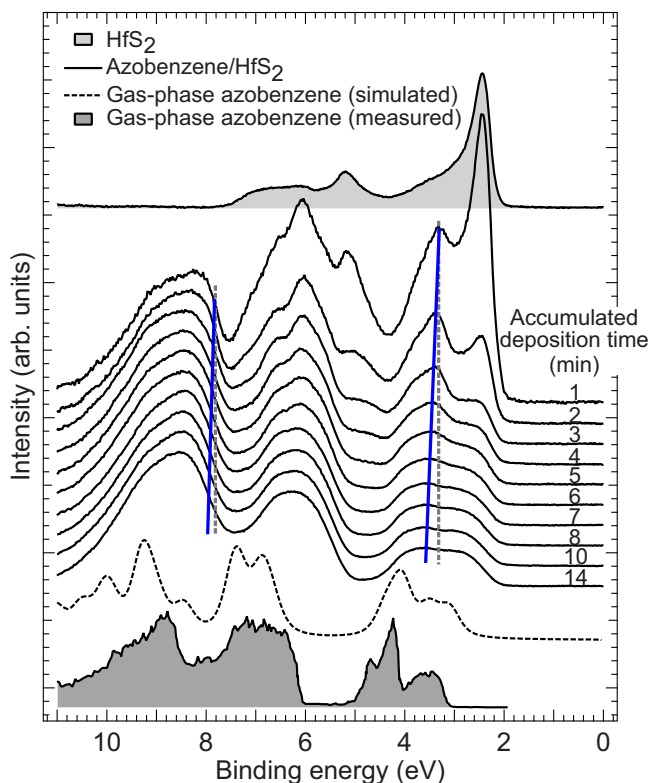a)Electronic mail: rossnagel@physik.uni-kiel.de.

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FIG. 2. (Color online) Valence-band photoemission spectra of azobenzene adsorbed on HfS₂ as a function of deposition time. Vertical (dashed gray) lines mark the initial positions of characteristic spectral features and off-vertical [solid blue (gray)] lines indicate spectral shifts in the course of deposition. The spectrum of pristine HfS₂ (top) and theoretical and experimental (Ref. 19) spectra of gas-phase *trans*-azobenzene (bottom) are shown for comparison.

FIG. 3. (Color online) (a) Valence-band photoemission spectra of an azobenzene multilayer system on HfS₂ upon alternating illumination with 365 nm and white light. A spectrum of the as deposited system (#1) and one with the light switched off (#3) are also shown. The gray bar marks the energy interval shown in (c). (b) Comparison of the spectra under illumination with 365 nm [blue (gray) line] and white (black line) light. Compared to (a), the intensity of the 365 nm radiation is higher. Arrows point to differences in the spectral shape. (c) Position of the valence band edge of the spectra shown in (a). A gray scale plot of the photoemission intensity is included.

gas-phase spectra were simulated using the results of outer valence Green's function (OVGF) calculations (basis set 6-311+G**).[17,18] To convert the calculated ionization energies to binding energies, the work function of the substrate was subtracted. The energy levels were broadened by Voigt profiles with Lorentzian and Gaussian full width at half maximum of 300 meV and for all molecular transitions equivalent matrix elements were assumed. In order to quantify the light-induced *trans*-to-*cis* conversion, first the experimental and simulated *trans*-azobenzene spectra were normalized to each other and then experimental and simulated difference spectra were computed by subtracting the pure *trans* spectra from the composite spectra. Estimates for the *trans*-to-*cis* conversion in photoequilibrium were finally obtained by comparing the absolute areas of experimental and simulated difference spectra.

Figure 2 shows how the valence electronic structure evolves while azobenzene is deposited on the HfS₂ substrate and compares the results to simulated and measured *trans*-azobenzene spectra in the gas phase. After a deposition time of about 3 min the prominent substrate features at binding energies of 2.4 and 5.1 eV are suppressed and the spectra are dominated by the molecular electronic structure. As to the overall spectral shape and the peak separations, the spectra of the azobenzene/HfS₂ system agree remarkably well with the simulated and measured[19] gas-phase spectra. The rigid spectral shift of only ~0.8 eV between adsorbed and gaseous azobenzene indicates that the combined effects of bonding to the substrate and photohole relaxation are rather weak. We
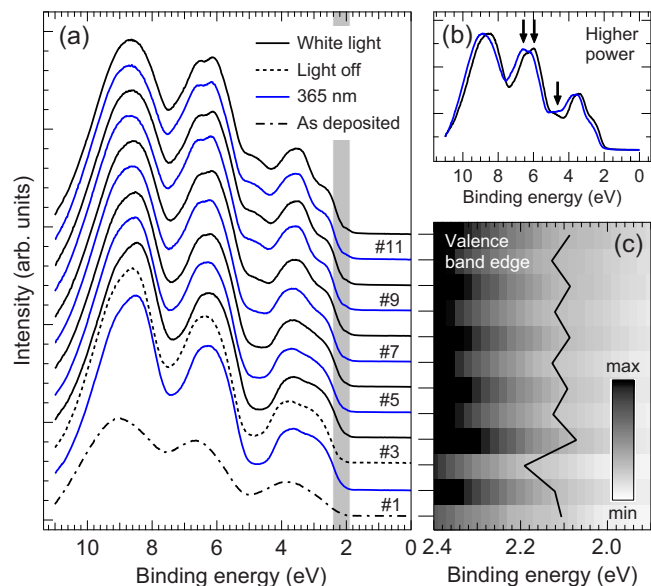
may conclude that the molecules adsorb intactly and that the molecule–substrate coupling is weak. The latter is corroborated by our observation that the azobenzene molecules readily desorb from the HfS₂ surface at a temperature of ~190 K. At longer deposition times we further note a small rigid shift of the spectral features toward higher binding energies (as indicated by the blue lines in Fig. 2). This shift is a spectroscopic signature of multilayer growth. It can be associated with a continuous reduction of the photohole–substrate interaction which naturally occurs when the distance between the substrate and the atomic site from which the photoelectron is emitted increases.[20]

