

Adsorption of ethanol on Si(1 0 0) from first principles calculations

Pier Luigi Silvestrelli *

*INFN (Udr Padova and DEMOCRITOS National Simulation Center, Trieste, Italy) and Dipartimento di Fisica “G. Galilei”,
Università di Padova, via Marzolo 8, I-35131 Padova, Italy*

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Abstract

The chemisorption of ethanol ($\text{C}_2\text{H}_6\text{O}$) on Si(100) is studied from first principles calculations, using a slab approach. Ethanol molecule initially interacts with the Si surface through the barrierless formation of a “dative bond”; from this physisorbed state ethanol can proceed to react with the surface via a number of possible pathways, the most relevant ones being characterized by O–H bond cleavage or O–C bond cleavage. We find that, although the product obtained by the O–C bond cleavage is thermodynamically more stable, the O–H bond cleavage process is kinetically favored. Other possible chemisorbed configurations and reaction paths have been investigated together with the effect of different surface coverages. Our results are in agreement with experimental findings; however they exhibit important differences with respect to those obtained in previous calculations based on a single-dimer cluster model.

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1. Introduction

The study of adsorbates on semiconductor surfaces and, in particular, on silicon substrates is an active area of basic research with relation to a number of technological applications. A very important process in semiconductor technologies is thermal oxidation: SiO_2 layers thermally grown on Si are used as a mask in diffusion doping of silicon, for passivation of p–n junctions and in

preparation of MOS structures. The demand for well-defined ultrathin silicon oxide films with good dielectric properties increases with each new generation of microelectronic devices; numerous methods of oxidizing silicon have been applied and proposed [1] and the challenge for current and future silicon oxide thin film fabrication methods is to be able to form well-defined, conformal silicon oxide films at temperatures which are sufficiently low so that dopant diffusion and interface degradation are not significant at length scales comparable to the dimensions of the device. Therefore a systematic investigation of the adsorption of carbon- and oxygen-containing molecules on Si is important because it can provide a better

* Corresponding author. Tel.: +39-0498277171; fax: +39-0498277102.

E-mail address: psil@pd.infn.it (P.L. Silvestrelli).

understanding of the interaction processes as well as hints for achieving synthesis and thermal oxidation under milder conditions.

Eng et al. [1], as part of continuing efforts to investigate the precursors of silicon oxide nucleation on silicon surfaces, studied adsorption of ethanol ($\text{C}_2\text{H}_6\text{O}$) on Si(1 0 0) using surface infrared absorption spectroscopy: according to their results, near room temperature, ethanol adsorbs dissociatively to form surface bound hydrogen and ethoxy ($\text{C}_2\text{H}_5\text{O}$) groups; the presence of features corresponding to Si–O stretching (at 756 cm^{-1}) and to Si–H stretching clearly indicate that O–H bond scission has occurred (it is assumed that the saturation coverage is 1.0 ML, i.e. one surface bound ethoxy group and one hydrogen per Si(1 0 0) dimer). The ethoxy groups are oriented such that the axis of the methyl group is nearly perpendicular to the surface, unlike the case for ethoxy groups bound to metal surfaces. *Ab initio* cluster calculations by the same group confirmed the proposed adsorption geometry and accurately reproduced the observed normal mode frequencies. Clearly, understanding the initial adsorption geometry of surface ethoxy species generated via the dissociative chemisorption of ethanol on Si(1 0 0) only represents the first step towards understanding the mechanism by which ethoxy decomposes.

The adsorption of ethanol on Si(1 0 0) at room temperature has been also investigated by Casaletto et al. using high-resolution synchrotron radiation photoemission [2]: their results support the dissociative adsorption scenario (with O–H scission) and suggest that no C–O bond rupture occurs, at variance with ethanol adsorption on Si(1 1 1) 7×7 [3].

