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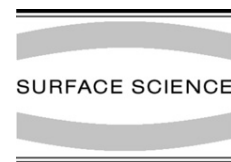


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# Fragmentation pathways of acetic acid upon adsorption on Si(100)2 × 1

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## Abstract

The reaction of acetic acid on the Si(100)2 × 1 surface has been investigated by density functional calculations on a two-dimers cluster model. We found that, once in the physisorbed state, acetic acid can proceed to react via two different pathways. In the first one, the cleavage of the hydroxylic bond is followed by a number of migrations of the dissociated hydrogen as well as structural rearrangements that eventually lead to the incorporation of an oxygen atom into the silicon surface, with a Si–O–Si structure. The second reaction pathway involves an initial C–H bond breakage, and evolves into a C–C bond cleavage and binding of the separate methyl and carboxylic fragments on top of a silicon dimer.

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## 1. Introduction

There is a growing interest in the functionalization of silicon surfaces in view of the development of new nanoelectronic devices [1,2], as well as bioelectronics such as biomolecules, DNA microarrays, protein chips, cell chips and neuron chips [3].

Carboxylic acid is a main constituent in the biomolecules, together with amines and alcohols. Therefore, a study on the reaction of carboxylic molecules with semiconductor surfaces will provide a clue to the understanding of biomolecules reactions as well.

Oxygen-containing functional groups are very good candidates to bind to the silicon surface, because of the strong Si–O bond. There are several examples of mono and bifunctional alcohol molecules such as methanol [4], ethanol [5], phenol [6] bonded through the oxygen to the silicon surfaces.

As far as the carboxylic acid is concerned, there are two similarly reactive oxygen atoms, which might give rise to the adsorption process. Theoretical and experimental investigations on formic acid show a preference for the monodentate (i.e. with one oxygen only) adsorption on Si(100)2 × 1 [7–9]. This is at variance with the behaviour on metals, where the bidentate (i.e. with both oxygen atoms) adsorption is observed [10].

However, when longer chains are attached to the carboxylic acid, other adsorption pathways may occur that involve a C–C bond breakage and C–Si bond formation.

In this paper, we present a theoretical investigation on the adsorption modes of acetic acid on Si(100)2 × 1.

We found that the first physisorption step occurs barrierless and, then, two possible fragmentations occur involving either a C–H or a O–H bond breaking.

We performed *ab initio* DFT based calculations using the CPMD code [11]. Since the accuracy in the description of the chemical processes on silicon surface has been shown to improve with respect to the pure local density approximation (LDA) when gradient correction is taken into account, we adopted the corrected gradient approximation

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(GGA) to the BLYP [12a,12b] functional for exchange energy.

## 2. Computational methodology

The calculations were carried out using norm-conserving Trouiller–Martins pseudopotentials [13]. The wave functions were expanded in plane waves with an energy cutoff of 60 Ry, a value for which the structural and binding properties of the systems are all well converged. The calculations were performed under periodic boundary conditions with the periodically repeated unit cells referred to as super-cell. A surface model is built with  $\text{Si}_{24}\text{H}_4$  corresponding to six layers of Si atoms and two ( $2 \times 2$ ) surface dimers. The silicon layers were included in this super-cell with vacuum regions of about 14 Å in the [001] direction (twice as much the slab dimension in the [001] direction, i.e. 12 interlayers). For such a super-cell the Brillouin zone was sampled by  $\Gamma$ -point approximation. A monolayer of hydrogen is used to saturate the dangling bonds on the lower side of the slab. The first two layers of silicon and the acetic acid are allowed to fully relax. The super-cell parameters were kept fixed during the optimization and geometry structures were relaxed until forces dropped below  $10^{-4}$  a.u.

The transition states were searched by the partitioned function rational optimizers (PRFO), implemented by Billster et al. [14].

## 3. Results and discussion

The adsorption of acetic acid on  $\text{Si}(100)2 \times 1$  may occur through different pathways, yielding different dissociation products. In order to interact with the surface, the acetic acid may break in different points. The hydroxylic bond, a methyl C–H or the backbone C–C bond may be involved in the interaction with the surface. In the first case, upon cleavage of the O–H bond, one or two oxygen atoms may be involved in the binding process with silicon. All those possibilities were investigated in the present paper and are presented in two sections. In the first one, the stable structures we found (local minima) are discussed. In the second one the pathway of different structural evolutions are presented.

