

Adsorption of carboxymethylester-azobenzene on copper and gold single crystal surfaces

M. Piantek · J. Miguel · M. Bernien · C. Navío ·
A. Krüger · B. Prieswisch · K. Rück-Braun · W. Kuch

Received: 21 January 2008 / Accepted: 9 July 2008 / Published online: 13 August 2008
© Springer-Verlag 2008

Abstract The adsorption of 3,3'-di(methoxycarbonyl)azobenzene (CMA) on Au(111) and on Cu(001) substrates was studied by X-ray absorption spectroscopy measurements at the C, N, and O *K* edges. We find the molecules physisorbed in a planar conformation flat on the Au(111) surface. At higher coverages, a molecular crystal is formed wherein the molecules have the same flat geometry. On Cu(001), additional chemical bonds are formed between the molecules and the surface via the nitrogen atoms. Here the methyl benzoate moieties are tilted out of the surface plane.

PACS 68.43.Fg · 68.55.am · 78.70.Dm

1 Introduction

Azobenzene and its derivatives are an important class of molecular switches. The *cis*–*trans* photoisomerization of azobenzene in gas phase or solution is one of the best-understood light-induced molecular functions [1, 2]. Azobenzene molecules undergo a reversible conformational transition of the N–N double bond between an extended (*trans*) and a compact (*cis*) conformation upon irradiation with light of ≈ 320 and ≈ 420 nm wavelength. With the prospect of a bottom-up assembly of molecular electronics, azobenzene molecules are attracting increased interest

as molecular switches converting light into mechanical motion. This is not possible without contacting and supporting the molecules. An important issue is thus the interaction with the environment, in particular, the adsorption on a solid surface and its effect on the switching characteristics.

Azobenzene derivatives adsorbed directly on Au(111) have been studied by scanning tunneling microscopy (STM) [3–8] and laser spectroscopy [9]. Generally, the molecules were found to adsorb in a *trans* or *trans*-rotated conformation. Lateral interaction between the molecules, depending on their functional end groups, leads to the formation of compact ordered islands. In some cases, the switching to the *cis* conformation or between the two nonequivalent *trans* conformations could be induced by tunneling electrons from the STM tip [5–7]. With a somewhat lower yield, a *trans*–*cis* isomerization after irradiation with light could also be observed [10, 11]. Conformation-dependent intermolecular interaction was evoked as a reason for the collective photoinduced switching behavior observed in azobenzene self-assembled monolayers [12].

Here we present an angle-resolved near-edge X-ray absorption fine structure (NEXAFS) study of 3,3'-di(methoxycarbonyl)azobenzene (carboxymethylester-azobenzene, CMA, see inset of Fig. 1) on Au(111) and Cu(001) single crystal surfaces. X-ray absorption spectroscopy has the advantage of elemental selectivity. From the angular dependence of spectral features, the orientation of the corresponding molecular orbitals can be determined. We find that CMA molecules adsorb in a flat configuration on Au(111) with electronic properties similar to the bulk material, suggesting a physisorption mainly by van-der-Waals interaction. In contrast, a tilted configuration is found on Cu(001), where X-ray absorption spectra suggest a chemisorption bonding to the substrate by N $2p$ π orbitals as the relevant mech-

M. Piantek · J. Miguel · M. Bernien · C. Navío · A. Krüger ·
W. Kuch (✉)
Institut für Experimentalphysik, Freie Universität Berlin,
Arnimallee 14, 14195 Berlin, Germany
e-mail: kuch@physik.fu-berlin.de

B. Prieswisch · K. Rück-Braun
Institut für Chemie, Technische Universität Berlin, Straße des 17.
Juni 135, 10623 Berlin, Germany