More recently, Zhang et al. [4] studied the reaction of ethanol with the Si(1 0 0)-(2 \times 1) surface, using Auger electron spectroscopy, thermal desorption spectroscopy, and *ab initio* computations, based on a single-dimer cluster model. Their calculations show that the ethanol molecule initially interacts with the Si surface through the formation of a “dative bond”, which occurs with no energy barrier; once in this physisorbed state ethanol can proceed to react with the surface via a number of possible pathways, the most relevant

ones being characterized by O–H bond cleavage or O–C bond cleavage. Zhang et al. [4] find that each of the reaction paths out of the dative bond well have significant barriers to reaction, when measured from the bottom of this well, except for O–H bond cleavage, which appears to have a small barrier ($3\text{ kJ/mol} = 0.03\text{ eV}$); this barrier is calculated to be below the energy of the separated subsystems (free ethanol molecule and bare Si cluster), differently from all the other bond cleavage channels investigated. Although the O–H bond cleavage appears to be the kinetically favored reaction, the O–C bond cleavage is found to be thermodynamically the most stable final product. Moreover, low-energy electron diffraction (LEED) patterns indicate that, after ethanol adsorption at room temperature, the underlying Si dimer σ bonds are intact, thus suggesting adsorption by either dative bond formation or by an O–H addition reaction.

Although these theoretical results are interesting and apparently in qualitative agreement with some experimental findings, the accuracy of the method used is somewhat questionable. In fact, if the Si(1 0 0) surface is modelled using a single-dimer cluster, as done in Refs. [1,4], it is not possible to reproduce the correct “buckling” of the surface Si dimers. It is well known, however, that the asymmetric electron distribution resulting from the buckling distortion of the surface dimers is a key factor for the chemistry of dissociative molecular adsorption on the Si(1 0 0) surface: in fact buckling is essential for establishing orbitals that can interact effectively with the incident molecules [5]. Note that, Zhang et al. [4] themselves, by discussing the binding energy of the physisorbed state, admit that the description would be improved by using a larger dimer cluster model to account for any charge delocalization or surface relaxation that may be important for accommodation of the dative bond by the Si surface.

In order to overcome the limitations of previous theoretical calculations and to clarify a number of experimental findings we performed a full first principles study of adsorption of ethanol on Si(1 0 0), by using the Car–Parrinello approach [6], with a slab geometry and periodic boundary conditions. Using a slab geometry, in contrast with the

cluster model adopted in the previous calculations, allows us to reproduce the characteristic “buckling” of the surface silicon dimer, to correctly describe the different electronic properties of the “up” and “down” Si atoms, and also to take into account possible strain effects on the Si(100) surface due to the adsorption of the ethanol molecule.

Basically, in agreement with the results of previous theoretical calculations, we find that the kinetically favored process is represented by the O–H bond cleavage, while the O–C bond cleavage is thermodynamically more stable. However our estimate of the dative bond well is significantly different from that obtained using the single-dimer cluster approximation; as a result also the values of the estimated energy barriers (particularly that relative to the O–H bond cleavage) exhibit pronounced differences. Moreover, our use of a slab approach allows us to investigate the effects of different surface coverages too.

2. Method

Calculations have been carried out within the Car–Parrinello approach [6] in the framework of the density functional theory, using gradient corrections in the BLYP implementation [7]. Gradient-corrected functionals have been adopted in the most recent theoretical studies of adsorption of organic molecules on Si(100) because they are typically more accurate than the local density functional in describing chemical processes on the Si(100) surface [8,9]. The calculations have been carried out by taking spin polarization into account, considering the Γ -point only of the Brillouin zone, and using norm-conserving pseudopotentials [10]. Wavefunctions were expanded in plane waves with an energy cutoff of 70 Ry. We have explicitly checked that, at this value of the energy cutoff, the structural and binding properties of our system are well converged.

In order to test our method, we have preliminarily calculated the structural properties of the free ethanol molecule and other alcohol molecules, such as methanol (CH_3O), finding a good agreement with available experimental results (the difference between calculated and experimental bond

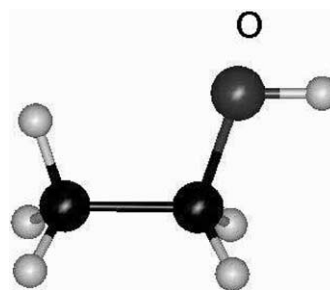


Fig. 1. Isolated ethanol molecule.