Throughout the paper, the adsorption and transition energies are calculated as difference between the energy associated to an adsorption or transition model and the energy of the separate acetic acid and silicon moieties.

### 3.1. Local minima

Acetic acid can give rise to many products upon adsorption on  $\text{Si}(100)$  surface. Our DFT calculations led to nine local minima of the adsorption energy, when adsorbed on the two-dimers model. They are shown in Fig. 1 (structure 1 through 7) and Fig. 2 (structures 1, 8 and 9) together with the geometrical parameters.

Acetic acid interacts with the electron-deficient down atom of the silicon dimer to yield the shallow minimum 1 in Figs. 1 and 2. This corresponds to an O → Si dative bond with a Si–O distance of 3.72 Å and an adsorption energy of  $-0.0396$  eV.

The local minima 2, 3 and 4 all represent a dissociative adsorption of the hydroxyl group giving rise to a monodentate adsorption of the acetate, i.e. with only one of the two carboxylic oxygen atoms bonded to the silicon surface. These structures differ for the positions of the dissociated hydrogen. Structure 2 corresponds to a bond breaking, where both resulting fragments remain on the same atom of a silicon dimer. The Si–O bond is 1.713 Å and the adsorption energy  $-0.686$  eV. In structure 3 the hydroxyl hydrogen and the acetate fragments are situated each on a silicon atom of the same dimer. In this case the Si–O is slightly shorter than in structure 2, i.e. 1.688 Å. The adsorption energy is  $-0.826$ . Structure 4, where the acetate and the hydrogen fragments occupy the silicon sites of two neighbouring dimers, is the most stable of the three monodentate structure ( $-1.14$  eV) and the Si–O bond length is 1.701 Å.

Upon adsorption of the acetic acid in the monodentate configuration, a rearrangement of the silicon dimers occur. In structure 2, the simultaneous adsorption of both acetate and hydrogen fragments on the same atom causes a swap of orientation of the silicon dimer involved, such that the down silicon atom is pushed upwards. The adsorption of the acetate and hydrogen fragments on each silicon atom of a dimer in structure 3 makes the dimer almost symmetric. In structure 4 both dimers of the cluster are involved in the adsorption. As a result, the dimer bearing the dissociated hydrogen is rather symmetric, and the one carrying the acetate is somewhat asymmetric, with a push upwards of the originally down atom.

Structure 5 represents a bidentate adsorption of the acetate fragment, with both oxygen atoms of the carboxylic group simultaneously bonded to each atom of same silicon dimer. The Si–O bonds are slightly longer than in the monodentate structures (1.849 Å and 1.856 Å) and the adsorption energy is lower ( $-1.931$  eV). The two-dimers carrying the fragments are completely (bidentate acetate) and almost completely (dissociated hydrogen) symmetric.

In structure 6, both oxygen atoms and the carboxylic carbon is at bonding distance with the silicon surface. The Si–O distances are 1.699 Å and 1.748 Å, the Si–C distance is 1.929 Å. In this case the silicon atom of the dimer interacting with the carbon is pushed upwards and the dimer carrying the dissociated hydrogen is symmetric. The binding energy is  $-1.171$  eV, similar to the monodentate structure 3.

In structure 7 one of the carboxylic oxygen atoms dissociates from the acetate, infiltrates into the surface and bridges between two silicon atoms yielding a Si–O–Si structure. The acetate fragment bridges to the silicon surface with the remaining oxygen atom (Si–O 1.854 Å) and the