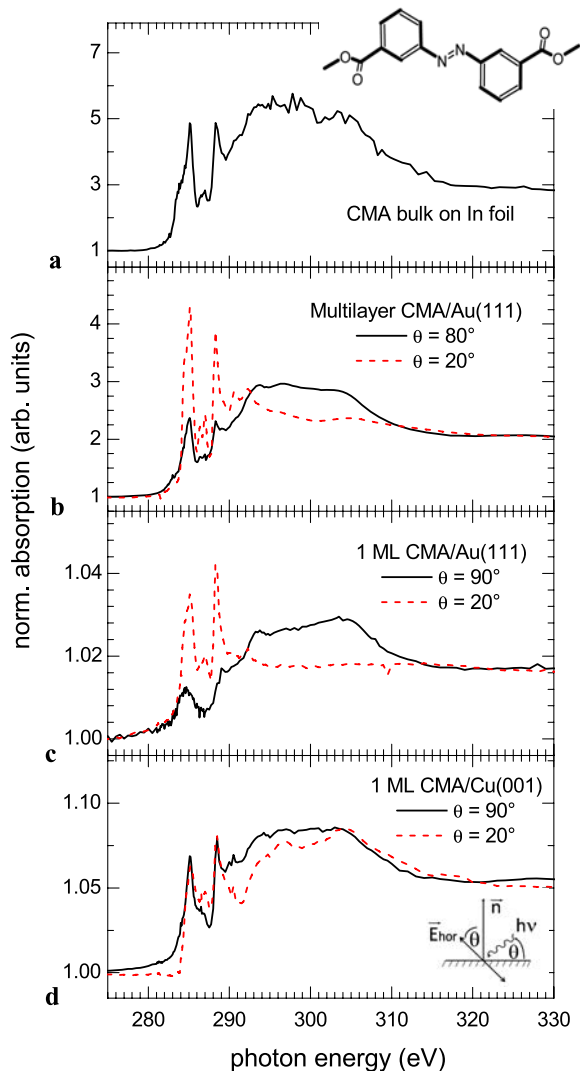


Fig. 1 From top to bottom: (a) C *K* edge absorption spectra of CMA bulk on In foil, (b) of a multilayer CMA on Au(111), (c) of 1 ML CMA on Au(111), (d) of 1 ML CMA on Cu(001). Continuous (dotted) lines correspond to spectra acquired at 90° or 80° near-normal (20° grazing) X-ray incidence. Inset in (a): Chemical structure of the 3,3'-di(methoxycarbonyl)azobenzene molecule. Inset in (d): Sketch of the experimental geometry defining the angle of incidence θ

anism. This has significant consequences for any *cis*–*trans* isomerization of adsorbed molecules.

2 Experimental

All experiments were performed in an ultrahigh vacuum system with a base pressure of 10^{-8} Pa, equipped with standard surface science tools. Au(111) and Cu(001) substrates have been cleaned by repeated cycles of Ar⁺ ion sputtering at 800 and 1000 eV, respectively, and subsequent annealing to 900 K until sharp low energy electron diffraction spots appeared, and no contamination of the surface could be detected by

X-ray photoelectron spectroscopy (XPS). CMA was synthesized from methyl 3-aminobenzoate and methyl 3-nitrosobenzoate by following the procedures described in [13]. The molecules were deposited by thermal evaporation from a resistively heated tantalum crucible onto the metal substrate. Typical evaporation temperatures were 365 K, at which deposition rates of ≈ 1 ML/min were obtained. The deposition rate was monitored by a quartz microbalance during deposition.

A thin film of CMA was prepared on Cu(001) at room temperature, at which the amount of adsorbed molecules saturates after a certain deposition time, as monitored by XPS. We refer to this coverage as one molecular monolayer (1 ML) in the following. The Cu substrate was kept at room temperature for the X-ray absorption measurements. For the preparation of CMA layers on Au(111) and for the subsequent NEXAFS measurements, the substrate was held at 155 K and the desired amount of molecules was evaporated with the same deposition rate as for the Cu substrate. No saturation occurred at that temperature, so that the deposited molecules do not desorb from the surface. The coverage was determined from XPS measurements and the edge jump of C *K* edge absorption spectra, taking into account the different background absorption signal caused by the different substrates. The sample labelled as “multilayer CMA/Au(111)” corresponds to a coverage of about 15–20 ML. As a reference, some grains of CMA powder were pressed into an indium foil and also measured.

