

## Comparative study of the adsorption and dissociation of vinylacetic acid and acrylic acid on silicon (001)

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In this work, we employ the state of the art pseudopotential method, within a generalized gradient approximation to the density functional theory, to investigate the adsorption process of acrylic acid (AAc) and vinylacetic acid (VAA) on the silicon surface. Our total energy calculations support the proposed experimental process, as it indicates that the chemisorption of the molecule is as follows: The gas phase VAA (AAc) adsorbs molecularly to the electrophilic surface Si atom and then dissociates into  $\text{H}_2\text{C}=\text{CH}-\text{COO}$  and H, bonded to the electrophilic and nucleophilic surface silicon dimer atoms, respectively. The activation energy for both processes correspond to thermal activations that are smaller than the usual growth temperature. In addition, the electronic structure, calculated vibrational modes, and theoretical scanning tunneling microscopy images are discussed, with a view to contribute to further experimental investigations.

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### I. INTRODUCTION

In the past few years, the success of the study of organic systems' intrinsic properties resulted in the search of new device development with tailorability inherent to these materials. The diversity of properties that make organic materials so appealing is exemplified by organic light emitting diodes (LEDs) that have allowed access to the entire visible color spectrum.<sup>1</sup> In addition to technological applications, the increasing number of studies devoted to the organic-inorganic interaction is related to its fundamental aspects. The adsorption study of multifunctional molecules on semiconductor surfaces is used to describe the competition selectively observed among surface reactions. Bifunctional molecules, such as vinylacetic acid (VAA) and acrylic acid (AAc), have attracted a great deal of interest, mainly due to the possibility of using their different functional groups in the design of new devices. Indeed, such systems offer a variety of possible combinations of its grafting and further reaction with different species, depending on the substrate.

Acrylic acid, also known as 2-propenoic acid, and vinylacetic acid, also called 3-butenic acid, are typical monomers having both vinyl ( $\text{H}_2\text{C}=\text{CH}-$ ) and carboxylic ( $-\text{COOH}$ ) groups, which make possible their use in a variety of systems. AAc and its polymeric form have been used by Li and Ruckenstein<sup>2</sup> in order to promote good photoluminescence stability in water solution for silicon nanocrystals to be employed for bioimaging. VAA bifunctionality was used by Hoare and Pelton to construct new temperature-responsive microgels.<sup>3</sup> They developed vinylacetic acid/*N*-isopropylacrylamide copolymer microgels, which contain carboxylic acid functional groups highly localized on the microgel surface. They suggest that this new configuration

would be ideal for use in biomolecule separation, medical diagnostics, and biodelivery applications. Another delivery system using VAA was proposed by Hillery *et al.*<sup>4</sup> They built a copolymeric nanoparticulate drug which VAA links to luteinizing hormone releasing hormone.

Recently, another investigation on the reactivity of the VAA functional groups was done by Hwang *et al.*<sup>5</sup> They studied the VAA adsorption on the silicon surface via low-energy electron diffraction, x-ray photoelectron spectroscopy, and synchrotron radiation photoemission spectroscopy. The experimental data suggest a breaking bond at the VAA carboxylic group whose final configuration would result in  $\text{H}_2\text{C}=\text{CH}-\text{COO}$  and H bonded to the silicon atoms of the (intact) Si—Si surface dimer. In an effort to help in the understanding of the interaction of VAA and AAc with the silicon (001) surface, we employ the state of the art pseudopotential method, within a generalized gradient approximation to the density functional theory, to investigate and compare the adsorption process of VAA and AAc on the silicon surface. Our total energy calculations and calculated vibrational modes for several models studied corroborate the experimental process for VAA. In addition, we present theoretically scanning tunneling microscopy (STM) images and an analysis of changes in the electronic structure of silicon upon VAA and AAc adsorption with a view to contribute to further experimental investigations.

### II. THEORETICAL CONSIDERATIONS

The surface was modeled in a supercell geometry, with an atomic slab of six Si layers and a vacuum region equivalent to eight atomic layers. The unit cell for the  $(2 \times 2)$  surface structure is spanned by vectors  $\mathbf{a}_1 = a(1, 1, 0)$  and  $\mathbf{a}_2 = a($

$-1, 1, 0$ ). The theoretical value of the bulk Si lattice constant  $a$  was used in the surface calculations. On the top side of the slab, we placed the VAA or AAc molecules in different configurations, and the back surface was passivated by H atoms arranged in a dihydride structure. Additionally, we made calculations for a single VAA (AAc) molecule placed in a cubic box of the 22 Å side. The electron-ion interaction between Si, C, O, and H atoms is described by projector augmented wave (PAW) potentials,<sup>6,7</sup> and the electron-electron exchange-correlation interactions were considered by using a generalized gradient approximation<sup>8</sup> to the density functional theory. The single-particle orbitals were expressed in a plane-wave basis up to the kinetic energy of 400 eV, whereas the cutoff for the augmentation charges is 460 eV. Increasing the energy cutoff to 450 eV did not change the key structural parameters by more than 0.4%. The difference between total energy values calculated using both plane-wave expansions is smaller than 0.1%. The electronic and ionic degrees of freedom were relaxed by adopting the Vienna *ab initio* simulation package (VASP) implementation.<sup>9</sup> For the Brillouin-zone summation, a single special  $\mathbf{k}$  point was used in all free molecule calculations, whereas four special  $\mathbf{k}$  points are used for the surface case. The atoms were assumed to be in their fully relaxed positions when the forces acting on the ions were smaller than 0.005 eV/Å.