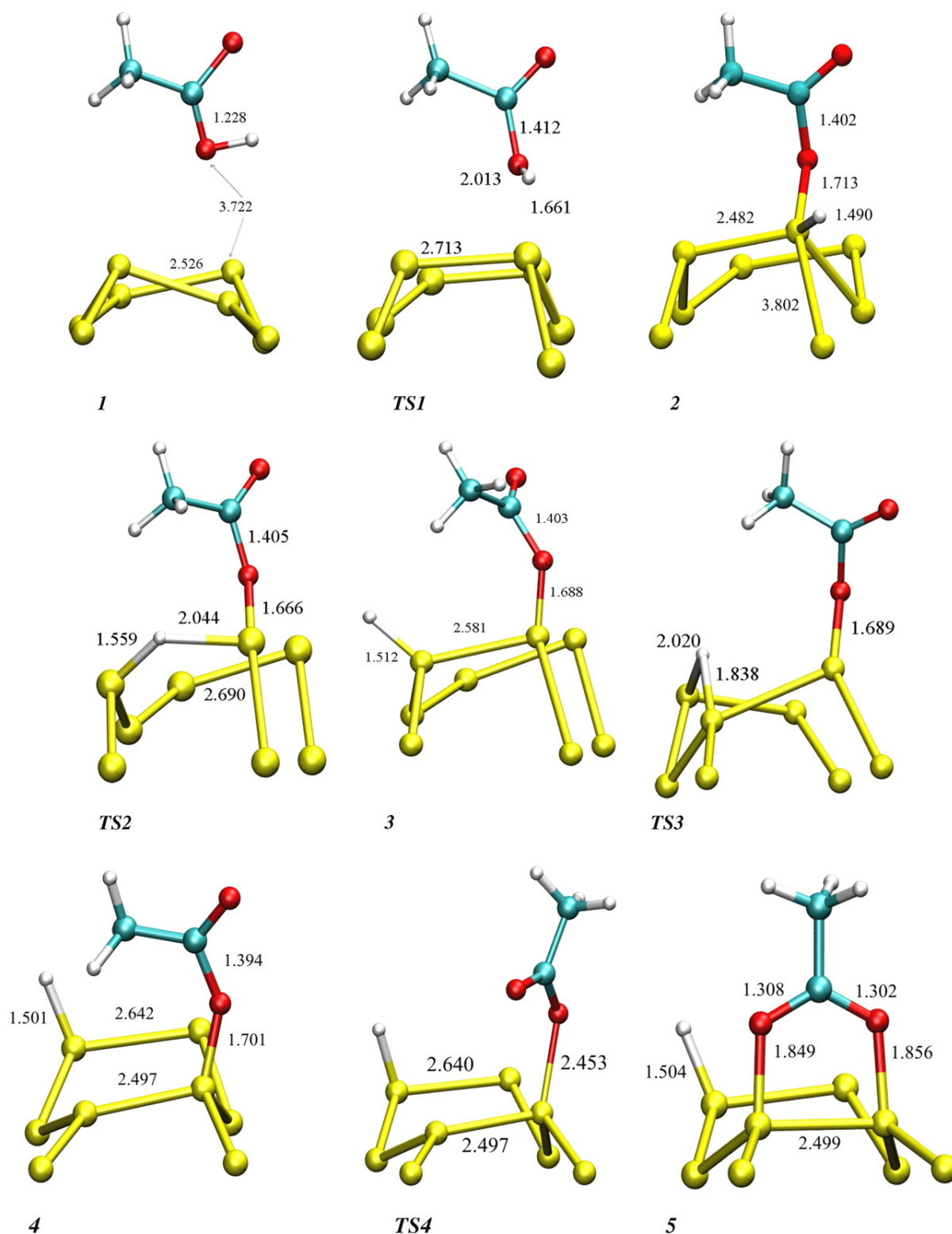


Fig. 1. First pathway of acetic acid adsorption on Si(100)2 × 1. **1** is the physisorbed state. In **2**, **3** and **4** the acetate fragment has monodentate configuration. **5** is a bidentate structure, **6** a bent-bidentate and **7** a dissociated acetate. **TS1**, **TS2**, **TS3**, **TS4**, **TS5** and **TS6** are optimized transition states, that evolve in the local minima **2**, **3**, **4**, **5**, **6**, and **7**, respectively. Only the top two silicon layers are represented. The main geometrical parameters are reported (distances are in Å).

carboxylic carbon (Si–C 1.949Å) in a cyclic Si–C–O–Si structure. The silicon dimer carrying the dissociated hydro-

gen remains symmetric also in this structure, where the dimer carrying the acetate is asymmetric as in the previous