Table 1
Calculated structural parameters of the free ethanol molecule (see Fig. 1)

	Calc.	Expt. [11]
$d(\text{O–H})$ (Å)	0.97	0.97
$d(\text{C–O})$ (Å)	1.46	1.43
$d(\text{C–C})$ (Å)	1.54	1.51
$\angle\text{C–C–O}$ (deg)	107.7	107.8
$\angle\text{C–O–H}$ (deg)	108.1	105.0
$\angle\text{C–C–H}$ (deg)	111.1	111.0
$\angle\text{C–C–H}$ (deg)	111.8	110.0

C–H bonds have lengths in the range 1.094–1.098 Å.

lengths [11] is in any case less than 2%). The structure of the isolated molecule is shown in Fig. 1, while geometrical parameters are reported in Table 1.

The Si(100) surface is modelled with a periodically repeated slab of 5 Si layers and a vacuum region of 10 Å: such a relatively large value is required in order to make the interactions between the ethanol molecule with its periodic images negligible. A monolayer of hydrogen atoms is used to saturate the dangling bonds on the lower surface of the slab. We have used a supercell with $p(\sqrt{8} \times \sqrt{8})R45^\circ$ surface periodicity, corresponding to 8 Si atoms/layer and with the 2×2 surface reconstruction, i.e. the lowest-energy reconstruction of the Si(100) surface which is compatible with this supercell. This surface reconstruction is characterized by Si dimers alternatively buckled (the buckling angle being about 17°) along a dimer row. The estimates of the energy barrier characterizing different reaction paths have been obtained using a recently proposed variant of the popular “Nudged Elastic Band” method, i.e. the

“Climbing Image Nudged Elastic Band” (CI-NEB) method [12], which has proven to be a very efficient technique to determine minimum energy paths in complex chemical reactions. Other details of our approach can be found in Refs. [13–18].

3. Results

Both ethanol and water are known to dissociate across single Si(100) dimers; therefore one could expect that the driving force which cause this behavior is the same for both cases. *Ab initio* investigation of Konečný and Doren [19] of the reaction pathway for water dissociation on Si(100) shows that the mechanism is governed by electrostatic interactions between the water molecule and the surface dimer: they argued that the asymmetric surface electron distribution of the Si(100) surface (due to dimer buckling) defines the water molecule’s geometry of approach prior to chemisorption; in particular the calculations show that the electron-poor, “buckled-down” side of the dimer attracts the lone pair electrons in the oxygen of the water molecule, whereas the electron-rich, “buckled-up” side attracts one of the H atoms of the water molecule. For ethanol the dissociation mechanism could be similar. An interesting question is whether the dissociation process is direct or implies the existence of a metastable undissociated state, as it seems to be the case for adsorption of methanol [20].

We find that the ethanol molecule initially interacts with the Si surface through the formation of a “dative bond” between the O atom and a “down” Si atom (the electrophilic one) of a surface dimer. In such a physisorbed state the ethanol molecule remains essentially intact (undissociated) but it can have different orientations with respect to the underlying Si surface (see Fig. 2 and Table 2): in particular, the direction of the O–H bond can be parallel (configuration U1 and U3, the U3 structure being obtained from the U1 one by a rotation of 180° with respect to the surface) or perpendicular to Si dimers (configuration U2); the three structures are almost degenerate in energy (the rotation of the ethanol molecule around the Si–O bond turns out to be rather facile), although

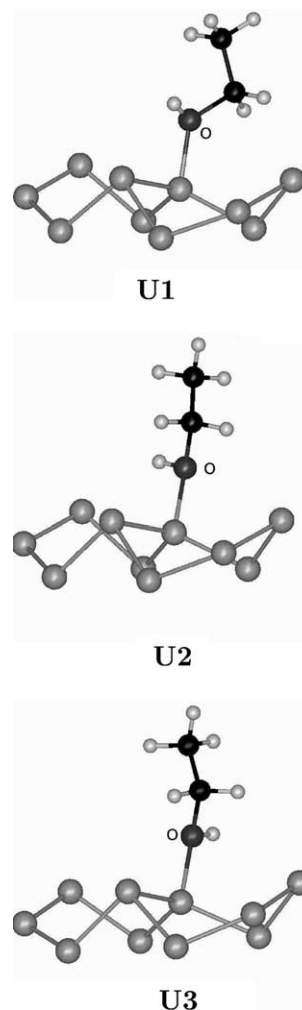


Fig. 2. Stable configurations for undissociative chemisorption of ethanol on Si(100). White, black, dark-grey, and light-grey balls indicate H, C, O, and Si atoms, respectively. For clarity only a few surface Si atoms are shown.