The most probable pathways and predicted energies from the gas-phase molecule to the adsorbed states were obtained by using the nudged elastic band (NEB) method,<sup>10,11</sup> as implemented in VASP. In this method, diffusion barriers were calculated via the determination of a local minimum energy diffusion path once the initial and final geometries are chosen. All NEB energy diffusion paths were calculated, considering the same supercell, the number of  $\mathbf{k}$  points, and the energy cutoff used in the total energy minimization. From the calculated NEB's diffusion barriers, we estimated the thermal energy barriers following the phenomenological approach in the form of the Arrhenius equation<sup>12</sup> (for a more complete description, see Ref. 13). The adsorption energy for the VAA or AAc molecule was calculated as  $E_{conf}^{ads} = -[E_{conf} - E_{ref}]$ , where  $E_{conf}$  is the total energy for the considered configuration and  $E_{ref}$  is the total energy for the free Si(001)-(2×2) surface plus the total energy for a free VAA or AAc molecule in a box of side 22 Å. The relaxed adsorption geometries were used to calculate the zone-center vibrational modes within the frozen-phonon scheme.<sup>14</sup> For setting up the dynamical problem, we considered the adsorbed system (the VAA or AAc molecule) and the Si dimer atoms. Following a conjugate-gradient algorithm, a series of initial unrelaxed configurations was submitted to the search of a minimum energy state whose final reconstructed structures are discussed in the next section. In order to obtain STM images from the calculated eigensolutions, we employed the Tersoff-Hamann formalism, as described in a previous work.<sup>15</sup>

### III. RESULTS

#### A. Preliminary results

For bulk silicon, our first-principles calculations produced 5.42 Å for the equilibrium lattice constant ( $a_0$ ), 0.86 GPa for

the bulk modulus, and 4.39 eV for the cohesive energy, all in good agreement with the experimental values presented in Ref. 16. The calculated theoretical lattice constant obtained for the bulk silicon is used in surface calculations. The clean Si(001)-(2×2) surface is characterized by alternated tilted Si—Si dimers, i.e., one dimer component is at a higher position than the other, but neighboring dimers present opposing tilting directions. The tilting of the dimer allows charge transfer from the “down” atom (which becomes more planar or  $sp^2$  bonded) to the “up” atom (which becomes nearly pyramidal or  $s^2p^3$  bonded). Thus, the down Si atom dimer is electron deficient, while the up Si atom is electron rich. Our calculations support this model: The Si—Si dimer is found to have a bond length of 2.30 Å and a vertical buckling of 0.73 Å, indicating a tilt angle of 17.8°. To test the reliability of the carbon, nitrogen, and hydrogen PAW potentials, we performed additional calculations. For cubic diamond, we obtained 3.60 (3.57) Å, 4.53 (4.42) GPa, and 7.28 (7.37) eV for the cubic lattice constant, bulk modulus, and cohesive energy, respectively, in good agreement with the experimental<sup>16</sup> values given in parentheses. The water molecule bond length O—H of 0.97 (0.96) Å and H—O—H bond angle of 104.4° (104.4°) are also in very good agreement with experimental data<sup>16</sup> given in parentheses. In a similar manner, for bulk ice in its Ih phase, we have found a lattice parameter of 4.43 Å and a cohesion energy of 0.67 eV, in agreement with the experimental findings of 4.50 Å for the lattice constant.<sup>17</sup> Although our calculated cohesion energy exceeds the experimental value of 0.58 eV,<sup>18</sup> it is in good agreement with other recent calculations (see Ref. 19 and references therein). Furthermore, our calculated bond lengths for the VAA and AAc molecules are C—C, C=C, C—O, C=O, O—H, and C—H are 1.49, 1.34, 1.37, 1.22, 0.98, and 1.09 Å, respectively, in good agreement with the experimental values usually found in organic molecules.<sup>16</sup>

#### B. Acrylic acid and vinylacetic acid adsorption on Si(2×2)-(001) surface

It is now well established that at low temperatures, the (001) surface of silicon exhibits a  $c(4\times 2)$  reconstruction. However, the limited time resolution of the measurements does not allow the proper resolution of the rapid dimer flipping at room temperature, creating the impression of a  $(2\times 1)$  surface reconstruction.<sup>20</sup> Although the majority of experiments are performed in such a way that only the  $(2\times 1)$  is observed, in order to clearly establish the role of interdimer interaction on the adsorption of VAA and AAc, we have considered a  $(2\times 2)$  surface reconstruction. The interaction of VAA and AAc with the silicon (001) surface was investigated by considering a series of possible adsorption sites. As many of the considered structures are found to be highly unstable (from the energetic point of view), in the present work we will focus our attention only to allow selected adsorbed structures obtained via an exothermic process, i.e., when the adsorbed system is lower in energy when compared to the products: the free molecule and the bare silicon (001) surface. We have determined the equilibrium