X-ray absorption spectra were taken using synchrotron radiation from the undulator beamline UE56/2-PGM2 and the bending magnet beamline PM-3 of BESSY in Berlin. Linearly *p*-polarized light with a degree of polarization $\geq 90\%$ was used. The incidence angle was varied between 20° and 90° with respect to the surface plane. A sketch of the experimental geometry is shown in the inset of Fig. 1d. Absorption spectra were acquired in total electron yield mode, recording the sample drain current as a function of photon energy. The energy resolution of the spectra acquired at the UE56/2-PGM2 (spectra of CMA reference sample and multilayer CMA/Au(111)) was 80 meV at the C *K* edge, 130 meV at the N *K* edge, and 200 meV at the O *K* edge. To minimize the effects of radiation damage, the photon intensity was reduced using higher constant fixed focus (c_{ff}) values of the monochromator. For the spectra taken at the PM-3 (1 ML CMA on Cu(001), 1 ML CMA on Au(111)) the resolution was better than 95 meV for spectra at the C *K* edge, 140 meV at the N *K* edge, and 215 meV at the O *K* edge, with higher resolution in the range of the π^* absorption maxima (variable- c_{ff} mode of the monochromator). At that beamline, the measuring position was moved out of the beam focus position to reduce the photon flux density on the sample. The estimated typical photon flux density at the sample was about 10^{13} s⁻¹ cm⁻² at both beamlines. From

the comparison of spectra taken immediately after preparation of the sample and at later times, we conclude that under these conditions radiation damage can be excluded for the measurements presented here.

3 Results and discussion

Figure 1 shows a comparison of angle-dependent absorption spectra at the C *K* edge. Spectra from top to bottom correspond to the CMA reference sample, to the multilayer of CMA on Au(111), to 1 ML of CMA on Au(111), and to 1 ML of CMA on Cu(001). The spectra were acquired at the incidence angles given in the legend (90° for the bulk reference sample). Solid and dotted lines correspond to spectra taken at normal/near-normal and grazing incidence, respectively. The spectra consist of a series of π^* resonances at photon energies between 280 and 290 eV, and broader σ^* resonances at photon energies above 290 eV. A strong angle dependence is observed in both samples of CMA on Au(111). While the π^* resonances show a significantly higher intensity for grazing incidence, the σ^* intensity at photon energies above 290 eV is higher for normal incidence. From these spectra we conclude a planar adsorption of the azobenzene molecules on Au(111), both in the monolayer and in the multilayer. The angle dependence is significantly less pronounced for CMA on Cu(001). This is attributed to the adsorption geometry as will be discussed below.

Figure 2 shows a magnified view of the spectra for grazing incidence as well as the reference sample in the region of the π^* resonances scaled to about the same height. All four spectra are qualitatively quite similar, indicating that the carbon atoms are not significantly influenced by the adsorption of the molecules to the substrate.

Angle-dependent NEXAFS spectra of the N *K* absorption edge are presented in Fig. 3. Panel (a) shows the absorption spectrum of the bulk reference sample, panel (b) shows the angular dependence measured for the multilayer film on Au(111), panel (c) that of 1 ML CMA on Au(111), and panel (d) that of 1 ML CMA on Cu(001). Continuous (dotted) lines represent spectra for normal (grazing) incidence, acquired at the angles as labelled in the figure.

Again a strong angle dependence is found for CMA on Au(111). The π^* resonances (lowest unoccupied molecular orbital, LUMO, at ≈ 398.6 eV, LUMO + 1 at ≈ 402.5 eV) show a significantly higher intensity for grazing incidence; for the monolayer on Au(111), they are even absent for normal incidence. We can thus conclude that besides the phenyl rings, also the central N–N double bond is aligned parallel to the surface plane.