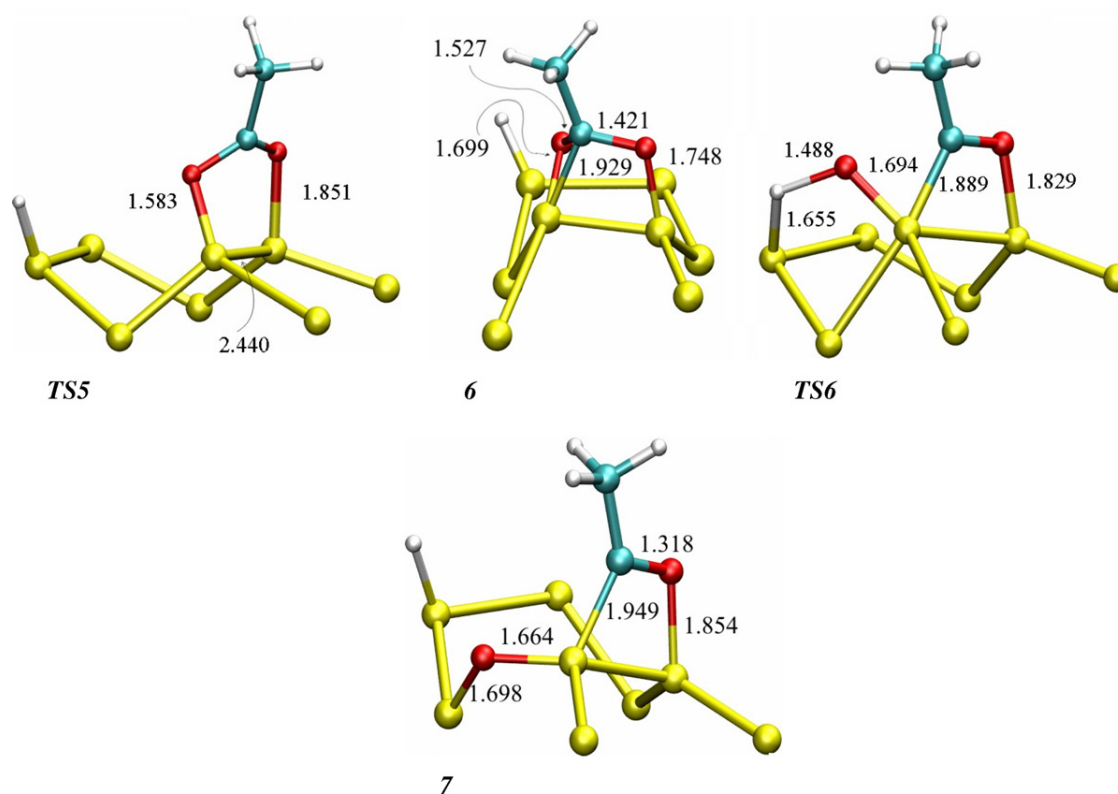


Fig. 1 (continued)

case. The adsorption energy is the lowest of all the investigated structures ( $-2.486$  eV).

The other minima correspond to a different dissociation pathway that yields structures where the cleavage of the acetic acid occurs at the level of the C–H and the C–C bonds (structures **8** and **9**, respectively).

Structure **8** is the outcome of a hydrogen extraction from a methyl group by a Si atom. In this case the acetate fragment is bonded through the methyl carbon to the silicon surface (Si–C  $1.962$  Å) and the dissociated hydrogen derives from the methyl group. Two neighbouring dimers are involved in the adsorption process, the one carrying the larger fragment is symmetric, the one carrying the hydrogen is only slightly asymmetric. The adsorption energy is  $-0.811$  eV.

In structure **9** a cleavage of the acetic acid carbon–carbon bond occurred and both the methyl and the carboxylic carbon atoms are simultaneously bonded to the same silicon dimer, which becomes symmetric (the other dimer, which does not carry any adsorbate remains asymmetric). The Si–C distances are  $1.905$  Å (methyl fragment) and  $1.969$  Å (carboxyl fragment) and the adsorption energy  $-0.584$  eV.

### 3.2. Reaction pathways

The pathways that lead structure **1** to the dissociation products **7** and **9** are reported in Figs. 1 and 2, respectively.

Furthermore, the corresponding energy diagrams are displayed in Fig. 3.

Acetic acid molecularly adsorbs without any energy barrier on the buckled-down silicon atom as expected for the formation of a dative bond through the donation of the oxygen lone pair to the electrophilic dimer site. Once adsorbed, the acetic acid can proceed to react with the surface via a number of pathways. As evidences in Fig. 1 and chart 1 (Fig. 3), seven transition states have been identified along the reaction pathway that leads from **1** to **7**. This pathway goes through a monodentate intermediate, which is followed by the migration of the dissociated hydroxyl hydrogen on the surface. Geometrical rearrangements change the configuration of the acetate from monodentate to bidentate and a further C–O bond cleavage results in the oxygen insertion into the silicon surface. This is accomplished by undergoing a series of geometrical and bond rearrangements and cyclic transition states.