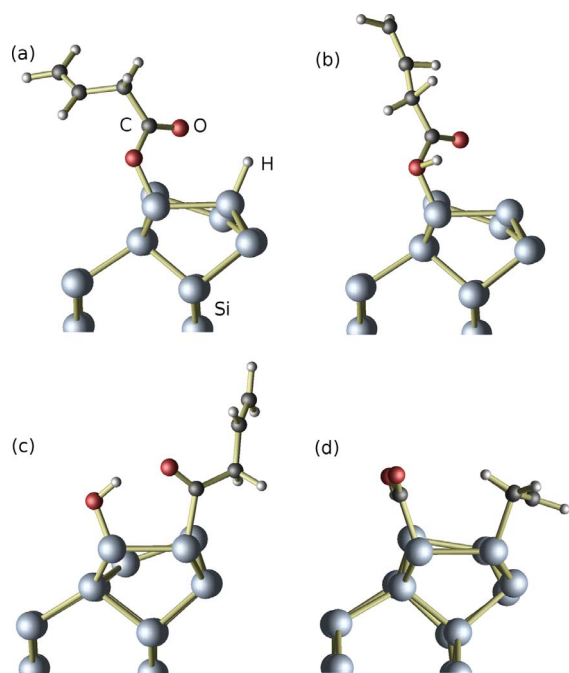


FIG. 1. (Color online) Schematic side view of the (a) dissociated [i.e.,  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{COO}$  (or  $\text{H}_2\text{C}=\text{CH}-\text{COO}$ ) and H bonded to different components of the dimer], (b) molecular [i.e., VAA (or AAc) bonded at one side of the Si dimer], (c) OH radical dissociation [i.e.,  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CO}$  (or  $\text{H}_2\text{C}=\text{CH}-\text{CO}$ ) and OH bonded to different components of the dimer], and (d) the carboxyl radical dissociation [i.e.,  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2$  (or  $\text{H}_2\text{C}=\text{CH}$ ) and COOH bonded to different components of the dimer] adsorption models for VAA and AAc on Si(001)-(2 $\times$ 2).

geometries of VAA and AAc adsorbed Si(001) surface for the molecular [i.e., VAA (or AAc) bonded at one side of the Si dimer, as in Fig. 1(b), and referred to as mol] and dissociated (i.e.,  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{COO}$  (or  $\text{H}_2\text{C}=\text{CH}-\text{COO}$ ) and H bonded to different components of the dimer, as in Fig. 1(a), and referred to as dis) models. In order to check the possibility of VAA (AAc) decomposition after adsorption, as pointed out by Hwang *et al.*,<sup>5</sup> we have also considered the following possible dissociative adsorption models: OH radical dissociation [i.e.,  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CO}$  (or  $\text{H}_2\text{C}=\text{CH}-\text{CO}$ ), as in Fig. 1(c), and referred to as  $\text{diss}_{\text{OH}}$ ] and the carboxyl radical dissociation [i.e.,  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2$  (or  $\text{H}_2\text{C}=\text{CH}$ ) and COOH bonded to different components of the dimer, as in Fig. 1(d), and referred to as  $\text{diss}_{\text{carb}}$ ].

The adsorption energies for possible models of the VAA (or AAc) interaction with the Si(001)-(2 $\times$ 2) surface are summarized in Table I. We have found that the dissociative adsorption model (diss), shown in Fig. 1(a), is energetically more favorable than the molecular (mol) state [Fig. 1(b)] by 2.28 eV for VAA and 2.36 eV for AAc. Our first-principles calculations also show that the molecularly adsorbed system is 0.01 (0.03) eV more stable than the system composed by the free silicon surface and the gas-phase VAA (AAc) molecule, suggesting that the molecularly adsorbed system corresponds to a metastable configuration. This is in agreement with experimental observations of a selective attachment of the carboxyl group concurrent with the dissociation of VAA

TABLE I. Adsorption energies (in eV) for possible adsorption models of VAA (or AAc) on the Si(001)-(2 $\times$ 2) surface presented in Fig. 1: (a) dissociated [i.e.,  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{COO}$  (or  $\text{H}_2\text{C}=\text{CH}-\text{COO}$ ) and H bonded to different components of the dimer], (b) molecular [i.e., VAA (or AAc) bonded at one side of the Si dimer], (c) OH radical dissociation [i.e.,  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CO}$  (or  $\text{H}_2\text{C}=\text{CH}-\text{CO}$ ) and OH bonded to different components of the dimer], and (d) the carboxyl radical dissociation [i.e.,  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2$  (or  $\text{H}_2\text{C}=\text{CH}$ ) and COOH bonded to different components of the dimer]. Negative adsorption values indicate an exothermic process.

Structure	(a)	(b)	(c)	(d)
VAA	-2.28	-0.01	-2.19	+0.94
AAc	-2.36	-0.03	-2.20	+1.01

to  $\text{R}-\text{COO}-\text{Si}$  and  $\text{H}-\text{Si}$  on the silicon surface under low coverage exposure<sup>5</sup> at room temperature.

