

Abstract

Stilbene (1,2-diphenylethylene) has shown an intriguing isomerisation behavior and may serve as a model system for “molecular switches” incorporating a C=C double bond. To evaluate the possible use of such molecules as molecular switches on semiconductor surfaces, the adsorption of cis- and trans-stilbene on Si(100) has been investigated. Identification of both isomers is achieved by differences in adsorption geometry as revealed by NEXAFS, and differences in electronic structure in the occupied and unoccupied molecular orbitals. For both isomers, bonding takes place via the C=C double bond to the Si dimer atoms allowing for free movement of the aromatic rings, a necessary prerequisite for photoinduced isomerisation on the surface. Our experimental results agree well with theoretical calculations.

1. Introduction

An intense search for digital optical data storage and novel electronic devices with increasing storage density has been pursued in the recent years. Promising results have been obtained for the use of molecular systems [1,2] with the advantage of easy fabrication, the possibility to shape organic compounds into desired structures by molecular engineering, and fine-tuning of many physical properties by small changes in molecular structure. Molecules with an extended π -electron-system are particularly 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 or inorganic molecular crystals, overlap between orbitals takes place only in one direction, leading to an anisotropy in physical properties, i.e. charge carrier mobility or optical absorption, as seen in for example perilene derivatives [3,4]. For large molecules with extended π -systems, the formation of bands has been observed [5] suggesting the occurrence of high carrier mobility due to band transport. A molecule with two different possible conformations incorporated into one-dimensional “molecular wires” would ideally serve as a “molecular switch”. The simplest model switch of this sort is the stilbene-molecule (1,2-diphenylethylene) shown in Fig. 1 for which the phenyl groups can be arranged in a Z-(“zusammen” i.e. on same side) or E-(“entgegengesetzt” i.e. on opposite sides) conformation around the central bridge, for cis- or trans-stilbene, respectively. This isomerisation around the C=C-double bond can be induced by UV irradiation, as already shown in the gas phase and in solution and described theoretically [6–9]. The molecule is chemically stable against radiation over a broad wavelength range, and is in fact used as a laser-dye [10–12]. Two possible pathways for isomerisation are currently discussed. The “one-bond flip” corresponds to a rotation around the double bond excited by the UV photons and leads to a transition state conformation of the two phenyl rings perpendicular to each other. The “hula-twist” mechanism shown by Fuß and coworkers [9], being a low-energy pathway, is a simultaneous rotation around the central double-bond and one of the adjacent C–C-single bonds, keeping the phenyl groups parallel to each other at all times. Photoinduction of the isomerisation process requires UV light in the wavelength range of 250–320 nm, with isomerisation times in the gasphase and in solution of 3 ps and 100 ps for the cis-to-trans- and the trans-to-cis-isomerisation, respectively [7].

In order for molecular switching to be a useful process in microelectronic circuits, such a pathway has to work on surfaces, i.e. in a constrained situation. Bonding with the substrate surface, however, must not hinder the switching process. This is possible for adsorbed stilbene, since bonding to a surface via the central C=C-double bond would be most favorable, and the freedom of movement is still sustained for the phenyl rings. We study the interaction of cis- and trans-stilbene with the Si(100) surface by means of core level (C1s and Si2p) X-ray photoelectron spectroscopy (XPS), valence band UV-photoelectron spectroscopy (UPS) and near edge X-ray absorption fine structure spectroscopy (NEXAFS). Our goal is to determine possible means of distinction of the two isomers on the surface to enable the spectroscopic investigation of the isomerisation discussed above.

2. Experiment

The experiments were performed at the UE56/2 PGM1 beamline of the BESSY II synchrotron radiation facility. The beamline can be operated at photon energies between 64 and 1400 eV. Photoelectrons were detected with a SPECS Phoibos 100 hemispherical analyzer (100 mm mean radius) equipped with a 2D CCD-detector. A sample of 2 mm x 5 mm cut from a p-doped Si(100) wafer (Virginia Semiconductor) was mounted on a sample holder which could be transferred on a manipulator with five axes of freedom. The Si(10 0) sample was cooled to a temperature of about 100 K using liquid nitrogen. Stilbene (Sigma–Aldrich, order nos. 139939 and S4808) was used without further purification. Both isomers were evaporated from a glass tube, in the case of trans-stilbene heated to 90 °C, through a leak-valve. The difference in evaporation temperature correlates with the higher boiling point of trans-stilbene under standard conditions. All photoelectron spectra were taken with a fixed angle of 54.6° between photon source and electron analyzer. Exposures were determined by means of pressure times exposure time [13]. In this work a monolayer coverage is defined as the saturation coverage at room temperature, which is reached after an exposure of 3 L.

