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Theoretical study of the local atomic and electronic structure of dimetacyano azobenzene molecules on Bi (111) substrate

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Abstract. The present work is devoted to the local atomic and electronic structure of dimetacyano (DMC) molecules deposited on a Bi (111) substrate before and after irradiation by X-rays and UV light using density functional theory (DFT) and a theoretical analysis of the X-ray absorption near edge structure (XANES) spectroscopy. As a result of the calculations the low-energy structure for DMC azobenzene molecules on a Bi (111) substrate was obtained.

1. Introduction

Using controlled reversible processes in molecules deposited on metal and non-metal surfaces develops new ways for the miniaturization of electronic devices. In particular the family of switchable molecules offers the possibility to reversibly control their properties by external parameters like photons, electrons, protons, temperature, or electrical currents – a so-called molecular switch. In this sense the direct adsorption of molecular switches on metallic and non-metallic surfaces is an interesting field in the ongoing development of bottom-up technologies. There are several classes of photoactive chemical compounds which are able to undergo reversible transformations between two or more stable molecular states. These states usually differ, e.g., in their chemical and/or geometric structure. Molecules for which the reversible process is given by a change between different stable geometries while the bond order of each atom is mainly preserved are referred to as conformational switches. For instance, the azobenzene molecules in gas phase and solution are subject to photoisomerization, during which changes are accompanied by corresponding changes in chemical structure. This property makes them suitable for using as building blocks in molecular motors and optical storage devices. On the other hand, deposition of molecules on surfaces leads to a restriction of the molecular switch, which occurs due to the fact that the isomerization process becomes influenced not only by an atomic bonding in the molecule but also by the electronic interactions between molecules and surroundings [1-3].

There are several scanning tunnel microscopy studies (STM) devoted to azobenzene molecules on Cu(001) and Au(111) surfaces [4,5,6]. The presence of an interaction between adsorbate and surface has been shown during the switching an azobenzene single molecule on Cu (001) surface at 5 K [4]. After switching, the resulting *cis*-isomer was found to be stabilized by chemisorption, preventing a reversible switching. It has been shown, that during the adsorption of an azobenzene monolayer on Cu (001) at the room temperature structures similar to the *cis*-form are formed, whereas, on Au(111) the

trans-form is more preferable [5]. It means that it is possible to use different types of substrates to control the switching process and provide reversibility. Also, it was revealed that the self-assembly and switching behavior is highly dependent on the chemistry and corrugation of the surface [6]. The atomic and electronic properties of DMC azobenzene molecules on Cu(001) were studied by angle-dependent near edge X-ray absorption fine structure (NEXAFS), X-ray photo electron spectroscopy (XPS) and DFT calculations [7]. It has been shown that the molecule coverage and chemical character of the substrate and its temperature have an influence on the adsorption state of DMC azobenzene molecules.

The present study provides additional structural information which leads to a more detailed picture of the mechanisms of adsorption. We used the density functional theory (DFT) and molecular dynamic simulations (MOPAC) to provide information on the atomic structure of adsorbed molecules.

2. Methods of calculation

The atomic geometry of DMC azobenzene molecules was analysed on the basis of density functional theory (DFT) and molecular dynamic simulations (MOPAC method) implemented in the ADF program code [8,9]. The electronic configuration of the cluster was described by a core double zeta, valence triple zeta, doubly polarized (TZ2P) basis set of Slater-type orbitals. The bismuth substrate was frozen during the geometry optimization and a double zeta (DZ) basis set was used.

The DFT-D3 exchange-correlation correction parameterized for B3LYP functional was applied during DFT calculations. The DFT-D3 dispersion correction is less empirical, i.e., the most important parameters are computed from first principles by standard Kohn-Sham DFT. The DFT-D3 implementation based on the paper by Grimme [10] was used to take into account weak van der Waals substrate – adsorbate interactions. This approach provides high accuracy for both "light" and "heavier" atoms.

3. Results and discussion

It is known that DMC azobenzene molecule change their geometric structure after irradiation during the photoisomerization of *trans*- and *cis*- isomers. The two isomers can be switched with particular wavelengths of light - ultraviolet or blue light. The *cis* isomer is less stable than the *trans* (for instance, it has a distorted configuration and is less delocalized than the *trans* configuration). Thus, *cis*-azobenzene will thermally relax back to the *trans* via *cis*-to-*trans* isomerization.