Figure 2 presents a schematic representation of possible reaction paths obtained via the NEB method. The thermal barriers were estimated following a phenomenological approach in the form of the Arrhenius equation,<sup>12</sup> with the choice for the A factor between  $10^{13}$  and  $10^{15}$  s<sup>-1</sup> (see Ref. 21), and considering the complete dissociation of the reactants into products; i.e., all molecules dissociate into  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{COO}$  (or  $\text{H}_2\text{C}=\text{CH}-\text{COO}$ ) and H bonded to different components of the dimer. Our results

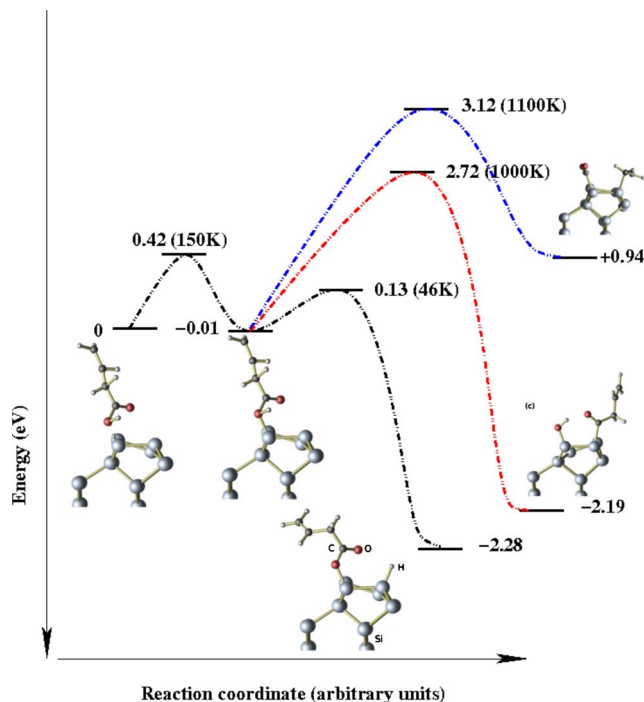


FIG. 2. (Color online) Profile of the energy surface diagram for possible adsorption models of a single VAA molecule on the Si(001):(2 $\times$ 2) surface. The values in parentheses correspond to the temperature range of thermal activation for the corresponding activation energies (without zero-point corrections). Note that the axis are guide to the eyes only, as different systems are in different scales.

indicate that molecular adsorption is possible and can occur either at higher coverages when VAA molecules are bonded to both sides of the Si dimer or at low temperatures where a thermal activation (around 150 K) would lead the system into the dissociative chemisorption state. A similar energy barrier (0.31 eV or 110 K) was found for the AAc molecular adsorption. The dissociation in both cases will take place with a very small energy barrier, corresponding to a thermal activation smaller than 50 K. This is consistent with the experimental dissociation of VAA at room temperature reported by Hwang *et al.*<sup>5</sup> and are coherent with the dissociation channels predicted by Pradyot.<sup>22</sup> It should be pointed out that the application of pseudopotentials and the density functional theory results in an underestimation of activation energies. The degree of underestimation is system dependent, and it was found to be around 10 kcal/mol for a Si<sub>2</sub>H<sub>6</sub> model of H<sub>2</sub> desorption from Si(001).<sup>23</sup> Indeed, Ortmann *et al.*<sup>24</sup> have recently shown that adsorption energies may change drastically when dispersion forces are included. Therefore, the numerical values presented here should be considered with caution. Besides the inherent modeling limitations, the reader must also bear in mind that all energy barriers are estimated, considering that all molecules are adsorbed onto the surface. In addition, the predicted reaction pathways do not necessarily correspond to the experimentally observed reactions, as local minima might play a decisive role in such processes. Therefore, our predicted dissociation pathway should be considered only as a general description of the reaction.

We have extended our study in order to investigate the possibility of the dissociative adsorption of a second VAA (or AAc) molecule (1 monolayer coverage). Our data indicates that the adsorption of a second molecule on a neighboring Si—Si dimer results in an energy gain that is very close to what is observed for the adsorption of the first molecule: around 2.1 eV. The calculated diffusion barriers (145 and 70 K for the molecular adsorption and dissociation processes, respectively) are also very similar to those obtained for a 0.5 monolayer coverage. This clearly suggests that the dissociative adsorption of a second molecule is as probable as the adsorption of a single molecule and is in agreement with the experimental data obtained by Hwang *et al.*<sup>5</sup>

