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Acetylene adsorption on the Si(001) surface

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Using a first-principles pseudopotential technique, we have investigated the adsorption of C_2H_2 on the Si(001) surface. We have found that, at low temperatures, the di-σ-bond configuration is the most stable structure from the energetic point of view. According to our calculations C_2H_2 adsorbs preferentially on the alternate dimer sites, corresponding to a coverage of 0.5 monolayer. Our calculated surface band structure suggests that the end-bridge configuration, recently pointed out as a more favorable configuration by first-principles calculations, presents a metallic character and thus is Peierls unstable. The di-σ adsorbed system is characterized by symmetric and slightly elongated Si–Si dimers, and by a symmetric C–C bond with length close to the double carbon bond length of the ethylene molecule. Our total-energy calculations suggest that other metastable configurations, like the 1,2-hydrogen transfer, the *p* bridge and the tetra-σ model are also possible. Available high-resolution electron-energy-loss spectroscopy experimental data are reinterpreted to support the existence of the tetra-σ model.

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I. INTRODUCTION

In the past few years a great deal of effort has been devoted to the study of the adsorption and surface reaction mechanism of organic molecules on the silicon surface. In particular, hydrocarbon molecules have attracted a great deal of interest due to their potential technological use in the heteroepitaxy of SiC and diamond film on the silicon surface.[1] In order to elucidate the elementary mechanisms of silicon carbide films production, the interaction of acetylene with the silicon surface has been the focus of many experimental works, involving different techniques. To our best knowledge, one of the first studies was carried out by Nishijima and co-workers,[2,3] using high-resolution electron-energy-loss spectroscopy (HREELS) and low-energy electron diffraction (LEED). Their LEED results clearly indicated the presence of a (2×1) structure, while their HREELS data suggest the absence of Si dangling bonds and the existence of a double carbon bond with a rehybridization very similar to the sp^3 configuration. Based on their combined experimental data, Nishijima and co-workers proposed that, between 80 and 300 K, the acetylene molecule predominantly chemisorbs nondissociatively to both atoms of a Si–Si dimer on the Si(001) surface, saturating the dangling bonds. This adsorption configuration is known as di-σ configuration [see Fig. 1(a)].

Auger electron spectroscopy (AES) and changes in the partial pressure of acetylene measured by a quadrupole mass spectrometer (QMS) were employed in the quantitative study of the adsorption of C_2H_2 on the silicon surface by Cheng *et al.*[4] In this work, the authors verified a saturation coverage corresponding to one hydrocarbon molecule per Si dimer site when the role of surface defects present on the Si(001) surface is considered, i.e., when the surface defect sites of the clean silicon surface are not counted as possible reaction sites for the adsorption of acetylene. The same group,[5] using AES, temperature-programmed desorption (TPD), low-energy electron diffraction/electron-stimulated desorption, and QMS, found, at low temperatures, a coverage of 0.83 monolayer (ML) for the adsorption of acetylene on the silicon (001) surface. As the remaining 17% of the surface silicon atom sites were thought to be defective, they concluded that one C_2H_2 molecule is adsorbed per Si–Si dimer, in