configuration U2 is slightly more favored. Note that Zhang et al. [4] reported only a physisorbed configuration similar to our structure U3 and found a binding energy (see Table 2) considerably smaller (less than a half) than ours: this discrepancy, found also in the case of methanol when comparison is made with other theoretical calculations [4], can be attributed to the fact that Zhang et al. use a single-dimer model, which turns not to be adequate in this case [4]. We have explicitly verified that adsorption into the U1, U2, or U3

Table 2

Binding energies and structural parameters of the configurations shown in Figs. 2 and 3, corresponding to 0.25 ML coverage

	U1	U2	U3	D1	D2	D3	D4	D5	D6
E_{bind} (eV)	0.88	0.91	0.86 (0.38)	2.55 (2.61)	3.15 (3.21)	1.46 (1.70)	1.51 (1.67)	2.59	1.91
$d(\text{O-H})$ (Å)	0.99	0.99	0.98	—	0.97	0.98	0.97	—	—
$d(\text{C-O})$ (Å)	1.52	1.52	1.53	1.46 (1.43)	—	1.47	1.46	—	1.28
$d(\text{C-C})$ (Å)	1.52	1.52	1.52	1.52 (1.52)	1.54	1.53	1.54	1.55	1.48
$d(\text{C-Si})$ (Å)	—	—	—	—	1.92	1.96	1.93	1.91	—
$d(\text{O-Si})$ (Å)	1.92	1.93	1.95	1.67	1.68	—	—	1.57	1.83
$d(\text{H-Si})$ (Å)	—	—	—	1.49 (1.68)	—	1.49	1.49	1.49	1.49
$d(\text{Si-Si})$ (Å)	2.43	2.46	2.46	2.42 (2.49)	2.46	2.44	2.44	2.48	2.44
Buckling (Si-Si) (deg)	11.3	12.1	11.7	0.6	0.1	0.8	1.3	2.2	3.6

Si-Si refers to the Si dimer on which the ethanol molecule, or its major fragment is bonded. In parenthesis we report the values obtained, using a simple-dimer cluster model, in Ref. [4] for the binding energies and in Ref. [1] for the bond lengths of the D1 configuration.

configuration, starting from an ethanol molecule far from the surface, is a barrierless reaction, so that it occurs spontaneously. Therefore, the undissociated U1, U2, and U3 structures (not clearly observed experimentally) represent shallow minima that the system can dynamically visit in a barrierless way at, e.g., room temperature.

Then, from such a physisorbed state ethanol can proceed to further react with the Si surface via a number of possible pathways, which imply breaking one or more molecule bonds, in order to realize more stable, dissociated configurations. A number of possible dissociated structures is shown in Fig. 3 (see also Table 2). The D1 structure can be obtained through breaking of the O-H bond, with the detached proton which forms a new bond with a Si surface atom; the most favorable configuration is one in which this proton is just attached to the Si atom of the same surface dimer to which the remaining ethoxy ($\text{C}_2\text{H}_5\text{O}$) fragment is bonded: in fact, for instance, if the H atom is attached to a Si atom of an adjacent dimer, the binding energy is reduced by about 0.3 eV; this result is in line with the absence of any spectral features attributable to the presence of H-Si-Si-H species [1]. In agreement with the results of Eng et al. [1] (and apparently differently from the findings of Zhang et al., looking at Fig. 2 of Ref. [4]), we find that the axis of the methyl group is nearly perpendicular to the Si(100) surface. Since in our case, with a single chemisorbed molecule, we realize a 0.25 ML coverage, we confirm the

suggestion of Eng et al. [1] that this “upright” orientation is not the result of repulsion between ethoxy groups at high coverages (note that, in contrast, ethoxy has been consistently observed to adopt a tilted configuration on metal surfaces). We also confirm that the O atom forms a single polar covalent bond with only one Si atom of the surface dimer (due to the localized and directed nature of the Si dangling bond), with the O lone pair electrons residing in nonbonding orbitals; instead in metals the tilted geometry for ethoxy suggests that the lone pair electrons of the O are closer to the metal surface, so that they might participate in some type of dative bonding interaction with the surface if there are unfilled surface states present [1]. A clear picture of the single polar covalent bond formed between the O and Si atom can be obtained by using the maximally-localized Wannier functions [21] which allow the total charge to be partitioned in a chemically transparent and unambiguous way. By looking at the distribution of the centers of these Wannier functions one finds that four centers are located around the O atom forming an almost tetrahedral geometry (due to spin degeneracy every center corresponds to a localized couple of electrons): two of them (whose distance from the O atom is about 0.3 Å) represent the lone pairs, one is located between Si and O (the distance from O and Si is 0.44 and 1.24 Å, respectively) and clearly describes the Si-O polar single covalent bond (this center is much closer to the more electronegative O atom), and another

