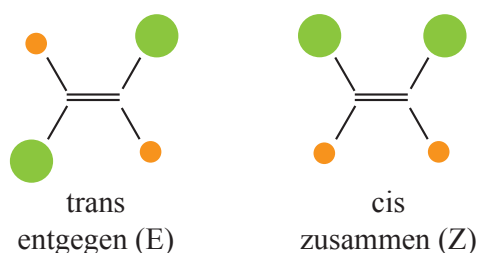


# 5 Isomerisation

## 5.1 Conformation and Isomerisation

### 5.1.1 Conformational Isomers

One of the most fascinating aspects of molecules is the diversity and complexity they exhibit in spite of the small number of different elements they are made of. Not only do several possibilities exist to connect the different atoms, only few of those constitutions[90] being chemically reasonable and every single one associated with one name<sup>1</sup>, but these entities of connected atoms have also several possibilities to order with respect to each other in all three dimensions. Though seeming endless, the actual number of possible orientations is restricted by the nature of their involved atoms – how many bonds can be formed, how can these bonds be arranged with respect to each other, and so on?



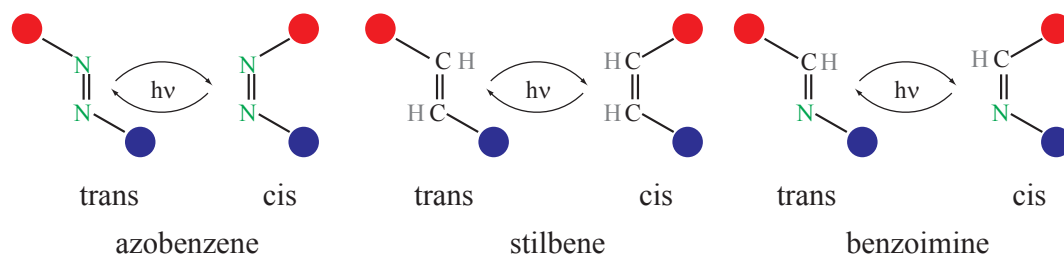
**Figure 5.1:** Molecules with a double-bond entity are named according to the order of the two largest ligands at the two ends of the double bond. These can be either on the same side (German: *zusammen* (Z)) or on the opposite side (German: *entgegen* (E)). They are named *cis* and *trans*, respectively.

A simple functional entity, allowing for two different conformations, is the C=C-double bond. Based on the arrangement of the two largest ligands, a *trans*-isomer (or *entgegengesetzt*-conformation (E; German for “opposite”)) where both ligands are on opposite sides of the double bond, and a *cis*-isomer (or *zusammen*-conformation (Z; German for

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<sup>1</sup>E.g. the molecule  $C_3H_8O$  can have the following three constitutions:  $H_3C - CH_2 - CH_2 - OH$  (Propan-1-ol),  $H_3C - CH(OH) - CH_3$  (Propan-2-ol) and  $H_3C - CH_2 - O - CH_3$  (Methoxyethane).

“together”))<sup>2</sup> where both ligands are on the same side of the double bond, can be realised. Both are shown in figure 5.1. As can be seen in figure 5.2, two other double bond entities exhibit the same behavior, the N=N-diazo group and the C=N-imine group.



**Figure 5.2:** The three important classes of photochromic molecular switches – azobenzenes, stilbenes, and benzoimines. The two large ligands represented by the two filled circles are in all cases functionalized phenyl-groups, i.e. benzene-ring derivatives.

For all three species it is well known, that the described isomerisation can be photo induced[8] making them a “photochromic molecular switch”<sup>3</sup>.

Such an isomerisation does not only change the position of two ligands with respect to each other, but, as can be seen in figure 5.2, also the shape of the complete molecule. The trans-isomers have a long almost linear shape with a slightly Z-like backbone. The cis-isomers are smaller, distorted and might even be tilted. This can have a dramatic impact on the properties of the whole molecule. A typical example is the stilbene molecule. Due to its planarity, stacking of trans-stilbene molecules and interaction of their  $\pi$ -system is simple, crystallisation under standard conditions thus possible - trans-stilbene is a solid. As the cis-isomer cannot stack that easily, it is a liquid under standard conditions.

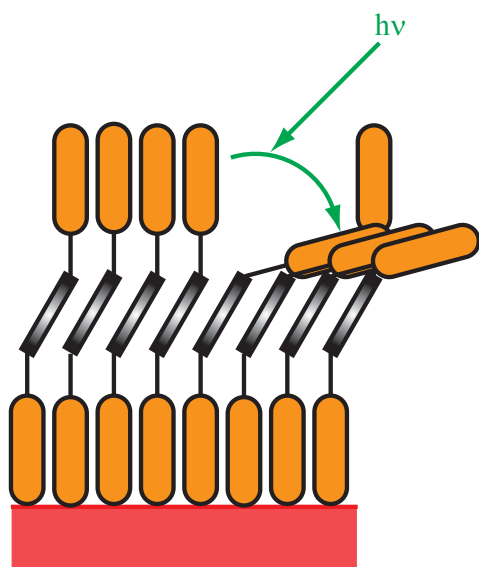
It may be thinkable, that switching is only possible in thin films such as monolayer coverages. For thicker films the molecules may regain their bulk properties and switching would lead to a solid-liquid phase transition.

These switching entities may now be coupled with ligands showing conductive properties. This would ultimately lead to “electronic molecular switches”. An idealized representation is shown in figure 5.3. Such conductive properties may be realized by the use of extended delocalized  $\pi$ -systems [7, 11] of which the smallest representative is the benzene ring. Thus the two simplest realizable optical switches are azobenzene and stilbene (see figure 5.2). Both of them have been extensively investigated, especially in view of their use as electrical switch (e.g. [91–93]). Investigations in the gas phase and in solution have revealed

<sup>2</sup>For historic reasons there exists the E,Z-nomenclature, which is based on the abbreviations of the German words describing the conformation. This nomenclature is still sometimes used in Chemistry. The cis-trans-nomenclature, though, is nowadays the international standard-descriptor for such conformations.

<sup>3</sup>Other classes of molecules that are considered as potential molecular switches are 1,2-dithienylethenes and spiropyrans.

insight into the isomerisation mechanisms, especially of stilbene. While for azobenzenes there have recently been attempts to transfer these molecules onto the surface[91, 92], for stilbene there is almost no such work[93, 94]. Still there is more work on stilbene.



**Figure 5.3:** *Idealized molecular switches on a surface..*

physical and chemical stability of stilbene. The previously described different state of aggregation for the cis- and trans-stilbene and different physical properties are experimental advantages of the pure hydrocarbon.

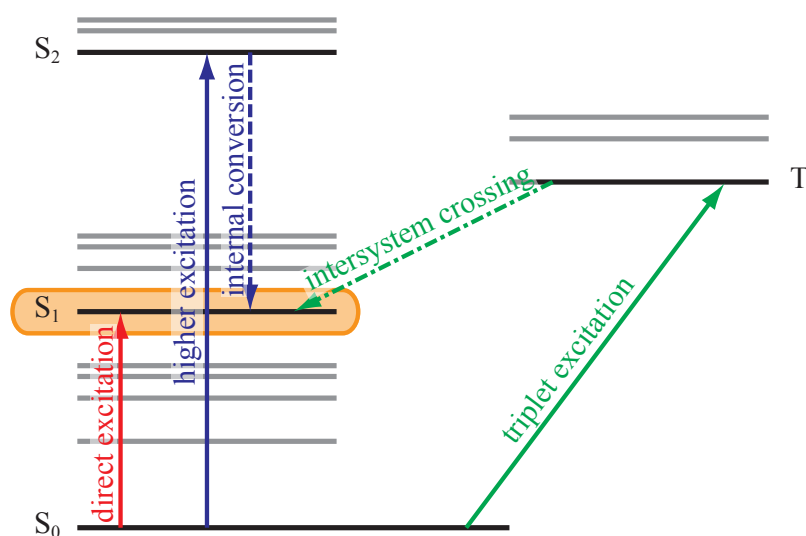
This is not surprising, as stilbene has some very practical experimental advantages over azobenzenes. Despite the fact, that both stilbene isomers are commercially available in very high purity while azobenzenes have to be separately synthesized (and are thus mainly available in the trans-form), the C=C group is of much higher physical and chemical stability than the N=N group. For investigations in absence of any perturbing material under UHV-conditions the latter is not so important, but the former may be very disadvantageous for every spectroscopic method. Stilbene and its derivatives have a broad range of application ranging from laser-dye[95–97] to washing powder as brightener (e.g. [98]). All applications are a prove of the high

### 5.1.2 Photoisomerisation of Azobenzenes and Stilbenes

In terms of conformation, stilbenes and azobenzenes are quite similar molecules[99]. Both planar trans-isomers exhibit a  $C_{2h}$  point group while the cis-isomers are being tilted.

For practical reasons, stilbene has been the wider investigated molecule. Especially gas phase studies and calculations contributed to the deeper understanding of the isomerisation process[12–15].

In principal isomerisation might be induced by several means. The isomers can be thermally activated into a transition state, where the vibrations of the molecule become strong enough to initiate a rotation and thereby transformation into the other isomer. For stilbene the activation barriers have been calculated to be 142-155 kJ/mol in solution[100] and 180 kJ/mol in the gas phase[101]. The bonding enthalpy of the C=C double bond is around 50 kJ/mol (52.318 kJ/mol for  $C_2H_4$ [102]) and thus thermal energy input in the order needed for isomerisation would directly lead to decomposition of the molecule.

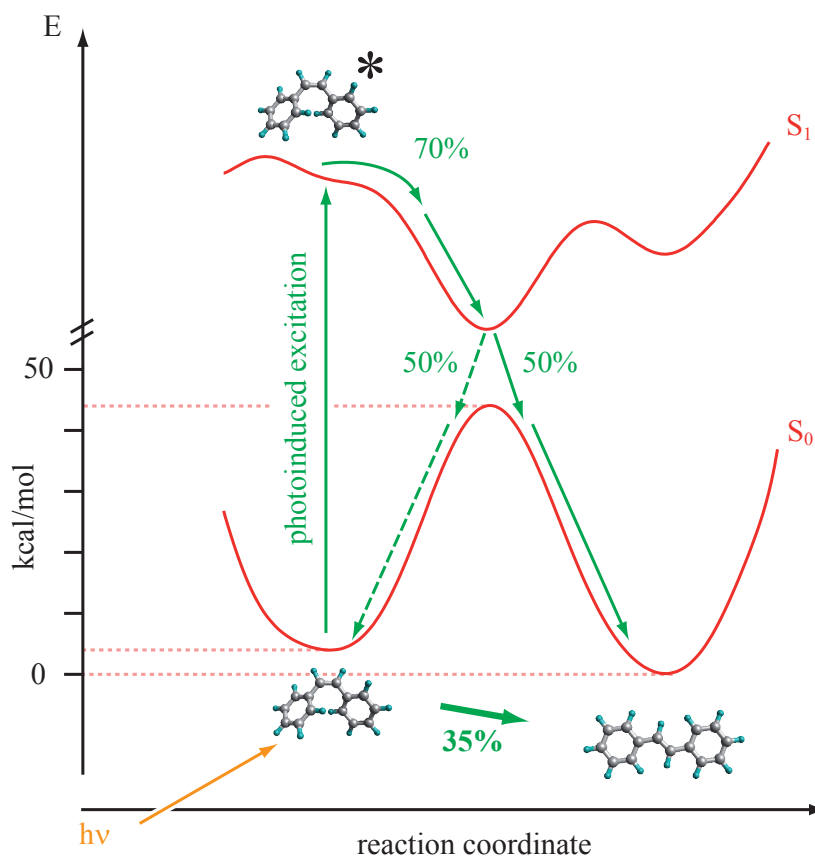


**Figure 5.4:** *Jablonski Diagram [103, 104] of photoexcitation and decay mechanisms possible in stilbene. The  $S_1$  state, in which electrons have to be excited for isomerisation (see figure 5.5) is highlighted. Three excitation mechanisms are available, the direct excitation (red), commonly used in gas phase and solution[13], excitation into higher  $S$  states and deexcitation via internal conversion (blue) and excitation into a triplet state (green). Intersystem crossing leads to a population of the  $S_1$  state[105, 106].*

Photoexcitation however, is a feasible pathway. Such reaction pathways can be displayed by means of a Jablonski scheme[103, 104] as depicted in figure 5.4. Excitation at 312 nm wavelength, corresponding to an excitation energy of 3.98 eV have been reported to be successful[13]. This excitation is actually capable of inducing either the cis-to-trans-reaction or the trans-to-cis-reaction. This corresponds to a  $\pi$ - $\pi^*$ -excitation into an  $S_1$  singlet state (red arrow in figure 5.4). The  $S_1$  state can also be accessed by an excitation with higher energy photons into a higher singlet state and subsequent deexcitation by means of internal conversion (blue arrows). A third pathway would be an excitation into a triplet state with subsequent intersystem crossing to reach the  $S_1$  state (green arrows). The existence of that pathway has been shown by Görner[105] and also by Bendig[106] who proposed a long wavelength excitation pathway. Görner and coworker[105] showed the existence of two intersystem crossing pathways via two triplet states of different energy. A pathway of a very high excitation and following inner conversion has to my knowledge not yet experimentally been shown. There are also only few indications for such a pathway in the literature [107, 108].

Hochstrasser and coworkers elaborated the energy diagram for the photoreactions between the stilbene isomers based upon the direct excitation into the  $S_1$  state[109]. Figure 5.5 shows the isomerisation from cis- to trans-stilbene. In the gas phase an additional reaction pathway is possible: the photoinduced transformation into dihydrophenantrene

(DHP)[109]. This reaction would involve an electron pair relocation away from the C=C-double bond. This site can be assumed the bonding site to the surfaces. Thus such a relocation will be hindered and such pathway can be excluded on surfaces.

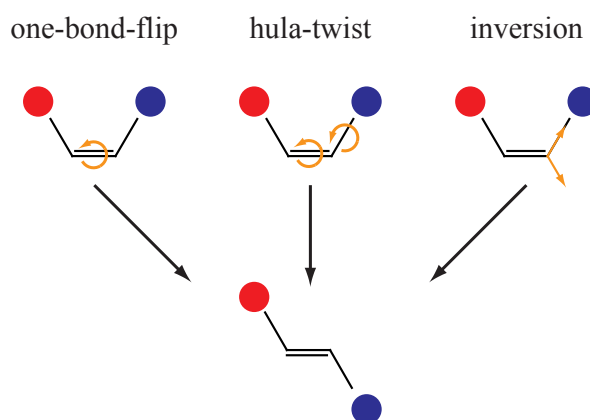


**Figure 5.5:** Energy diagram for conversion between stilbene isomers. For the cis-to-trans isomerisation a total yield of 35% has been reported[110].

For the complete reaction, Vachev and coworkers theoretically predicted an overall conversion from cis-stilbene into trans-stilbene of about 20%[111]. This seems rather low in comparison to the aforementioned experimental value. Assuming the quantum yield of 70% reported by Hochstrasser for the photoexcitation into the isomerisation pathway[109] and the equal possibility for the cis- and trans-pathway (see figure 5.5) at the intersection, a yield of 35% is reasonable.

For azobenzene the thermal activation barrier lies at an energy of 96 kJ/mol [112]. Anderson and coworkers have shown in detail that this excitation mechanism is present for the cis-to-trans-isomerisation of azobenzenes[113, 114]. For photoinduced isomerisation, the excitation energies (wavelengths) are 3.55 eV (350 nm) for the trans-to-cis and 2.82 eV (440 nm) for the cis-to-trans-isomerisation[115, 116]. These are again direct  $n-\pi^*$  excitations from an unbinding into an excited antibonding  $\pi^*$  state of azobenzene comparable to the  $S_1$  state shown for stilbene in figure 5.5. While for stilbene only photoisomerisation

has been investigated, for azobenzenes additional excitation mechanisms have been sought for. Besenbacher and coworkers showed for azobenzene on Cu(110) that the substrate - adsorbate interactions are as strong that additional thermal activation might be needed in conjunction with the photoexcitation[117]. In this case, the azobenzenes adsorbed at the Cu bridge sites and with a small tilt angle along the  $[1 \bar{1} 0]$  direction. Morgenstern and coworkers showed that direct excitation of single azobenzene molecules by inelastic electron tunneling can induce the cis-to-trans and trans-to-cis isomerisation[116]. Excitation energies of about 640 meV and 650 meV had to be applied, respectively. Grill and coworkers showed, that also the electric field between STM-tip and metal (Au(111)) surface can induce isomerisation of azobenzene molecules[118].

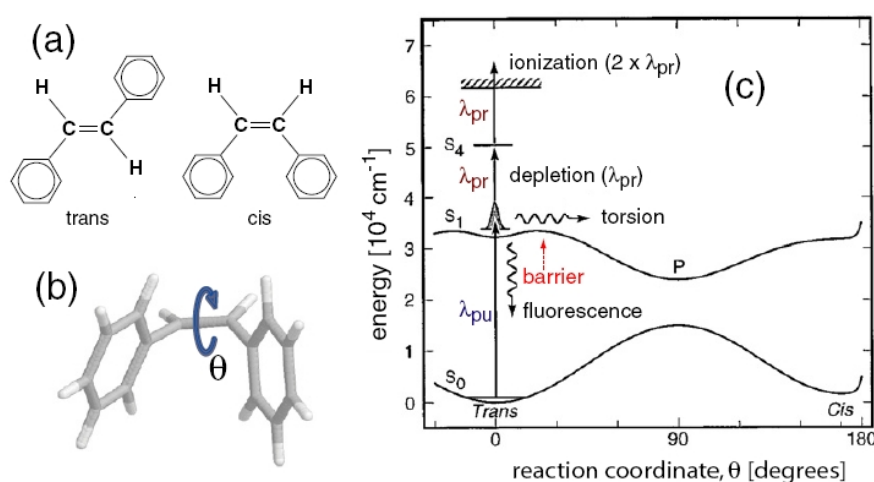


**Figure 5.6:** Three possible isomerisation are thinkable for the stilbene isomerisation. The one-bond flip corresponds to a rotation around the central bridge bond, the hula-twist to a rotation around the central and one adjacent bond. As a third mechanism an inversion around one of the bridge atoms is possible.

Three different mechanisms shown schematically in figure 5.6 are possible for the conversion of a double-bond cis-isomer into the according trans-isomer. The *one-bond-flip* is the most simple mechanism and represents a rotation around the central double bond. It begins with the photoexcitation of the starting material. From this photoexcited state, the molecules relax into a phantom state  $P$  (marked as such in figure 5.7), where the two phenyl groups are tilted by  $90^\circ$  toward each other, which is halfway between the angles for both conformers. Following the one-bond flip, the molecule subsequently reaches the ground state via a conical intersection resulting in vibrationally excited molecules. Such a rotation requires a free rotation cone around at least one ligand, as in the intermediate situation both ligands have a dihedral angle of  $90^\circ$ . A mechanism requiring less space is the *hula-twist*. During the simultaneous rotation around the double bond and one of the adjacent single bonds, both ligands are parallel to each other throughout the whole reaction. This is of importance in a constrained environment like adsorbed on a surface, where one halfsphere of space is blocked by the substrate. In such an environment the hula-twist mechanism seems much more feasible than the one-bond flip. This also holds

true for the *inversion* reaction, where the ligand and the adjacent hydrogen atom (in the case of stilbene) or electron lone pair (in the case of azobenzene) exchange places.

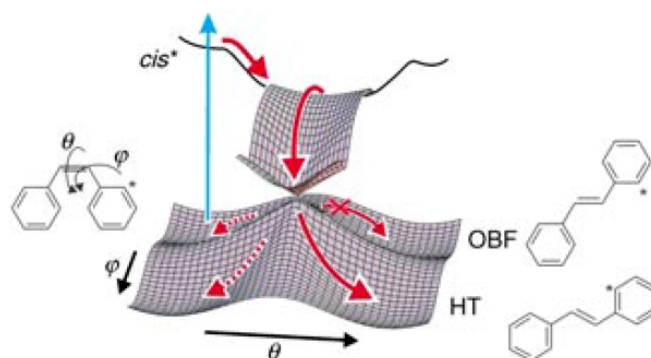
All three mechanisms have been considered for the isomerisation of stilbene and azobenzene. In the early stages, the one-bond-flip, as the most simple mechanism, was assumed to appear. It is still supported by several theoretical papers from Baskin and coworkers[14, 119]. In contrast to this the hula-twist, a pathway that would be more feasible especially in the constrained situation on a surface, was supported by the works of Fuß and coworkers[15]. It has to be noted that Baskin has investigated the trans-to-cis-isomerisation, while Fuß investigated the cis-to-trans-pathway. The appearance of such a twisted state along the reaction pathway was also proposed by Hochstrasser, who investigated the cis-to-trans-isomerisation in solvents [120].



**Figure 5.7:** The one-bond flip mechanism for the trans-to-cis isomerisation (a) of stilbene (b) as proposed by Hochstrasser, Baskin and Zewail[14, 119]. On the right the energy diagram (c) is shown, with the phantom state P, where the two phenyl-rings are in an  $90^\circ$  angle to each other, indicated. – Figure reproduced from [119].

Fuß[15] tested both pathways using marked stilbene molecules. Depending on the mechanism two different isomers might result, as shown in figure 5.8. Subsequent to a one-bond-flip the marker would point away from the C=C-bridge. A hula-twist mechanism would have the marker pointing toward the bridge. As only the latter product could be detected, the hula-twist pathway was supposed to be valid for the cis-to-trans isomerisation. This pathway has now also been confirmed theoretically[121].

