X-Ray-Induced Reversible Switching of an Azobenzene Derivative Adsorbed on Bi(111)

A. Krüger*, M. Bernien, C. F. Hermanns, and W. Kuch*

Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

E-mail: a.krueger@fu-berlin.de

Abstract

We report on the adsorption of a submonolayer of di-meta-cyano-azobenzene (DMC) on Bi(111) and on the reversible switching of these molecules induced by resonant X-ray illumination. DMC adsorbs in at least two configurations, the flat *trans* and the non-flat *cis* isomer. We find that in 0.8 monolayers at least 26% of the molecules change their configuration at 110 K by excitation of the N1$s \rightarrow$ LUMO transition at the azo group, and by a thermally induced back reaction at 120 K. Non-resonant excitation with X-ray light does not induce any reversible changes.

Keywords: Photochromic molecules, reversible switching, X-ray induced, azobenzene on surface.

*To whom correspondence should be addressed

Introduction

Switches are an omnipresent component of our electronic world and their ongoing miniaturization leads to continuous improvements. Bottom-up epitaxy with bistable molecules will allow to employ switches with a structure size down to 1 nm. In the case of photochromic molecules the photon-triggered transition between two different isomers offers the possibility to switch between two metastable states.[1] By means of X-ray absorption measurement techniques like near-edge X-ray absorption fine structure (NEXAFS) or X-ray photoelectron spectroscopy (XPS), the adsorption geometry of molecules on the surface can be observed as well as the interconversion between their metastable states. The influence of X rays on the metastable states of photochromic molecules is until now not well studied.

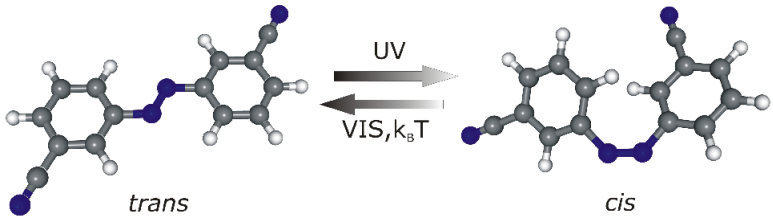


Figure 1: Schematic structure of DMC in *trans* and *cis* configuration. Atoms: blue - nitrogen, gray - carbon, white - hydrogen.

Azobenzene derivatives are prototypical photoswitches.[2–5] Here, we study a symmetrically cyano-functionalized azobenzene molecule, di-meta-cyano-azobenzene (DMC). Its geometric structure is shown in Fig. 1. The central N=N azo bridge connects two benzene rings that are substituted with cyano groups in meta positions. Cyano-functionalized molecules have the advantage that by angle-resolved NEXAFS experiments the angles between the surface and each of the two orthogonal π bonds of the cyano triple bond can be measured independently, allowing a full determination of the orientation of the cyano group in space. Besides, the electronegative cyano groups may withdraw electron density from the central N=N azo bridge, facilitating the switching between the *cis* and *trans* isomers. This azobenzene derivative shows typical switching behavior[2–5] in solution and the gas phase with *trans* $\rightarrow$ *cis* isomerization under illumination with ultraviolet (UV)

light with a wavelength around 320 nm. The *cis* $\rightarrow$ *trans* isomerization can be induced by visible light (vis) with a wavelength around 430 nm or by annealing above the thermal barrier. The UV-vis absorption spectrum of DMC solved in benzene is provided in the Supporting Information. Molecules directly adsorbed on metallic surfaces show considerably reduced switching yields.[8] In a few systems the switching process was found to be reversible when it was induced by tunneling electrons from the tip of a scanning tunneling microscope.[9–11] The influence of the X rays on the molecules is not well studied and can be two-fold. Analogous to irradiation with UV/vis light, the X rays may induce switching between the two isomers or they may induce a chemical modification that affects the properties of the molecules. Previous theoretical calculations of the adsorption geometry of neutral *trans* and *cis* isomers of DMC on Bi(111) also do not describe the effect of X-ray-induced isomerization.[7] It is hence important to understand the influence of X-ray light on the photochromic molecules grown in bottom-up epitaxy mode. Here, we present evidence for the switching of DMC on Bi(111) at 110 K, even at submonolayer coverage. In a simplified picture the Bi(111) crystal can be described by a stack of covalent bi-layers held together by Vander-Waals-like bonds with unique electronic structure.[12–15] The lattice constant is $a = 4.35$ Å, the distance between the first and second layer is 1.59 Å, and the distance between bilayers is 2.35 Å.[13] This bilayer structure of the Bi(111) surface is inert. This leads to weak chemical interaction between adsorbed molecules and the surface. Special to Bi(111) is also that the surface is much more metallic than the bulk. In the ideal crystal and thin layers, the bulk is insulating and the surface is metallic.[13,16]

