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Reversible isomerization of an azobenzene derivative adsorbed on Au(1 1 1): Analysis using vibrational spectroscopy

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Dedicated to Professor Eugen Illenberger on the occasion of his 65th birthday.

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ABSTRACT

High resolution electron energy loss spectroscopy (HREELS) is employed to analyze reversible changes in the geometrical structure of the molecular switch di-methoxy-tetra-*tert*-butyl-azobenzene (diM-TBA) adsorbed on Au(1 1 1), which are induced by UV-light and thermal activation. While for 1 monolayer (ML) coverage no changes in the vibrational structure due to UV-light exposure at 3.5 eV are observed, illumination of 2 ML of diM-TBA leads to a pronounced modification of the vibrational spectra, which we assign to a *trans* → *cis* isomerization. The reverse process, i.e., the *cis* → *trans* isomerization, can be stimulated by thermal activation. We propose that the photoisomerization is driven by a direct (intramolecular) electronic excitation of the adsorbed diM-TBA molecules in the second ML analogous to diM-TBA in the liquid phase.

1. Introduction

Molecular switches such as azobenzene and its derivatives adsorbed on surfaces, are promising systems for the future development of new technologies with possible applications in the field of molecular electronics and functional surfaces [1–3]. Azobenzenes constitute one of the most thoroughly investigated molecular switches and allows for the reversible control over various properties by light, i.e., photochromism. In the liquid phase they undergo a photochemical interconversion between the planar *trans*-isomer and the three-dimensional *cis*-form, which involves an electronic excitation at appropriate wavelengths [4–6]. The switching properties and excitation mechanism of the surface-adsorbed species are expected to be different compared to the free molecules since quenching of electronic excitations [7] as well as changes of the geometric and electronic structure occur in the presence of a (metal) substrate. Besides knowledge about the electronic structure of the molecules bound on a metal surface, detailed insights into the adsorption geometry (molecular orientation) are essential.

Recent scanning tunneling microscopy (STM) studies have shown that excitations by a resonant [8] and inelastic [9] tunneling current or by an applied electric field [10] can induce reversible *trans*/*cis* isomerization in various azobenzenes absorbed on Au(1 1 1). Photoisomerization has been demonstrated for the tetra-*tert*-butyl-azobenzene (TBA) adsorbed on Au(1 1 1), a molecule in which the bulky *tert*-butyl groups lead to a decoupling of the functional azobenzene backbone from the metallic substrate [11–14]. Thereby, it has been shown that TBA can be switched bidirectionally by UV-light and thermal activation resulting in reversible changes in the vibrational and electronic structure. For TBA on Au(1 1 1) these effects have been studied by surface vibrational spectroscopy [13] and two-photon photoemission [11,14], respectively. On the other hand, light-induced switching could not be achieved for TBA on Ag(1 1 1) [15] and the parent unsubstituted azobenzene on Au(1 1 1) [12], presumably due to the stronger interaction with the metal substrate and corresponding differences in the geometric and electronic structure as well as lifetime of the excited states.

In this contribution, we investigate UV-light induced changes in the vibrational structure of 4,4′-di-methoxy-3,3′,5,5′-tetra-*tert*-butyl-azobenzene (diM-TBA, see Fig. 1) absorbed on Au(1 1 1) and the reverse process stimulated by thermal activation using high-resolution electron energy loss spectroscopy (HREELS). This study is motivated by our previous work on the TBA/Au(1 1 1) system [13] with the intention to utilize the methoxy-group as a marker group

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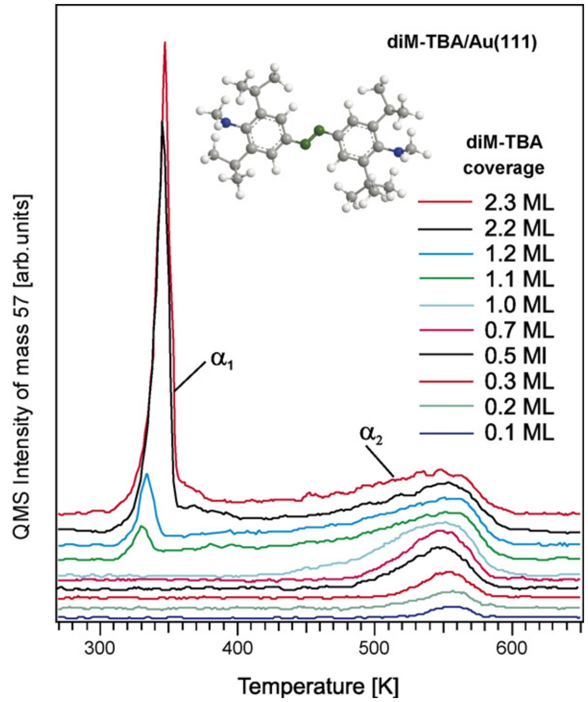