Following theoretical calculations, azobenzenes were also sought to follow the one-bond-flip[122]. Yet this could not be shown experimentally. For the thermally activated isomerisation Andersson and coworkers deduced an inversion pathway from their experiments[113, 114]. The calculations of Wettermark and Ljunggren, who obtained activation barriers of  $293 \text{ kJ/mol}$  for a one-bond-flip and  $138 \text{ kJ/mol}$  for an inversion[123], which



**Figure 5.8:** Energy diagram of the *cis*-to-*trans*-isomerisation of stilbene as proposed by Fuß and coworkers[15]. The two possible products of a one-bond flip or a hula-twist of a marked stilbene are shown. Only the latter one could be detected by Fuß and coworkers. – Figure reproduced from [15].

agrees more with the experimentally determined activation barrier of  $96 \text{ kJ/mol}$  [112], support this finding. The hula-twist mechanism was instead found for the photoinduced isomerisation in gas phase[124]. Still, the inversion pathway seems to be the preferred mechanism for azobenzene isomerisation, while it is not present at all for stilbene. This is not surprisingly, as an inversion of a bond and an electron lone pair is easier carried out than the inversion of two covalent bonds.

Above findings may or may not apply when the molecules are adsorbed on the surface. The bonding interaction with the surface will alter the electronic structure of the molecules. Thereby the excitation pathways for isomerisation can be either promoted or inhibited. Additionally the steric hindrance due to the surface may make certain pathways, e.g. simple rotations, impossible. Consequently for stilbene Wang and coworkers observed a one-bond-flip after light induced isomerisation of *trans*-molecules adsorbed on  $\text{Ag/Ge}(111)\text{-}(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ . After irradiation with 248 nm (5 eV) UV-light, i.e. at shorter wavelength than in the gas phase, single molecules could be observed by STM to have undergone isomerisation. They proposed a complicated exciton propagation pathway for excitation and a subsequent one-bond flip for isomerisation. This pathway seems highly complicated in contrast to the direct excitation known from gas phase. Also a mere one-bond flip seems rather surprising under the constrained conditions on the surface. The isomerisation of only single molecules within a whole assembly on the surface still leaves several questions open.

Only very recently also photo-induced isomerisation of azobenzenes lying flat on  $\text{Au}(111)$  surfaces has been achieved, e.g. by Wolf and coworkers[125, 126]. Crommie and coworkers have shown that poly-*tert*-butyl-substituted azobenzenes can be reversibly isomerised upon UV-irradiation of 375 nm[127]. The overall conversion was at about 4%. For upright

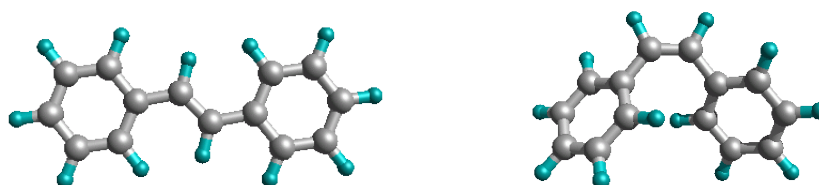


azobenzenes attached to silicon samples via a  $SiCl_3$ -anchor Heinzmann and coworkers determined a 360 nm excitation wavelength[128]. The other excitation mechanisms mentioned before were more successful up to now. Excitation by inelastic electron tunneling, as performed by Morgenstern and coworkers, induced an isomerisation (in both directions) following a pathway that is due to an inversion of an N-C bond[116].

## 5.2 Isolated Molecular Switches - Gas Phase Stilbene

### 5.2.1 Stilbene in the Gas Phase

In the gas phase, *cis*- and *trans*-stilbene have their initial configuration, as can be seen in figure 5.9. Lacking any sterical constraints from the environment, the *trans*-isomer is planar while the *cis*-isomer is twisted.



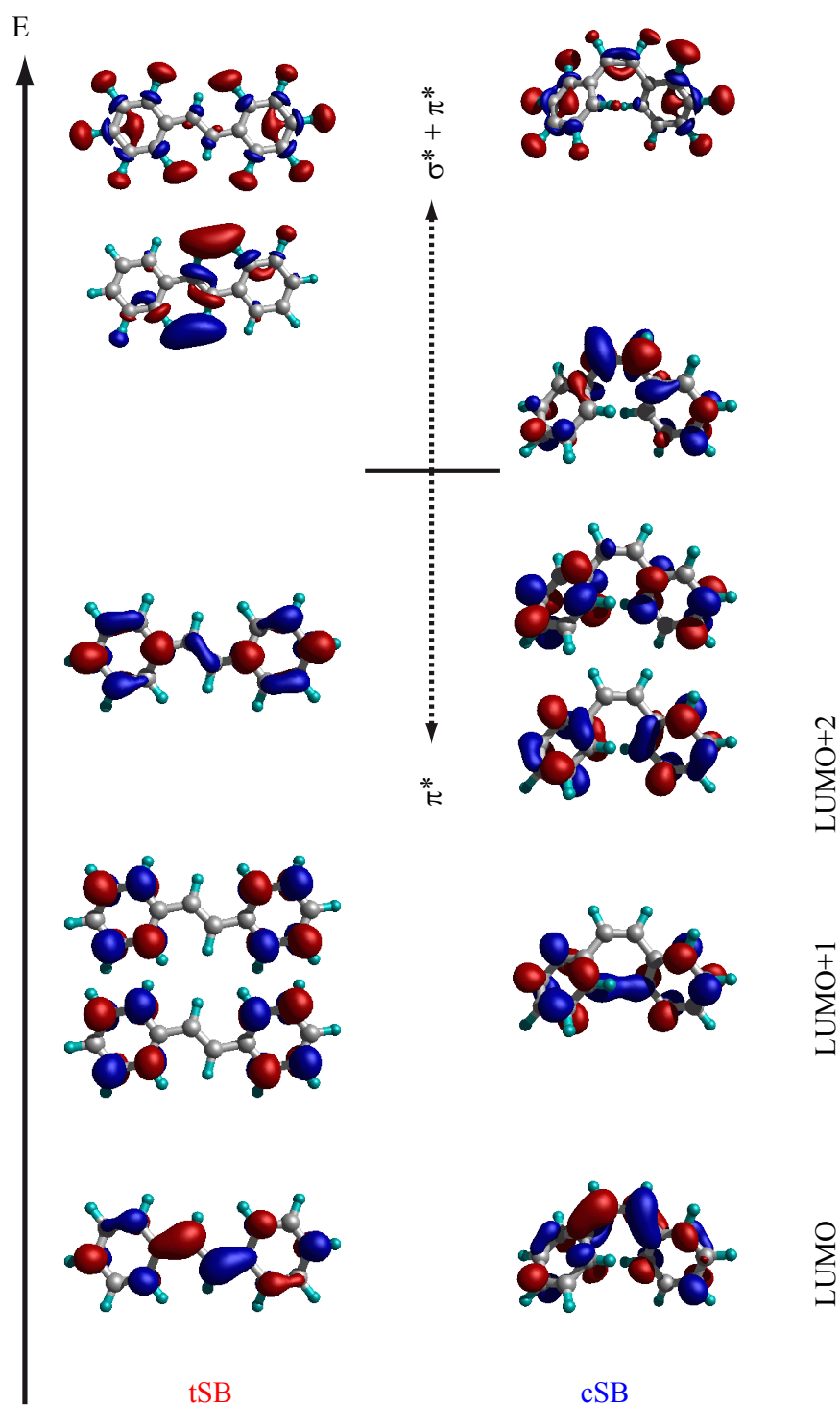
**Figure 5.9:** Conformation of *cis*- and *trans*-stilbene in gas phase.

For the planar *trans*-isomer it is reasonable to assume that the  $\pi$ -orbitals of the three entities phenyl-group/C=C bridge/phenyl-group can overlap and form a fully conjugated  $\pi$ -system. This can easily be derived in the Hückel molecular orbital picture[67], where the atomic  $p_z$  orbitals, i.e. the orbitals perpendicular to the molecular plane, are added up. The best representation of this fact should be the HOMO and the LUMO, but also the other molecular orbitals should be symmetric around the center of the C=C bridge.

DFT calculations using the Gaussian program and subsequent visualization in figure 5.10 support these assumptions. Using a 6–31g basis set and the B3LYP functional, the ground state of a single *trans*-stilbene molecule was calculated using Gaussian. After geometry optimization, the binding energies of occupied and unoccupied molecular orbitals were determined. From the calculated electron density, the geometry of the molecular orbitals was deduced. The LUMO-orbital is a pure  $\pi$ -type orbital, it is delocalized over the full molecule, and the sign changes with every lobe (indicated by red and blue color in figure 5.10). Therefore the LUMO represents a fully conjugated  $\pi$ -system. The same holds true for the LUMO+2; though the degenerate LUMO+1 is localized at the two phenyl groups, it is fully symmetric around the center of the molecule. The higher orbitals depicted show a more complex geometry, but still show the significant characteristics: full conjugation, delocalisation over the whole molecule, symmetric around center of the C=C bond.

For the *cis*-stilbene, this is by far not so intuitive. Due to the twist of the molecule, the  $\pi$ -orbitals of the different entities still can overlap in the concave or inner side of the molecule, but the interaction is not as collinear as for the flat *trans*-isomer. And on the outer or convex side, overlap is much less than for *trans*-stilbene. Thus a distortion of the overall  $\pi$ -system due to the twist in the backbone can be assumed. On the other hand, a

fully conjugated  $\pi$ -system is energetically favored and it resists against a certain amount of sterical strain before loosing its conjugation.



**Figure 5.10:** Unoccupied Molecular orbitals of *cis*- and *trans*-stilbene.

To reveal this question, the same calculations as for *trans*-stilbene were performed on the *cis*-isomer. As figure 5.10 shows, the unoccupied molecular orbitals of *cis*-stilbene

still exhibit a full conjugation. This can be seen nicely in figure 5.10. The LUMO of the cis-isomer is delocalized over the whole molecule, purely  $\pi$ -type and changing sign with every lobe. In fact, the similarity between the orbitals for both isomers is evident. The two LUMOs of both isomers show a comparable electron distribution, in spite, of course, of the different conformation. The next two orbitals (LUMO+1 and LUMO+2) in case of the cis-isomer exhibit an energy difference mainly due to the bent cis-conformation. Thus for the trans-stilbene these two orbitals are the degenerated LUMO+1. Also the cis-LUMO+3 and trans-LUMO+2 are of comparable shape and energy. For completeness it shall be mentioned that higher unoccupied MOs exhibit also a  $\sigma$ -contributions, thus reducing the favorable influence of the fully conjugated  $\pi$ -system. The differences between the isomers become larger and are not only due to the different conformation. Two examples are shown in figure 5.10. In this work, the previously described  $\pi^*$ -orbitals will be of main interest.

Indeed, if the molecular orbitals, calculated for trans-stilbene are twisted in a way analogous to the twist the cis-isomer exhibits, almost identical isomers are obtained than calculated directly for the cis-stilbene. These findings show the strong similarity in electronic structure of both isomers.

Ideally this similarity will help to distinguish stilbene from other molecules like benzene. The fact that the electronic structure is not identical will then provide a tool to distinguish the isomers. Nevertheless two important aspects are up to now neglected. These calculations are determinations of energy and geometry of orbitals in single molecules – and not in molecular assemblies, either in gas phase or adsorbed on a surface. And the overlap of final and initial orbital, which determines NEXAFS intensity, is up to now neglected.

## 5.2.2 Identification of Isomers - NEXAFS

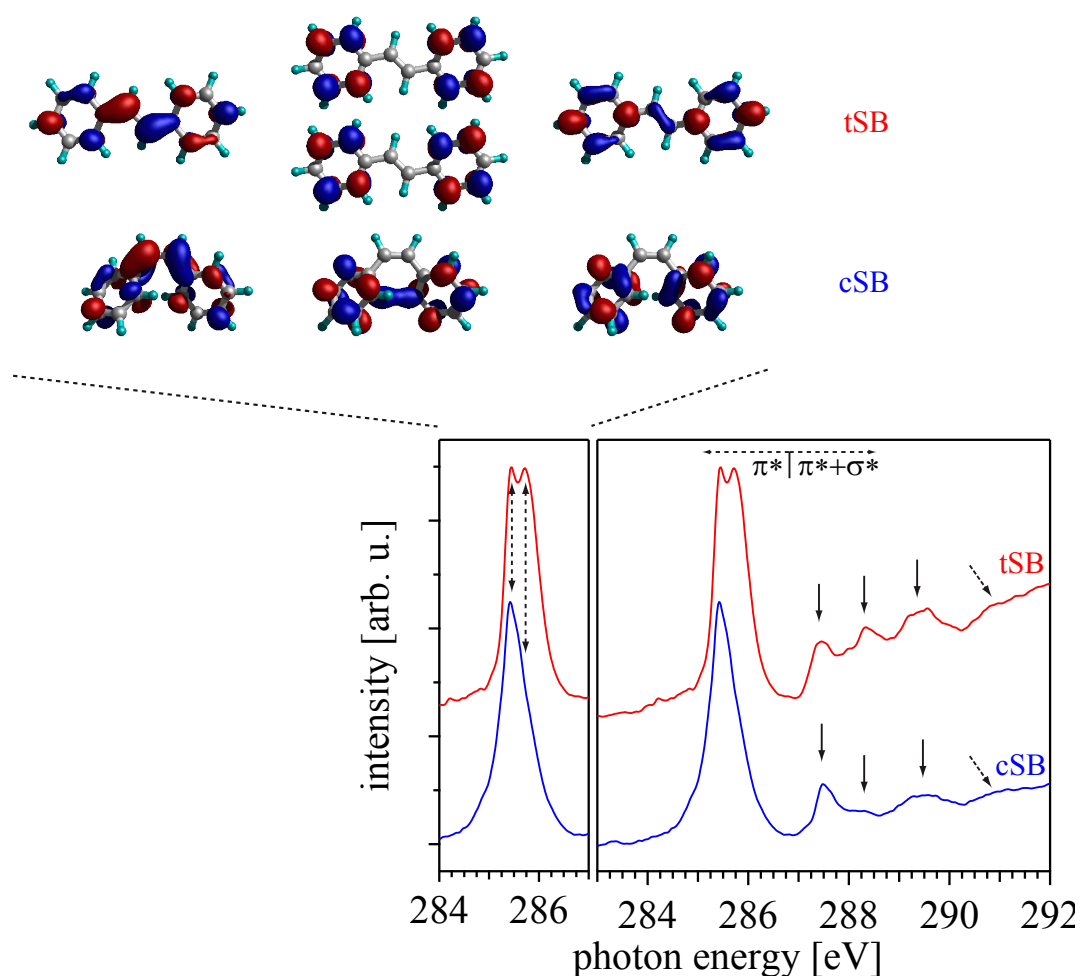
### Experimental NEXAFS spectra

NEXAFS is a very powerful but yet straightforward technique to investigate the structure of molecules[129] and the interaction of these molecules with their environment[62]. NEXAFS is the only spectroscopic tool, that joins so much supplementary information in a single spectrum. Still the interpretation of NEXAFS spectra is, as mentioned in chapter 4.3, very straightforward following intuitive concepts, such as the MO theory. Thus NEXAFS appears to be the ideal method to investigate the two isomers of stilbene and follow the isomerisation process.

Figure 5.11 shows gas-phase Carbon-K-edge NEXAFS spectra (CK-NEXAFS) of both stilbene isomers[130]. Both spectra for the cis- and trans-isomer show two spectral regions,

which are analysed separately. Up to about 286.2 eV photon energy the sharp and intense  $\pi^*$ -resonance can be seen while for higher energies, combined  $\pi^*$ - and  $\sigma^*$ -resonances are visible as indicated in the figure.

### CK-NEXAFS



**Figure 5.11:** Carbon  $K$ -edge NEXAFS spectra (CK-NEXAFS) of gas phase *cis*- (blue) and *trans*-stilbene (red). Full spectrum on the right, detail of  $\pi^*$ -resonance on the left.

From the line shape, and a comparison of the *cis*- and *trans*-spectra, it is clear that the  $\pi^*$ -resonance is a multi-component signal. While for the *trans*-stilbene two components at 284.85 eV and 285.1 eV photon energy with a clear splitting between each other are detectable, the  $\pi^*$ -resonance of the *cis*-isomer exhibits only one peak at 284.82 eV photon energy. The second component, as indicated by the dashed arrows, vanishes in the shoulder. In fact, more than just two components determine the  $\pi^*$ -resonance - that is, excitation from every atom in the molecule into the three lowest unoccupied molecular orbitals, as is indicated in figure 5.12. As shown in figure 5.11, these orbitals exhibit a certain similarity, thus the differences in spectra can only result from the different confor-

mation of the isomers. This difference in conformation directly influences the overlap of the unoccupied molecular orbitals (final state) with the C1s orbital of the different atoms (initial state).

The  $\pi^*$ -resonance with its direct dependence on the molecular conformation is a key-feature to clearly identify both isomers.

In the region above 286.8 eV photon energy, several smaller peaks can be found. These can be attributed to excitations into molecular orbitals that are either of pure  $\sigma^*$  or combined  $\pi^*$  and  $\sigma^*$  nature. These features are of much lower intensity than the  $\pi^*$ -resonance and also sit on top of a strongly increasing background. As these are gas-phase spectra, there does not exist a continuum-step to be subtracted. Both isomers exhibit three well visible resonances (indicated by arrows in figure 5.11) in this region at about 287.45 eV, 288.35 eV and 289.37 eV photon energy. The first resonance is slightly sharper and more intense for the cis-isomer, while the second signal, shifted to minimal lower energies, is less intense there. The third signal, broad and small for the cis isomer, even exhibits a substructure for the trans-stilbene.

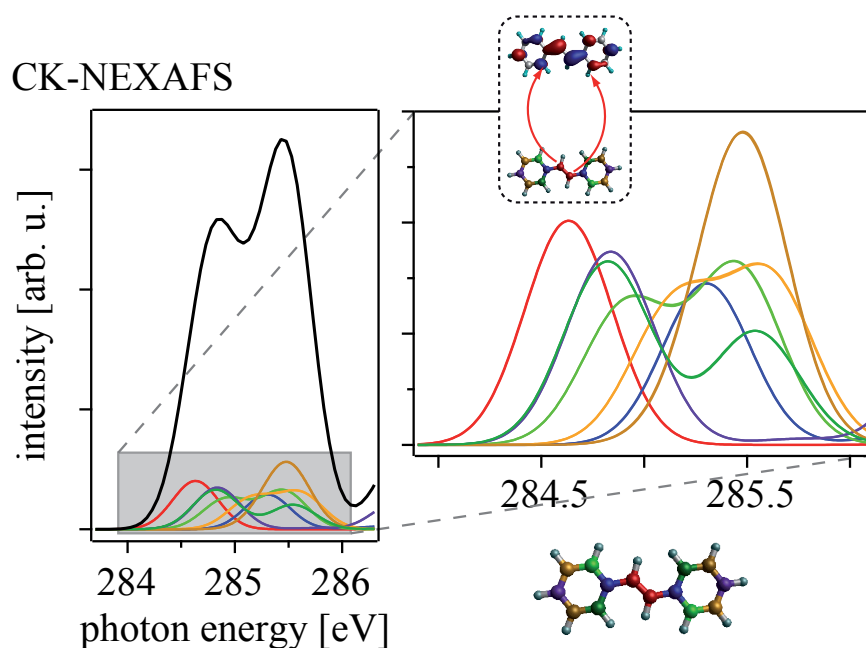
Additional signals, e.g. at 291 eV (dashed arrow), are very small in comparison to the background and an assignment is rather speculative here.

### **Theoretical calculations of NEXAFS spectra**

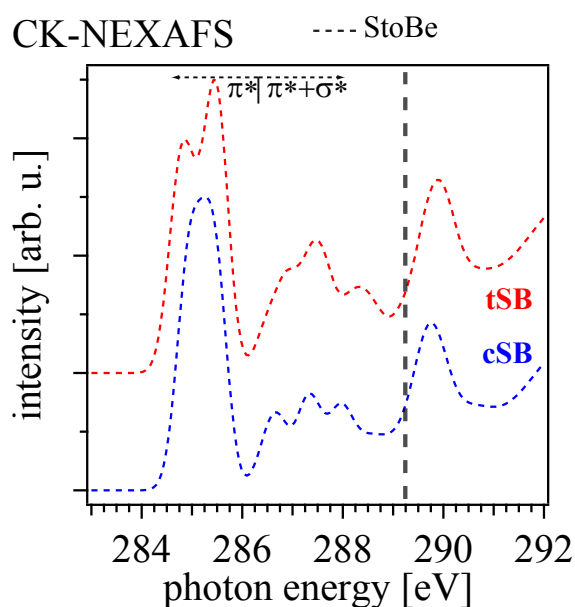
Up to now, only DFT calculations of molecular orbital geometries and binding energies have been shown. These were used for a qualitative comparison with the experimental data. A reasonable assignment of the peaks in the NEXAFS-spectra could be obtained. For further interpretation, in order to gain better insight into the experimental data, the StoBe[87] package has been used for a theoretical prediction of actual NEXAFS spectra. Figure 5.12 shows the results of these transition state calculations for trans-stilbene.

As described before in chapter 4.6, StoBe-calculated spectra are based on the excitation of electrons from every single atom into every unoccupied orbital. These atom-specific spectra are the color-coded lines in figure 5.12. Exemplarily the transition from the C-K-shell of the red-coded atoms into the LUMO are indicated in the figure. The superposition of all these transitions results in the solid black spectrum in figure 5.12.