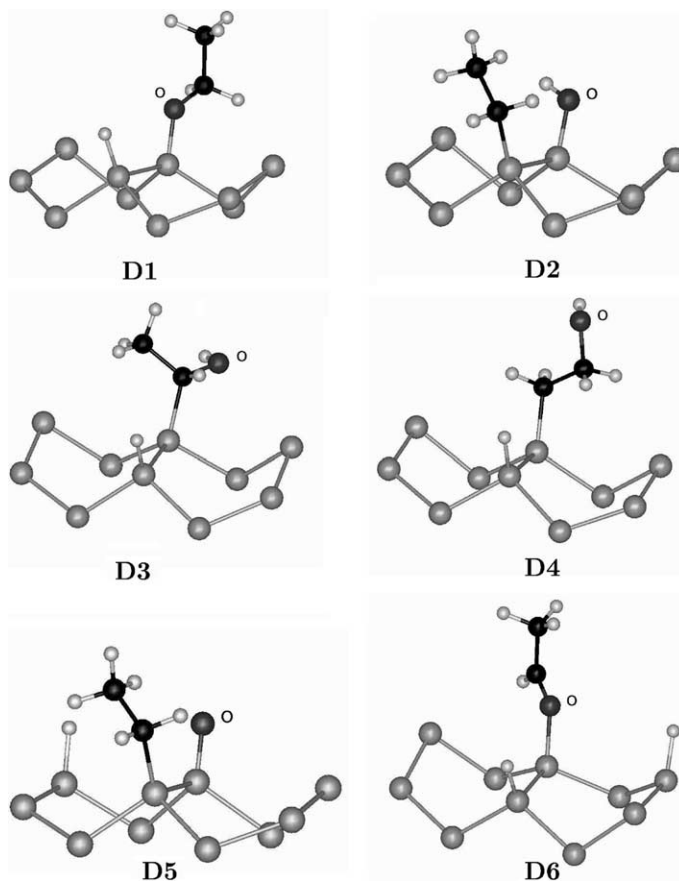


Fig. 3. Stable configurations for dissociative chemisorption of ethanol on Si(100).

one is between O and C (the distance from O and C is 0.50 and 0.96 Å, respectively) and corresponds to the polar covalent bond between O and C.

The D2 configuration is characterized by the C–O bond cleavage, with the axis of the methyl group which is now tilted; it is clearly thermodynamically more stable than the D1 one. Also in this case the most favored structure has the OH group and the C₂H₅ fragment bonded to the same Si dimer (the configuration with the two fragments on adjacent dimers is higher in energy by about 0.4 eV). Chemisorption in the D3 structure is obtained by breaking a C–H bond (of the C atom bonded to the O atom); although this configuration is possible, it is evidently less stable than both D1 and D2 (also in this case the axis of the methyl group is tilted). Configuration D4 has a binding energy

comparable to that of the D3 one and is characterized by cleavage of a C–H bond of the methyl group; note that, in contrast to the findings of Zhang et al. (see Fig. 4 of Ref. [4]), the C–O bond is nearly perpendicular to the Si surface. The configuration D5 can be obtained from the D2 one by breaking the O–H bond and attaching the detached proton to an adjacent dimer; as can be seen this structure is energetically less favored than the original D2. Also D6 is realized by an O–H bond cleavage but starting from the D1 configuration; again the new configuration is higher in energy than the original one by more than 0.6 eV. The energy trend relative to these different chemisorbed structures is in line with the general chemical picture: ethanol (and, in general, any alcohol) tends to dissociate by losing the OH group and, on a

secondary instance, H as a result of the deprotonation of OH, while breaking C–C or C–H bonds is energetically less favorable.