Fig. 1. Thermal desorption spectra of diM-TBA on Au(1 1 1) at different coverages recorded with a heating rate of 1 K/s at the fragment-mass of 57 amu ($C_4H_9{}^+$).

for the vibrational spectroscopy in order to monitor the switching process. We found that in the case of diM-TBA in direct contact with the Au(1 1 1) surface, i.e., in the monolayer (ML) coverage regime, UV-light exposure at 355 nm (3.5 eV) stimulated no conformational changes, in contrast to the TBA/Au(1 1 1) system [13]. On the other hand, at a diM-TBA coverage of 2 ML reversible changes in the vibrational structure due to illumination and thermal activation, respectively, are observed, which we assign to a *trans*/*cis* isomerization. The underlying photoexcitation mechanism for the *trans* → *cis* isomerization in the *second* adsorbate layer is attributed to a direct (intramolecular) electronic excitation.

2. Experimental

The experiments were performed in an ultrahigh vacuum (UHV) apparatus consisting of two chambers separated by a gate valve. The upper chamber was used for sample preparation whereas the lower chamber houses a high resolution electron energy loss (HREEL) spectrometer for recording vibrational spectra.

The HREEL spectrometer (Ibach-type) consists of two subsystems the electron monochromator and analyzer, both with double-pass 127° cylindrical deflectors [16]. HREEL spectra were recorded at a sample temperature of 90 K and in both specular ($\theta_i = \theta_r = 60^\circ$) and off-specular ($\theta_i = 50.8^\circ$, corresponding to 9.2° off-specular; $\theta_r = 60^\circ$) scattering geometry. The energy of the primary electrons was set to 3.7 eV with an overall resolution of ≤ 4 meV, measured as the full width at half maximum (FWHM) of the elastic peak. In the specular spectra of HREELS, the signals contain both dipole- and impact scattering components [17]. The selection rule for dipole scattering, i.e., only vibrations with a component of the dipole moment change normal to the surface are observable, is the same as that for infrared reflection absorption spectroscopy [18,19]. Therefore it is useful for characterizing the geometrical structure and predominantly the orientation of adsorbates. To separate the dipole-scattering components, off-specular spectra consisting only of impact-scattering components were measured.

The Au(1 1 1) crystal was mounted on a liquid nitrogen cooled cryostat which in conjunction with resistive heating enables temperature control from 90 to 750 K. The crystal was cleaned by cycles of Ar^+ sputtering and annealing. The diM-TBA was dosed by means of a home-built effusion cell held at 380 K at a crystal temperature of 250 K. The coverage was analyzed with thermal desorption spectroscopy (TDS). In the TDS experiments, the substrate was resistively heated with a heating rate of 1 K/s, and desorbing diM-TBA was detected with a quadrupole mass spectrometer at the diM-TBA-fragment mass of 57 amu ($C_4H_9{}^+$).

A viewport at the spectrometer level allows to illuminate the sample at the same position where also the HREEL spectra were recorded. For the illumination of the diM-TBA-covered Au(1 1 1) a pulsed (10 Hz, pulse length: 5 ns) Nd:YAG laser at a wavelength of 355 nm (3.5 eV) was used. The output power of the laser beam was set to 140 mW/cm^2. The laser spatial profile was characterized by a CCD camera located at a position outside the UHV chamber, which is equivalent to the sample position. A rather large spotsize with a diameter of ≈ 5 mm was chosen to guarantee an overlap between the illuminated area and the electron beam in the HREEL spectrometer. The annealing experiments were carried out by heating up the sample from 90 to 260 K, staying there for 5 min and subsequently cooling down to 90 K. Changes in the vibrational structure of diM-TBA upon UV-light exposure and annealing, respectively, are monitored by HREELS.

