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Full Length Article

A density functional theory computational study of adsorption of Di-Meta-Cyano Azobenzene molecules on Si (111) surfaces

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ABSTRACT

The adsorption of di-meta-cyano azobenzene (DMC) *cis* and *trans* isomers on non-passivated and passivated Si (111) (7 × 7) surfaces is studied using density functional theory (DFT) calculations. Our results reveal that on the non-passivated surface the 12 Si adatoms are accessible to form chemical bonds with DMC molecules. Interestingly, the *trans* isomer forms two chemical bonds near the corner hole atom in Si (111) (7 × 7) surface, which is not observed in the widely studied metallic surfaces. The DMC isomers show significant structural distortion in the chemisorption case. The strong chemical bonds (and high bonding energy) could be detrimental to conformation switching between these two isomers under external stimuli. The physisorption case is also examined. Monte Carlo (MC) simulations with empirical force fields were employed to search about 10^6 different adsorption positions and DMC molecule orientations to identify the stable adsorption sites (up to six). The DFT-PBE and DFT-D2 calculations were then carried out to obtain the relaxed atomistic structures and accurate adsorption energy. We find that it is imperative to take van der Waals (vdW) interaction into account in DFT calculations. Our results show that the adsorption sites generally are encompassed by either the Si adatoms or the passivated H atoms, which could enhance the long-range dispersion interaction between DMC molecules and Si surfaces. The molecular structures of both isomers remain unchanged compared with gas phase. The obtained adsorption energy results ΔE_{ads} are moderate (0.2–0.8 eV). At some adsorption sites on the passivated surface, both isomers have similar moderate ΔE_{ads} (0.4–0.6 eV), implying promises of molecular switching that should be examined in experiments.

1. Introduction

Smart surfaces that can change their surface properties under external stimuli have attracted enormous attention in last decade [1–11]. Controlling the surface properties such as wettability, optical properties, thermal stability, and chemical reactivity lead to a wide range of applications, such as micro and nanofluidic devices, self-cleaning surfaces, anti-fog surfaces, molecular motors, data storage devices, medical devices, drug delivery systems, and microelectronic applications. One approach toward this goal is adsorption of molecular switches on a surface [1–5,12–14]. These switchable molecules can change their geometrical structure, spin, color, conjugation, dipole moment or other properties under external stimuli like light, electric field, electron injection, and heat [7,10,11,15,16].

Azobenzene is a family of molecules that are extensively studied as molecular switches due to their capability in reversible switching upon optical excitation. Azobenzene molecules can exist in two forms: the planar *trans* isomer and the *cis* isomer with three-dimensional bent conformation. In the gas and solution phase, the *trans* isomer can be transformed into *cis* form by UV light, meanwhile the reversible switching can be induced by visible light or thermal annealing [17,18]. Recently, extensive studies have been conducted to examine the switching process and mechanism of azobenzene derivatives on different metallic materials [19–25]. Reversible switching of DMC molecules on Bi (111) surface induced by resonant X-ray illumination was observed in experiments [23,24]. Unlike the gas and solution phases, switchable molecules adsorbed on a surface are subject to restrictions aris-

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ing from the interactions between the molecules and the surface [1,26,27]. The interaction between the azobenzene derivative and substrate plays a pivotal role on the switching performance. At present, the molecular switches are either attached to the substrates via ligands [28,29] or directly deposited on substrates [19–25]. The latter option is appealing since no complex chemical process is required.

It is fundamentally important to explore how the structure and the conformational dynamics of molecular switches, such as azobenzene-based compounds, are modified when directly adsorbed on solid surfaces. The previous studies of adsorbed states of azobenzene derivatives on different metallic materials, such as Au, Ag, and Cu, have identified two main physical or chemical interactions[19,26,27], (i) the tendency of the nitrogen in the azo bridge (—N═N—) to form chemical bond with the surface and (ii) the long range intermolecular interaction between the phenyl ring moieties with the surface. The formation of chemical bonds shortens the distance of the molecule from the surface, often causing the Pauli repulsion force to the phenyl moiety. Hence, the *cis* isomer usually has a better chance to form stronger chemical bonds, due to its bent conformation. A chemical bonding results in strong adsorption energies, distortion of atomic structures, and changes of the electronic properties, which often cause loss of the switching capability. If the isomers are physisorbed, owing to its planar conformation, the *trans* isomer forms a stronger intermolecular van der Waals (vdW) interaction. A strong vdW interaction could cause adverse effect on the switching process [20,23,30]. However, if the interaction of the molecule with the surface is too weak, the adsorption may not be stable. Hence, it is reasonable to expect that a surface that can facilitate switching process should be the one with a balanced interaction with the molecule switch.