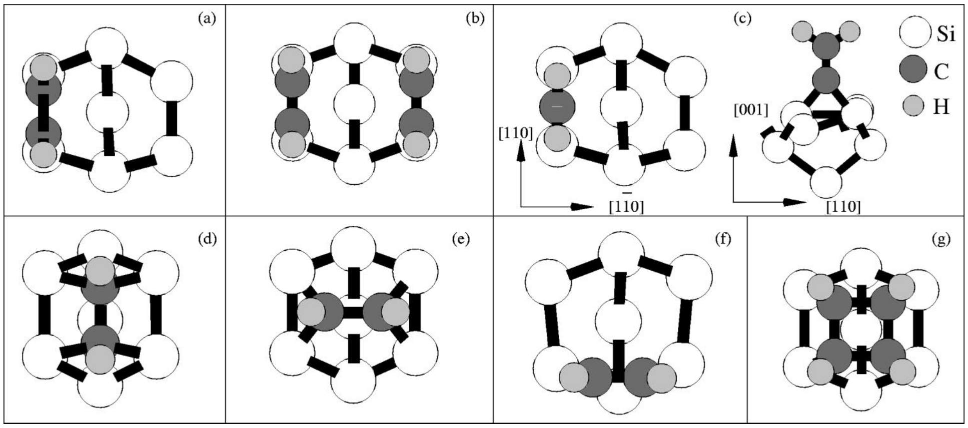

FIG. 1. Schematic views of the adsorption models of C_2H_2 on the Si(001)–(2×2) surface: (a) di-σ (0.5-ML coverage), (b) di-σ (1-ML coverage), (c) 1,2-hydrogen transfer, (d) tetra-σ, (e) *r* bridge, (f) end bridge (0.5-ML coverage), and (g) end bridge (1-ML coverage). All drawings are on the [110]-$[1\hat{1}0]$ plane, unless otherwise indicated.

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agreement with the earlier findings by Nishijima and co-workers.[2] However, Taylor *et al.*[5] proposed that the di-σ bonding will only occur with the breaking of the Si–Si dimer. The authors also estimated a molecular desorption energy of 2.00 ± 0.09 eV.

The existence of the double C–C bond was lately confirmed by Huang *et al.*[6] who combined HREELS, LEED, AES, and thermal-desorption spectroscopy. In their work, Huang *et al.* assigned the 1050-cm^{-1} loss vibration to a C–H asymmetric out-of-plane bending mode (which was earlier assigned as a C–C stretch mode by Nishijima and co-workers[2]), and assigned a 1450-cm^{-1} peak not observed by Nishijima's group to the C–C stretch mode. This new interpretation of the vibrational spectra was seen as strong evidence of the breaking of the Si–Si dimer bond. Widdra *et al.*,[7] based on studies using HREELS, LEED, AES, and TPD spectroscopy, favored the di-σ-bonding structure. Their experiments showed that atomic hydrogen could be coadsorbed onto the silicon surface already saturated with C_2H_2, thus reestablishing the Si–H bonds. This again was interpreted as a clear indication of the breaking of the Si–Si dimer bonds. Despite some common evidence for the breaking of the Si–Si dimer, the assignment of the vibrational modes remained a question of debate. Although Widdra *et al.* observed a C–C stretch mode around 1450 cm^{-1} as in the work by Huang *et al.*,[6] the loss peak at 1050 cm^{-1} was assigned to an in-plane C–H bending mode, and not to a symmetric out-of-plane bending mode as proposed earlier by Huang *et al.*

Following the pioneering works by Mayne and co-workers,[8] Li and co-workers[9] performed scanning tunneling microscopy (STM) studies of C_2H_2 adsorption on the silicon surface. The authors observed a saturation coverage of 0.5 monolayer, in contrast to the previous observation of 0.83 ML by Taylor *et al.* The authors also claim that their STM images are consistent with the di-σ adsorption model where the C_2H_2 molecule bonds across the silicon dimer with the Si–Si dimer bond, remaining intact. Matsui *et al.*[10] used near-edge x-ray-adsorption fine structure (NEXAFS) and ultraviolet photoemission spectroscopy (UPS) and concluded that the Si dimers beneath adsorbates are preserved. The authors also suggested that the di-σ model is the most appropriate model for the adsorption process. The di-σ configuration is also supported by the x-ray photoelectron spectroscopy studies by Liu and Hamers.[11] Their results, however, indicate that some C atoms are probably not bonded directly to the Si surface. These authors therefore proposed an alternative bonding configuration: the 1,2-hydrogen transfer model, shown in Fig. 1(c). In this geometry the C atom nearest the Si surface is in a bonding configuration similar to that adopted by a CH_2 (methylene) group on Si(001).