3. Results and discussion

3.1. The Si2p core level

The Si2p core level has been studied in many related studies of molecular adsorption on silicon surfaces [14,15] since it may indicate details of the bonding geometry. Si2p core levels for coverages of one monolayer (3 L) and multilayers (15 L and 30 L for cis- and trans-isomer, respectively) stilbene were measured at a photon energy of 140 eV. The respective spectra for the cis-isomer are shown in Fig. 2. For the clean surface, the Si2p signal was fitted using symmetric Voigt-doublets as described in the literature [16,17] and a Shirley type background component [18,19]. For the clean surface, five spin-orbit-split components are required. These contributions are assigned to the emission from the up dimer (S), the down dimer (SS), bulk-atoms (B), defects (C) and second layer (S2) atoms at binding energies of 98.69 eV, 98.95 eV, 99.21 eV, 99.41 eV, and 100.59 eV, respectively. For the clean surface (bottom spectrum in Fig. 2) the defect contribution is very small. The Si2p spectra for different coverages of cis- and trans stilbene on the Si surface can also be fitted by five Voigt-doublets. Fig. 2 shows spectra for monolayer and multilayer coverage of cis-stilbene with the respective spectra of the clean surface used for the experiments. Relative peak positions are constant for all coverages, implying that the chemical environment does not change throughout stilbene deposition. In addition, absolute positions are constant as well within experimental resolution. Analogous results apply

for trans-stilbene. Thus no change in bandbending of the Si(100) appears as the bulk Si2p component experiences no energy shift. Both cis- and the trans-stilbene thus appear to be only weakly bound to the Si(100) surface, since no additional chemically shifted components are detected in the Si2p spectra. The overall intensity of the Si2p signal decreases with increasing stilbene coverage. Only the relative intensities of dimer up (S) contribution decrease with coverage, while all other contributions remaining at the same relative intensity. This indicates that an interaction between the adsorbed molecules and the surface mainly takes place with the dimer rows. The additional signal at high binding energy for the spectra of the covered surface can be attributed to a defect contribution to the surface. More defects may occur during experiment.

3.2. The C1s core level

The C1s core level is an important indicator of the chemical environment of the adsorbed molecule and gives insight into the bonding [20,21]. Fig. 3 shows C1s core level spectra for coverages of a monolayer (3 L) and multilayers (15 L and 30 L for cis- and trans-isomer, respectively) of stilbene obtained at 330 eV photon energy. Peak maxima for both isomers occur at 284.3 eV binding energy. Differences in linewidth of 1.0 eV and 1.3 eV for cis- and trans-stilbene, respectively, are again due to a different experimental resolution. The C1s peaks for cis- and trans-stilbene are different in shape. While the C1s signal from the cis-stilbene covered surface is symmetric, the C1s-spectra of trans-stilbene show an additional asymmetric contribution on the higher binding energy side of the signal. Asymmetric lineshapes have been described previously in the literature for benzene adsorbed on Si(100) surfaces [20] and could be due to unresolved vibrational progressions. A comparison with the lineshape of the Si2p emission with an experimental resolution of 0.28 eV and 0.46 eV for the cis- and trans-isomer, respectively, indicates a contribution of several components to the C1s signal with separations smaller than the half width of the peak.