As far as the structural properties are concerned, we note that (see Table 2), as one can expect, the lengths of the bonds formed by the O atom, with Si or C, decreases by decreasing the total number of bonds of O. Moreover, the buckling angle of the Si dimer on which the ethanol molecule (or its major fragment) is bonded remains substantial for the undissociated, U1, U2, and U3 configurations, while it tends to vanish in the case of the dissociated ones. Interestingly, in the cases where a comparison with the binding energies obtained by Zhang et al. [4] is possible (see Table 2), our results are in reasonable agreement for the dissociated structures (where the buckling angle is vanishing) while, as already mentioned above, the difference in the case of the undissociated structures is large; this further supports the idea that a cluster approach based on a single dimer (where an accurate description of the Si dimer buckling is not possible) is not entirely reliable for studying such a system since some configurations are predicted to have a too small binding energy. In the case of the D1 configuration a comparison is possible for some bond lengths obtained by Eng et al. [1]: as can be seen from Table 2, there is a substantial agreement with the exception of the Si–H (on dimer) bond length which we find considerably shorter than in Eng et al. [1].

Clearly, in order to predict the probability of a possible stable adsorption configuration it is important not only to estimate its thermodynamical stability (i.e. the binding energy of the system in a given configuration), but also to take kinetic effects into account by evaluating the energy barrier (if any) that the system must overcome to arrive at this configuration. Therefore we have estimated the energy barriers relative to different possible chemisorption mechanisms (the most interesting processes are reported in Table 3). As mentioned above the adsorption into the undissociated, U1, U2, and U3 structures is a barrierless reaction. Therefore it appears reasonable to investigate the reaction paths going from these configurations to the dissociated ones. In particular, for

Table 3

Estimated energy barriers, E_b , and transition state energy levels, E_{TS} (with respect to the energy of the separated subsystems) for different possible dissociation processes (see discussion in the text)

Reaction	E_b (eV)	E_{TS}
(C ₂ H ₆ O + Si(1 0 0)) → U2	0.00 (0.00)	–
U1 → D1	0.50 (0.03)	–0.37 (–0.35)
U2 → D2	1.00 (0.78)	+0.10 (+0.39)
U2 → D2'	2.29	+1.39
D1 → D6	3.17	+0.62

In parenthesis we report the values obtained, using a simple-dimer cluster model, in Ref. [4] (in this case the starting configuration was similar to our U3 structure).

the transformation to the D1 structure, we considered, as a starting configuration the U1 one; in fact, among the undissociated configurations this appears to be the optimal initial structures since it is characterized by a O–H bond already oriented parallel to the underlying Si dimer (however one expects that the energy barrier of similar reactions starting from the U2 or U3 configurations have only slightly higher energy barriers because the rotation around the O–Si bond is rather facile: for instance we estimate that the barrier starting from U2 is only 0.1 eV higher). As can be seen in Fig. 4 this reaction is characterized by an energy barrier of 0.5 eV; since the binding energy of the U1 structure is about 0.9 eV this means that the barrier for the whole process (adsorption into the U1 structure and subsequent transition to the D1 configuration) is calculated to be below the initial energy of a free ethanol molecule and a bare Si(100) surface, so that the whole reaction is *exothermic*. In strict analogy with the case of reactions of methylamines on Si(100) [22] this reaction can also be seen as a proton transfer process from oxygen to the electron-rich, nucleophilic “up” silicon atom of the dimer. Note that, although our results are in qualitative agreement (see Table 3) with the findings of Zhang et al. [4] (the whole process is found to be exothermic), our estimated energy barrier value is an order of magnitude larger than in Ref. [4]; again this is related to the underestimation by Zhang et al. [4] of the binding energy of the undissociated configuration.