The NEXAFS spectra derived from the StoBe calculations, as shown in figure 5.13, show a peak structure very similar to the experimental spectra shown before. Both exhibit a strong  $\pi^*$ -resonance at energies around 285 eV photon energy and a three-peak structure between 286 eV and 289 eV photon energy, which can be attributed to combined  $\pi^*$ - $\sigma^*$ -resonances. At 290 eV photon energy a very dominant peak is predicted for both isomers. The  $\pi^*$ -resonance is differently predicted for both isomers. While for the cis-stilbene a



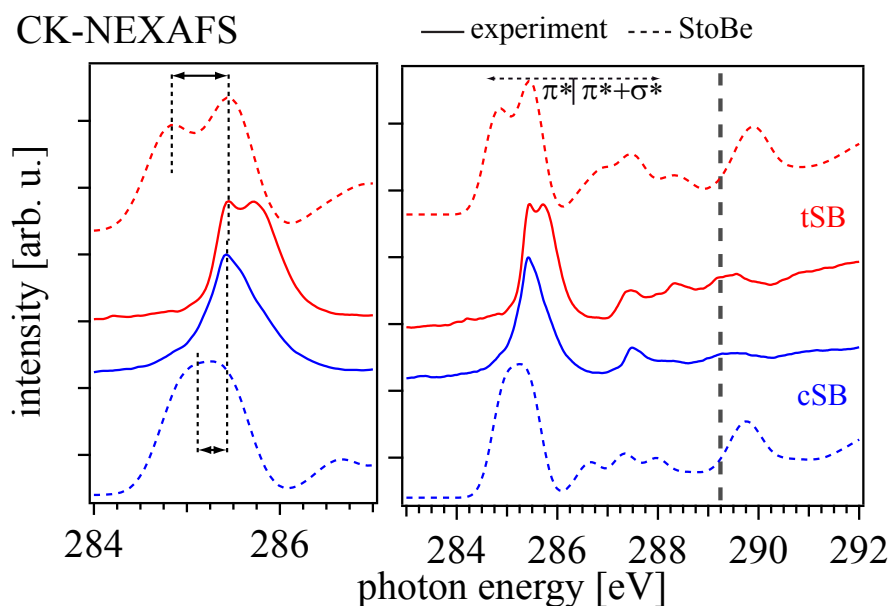
**Figure 5.12:** *StoBe*-calculations of CK-NEXAFS spectra for stilbene. The thick black line is the calculated NEXAFS spectrum (shown is the  $\pi^*$ -resonance of *trans*-stilbene), the colored lines represent hypothetical spectra, which would be obtained, if electrons would be excited from only one atom in the molecule into the different unoccupied orbitals. The assignment to the different atoms is given in the inset.



**Figure 5.13:** NEXAFS spectra of *cis*- and *trans*-stilbene resulting from *StoBe* calculations.

single peak results from the calculations, the *trans*-isomer exhibits a split  $\pi^*$ -resonance. Also the intensity distribution in the combined resonances is different for the isomers. While for the *trans*-isomer the central peak is of higher intensity, for the *cis*-isomer all

three features are more or less of equal intensity.



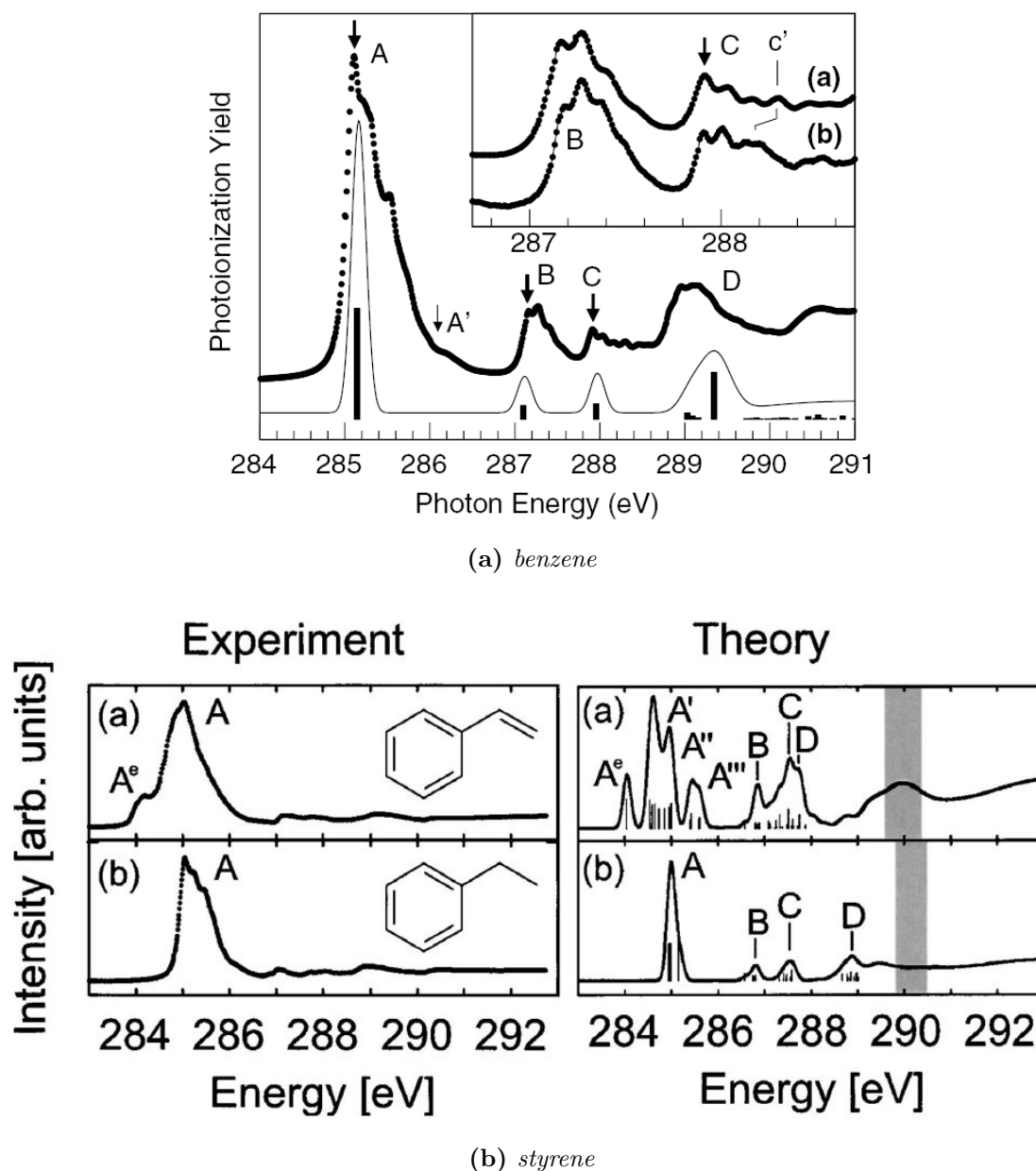
**Figure 5.14:** CK-NEXAFS spectra of gas phase cis- (blue) and trans-stilbene (red). Comparison of experimental data (solid line) and StoBe calculations (dashed line). The energy shift in the  $\pi^*$ -resonance is indicated by the two arrows. The dashed vertical line marks the ionisation potential of the carbon atoms.

At first glance, the StoBe-calculations in figure 5.14 seem in a certain way resemble the experimental data. They exhibit a  $\pi^*$ -resonance that is of different shape for each isomer and then a number of  $\sigma^*$  and mixed  $\pi^*$ - $\sigma^*$ -resonances. Closer investigation of the different regions of the spectra reveal, that the agreement of calculation and experimental data does not exceed this qualitative resemblance.

The  $\pi^*$  of the StoBe calculations show a behavior for the two isomers that has also been observed in the experiment: the trans-stilbene spectrum is split and shows two pronounced maxima, the cis-stilbene spectrum shows one maximum at lower photon energies while the second signal is hidden in the shoulder of the  $\pi^*$ -resonance. Apart from this overall agreement in general peak shape, the calculations exhibit major differences in comparison with experiment. The low-energy-peak of the trans-spectrum is shifted by 0.6 eV to lower photon energies. For the cis-isomer the shift is only about 0.3 eV to lower energies. These shifts are indicated in figure 5.14. In the experiment both low-energy-peaks were located at the same excitation energy. This is not the case in the calculation, here the signal derived for the trans-isomer is about 0.3 eV lower in energy. Especially striking is the difference in splitting and linewidth. The broader linewidth of the calculated spectra can partially be explained. In the calculation, the cross sections for every transition from every atom core level into every unoccupied molecular orbital are determined. These are convoluted with a gaussian of 0.5 eV width that determines the peak broadening. This value has



shown to be realistic for organic gas phase molecules[131, 132]. Different broadening and different functions (i.e. a Lorentzian and the vibrational decay measured for benzene[131]) did not provide better results. But the splitting itself, which is 0.3 eV in the experiment and 0.65 eV in the calculation is due to the energies calculated for every transition. This difference of a factor of more than two between calculation and spectra already indicates major problems in the calculations.

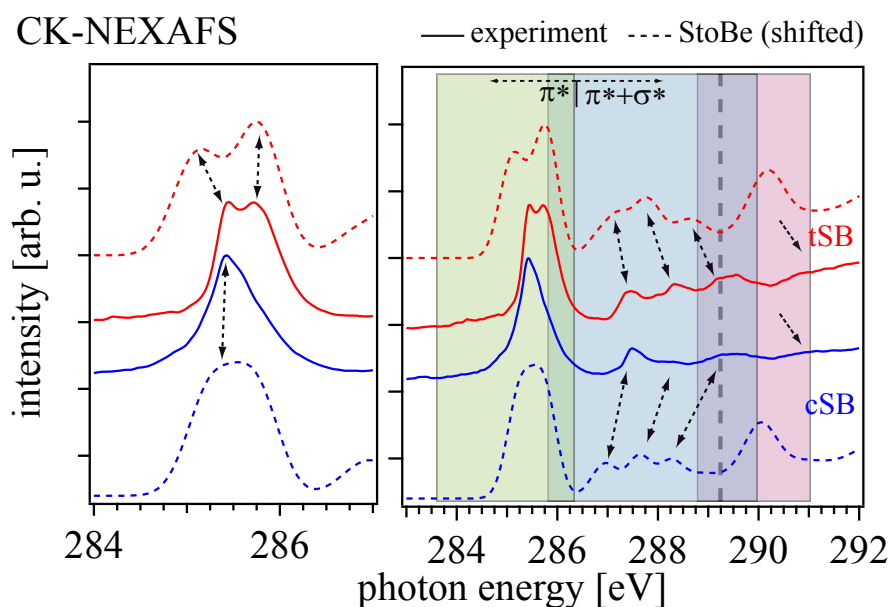


**Figure 5.15:** Two examples from literature comparing experimental gas phase NEXAFS spectra and StoBe calculations. Both cases exhibit the same discrepancies between experimental and theoretical spectra as observed here. – Figures reproduced from [131] and [132].

The experimental findings for the  $\pi^*$ -resonance are qualitatively confirmed by the calculations in terms of peak-appearance. The  $\pi^*$ -resonance can really be seen as “spectroscopic

identification tag”.

Obviously, this is not the first work, where experimental NEXAFS spectra are compared with calculations using the StoBe code. Püttner and Kolczewski have demonstrated with their work on small aromatic hydrocarbons how powerful this method may be [131, 132]. Figure 5.15a shows the NEXAFS spectra of benzene. Below 289 eV photon energy the agreement between theory and experiment is remarkable. The energy positions and, for the  $\pi^*$ -resonance, also the lineshape are resembled well by the calculations. The peak fine structure, that is shown in the inset for benzene and deuterated benzene, is nevertheless not resembled by the calculations. The agreement in energy position seems remarkable, but has only been achieved after shifting the calculated spectrum to 0.2 eV higher photon energies [131]. This shift is, though slightly smaller, still comparable with the 0.3 eV shifts observed here. With this in mind, the energetic resemblance of the measured spectra of stilbene and the StoBe-calculation is better.



**Figure 5.16:** CK-NEXAFS spectra of gas phase *cis*- (blue) and *trans*-stilbene (red). Comparison of experimental data (thick line) and StoBe calculations (thin line). The different areas of the spectrum are marked in colors (see text). The dashed line marks the ionisation potential of the carbon atoms.

Upon application of a shift of 0.3 eV on the calculated spectra, in accordance with the literature examples shown before [131, 132], the agreement of the StoBe calculations with the experimental data increases. This is shown in figure 5.16. Still there is no absolute agreement of the calculated and measured  $\pi^*$ -resonances. For the *cis*-stilbene, the peak-centers of the  $\pi^*$ -resonance are both at 285.25 eV, for the *trans*-isomer these are still by 0.3 eV apart.

In the blue area of the spectrum, the calculations show three signals for both isomers. The middle peak is stronger in intensity in the case of the trans-isomer. Qualitatively, this resembles the experimental findings - three  $\sigma^*$ -resonance-resonances with a stronger middle peak for trans-stilbene. On a quantitative scale the agreement is not very good. The shape of the signals, especially the low-energy signal of the cis-isomer, is not in agreement. The overall intensity is bigger in the calculation than in the experiment. The  $\sigma^*$ - and combined  $\pi^*$ - $\sigma^*$ -resonances show the opposite behavior of the  $\pi^*$ -resonance. The latter one is too broad in the calculation. The former three-peak structure, on the contrary, is wider in the experiment than in the calculation. Thus an energy difference of 0.3 eV, 0.6 eV and 0.9 eV for the first, second and third peak, respectively, exists between the StoBe calculation and experiment.

Major differences do occur in the red region. While the StoBe calculation predicts an intense signal at about 289.75 eV and 289.88 eV photon energy for trans- and cis-stilbene, respectively, in the experiment only minimal signals at about 291 eV can be observed (dotted arrows, see also figure 5.11). The ionisation potential of the carbon atoms in stilbene is at about 289.15 eV (indicated by the dashed line). As explained in chapter 4.3, here the decay path of the excited electron might lead into continuum states and thus these resonances might exhibit a strong broadening and suppression. This could explain a slightly lower intensity of a signal at this point but not the large difference observed here. As the calculations show, the resonance here is a resonance into a fully antibonding, fully conjugated  $\pi^*$  orbital, i.e. a higher  $\pi^*$ -resonance (figure 5.12). This state does seem to have a totally different decay pattern than the other state, rendering it inaccessible by NEXAFS spectroscopy.

For energies above 289 eV the StoBe calculations for organic molecules generally seem to predict one very strong signal (labeled as “D” in figure 5.15), which in the case of benzene is situated at lower photon energies and with a completely different line shape. Though in the case of benzene, the predicted high energy resonances do not vanish completely, as for stilbene, but appear differently, this publication already indicates the problems and limitations of the StoBe program at these energies. A sufficient explanation for the suppression has not yet given there[131].

Even more pronounced is this effect for the styrene molecule, which is seen in figure 5.15b top[132]. At about 290 eV photon energy, a very intense signal is predicted, which cannot be found in the experimental data. This discrepancy suggests a suppression of these orbitals in NEXAFS. Electron energy loss spectra have proven the existence of these states[131]. Still in literature no direct explanation of this phenomenon could be given. Püttner and Kolczewski have suggested a few lines of argument: the theory calculates photoabsorption cross sections while in the experiment the total photoionization yield is measured; the molecules in their excited  $\pi^*$ -states emit Auger cascades of many slow

electrons, detected as the low energy signals, higher excited states result in emission of only a few fast Auger electrons, which are then not being detected any more; finally, the spectrometer geometry might play a role.

All these hypotheses do not explain why and to which extent the calculated spectra are really in accordance with the measured ones. But it is apparent from these literature examples, that the StoBe calculations may describe the signal distribution with an energy uncertainty of a few tenth eV and above the carbon atom ionization potential the calculations are not able to describe the experimental data.

This fully coincides with my findings above, i.e. the StoBe calculations support the experimental finding, that the  $\pi^*$ -resonance is a key-feature to distinguish between cis- and trans-stilbene, by means of a qualitative reproduction of the  $\pi^*$ -resonance peak shape.

NEXAFS spectra provide a direct access to the investigation of isomerisation, as the  $\pi^*$ -resonance is a key feature that allows for the clear identification of cis- and trans-stilbene. The characteristic lineshape of the  $\pi^*$ -resonance can be seen not only in experiment but also in the theoretical calculations.

## 5.3 Molecular Switches on a Semiconductor - Stilbene on Si(100)

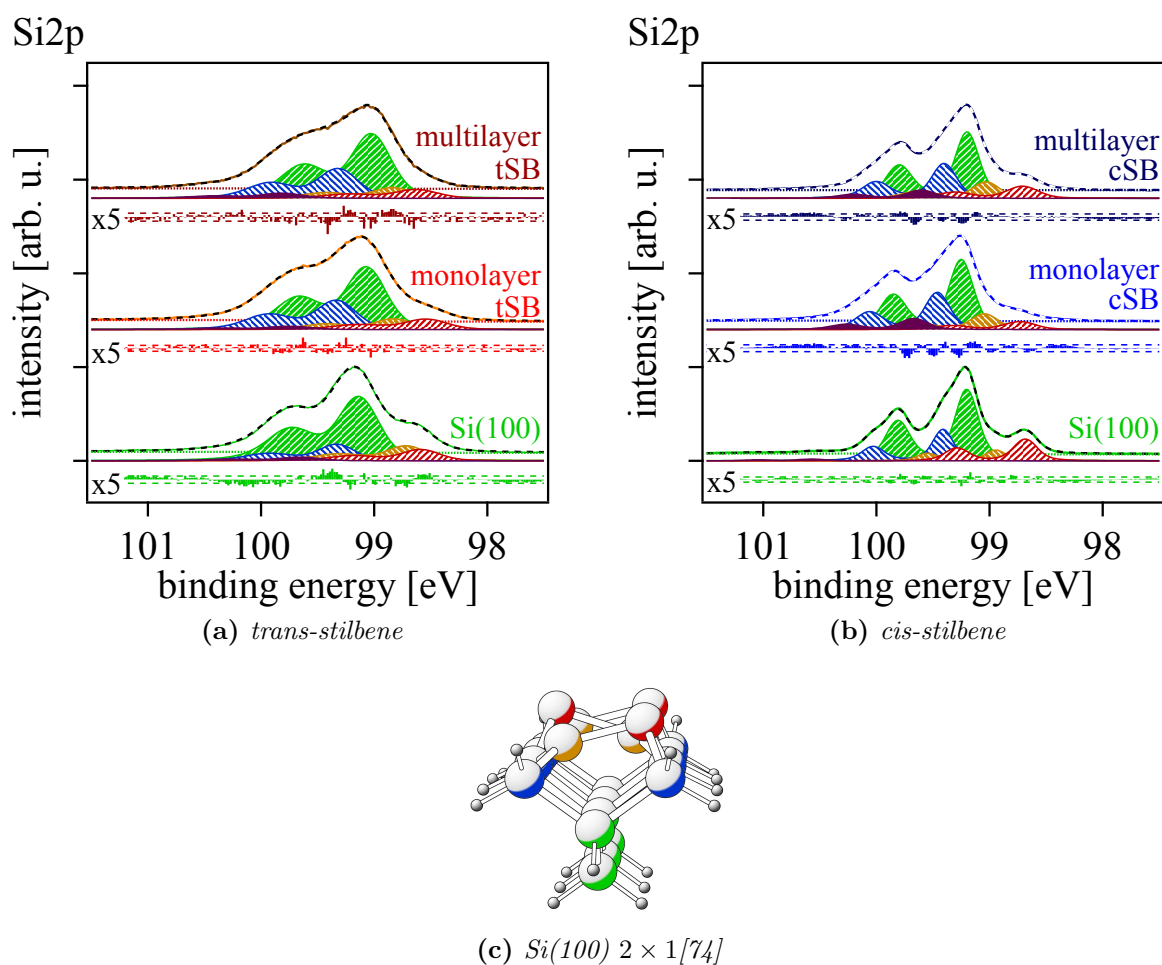
### 5.3.1 Adsorption on Si(100)

Many organic molecules, especially with extended  $\pi$ -systems strongly bind to silicon[133] with visible changes in photoemission spectra[134, 135]. This is not the case for stilbene. Adsorption on Si(100) at room temperature results in formation of one monolayer, at 100K multilayers could be adsorbed as well. Upon increase of temperature up to 300K, the multilayers desorb. Spectroscopically this corresponds to a C1s to Si2p(bulk) intensity ratio of 1.74 in core level photoemission.

Core level spectra from the substrate (Si2p) and the adsorbate (C1s) are useful for a study of stilbene on Si(100); especially the Si2p level might reveal information about adsorption site and bonding geometry[136, 137]. From the C1s level, information about the atoms interacting with the surface might be deduced.

Figure 6.12 shows the Si2p spectra of mono- and multilayers (30 L for trans-stilbene, 15 L for cis-stilbene) of both isomers adsorbed on the Si(100) surface. Due to experimental conditions the spectra for trans-stilbene are broadened with respect to the cis-isomer.