3. Results and discussion

In order to obtain insights into the adsorption properties of diM-TBA/Au(1 1 1) and to quantify the coverage, thermal desorption spectra were recorded as a function of coverage (see Fig. 1). At low coverage a broad desorption peak (α_2) is observed around 555 K, which extends to lower temperatures with increasing coverage. After saturation of this peak a second desorption feature α_1 develops at 330 K. The α_1 peak increases in height and width with increasing coverage, showing a typical zero-order desorption behavior. We therefore assign this peak to desorption from the multilayer while the α_2 peak is associated with desorption from the first monolayer (ML). The thermal desorption behavior of diM-TBA from Au(1 1 1) is very similar to those of other aromatic compounds on noble metal surfaces, for example, benzene [20,21] hexafluorobenzene [22], and pyridine [23], respectively. A common observation in these systems is the substantial broadening of the desorption peak with increasing coverage in the monolayer regime. This can be attributed to repulsive interactions between the adsorbed molecules (for example due to dipole–dipole interactions).

Fig. 2(a) shows the HREEL spectrum of 1 ML diM-TBA adsorbed on Au(1 1 1) recorded in specular scattering geometry. For comparison, the solid state (in KBr) infrared (IR) data are displayed in Fig. 2(b). The vibrational frequencies and their assignments for both the adsorbed and condensed diM-TBA are listed in Table 1 together with the literature values of vibrational modes of tetra-*tert*-butyl-azobenzene (TBA) [13], anisole [24–26], and *trans*-azobenzene [27].

The HREEL spectrum for the adsorbed diM-TBA agrees well with the IR data of the condensed phase diM-TBA. While in the condensed phase the C–N stretch mode (υ: 1220 cm^{-1}), the stretch mode of the aromatic rings (υ(C–C)) at 1406 cm^{-1}, and the asymmetric CH_3 stretch mode (υ_{as}: 2963 cm^{-1}) of the *tert*-butyl-groups result in the most intense infrared absorption, in the HREEL the torsion mode (out-of-plane) of the phenyl rings (τ(C–C)) at 895 cm^{-1} and O–CH_3 stretch vibration at 1009 cm^{-1} show the highest intensity. The latter is also very intense in the condensed diM-TBA (1006 cm^{-1}). The C–C stretch modes of the phenyl-ring at 1109 and

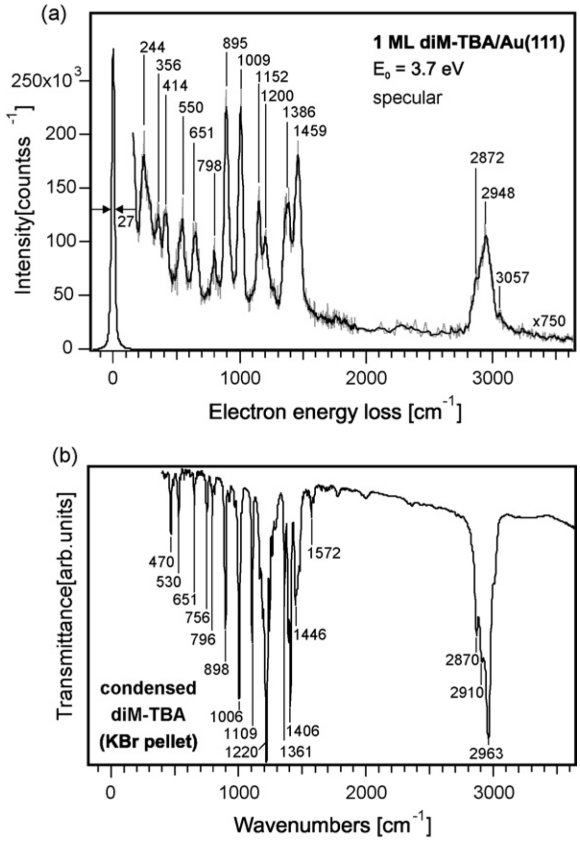

Fig. 2. (a) HREEL spectrum of 1 ML diM-TBA adsorbed on Au(1 1 1) recorded in specular geometry with a primary electron energy of 3.7 eV. The FWHM of the elastic peak is 27 cm^{-1} (3.3 meV). (b) Fourier-transform infrared spectrum of solid diM-TBA (KBr-pellet) measured with a resolution of 4 cm^{-1}.

1406 cm^{-1}, respectively, observed in the condensed molecule are not seen in the adsorbed diM-TBA. Note that the N=N stretching mode of the adsorbed diM-TBA is not observed, since the intense CH_3 bending vibration is located in this energy range.

For a 2 ML diM-TBA coverage, shown in Fig. 3, the overall peak intensities are higher and thus some of the features are better resolved compared to the monolayer spectrum. Two new vibrational modes at 481 and 1570 cm^{-1}, which can be assigned to the C–C in-plane bending mode and the C–C stretch vibration of the aromatic rings, respectively, are observed (see Table 1). In addition, the peak around 1234 cm^{-1} (δ(C–N) or υ(C–O)) is very intense compared to the barley visible feature of 1 ML diM-TBA/Au(1 1 1).