Experimental Section

All experiments were performed in an ultrahigh vacuum system with a base pressure of 5×10^{-10} mbar equipped with standard surface science tools. The Bi(111) single crystal was cleaned by repeated cycles of Ar^+ ion sputtering at 600 eV and subsequent annealing to 350 K until sharp low-energy electron diffraction spots appeared, and no contamination of the surface could be de-

tected by XPS. Sample preparation was done by deposition of DMC[21,22] molecules from a Knudsen cell at around 345 K onto a clean Bi(111) surface stabilized at a temperature of 110 K. The deposition rate was monitored by a quartz microbalance during deposition. X-ray absorption spectroscopy was performed at the undulator beamline UE56/2-PGM1 of BESSY II in Berlin. Absorption spectra were acquired in total electron yield mode by recording the sample drain current with a low-noise current amplifier DDPCA-300 (Femto) as a function of photon energy. Beam intensities were monitored by the total electron yield from a freshly evaporated gold grid. The molecular coverage was calibrated by dividing the NEXAFS sample signal by the signal of the gold grid. This provides normalized NEXAFS spectra, the intensity of which is proportional to the coverage. Using the signal of 1 ML of previous NEXAFS experiments of DMC on Au(111) and Cu(111)[6] and considering the different absorption cross sections of the substrates at the N-*K* edge gives the molecular coverage on the sample. To avoid radiation damage of the molecules, the X-ray photon flux was reduced by moving the sample out of the beam focus and closing the aperture of the beamline. To ensure that the probed sample area is homogeneously illuminated, the spot size for measurements was decreased to 0.4 mm horizontally and 0.9 mm vertically with a typical photon-flux density of $5(4) \times 10^9$ $s^{-1}mm^{-2}$ per 100 mA ring current and a photon energy resolution around 50 meV. Typical ring currents were between 200 and 300 mA. The photon flux was measured with a GaAs diode. For X-ray illumination of the sample the apertures of the beamline were opened and the spot size increased to 0.5 mm horizontally and 1.2 mm vertically with a typical photon flux density of 2×10^{11} $s^{-1}mm^{-2}$ per 100 mA ring current and an energy resolution of 300 meV. The position of the sample was kept fixed for all experiments with an incidence angle of 70° between the X-ray wave vector and the surface normal. Polarization-dependent NEXAFS measurements were performed by setting the undulator to yield horizontally and vertically polarized X rays with the electric field vector 20° off the surface normal and in the surface plane, respectively. XPS measurements were performed using a SPECS Phoibos 100 electron analyzer set to an energy resolution of 600 meV with 20 eV pass energy. *P*-polarized X rays with 45° incidence angle and fixed sample position with normal emission were used for all XPS experiments. The

excitation energy was 680 eV with a photon energy resolution of 300 meV. All binding energies have been calibrated to the Bi $4f_{7/2}$ binding energy at 157.0 eV.[23]

Results and Discussion

We find that the DMC molecules switch from *trans* to *cis* after resonant X-ray excitation of the N1$s \rightarrow$ LUMO transition and show a thermally induced back reaction.