Structure **1** evolves into the optimized transition state **TS1**, which shows an elongation of the C–O bond and simultaneous shift upwards of the down silicon atom (to yield a symmetric structure) and consequent lengthening of the Si–Si dimer bond by  $0.213$  Å. In this state the Si–O distance is  $2.013$  Å. The hydroxyl hydrogen is still bonded, but stretched to  $1.661$  Å. The transition energy is  $0.36$  eV. The transition state **TS1** relaxes into the local minimum **2**, where the hydroxyl group is dissociated and the hydrogen and acetate fragments both bind to the same silicon atom.

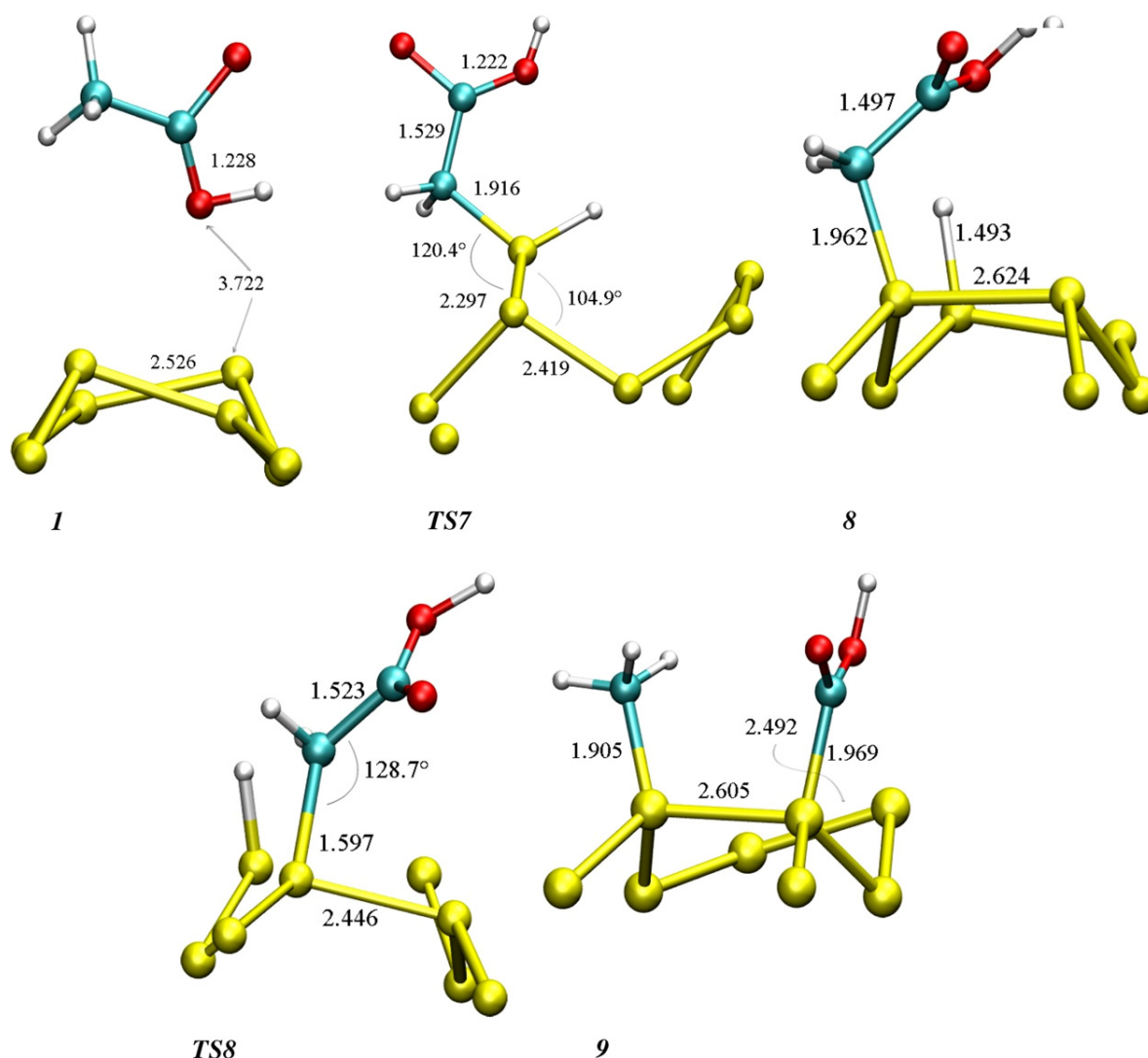


Fig. 2. Second pathway of acetic acid adsorption on Si(100) $2 \times 1$ . **1** is the physisorbed state. Structures **8** and **9** correspond to methyl C–H and C–C cleavage, respectively. **TS7** and **TS8** are optimized transition states, that evolve in the local minima **8**, **9**, respectively. **TS7** is  $90^\circ$  rotated, compared to the other projections, in order to show the geometrical parameters. Only the top two silicon layers are represented. The main geometrical parameters are reported (distances are in Å).

This minimum is followed by a first hydrogen migration from one atom of the silicon dimer to the other (**TS2**), a relaxation into the local minimum **3** and another migration of the hydrogen originally belonging to the hydroxyl group from one dimer to the neighbouring one (**TS3**). Cyclic Si–H–Si intermediates are formed in the transition states **TS2** and **TS3**. In **TS2** the two Si–H distances are 1.559 Å and 2.044 Å and the transition energy 0.46 eV. This