As already seen from the Si2p core level, the interaction between the molecule and the surface is weak. Hence contributions to the C1s emission are likely to arise from different bonding environments in the molecules themselves. The binding energy of core level electrons, in a strict initial state picture, depend on inter- and intramolecular bonding. In order to obtain insight into the intramolecular bond structure for both isomers, the charge distribution around the carbon atoms for a single isolated molecule has been determined through density-functional calculations, following a geometric optimization and determination of molecular orbitals (MOs) using a restricted hybrid functional B3LYP [22] method with a 6-31G basis set on Gaussian03 [23]. For trans-stilbene, six different charge distributions may be identified, namely the bridge-atoms (B), the substituted atoms (S) of the phenyl-rings and the atoms in para-(P), meta-(M) and ortho-position to the bridge-substituent, while the latter one is split into the atoms towards (O1) and away from (O2) the bridge, with a ratio of 2:2:2:4:2:2 (S:P:O1:M:B:O2). For cis-stilbene the intramolecular center of inversion in the C=C double bond is broken due to the Z-configuration, and the resulting tilt with respect to the molecular plane of the trans-isomer. Therefore charges are not equally distributed in cis-stilbene, and for atoms around the bond, namely B and S, an additional splitting may occur. Thus eight components with a ratio of 1:1:2:2:4:2:1:1 (S:S0:P:O1:M:O2:B:B0) are possible for cis-stilbene. On the basis of these calculations, the C1s-spectra may be modeled by eight and six contributions for trans- and cis-stilbene, respectively. The different

charge distribution over the C atoms calculated for both isomers gives an indication of the origin of the different shapes of the observed C1s core level emissions.

Limitations of these calculations, based on one molecule in the gasphase instead of a molecular assembly on a surface, are obvious, such that this kind of analysis of the shape of the core level line may only be seen as an approximation of the real situation.

The monolayer coverage, i.e. saturation coverage at 300 K substrate temperature, has been determined to correspond to a C1s to Si2p(bulk) intensity ratio of 1.74. For multilayer coverages, a broadening of the signal towards higher binding energies occurs, which might be attributed to the emergence of a new contribution to the signal. As shown before, interactions between the adsorbed stilbene-molecules and the substrate are weak. For higher coverages, additional interactions between overlapping π -systems among neighboring molecules may take place. Charge transfer due to these carbon π - π -interactions may be considered to be slightly stronger than in carbon π -Si-interactions at the surface – as can also be seen for covalent bonds due to differences in electronegativity [24]. These purely intermolecular interactions may explain binding energy shifts in the C1s core level signals not observed for the Si2p emission. The better stacking of the trans-isomer due to its flat conformation may enhance this effect, explaining the stronger broadening of the trans- compared to the cis C1s-signal upon multilayer coverage.

3.3. Valence band spectra

For the clean Si(100) surface and for a monolayer (3 L) and multilayers of stilbene, valence band spectra have been recorded at a photon energy of 98 eV. In Fig. 4 spectra for the clean surface and one monolayer of cis- and trans-stilbene, respectively, are shown. A Shirley-type background has been subtracted in all spectra. The spectrum of the clean Si-substrate shows the surface state at 0.95 eV binding energy. Furthermore the Si sp-bands give rise to features down to 12 eV [20]. Upon adsorption of stilbene, the Si surface state decreases in intensity. The low binding energy occupied molecular orbitals (MO) lie in the energy range of the Si bulk bands. Thus it is difficult to clearly identify contributions arising from the molecular adsorbates. However, new features appear which can clearly be attributed to these, as indicated in the lower part of Fig. 4. These new signals arise at binding energies relative to the Fermi level of 2.0 eV, 3.4 eV, 4.9 eV, 6.6 eV, 9.2 eV, 13.0 eV, 16.9, and 20.0 eV for trans-stilbene and at binding energies of 2.2 eV, 3.4 eV, 4.6 eV, 6.6 eV, 9.7 eV, 12.9 eV, 16.9, and 20.0 eV for the cis-isomer. Binding energies of MOs have been calculated for an isolated molecule of both isomers using the methods described above.