The spectra were measured at photon energies of 140 eV. For the clean surface, the Si2p signal was fitted with symmetric Voigt doublets[136–138] after subtraction of a Shirley-type background (see chapter 4.2). Five spin-orbit split components were required, which are assigned to 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[139, 140]. Especially for the cis-spectra, the defect contribution is very small for the clean surface and increases only slightly during the experiment as the defect density increased due to continuous sample cleaning and adsorption. The spectra of the stilbene covered surfaces can also be fitted using five symmetric spin-orbit split Voigt doublets. The relative peak positions are constant for all coverages, implying that the chemical environment does not change throughout stilbene deposition. In addition, the absolute positions are constant as well within experimental resolution. As the bulk component (B) does not exhibit any energy shift, there is no indication of band bending at the Si(100) surface which would result from charge-transfer between substrate and adsorbate. Therefore only a weak bonding seems to occur between stilbene and Si(100). This is supported by the absence of any additional energy-shifted components. As can be expected, an increased coverage leads to a decreased overall intensity of the Si2p signal. Only the relative intensities of the up-dimer (S) contribution decrease with coverage, while all other contributions remain at the same



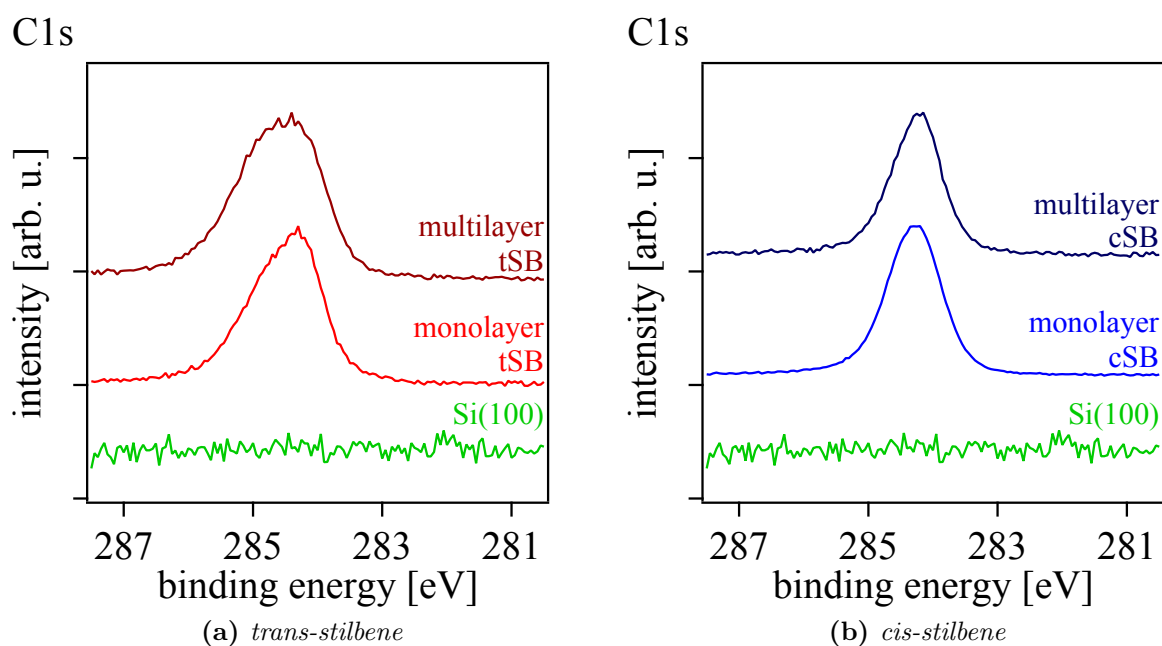
**Figure 5.17:** *Si2p* core-level spectra from the clean *Si(100)* surface, and adsorbed *cis-* (a) and *trans-stilbene* (b). Also shown is a line shape analysis using five symmetric Voigt-doublets which can be attributed to the up- (*S*) and down-dimers (*SS*), bulk (*B*), 2nd layer (*S2*) atoms and defects (*C*). Assignment of the respective contributions is shown below in (c). *Si2p* core-level spectra of *cis-* and *trans-stilbene* show no significant differences compared to clean *Si(100)* surface.

relative intensity. This indicates that an interaction between the adsorbed molecules and the surface mainly takes place with the dimer rows.

These findings are rather surprising in the sense that upon adsorption of organic adsorbates onto *Si(100)* a surface core level shift has been reported[134, 141]. For  $C_2H_2$  adsorption an overall shift of up to 0.2 eV at saturation has been observed together with the emergence of new spectral features[141]. Similar results have been reported by Widdra and coworkers[134, 142] and also Piancastelli, Horn and coworkers[143–146], who find additional components and surface core level shifts for the adsorption of various organic molecules on *Si(100)*. This coincides with a depletion of the up-dimer contribution with increasing coverage, which has been interpreted as an indication of the bonding site for the molecule. Such finding is in close agreement with the results obtained here. Widdra and coworkers showed using STM that the adsorption of benzene occurs directly via the dimer

atoms of the Si(100)[147]. Yeom and coworkers confirmed this spectroscopically[139]. As reported for other organic compounds, a surface core level shift of about 0.2 eV and a strong depletion of the up-dimer signal was observed for benzene adsorption, together with the emergence of a new component in the Si2p signal.

The C1s core level spectra can be used to investigate changes in the chemical environment of the single atoms of stilbene upon adsorption, i.e. the bonding of the atoms either in the molecule and to the surfaces[134, 135, 142]. Spectra obtained at 330 eV photon energy for the same coverages as before are shown in figure 5.18.

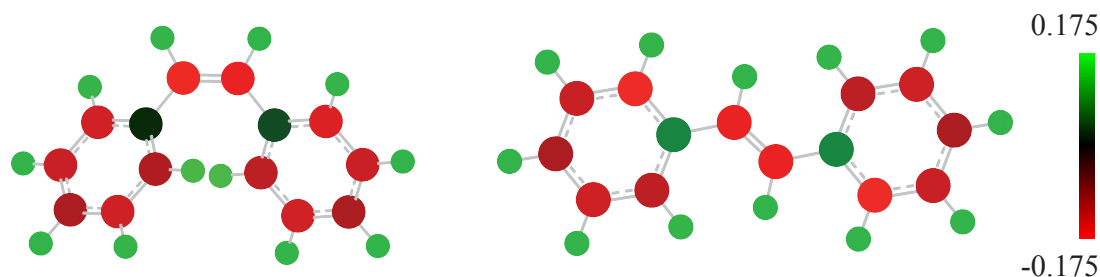


**Figure 5.18:** C1s core-level spectra from the clean Si(100) surface, and adsorbed cis- (a) and trans-stilbene (b). While cis-stilbene shows a symmetric lineshape, trans-stilbene spectra are asymmetric. For larger coverages peak broadening can be observed due to different interactions between adjacent molecules and molecules with the Si surface.

Both isomers exhibit a strong peak with a maximum at 284.3 eV binding energy. The difference in linewidth of 1.0 eV and 1.3 eV for cis- and trans-stilbene, respectively, is again due to a different experimental resolution. Although no substructure can be detected, the contribution of several components to the peak can be assumed, as the peak width is much broader than the experimental resolution seen in the Si2p spectra (0.28 eV and 0.46 eV for the cis- and trans-isomer, respectively).

A different lineshape for the two isomers can be detected. While cis-stilbene exhibits a symmetric signal, the signal from the trans-isomer shows an additional asymmetric contribution on the higher binding energy side. One explanation for these differences can be sought in the different chemical environment of the carbon atoms in the two isomers. The two atoms in the C=C bridge have to be considered different from the phenyl group atoms,

but the latter ones also have to be distinguished by the exact position and the neighboring atoms. The chemical environment is physically reflected in the charge distribution of the nuclei. Figure 5.19 shows the charge distribution in the free stilbene molecules determined through the same Gaussian DFT calculations of the molecular ground state, used for the determination of molecular orbitals.

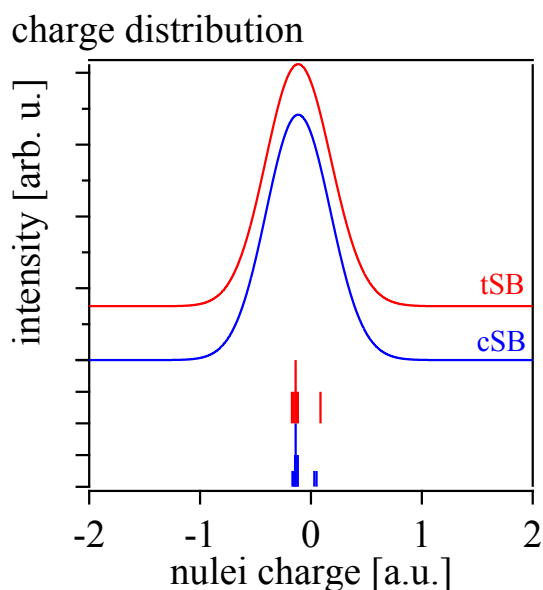


**Figure 5.19:** Charge distribution in *cis*- and *trans*-stilbene (left) as calculated for single gas phase molecules.

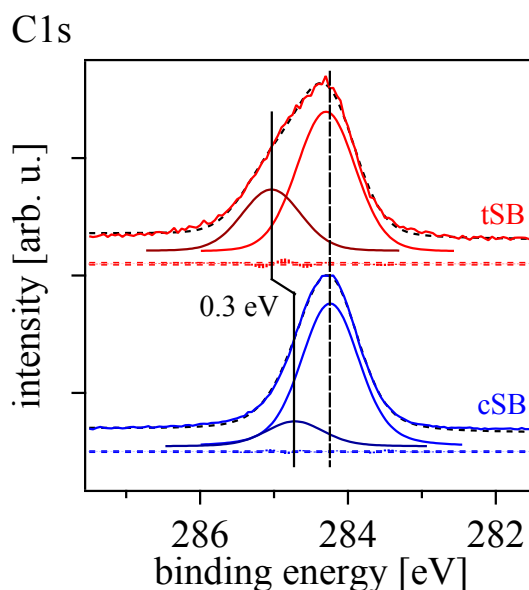
For *trans*-stilbene, six different charge distributions may be identified, namely the bridge atoms (*B*), the substituted atoms (*S*) of the phenyl-rings and the atoms in *para*-(*P*), *meta*-(*M*) and *ortho*-position to the bridge substituent, while the latter one is split into the atoms toward ( $O_1$ ) and away from ( $O_2$ ) the bridge, with a ratio of 2 : 2 : 2 : 4 : 2 : 2 ( $S : P : O_1 : M : B : O_2$ ). 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 ( $S : S' : P : O_1 : M : O_2 : B : B'$ ) are possible for *cis*-stilbene. The charge distribution in polyatomic molecules has a direct influence on the core level photoemission[148]. Thus it may seem reasonable to assume that the different charge distributions for the two isomers originate the different lineshape. Figure 5.20 displays the resulting spectra upon convolution of the charge distribution of a gaussian with 0.4 eV width. It is clearly visible that the influence on the charge distribution is only marginal and the base component of *cis*- and *trans*-stilbene on the C1s emission is almost identical.

Such asymmetric lineshapes as observed here have been described already in the literature for benzene adsorbed on Si(100) by Widdra and coworkers[134], but a convincing explanation has not been given. Hergenbahn and coworkers were able to fit this asymmetric signal with two vibrational progressions[149], following and extending the model of Sæthre and coworkers[150]. They proposed that the asymmetry is due to a shortening of the CH bond upon C1s ionization, and that the amount of shortening is a universal quantity that depends only on the number of CH bonds on the ionization site. Yeom and coworkers have investigated the adsorption of  $C_2H_2$  and  $C_2H_4$  on Si(100)[141]. They





**Figure 5.20:** Simulated  $C1s$  core level spectra. Convolution of charge distribution shown in figure 5.19 convoluted with a gaussian of  $0.4\text{ eV}$  width.



**Figure 5.21:**  $C1s$  spectra fitted with two components. The base peak at  $284.3\text{ eV}$  binding energy for both isomers and a vibrational component at  $285\text{ eV}$  and  $284.7\text{ eV}$  for trans- and cis-stilbene, respectively.

also observe an asymmetric lineshape of the  $C1s$  spectrum for both molecules. They were able to fit the asymmetric signal with two symmetric components. Both components are intrinsic to the molecule, the higher binding component they assigned to a vibrational satellite due to the C-H stretching mode. A satellite with the same shift had previously been detected for both molecules in the gas phase[151, 152]. Yeom and coworkers pointed out that for  $C_2H_4$ , the shift of the vibrational component is different in the gas phase and in the adsorbed phase[141], in the latter case being located closer toward the main peak. They attributed this to the higher distortion of the molecule due to adsorption. For stilbene the interaction with the surface is by far not as strong as for ethane, ethene or benzene, as seen by the lack of silicon band bending (see before). Thus the effect of adsorption can be considered equal for both isomers. But as can be seen in the molecular models in figure 5.9, the cis-isomer is much more strongly distorted than the trans isomer. Following the argument of Yeom and coworkers the vibrational component for cis-stilbene has to be much closer to the main peak than for trans-stilbene. Indeed fitting of the  $C1s$  emission with two gaussian components nicely resolves the two different lineshapes, as can be seen in figure 5.21. Both isomers exhibit the base peak at the same binding energy ( $284.3\text{ eV}$ ). This is in the range of benzene, which exhibits a binding energy of  $284.52\text{ eV}$  in the deuterated form on Si(100)[134]. This can be expected, as the difference in chemical environment for the carbon atoms in the isomers is negligible from the photoemission point of view (see figure 5.20). Trans-stilbene shows a vibrational component at  $0.7\text{ eV}$  higher binding energy (i.e.  $285\text{ eV}$ ). For ethane, Yeom and coworkers observe a shift of

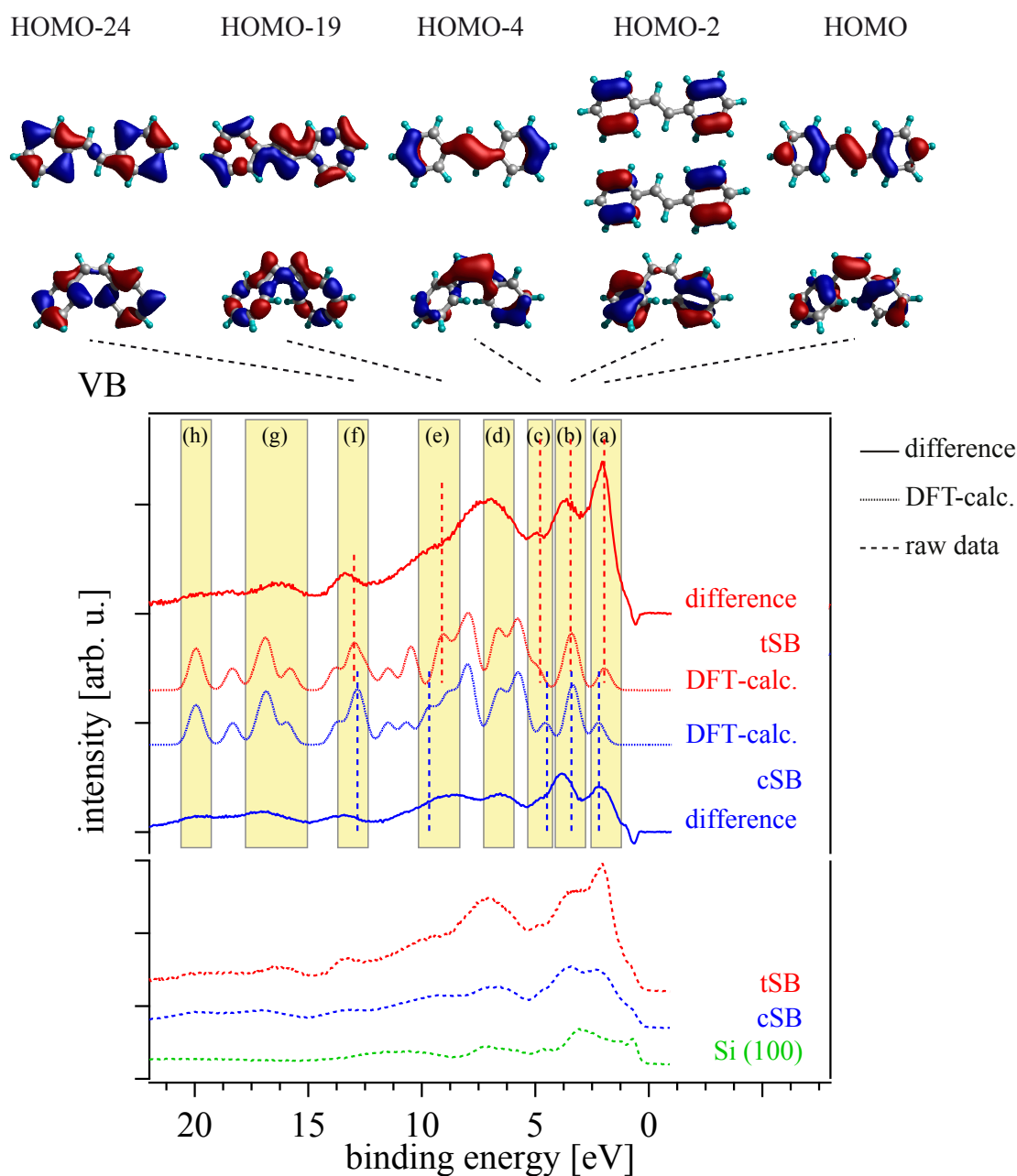
only 0.41 eV[141]. The stronger shift in stilbene can be attributed to the aromatic C-H stretch components, which are completely absent in ethane. The C-H stretching frequency for alkanes lies around  $2850\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$  (corresponding to 0.35 eV to 0.37 eV), for aromatic compounds between  $3000\text{ cm}^{-1}$  and  $3100\text{ cm}^{-1}$  (corresponds to 0.37 eV to 0.38 eV)[153]. The cis-isomer is more strongly distorted than the trans-isomer. Consequently the vibrational component can be found at 284.7 eV binding energy, i.e. shifted by 0.4 eV relative to the base peak.

Yeom and coworkers suggest a different interpretation of the C1s spectra for benzene adsorbed on Si(100)[139]. They distinguish between a  $C_\pi$  and a  $C_\sigma$  component separated by 0.3 eV. Upon adsorption of benzene they predict a covalent bonding between some benzene atoms and the Si dimers. This bonding leads to a rehybridization of the initially  $sp^2$ -hybridized atoms ( $C_\pi$ ) into  $sp^3$ -hybridization ( $C_\sigma$ ). As a covalent bonding of stilbene to the silicon surface can be ruled out, such a splitting of the C1s emission cannot be expected here. Especially for submonolayer and monolayer coverages, Yeom and coworkers determined the two components being of almost equal intensity, leading to an overall symmetric lineshape of the C1s emission. This is also in contradiction to the emission from the trans-stilbene. Thus their approach is not applicable to stilbene, where the emission profiles can much better be explained by the vibrational components mentioned before.

Shakeup-contributions at higher binding energies, as have been detected by Svensson and coworkers[154] for aromatic carbon ring systems were not detected for stilbene.

Comparing mono- and multilayer coverage, the trans-isomer exhibits an additional signal at the high energy shoulder, for cis-stilbene this cannot be observed. This additional signal, though not strong in intensity, can be attributed to  $\pi$ - $\pi$ -interactions between the molecules, which may only appear for coverages higher than a monolayer. As the only the trans-isomer is flat, stacking between the molecular layers, and therefore  $\pi$ -system overlap, is only supported for this isomer. Charge transfer due to these carbon  $\pi$ - $\pi$ -interactions[155, 156] may be considered to be slightly stronger than in carbon  $\pi$ -Si-interactions at the surface as can also be seen for covalent bonds due to differences in electronegativity[157].

The valence band spectrum for the clean Si(100) surface (figure 5.22) recorded at photon energies of 98 eV displays, after subtraction of a Shirley-type background, features attributed to the Si sp-bands down to binding energies of about 12 eV[142]. The most prominent signal at 0.95 eV binding energy is the Si(100) surface state. Upon adsorption of stilbene, Si surface state emission is suppressed. This can be seen very well in the difference spectra in figure 5.22, where negative intensities occur at the position of the surface state. Such a suppression of the surface state has also been observed by Piancastelli and coworkers for the adsorption of benzene on Si(111)[137]; not as drastically as here but over a wide coverage range. This has been attributed to the bonding interaction of the



**Figure 5.22:** 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.

molecules to the surface. The low binding energy occupied molecular orbitals (MO) lie in the energy range of the Si bulk bands. No shift of these Si signals can be detected. This confirms the non-appearance of band bending as has already been indicated by the Si2p core level spectra. Therefore it is difficult to clearly identify molecular contributions in

the original spectra.

The top part of figure 5.22 shows substrate subtracted spectra of monolayer cis- and trans-stilbene showing the molecular contributions to the spectra. These new signals arise at binding energies relative to the Fermi level as listed in table 5.1 and indicated in figure 5.22.

isomer	valence band signals [eV]							
	a	b	c	d	e	f	g	h
trans	2.0	3.4	4.9	6.6	9.2	13.0	16.9	20.0
cis	2.2	3.4	4.6	6.6	9.7	12.9	16.9	20.0

**Table 5.1:** Binding energies of valence band signals of monolayer stilbene on Si(100).

Also shown are calculated spectra derived from binding energy calculations of molecular orbitals I performed with Gaussian (see chapter 4.6). These have been calculated for isolated molecules in the ground state (see chapter 5.2) and afterwards convoluted with a gaussian function of 0.4 eV width to model broadening. These model spectra have been aligned with the valence band maximum of Si(100), which has been found at 0.14 eV below the Fermi energy. These calculations cannot be used quantitatively to analyse measured valence band spectra, as 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 need not, and do not resemble the intensities measured. Still, a qualitative analysis may be used for interpretation. The measured valence band signals actually do appear at the energies indicated by calculation. This can be seen as a first indication that these features can solely be attributed to stilbene. The calculated spectra are remarkably similar. Only a few peaks are shifted with respect to each other. Thus only a few molecular orbitals are distorted by conformational changes. As can be seen in the visualizations in figure 5.22 (top), these are mainly molecular orbitals that are extended over the whole molecular framework. As these visualizations also show, cis-MOs can be transformed into trans-MOs by twisting them from a cis- into a trans-conformation. The mentioned orbitals can be found at binding energies as listed in table 5.2.

The values for calculated and measured spectra are thus in good agreement. While the signals at around 2 eV, 3.4 eV, and 13 eV binding energy show only a different intensity for cis- and trans-stilbene but exhibit the same binding energy, the signals at 4.6 eV and 9.7 eV for cis-stilbene, and 4.9 eV and 9.2 eV for trans-stilbene respectively, differ also in binding energy.

Typical dissociation products of stilbene would include benzene and ethene. Benzene valence band spectra are well documented. They exhibit distinct features at 2.3 eV, 4.0 eV,

isomer	valence band signals [eV]				
HOMO	0	-2	-4	-19	-24
trans (experiment)	2.0	3.3	4.9	9.2	13.0
trans (Gaussian)	1.96	3.32	4.92	9.22	13.00
cis (experiment)	2.2	3.4	4.6	9.7	12.9
cis (Gaussian)	2.21	3.36	4.55	9.67	12.83

**Table 5.2:** Binding energies of valence band orbitals that can be used to distinguish between *cis*- and *trans*-stilbene.