Very recently, Xu and co-workers,[12,13] using high-resolution photoemission spectroscopy and photoelectron diffraction (PhD), proposed a tetra-σ-bonded model for the C_2H_2 adsorption on the silicon surface. In this model, each C atom bonds back to two Si atoms of two adjacent dimers, as shown in Fig. 1(d), and thus each C atom is naturally in its sp^3 hybridization state. This model proposed by Xu and co-workers is also in agreement with the 0.5-ML coverage proposed earlier by Li and co-workers.[9] On the other hand, another recent work based on the same PhD technique by Terborg and co-workers[14] favors the di-σ-bond model and not the tetra-σ-bond model, although the authors pointed out the poor value of their R factor for their best-fit structure, directly influencing their experimental error bars. Matsui and co-workers[15] have analyzed the di-σ- and tetra-σ-bond models using NEXAFS and UPS experiments. The authors concluded that the tetra-σ-bond model, with the C–C bonds lying parallel to the surface dimers, is irreconcilable with their experimental electronic spectra, and supported the di-σ-bonding model with a coverage around 0.5 ML.

From the theoretical point of view, Craig and Smith[16] used the intermediate neglect differential overlap semiempirical procedure to study a large number of different adsorption sites. Their calculations favored the di-σ adsorption model with the breaking of the Si–Si dimer and with no distinct preference between the (2×1) and $c(2\times2)$ phases. Cramer, Weiner, and Frenklach[17] combined quantum-mechanical and empirical potential-energy functions in molecular-dynamics calculations. In their work, Cramer, Weiner, and Frenklach found that the direct reaction of C_2H_2 with dimer sites on the Si(001) surface is dependent on the initial orientation and the kinetic energy of the incident molecule. They verified that molecules not aligned parallel to the dimer bond direction were scattered from the surface without reaction. The authors suggested that the di-σ-bond structure with the breaking of the Si–Si dimer is the most stable configuration from the energetic point of view. However, they have shown that initially the most likely scenario is for one of the carbon atoms to bond at a single dangling-bond site, giving rise to the mono-σ structure. Their empirical potential calculations suggest that di-σ adsorption with an intact Si–Si dimer is unstable. They have also suggested that chemisorption to form bridging structures between dimers in adjacent rows is unlikely. The atom-superposition and electron-delocalization molecular-orbital theory was employed by Zhou, Cao, and Lee[18] to study the adsorbed states and vibrational properties of acetylene on Si(001)–(2×1). Their total-energy calculations and vibrational data indicate that the di-σ-bond structure is the preferred adsorption site for the acetylene molecule. However, Zhou, Cao, and Lee provided no information about the Si–Si dimers beneath the adsorbed molecule, as no relaxation of the substrate is considered in their work.

Investigations by Imamura and co-workers,[19] using first-principles pseudopotentials and a generalized gradient approximation, found that the dimerized structure proposed originally by Nishijima and co-workers[2] is more stable than the dimer-cleaved structure proposed by Taylor *et al.*[5] Their vibrational mode analyses also favored the di-σ model with the dimerized structure. Feng, Liu, and Lin[20] performed discrete variation X_α calculations and found that C_2H_2 is easily adsorbed at bridge sites with a binding energy of 3.45 eV. Liu and Hoffmann[21] used a variety of theoretical procedures, including extended Hückel, restricted Hartree-Fock, and unrestricted Hartree-Fock models, as well as pseudopotential calculations within the local-density approximation (LDA). Their results favor an acetylene adduct with an unbroken symmetric Si–Si dimer bond. More recently, Fisher, Blöchl, and Briggs[22] have used a projector-augmented wave method within the LDA to examine the coadsorption of C_2H_2 and hydrogen on the silicon surface. Their calculations support the intact-dimer structure and show that the dimer bond is broken only in the process of hydrogen coadsorption and that hydrogen does not attach to preexisting dangling bonds.