The present research was concentrated on the theoretical prediction of the atomic and electronic structure of DMC azobenzene molecules deposited on a Bi(111) substrate before and after irradiation by UV light. In order to study the geometric structure the relaxation of DMC azobenzene molecules deposited on the bismuth surface density functional theory was performed. At first, we studied the structural changes of the free DMC molecules depending on the spin state. Figure 1 shows the proposed changing the *trans*- DMC azobenzene molecule geometry as a result of changing its spin state. The initial structure corresponds to the *trans*-isomer of the molecule in the ground state S_0 (1). After photoexcitation the molecule passes into the excited electronic state S_2 , which corresponds to the *cis*-isomer of DMC azobenzene molecules (2). The excited state is a triplet. In the process of relaxation of the molecule it can take the geometry 3 or 4 with equal probability (the bonding energy for these two configurations has almost the same value). In the DFT approach used there, the bonding energy is calculated as the energy of the cluster minus the energy of the constituent atoms.

In the next step the most probable geometry of the DMC azobenzene molecule on a Bi(111) substrate in the ground and excited state (corresponding to the states before and after irradiation) was found. The simulation results are presented in table 1. The geometrical optimization was performed using ab initio DFT. For each of the resulting structures the values of a bonding energy in order to select energetically the most favorable configuration were calculated. For *trans* isomer of DMC azobenzene molecule only the model with a highest bond energy is presented. The DMC azobenzene molecule in this model is arranged horizontally with respect to the substrate and the azo nitrogen atoms are located directly above the bismuth atoms.

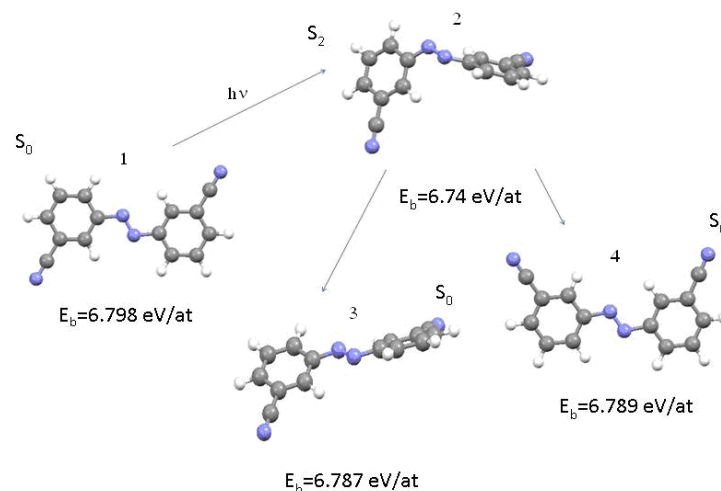


Figure 1. Schematic representation of the *trans-cis* photoisomerization pathways of DMC azobenzene molecules. E_b is a bond energy per atom.

In table 1 the two models for the excited DMC azobenzene molecule on the Bi(111) substrate are shown. They are quite close in bonding energies and in order to choose the more reasonable model in a follow-up study the analysis of angle-depended NEXAFS spectra should be done.

Table 1. The relaxed geometry structures of a single DMC azobenzene molecule on top of a Bi cluster from a Bi(111) substrate, resulting from DFT geometry optimization. The substrate atoms were fixed during optimization.

Spin state	Optimized DMC molecule on the Bi(111) substrate	Bonding energy per atom, eV
S_0 <i>trans</i> -DMC		4.242
S_2 <i>cis</i> -DMC		4.042
S_2 <i>cis</i> -DMC		4.054

We calculated angle-dependent N K-edge NEXAFS spectra for *trans*- and *cis*- isomers of the DMC azobenzene molecule in order to understand the geometry of the molecules related to a Bi(111) surface. On the figure 2 the theoretical spectra for two isomers and experimental spectra for *trans*-DMC azobenzene molecule deposited on a Bi(111) are compared. The inserted pictures show the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) at the DMC azobenzene molecule. The energy position and relative intensity of the features on the simulated N K-edge NEXAFS spectra for *trans*- isomer well describe the experimental spectrum which let us to assume the flat settle of DMC molecules on the Bi(111) substrate. As one can see from the bottom two pictures of the figure 2 the simulated spectra for *cis*- isomer are characterized by the high intensity resonance from cyano nitrogen group which lies perpendicular to a surface for both normal and grazing X-ray incidence.