5.7 eV, 13.3 eV, and 14.1 eV[135, 139, 142]. As none of these energies signals are detected for stilbene, demonstrating that a possible dissociation of the stilbene molecule into benzene and ethene during deposition does not take place.

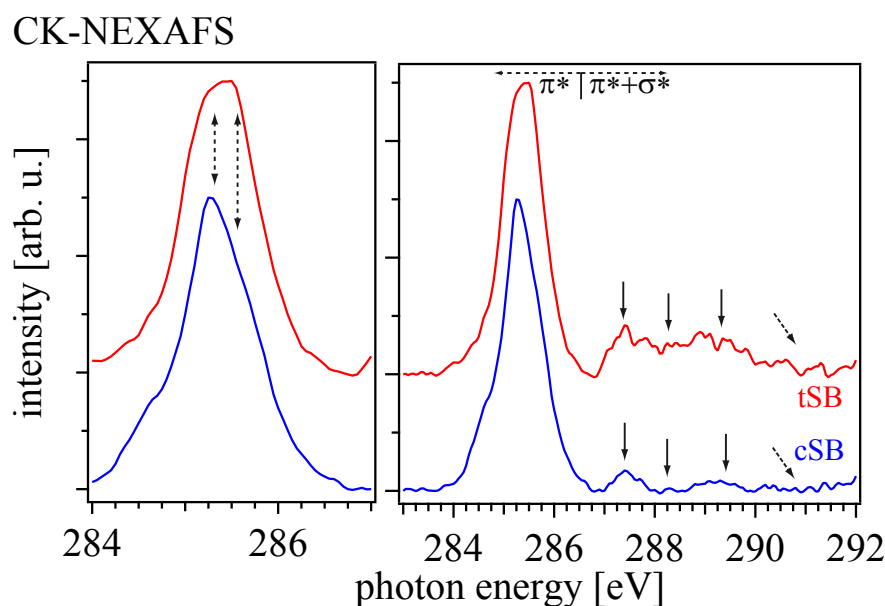
The fact that differences in valence band spectra calculated for isolated molecules are visible in the spectra of the adsorbed species indicate that the bonding interaction of both isomers with the Si substrate is similar, leading to the conclusion that this interaction most likely takes place via the atoms of the C=C-bridge.

### 5.3.2 Identification of Isomers - NEXAFS

#### Experimental NEXAFS spectra

For the investigation of gas phase stilbene, NEXAFS has shown to be a straightforward method to identify the two isomers of stilbene by the  $\pi^*$ -resonance. Additionally information about the molecular backbone could be gained. For adsorbed molecules, NEXAFS allows an insight into the bonding between substrate and adsorbate[63, 129, 158]. Especially, quantitative information on the adsorption geometry and the orientation of the molecules on the surface can be gained[63].

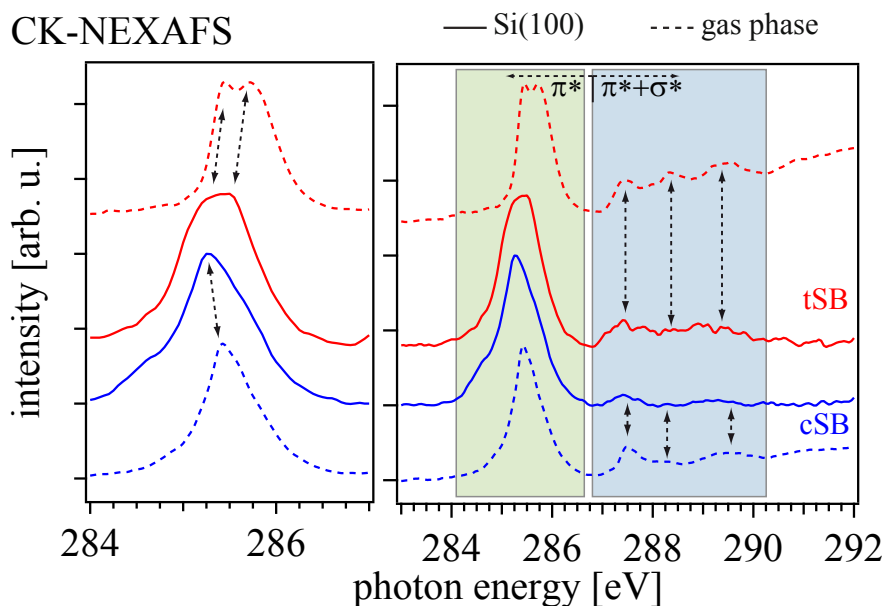
For monolayer coverage of both isomers on Si(100), C1s-NEXAFS spectra have been recorded, shown in figure 5.23. These spectra are also dominated by the  $\pi^*$ -resonance around 285 eV photon energy. While the  $\pi^*$ -resonance maximum of *trans*-stilbene consists of two components with the more intense component at higher photon energies, for the *cis*-isomer this second component has a lower intensity and vanishes in the shoulder of the  $\pi^*$ -resonance. At higher photon energies a substructure can hardly be identified, both isomers display a three peak structure with a slightly less intense middle peak, indicated by arrows in figure 5.23 right. These peaks can be attributed to  $\sigma^*$ -resonances. At 291 eV photon energy, where the higher  $\pi^*$ -resonances would be expected, no signal can be found (dashed arrows).



**Figure 5.23:** CK-NEXAFS spectra of monolayer cis- (blue) and trans-stilbene (red) adsorbed on Si(100). Full spectrum on the right, detail of  $\pi^*$ -resonance on the left.

On a qualitative scale, this signal behavior is analogous to gas phase stilbene. A comparison between gas phase and adsorbed molecules is shown in figure 5.24. Here, the  $\pi^*$ -resonance of stilbene adsorbed on Si(100) is almost identical to the gas phase signal, especially for the cis-isomer. For the adsorbed molecule the whole peak is shifted by 200 meV to lower photon energies. For trans-stilbene the  $\pi^*$ -resonance is also shifted by the same amount. Additionally, the lower energy component is of less intensity and thus the splitting which was visible in the gas phase, remains only as a step in stilbene adsorbed on Si(100). This energy shift indicates an interaction of the molecular  $\pi$ -system with the substrate. The unoccupied orbitals involved are the fully conjugated  $\pi$ -system and the orbitals located at the phenyl groups. Due to the conformational difference of cis- and trans-stilbene, only the C=C-bridge can be seen as a common binding site to the surface for both isomers. Because of the conjugation, the complete  $\pi$ -system would be influenced, if the  $\pi$ -system at the bridge were manipulated in the bonding interaction with the surface.

For the  $\sigma^*$ -resonances at higher binding energies an energy shift cannot be detected. Although the resonances are very small already for the gas phase molecules, upon adsorption to the surfaces they are even less detectable. As indicated on the right hand side in figure 5.24, a signal pattern analog to the  $\sigma^*$ -resonances seen for gas phase molecules can be detected. These signals show a similar three-peak pattern as in the gas phase. For trans-stilbene, the three peaks are of comparable intensity, while for the cis-isomer the middle peak is lower and almost vanishes in the background between the two other peaks. Here no



**Figure 5.24:** CK-NEXAFS spectra of monolayer cis- (blue) and trans-stilbene (red) adsorbed on Si(100). Comparison of adsorbed molecules (solid lines) with gas phase molecules (dashed lines).

energy shifts appear, leading to the conclusion that the molecular framework of  $\sigma$ -bonds is not changed upon adsorption. In comparison with the gas phase spectra, the adsorbed molecules show a much more similar structure in the  $\sigma^*$ -resonance. This can be seen as an indication that the molecular backbone, i.e. the conformation of both isomers, converges upon adsorption. The higher  $\pi^*$ -resonance at 291 eV photon energy, barely visible in the gas phase cannot be detected.

These results strongly support the conclusions drawn from the core level spectra. As bonding interaction with the surface is of physisorptive nature, no covalent bonds, which would have been detectable in core level spectra, are formed. The molecular framework with its sigma bonds remains unchanged. The direct chemical environment of the single atoms seems unperturbed, again indicating that there is no covalent bonding to the surface, and the interaction with the surfaces merely takes place via the  $\pi$ -orbitals. This is in accordance with our findings from the core level photoemission.

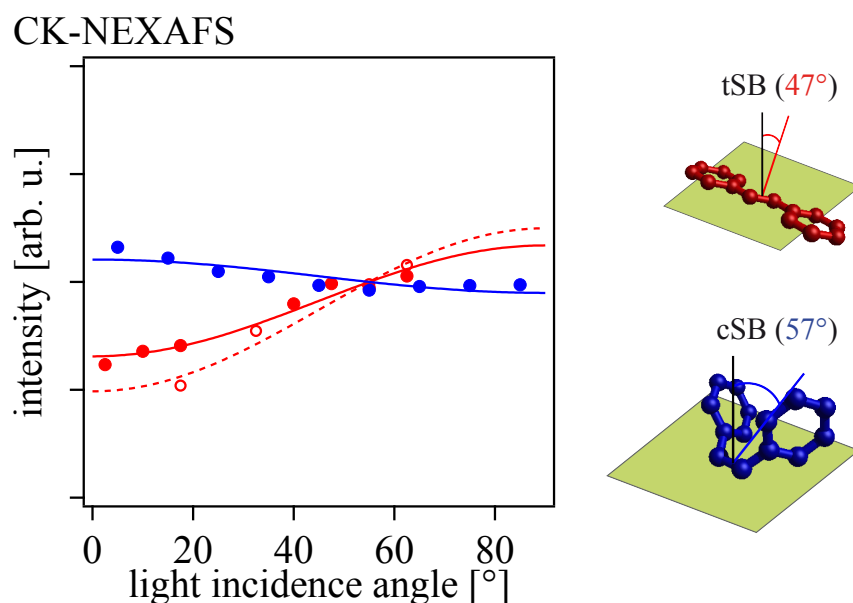
In order to identify the adsorption geometry of stilbene on the Si(100) surface angle resolved NEXAFS spectra have been recorded. The change of signal intensities with respect to the light incidence angle provides information about the orientation of the adsorbates with respect to the surface[62].

After background subtraction and normalisation to the step function, the intensity of the  $\pi^*$ -resonance was determined. Figure 5.25 shows the  $\pi^*$ -intensity with respect to the light incidence angle. The data points have been fitted with the  $\cos^2$ -function (4.21) given in

chapter 4.3.

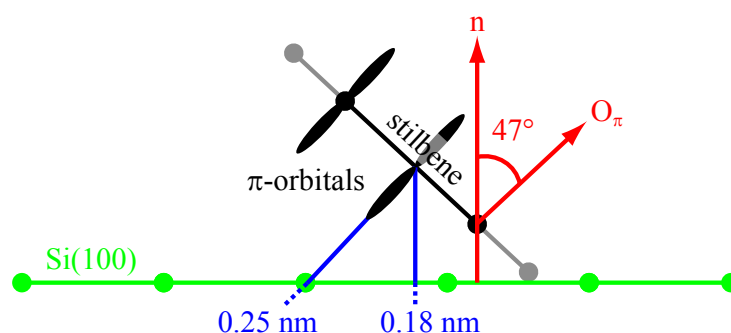
For cis-stilbene, these measurements have been performed along the Si dimer rows. For trans-stilbene, two data sets are shown in figure 5.25 – at  $+45^\circ$  and  $-45^\circ$  to the dimer rows. Three reasons can be found for the well agreement of both data sets. Either the molecules are perfectly aligned along the Si dimer rows, or it can be assumed that no special ordering along one of the crystal axes occurs. The substrate used was a Si(100)  $2 \times 1$  surface having two domains. These two domains would also lead to this agreement. The fits give an overall tilt angle  $\alpha$  of  $47^\circ$  for the trans-isomer and  $57^\circ$  for the cis-isomer. These are the angles of the molecular orbital vector  $O_\pi$ , representing the total delocalised  $\pi$ -system, to the surface normal  $n$ . As mentioned before (chapter 4.3) the vector  $O_\pi$  is the superposition of all molecular orbital vectors of the  $\pi$ -system at each point of the molecule. For a twisted molecule this vector might just have an odd direction.

In a simple picture the flat trans-isomer (in gas phase) can be assumed to adsorb also in a flat conformation on the Si(100) surface, as shown in figure 5.26. In that case, the whole molecule would have to adsorb with the same angle as the  $\pi$ -system, i.e. an angle of  $47^\circ$  with respect to the surface. The diameter of a benzene ring is roughly 0.5 nm. Tilted by  $47^\circ$  the center of the benzene ring and thus the C=C bridge would have to be 0.18 nm away from the surface. This corresponds to the Si-Si distance in the dimers of about 0.22 nm[159, 160]. The distance from the molecule to the surface along the  $\pi$ -system, i.e. in a direction perpendicular to the molecular plane, would be 0.25 nm. The distance between two layers of graphite is 0.33 nm[102], thus a typical carbon  $\pi$ -system extends



**Figure 5.25:** Angular dependence of the  $\pi^*$ -resonance-intensity for cis- and trans-stilbene on Si(100) (dots). A  $\cos^2$ -fit (lines) reveals an adsorption tilt angle of  $47^\circ$  for trans- and  $57^\circ$  for cis-stilbene, both are sketched in the simplified model on the right.





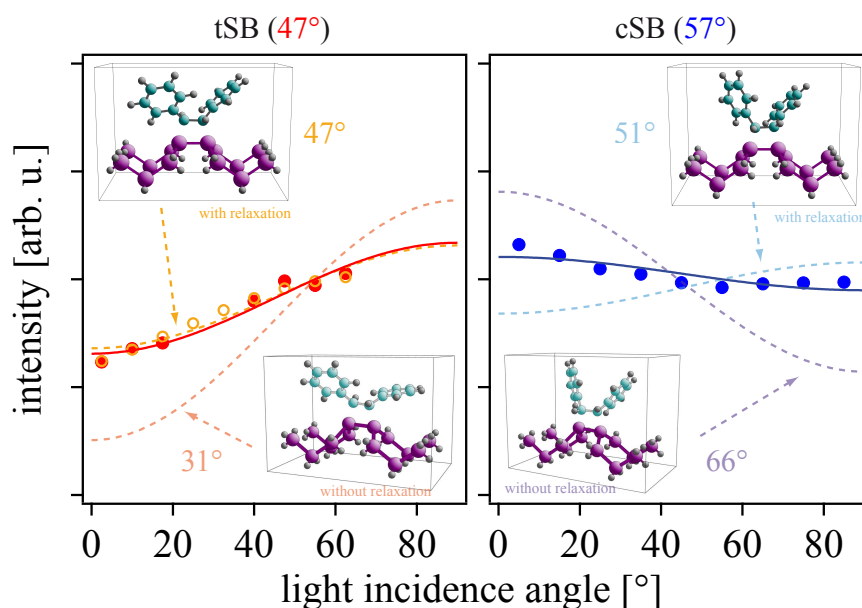
**Figure 5.26:** Simple adsorption model assuming, that the trans-stilbene remains flat upon adsorption on Si(100) under a tilt angle of  $47^\circ$ . The distance of the C=C bridge in the center of the molecule to the surface would be 0.25 nm, which is larger than the length of a  $\pi$ -orbital with 0.16 nm. Two exemplary  $p_z$ -orbitals, which constitute the  $\pi$ -system are indicated in the scheme.

about 0.16 nm away from the surface. This length is too small to bridge the 0.25 nm gap to the surface. Thus this picture can be considered fairly unrealistic, especially as such an adsorption would result in a distortion of the  $\pi$ -system. The MOs would split into a contribution of the atoms near the surface and further away from the surface. This process is not reflected in the spectra. As the NEXAFS spectra shown in figure 5.23 indicate a bonding via the bridge atoms, the tilt angle detected has to be interpreted as an intermolecular tilt around the bridge, i.e. the phenyl groups have to be bent up upon adsorption, and the whole molecule is slightly tilted with respect to the surface. This is also in agreement with the observation of similar  $\pi^*$ -resonances for both isomers in the adsorbed case. For the cis-isomer, which is already bent before adsorption, this remains and therefore it is also more strongly tilted with respect to the surface, resulting in an  $\alpha$ -value of  $57^\circ$ .

### StoBe Calculations

In analogy to the calculations performed for gas phase spectra shown in chapter 5.2.2, theoretical results from StoBe calculations have been obtained for both isomers adsorbed on the Si(100)-surface. One molecule has been adsorbed on a  $Si_{14}H_{28}$  cluster, which is believed to represent the behavior of the Si(100) surface[161]. In a first energy optimization, only the position of the atoms in the stilbene-molecules were allowed to relax. The two dimer atoms were assumed to have relaxed out of the up-down-configuration into a position parallel to the surface. In a second step, relaxation of the two dimer atoms was also allowed during optimization. For these geometries, NEXAFS spectra were obtained using the StoBe-package. These background-free spectra were normalised to be of the same  $\pi^*$ -resonance intensity as the measured spectra in normal emission, i.e. at the magic angle. Intensities of the  $\pi^*$ -resonances were determined and fitted with the previously described  $\cos^2$ -function from equation (4.21). Results for both isomers are shown in figure

5.27.

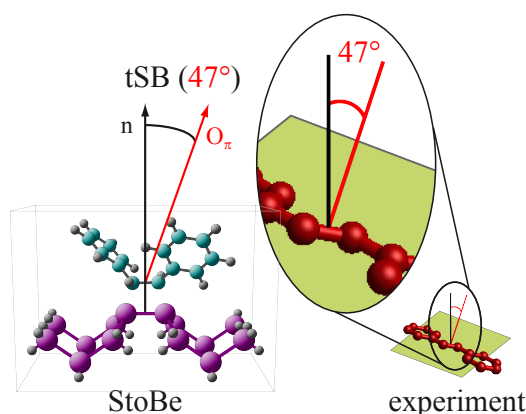


**Figure 5.27:** Comparison between calculations and experiment for angle resolved NEXAFS spectra. Shown are the  $\pi^*$ -intensities for different light incidence angles, on the left for the trans-stilbene (red), on the right for the cis-stilbene (blue). Shown are the experimental values (filled dots). The angle derived from the fits (solid lines) are given in the top of the graph. In comparison the results for the different theoretical calculations are shown (open circles, dashed lines). The insets show the used geometry. The models with relaxation of the Si-dimer shown in the top corners, the models without relaxation shown in the bottom corners. The resulting data points are indicated by arrows, the fitted angle is also given.

For trans-stilbene the relaxed and unrelaxed model both predict an intermolecular tilt upon adsorption of the molecule on the Si surface, while bonding interaction takes place via the C=C-bridge to the Si dimer. This prediction is in good agreement with the experimental findings shown before. Upon relaxation of the dimer atoms, this tilt becomes stronger. The calculated  $\pi^*$ -resonance intensities show a positive slope in both cases, with a much steeper increase for the relaxed dimer model. A comparison with the experimental results shows that the more complex model - with dimer relaxation - describes the actual system quite well. In fact, calculated and measured data points are almost identical, i.e. the calculated tilt angle ( $47^\circ$ ) corresponds to the measured one. The simpler model provides too small an angle ( $31^\circ$ ).

For the cis isomer, the relaxed and unrelaxed model lead to seemingly similar adsorption geometries, as can be seen in the insets in figure 5.29, however the predicted NEXAFS intensities vary quite drastically. Two regimes can be determined - intensities below and above  $55^\circ$  incidence angle. While for light incidence angles above  $55^\circ$  both models provide similar NEXAFS intensities, which, though a little bit too high, are also in fair agreement with the measured values, for smaller light incidence values the discrepancy between

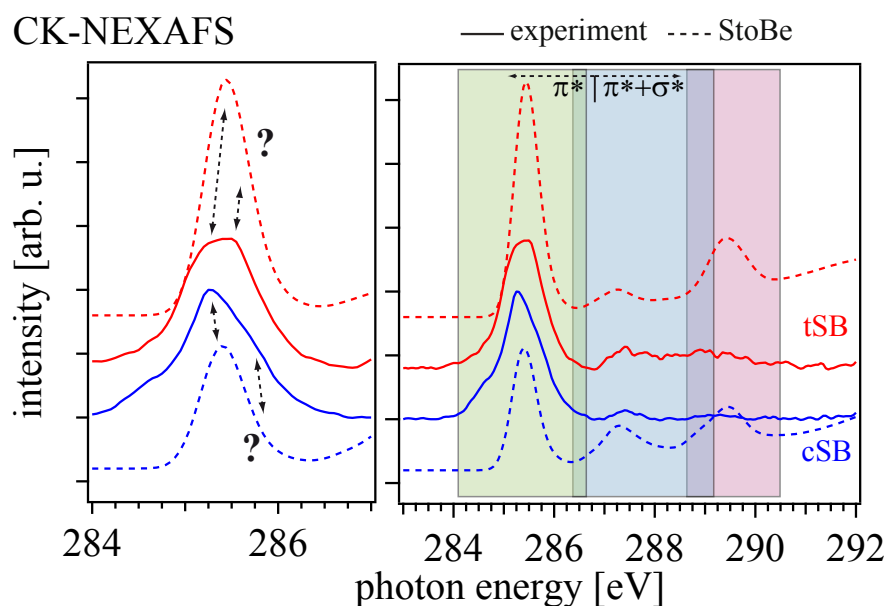
experiment and calculation becomes rather large. The unrelaxed model predicts NEXAFS intensities that are too high, the relaxed model intensities that are too small. The results retrieved from the dimer-relaxed model do not even follow the  $\cos^2$  behavior of equation (4.21). Only for incidence angles below normal emission can the data points be fitted. The resulting tilt angle is  $66^\circ$ . Although this tilt angle retrieved from the relaxed model with its value of  $51^\circ$  is only  $6^\circ$  off the experimental value (corresponding to 12%), the positive slope of the intensity plot is in contradiction to the negative slope of the experimental values.