Dyson and Smith[23] combined the extended Brenner empirical potential and Hartree-Fock techniques in order to identify possible chemisorption sites for acetylene on the Si(001) dimerized surface. These authors considered a series of structures, including the adjacent cross-dimer site (the C_2H_2 molecule adsorbed between two adjacent dimer rows and oriented parallel to the dimer rows), dimer-bridge site [the standard di-σ model, as in Fig. 1(a)], the *p*-bridge site [the standard tetra-σ model, as in Fig. 1(d)], the *r*-bridge dimer site [the C_2H_2 molecule adsorbed in a tetracoordinated structure binding to the four Si atoms of two adjacent surface dimers in a dimer row at right angles to the dimers, as in Fig. 1(e)], and the end-bridge site [C_2H_2 bonded to the silicon atoms from two adjacent dimers in the dimer row direction and oriented perpendicular to the dimer row, as in Fig. 1(f)]. According to their empirical calculations, the end-bridge, dimer-bridge, cross-dimer, and *r*-bridge chemisorption sites are characterized by an increasing order of binding energy. Two points are worthy of note regarding their work. First, while their empirical calculation suggests that the di-σ structure with a broken Si–Si dimer is metastable, from their cluster Hartree-Fock calculation the broken dimer structure is found to be unstable. Second, while their empirical calculations reveal that the end-bridge site has the highest binding energy, their Hartree-Fock calculations find that the binding energy of the dimer-bridge site is almost 1.3 eV higher than that of the bridge site. It should be stressed that Dyson and Smith supposed that their *ab initio* calculations were likely to underestimate the binding energies for the end-bridge structure due to the small cluster used in their simulations.

Meng, Maroudas, and Weinberg[24] used first-principles pseudopotentials and LDA to study the chemisorption of acetylene with and without the coadsorption of hydrogen. Based on their total-energy calculations, the authors found that the cleaved-dimer structure is unstable and that hydrogen coadsorption onto the Si–Si dimer breaks the bond leading to a separation of the two silicon atoms. Konecný and Doren[25] used density-functional theory (DFT) with the $B3LYP$ functional to study reactions of a series of unsaturated hydrocarbons on the silicon surface. Their results favored the di-σ-bonded adsorbate complex within the unbroken dimer model. The calculated adsorption energy for this model is 2.87 eV, far from the experimental value of 2.00 eV reported by Taylor *et al.*[5] Tanida and Tsukada[26] employed ultrasoft pseudopotentials within the generalized gradient approximation (GGA) to study the coverage dependence of the Si(001)-C_2H_2 chemisorbed surface. According to their first-principles calculations, this system prefers to form the structure at the saturation coverage of 1.0 ML, i.e., one acetylene molecule per Si–Si dimer.

Sorescu and Jordan[27] based their non-norm-conserving pseudopotential calculations within the GGA framework on experimental data obtained from an unpublished article by Mezhenny *et al.*[28] Sorescu and Jordan revisited, among others, the dimer-bridge, *p*-bridge, *r*-bridge, and end-bridge sites investigated earlier by Dyson and Smith.[23] Their *ab initio* calculations suggested that at low coverages the dimer-bridge site is the most stable configuration, with an adsorption energy of 2.74 eV (at 0.125 ML), while for high coverages the end-bridge configuration is the most probable one, with an adsorption energy of 2.93 eV (at 1.0 ML). The same structures were the subject of the study by Lu and Lin[29] who made DFT calculations using the $B3LYP$ functional in combination with cluster surface models. Their studies also indicated that the end-bridge site is slightly more favorable than the dimer-bridge site (2.89 against 2.73 eV) for 0.5-ML coverage. However, their calculated vibrational frequencies for the di-σ configuration fit better with the experimental HREELS data. This suggests that the adsorbed species experimentally detected by HREELS indeed represents the di-σ-bonded dimer-bridge configuration. More recently, Morikawa,[30] using non-norm-conserving pseudopotentials in the GGA framework, has found that the dimer-bridge site corresponds to the most stable configuration at low coverages, while the end-bridge configuration becomes the most stable configuration at 1.0 ML, in agreement with the work of Sorescu and Jordan. According to Morikawa, a comparison of his theoretical vibrational modes with experimental data clearly indicates that both the end-bridge and di-σ configurations can coexist. However, it must be pointed out that this analysis is entirely based on the assignment of vibrational modes around 600 cm^{-1}, which is in the tail of the elastic peak region (600–900 cm^{-1}), making an accurate experimental determination of the peak position rather difficult.[6] In addition to sitting on the tail of the strong elastic peak, several peaks in this region, such as hydrogen bending, the surface Si–C stretch, and the amorphous SiC peak, overlap each other considerably.[6]