In Fig. 4 calculated valence band spectra are shown. In the top part binding energies for MOs derived from DFT calculations are shown convoluted with a Gaussian function of 0.4 eV width to model broadening. Calculated binding energies have been aligned to the Si(100) valence band maximum which is found at 0.14 eV below the Fermi energy. A comparison between the valence band spectra of the adsorbed molecules subtracted from the substrate valence band and the calculations show significant differences for the cis- and trans-isomer as indicated in Fig. 4 (dotted lines). The signals arising at these energies can be attributed to the occupied molecular orbitals as indicated by dashed lines in the figure. These can be found at binding energies (calculated values in brackets) of 2.2 eV (2.21 eV), 3.4 eV (3.36 eV), 4.6 eV (4.55 eV), 9.7 eV (9.67 eV), 12.9 eV (12.83 eV) and 2.0 eV (1.96 eV), 3.3 eV (3.32 eV), 4.9 eV (4.92 eV), 9.2 eV (9.22 eV), 13.0 eV (13.00 eV) for cis- and trans-

stilbene, respectively. The values for calculated and measured spectra are thus in good agreement. This is especially remarkable since the DFT calculations have been performed for single isolated molecules, and bonding interaction between the adsorbed molecules and the surface are thus neglected. Hence intensities in the calculated spectra may and do not resemble the intensities measured. Still the calculated binding energies for the MOs are in good agreement with measured values as shown before. This can be explained by the weak interaction of the molecules with the substrate as indicated by core level XPS. Measured as well as calculated spectra for the two isomers are similar to a large extent as can be expected. However the small differences mentioned before are visible. A visualizations of these MOs using GaussView [25] as depicted in Fig. 4 suggests that differences in shape and thus in the binding energy of the respective MOs are due to the different conformation of the molecules. This interpretation is further supported by the fact that the trans-stilbene MOs can be transformed into the respective cis-stilbene MOs by bending the orbitals according to the trans-to-cis isomerisation of the molecular backbone. The fact that differences in valence band spectra calculated for isolated molecules are visible in the spectra of the adsorbed species indicate that the bonding interaction of both isomers with the Si substrate is similar, leading to the conclusion that this interaction most likely takes place via the atoms of the C=C-bridge.

The valence band spectra of cis- and trans-stilbene differ significantly from valence band spectra obtained for benzene, where features at 2.3 eV, 4.0 eV, 5.7 eV, 13.3 eV, and 14.1 eV binding energy are found [17,20]. This difference demonstrates that a possible dissociation of the stilbene-molecule into benzene and ethene during deposition does not take place.

The valence band spectra of cis- and trans-stilbene not only show isomer-characteristic differences in peak intensity, e.g. at around 2 eV, 3.4 eV, and 13 eV binding energy, but also peaks specific for only one isomer, at 4.6 eV, 9.7 eV, 4.9 eV, and 9.2 eV for cis- and trans-stilbene respectively. These differences are large enough to permit a clear differentiation between the adsorbed isomers which is a prerequisite for the investigation of the stilbene isomerisation. Although other methods for the differentiation of both isomers are possible, e.g. through vibrational spectra [26], only the valence band spectra give direct access to the electronic structure of the molecule and permit an investigation of the change in electronic structure upon isomerisation.

3.4. Near-edge X-ray absorption fine structure (NEXAFS)

In C1s NEXAFS, electrons from the carbon K shell are excited into unoccupied MOs of the adsorbate complex. Here we use partial electron yield measurements to detect the carbon Auger electrons at 260 eV kinetic energy. Upon variation of the excitation energy, transition into different unoccupied MOs occur. The intensities of these resonances depend on the overlap of the E-vector of the exciting light and the vector matrix element of the final state orbital, such that π^* - and σ^* -orbitals can be probed selectively. The intensity dependence of single resonances with respect to the light incidence angle, here probed by varying the sample polar angle, may thus provide information about the adsorption geometry on the surface [27,28]. Since conformational switching is likely to induce a change in adsorption geometry, NEXAFS may identify and distinguish the two different isomers and allows an insight into the influence of the isomerisation process onto the adsorption geometry. NEXAFS spectra shown in Fig. 5 were recorded for a monolayer of either cis- and trans-stilbene for different light incidence angles. NEXAFS spectra in normal incidence, i.e. at a light incidence angle of 54° with respect to the surface normal,