**Figure 5.28:** Model of adsorption for trans-stilbene on Si(100) as derived from StoBe calculations. The molecule interacts with the silicon surface through the relaxed dimers. The phenyl groups are twisted upwards.

Thus for the adsorbed stilbene the StoBe calculations fail to provide a reliable description of the data. Only for trans-stilbene a good agreement between calculations and experiment exists. The model which provides this good agreement is shown in figure 5.28. Trans-stilbene adsorbs on top of the dimer rows of the Si(100). The buckling of the dimers is leveled out; a result in accordance with the depletion of the up-dimer contribution in the Si2p emission. Bonding interaction takes place via the C=C-bridge, specifically the  $\pi$ -system of the bridge; this already being indicated by the shift of the  $\pi^*$ -resonance to lower excitation energies. Upon adsorption the two phenyl rings bend upwards, leading to an overall twisted  $\pi$ -system. In figure 5.28, the surface normal  $n$  and the orbital vector  $O_\pi$  of the twisted  $\pi$ -system are indicated to symbolize the effect of this up-bending. As can be seen in comparison to the sketch derived from the experimental findings, this up-bending reasonably explains the tilt angle observed for trans-stilbene.

The StoBe calculations lead to the same results that can be derived from the interpretation of NEXAFS and core level spectra for trans-stilbene. Thus it can be assumed, that the similar interpretation of the spectra of the cis-isomer is also valid. The StoBe calculations up to now do not provide a reasonable representation of the cis-stilbene adsorption, as can be seen in the large discrepancy of the angular dependence.



**Figure 5.29:** NEXAFS spectra of *cis*- and *trans*-stilbene in monolayer coverage on *Si*(100). The dotted lines show the spectra derived from the StoBe calculations. The huge discrepancies especially in the  $\pi^*$ -resonance and also in higher resonances are clearly visible. Highlighted are the three spectral regions,  $\pi^*$ -resonance (green),  $\sigma^*$ -resonances (blue) and higher resonances (red).

This becomes even more evident upon direct comparison of the theoretically predicted NEXAFS spectra and the experiment (figure 5.29). In contrast to the gas phase results, now the calculated spectra do not have to be shifted to overlap with the center of the  $\pi^*$ -resonance. The calculated spectra of both isomers are very similar. Especially the  $\pi^*$ -resonance, the key identification feature in the experiment, shows a strong single component for both isomers. Although a slight asymmetry is visible which points into the opposite direction for *cis*- and *trans*-stilbene, the typical two-component signal is not at all represented by the calculation. Even under the assumption that too large a broadening has been used for convolution of the spectra (compare with chapter 5.2.2) the difference in the resonances should have been clearly visible. For the  $\sigma^*$ -resonances no better agreement can be found between calculation and experiment.

The StoBe calculations fail to provide NEXAFS spectra comprising at least the key features identified in experiment. This is most evident in the lacking resemblance of the  $\pi^*$ -resonance. Only in the description of the angular dependency of the  $\pi^*$ -resonance for adsorbed *trans*-stilbene an agreement with experiment exists. The underlying model providing this dependency well agrees with the interpretation derived from experimental core level and NEXAFS spectra. The validity of the description of the stilbene adsorption provided by the StoBe calculations may thus not completely be negated. But especially the disagreement in the  $\pi^*$ -resonance only allow for the conclusion, that the interpretation of the further results should merely be based on the experimental interpretation.

These experimental findings allow for two major conclusions. The absence of core level shifts already indicated that no covalent bonding takes place between stilbene and Si(100). The NEXAFS spectra confirm these results, as only shifts in the  $\pi^*$ -resonance can be detected. Furthermore these shifts allow for the assumption that Si- $\pi$ -interactions are the main bonding mechanism. From the angular dependence of the  $\pi^*$ -resonance it is clear, that both isomers are twisted upon adsorption. This twist leads to a dislocation of the phenyl groups away from the substrate surface. Thus only the C=C bridge is in close vicinity to the Si atoms to perform the bonding. The strength of the twisting depends on the original conformation, cis-stilbene is more strongly twisted than the trans-isomer.

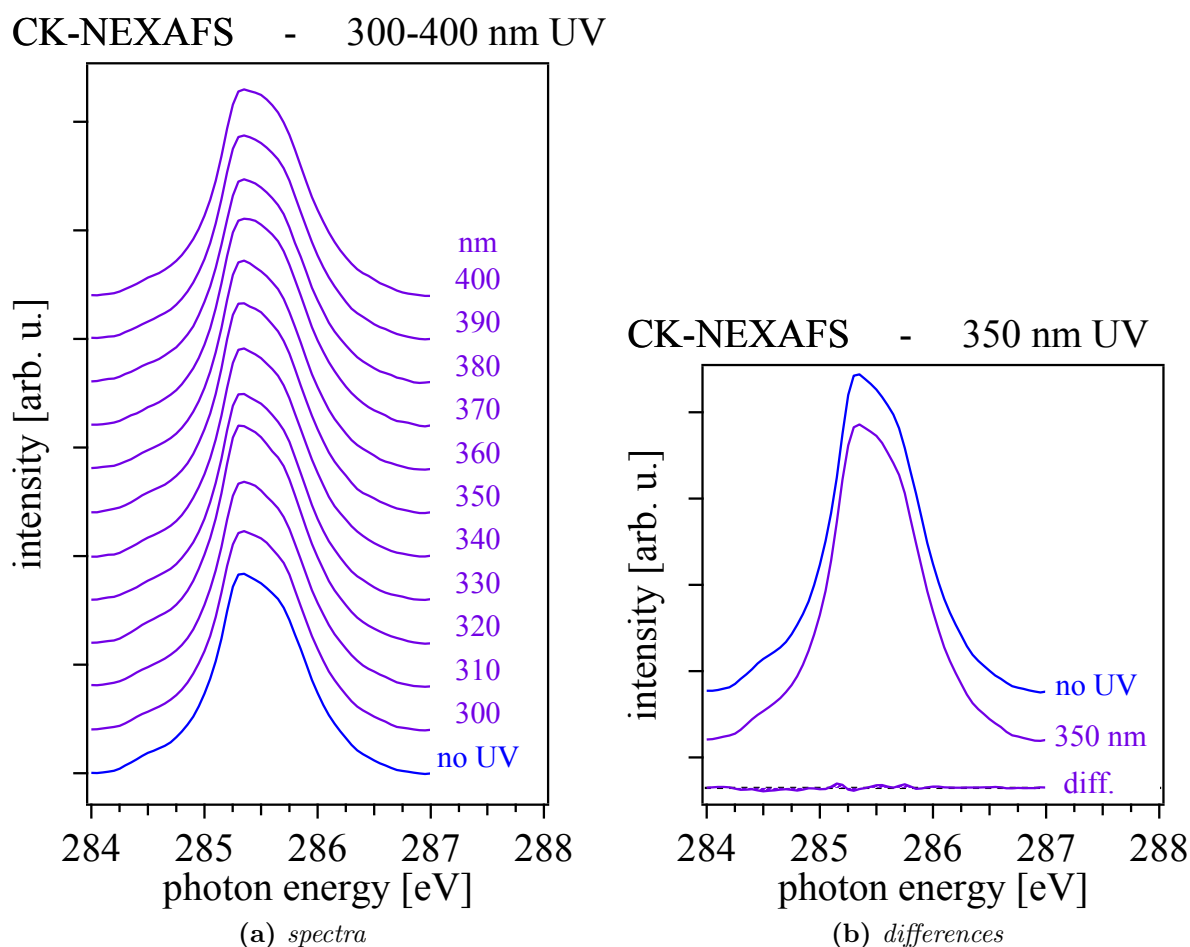
### 5.3.3 Photoinduced Isomerisation on Si(100)

The analysis of NEXAFS spectra for adsorbed stilbene indicated a bonding of the molecule via the  $\pi$ -system of the C=C-bridge to the surface leaving the adjacent phenyl groups free to move in space. As an intramolecular twist is introduced into the formerly flat trans-isomer upon adsorption, it should now be easier to transform into from the cis-conformer, making the latter one especially prone to light induced isomerisation.

In order to check this hypothesis, one monolayer of cis-stilbene was exposed to UV light of different wavelength in the discrete exposure mode (compare chapter 4.5) as shown in figure 5.30. Cis-stilbene has been chosen as the cis-to-trans isomerisation is well known and the mechanism in the gas-phase and solution well understood (see chapter 5.1.2). It is clearly visible that no changes in NEXAFS spectra occur upon UV irradiation. This proves the high UV stability of stilbene.

Trans-stilbene was also exposed to UV-irradiation to ensure that there is no preference for either the cis-to-trans or the trans-to-cis pathway. Again consecutive illumination with UV light of a broad wavelength range yielded no change in the NEXAFS spectrum.

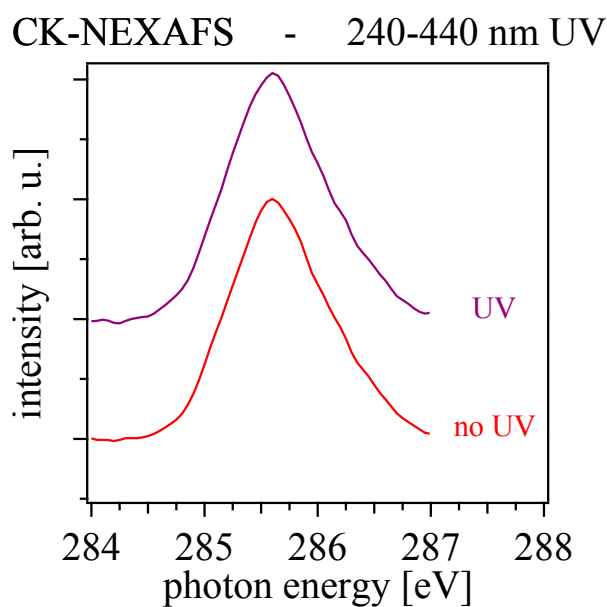
Why is the well known light induced isomerisation inhibited in this case? Two factors determine the feasibility of the process. As shown before, the photoisomerisation pathway is a combination of one or more rotatory movements. To perform these movements, a certain amount of free space around each rotation axis is required. These axes are the main C=C bridge and, depending on the actual pathway on the surface, an adjacent single bond. For the cis-isomer, adsorbed via the C=C bridge, the adjacent single bonds are pointing away from the surface. Therefore a sterical hindrance of the rotation around one of these bonds is not given. The interpretation of the NEXAFS spectra has shown that in the adsorbed trans-isomer the phenyl groups are also pointing away from the surface. Thus a full 180 ° rotation around the bridge bond is not required to transform the cis- into the trans-isomer. Thus isomerisation should be possible.



**Figure 5.30:** NEXAFS  $\pi^*$ -resonance of monolayer *cis*-stilbene adsorbed on Si(100) before and after exposure to UV-light of different wavelengths. No changes in the signal can be observed upon irradiation. All spectra are shown in (a), an exemplary difference spectrum is depicted in (b).

As has been discussed in chapter 5.1.2, the crucial step in the photoisomerisation process is the excitation into an unoccupied  $\pi$ -orbital located at the C=C bridge. Although no covalent bonding could be detected in the core level and NEXAFS spectra, an interaction between molecules and surface is inevitable. On the substrate side, the adsorption site are the Si dimers, as indicated through the Si2p emission. In the molecules an interaction originating from the  $\pi$ -system can be assumed, considering the shift in the NEXAFS  $\pi^*$ -resonance. As the angular dependence of the  $\pi^*$ -resonance showed, both isomers are twisted in the adsorbed phase, such only the C=C bridge is in the vicinity of the surface, representing the bonding site on the stilbene side. This means that a directed interaction takes place between the unoccupied  $p_z$  orbitals of the bridge carbon atoms and the Si dimers. These orbitals are thereby blocked for population by photoexcited electrons from the molecule, and thus the isomerisation is not feasible on Si(100).

As the incorporation of the C=C bridge  $\pi$ -system seems crucial to perform the isomeri-



**Figure 5.31:** NEXAFS  $\pi^*$ -resonance of monolayer *trans*-stilbene adsorbed on Si(100) before and after exposure to UV-light of 240 nm to 440 nm wavelength. No changes in the signal can be observed upon irradiation.

sation, the  $\pi$ -system-substrate interaction needs special attention. A system where this interaction is significantly weaker than on the silicon (but still strong enough for molecular adsorption) should be found. The copper surfaces would seem feasible, as the interaction of the  $\pi$ -orbitals with the diffuse metal bands should be weaker than with the directed orbitals at the semiconductor silicon. Thus we address exactly this interaction between stilbene and Cu in the next section.

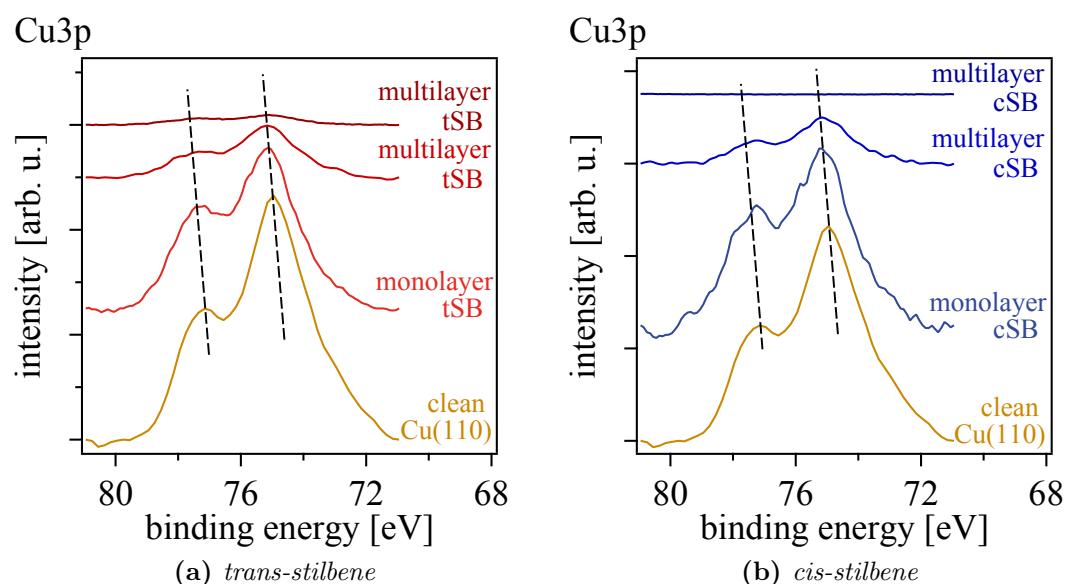
## 5.4 Molecular Switches on a Metal - Stilbene on Cu(110)

### 5.4.1 Adsorption on Cu(110)

Copper seems to be a suitable candidate for the adsorption of stilbene and light induced isomerisation. The adsorption of  $\pi$ -system-bearing molecules has already been studied in various cases [7, 9]. The Cu(110) surface in particular was chosen, as it is experimentally well known from the experiments shown in chapters 6 and 7.

For the investigations on stilbene two coverages have been investigated – monolayer and multilayer coverage.- The multilayer coverage corresponded to ten and five layers for trans- and cis-stilbene, respectively. For the investigations on copper, more attention was paid to the coverage dependence. Especially for the UV light induced isomerisation, a better decoupling of the topmost stilbene layer, which is exposed to irradiation, from the substrate might be of importance. Such decoupling can be achieved by several buffering layers of stilbene. Therefore monolayer coverage and two multilayer coverages were investigated. The “thin” multilayer corresponded to five, the “thick” multilayer to 35 layers of stilbene.

As in the case of Si(100) core level spectra, that can provide valuable information about the adsorption interaction between the molecules and the surfaces, were acquired.

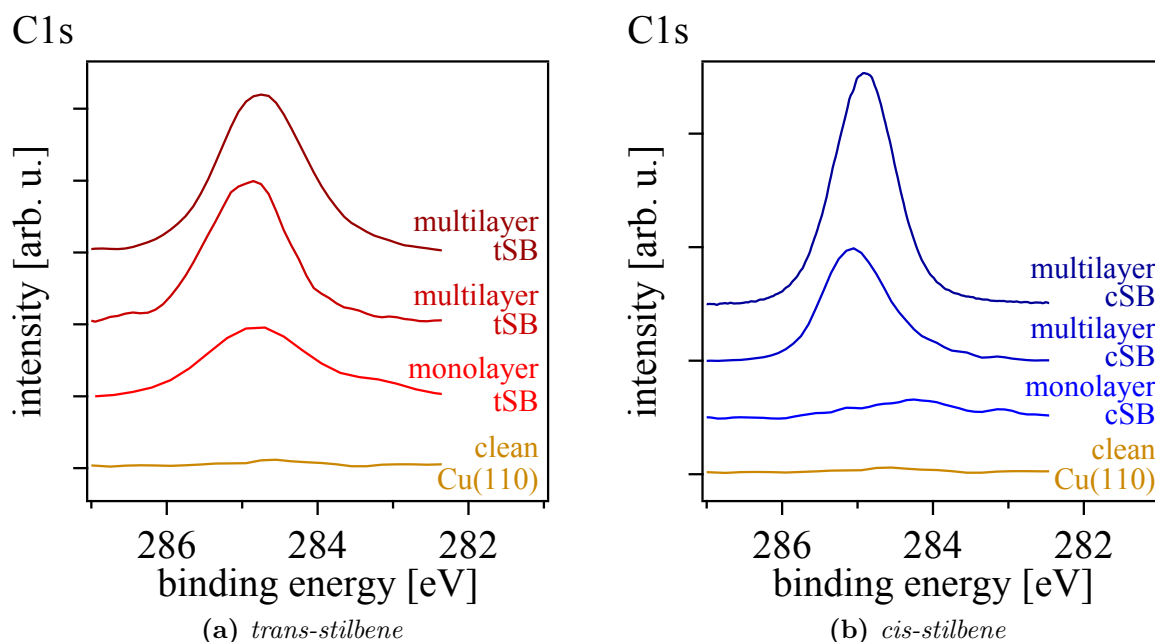


**Figure 5.32:** *Cu3p* core level of *cis*- and *trans*-stilbene adsorbed on Cu(110). Shown are monolayer and two multilayer coverages for both isomers. The spectral shift is indicated by the dashed lines.

The Cu3p spectrum in figure 5.32 shows a spin-orbit split doublet signal for the clean

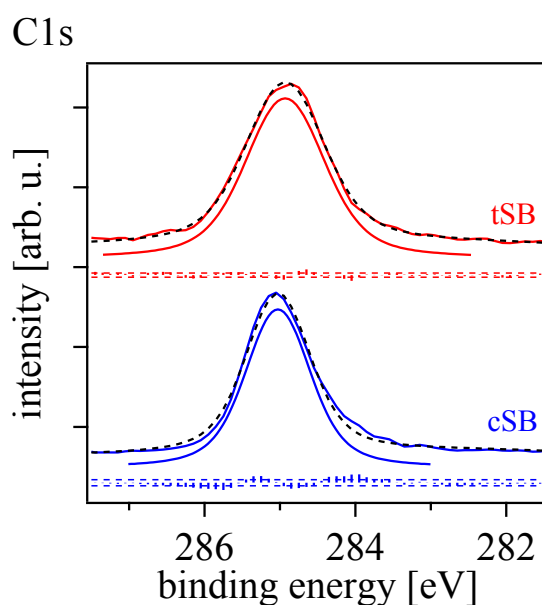


surface with a peak at 75 eV binding energy, split by 2.2 eV. In contrast to the Si2p signal of the Si(100) surface, the Cu3p signal shows now significant substructure. Upon adsorption of stilbene, no new features appear in the spectra, but the complete signal is shifted toward higher binding energies upon coverage. For monolayer coverage the signals are shifted by 0.2 eV. Such core level shifts can be explained by a change of the substrate workfunction. Such workfunction changes at metal surfaces upon the adsorption of organic molecules is well known[7]. As there are no relative changes in the Cu3p core level emission, like in the Si2p emission, the direct interaction between stilbene molecules and surface atoms can be assumed to be analogous to the case on Si(100). Therefore a  $\pi$ -metal interaction without any covalent nature can be expected.



**Figure 5.33:** C1s core level emission from *cis*- and *trans*-stilbene adsorbed on Cu(110) in monolayer and two multilayer coverages.

