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Conformation-selective adsorption of 2,3-butanediol on Si(001)

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Abstract

The adsorption of 2,3-butanediol on the Si(001) surface is studied by means of *first-principles* pseudopotential calculations. Molecular adsorption on top of the Si dimers resulting in a 6-membered ring of the O–C–C–O segment with the dimer atoms is energetically favored, in agreement with the interpretation of recent experiments. The adsorption energy difference for butanediol adsorbed in either gauche or anti conformation is nearly one order of magnitude larger than the energy difference between the respective conformers in gas phase, pointing to a conformation-selective adsorption.

Keywords: Silicon surface; Alcohols; Density functional calculations; Chemisorption

The chemistry of small organic molecules on semiconductor surfaces is of both fundamental and technological interest [1–3]. This interest arises from the vast range of qualities that organic molecules can be designed to have, and the hope of adding their functionality to semiconductor technology. Of particular interest are therefore surface reactions with polyfunctional organic molecules.

As an example for the adsorption of diols on semiconductor surfaces, Kim et al. [4] have recently studied the reaction of 2,3-butanediol ($C_4H_{10}O_2$) with the Si(001) surface using photoelectron spectroscopy. 2,3-Butanediol is a small molecule containing two hydroxyl (–OH) groups which is interesting from the stereo-chemical point of view. Firstly, it is chiral: The carbon atoms bonded to –OH groups are chiral centers. Secondly, because rotation around a single C–C bond is relatively free, the molecule exists in a large variety of confirmations. Not all of them are suitable for adsorption on Si(001): If the bonding

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is to occur via the hydroxyl groups, these should for steric reasons be in gauche conformation. Anti conformation of the hydroxyl groups should not occur. However, the orientation of the methyl groups seems to remain as degree of freedom. Fig. 1 shows ball-and-stick models and Newman projections for the energetically favored $g^-G^-g'^+$ (CH_3 gauche) and g^-G^+t' (CH_3 anti) conformers of (*R*,*R*)-2,3-butanediol [5,6]. According to B3LYP/6-31G* calculations [5], the gauche conformation, with a dihedral angle between the methyl groups of about 60°, is slightly (by 19 meV) more stable than the anti conformation. We focus on these two conformers in our adsorption study.

The calculations are performed using the Vienna Ab-initio Simulation Package (VASP) implementation [7] of the gradient-corrected density functional theory (DFT–GGA) [8]. The electron–ion interaction is described by non-normconserving ultrasoft pseudopotentials [9]. We expand the valence wave functions into plane waves up to an energy cutoff of 25 Ry. The Brillouin zone integrations are performed using sets corresponding to 64 **k** points in the full (1×1) surface Brillouin zone. All calculations are performed using the calculated Si equilibrium lattice constant of 5.456 Å. The surface structure is considered to be in equilibrium when the forces are below 50 meV/Å. To calculate the density of state, the energy spectrum is Gaussian broadened by 0.2 eV.

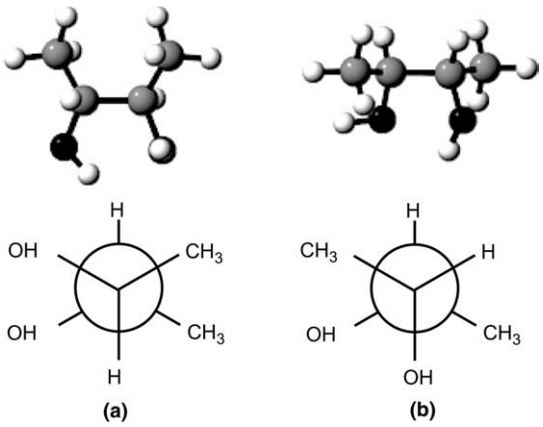

Fig. 1. Ball-and-stick models and Newman projections for (a) the $g^-G^-g'^+$ and (b) the g^-G^+t' conformers of (*R*,*R*)-2,3-butanediol. Black, gray and white balls indicate O, C and H atoms, respectively.