The angle-dependent spectra measured for the 1 ML film are qualitatively identical to the ones of the much thicker

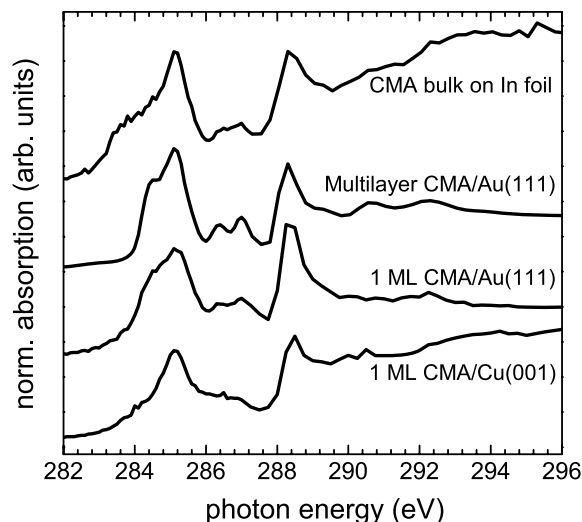


Fig. 2 Magnified view of the π^* region of the spectra of Fig. 1 measured at $\theta = 20^\circ$ and the bulk spectrum ($\theta = 90^\circ$)

multilayer film, which we consider as being representative for molecules not interacting with the substrate, as well as to the spectrum of bulk CMA.

Assuming that the measurement averages over all possible azimuthal orientations of adsorbed molecules and that all molecules are adsorbed in the same manner, we calculate the angle between the molecular π^* orbitals and the surface normal from the angular dependence of the corresponding spectral features [14]. In this case, the absorption intensity is proportional to the projection of the molecular orbital onto the polarization vector of the light. To do so, the heights of the π^* absorption peaks with respect to the pre-edge absorption were evaluated from the spectra of Fig. 3 without further peak decomposition. For 1 ML CMA on Au(111), the molecules are basically lying flat on the surface. For the multilayer film, the tilt angle between the surface normal and the π^* orbital of the LUMO results as $\approx 24^\circ$, calculated from the ratio of the absorption intensities at 398.6 eV. Because a molecular disorder would cause a stronger decrease in the angular dependence than the one observed for CMA/Au(111), we conclude the formation of a highly ordered molecular crystal.

The same behavior is observed at the C *K* edge (Figs. 1b and c). This indicates a flat adsorption of the entire CMA molecule on the Au surface, in which the N–N double bond is oriented parallel to the surface of the substrate. The conformation has therefore to be either the *trans* or the *trans*-rotated one, in agreement with STM measurements [8]. The shape of the N *K* absorption spectra does not change for thicker films and agrees with the one measured at the bulk reference sample (Fig. 3a). This means that no significant hybridization between the electronic states of the molecules and the substrate takes place. The conclusion

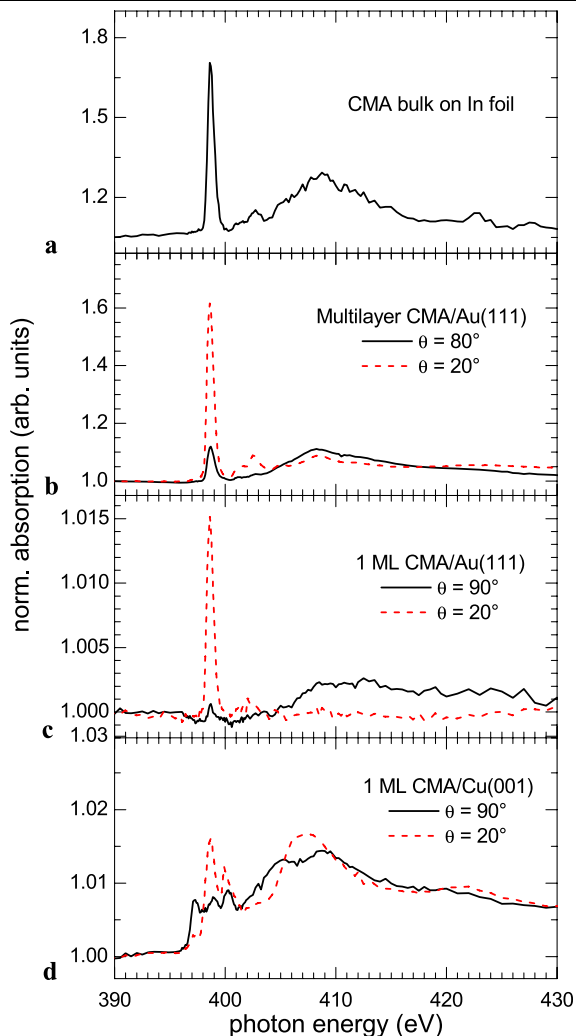


Fig. 3 N *K* edge absorption spectra of (a) the bulk CMA reference sample, (b) multilayer CMA on Au(111), (c) 1 ML CMA on Au(111), and (d) 1 ML CMA on Cu(001). Continuous (dotted) lines correspond to spectra acquired at 90° or 80° near-normal (20° grazing) X-ray incidence

is thus that carboxymethylester-azobenzene adsorbs on the Au(111) surface by van-der-Waals interactions.