reveal significant differences for both isomers. The π^* -resonance signal at around 285 eV photon energy shows an asymmetric lineshape that is different for each isomer. DFT-calculations (see above) for isolated stilbene molecules show that for the case of trans-stilbene at least two unoccupied MOs (one with a twofold degeneracy) contribute strongly to the π^* -resonance, while in the case of cis-stilbene contributions from at least three unoccupied MOs may be expected. A comparison of the calculated binding energies of the lowest unoccupied MOs shows different values for trans- and cis-stilbene. This can explain the differences in lineshape of the π^* -resonances. For the trans-isomer the MOs have – in comparison to the respective MOs in cis-stilbene – lower binding energies, giving account for the stronger shoulder in the π^* -resonance at higher photon energies. The MOs for the cis-isomer, on the other hand, have relatively higher binding energies, explaining the stronger shoulder at lower photon energies in the π^* -resonance of the cis-stilbene. Calculations yield an unoccupied MO for both isomers at lower binding energies. Indeed, a weak resonance can be found in spectra for both isomers at 0.5 eV lower photon energies than the π^* -resonance. The σ^* -resonances of trans- and cis-stilbene also correspond to the calculated unoccupied MOs, which for higher LUMO + 5 are not purely π^* -orbitals but incorporate also σ^* -contributions. In addition the σ^* -resonance signal at 287.7 eV photon energy is stronger for trans-stilbene.

These differences, especially for the π^* -resonance signal, again permit a clear distinction between cis- and trans-isomer, which is essential for the detection and characterization of the isomerisation on the surface. To determine the orientation of the molecules on the Si(10 0) surface, NEXAFS spectra were recorded for several light incidence angles. In the case of trans-stilbene the sample was investigated under two different azimuth angles. The intensity of the π^* -resonance for different incidence angles are shown in Fig. 5. Angle values are given with respect to the surface normal.

$$I = A \cdot \left(1 + 0.5 \left(3 \cos^2(90 - x) - 1\right) \left(3 \cos^2 \alpha - 1\right)\right)$$

A \cos^2 -function describing the interaction of the E-vector of the exciting light and the vector matrix element of an s-type initial and a p-type final state [28] was used to fit the curves connecting the datapoints. Here, α is the tilt angle of the molecular π -system plane normal with respect to the surface normal, and x the angle between the incoming light and the surface normal; A is a normalization factor. From these fits we find the tilt angles of the molecular orbitals with respect to the surface normal. In the direction of the Si dimer rows this angle for cis-stilbene is about 57° while for trans-stilbene it is about 36° . In the direction perpendicular to the dimer rows the tilt angle is only slightly larger with 41° for trans-stilbene. For cis-stilbene the tilt angle has been determined in one direction only, as the differences for both directions are rather small as seen for the trans-isomer. These angles indicate that trans-stilbene is only tilted slightly upwards while the phenyl groups of cis-stilbene are pointing away from the surface as indicated in Fig. 5.

Following the hula-twist mechanism as the assumed isomerisation pathway, only the C–H-bonds on the C=C bridge are rotated out of the molecular plane while the actual cis–trans-rearrangement takes place within the molecular plane [9] and only afterwards the tilt within the cis-isomer is established. For such a mechanism, the molecule should not be significantly hindered by the substrate. With the calculated tilt of below 36° the trans-isomer is still adsorbed in a fashion to allow that mechanism to apply in the trans-to-cis direction. The indicated upright position of the cis-isomer, on the other hand, leaves enough room for unfolding from the tilted conformation upon

reaction in the cis-to-trans direction. Thus isomerisation of stilbene should be possible even in the constrained environment of an adsorbed molecule on a Si(100) surface. Attempts to induce this isomerisation by UV light exposure are planned.

4. Summary

The adsorption of cis- and trans-stilbene on Si(100) surfaces has been investigated by means of photoemission spectroscopy and NEXAFS. C1s and Si2p core level XPS show for stilbene on Si(100) only weak bonding in the order of π - π -interactions with adjacent molecules. The Si dimer rows could be identified as interaction sites on the surface. We show that using photoemission spectra of molecular orbitals recorded at low binding energies we are able to identify and distinguish the cis- and trans-isomer of stilbene on the surface, both of which are shown to adsorb undissociated. The experimental binding energies of the MOs are in good agreement with results of DFT calculations. We use NEXAFS not only to identify the adsorbed isomer by means of different lineshape, but also show two different adsorption geometries characteristic for each isomer. In these geometries the assumed isomerisation pathway is feasible and not hindered due to the constrained environment. These studies are important for an analysis of molecular switching processes on surfaces.