In order to gain insights into the excitation mechanism, i.e., dipole-scattering versus impact-scattering, and to analyze the adsorption geometry of diM-TBA on Au(1 1 1) we performed angular dependent measurements. Fig. 4 shows a comparison of HREEL spectra recorded in specular and 9.2° off-specular geometries for 1 and 2 ML diM-TBA adsorbed on Au(1 1 1). Regarding the monolayer-covered surface, most striking is the huge intensity decrease of the torsion mode of the phenyl rings ((τ(C–C)) at 895 cm^{-1} and of the O–CH_3 stretch vibration (υ (O–CH_3)) at 1009 cm^{-1} in the off-specular spectrum, indicating that their intensity is originating mostly from dipole scattering in the specular spectrum (see Table 1 for the assignment of the dipole active modes).

The strong dipole activity of the phenyl ring torsion and O–CH_3 stretch modes points towards a preferential orientation of the diM-TBA parallel to the Au(1 1 1) surface, *viz.* a planar (*trans*)-geometry, since in this orientation these modes have a strong dipole moment change upon vibration perpendicular to the surface. Note that the C–O–C angle of the methoxy-group is approximately 120° and due to steric effects between the bulky *tert*-butyl-groups and the methoxy CH_3-group it is likely to assume that the methoxy CH_3-group points upwards or downwards, i.e., perpendicular to the molecular plane. Moreover, the in-plane modes of diM-TBA, e.g., the stretch vibrations of the phenyl rings at 1109 and 1406 cm^{-1} and the C–N stretch mode at 1220 cm^{-1}, observed with high intensities in

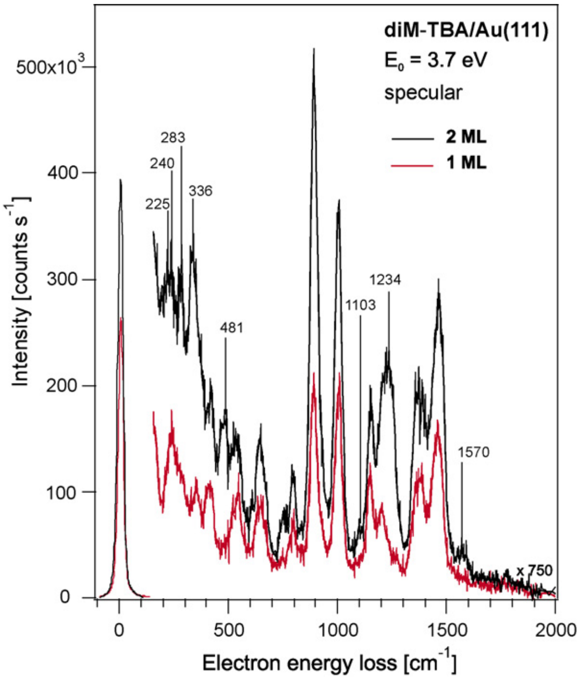

Fig. 3. HREEL spectra of 1 and 2 ML diM-TBA adsorbed on Au(1 1 1) recorded in specular geometry with a primary electron energy of 3.7 eV.

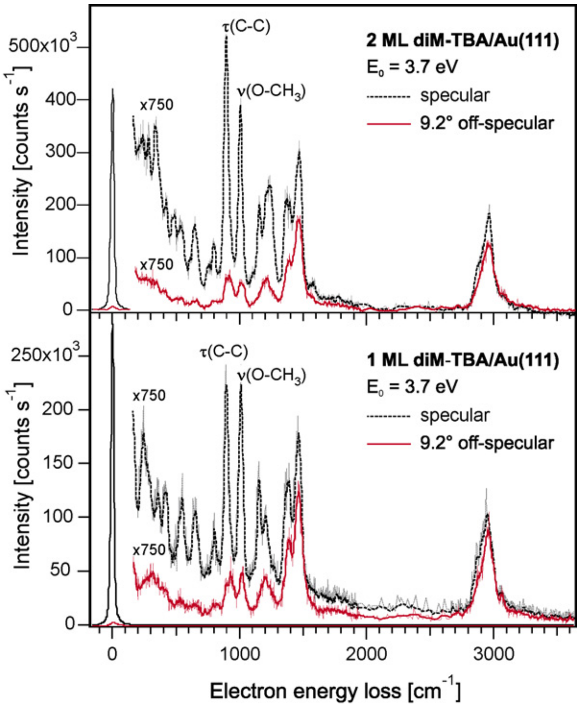

Fig. 4. HREEL spectra of 1 and 2 ML diM-TBA adsorbed on Au(1 1 1) recorded in specular and 9.2° off-specular scattering geometry, respectively, with a primary electron energy of 3.7 eV.