From Table I, it is clear that there is at least another possible dissociative reaction involving the formation of an OH radical and a CO—R group for both VAA and AAc. However, our predicted reaction pathways ruled this configuration out, as our data suggest that this dissociation path involves a thermal activation energy around 1000 K for both VAA and AAc. We have also investigated a possible [2+2] cycloaddition reaction, which is a well-known mechanism involving the adsorption of a C=C bond of the unsaturated hydrocarbon molecule with the  $\sigma$  orbital of the Si—Si dimer. However, all configurations based on the [2+2] cycloaddition reaction evolves to the desorption of the VAA or AAc molecule. A recent theoretical study of the interaction of acetic acid with the silicon surface by Kim and Cho<sup>25</sup> suggests that the attraction of the carbonyl oxygen to the down Si atom leads to the formation of a di- $\sigma$  configuration where the  $\pi$  bond in the double C=C bond is broken to form two new  $\sigma$  bonds with the Si dimer. The authors suggest that the di- $\sigma$  chemisorbed species can easily desorb into the gas state and

indicate that this is in agreement with experimental findings for formic acid adsorption on the silicon surface by Ikeura-Sekiguchi and Sekiguchi<sup>26</sup> and high resolution electron energy loss spectroscopy investigations on the adsorption of benzoic<sup>27,28</sup> and 4-aminobenzoic<sup>29</sup> acid on the same surface by Richardson's group. Although their results for formic acid are in contrast with the absence of any evidence of a Si—C bond in the case of VAA adsorption investigated via surface core level shift data,<sup>5</sup> we have also tried hybrid di- $\sigma$  structures and dissociation paths involving carbon bonds, as presented in Fig. 1(d). However, in agreement with experimental data, all theoretically considered cases are found to be unstable from the energetical point of view, as indicated in Table I. In addition, the calculated dissociation pathways of some of these structures always involve thermal energy barriers around 1000 K, as clearly seen for the carboxyl radical dissociation [i.e., H<sub>2</sub>C=CH—CH<sub>2</sub> (or H<sub>2</sub>C=CH) and COOH bonded to different components of the dimer] depicted in Fig. 2. It is also of interest to note that the adsorption energies and reaction pathways for VAA and AAc for all considered structures are very close to each other. This is a clear indication that the elongation of the organic chain does not decisively affect the interaction of the carboxyl group with the silicon substrate and that the interaction of the vinyl group with the substrate is probably very small.

Upon the adsorption of VAA in either the molecular or dissociated model, the Si dimer gets elongated by approximately 6% with a bond length of 2.40–2.41 Å. However, while for the molecular adsorption the Si—Si dimer retains its asymmetric configuration with a tilt angle of 12.0°, for the dissociated system it becomes almost symmetric with a tilt angle of 1.7°. The expanded Si dimer length predicted in our work for both models would indicate softening of the dimer bond. Similar findings for the softening of the Si—Si dimer were obtained upon adsorption of other species like such as NH<sub>3</sub> (Ref. 30) and NF<sub>3</sub> (Ref. 31). For the molecular model, we calculated a Si—O bond length of 1.95 Å in contrast to a much smaller value of 1.73 Å obtained for the dissociated model. The weakening of the Si—O bond observed for the molecular model is probably related to charge transfer from oxygen to silicon. With respect to the surface normal, we calculated the inclination of the Si—O bond as  $\theta=22^\circ$  for the molecular model, but only 12° for the dissociated model. This difference is a direct consequence of the dimer tilt: 12° for the molecular case, but only 1.7° for the dissociated case. In other words, if the Si—Si dimer tilt angle is subtracted from  $\theta$ , then both inclinations are very similar. In addition, we have found that the VAA as well as the H<sub>2</sub>C=CH—COO group preserve their molecular structure to be almost intact; i.e., bond angles and bond lengths of the adsorbates are very similar to those observed for the free molecule. When the dissociated model is considered, the H adsorbed by the other Si dimer component is at a distance of 1.51 Å, exactly the same value obtained by us for this bond length when the adsorption of the ammonia molecule is considered.<sup>30</sup> The same level of agreement was observed for the Si—H bond tilt:  $\phi=20.7^\circ$  with respect to the surface normal. Our structural data are also consistent with the theoretical findings by Kim and Cho<sup>25</sup> for the adsorption of acetic acid with the silicon surface.

TABLE II. Selected calculated vibrational modes for the molecular [i.e., VAA (or AAc) bonded at one side of the Si dimer], and dissociated [i.e.,  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{COO}$  (or  $\text{H}_2\text{C}-\text{CH}-\text{COO}$ ) and H bonded to different components of the dimer], and OH radical dissociation [i.e.  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CO}$  (or  $\text{H}_2\text{C}=\text{CH}-\text{CO}$ ) and OH bonded to different components of the dimer] models for the adsorption of VAA (or AAc) on the  $\text{Si}(001)-(2\times 2)$ . Our theoretical results (Theor.) for the free VAA (or AAc) molecule and available experimental (Expt.) data (Ref. 32) for AAc are also presented. All values are in  $\text{cm}^{-1}$ . (*s*=symmetric, *as*=antisymmetric, *op*=out of phase, and *ip*=in phase.)