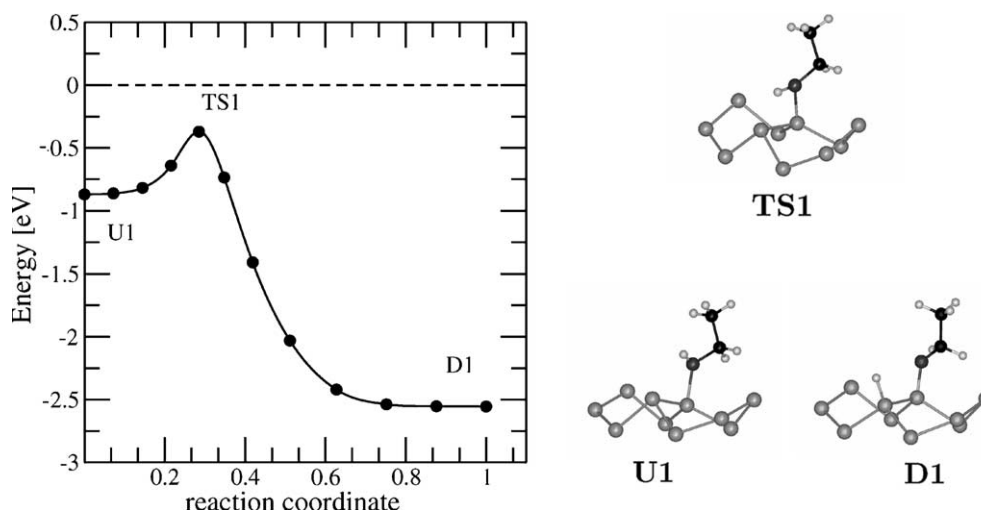


Fig. 4. Dissociative reaction path from U1 to the D1 configuration. The zero of the energy is the vacuum level and corresponds to the separated subsystems (free ethanol molecule and clean Si(100) surface).

Starting from the ethanol molecule physisorbed in an undissociated structure the C–O bond cleavage can occur through two basic, different processes: either the OH group remains attached to the Si atom and the ethoxy group is detached and forms a new bond with the other Si atom of the surface dimer (this U2–D2 reaction is similar to that proposed by Zhang et al. [4], see Fig. 5), or it is the OH group which moves away and form a

new bond with the other Si atom, while, at the same time, the C atom of the ethoxy group forms a bond with the original Si atom (reaction U2–D2'). As can be seen from Table 3 the former reaction is largely favored, although its energy barrier of about 1.0 eV (note that Zhang et al. [4] obtained 0.8 eV) is twice as large as that of the U1–D1 reaction discussed previously and makes the whole process *endothermic*.

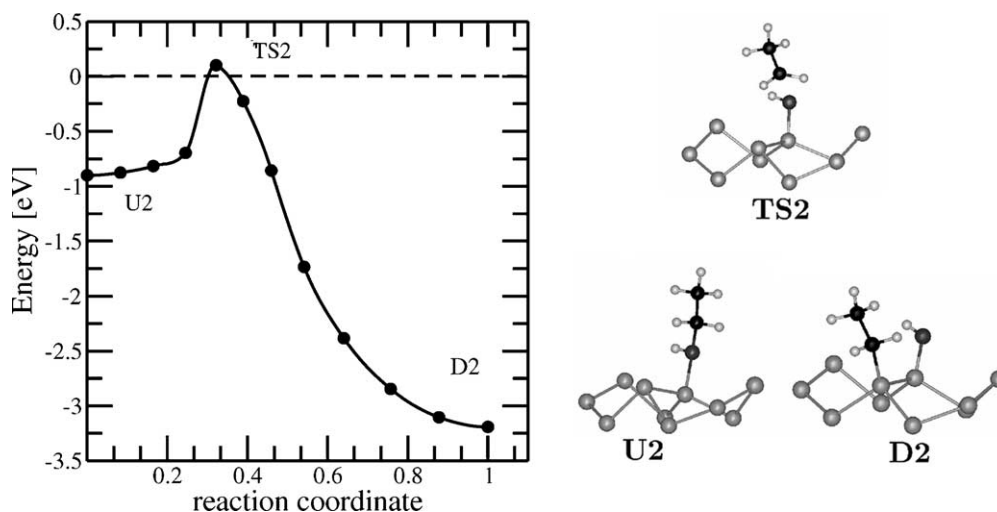


Fig. 5. Dissociative reaction path from U2 to the D2 configuration. The zero of the energy is the vacuum level and corresponds to the separated subsystems (free ethanol molecule and clean Si(100) surface).

Therefore, according to our calculations, although the dissociated D2 configuration turns out to be thermodynamically more stable than the D1 one, we expect that it is kinetically less favorable, particularly at room (or lower) temperature. This scenario is similar to that proposed for adsorption of methanol on Si(1 0 0) [20].