Table 1

Vibrational frequencies (in cm^{-1}) and assignments for 1 and 2 ML diM-TBA adsorbed on Au(1 1 1), and condensed diM-TBA, respectively

Vibrational mode [a]	1 ML diM-TBA [b]	2 ML diM-TBA [b]	Condensed diM-TBA [c]	0.9 ML TBA [d]	Anisole [e]	*t*-Azo [f]
δ(C–N), δ(COC)		225 sh [g]			209	219
τ(C–C)$^{\text{Ar}}$	244 (da) [h]	240				251
δ(COC)	283 sh	283			263	
δ_{as}(CC$_3$)^t		336				
τ(C–C)$^{\text{Ar}}$, δ_{as}(CC$_3$)^t	356 (da)			352		
τ(C–C)$^{\text{Ar}}$	414 (da)	421		403	415	403
δ(C–C)$^{\text{Ar}}$		481	470		443	
δ(C–N)	526 sh	535	530	512		521
τ(C–C)$^{\text{Ar}}$	550 (da)	547 sh	572	543	554	545
τ(C–C)$^{\text{Ar}}$	651 (da)	644	651	696	690	689
δ(C–C)$^{\text{Ar}}$	752	752	756		752	755
τ(C–C)$^{\text{Ar}}$	798 (da)	796	796		782	776
τ(C–C)$^{\text{Ar}}$	895 (da)	893	898	879	880	
υ (O–CH$_3$)	1009 (da)	1004	1006		1039	
υ(C–C)$^{\text{Ar}}$, δ(C–C)$^{\text{Ar}}$		1103	1109			1146
ρ(CH$_3$)$^{t,\text{m}}$	1152 (da)	1154	1166	1153	1151	
υ(C–N)	1200	1207	1220	1189		1223
δ(C–N), υ(C–O)$^{\text{Ar}}$	1234 sh	1234	1246	1230	1247	1300
δ_{s}(CH$_3$)^t	1362	1365	1361	1359		
δ_{s}(CH$_3$)^t	1386	1389	1394	1385		
υ(C–C)$^{\text{Ar}}$			1406		1450	1441
δ_{s}(CH$_3$)$^{t,\text{m}}$, δ_{as}(CH$_3$)$^{\text{m}}$	1459	1461	1446, 1475	1453	1497	
υ(C–C)$^{\text{Ar}}$		1570	1572	1584	1599	1585
υ_{s}(CH$_3$)$^{t,\text{m}}$	2872	2877	2870	2878	2892	
υ_{as}(CH$_3$)$^{t,\text{m}}$	2948	2953	2963	2951	2946	
υ(C–H)$^{\text{Ar}}$	3057	3058		3057		3065

[a] s, indicates symmetric; as, asymmetric; υ, stretch; $\delta_{\text{s,as}}$, bending of the *t*-butyl; δ, in-plane bend; τ, torsion; ρ, rocking; Ar, aromatic ring; *t*, *tert*-butyl group; m, methoxy group.

[b] Obtained by HREELS; present study.

[c] IR spectrum recorded in KBr; present study.

[d] HREELS data from tetra-*tert*-butyl-azobenzene (TBA) adsorbed on Au(1 1 1) adapted from ref. [13].

[e] IR and Raman data adapted from refs. [24–26].

[f] IR and Raman data from *trans*-azobenzene adapted from ref. [27].

[g] sh: shoulder.

[h] The 'da' indicates a strong dipole activity.

the IR spectrum of condensed diM-TBA, are absence or barley visible in HREELS (note that the C–N stretch mode at 1200 cm^{-1} shows no strong dipole activity). This result corroborates the proposed planar adsorption geometry. In addition, STM measurements show that in the low-coverage regime diM-TBA form well-ordered islands with the molecules adsorbed in a planar (*trans*)-configuration,[1] as observed for the TBA on Au(1 1 1) [10,12]. Also in the liquid phase the *trans*-isomer is established to be the energetically favorable configuration [4–6]. In the case of 2 ML diM-TBA adsorbed on Au(1 1 1) (see Fig. 4) we also assume a planar adsorption geometry, since the torsion modes of the phenyl rings (τ(C–C)) at 895 cm^{-1} and the O–CH$_3$ stretch vibration (υ (O–CH$_3$)) at 1009 cm^{-1} show a pronounced intensity loss in the off-specular spectrum and similar to the 1 ML coverage the in-plane modes are not observed or show very low intensities compared to the condensed diM-TBA. Note that in the specular scattering geometry, the intensity of the (C–C) torsion vibrations is even higher than that of the stretch O–CH$_3$ vibration, while for the monolayer these intensities are equal.