Upon adsorption of stilbene on Cu(110) a single broad C1s signal can be detected at a binding energy of 285 eV which is comparable to the binding energy observed on Si(100). As already seen on Si(100), the C1s signal for the *cis*- and *trans*-isomer is not identical. All coverages exhibit a similar lineshape. Thus the low multilayer coverage, displaying a stronger signal than the monolayer coverage, was chosen for fitting. Figure 5.34 displays the spectra for both isomers. Each spectrum can be fitted with a single Voigt function at the same binding energy, with a width of 1.1 eV for *trans*- and 0.9 eV for *cis*-stilbene, at the same lineshape. A possible second vibrational component could not be resolved. The larger broadening of the *trans*-stilbene spectra indicates a stronger interaction of the *trans*-stilbene molecules. As the Cu3p emission shows no difference between both isomers, this interaction has to be of intermolecular nature. In analogy to the explanation given



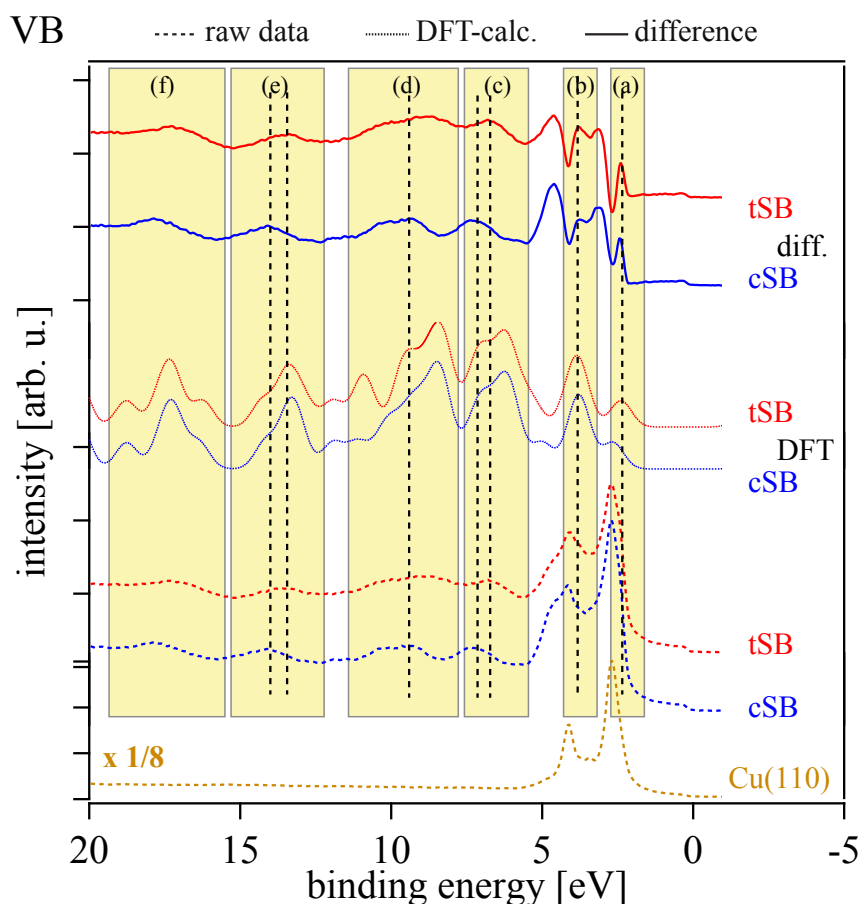
**Figure 5.34:** The C1s core level from a thin multilayer stilbene adsorbed on Cu(110) can be fitted with a single Voigt profile. No additional vibrational component can be detected.

before for the adsorption on Si(100), where a strong broadening occurred from monolayer to multilayer coverage of the trans isomer, the planarity of the trans-stilbene molecules allows for a good stacking and  $\pi$ - $\pi$ -interaction. This  $\pi$ - $\pi$ -interaction seems to appear already from low coverages on. This already indicates, that the bonding to the surface via the C=C bridge is weaker and the subsequent twisting of the isomers is less than for the Si(100) substrate.

For the investigation of valence band spectra from molecular adsorbates, Cu(110) is advantageous to Si(100) as substrate. While the Si bulk-bands are visible over a broad energy range, Cu only displays sharp but also very intense d-band signals between 2 eV and 5 eV binding energy. Thus detection and identification of adsorbates is much more simplified. Very low lying molecular orbitals can easily be detected, and between 5 eV and 20 eV binding energy no significant background exists.

Figure 5.35 shows valence band spectra of one monolayer cis- and trans-stilbene on Cu(110). Already in the range of the Cu bulk d-bands, new contributions from the adsorbate can be seen. These are even more pronounced at higher binding energies on top of the flat background signal from the Cu(110) surface. In normal emission geometry, as used here, the sp-bands and the surface state are not seen as for Si(100).

Both valence band spectra are quite similar. Nevertheless, small but distinct differences can be detected. A comparison of the experimental spectra with the single molecule calculations, which were already used for the interpretation of the Si(100) data, shows qualitative agreement. Especially the signals at binding energies listed in table 5.3 are well



**Figure 5.35:** Valence band spectrum of pure Cu(110) and monolayer coverages of *cis*- and *trans*-stilbene. At the bottom the raw data is shown, at the top the substrate-subtracted spectra of both isomers. Orbital binding energy spectra (deconvoluted with a gaussian) are displayed in the middle for comparison. Areas in the spectra, where stilbene signals can be detected are highlighted, energies are given in table 5.3. Characteristic features used for identification of the isomers are indicated by dashed lines.

reproduced.

isomer	valence band signals [eV]					
	a	b	c	d	e	f
trans (exp.)	2.4	3.8	6.7	9.4	13.5	17.3
trans (gaussian)	2.38	3.8	6.7	9.4	13.5	
<i>cis</i> (exp.)	2.45	3.8	7.2	9.4	14.1	17.6
<i>cis</i> (gaussian)	2.5	3.8	7.1	9.4	14.0	

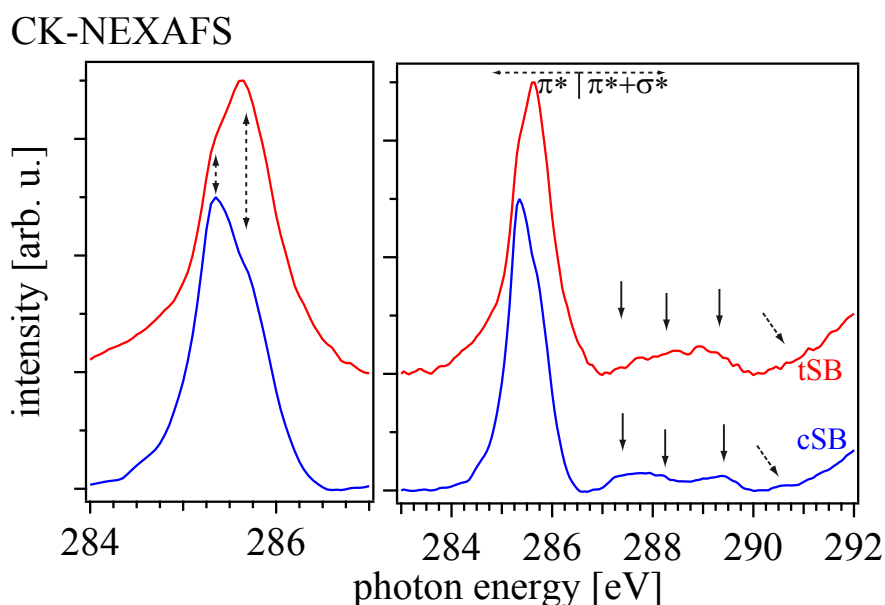
**Table 5.3:** Binding energies of valence band signals of monolayer stilbene on Cu(110).

All energies are shifted by 0.4 eV to higher binding energies in comparison to the Si(100) surface. This behavior is due to the higher surface potential due to the adsorbed molecules [7], as has already been indicated in the Cu3p emission. At the energy positions indicated

by dashed lines in figure 5.35, differences between both isomers are visible in the subtracted spectra. These differences are well reproduced by shifts and intensity differences in the simple single molecule calculations. Already the raw data spectra at the bottom show these differences, although they are not as prominently visible as in the substrate subtracted spectra. This strongly indicates that purely cis- and trans-stilbene are adsorbed onto the surface. Again valence band spectra can be used to distinguish both isomers. Due to the overall shift to higher binding energies, stilbene features are now very close to those detected for benzene on Si(100), at 2.3 eV, 4.0 eV, 5.7 eV, 13.3 eV, and 14.1 eV[135, 139, 142]. If a corresponding energy shift can be assumed for benzene upon adsorption on Cu(110), at these energies (shifted values: 2.7 eV, 4.4 eV, 6.1 eV, 13.7 eV, and 14.5 eV) no signals can be detected. Thus the appearance of benzene due to dissociation of stilbene can be excluded.

#### 5.4.2 Identification of Isomers - NEXAFS

Figure 5.36 shows NEXAFS spectra of a thick multilayer stilbene on Cu(110). At such high coverages the molecular features in the spectra are well pronounced. As seen before NEXAFS spectra consist of two parts, the strong  $\pi^*$ -resonance at energies below 287 eV photon energies and  $\sigma^*$ -resonances at higher photon energies.

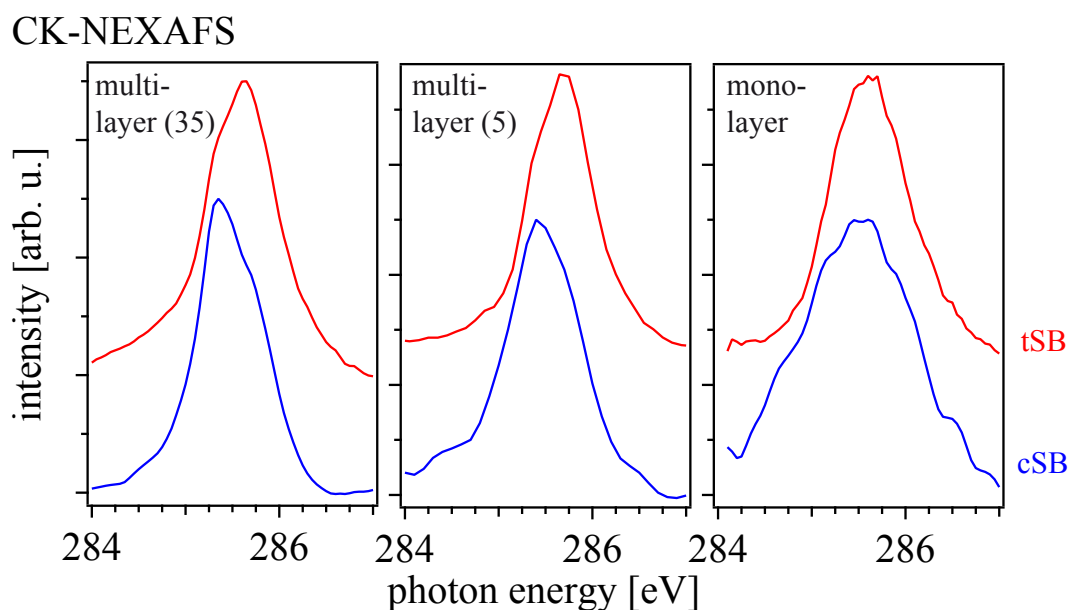


**Figure 5.36:** CK-NEXAFS spectra of monolayer cis- (blue) and trans-stilbene (red) adsorbed on Cu(110). Full spectrum on the right, detail of  $\pi^*$ -resonance on the left.

The  $\pi^*$ -resonance of both isomers shows two main components. For the trans-isomer the high energy component is stronger, while for the cis-isomer the low energy component

dominates. The other component, respectively, is not strongly separated and thereby manifested in a splitting, but detectable in the shoulder of the stronger component. This behavior is already seen in the gas-phase, thus the characteristic feature of stilbene is preserved also upon adsorption onto the copper surface.

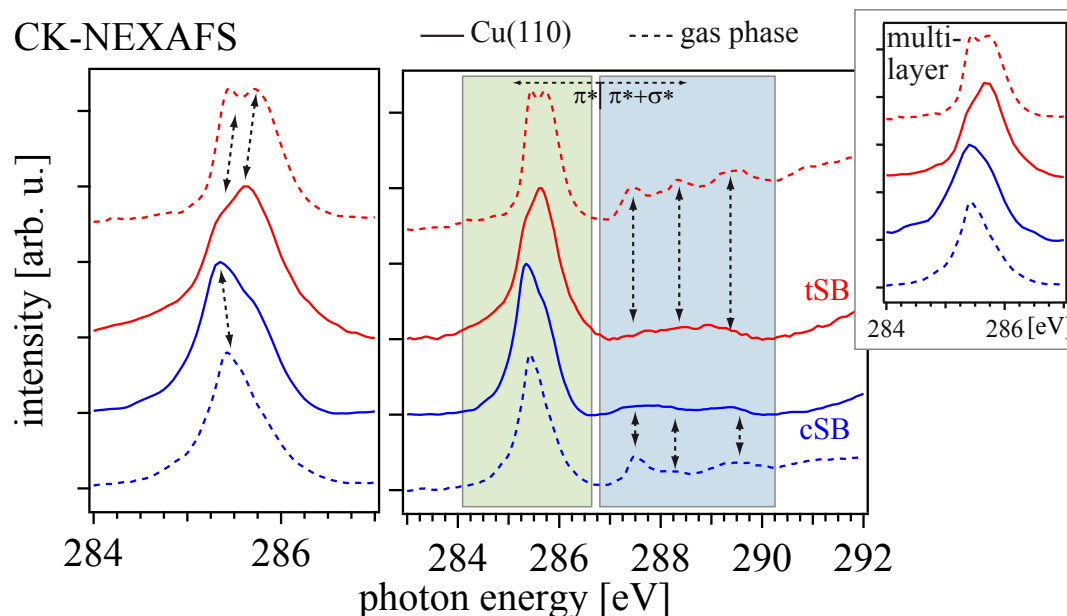
Both isomers also exhibit the characteristic three-peak-structure for higher  $\sigma^*$ -resonances. As described previously in chapters for the cis-isomer, the middle peak is slightly lower in intensity than the outer ones, while for the trans-isomer the middle one is slightly more intense. At about 291 eV photon energy no higher  $\pi^*$ -resonance can be detected. This result also corresponds to the findings in the gas phase and on Si(100)



**Figure 5.37:** NEXAFS- $\pi^*$ -resonance of cis- and trans-stilbene for the three investigated coverages (from right to left), monolayer, multilayer of five and 35 layers thickness. Despite the less quality of the monolayer spectra the specific spectral features can be observed for all coverages.

A comparison of the  $\pi^*$ -resonance for the monolayer and a thin multilayer with the thick multilayer spectra shown in figure 5.36 reveals no change. For lower coverages, i.e. the monolayer, detection of the isomers becomes more difficult, as the molecular contributions to the spectra become rather small in comparison to the contributions from carbon-contaminations of the beamline. In spite of the lower quality of the spectra for lower coverages indicating the approach to detection limit, spectra for all coverages look similar. Especially the prominent identification feature and the behavior of the two components - stronger signal at higher or lower photon energies for trans- and cis-stilbene, respectively - is preserved. Thus even for low coverages NEXAFS proves to be able to clearly identify both isomers.

Figure 5.38 shows the  $\pi^*$ -resonance of thin multilayer and thick multilayer stilbene on



**Figure 5.38:** CK-NEXAFS spectra of thick multilayer *cis*- (blue) and *trans*-stilbene (red) adsorbed on Cu(110). Comparison of adsorbed molecules (solid lines) with gas phase molecules (dashed lines). Inset top right shows spectra for thin multilayer for comparison. No differences compared to spectra for the thick multilayer can be detected.

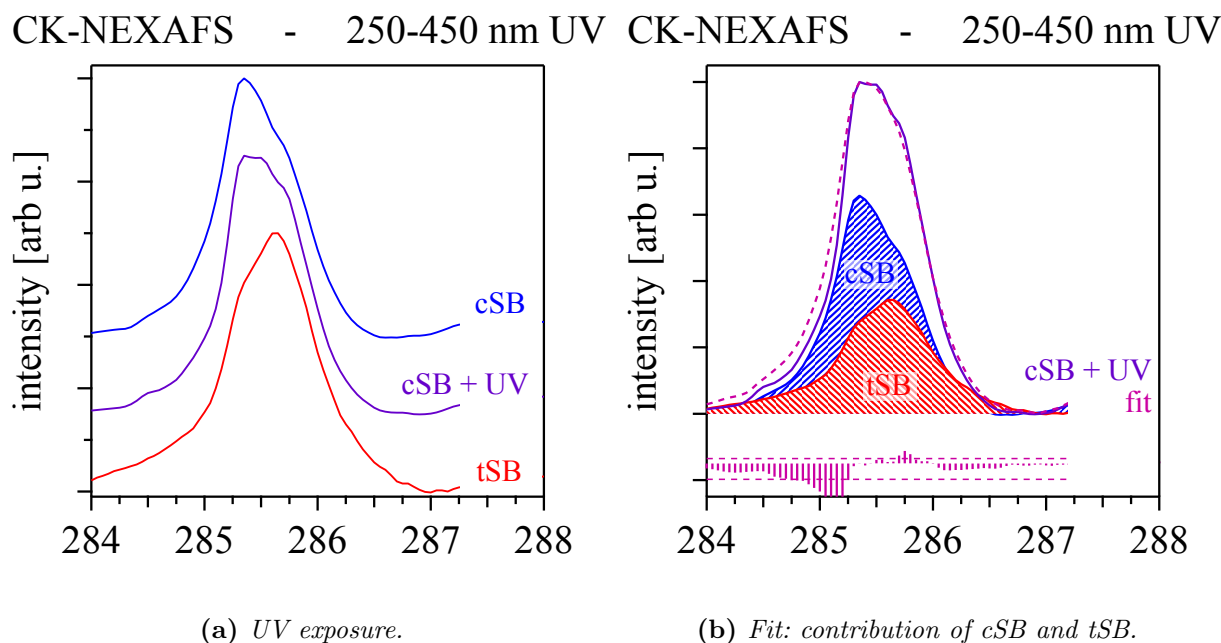
Cu(110) in comparison to the gas phase spectra. Upon adsorption, the  $\pi^*$ -resonance is shifted by 0.03 eV to lower excitation energies due to interaction of the molecular  $\pi$ -system with the substrate. This shift is much smaller than for adsorption on Si(100). Although a direct relation between the bond strength and the spectral shift cannot be assumed, this is already an indication that the interaction strength is weaker here. Thus the unoccupied molecular orbitals are less influenced by the adsorption interaction. Hence it seems that isomerisation might be possible on the Cu(110) surface. Figure 5.38 shows that again the  $\sigma^*$ -resonances are not influenced in position and are just smaller in intensity in the adsorbed phase. This supports the assumption that bonding interaction takes place mainly due to the molecular  $\pi$ -system.

### 5.4.3 Photoinduced Isomerisation on Cu(110)

#### UV induced Photoisomerisation

In the multilayers, the upper molecular layers are well decoupled from the substrate than the immediate monolayer[162]. As shown for adsorption on the Si(100) surface the coupling of the molecular  $\pi$ -system to the substrate may inhibit the ability for isomerisation (see chapter 5.3.3). Therefore multilayer coverages on the Cu(110) surface, where the smaller shift in the  $\pi^*$ -resonance already indicates weaker bonding to the surface, seem most

promising for UV-induced isomerisation.



**Figure 5.39:** A thick multilayer of *cis*-stilbene exposed to UV-light. Spectral changes are clearly visible in 5.39a. For details on the fitting see text.

Figures 5.39 and 5.40 show the  $\pi^*$ -resonances of thick multilayer *cis*- and *trans*-stilbene on Cu(110) exposed to UV-light. Cumulative UV exposure with wavelengths ranging from 250 nm to 450 nm has been applied. Only the *trans*-isomer was additionally exposed to 365 nm UV-light in the discrete operation mode (see chapter 4.5).

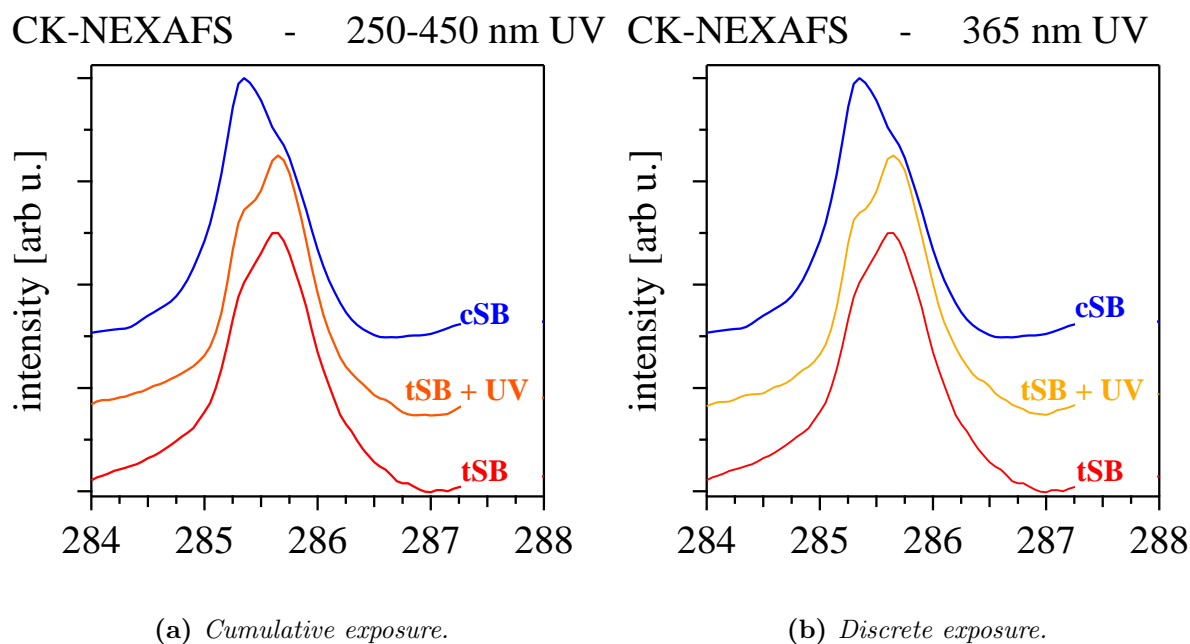
Upon exposure of *cis*-stilbene in the thick multilayer coverage to UV-light, clear spectral changes in the  $\pi^*$ -resonance can be detected. While the low energy component at 285.35 eV (which higher intensity is characteristic for the *cis*-isomer) decreases, an increase of the high energy feature at 285.65 eV, which is more intense for *trans*-stilbene, can be detected. This indicates a partial conversion of the *cis*- into the *trans*-isomer. To identify the overall amount of conversion, the  $\pi^*$ -resonance intensity acquired has been compared to a calculated spectrum

$$I_{calc} = (1 - \alpha) \cdot I_{tSB} + \alpha \cdot I_{cSB} \quad (5.1)$$

where  $I_{tSB}$  and  $I_{cSB}$  are the experimentally determined spectra for pure *trans*- and *cis*-isomer and  $\alpha$  is the overall conversion factor. An overall conversion of about 34% *cis*-stilbene into *trans*-stilbene could thereby be determined. This is almost exactly the number that Hochstrasser and coworkers report for the gas-phase[109, 110] (see chapter 5.1.2).