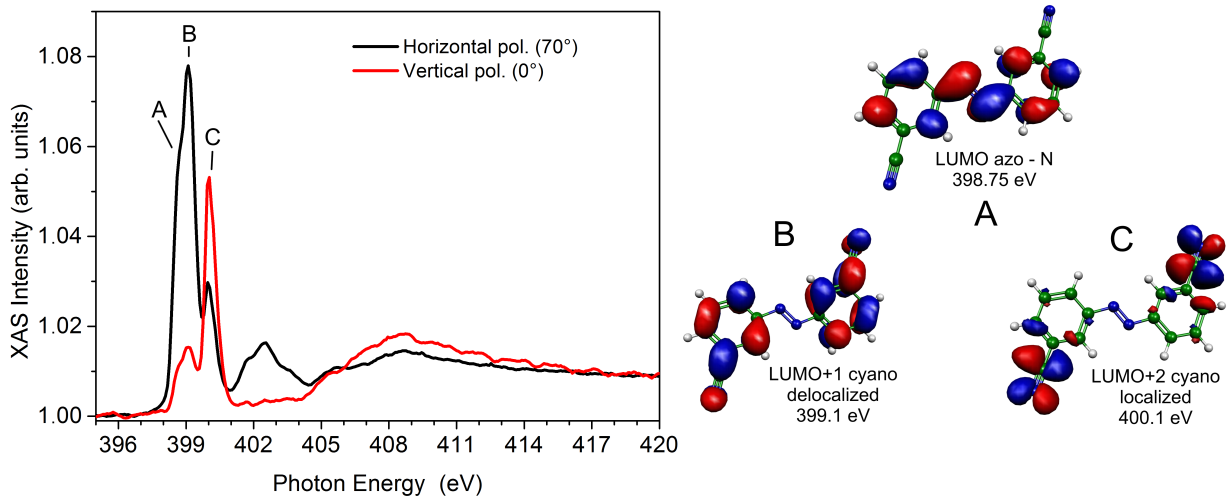


Figure 2: N-*K* NEXAFS spectra of 0.8 ML of DMC on Bi(111) at *T*=110 K and assignment of the first three N1*s* to LUMO+X transitions. The orbitals were calculated by means of DFT for a free *trans* DMC molecule. NEXAFS resonance positions were obtained by the transition state method as implemented in the StoBe code.[6]

Figure 2 shows polarization-dependent N-*K* edge NEXAFS spectra of 0.8 monolayer (ML) of DMC on Bi(111), measured after deposition at 110 K substrate temperature with low X-ray photon flux. The N-*K* spectrum recorded with horizontal polarization (p-polarization, black line) displays two sharp resonances at 399.1 (B) and 400.1 eV (C) and one shoulder at 398.7 eV (A), which can be identified as well in the spectrum recorded with vertical polarization (s-polarization, red line). The strong dependence of the resonance intensity on the polarization of the X rays indicates that the molecules are oriented almost flat on the surface.

Previous results[6] on the electronic structure of free *trans* DMC molecules by means of density

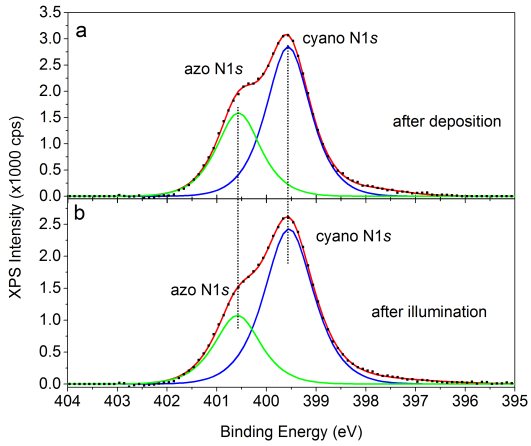


Figure 3: XP spectra of 0.8 ML DMC/Bi(111) (a) after deposition and (b) after resonant illumination with intense X rays of 398.7 eV for 20 min. Points are experimental data, blue lines are the fitted peaks of cyano nitrogen, green lines are fitted azo nitrogen components, red lines are the sum of both.

functional theory and simulation of NEXAFS spectra are in very good agreement with the line shape of the experimental NEXAFS. Hence we conclude that DMC is physisorbed on Bi(111). Based on these calculations we can assign the transition energies to molecular orbitals. The shoulder at 398.7 eV (A) belongs to the azo N1s $\rightarrow$ LUMO transition. The sharp peak at 399.1 eV (B) stems from the cyano N1s $\rightarrow$ LUMO+1 (delocalized cyano orbital) and the peak at 400.1 eV (C) from the cyano N1s $\rightarrow$ LUMO+2 (localized cyano orbital) transition.

It is known by means of XPS measurments that the binding energy of the N 1s electrons of chemisorbed DMC molecules is completely different compared to physisorbed DMC molecules.[6] Figure 3a shows XP spectra of freshly deposited DMC molecules on Bi(111) at 110 K. Two species of nitrogen can be identified as cyano (399.6 eV) and azo (400.6 eV) nitrogen of physisorbed DMC molecules. Figure 3b shows the XP spectrum of the same sample after illumination with intense X rays of 398.7 eV for 20 min. The absence of additional species in both spectra and identical binding energies for N1s cyano and azo nitrogen let us conclude that the DMC molecules are physisorbed on the surface and do not perform any chemical reaction with the surface after illumination.