In the following we investigate the effect of illumination on the vibrational structure of the diM-TBA/Au(1 1 1) system. UV-light ($h\nu = 3.5$ eV) exposure of $\leq$1 ML diM-TBA adsorbed on Au(1 1 1) provoked no changes in the vibrational structure, *viz.* no modification of the adsorption geometry is observed. For comparison, illumination of TBA on Au(1 1 1) with 3.5 eV photons in the low-coverage regime (<1 ML) caused significant changes in the vibrational structure due to a *trans* → *cis* isomerization [13]. The different behavior of the TBA compared to the diM-TBA is presumably due to a different electronic structure of the diM-TBA/Au(1 1 1) system. For the isomerization of TBA in direct contact with the Au(1 1 1) surface, it has been proposed that in the photon energy regime between ~2.0 and 4.4 eV excitation of holes in the Au *d*-band, which relax to the top of the *d*-band followed by a hole transfer to the highest occupied molecular orbital (HOMO) of TBA, drives the isomerization process [28]. Therefore, a different energetic position of the diM-TBA HOMO level, i.e., a position or a wave function overlap, which does not allow a hole transfer from the metal *d*-band, would prevent the isomerization. In order to elucidate the different performance of diM-TBA a detailed knowledge about the electronic structure of the molecules adsorbed on Au(1 1 1) is essential.

Fig. 5 shows HREEL spectra recorded before and after illumination with UV-light ($h\nu = 3.5$ eV; photon dose of 1×10^{21} photons/cm^2) for 2 ML diM-TBA adsorbed on Au(1 1 1). UV-light exposure leads to an intensity decrease of the elastic peak and all dipole active modes, most demonstrative for the phenyl-ring torsion vibration (at 895 cm^{-1}) and the O–CH$_3$ stretch mode (at 1009 cm^{-1}), while the impact scattering components do not change (see inset of Fig. 5). The intensity drop in the dipole-scattering components could in principle be due to an order-disorder phase transition or a structural change in the ordered layer. A possible disorder could be generated either by a local transient heating effect of the laser pulses (i.e., the diM-TBA molecules in their *trans*-form but with a random adsorption geometry) or by electronic excitation of the diM-TBA molecules leading to *trans* → *cis* isomerization. However, a disorder created by a higher transient lattice temperature is implausible since heating under equilibrium conditions usually causes ordering in adsorbate layers. This was also our experience,

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[1] L. Grill, Freie Universität Berlin, private communication.

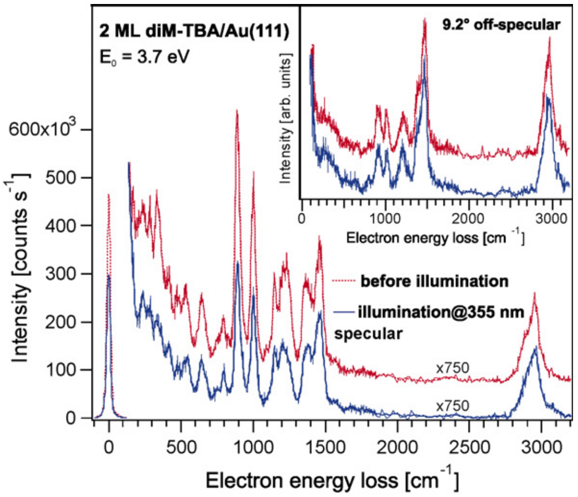

Fig. 5. HREEL spectra of 2 ML diM-TBA adsorbed on Au(1 1 1) before and after UV-light exposure at 355 nm with a photon dose of 1×10^{21} photons/cm^2 recorded in specular geometry at a primary electron energy of 3.7 eV. Inset: 9.2° off-specular spectra before and after illumination at 355 nm.