structure relaxes into the minimum with the acetate and the hydrogen fragment each on top of two silicon atoms of the same dimer (**3**). The next hydrogen migration on a neighbouring atom shows a higher transition energy, i.e. 1.03 eV. In this transition state the Si–H distances are 1.838 Å and 2.020 Å, longer than in **TS2**. Furthermore, a partial rearrangement of the monodentate structure occurs, with a rotation of the acetate around the Si–O bond, in order to minimize the repulsion of the bridged hydrogen.

The state **TS3** relaxes into the structure **4**, which corresponds to a deeper minimum compared to the monodentate structures **2** and **3**.

The migration of the hydrogen atom on a neighbouring dimer allows the monodentate acetate to undergo a transition through the state **TS4** and relaxation into the lower energy state **5**, with both oxygen atoms of the acetate fragment bridged on a silicon dimer, i.e. in a bidentate conformation. The transition energy is 0.45 eV, and the adsorption energy 1.93 eV. In the transition state **TS4** the acetate rotates around the Si–O bond till the C–C axis is almost perpendicular to the surface and the Si–O bond is elongated to 2.453 eV.

In a theoretical investigation of acetic acid adsorption on Ge(100) [15] several monodentate and bidentate configurations were calculated, with the dissociated hydrogen in different positions relative to the acetate fragment. In

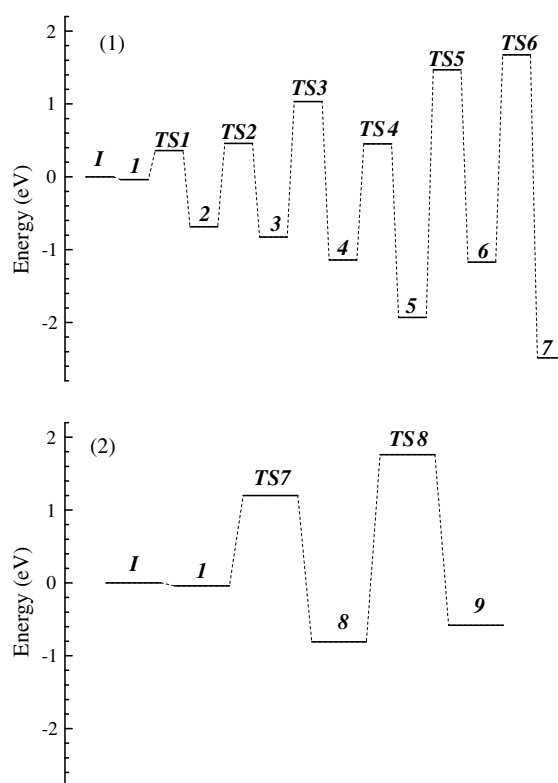


Fig. 3. Energy charts of the two reaction pathways of acetic acid on Si(100) $2 \times 1$ . **I** represents the level of the separate acetic acid + silicon surface moieties.