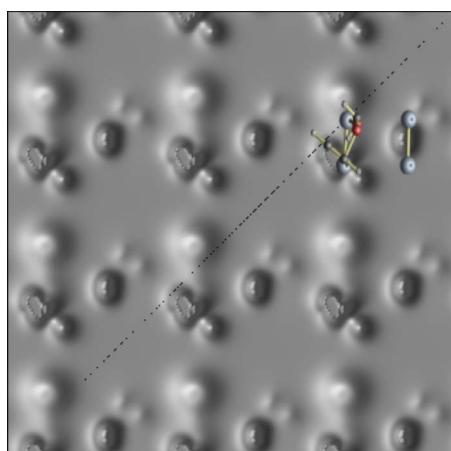
Assignment	Gas phase			mol		diss		diss <sub>OH</sub>	
	VAA Theor.	AAc		VAA Theor.	AAc Theor.	VAA Theor.	AAc Theor.	VAA Theor.	AAc Theor.
		Theor.	Expt.						
O—H <sub>s</sub>	3702	3612		3452	3405			3378	3300
C—H <sub>as</sub>	3180	3192	3112	3181	3250	3166	3185	3173	3152
C—H <sub>s</sub>	3131	3104	3076	3108	3112	3091	3123	3107	3080
Si—H <sub>s</sub>						2151	2147	2113	2124
C=C <sub>op</sub>	1749	1776	1728	1817	1789	1696	1667	1657	1694
C=O <sub>ip</sub>	1651	1637	1660	1660	1646	1615	1623	1613	1593
CH <sub>scissors</sub>	1411	1389	1434	1411	1418	1412	1395	1414	1397
CH <sub>bend</sub>	1376	1368	1395	1388	1391	1398	1363	1356	1357
OH <sub>bend</sub>	1296	1307	1296	1295	1311	1285	1268	1288	1256
Si—O <sub>s</sub>				1101	1103	1214	1239	1280	1187
C—C <sub>ip</sub>	1201	1154	1232	1111	1147	1178	1010	1177	1078
CH <sub>2rock</sub>	1098	1055	1069	1027	1012	1080	996	1098	1000

For calculating the zone-center optical phonon modes, we set up a  $42\times 42$  ( $36\times 36$ ) eigenvalue problem for VAA (AAc) and identified selected modes that describe a pronounced surface character. The results of our calculations and available experimental data, molecular and dissociative adsorption models, as well the data for the VAA and AAc molecules in their gas phase, are presented in Table II. For the free AAc molecule, our calculated vibrational frequencies are in good agreement with the corresponding experimental values,<sup>32</sup> suggesting that the present calculations indeed describe properly the studied systems. In a general sense, both the molecular and dissociative adsorption model vibrational modes are close to those calculated for the respective gas-phase molecules. As expected, the main differences are observed for the oxygen bonds interacting with the silicon dimers. Having established that the main difference for the vibrational frequencies for the molecular and dissociative models for the interaction of VAA and AAc with the silicon surface is oxygen related, we understand that an experimental investigation of the dynamical properties of the first stages of the interaction of VAA and AAc with the silicon surface would be of great value in validating the adsorption paths discussed in the present manuscript.

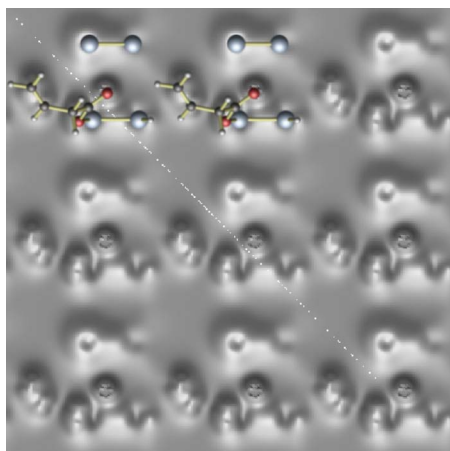
In the next step of our study, we simulated the STM images for the molecular and dissociative adsorption models in order to establish if, indeed, mixed domains might coexist on the silicon surface. STM images were obtained from the calculated electronic eigensolutions, following the Tersoff-Hamann formalism, as described in Ref. 15. Figure 3 shows the theoretical STM images obtained for a bias voltage of  $-2.0$  eV for the occupied states of the VAA:Si(001)-(2 $\times$ 2) system considering (left) molecular (i.e., AAc bonded at

one side of the Si dimer) and (right) dissociated (i.e.,  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{COO}$  and H bonded to different components of the dimer) adsorption models. The (2 $\times$ 2) reconstruction is easily identified in all theoretical images. It is worth pointing out that the present image is much richer than a constant-current experiment. In contrast to experimental conditions, in our simulation a range of tunneling currents is considered and represented by different brightnesses. Considering the brighter regions, only the adsorbate and the Si—Si dimer rows can be identified. VAA and AAc are very similar, and in order to clearly show this fact, we show in Fig. 3 the molecular adsorption model for AAc (left) and the dissociative adsorption model for VAA (right). The differences between the two simulated STM images are very small. Although we acknowledge that STM is a very powerful surface analysis technique, it is accepted that the structural analysis based on STM images should be interpreted with great care. It is now well established that the STM image should be interpreted as the manifestation of the electronic structure near the Fermi level rather than the surface atomic geometry.<sup>33</sup> Therefore, we believe that STM images are not a good candidate to distinguish the molecularly and dissociatively adsorbed structures that can coexist in a mixed domain pattern.