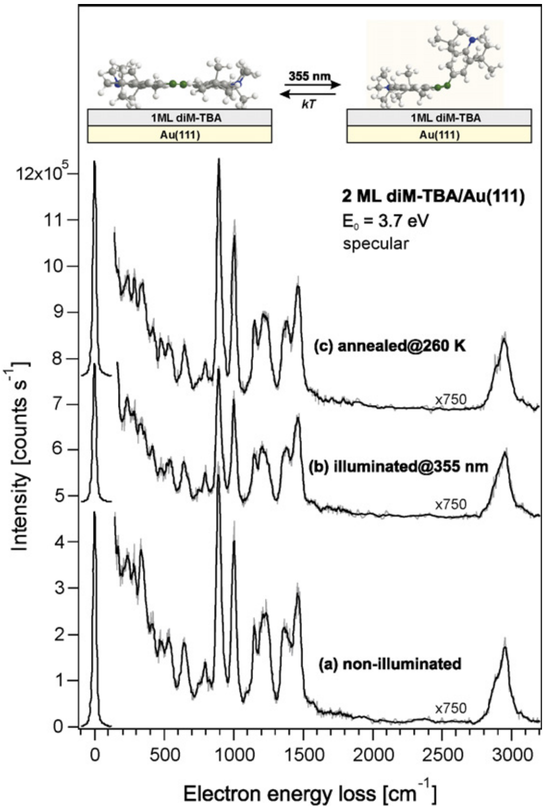

Fig. 6. Reversible switching of diM-TBA molecules induced by light and thermal activation. HREEL spectra of 2 ML diM-TBA adsorbed on Au(1 1 1) (a) before and (b) after UV-light exposure at 355 nm ($n_p = 1 \times 10^{21}$ photons/cm^2) as well as (c) after annealing the illuminated sample to 260 K for 300 s recorded with a primary electron energy of 3.7 eV. Inset: Scheme of the reversible isomerization process. Note that the exact structure of the adsorbed *cis*-diM-TBA is unknown (see text).

deposition of diM-TBA at a surface temperature of 90 K and subsequently heating to 250 K resulted in an *higher* intensity of the elastic peak and all dipole active modes compared to the intensities observed at 90 K. Note that during UV-light exposure the transient lattice temperature, estimated by using the equation proposed by Burgess et al. [29], is kept well below 300 K in order to exclude desorption of diM-TBA molecules. Hence, we conclude that the process leading to the decrease in the intensity of the elastic peak and the dipole active modes is driven by an electronic excitation of the diM-TBA molecules followed by *trans* → *cis* isomerization. Note that exposure of the sample to the electron beam at an electron energy of 3.7 eV in the absence of light does not induce any change in the vibrational features.

One might expect the appearance of new vibrational features, which are associated with the diM-TBA molecules in its modified configuration (*cis*-form). Vibrational (IR [30] and Raman [31]) spectroscopy of the *trans*- and *cis*-azobenzene in the condensed phase determined only small differences in the vibrational structure between the two isomers. The main difference is a shift of the N═N stretching mode to higher energies from 1443 to 1511 cm^{-1} when going from the *trans*- to the *cis*-form. However, the intense CH$_3$ bending modes of the *tert*-butyl-groups in the diM-TBA adsorbed on Au(1 1 1) are also located in this frequency range, which inhibits the discrimination between the *trans*- and *cis*-isomer *via* the detection of the N═N stretch mode.

For the *cis*-TBA adsorbed on Au(1 1 1) a molecular structure has been proposed, based on observed STM images and a structural model [10,12,32]. Thereby one phenyl moiety remains parallel to the surface, while the second phenyl ring is pointing upwards. Assuming a similar structure for the *cis*-diM-TBA, the strong intensity decrease of the dipole active modes, in particular the phenyl torsion and O–CH$_3$ stretch vibrations, can be rationalized, because in the switched state one phenyl-ring per molecule is no longer orientated parallel to the surface (see Fig. 6). In addition, the tilted geometry of one phenyl ring in the *cis*-diM-TBA leads to a less-ordered molecular film, resulting in a broader scattered elastic electron beam (diffuse scattering), which causes a decrease in the elastic peak intensity and consequently an intensity drop of all dipole active modes. Note that the decrease in the elastic peak intensity could also result from a change in the electronic density-of-states above the vacuum level [33,34] due to the isomerization process. Thereby, resonant electron scattering, i.e., creation of a negative ion resonance, may play a role and would lead to an intensity drop of the elastic peak.

Since it is known that the reverse process, i.e., the *cis* → *trans* isomerization of TBA adsorbed on Au(1 1 1) can be stimulated by thermal activation [11,13], annealing experiments were performed. Indeed, these measurements indicate that by annealing the sample to 260 K (for 300 s) the same HREEL spectrum with respect to intensity and shape can be retrieved as without illumination (see Fig. 6). We propose that the observed reversible changes in the vibrational structure of diM-TBA adsorbed on Au(1 1 1) are due to a structural change of the adsorbate, associated with the switching process. The UV-light induces the *trans* → *cis* isomerization whereas the reverse process (*cis* → *trans*) can be stimulated by thermal activation as illustrated in Fig. 6.