The ratio of the NEXAFS resonance intensity between horizontal and vertical polarization

allows to determine the mean angle between these orbitals and the surface normal.[18] The ratio $R_1 = 5.40$ of the delocalized cyano orbital (B) yields an average angle of $(29 \pm 5)^\circ$ with respect to the surface normal and the ratio $R_2 = 0.64$ of the localized cyano orbital (C) gives an average angle of $(61 \pm 5)^\circ$. In contrast to the adsorption geometry of DMC on Au(111),[6] DMC does not adsorb in a completely flat configuration on Bi(111). The observed average orbital angles can be the result of a common tilt angle for all cyano groups or of a mixture of differently oriented groups.

Trans DMC is expected to adsorb in a completely flat configuration,[6,11,17] where the cyano delocalized orbital is oriented perpendicular and the cyano localized orbital parallel to the surface. We assume in the following that there are two species of cyano groups, one of which is oriented flatly on the surface and the other not. Since we do not know how many of each species are present, we introduce the free parameter K as the portion of tilted cyano groups. The orientation of the non-flat phenyl rings can then be calculated by means of:

$$R = \frac{(1-K)I_{sum}[P,\theta,\alpha_1] + K\,I_{sum}[P,\theta,\alpha_2]}{(1-K)I_{sum}[P,\pi/2,\alpha_1] + K\,I_{sum}[P,\pi/2,\alpha_2]}, \tag{1}$$

where $R = \frac{I_{p-pol.}}{I_{s-pol.}}$ and I_{sum} is

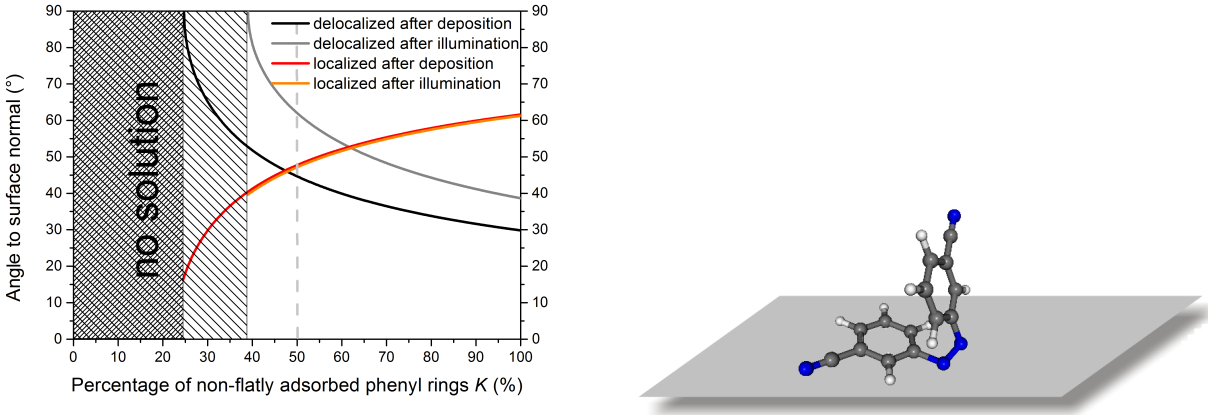
$$I_{sum}[P,\theta,\alpha_{1,2}] = P * I[\theta,\alpha_{1,2}] + (1-P) * I[\pi/2,\alpha_{1,2}]. \tag{2}$$

I is the normalized intensity for horizontal and vertical polarization, respectively, of vector-like orbitals on substrates with 3-fold or higher symmetry,[18] with

$$I[\theta,\alpha_{1,2}] = \cos^2\theta\cos^2\alpha_{1,2} + 1/2\sin^2\theta\sin^2\alpha_{1,2}, \tag{3}$$

P the linear polarization degree, and $\alpha_1 = 90^\circ$ or $\alpha_1 = 0^\circ$ the angle of the cyano localized and delocalized orbital of the flatly adsorbed phenyl rings, respectively. α_2 is the angle of the cyano orbitals of the non-flat phenyl rings and θ the angle of the $\vec{E}$ vector of the incoming beam with respect to the surface normal $\vec{n}$.