In contrast, the spectra of 1 ML CMA on Cu(001) (Fig. 3d) are strikingly different. In the region of the σ^* resonances, additional intensity at ≈ 407 eV is visible, which shows the opposite angular dependence compared to the peaks at ≈ 408 and ≈ 412.5 eV of the CMA/Au(111) spectra. The higher intensity at grazing incidence suggests nitrogen σ bonds oriented predominantly perpendicular to the surface, with different bond length and/or chemical shift compared to CMA on Au(111) or bulk CMA. Two additional peaks are also observed in the region of the N π^* resonances at 397.2 and 400.3 eV. The former exhibits an opposite angular behavior compared to the peak at 398.6 eV, with higher intensity at normal incidence. This implies an N double bond perpendicular to the surface. In addition, the

angle-averaged integrated intensity of the π^* resonances relative to the intensity of the σ^* region and the overall edge jump is smaller in the case of CMA/Cu(001).

From these N *K* edge spectra we conclude that the nitrogen atoms are significantly influenced by the adsorption of the molecule on the copper substrate. The appearance of spectral features indicating perpendicular bonds of the N atoms points towards a hybridization of nitrogen-related molecular orbitals with the electronic states of the substrate. The conclusion is that CMA chemically bonds to the Cu(001) surface via one or both of the nitrogen atoms. Such a chemisorption most likely comes along with a change of the molecular conformation as already mentioned in the discussion above.

This is reflected by the observed angular dependence of the spectra. Under the same assumptions as before, the tilt angles to the surface normal of the orbitals corresponding to the peaks at 397.2 and 398.6 eV are evaluated as 71° and 40°, respectively. The C *K* edge absorption spectra (Fig. 1d), in contrast, do not exhibit a pronounced angular dependence, pointing towards a tilt angle of the phenyl moieties close to 54°. This means that the molecules are adsorbed on the copper surface in a bent geometry with the benzene rings in an upright position, while the N–N bond hybridizes with the substrate and stays more parallel to the surface plane. It should be noted that, as a consequence of chemisorption, the shape of the involved orbitals may also be significantly distorted, and a simple analysis may not lead to the correct results. In any case, the presence of N-derived π^* orbitals both with more parallel as well as more perpendicular orientation to the surface is clearly seen from Fig. 3d.

The angular dependence of the absorption intensity at 412–417 eV also points towards an N-derived σ bond more or less parallel to the surface, indicating the integrity of the molecules. The additional σ^* intensity at ≈ 407 eV could be related to the modified C–N bonds, now pointing upright. On the basis of the presented NEXAFS data, however, we cannot rule out a scenario in which a part of the molecules is dissociated by a breaking of the N=N bond while chemisorbed to the copper surface by the nitrogen atoms, and the other part of the molecules is physisorbed in a flat geometry.

Note that from the angular dependence of the absorption spectra it is also not possible to distinguish between bent configurations of the adsorbed molecules with a symmetric or asymmetric tilt. The angles given above are for a symmetric configuration in which both benzene rings make the same angle to the surface. An asymmetric configuration in which, for example, one of the benzene rings is tilted more and the other one less would be indistinguishable from the angular dependence of the absorption spectra. Nevertheless, we can affirm that, compared to the Au case, the moieties of the adsorbed molecules on Cu(001) are tilted out of plane.