Can the azobenzene multilayer system be reversibly switched by light? To answer this question, the surface was alternatingly illuminated with ultraviolet and white optical light. The corresponding photoemission spectra are shown in Fig. 3(a) and reveal two major effects: First, as soon as the illumination starts and then with increasing illumination time the spectra sharpen up and substrate features, particularly the one around 5 eV binding energy, begin to emerge. Since this process partly appears as the reverse of the deposition process shown in Fig. 2, we may conclude that azobenzene desorption occurs under illumination. Second, and more importantly, we observe a reversible rigid shift of 30–40 meV between the spectra taken under illumination with 365 nm light (*trans* to *cis*) and the spectra taken under the white light of the halogen lamp (*cis* to *trans*) [Fig. 3(c)]. We argue here that this shift is caused by a change in the surface conductance upon changing the concentrations of *trans*- and *cis*-azobenzene in the multilayer system.

It is well known that surface charging does occur in photoemission of organic thin films and that it can be compensated for by continuously illuminating the sample with
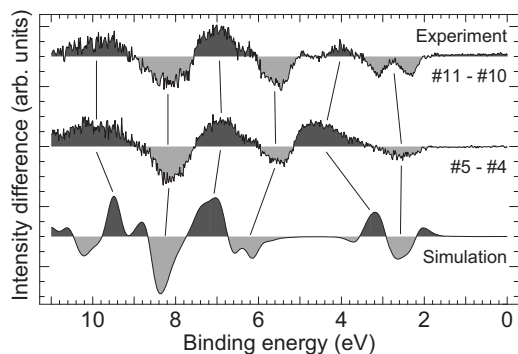
FIG. 4. Top and middle: experimental difference spectra for spectra shown in Fig. 3(a). Bottom: simulated difference spectrum (composite spectrum for 7% *cis*- and 93% *trans*-azobenzene minus spectrum for 100% *trans*-azobenzene).

optical light, thus increasing the conductivity by the creation of free charge carriers.[21] This effect is seen in the data of Figs. 3(a) and 3(c). Without additional irradiation the charging is strongest as the position of the valence band edge appears at the highest binding energy (lowest kinetic energy). With additional irradiation the charging is reduced and the band edge shifts to lower binding energies (higher kinetic energies). Yet, the size of the back shift depends on the wavelength and the intensity of the light source. The back shift is larger for the less intense halogen lamp [Fig. 3(c)], whose light supposedly increases the surface conductance by increasing the concentration of the more conductive *trans*-azobenzene, and it becomes smaller when the intensity of the ultraviolet source is increased [cf. Figs. 3(a) and 3(c)], which should shift the photostationary equilibrium in favor of the less conductive *cis* isomer. We note that the latter observation rules out band bending at a semiconductor interface as a cause of the spectral shifts because in the present situation light-induced back bending would become larger, if the light intensity was increased.[22]

Further evidence for azobenzene photoisomerization in the multilayer system comes from spectral changes that go beyond a simple rigid shift of the entire spectrum [see arrows in Fig. 3(b)]. These changes are brought to light in Fig. 4, which reveals a surprisingly good agreement in the shape of experimental and simulated difference spectra. From the absolute area under the experimental difference curves, the *trans*-to-*cis* conversion obtained at 365 nm can be estimated to about 7%. Compared to liquid environments,[6] this is lower by more than a factor of 10. We believe that this suppression reflects the effects of the particular condensed-matter environment and the irradiation with the 58.5 nm He line during measurements.

In conclusion, we have found spectroscopic evidence that *trans*-to-*cis* and *cis*-to-*trans* photoisomerization is possible in azobenzene multilayers when they are adsorbed on a layered semiconductor. The photoinduced changes of the *trans*-*cis* population are of the order of 5%–10% and manifest themselves in ultraviolet photoemission spectra in two ways: (i) as a small change of the spectral shape due to changes in the azobenzene electronic structure and (ii) as a relaxation shift of 30–40 meV due to a change in the conductance of the azobenzene multilayer system. Being able to switch the conductance of azobenzene on semiconductor surfaces may prove useful in the fields of molecular electronics and functionalized surfaces.

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