In Figure 4a we show numerical solutions for α_2 based on the experimentally obtained ratios



(a) (b)

Figure 4: a) Calculated orientations of delocalized and localized cyano orbitals as a function of the percentage of not-flatly adsorbed phenyl rings. Black and red lines show the orientations of the orbitals of the non-flat species after deposition. The gray and yellow lines show the orbital orientations after illumination with X rays of 398.7 eV for 20 minutes. The dashed line at 50% indicates the orientation for the molecules under the assumption that exactly one out of two phenyl rings changes its orientation. b) Schematic sketch of adsorption geometry of DMC after deposition on Bi(111) for K = 25%.

R_1 and R_2 and (1) (black and red curves). It shows that at least 25% of the phenyl rings adsorb in a non-flat configuration on Bi(111). If K were 25%, these phenyl rings would be standing upright with the delocalized cyano orbital aligned parallel to the surface, whereas the angle between the localized cyano orbital and the surface normal would be around 15°. Assuming an increasing amount K of non-flat phenyl rings, the angle between the delocalized cyano orbital and the surface normal decreases until it reaches 29° at K=100%. The angle of the localized cyano orbital increases correspondingly up to 61°. In the literature it is well known that in case of a non-trans configuration of azobenzene derivatives adsorbed on metal surfaces, one of the phenyl rings is tilted and the other flat to maximize Van-der-Waals interaction with the surface.[24–26] This means that the highest possible amount of phenyl rings with non-flat configuration should be 50%. In this case all molecules would be adsorbed in a non-flat non-trans configuration. Since, on the other hand, below 25% of non-flat phenyl rings, no solutions are obtained for (1), at least 50% of the DMC molecules would be in a non-trans configuration, under the assumption that always one phenyl ring per molecule is fully flat on the surface.

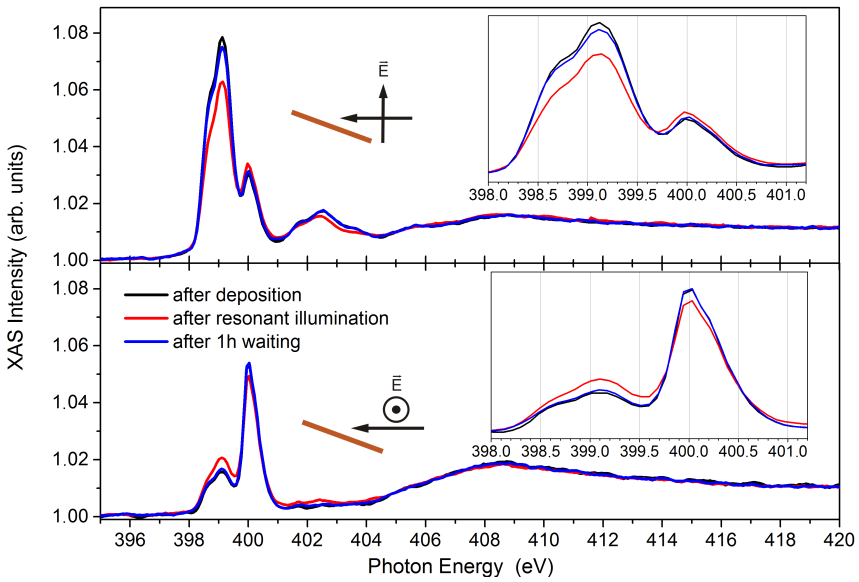


Figure 5: N-*K* NEXAFS spectra of 0.8 ML DMC on Bi(111) at 110 K. Upper and lower panel spectra are recorded with p- and s-polarized light, respectively. The insets show close-ups of the π^* regions. Black lines depict the spectra after deposition of the molecules. Red lines correspond to spectra after illumination with high-intensity p-polarized X rays of 398.7 eV photon energy. Blue lines show spectra after subsequent waiting for 1 hour without illumination.

To induce a change of the orientation of the molecules we illuminate the sample with intense X rays with the photon energy tuned to the N1*s* azo→LUMO transition (398.7 eV). After resonant illumination for 20 min, the NEXAFS signal for p-polarized light of the delocalized cyano orbital decreased by 25% and the signal of the localized cyano orbital increased by 15%, as shown in Fig. 5 (top panel). In the NEXAFS spectra recorded with s-polarized light (bottom panel) the changes are opposite, see also Tab. 1. After waiting without illumination at 120 K for one hour, more than 95% of the intensity before illumination of all resonances in the N-*K* NEXAFS spectra for both polarizations is recovered, see Fig. 5. The opposite changes in spectra recorded with p- and s-polarized light, the reversibility, and the unmodified XP spectra suggest that illumination with 398.7 eV induces changes of the orientation of the phenyl rings, but does not affect the chemical structure of the DMC molecules.