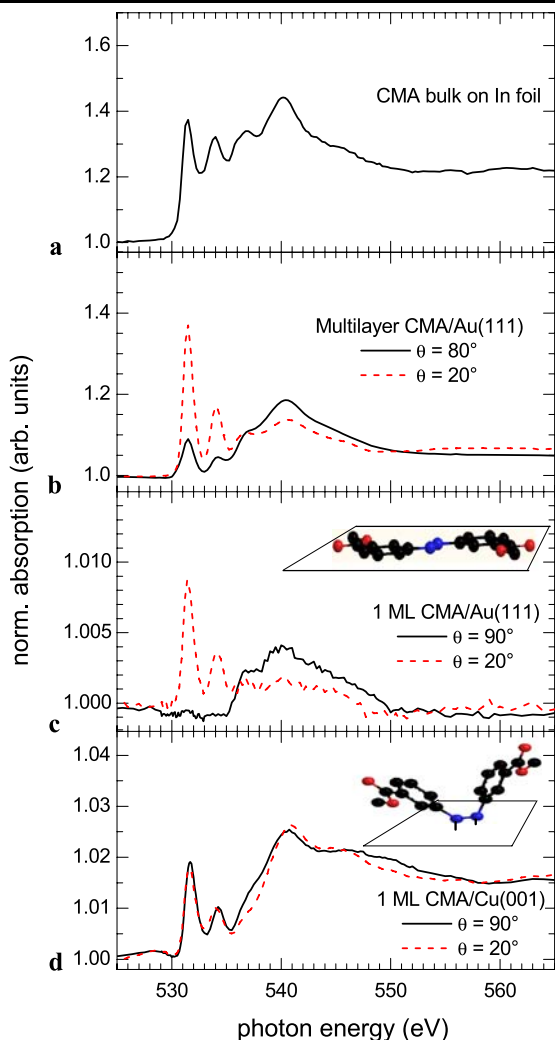


Fig. 4 Angular dependence of O *K* edge absorption spectra of (a) the bulk CMA reference sample, (b) the multilayer CMA on Au(111), (c) 1 ML CMA on Au(111), and (d) 1 ML CMA on Cu(001). Continuous (dotted) lines correspond to spectra acquired at 90° or 80° near-normal (20° grazing) X-ray incidence. The insets in (c) and (d) are sketches of the corresponding adsorption geometries

Figure 4 shows X-ray absorption spectra at the O *K* edge of the bulk reference sample (a), the multilayer of CMA on Au(111) (b), 1 ML of CMA on Au(111) (c), and 1 ML of CMA on Cu(001) (d). Continuous (dotted) lines represent spectra for normal (grazing) incidence, acquired at the angles as labeled in the figure. In contrast to the nitrogen absorption spectra, the overall angle-averaged spectral shape of the O *K* edge is the same for the two substrates and the different CMA layer thicknesses. The oxygen atoms, like the carbon atoms, are thus not involved in the chemisorption to the substrate. The main difference between the spectra for the Cu and Au substrates is their angular dependence. For the thick CMA layer on Au(111) (Fig. 4b), the angular dependence of the π^* resonance at 531.5 eV corresponds to an orientation of the C–O π^* orbital of 30° to the surface nor-

mal. The carboxymethylester end groups are thus supposed to be only slightly tilted with respect to the molecular plane.

In the case of the CMA monolayer on Cu(001), the tilt angle of the C=O π^* orbitals with respect to the surface normal would be close to the magic angle of 54° if one assumed that all the end groups were oriented in the same way. The angular dependence is thus similar to the one of the C *K* edge spectra, indicating that the plane of the carboxymethylester groups is roughly aligned with the plane of the benzene rings, as for CMA/Au(111). The insets in Figs. 4c and d sketch the respective adsorption geometries of the monolayer CMA on Au(111) and Cu(001), assuming a symmetric tilt of the benzene moieties in the case of the copper substrate. While for a planar molecule lying flat on the metal surface, a rotation of the end group around the benzene–C single bond is simply inhibited by steric hindrance by the substrate surface, in the case of the chemisorbed CMA molecules on Cu(001), the molecules are bent upwards, in principle allowing a rotation of the end groups. A geometrical order of the end groups could be induced by intermolecular interaction. Note that due to the small angular dependence, the spectra would be also consistent with a certain disorder in the rotational orientation of the end group.