In order to evaluate the underlaying mechanism responsible for the photoinduced isomerization of the diM-TBA molecules in the *second* adsorbate layer, two possible scenarios can be considered: (i) The UV-photons induce a *direct* (intramolecular) electronic excitation within the adsorbate and (ii) the incident photons *indirectly* drive the process, *viz.* a substrate-mediated photochemical process, where hot electrons (or holes) are attached to the adsorbate, creating a negative (or positive) ion resonance. As discussed before, in the case of TBA adsorbed on Au(1 1 1) the photoinduced isomerization within the first monolayer is supposed to be driven by a hole transfer from the Au *d*-bands to the HOMO of TBA (formation of a positive ion resonance) [28].

In the liquid phase *direct* electronic excitation induces isomerization of azobenzenes and its derivatives *via* a $n \rightarrow \pi^*$ (S_1) and

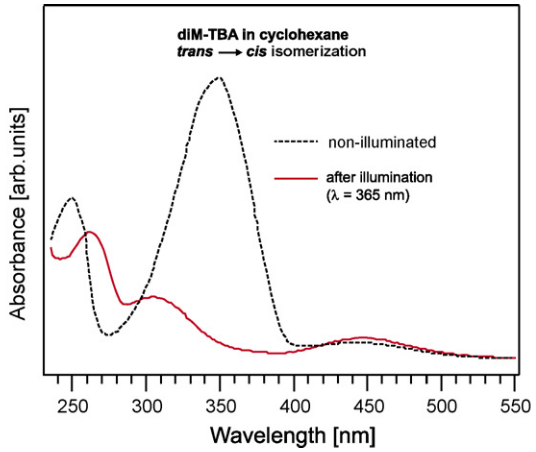

Fig. 7. UV–vis absorption spectra of diM-TBA in cyclohexane before and after illumination with UV-light at 365 nm. Exposure at 365 nm leads to a decrease of the absorbance around 350 nm due to *trans* → *cis* isomerization.

$\pi \rightarrow \pi^*$ (S_2) electronic excitation, respectively. Fig. 7 shows UV–vis spectra of diM-TBA in solution (cyclohexane). The strong absorption band at ≈350 nm belongs to the S_2 transition, whereas the band around 450 nm corresponds to the symmetry forbidden S_1 transition. The intensity loss of the absorption band at 350 nm due to illumination at 365 nm can be assigned to the *trans* → *cis* isomerization. In the case of the adsorbed diM-TBA we propose that a direct optical electronic excitation drives the isomerization, since the second adsorbate layer is most likely electronically decoupled from the metal substrate. Hence, the electronic structure of the adsorbed molecule will be very similar to the molecule in the liquid phase, i.e, the absorption bands should be barely modified. Photoexcitation at 355 nm (3.5 eV), which corresponds to the maximum of the absorption band for the $\pi \rightarrow \pi^*$ (S_2) transition, leads to isomerization of the adsorbed molecules analogous to the liquid phase.

4. Conclusion

In summary, high resolution electron energy loss spectroscopy (HREELS) is utilized to investigate the adsorption geometry of the molecular switch 4,4′-di-methoxy-3,3′,5,5′-tetra-*tert*-butyl-azobenzene (diM-TBA) adsorbed on Au(1 1 1). Furthermore HREELS is employed to study reversible changes in the vibrational structure of diM-TBA, which are induced by UV-light and thermal activation, respectively. For a coverage of 1 ML as well as for 2 ML the phenyl ring torsion and O–CH_3 stretch modes possess a strong dipole activity indicating that diM-TBA adsorbed in the planar (*trans*)-configuration. UV-light exposure at 355 nm (3.5 eV) of the monolayer-covered Au(1 1 1) surface induced no changes in the vibrational structure of the diM-TBA. In contrast, illumination of the second adsorbate layer resulted in a pronounced intensity decrease of the elastic peak and all dipole active modes, in particular, the phenyl ring torsion and O–CH_3 stretch vibrations. After annealing to 260 K these peaks are recovered with respect to the shape and intensity. We assigned the reversible changes in the vibrational structure to *trans*/*cis* isomerization of the diM-TBA molecules. We proposed a direct intramolecular electronic excitation to be the underlying excitation mechanism in the photoisomerization, since the second adsorbate layer is decoupled from the metallic substrate.

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