Whereas the dative bonded undissociated structures, U1, U2, and U3 can be considered to be metastable precursors to the more stable D1 configuration, they probably have not a sufficiently large binding energy at room temperature to compete as observable reaction products (we expect that the majority of the ethanol molecules adsorbed into the undissociated configurations will not remain trapped in these structures for a long time). Note that this scenario is substantially different from what happens, for instance, in the case of 3-pyrroline on Si(1 0 0) [18]. In fact organic molecules containing nitrogen atoms (such as primary and secondary amines) are instead characterized by a more stable physisorbed, dative bond well [18,22–24] so that thermal desorption experiments detect a small parent desorption channel due to trapping in this well [24]. In the case of ethanol on Si(1 0 0) the extra stabilization of the O–Si bond relative to the N–Si bond is consistent with the lack of any observed alcohol parent recombination products for primary alcohols [4].

Finally, we consider the transition from configuration D1 to D6, which occurs by detaching a H atom from the ethoxy group. This reaction path is related to a proposal of Zhang et al. [4] who suggest that, after initial O–H bond cleavage (i.e. chemisorption into the D1 structure), there could be a hydrogen elimination reaction to produce aldehydes and hydrogen, which is also observed as a desorption product. As can be seen from Table 3 the energy barrier for this process is relatively large, thus suggesting that the reaction is highly unfavored. The same is true for a similar transformation in which the C–O bond is broken and the C₂H₅ group bonds to a Si atom of a surface dimer adjacent to that already saturated by the O and H atoms. These conclusions are in agreement with the experimental findings of Casaletto et al. [2] who found, in their high-resolution photoemission study, no evidence of fragmentation of

the ethoxy group, at variance with the case of ethanol adsorption on Si(1 1 1) [3].

In summary, for the cases in which a direct comparison with the results of Zhang et al. [4] is possible, we note that, although the energy level of the transition state of the U1–D1 transformation is in reasonable agreement, there are instead substantial differences in the value of the energy barrier of this transformation and in both the energy level of the transition state and the energy barrier value relative to the U2–D2 transition. Again this is directly related to the large underestimate in Ref. [4] of the binding energy of the physisorbed state due to the use of a single-dimer cluster approximation.

The fact that we adopt a slab approach, instead of a single-dimer cluster model, allows us to simulate adsorption of ethanol on Si(1 0 0) at different coverages too, for the basic configurations, U2, D1, and D2; in particular, given our choice of the supercell (with four surface Si dimers), by putting one, two, and four ethanol molecules on top of the Si(1 0 0) surface corresponds to a 0.25, 0.50, and 1.00 ML coverage, respectively. In the case of the 1.00 ML coverage we considered a 2 × 2 periodicity in which the ethanol fragments are alternated on adjacent Si dimers. The values of the binding energy per ethanol molecule are reported in Table 4. As can be seen, even at high coverage, the energetic ordering remains the same, however the binding energy per molecule does not vary appreciably by increasing the coverage for the D1 structure, while it decreases both for the U2 and D2 (particularly going from 0.5 to 1.0 ML coverage), thus indicating a significant repulsive interaction among sufficiently close ethanol molecules chemisorbed into these latter structures. Therefore, taking also kinetic effects into account (see the previous discussion) we can conclude that the

Table 4
Binding energies (in eV/molecule) of the basic configurations of ethanol on Si(1 0 0) at different surface coverages

Coverage	U2	D1	D2
0.25 ML	0.91	2.55	3.18
0.50 ML	0.85	2.54	3.18
1.00 ML	0.67	2.57	2.97

D1 dissociated structure is favored also at high coverages, the 1.0 ML coverage appearing as the saturation coverage; note that this corresponds to 0.5 ML coverage following the convention of Zhang et al. [4], who, on the basis of Auger spectroscopy measurements, estimate a saturation coverage of 0.42 ± 0.10 (i.e. roughly one molecule per surface dimer).

4. Conclusions

In conclusion, our first principles study, based on a slab approach, of chemisorption of ethanol on the Si(100) surface confirms the qualitative scenario proposed by previous theoretical and experimental papers: the ethanol molecule initially interacts with the Si surface through the barrierless formation of a dative bond; from this physisorbed state the O–H bond cleavage process is the kinetically favored dissociation reaction. However, some relevant quantitative differences from the results of previous studies clearly show the limitations of a single-dimer cluster model. Moreover, our use of a slab approach allowed us to study the system at different surface coverages.

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