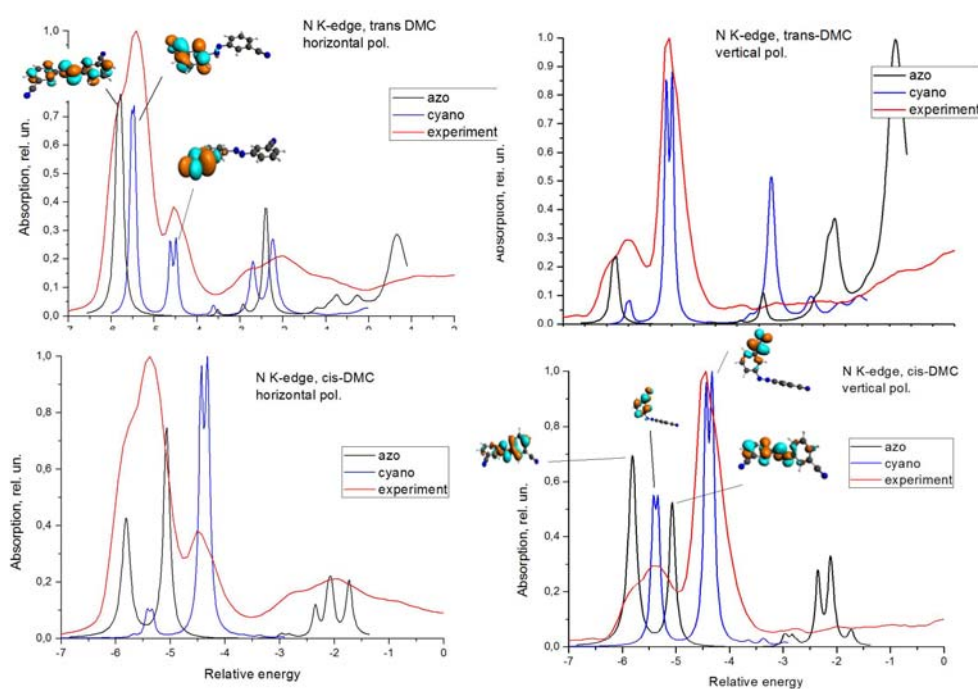
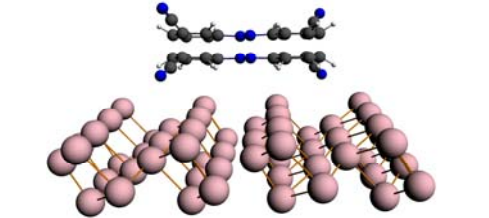
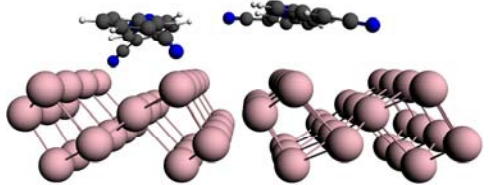
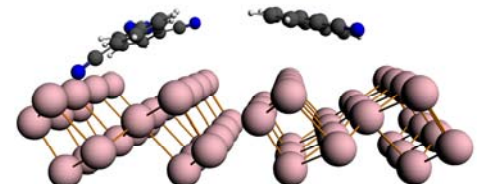
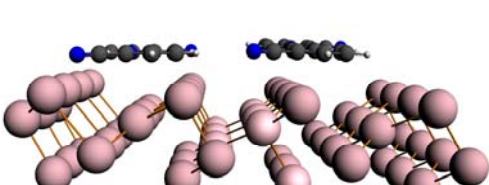


Figure 2. Angle-dependent N K-edge absorption spectra of 1 multilayer DMC molecules evaporated on Bi(111) substrate at 110 K temperature compared with simulated NEXAFS spectra of free *trans*- and *cis*- DMC molecules. The black and blue curves correspond to the azo and the cyano excitation centers. The red lines correspond to experimental spectra at 90° (normal) and 20° (grazing) X-ray incidence.

In order to predict a possible arrangement of DMC azobenzene molecules on a Bi(111) substrate the geometrical optimization by a semiempirical MOPAC method implemented in the code ADF2012 was performed. We optimized several models in which two DMC azobenzene molecules were placed on the top of a bismuth cluster. Some of the models are presented in table 2. The energetically most preferable for a non-excited DMS molecule is to symmetrically settle parallel to the bismuth surface.

Table 2. The relaxed geometric structure of two DMC azobenzene molecules on top of a Bi cluster from Bi(111) substrate resulting from MOPAC geometry optimization. The substrate atoms were fixed in space during optimization.

Optimized DMC molecules on the Bi(111) substrate	Total energy, eV
	-12 204.153
	-12 214.250
	-12 213.277
	-12 214.617

4. Conclusions

The research has involved the theoretical modelling of the atomic and electronic structures of DMC azobenzene switchable molecules on a Bi(111) substrate using the density functional theory (DFT) and molecular dynamics (MOPAC) techniques.

The most probable structure of *trans*- and *cis*- isomers of the DMC azobenzene molecule on a Bi(111) substrate was found by means of DFT calculations. In order to proof our theoretical predictions, the combination of experiment and theory of angle-dependant X-ray absorption near fine structure (NEXAFS) spectroscopy for the DMC azobenzene molecule on a Bi(111) substrate was applied. We found the planar geometry of the *trans*- DMC azobenzene molecule relative to a Bi(111) substrate.

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