general, it was found that the bidentates configurations were more stable than the monodentate ones. Furthermore, a nudged elastic band calculation was performed to evaluate the barrier for the transition of a specific monodentate (NA1), similar to structure 3 in the present study, with the acetate and the hydrogen atoms each on top of an atom of a germanium dimer, to a bidentate configuration with the carboxylic oxygen atoms bridging over two dimers (end-bridge configuration EB). An energy barrier of 0.28 eV/molecule was found. It is worth noticing that the EB structure is not the most stable of all the bidentate ones (it is 0.29–0.35 eV less stable than the deepest lying bidentate configuration, depending on the coverage), but it does not require any hydrogen migration for the monodentate-to-bidentate transition to occur. In this case, the energy barrier is attributed to the switch of the dimer buckling that occurs in the transition and that may induce buckling change in a complete dimer row.

As for the adsorption of the acetic acid on Si(100), the buckling switch is more likely related to the early stages of adsorption and the hydrogen migrations, than to the monodentate-to-bidentate transition itself. However, the possibility for the acetate to transform from monodentate to bidentate requires both the hydrogen migrations to occur prior the transition itself. As a consequence, it would not be surprising if also the acetate stays monodentate as it was found for formic acid [6–8].

Acetic acid may undergo a further fragmentation on the silicon surface. The bidentate structure may bend asymmetrically towards the surface into transition state **TS5**, which also displays a shortening of one of the Si–O bonds to 1.583 Å. This state, which has a transition energy of 1.469 eV, then relaxes into structure 6 (bent bidentate) where both the carbon and one oxygen atoms of the carboxylic group are at binding distance with one silicon atom of the dimer. The adsorption energy of the latter structure is comparable to that of the monodentate structure 4.

A further evolution of the system is possible, i.e. the bent bidentate may undergo another transition assisted by the hydrogen on the neighbouring dimer (**TS6**), with final incorporation of one oxygen atom into the silicon surface to yield a Si–O–Si structure (7). The local minimum of structure 7 is the deepest of the series (–2.49 eV), but also the transition energy to overcome the last transition is high, 1.67 eV.

An alternative pathway to the hydroxyl dissociation and acetate adsorption through one or two carboxylic oxygen atoms is the cleavage of the C–C bond and the formation of two fragments both bonded to the silicon through Si–C bonds. The latter pathway is sketched in Fig. 2 and chart 2 (Fig. 3). The process occurs in two steps. State 1 may undergo a transition to the state **TS7** and relax into the state 7, which is a fragmentation of acetic acid into an end-bridge configuration. In the optimized state **TS7** the up atom of the silicon dimer is further shifted upward to interact with the methyl group of the acetic acid. The outcome is a transition state with a dissociated methyl group where the resulting acetyl and hydrogen fragments are bonded simultaneously to the same silicon atom. In Fig. 2 the transition state **TS7** is 90° rotated with respect to the projection of the other structures, in order to show the geometrical parameters more clearly. The large upward shift of the silicon atom and the methyl dissociation cause a transition energy of 1.202 eV. This state relaxes into structure 8, where the silicon dimers are lowered back into the surface. In the downward movement the hydrogen fragment hops onto a neighbouring dimer. The adsorption energy of structure 8 is 0.81 eV. A further fragmentation of the acetate is possible and involves the C–C backbone. Structure 8 may evolve into the transition state **TS8**, where the acetyl fragment bends towards the surface and the Si–C bond is shortened to 1.597 Å. The hydrogen atom is also bent towards the acetyl fragment. The transition energy is 1.76 eV. The relaxation of this state yields the final conformation 9, with Si–methyl and Si–carboxyl on either atoms of a single dimer, and an adsorption energy of 0.58 eV.

#### 4. Conclusion

We have investigated the acetic acid adsorption on Si(100) $2 \times 1$  by first principle calculations. We found a first barrierless physisorption, which may evolve in two possible fragmentation pathways, one involving an initial O–H bond, the other one an initial C–H bond cleavage.

The first reaction pathway proceeds via a dissociative adsorption on a single atom of a silicon dimer followed by several rearrangements of the dissociated hydrogen on the silicon dimers. The system evolves by forming a bidentate adsorbate and eventually an incorporation of an oxygen atom into the silicon surface, with a Si–O–Si structure.

The second pathway goes through an hydrogen extraction from a methyl group, followed by a rearrangement that ends up in a the cleavage of the C–C backbone bond.

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