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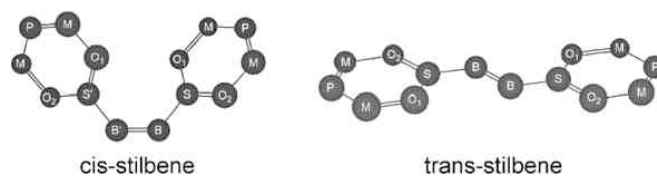


Fig. 1. The two isomers of the stilbene (1,2-diphenylethylene) molecule. On the left hand side the cis-isomer, with both phenyl groups on one side of the C=C-bond (“Z”usammen conformation), on the right hand side the trans-isomer, with phenyl groups on opposite sides of the C=C-bond (“E”ntgegengestzt conformation). C atoms are labeled as used throughout the text.

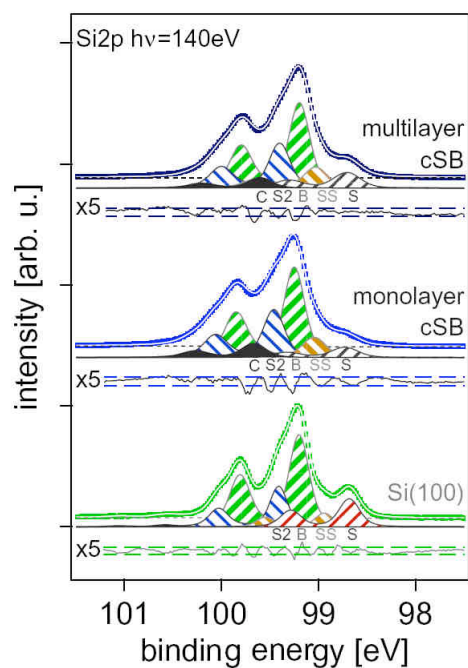


Fig. 2. Si_{2p} core-level spectra from the clean Si(100) surface, and adsorbed cis-stilbene. Also shown is a line shape analysis using five symmetric Voigt-doublets which can be attributed to the up- (S, upright light pattern) and down-dimers (SS, upleft dark pattern), bulk (B, upright dark pattern), 2nd layer (S2, upleft light pattern) atoms and defects (C, solid). Si_{2p} core-level spectra of cis- and trans-stilbene show no significant differences compared to clean Si(100) surface.