The surface is modeled with a periodically repeated slab, consisting of 12 atomic Si layers plus adsorbed butanediol. We use supercells with $p(4\times2)$ and $p(2\times2)$ or $c(4\times2)$ surface periodicities for studying coverages of 0.25 and 0.5 monolayers (ML), respectively. Here 1 ML is defined as one molecule adsorbed per Si surface dimer. The topmost five layers of the slab as well as the adsorbed molecules are allowed to relax.

Calculations for gas-phase 2,3-butanediol were performed using a $18\times18\times18$ Å^3 supercell and enforcing a force limit of 5 meV/Å. In agreement with Ref. [5], we find the gauche to be favored over the anti conformer. The calculated energy difference of 41 meV is somewhat larger than the result of Ref. [5], however. Intramolecular H···O–H hydrogen bonds between the two hydroxyl groups are formed. The predicted bond lengths are 2.12 and 2.30 Å for the gauche and anti conformers, respectively.

Alcohols adsorb on Si(001) by a dissociative reaction via the hydroxyl groups [10–14]. Ethanol, for example, first forms a dative bond, before either an O–H or an O–C cleavage occurs [13]. The energy barrier of the latter reaction renders the hydrogen dissociation more likely at room temperature. A similar reaction is found for water adsorbed on Si(001) [15–17].

The measured core-level spectra [4] also indicate O–H cleavage for the adsorption of 2,3-butanediol: The spectra are interpreted in terms of the formation of Si–H and Si–O bonds. Apart from the H dissociation, no further fragmentation of the molecule should occur. Based on this experimental information, we study a number of conceivable bonding sites for the two conformers shown in Fig. 2. We consider positions where butanediol adsorbs on top of one Si dimer (T), bridges the ends of two adjacent dimers within the dimer row (E), and bridges two dimers of neighboring dimer rows (B). The dissociated hydrogen atoms are adsorbed on the adjacent dimer in case (T) or saturate the remaining dimer dangling bonds in the cases (E) and (B). The adsorption energies for these interface geometries are summarized in Table 1 for coverages of 0.25 and 0.5 ML. We find that the top-dimer model (T) with the gauche conformation leads to the

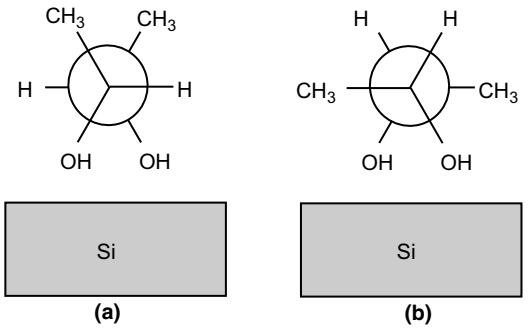

Fig. 2. Schematic illustration of (*R*,*R*)-2,3-butanediol adsorption in gauche (a) and anti conformation (b) on Si(0 0 1).

Table 1
Calculated adsorption energies in eV/molecule with respect to the clean Si(0 0 1)c(4 × 2) surface and the respective conformer in gas phase

Conformation	Adsorption site	0.25 ML	0.5 ML
a	T	4.48	4.48
a	E	4.26	4.27
a	B	4.04	4.07
b	T	4.28	4.29
b	E	4.23	4.22
b	B	3.99	3.98

The notation refers to Fig. 2 and the text.

lowest-energy configuration, both for coverages of 0.25 and 0.5 ML. Also for the less favored adsorption sites (E) and (B), the gauche conformation of the methyl groups is clearly favored over the anti conformation. In all cases, the coverage dependence of the adsorption energy is very small, indicating a nearly vanishing interaction between the adsorbed molecules, once their separation exceeds the steric interaction.

The adsorption of 2,3-butanediol on top of one Si dimer leading to the formation of a Si–O–C–C–O–Si ring structure supports the conclusions drawn by Kim et al. [4]. However, from the total-energy results in Table 1 it appears that the anti conformation of the methyl groups assumed by the experiment is less likely to be observed than the gauche conformation.