To see whether these reversible changes in the NEXAFS transition intensities can be evoked also by X-ray illumination with a photon energy different from that of the N1*s* → LUMO transition,

we first performed resonant illumination with X rays of 399.1 and 400.1 eV photon energy. The illumination with resonant X rays with a photon energy of the N1s $\rightarrow$ LUMO+1 transition (399.1 eV) results in very small changes. The intensity of the N1s $\rightarrow$ LUMO+1 peak reduces by about 6% while changes of the intensity of the N1s $\rightarrow$ LUMO+2 peak are less than 1%. Both seem to be reversible (see supporting information). Due to the energy resolution of 0.3 eV during the illumination and the small energy difference between both LUMOs of only 0.4 eV, the changes in the NEXAFS spectra after illumination with a photon energy of 399.1 eV could also result from the excitation of the N1s $\rightarrow$ LUMO transition at 398.7 eV with reduced intensity. After illumination with a photon energy corresponding to the N1s $\rightarrow$ LUMO+2 transition (400.1 eV), the changes in the NEXAFS spectrum are significant but not reversible (see supporting information).

Also exposure to non-resonant X rays did not induce any reversible changes of the orientation of the phenyl rings. After illuminating the sample with X rays of 270.0 eV photon energy for 20 minutes, the NEXAFS signal for p-polarized light of the delocalized cyano orbital decreased by 5% and the change of the NEXAFS signal of the localized cyano orbital was below the detection limit of the experimental setup (<1%), see Table 1. The line shape of the NEXAFS spectra recorded with s-polarized light does not show any X-ray-induced changes. By illumination with X-rays of 500 eV for 20 minutes, the signal of the delocalized cyano orbital decreased by 15% in the NEXAFS spectrum recorded with p-polarized light as well as in the spectrum recorded with s-polarized light, see Table 1. No change was observed in the signal of the localized cyano orbital in NEXAFS spectra for both polarizations. After waiting for one hour at 120 K without illumination, the signal of all transitions for both polarizations did not change, indicating that the molecules undergo irreversible modifications induced by these off-resonant X rays.

Hence, only resonant illumination with a photon energy corresponding to the azo N1s $\rightarrow$ LUMO transition induces a geometrical change of the molecules with high reversibility. After the illumination, the ratio of the delocalized and localized cyano orbitals changes to R_1= 2.83 and R_2= 0.65, respectively. This corresponds to an average angle of $(38 \pm 5)^\circ$ for the delocalized cyano orbitals and $(60 \pm 5)^\circ$ for localized cyano orbitals after illumination. Using (1) and

Table 1: Comparison of illumination and measuring conditions with respect to the photon flux-density as well as the relative change in resonance intensity of the N1s→LUMO+0,1,2 transitions in N-K NEXAFS spectra.

Photon energy (eV)	Photon flux-density $s^{-1}mm^{-2}$ per 100 mA r.c.	I_h(399.1 eV)		I_h(400.1 eV)		Reversibility
		p-pol.	s-pol.	p-pol.	s-pol.	
270.0 eV	$2.1(1)\times10^{11}$	< -5%	<-2%	< 1%	<1%	No
398.7 eV	$2.5(1)\times10^{11}$	-25%	+22%	+15%	-11%	> 95%
399.1 eV	$2.5(1)\times10^{11}$	-6%	+2%	<1%	<1%	$\sim$ 50%
400.1 eV	$2.5(1)\times10^{11}$	-12%	-10%	<1%	<1%	No
500.0 eV	$2.8(1)\times10^{11}$	-15%	-15%	< 1%	<1%	No
Measurement	$5(4)\times10^{9}$	< 1%	< 1%	< 1%	< 1%	-

the same assumptions as before, we calculate the angles of the cyano orbitals as a function of the amount of non-flatly adsorbed phenyl rings, see Fig. 4a. Assuming, as before, that one phenyl ring of each molecule is always flat, the amount of switched molecules after illumination is at least 2×38%=76%.