Finally, we have studied changes in the electronic structure of the silicon substrate upon the adsorption of VAA and AAc. Figure 4 shows the electronic density of states (DOS) for the free Si(001)-(2 $\times$ 2) surface and for the same system after its interaction with the VAA molecule, considering only the dissociative adsorption model. In order to make the analysis of the changes in the electronic structure clearer, we have considered a full monolayer adsorption, i.e., one VAA



(a)



(b)

FIG. 3. (Color online) Theoretical STM image obtained for a bias voltage of  $-2.0$  V for the molecular (left) and dissociative (right) adsorption models of AAc and VAA, respectively. A schematic representation of the adsorbed system is also presented.

molecule per silicon dimer. The DOS spectra suggest that the silicon surface is passivated upon the adsorption of VAA, as the surface state in the midgap vanishes. The same spectra suggest that the adsorption of VAA induces new surface states just below the Fermi level. From Fig. 5, it is clear that these new electronic states are VAA related, as the charge density for the highest occupied molecular orbital (HOMO) is concentrated not only on the underneath Si—Si dimer, but also around the oxygen atoms. We would like to stress that in order to allow for a better visualization of the charge density contour plots, only one VAA molecule is shown. The surface passivation effect that follows the dissociative adsorption process was already observed for both inorganic<sup>30</sup> and organic molecules even when different radical groups are considered.<sup>34,35</sup> A similar result (not shown here) was obtained for the AAc adsorbed system, which is another clear indication that the interactions of both molecules with the silicon surface are very similar.

#### IV. SUMMARY

In this work, the interaction of AAc and VAA with the silicon (001) surface is investigated using the density func-

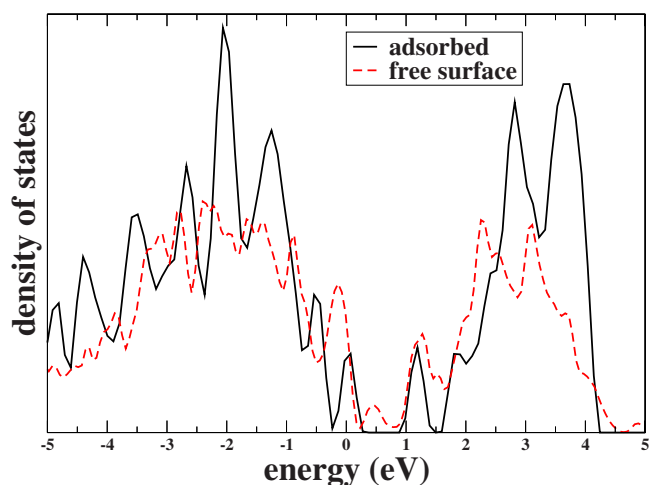


FIG. 4. (Color online) Electronic density of states (DOS) for the free Si(001)- $(2 \times 2)$  surface (dotted line) and for a full monolayer coverage (i.e., one VAA molecule per Si—Si dimer) of the dissociated adsorption model of VAA on the same surface (full line). Note that the density of state axis is in relative units, as different systems present different numbers of electrons.

tional theory. The most probable pathways and predicted energies from the gas-phase molecule to the adsorbed states indicate that the chemisorption of the molecule is as follows: The gas-phase VAA adsorbs molecularly to the electrophilic surface Si atom and then dissociates into  $\text{H}_2\text{C}=\text{CH}-\text{COO}$  and H bonded to the electrophilic and nucleophilic surface silicon dimer atoms, respectively, with an energy barrier corresponding to a thermal activation smaller than 150 K for VAA and 110 K for AAc. This is a clear indication that VAA and AAc molecules will be observed in their dissociated states at room temperature and is consistent with the experimental findings by Hwang *et al.* (Ref. 5). Our DOS spectra

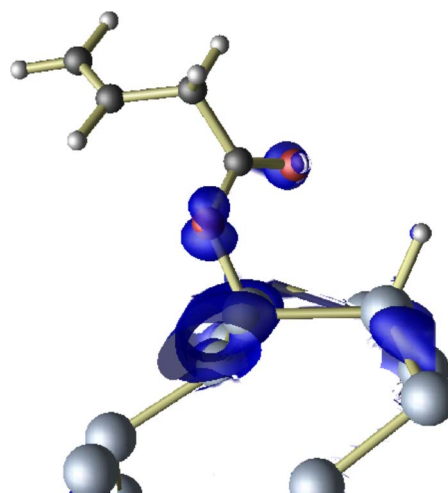


FIG. 5. (Color online) Charge density plots for the HOMO for the dissociated adsorption model of VAA on the silicon (001) surface. For simplicity, only one VAA molecule is shown. The drawing is in the  $[001]$ - $[110]$  plane. The contour values are in units of  $10^{-3}$  electrons per unit cell volume.

suggest that VAA and AAc adsorption on the silicon surface is responsible for a partial passivation of the silicon surface states. In addition, calculated vibrational modes and theoretical STM images are presented, with a view to contribute to further experimental investigations.