Fig. 3 shows the structurally relaxed top-dimer model for gauche conformer adsorption on Si(0 0 1). For a coverage of 0.25 ML we calculate bond lengths of 2.36, 1.67 and 1.49 Å for the Si dimer beneath the $C_4H_8O_2$ fragment, the Si–O bond, and the Si–H bond, respectively. The distance between the two oxygen atoms in gauche and anti conformations amounts to 3.02 and 3.07 Å, respectively. The respective distances for the gas-phase conformers are 2.72 and 2.78 Å.

The adsorption energies compiled in Table 1 refer to the gas-phase energies of the respective conformers of 2,3-butanediol. Therefore, the energy difference between the conformers has to be added, to compare the total surface energies. Thus one obtains an energy difference of 0.25 eV for butanediol adsorbed in either gauche or anti conformation. This is nearly one order of magnitude larger than the energy difference between the conformers in gas phase. The reason for this enhancement is the repulsive interaction between the molecular methyl groups and the surface: We find that the methyl groups of adsorbed anti

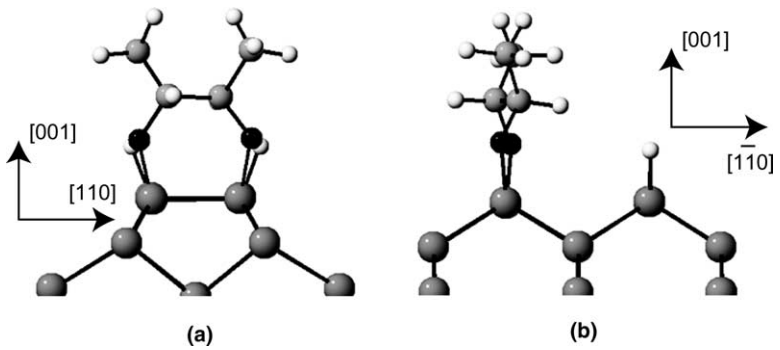

Fig. 3. Side views of the relaxed top-dimer adsorption configuration of (*R*,*R*)-2,3-butanediol in gauche conformation on Si(0 0 1). Large (black, gray, white) circles denote Si (O, C, H), respectively.

conformers bend upwards by 1–2°, compared to the gas-phase geometry. According to the population based on Gibbs energies from the B3LYP/6-31G* calculations for the predominant conformations of (*R*,*R*)-2,3-butanediol [5], both gauche and anti conformers exist. From the repulsive interaction between the methyl groups and the Si(0 0 1) surface it can be expected that not only the final adsorption energies but also the reaction kinetics favor the adsorption of the gauche conformer. A conformation-selective adsorption appears thus likely. A transformation of the gauche to the anti conformer, on the other hand, appears unlikely: For the gas-phase molecule we calculate a transition barrier of about 0.5 eV. Due to the bonding to the substrate, the barrier will be substantially higher for adsorbed species.

According to the calculations, the adsorption may be conformation-selective. However, since the surface chemical bonds involved are identical, an experimental confirmation of this prediction using standard experimental techniques such as vibrational or core-level spectroscopy will be difficult. In Fig. 4 we compare the modification of the bulk Si density of states due the adsorption of either the gauche or anti conformer. The differences are relatively small, much smaller than compared to the results for the clean surface that are shown for comparison. Both spectra seem compatible with the valence-band measurements by Kim and co-workers [4], as indicated by the labeling of the peaks adopted from the experiment. Interestingly, the energies of most of the additional peaks in the density of states correspond quite well to the