The same X-ray-induced switching effect is also observed in a multilayer of DMC on Bi(111). 14 ML of DMC on Bi(111) were resonantly illuminated with X rays of 398.7 eV photon energy at 110 K. The evaluation of the tilt angles is not meaningful because of the relatively long acquisition time of the NEXAFS spectra under grazing and normal incidence of around 7 minutes and the fast changes of the geometrical orientation during this time. However, the NEXAFS spectra in Fig. 6 show clearly that the effect of the resonant illumination is even more pronounced than in the submonolayer and is fully reversible in all resonances. The first adsorbed layer on Bi acts as a decoupling layer for all other molecular layers on top. Consequently the Bi(111) surface does not actively participate in the *cis* isomerization. The similarity of the effect of resonant X-ray illumination on both submonolayer and multilayer coverages supports our conclusion that also for the first adsorbed layer the Bi surface does not play an active role during the X-ray-induced switching.

A possible explanation for the observed X-ray-induced reversible switching is that after resonant excitation of a nitrogen 1s electron into the LUMO followed by an Auger decay of the core hole, a metastable DMC^+ cationic state is formed, with a HOMO-1/LUMO exciton. This is

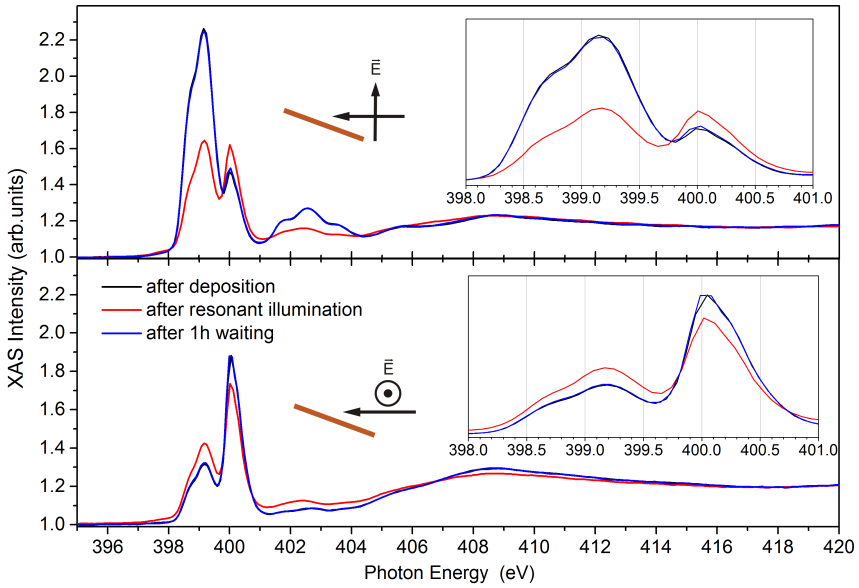


Figure 6: N-*K* NEXAFS spectra of 14 ML DMC on Bi(111) at 110 K. Upper and lower panel spectra are recorded with p- and s-polarized light, respectively. The insets show close-ups of the π^* regions. Black lines depict the spectra after deposition of the molecules. Red lines correspond to spectra after illumination with high intensity p-polarized X rays of 398.7 eV photon energy. Blue lines show spectra after subsequent waiting for 1 hour without illumination.

schematically depicted in Fig. 7. The left-hand side shows a possible electronic configuration after resonant 1*s* $\rightarrow$ LUMO excitation and Auger core hole decay. Compared to the UV-light-induced switching in solution, see Fig. 7 (right), the difference is the additional hole in the case of the 1*s* $\rightarrow$ LUMO excitation (one electron in the LUMO and two holes), while after HOMO-1 $\rightarrow$ LUMO excitation by the UV light the molecule is neutral (one electron in the LUMO and one hole). In Fig. 7 we show both holes in the HOMO–1, but also other configurations are conceivable, and density functional theory investigations may be necessary to reveal all details of the electronic configuration during switching.