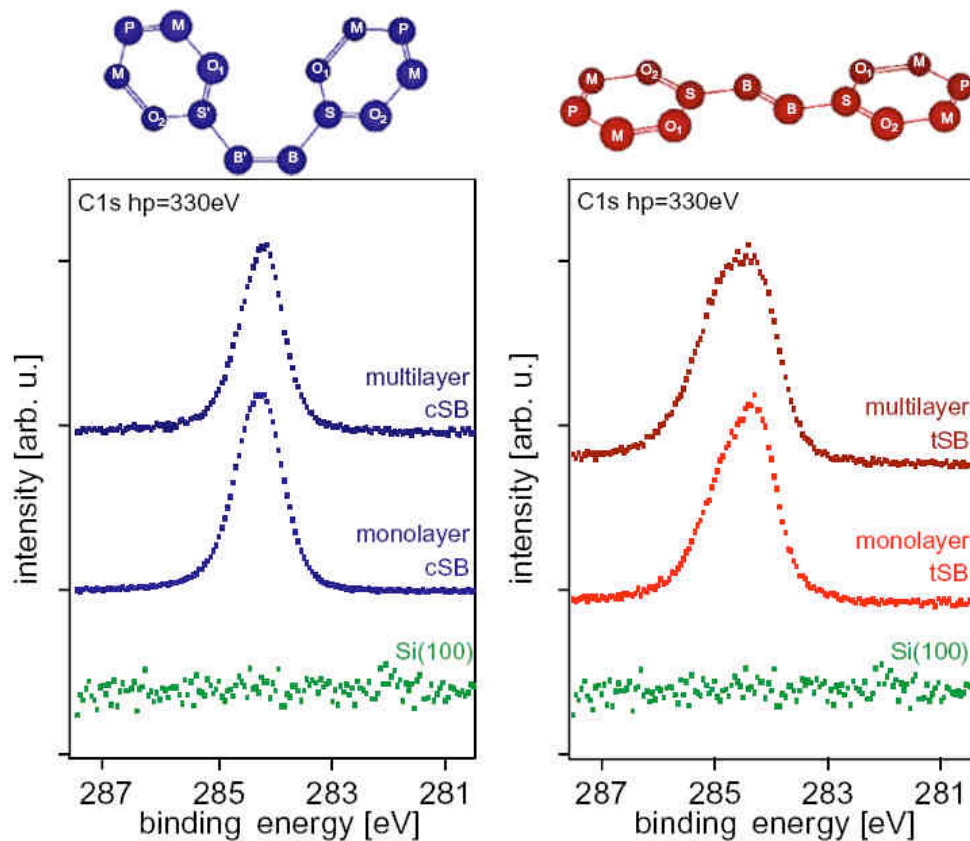


Fig. 3. C1s core-level spectra from the clean Si(100) surface, and adsorbed cis- and trans-stilbene. While cis-stilbene shows a symmetric lineshape, trans-stilbene spectra are asymmetric. For larger coverages peak broadening can be observed due to different interactions between adjacent molecules and molecules with the Si surface.