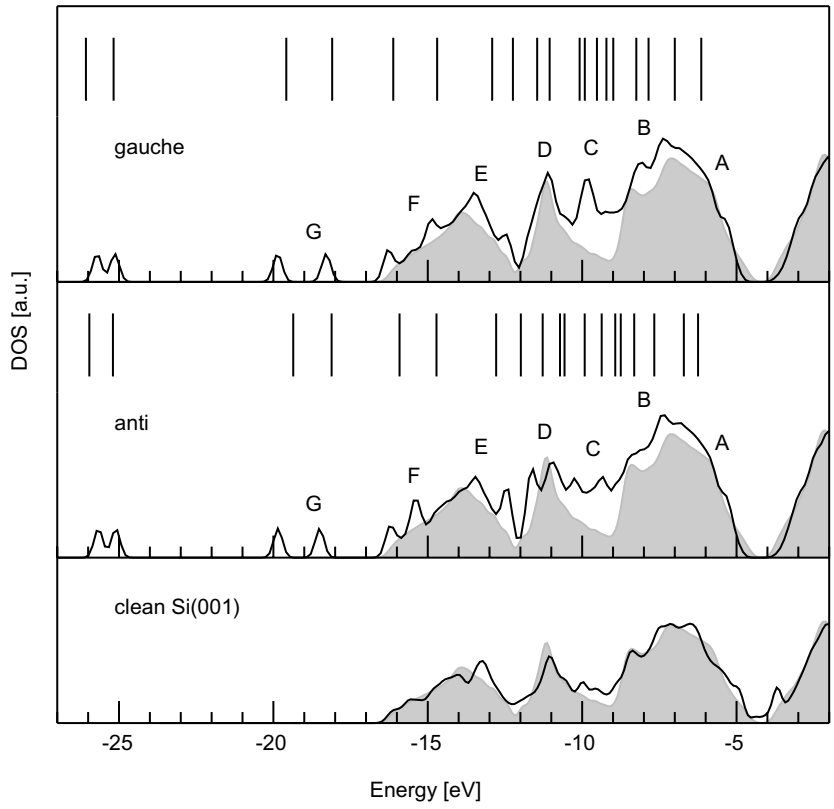

Fig. 4. Comparison of the calculated ionization potentials for (*R*,*R*)-2,3-butanediol (vertical lines) and the interface density of states (DOS) for the respective adsorbed configurations (0.5 ML) as well as the clean Si(0 0 1)-(4 × 2) surface. The bulk Si density of states is indicated in gray. The peaks are labeled following the notation from Ref. [4].

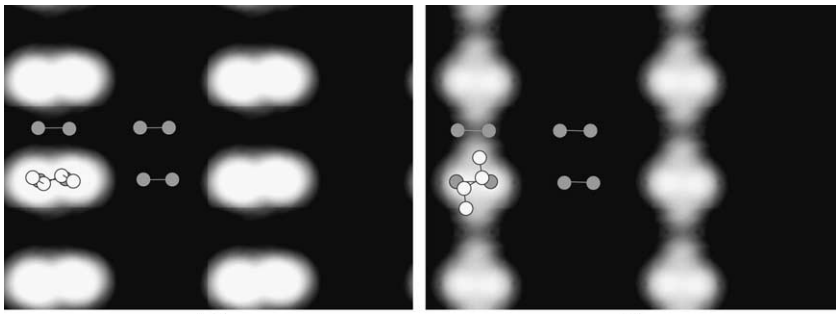

Fig. 5. STM images simulated for top-dimer adsorption of the gauche (a) and anti conformation (b) of butanediol on Si(0 0 1). White and gray circles indicate the lateral positions of C and first-layer Si atoms, respectively.

ionization energies of the molecular orbitals from gas-phase calculations.

We also simulate scanning tunneling microscopy (STM) images using the scheme devised by Tersoff and Hamann [18]. The resulting filled-state images for a bias voltage of −2.0 V (such as typically used for exploration of organic overlayers [19]) are shown in Fig. 5. As one might expect from the molecular structure, the STM features predicted for the gauche conformation are more compact and confined to the area above the Si dimer, whereas the anti conformation gives rise to a more continuous distribution of the energy resolved probability density along the Si dimer row. According to the simulations, it should thus be possible to distinguish between the adsorbed conformers by STM.

In summary, we have examined the chemisorption of 2,3-butanediol on the Si(0 0 1) surface by *first-principles* calculations. The molecule prefers to adsorb on top of a single Si surface dimer. The calculations support the formation of a 6-membered ring of the O–C–C–O segment with the Si dimer atoms. Beyond the steric repulsion, there is very little interaction with neighboring ad-molecules. Interestingly, the conformation of the molecule strongly influences its adsorption energy, which can be expected to lead to a conformation-selective bonding behavior. According to the simulated images, STM experiments should be able to discriminate between different types of adsorbed conformers.

Acknowledgements

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