The energy barrier for the *trans* to *cis* transformation of the charged molecule could be much lower than for the neutral one.[19] Comparison of our NEXAFS measurements with the XP spectra shown in Fig. 3 shows that the energy level of the excited LUMO after photon absorption at 398.7 eV is below the Fermi energy of 400.6 eV relative to the N1*s* level at the azo group. Since the X-ray-induced switching is observed only after resonant excitation of the N1*s* electron into the

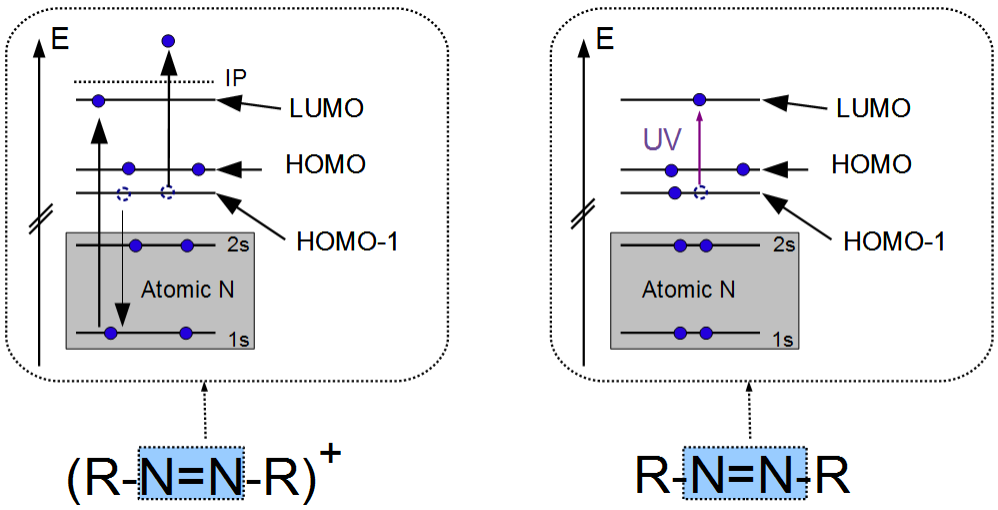


Figure 7: Comparison of the proposed mechanism for resonant X-ray light induced switching (left) and UV-light induced switching (right).

LUMO, but not after non-resonant excitations, we conclude that the occupied LUMO after photon absorption is important for the switching mechanism and must have a long lifetime after the Auger decay of the core hole.

Recently also a non-reversible switching of DMC molecules on Bi(111) by UV light has been reported.[20] Note that the photon dose per area applied in our case (3×10^{16} cm^{-2}) is orders of magnitude smaller than the one by UV photons reported in Ref.[20]. Interestingly, a different switching mechanism has been suggested for the UV-induced switching of DMC on Bi(111), where Bi states are directly involved. In that case, the excitation is supposed to go from occupied *p* bands to unoccupied *p* bands and then by a tunnel process to the DMC LUMO, creating a negative DMC ion, which then is proposed to lead to the switching to the *cis* state.[20]

The energy barrier of the thermal *cis*→*trans* backreaction for DMC on Bi(111) is obviously much smaller than the barriers of close to 1 eV typically observed for thermal *cis*→*trans* switching of azobenzene derivatives in solution[27,28] or calculated for free azobenzene molecules[19]. The rate of the thermal *cis*→*trans* conversion in our experiment is also higher than that of tetra-*tert*-butyl-azobenzene adsorbed on Au(111)[28]. This ease of thermal *cis*→*trans* backswitching has to be attributed to the influence of the Bi(111) surface on the energetics of the adsorbed *cis* and *trans* isomers of DMC.

Conclusions

In conclusion, we have demonstrated that a submonolayer of DMC molecules adsorbed on Bi(111) can be effectively switched by illuminating the sample with monochromatic X-ray light with an energy corresponding to the N1*s* azo $\rightarrow$ LUMO transition (398.7 eV). The switched species is chemically very similar, but shows a geometric change towards higher angles between phenyl rings and the surface plane, indicative of a *trans* $\rightarrow$ *cis* isomerization. These X-ray-induced changes show a high reversibility at 120 K surface temperature. The absence of reversible changes when illuminating with non-resonant X rays indicates that the occupation of the LUMO orbital must play an important role for the switching mechanism, analogous to the UV-induced *trans* $\rightarrow$ *cis* isomerization in solution. We propose that the mechanism for X-ray-induced switching is based on a cationic transition state of the DMC molecule with a long life time.

Supporting Information Available: UV–vis spectra of DMC in solution and spectra after X-ray excitation with different photon energies. This material is available free of charge via the Internet http://pubs.acs.org.

Acknowledgments

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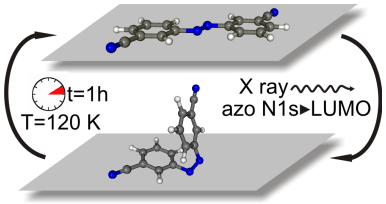
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