4 Conclusion

We have used X-ray absorption spectroscopy to study the adsorption of the photoswitch CMA on two different metallic single crystal surfaces, namely on Au(111) and on Cu(001). We find that electronic and geometric properties of the molecules depend strongly on the substrate. The molecules are adsorbed flat on the chemically more inert gold surface, with their electronic properties being very much undisturbed by the presence of the substrate. We conclude thus that a physisorption by van-der-Waals forces takes place on Au(111). On Cu(001), in contrast, a stronger interaction between the nitrogen atoms of CMA and the substrate occurs, with significant effects on the nitrogen-related molecular orbitals. The N *K* edge absorption spectra suggest a bond between the Cu(001) substrate and the N π orbitals of the CMA molecules. As a consequence, also the geometric structure of the molecules is altered. A nonplanar configuration, in which the methyl benzoate moieties bend up from the surface, is concluded.

Such a strong dependence of the adsorption properties on the substrate has consequences for a possible conformational switching of adsorbed CMA molecules. Neither a pure van-der-Waals physisorption involving the benzene π system nor a strong chemisorption at the nitrogen atoms is a favorable situation for an effective isomerization of the azobenzene molecules. Most beneficial could be to achieve

the right balance between both types of bonds, which could lead to energetically comparable adsorption of both the flat *trans* and the bent *cis* isomers.

Acknowledgement This work is supported by the DFG (Sfb 658). We thank B. Zada, W. Mahler, and T. Kachel for their technical support during the measurements at BESSY, and J.I. Pascual, K. Franke, and N. Henningsen for fruitful discussions.

References

1. T. Ikeda, O. Tsutsumi, *Science* **268**, 1873 (1995)
2. J. Wachtveitl, S. Sporlein, H. Satzger, B. Fonrobert, C. Renner, R. Behrendt, D. Oesterhelt, L. Moroder, W. Zinth, *Biophys. J.* **86**, 2350 (2004)
3. A. Kirakosian, M.J. Comstock, J. Cho, M.F. Crommie, *Phys. Rev. B* **71**, 113409 (2005)
4. M.J. Comstock, J. Cho, A. Kirakosian, M.F. Crommie, *Phys. Rev. B* **72**, 153414 (2005)
5. J. Henzl, M. Mehlhorn, H. Gawronski, K.-H. Rieder, K. Morgenstern, *Angew. Chem. Int. Ed.* **45**, 603 (2006)
6. B.-Y. Choi, S.-J. Kahng, S. Kim, H. Kim, H.W. Kim, Y.J. Song, J. Ihm, Y. Kuk, *Phys. Rev. Lett.* **96**, 156106 (2006)
7. N. Henningsen, K.J. Franke, I.F. Torrente, G. Schulze, B. Priewisch, K. Rück-Braun, J. Dokić, T. Klamroth, P. Saalfrank, J.I. Pascual, *J. Phys. Chem. C* **111**, 14843 (2007)
8. N. Henningsen, K.J. Franke, G. Schulze, I. Fernández-Torrente, B. Priewisch, K. Rück-Braun, J.I. Pascual, *Chem. Phys. Chem.* **9**, 71 (2008)
9. P. Tegeder, S. Hagen, F. Leyssner, M.V. Peters, S. Hecht, T. Klamroth, P. Saalfrank, M. Wolf, *Appl. Phys. A* **88**, 465 (2007)
10. M.J. Comstock, N. Levy, A. Kirakosian, J. Cho, F. Lauterwasser, J.H. Harvey, D.A. Strubbe, J.M.J. Fréchet, D. Trauner, S.G. Louie, M.F. Crommie, *Phys. Rev. Lett.* **99**, 038301 (2007)
11. S. Hagen, F. Leyßner, D. Nandi, M. Wolf, P. Tegeder, *Chem. Phys. Lett.* **444**, 85 (2007)
12. G. Pace, V. Ferri, C. Grave, M. Elbing, C. von Hänisch, M. Zharnikov, M. Mayor, M.A. Rampi, P. Samor, *Proc. Nat. Acad. Sci.* **104**, 9937 (2007)
13. B. Priewisch, K. Rück-Braun, *J. Org. Chem.* **70**, 2350 (2005)
14. J. Stöhr, *NEXAFS Spectroscopy* (Springer, Berlin, 1992)