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- <sup>1</sup>C. W. Tang and S. A. Van Slyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- <sup>2</sup>Z. F. Li and E. Ruckenstein, *Nano Lett.* **4**, 1463 (2004).
- <sup>3</sup>T. Hoare and R. Pelton, *Macromolecules* **37**, 2544 (2004).
- <sup>4</sup>Anyia M. Hillery, Istvan Toth, Andrew J. Shaw, and Alexander T. Florence, *J. Controlled Release* **41**, 271 (1996).
- <sup>5</sup>Han-Na Hwang, Jae Y. Baik, Ki-Seok An, Sun S. Lee, Yunsoo Kim, Chan C. Hwang, and Bonsoo Kim, *J. Phys. Chem. B* **108**, 8379 (2004).
- <sup>6</sup>P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- <sup>7</sup>G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- <sup>8</sup>M. Kraus, W. Wintz, and U. Seifert, and R. Lipowsky, *Phys. Rev. Lett.* **77**, 3685 (1996).
- <sup>9</sup>G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- <sup>10</sup>G. Mills, H. Jonsson, and G. K. Schenter, *Surf. Sci.* **324**, 305 (1995).
- <sup>11</sup>H. Jonsson, G. Mills, and K. W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B. J. Berne, G. Ciccotti, and D. F. Coker (World Scientific, Singapore, 1998).
- <sup>12</sup>M. J. Pilling and P. W. Seakins, *Reaction Kinetics* (Oxford Science, Oxford, 1995).
- <sup>13</sup>R. Miotto, G. P. Srivastava, and A. C. Ferraz, *Phys. Rev. B* **63**, 125321 (2001).
- <sup>14</sup>G. P. Srivastava, *The Physics of Phonons* (Adam Hilger, Bristol, 1990).
- <sup>15</sup>R. Miotto, G. P. Srivastava, and A. C. Ferraz, *Phys. Rev. B* **62**, 13623 (2000).
- <sup>16</sup>D. R. Lide, *Handbook of Chemistry and Physics* (CRG Boca Raton, FL, 1995).
- <sup>17</sup>R. Brill and A. Teppe, *Acta Crystallogr.* **23**, 343 (1967).
- <sup>18</sup>E. Whalley, *Trans. Faraday Soc.* **53**, 1578 (1957).
- <sup>19</sup>C. Thierfelder, A. Hermann, P. Schwerdtfeger, and W. G. Schmidt, *Phys. Rev. B* **74**, 045422 (2006).
- <sup>20</sup>J. Dabrowski and H.-J. Mussig, *Silicon Surfaces and Formation of Interfaces* (World Scientific, Singapore, 2000).
- <sup>21</sup>Typical values for the  $A$  factor are around  $10^{13} \text{ s}^{-1}$ , while large  $A$  factors ( $10^{15}$ – $10^{16}$ ) usually arise if there is a gross change of geometry during the activation process (see, for example, Ref. 12).
- <sup>22</sup>Pradyot K. Chowdhury, *Chem. Phys. Lett.* **367**, 253 (2003).
- <sup>23</sup>P. Nacthigal, K. D. Jordan, A. Smith, and H. Jónsson, *J. Chem. Phys.* **104**, 148 (1996).
- <sup>24</sup>F. Ortman, W. G. Schmidt, and F. Bechstedt, *Phys. Rev. Lett.* **95**, 186101 (2005).
- <sup>25</sup>Hyung-Jin Kim and Jun-Hyung Cho, *Phys. Rev. B* **72**, 195305 (2005).
- <sup>26</sup>H. Ikeura-Sekiguchi and T. Sekiguchi, *Surf. Sci.* **433-435**, 549 (1999).
- <sup>27</sup>T. Bitzer, T. Alkumshalie, and N. V. Richardson, *Surf. Sci.* **368**, 2002 (1996).
- <sup>28</sup>T. Bitzer and N. V. Richardson, *Surf. Sci.* **427-428**, 369 (1999).
- <sup>29</sup>A. Lopez, T. Bitzer, T. Heller, and N. V. Richardson, *Surf. Sci.* **480**, 65 (2001).
- <sup>30</sup>R. Miotto, G. P. Srivastava, and A. C. Ferraz, *Phys. Rev. B* **58**, 7944 (1998).
- <sup>31</sup>R. Miotto, A. C. Ferraz, and G. P. Srivastava, *Surf. Sci.* **454-456**, 152 (2000).
- <sup>32</sup>W. R. Fearheller, Jr. and J. E. Katon, *Spectrochim. Acta, Part A* **23**, 2225 (1967).
- <sup>33</sup>For a more detailed discussion on the use of STM as a probe in surface structure analysis, please refer to G. P. Srivastava, *Theoretical Modelling of Semiconductor Surfaces: Microscopic Studies of Electrons and Phonons* (World Scientific, Singapore, 1999), p. 305. Another useful discussion is the analysis of the  $\beta 2(4 \times 2)$  and  $\zeta(4 \times 2)$  GaAs(001) surfaces proposed by Schefler's group [*Phys. Rev. Lett.* **85**, 3890 (2000)], where two very different structures present similar STM patterns.
- <sup>34</sup>R. Miotto, M. C. Oliveira, M. M. Pinto, F. de Leon-Perez, and A. C. Ferraz, *Phys. Rev. B* **69**, 235331 (2004).
- <sup>35</sup>R. Miotto, G. P. Srivastava, and A. C. Ferraz, *Surf. Sci.* **575**, 287 (2005).