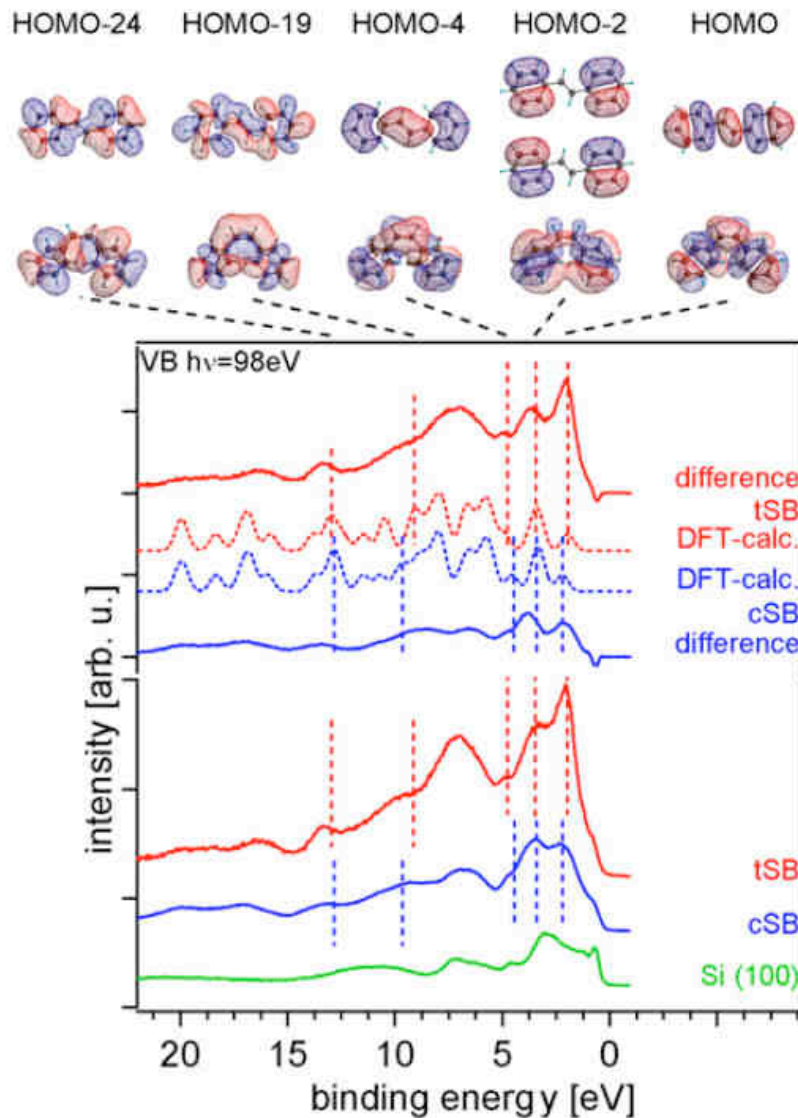


Fig. 4. Valence band spectra of one monolayer cis- and trans-stilbene adsorbed on Si(100) in comparison to the clean surface (lower part). Adsorbate spectra with the substrate components subtracted are shown in comparison to spectra derived from DFT calculated binding energies convoluted with a gauss function (upper part). Differences in spectra from adsorbed cis- and trans-stilbene in measured and calculated spectra are indicated by a “difference-spectrum” and dotted lines, the corresponding molecular orbitals are displayed above.

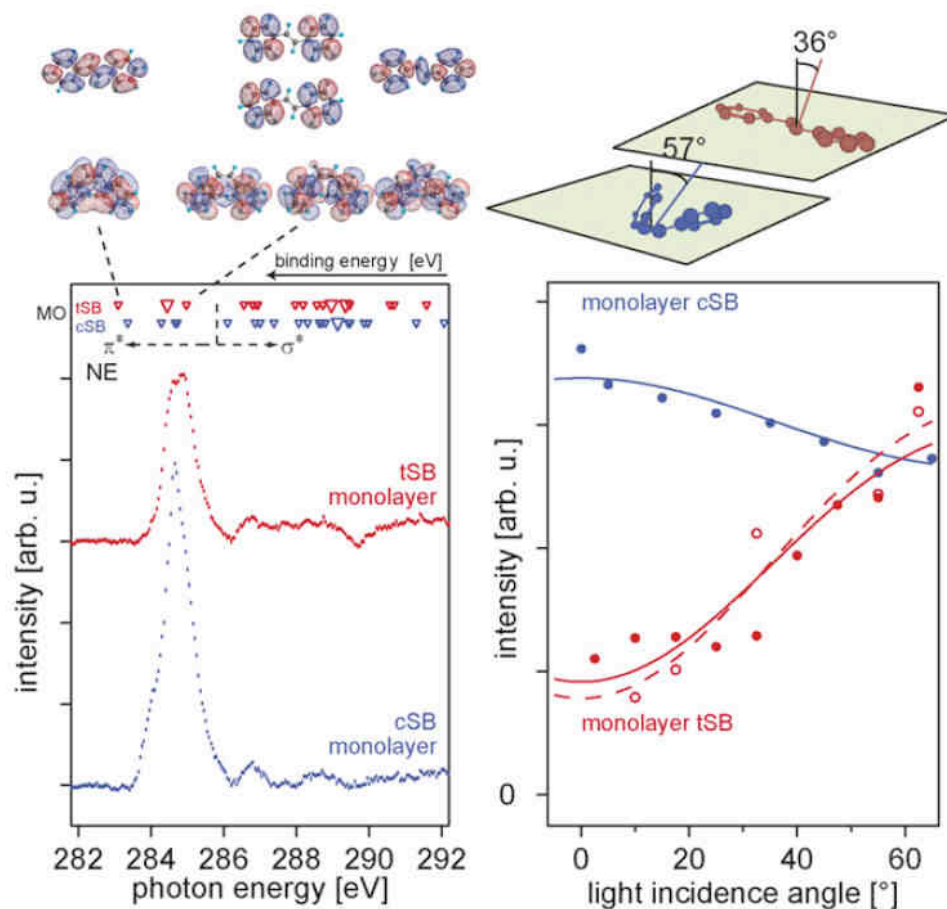


Fig. 5. NEXAFS-spectra of one monolayer cis- and trans-stilbene in normal emission (55° light incidence angle) (left) show different π^* - and σ^* - resonances for both isomers. The calculated binding energy of unoccupied molecular orbitals and their geometry (π or σ) is indicated. Also shown is the intensity change of the π^* -resonance with varying light incidence angle (right) for cis-(filled: 0° azimuth) and trans-stilbene (filled: 0° azimuth, unfilled: 90° azimuth) and the applied \cos^2 -fit (solid line: 0° azimuth, dotted line: 90° azimuth). The derived stilbene adsorption geometry is sketched.