Silicon is the most widely used substrate material in semiconductor industry and in semiconductor physics research field. There are many well-developed technologies available to manipulate and control the Si surfaces. It is promising and valuable to develop Si based smart surfaces. But there are no studies to understand how the surface adsorption modifies the conformation of DMC isomers and energetic properties of adsorption complexes. In this paper, the adsorption properties of DMC on Si (111) (7 × 7) surface and hydrogen passivated Si (111) surfaces are investigated using DFT calculations, which should provide valuable clues for experimental development of Si based smart surfaces. For the physisorption case, Grimme's scheme (DFT-D2) was employed to account for the long-range dispersion interaction, which has an essential effect on calculated adsorption energy results [27]. To understand how the molecule interacts with the substrate, electron charge analysis was performed as well.

2. Adsorption sites on Si (111) surfaces

Different from the mostly studied (111) surfaces of Au, Ag, and Cu, Si (111) (7 × 7) surface has a complex structure, which could lead to many local meta-stable adsorption sites. Locating the adsorption sites on such a complex surface through DFT calculations is a challenging task. Thus for the case of chemisorption, we examine the most plausible adsorption sites (details later). As for the physisorption case, we used MC simulations to explore the surfaces and identify possible adsorption sites. Note that the adsorption structures and energetics often depend on coverage [31,32]. We only consider the low coverage case, influence of coverage density on adsorption stability can be neglected [33]. Moreover, influence of the adsorbed molecules on Si surface structure should be minor [34].

2.1. Non-passivated surface

Fig. 1a demonstrates the atomistic structure of Si (111) (7 × 7) surface. The lattice constants of Si (111) (7 × 7) within the surface plane are $a = b = 27.06$ Å. The four top atomic layers undergo structural reconstruction [35]. As a result, there are 19 atoms with dangling bonds and different reactivities [36]. These unsaturated atoms are classified into three groups: 12 adatoms (top layer), 6 rest atoms (2nd layer), and 1 corner hole atom (bottom layer).

It is reasonable to expect that the Si atoms with dangling bonds would have a high reactivity and thus a high tendency to form chemical bonds with DMC molecule. Among them, the 12 adatoms are the most accessible unsaturated atoms since they are arranged in the top layers. Indeed, our DFT calculations confirmed that other unsaturated atoms were not accessible for DMC molecules to form a chemical bond. Hence, only the adatoms are recognized as plausible chemisorption sites on Si (111) (7 × 7) surface. These adatoms have been numbered in Fig. 1b. Note that due to the structural symmetry, some adatoms such as 2&3, 4&6, 7&9, and 10&11 are similar. In following, we will use adatom IDs to label chemisorption sites.

To locate the stable physisorption regions, we scanned the Si (111) (7 × 7) surface by using Monte Carlo (MC) simulations. We expect the phenyl ring – surface interaction would be the driving adsorption mechanism in these sites. The Lennard-Jones force fields with parameters from References [37,38] were used to describe the van der Waals interactions between the DMC molecule and Si surface. We explored a large number of surface locations and molecular orientations for both *cis* and *trans* isomers. Ten runs (with different initial guesses) were carried out. In each run, following the Markov chain model, 1×10^6 random configurations were examined and the one with the lowest energy was identified. Then, the obtained structures were further minimized through DFT calculations.

Fig. 1c shows the identified adsorption sites. All MC simulations yielded only one adsorption site for the *cis* isomer (Site I), while five different sites were obtained for the *trans* isomer. Site I is located on the top of the corner hole atom and surrounded by 6 adatoms (corner adatoms). Site II is surrounded by 6 adatoms (2 corner adatoms and 4 center adatoms) and encompasses one rest atom. The geometry of site III is similar to that of site II except that it is placed in the faulted half of the Si (111) (7 × 7) surface. Sites IV and VI are similar to sites III and II, respectively. They are encompassed by 4 center adatoms. Site V is located at the boundary between the two halves and is surrounded by 6 adatoms (4 corner adatoms and 2 center adatoms).

Analyzing the Si (111) (7 × 7) surface structure helps us rationalize these adsorption sites. The *cis* isomer prefers site I because the concave hole shape of site I should well accommodate its bent molecular conformation. The N atom of *cis* isomer sits close to the corner hole Si atom, meanwhile the phenyl rings are near the adatoms. In Fig. 1c, all stable sites for *trans* isomer are flat regions confined by the adatoms. Such configurations allow DMC *trans* isomer to sufficiently interact with the adatoms, meanwhile the flat phenyl rings have a smaller distance from the surface.

2.2. Passivated surface

The reactive dangling bonds of Si (111) (7 × 7) surface could be potentially detrimental to the switching process of the adsorbed DMC. Its reactivity can be significantly reduced via passivation. Note that at finite temperature, the Si (111) surface is often passivated [39–41].

It is known that the passivation of Si (111) (7 × 7) by hydrogen atoms depends on temperature and hydrogen concentration [40]. For a low coverage case, hydrogen atoms react with dangling bonds without changing the reconstructed surface structure, whereas a