Valence band spectra of the sample after irradiation (not shown here) confirm these

results. A combined valence band spectrum, bearing the features of cis- and trans-stilbene was found. No indications of additional components, e.g. dissociation products such as benzene, could be found. Thus it seems clear that solely the cis-to-trans isomerisation has taken place.

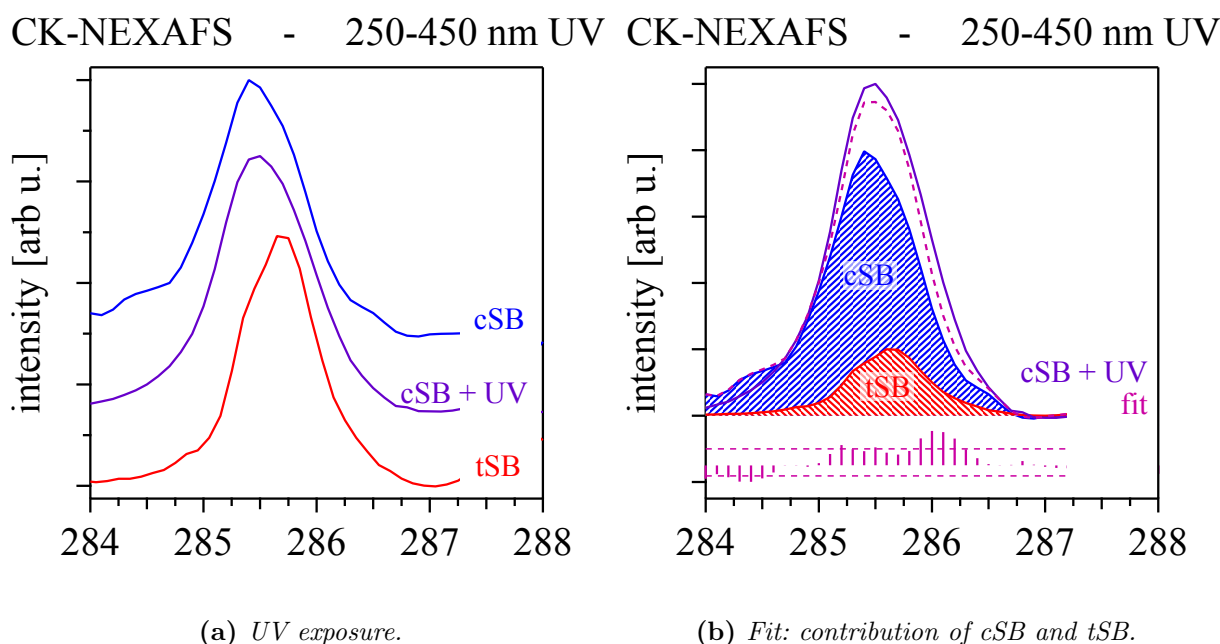


**Figure 5.40:** Thick multilayer of trans-stilbene exposed to UV-light in different exposure modes. The unchanged spectra clearly show that the isomerisation could not be induced.

Upon further exposure to UV-light the spectra did not change any more. Thus no higher conversion could be achieved, but also no back-reaction from trans-stilbene to cis-stilbene could be initiated. Figure 5.40 shows data for monolayer coverages of trans-stilbene exposed to UV-light in different exposure modes. No changes in the spectral features are detectable for the UV exposed samples. At first glance, this is astonishing as the trans-isomer is the thermodynamically more stable isomer in the gas phase and in solution. However, in the constrained environment such as in the adsorbed state on a surface, the strength of interaction between adjacent molecules and molecules and the surface influences the stability of the single molecules. As has been mentioned before in chapter 4.7.3, the planarity of the trans-isomer favors stacking and crystallization of the molecule due to better  $\pi$ - $\pi$ -overlap. The same argument holds true adsorbed on the surface, as has been shown on the basis of the C1s emission of both isomers. Thus trans-isomers on the surface are stabilized with respect to the cis-isomers. This hinders the transformation from trans-stilbene into cis-stilbene - as seen for the pure trans-covered surfaces and in the lack of back reactions after cis-to-trans isomerisation. Not only the  $\pi$ - $\pi$ -interactions[155, 156] between adjacent molecules act in a stabilizing way, as shown before (chapter 5.4.2) bonding between stilbene and the Cu surface takes place via the C=C-bridge. In the



trans-conformation the two phenyl groups are placed more parallel to the surface and  $\pi$ -Cu-interactions may occur, further stabilizing the isomer on the surface. Additionally the trans-isomer occupies more space on the surface. The more space is covered, the less space is available for rotation of the phenyl-groups of stilbene in the isomerisation process. Due to this, trans-isomers also do hinder themselves in isomerisation. These reasons provide a sufficient explanation for the inability of trans-to-cis isomerisation in this context. Thus thick multilayer stilben on Cu(110) can be partially photoisomerised only from the cis- into the trans-configuration.



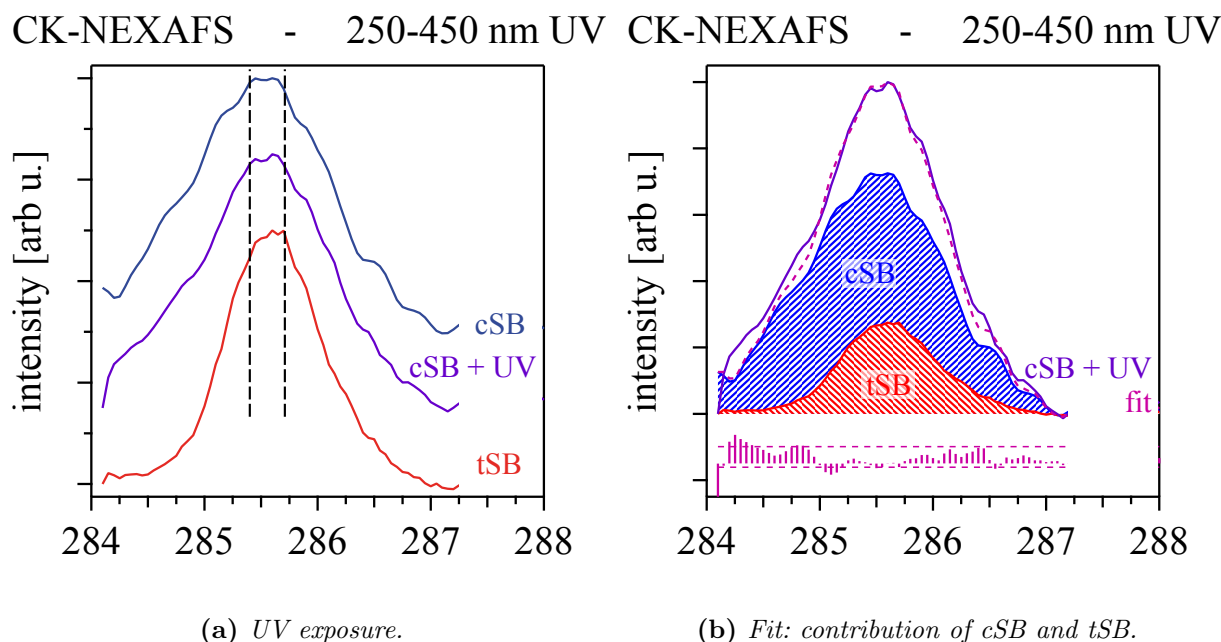
**Figure 5.41:** Thin multilayer of cis-stilbene exposed to UV-light. Spectral changes are clearly visible in 5.41a. For details on the fitting see text.

Coverages of thin multilayer (figure 5.41) and monolayer (figure 5.41) cis-stilbene have also been exposed to UV-irradiation in the cumulative exposure mode.

UV-exposed cis-stilbene at thin multilayer coverage shows the same behavior as the thicker layers shown before. While the low energy component is depleted, the high energy component of the  $\pi^*$ -resonance increases, indicating a partial conversion from cis- to trans-stilbene. Valence band spectra were again used to support this finding and exclude dissociation or other beam damage.

Modelling of the spectrum using equation (5.1) yielded an overall conversion of about 20% for the thin multilayer coverage, which is about 57% of the value for the thick multilayer and the gas phase value from Hochstrasser[109]. No further cis-to-trans reaction upon additional exposure could be detected. The trans-to-cis isomerisation from a pure trans-stilbene surface has not been probed. But as no back reaction could be observed on the

converted samples, it is feasible to assume this as again hindered for the same reasons as meant before.



**Figure 5.42:** Monolayer of *cis*-stilbene exposed to UV-light. Spectral changes are clearly visible in 5.39a. For details on the fitting see text.

As for the low coverage, i.e. monolayer, NEXAFS spectra contain a huge amount of “contamination-signal”, as has been shown in figure 4.19. The differentiation of the two isomers and determination of a conversion amount becomes rather difficult and error prone. Figure 5.42 shows the three experimental spectra (and the modeling calculation). The strong noise in comparison to the previously shown spectra is clearly visible. Several of the shoulders and supposed features can be attributed to this noise. Though differences are not as concise any more, it can still be fathomed that the *cis*-spectrum bears its  $\pi^*$ -resonance maximum at lower photon energies than the *trans*-spectrum. Two dashed lines are inserted in figure 5.42a to guide the eye. Also the change in intensities of the two contributions upon UV-exposure is visible. Modelling yielded in an overall conversion of about 27.5%. Depending on the range of the  $\pi^*$ -resonance over which the modelling has been performed conversion amounts of up to 37% have been determined.

Thus on the Cu(110) surface the isomerisation from *cis*-stilbene to *trans*-stilbene seems possible. Independent of the amount of stilbene buffer layers (none for the monolayer up to 34 for the thick multilayer) between the topmost *cis*-stilbene layer and the substrate, overall conversion between 20% and 38% could be achieved. Although the modelings shown in figures 5.39, 5.41 and 5.42 resemble somewhat the peak of the exposed stilbene, the signal shoulders are not very well fitted. Therefore the determined conversion percentages should be considered with some care. The coverage (and therefore the separation of

topmost layer from the substrate) does not seem to have a direct influence on the conversion, as conversion is least for the thin multilayer and not for the monolayer (or thick multilayer). It is probably most reasonable to assume an average conversion rate of about 27.5%. This is slightly less but still in the range of the value reported by Hochstrasser and coworkers in the gas phase – 35%[109]. Sterical reasons do not seem to play a role, otherwise with increasing coverage, i.e. increasing number of molecules on the surface, the conversion would have to decrease. Thus this rate can be assumed to be determined by the yield of photoexcitation.

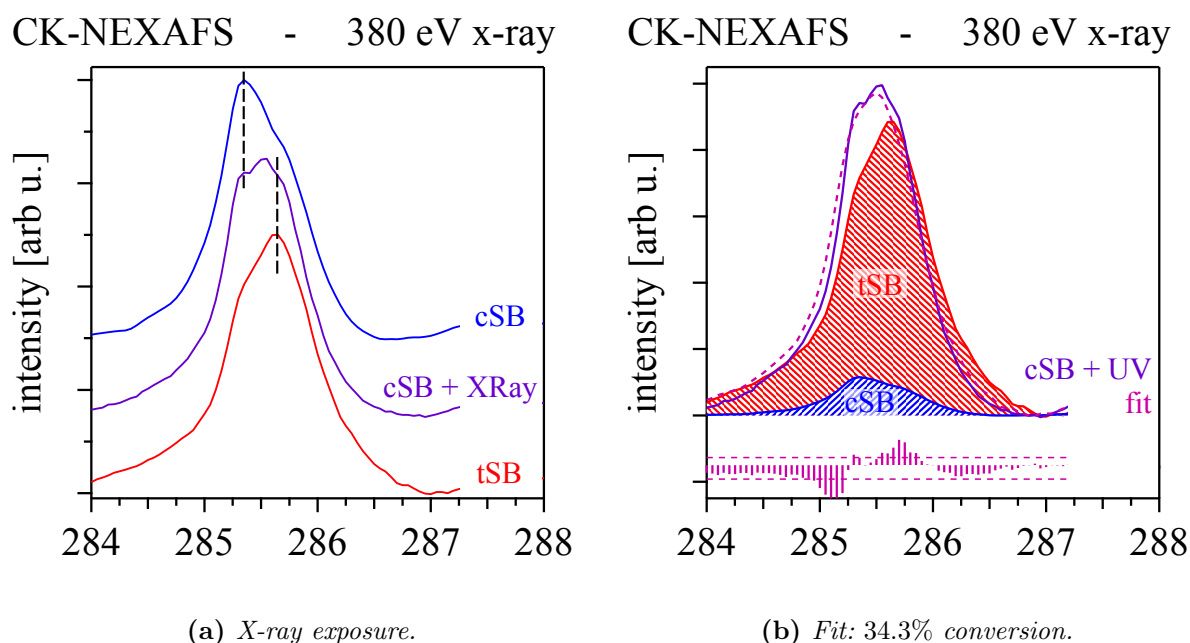
The trans-stilbene has been observed not to react at all, neither in form of the back reaction following cis-isomerisation, nor from the pure trans-stilbene covered phase. This can be explained by the stronger stabilisation of the less twisted trans-conformation. Intermolecular stabilization due to good stacking and  $\pi$ - $\pi$ -interactions as well as probably better interaction of the more planar  $\pi$ -system with the metal surface.

Thus under certain conditions, i.e. decoupling of the unoccupied “switching state” from the substrate surface, the isomerisation from cis-stilbene to trans-stilbene seems possible. The stronger stabilization of the trans-isomer due to intermolecular interactions and interaction with the substrate and its bigger space consumption hinder the trans-to-cis-isomerisation, independent if as back reaction or as reaction from the pure trans-stilbene surface.

## X-Ray induced Photoisomerisation

In chapter 5.1.2 additional excitation pathways for the stilbene isomerisation have been described. While longer wavelengths have not been tested in this work, light of a much shorter wavelength has been applied to a thick multilayer coverage of cis-stilbene. Synchrotron x-rays of 380 eV photon energy, corresponding to 3.3 nm wavelength, were used in a five minute exposure; i.e. a C1s-scan was performed with this photon energy. For such short wavelength the photon induced dissociations and fragmentations of molecular adsorbates has been reported[163]. Thus extra attention has been paid to the risk of these reactions. Valence band spectra contained no sign of newly emerging fragmentation products, in fact no molecular features other than from cis- and trans-stilbene could be detected. Therefore it seems reasonable to assume that indeed a cis-to-trans isomerisation has been induced via an ISC-pathway (compare figure 5.4).

Figure 5.43 shows the  $\pi^*$ -resonance of thick multilayer cis-stilbene exposed to 3.3 nm irradiation. Besides the decrease of the low energy component and the increase of the high energy component, the rise of a peak in the middle of both components can be seen. Such a peak is typical for an overlap of two adjacent signals. Again equation (5.1) was used to model the conversion. An overall conversion amount of about 70% could be determined.



**Figure 5.43:** Thick multilayer of *cis*-stilbene exposed to UV-light. Spectral changes are clearly visible in 5.39a. Conversion of 88.5% is derived from fitting with pure isomer spectra in 5.43b.

Valence band and core level spectra (both not shown here) were used to verify that no photodissociation or beam damage has occurred. The sterical situation of the *cis*-stilbene molecules in this case is identical than under UV exposure, and can therefore not used as an explanation for the high conversion. Such high conversion can only be explained by a much better excitation. Which is quite obvious as a much better excitation source has been used - the synchrotron with a much smaller focus, a higher flux density and a wavelength that is at the carbon absorption edge.

The back reaction or further conversion after additional irradiation could not be observed, as the spectrum remained unchanged.

## 5.5 Photoisomerisation of Stilbene

Stilbene is a very nice example, how the different structure of the two isomers has a huge impact on macroscopic properties, e.g. the aggregate state (liquid for cis-stilbene, solid for the trans-isomer at room temperature). The investigations in this work show very nicely that these macroscopic differences can be detected on a very microscopic level. Core-level photoemission, sensitive to the single atoms in molecules can be used as a method to distinguish between the two isomers of stilbene. A characteristic lineshape in the C1s core level emission can be detected independent on the substrate the molecules are adsorbed onto. This effect is even more prominent in the emission from valence band molecular orbitals, which are delocalized over the whole molecule and thus much more structure sensitive. Again isomer-specific signals can be detected substrate-independently. These signals can not only be unambiguously assigned to the cis- or trans-isomer, but also correlate with DFT calculations for single molecules. These correlations are prevailed as well for adsorption on a semiconductor as on a metal, which is quite surprising, as the molecule-substrate interactions are different for both substrates.

Together with core level spectra from the substrates information about the strength and site of this bonding interaction could be revealed. Both on silicon and copper the molecules attach via the C=C-bridge to the outstanding atoms, i.e. the dimers in Si(100) and the Cu-rows on Cu(110), with an increased bonding strength of the  $\pi$ system-substrate-atom interaction for the semiconductor compared to the metal.

For the isomerisation process knowledge about the unoccupied molecular orbitals is crucial. NEXAFS has proven to be an ideal method for this purpose. The characteristic and isomer specific  $\pi^*$ -resonance observed for gas phase stilbene was preserved upon adsorption on Si(100) and Cu(110) and therefore served as an identification tag for the two isomers.

Changes in the absolute energy position of the  $\pi^*$ -resonance gave an insight into the bonding strength to the surface. The interaction of the lower energy unoccupied  $\pi$ -orbitals with the silicon surface is stronger in comparison with the copper surface. As this orbital is responsible for the isomerisation, this finding explains why the isomerisation is hindered on Si(100) and feasible on Cu(110). Analysis of the higher resonances, which are due to excitations into the  $\sigma^*$ -orbitals, provide an insight into the molecular backbone of the molecules. It could be shown that the backbone, despite its different conformation, is comparable for both isomers. Also, as no changes in the signal pattern occur, it could be shown, that no covalent bond to the surfaces is formed and the molecular backbone is preserved. Energy shifts do only occur in the  $\pi^*$ -resonance. This directly points to the fact, that only the molecular  $\pi$ -system is involved in bonding to the surface.

Not only is NEXAFS a powerful tool to elucidate the adsorption behavior of cis- and

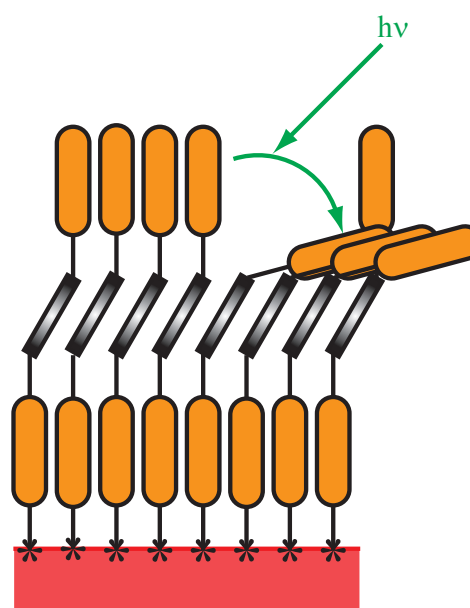
trans-stilbene on different surfaces. Due to the different form of the signal and different maximum energy positions possible mixtures of cis- and trans-stilbene could be analysed. The spectra of UV-illuminated cis-stilbene on Cu(110) appeared to be a linear combination of the pure-isomer spectra. No additional components arising from decomposed molecules were detected. This proved the isomerisation of cis-stilbene and a ration of around 20% trans-isomers could be determined.

Though this is the first time the isomerisation of stilbene and “molecular switches” in general on a surface could be shown on a hyper-single-molecular level, these experiments directly pinpoint to the limitations of this system. In both cases, the stilbene molecule adsorbed in a parallel manner to the surface. Despite the occurring spatial restrictions hindering the isomerisation process, this adsorption fashion enables the interaction of the molecular  $\pi$ -system with the substrates. In the worst case – Si(100) – this interaction completely withdraws the  $\pi^*$ -state and completely inhibits isomerisation. For the metal substrate this effect might still be the reason for the small cis-to-trans conversion ration. On Cu(110) the interaction of the overall  $\pi$ -system hindered a back-reaction of the cis-to-trans and inhibited the trans-to-cis-isomerisation at all, respectively.

In an ideal “molecular switch” there would be no interaction between its  $\pi$ -system and the substrate and the switching entity would not experience any spatial restrictions. These pre-conditions would be fulfilled, if the molecules were standing upright on the surface, as idealized in figure 5.44. Then the  $\pi$ -systems of the molecule would stand perpendicular to the surface, i.e. interaction would be impossible due to zero overlap. Also no surface would restrict the isomerisation-motion. Such a configuration would have another advantage. In a defined assembly the  $\pi$ -orbitals of the molecules would overlap and lead, as shown, to a band formation[11, 164] and consequently to conduction along the molecular chain. A “real switch” would have been produced.

The experiments on silicon and on copper have shown that such an assembly is not reachable with the pure molecule. Modification on the molecule, the addition of an anchor group, fixating the molecule in a defined upright position onto the surface, is necessary.

For azobenzenes the use of such anchor groups is already quite common. These can either



**Figure 5.44:** Idealized molecular switches connected to the surface via an anchor group.

be two tert-butyl-groups on either phenyl-ring, as Grill used as sort of small tripod-feet[118], or nitro- and amino-groups used by Morgenstern[116], to name a few examples. Yet there is no work on single-anchored stilbenes.

The stilbene derivative commercially available, where a possible anchor-group is substituted in the ortho-position of the benzene ring opposite to the bridge is 4-4'-stilbene dicarboxylic acid ( $HOOC - stilbene - COOH$ )<sup>4</sup>.

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<sup>4</sup>This is based on a Chemical Abstracts database[165] search for stilbene derivatives containing a substituent only in 4 and/or 4' position, that had an anchor group functionality, i.e.  $COOH, OH, SH$ . From the resulting possible candidates only the above mentioned was actually commercially available at the time of this work.