A detailed investigation of the acetylene adsorption for coverages of 0.5 and 1.0 ML was done by Cho and co-workers[31] using non-norm-conserving pseudopotentials in the GGA framework. In this work, only the di-σ and the tetra-σ configurations are studied with the former being a more stable configuration by 1.6 eV. Both coverages (0.5 and 1.0 ML) are found to have similar adsorption energies: 2.72 and 2.74 eV, respectively. Hofer, Fisher, and Wolkow[32] have also used non-norm-conserving pseudopotentials in the GGA framework to compare the dimer-bridge, end-bridge, *p*-bridge, and *r*-bridge sites using theoretical STM images. The calculated adsorption energies for the four studied models are 2.97, 2.87, 2.00, and 1.20 eV, respectively. Their results are consistent with previous calculations, as the dimer-bridge configuration is found to be the most stable structure at 0.5-ML coverage. A comparison of their calculated STM images with experimental observations shows a preference for the tetra-σ structure while energy considerations suggest that the di-σ configuration is the most stable one for 0.5-ML coverage. They suggest that kinetic effects might play a decisive role in the local minimum tetra-σ structure to be stabilized.

It is interesting to note that despite numerous theoretical and experimental efforts in the study of the adsorption of acetylene on the Si(001) surface, to our best knowledge, there is no general consensus. While many theoretical studies point to the end-bridge structure, all experimental results, with the exception of an indirect report from the unpublished work by Mezhenny *et al.*,[28] point to the di-σ structure. According to Hamers *et al.*,[33] adsorption of organic substituents to the Si(001) surface can take place at room temperature with the formation of strong covalent bonds, as the reactions do not involve the cleavage of any C–H or C–C bonds. Thus, in general most simple organic species, like acetylene and ethylene, bind irreversibly to the surface.[33] This would allow the formation of a series of metastable configurations, as predicted by first-principles calculations. What is surprising in this context is the nonexperimental observation, even considering the range of techniques employed, of the end-bridge structure, predicted to be the most stable configuration from the theoretical point of view. In this work we attempt to provide an explanation for the discrepancy between the experimental and theoretical studies available so far. In order to achieve this goal, we employ the first-principles pseudopotential method in the GGA framework to accurately describe the structural and electronic structures of a series of adsorption sites for acetylene on the Si(001) surface. In addition, in the light of the findings provided by our structural and electronic analyses, we calculate vibrational modes and compare with the available experimental results.

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 (2×2) 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 C_2H_2 molecule in different configurations, and the back surface was passivated by H atoms arranged in a dihydride structure. Additionally, we made calculations for a single C_2H_2 molecule placed in a cubic box of 22 atomic units (a.u.) per side. The pseudopotentials for Si, C, and H were derived by using the scheme of Troullier and Martins[34] and the electron-electron exchange-correlation interactions were considered by using a GGA (Refs. 35 and 36) of the density-functional theory. As for the surface calculations, the single-particle orbitals were expressed in a plane-wave basis up to the kinetic energy of 35 Ry. For the Brillouin-zone summation, four special **k** points were used for surface calculations while for the isolated molecule we considered eight special **k** points. Increasing the energy cutoff to 50 Ry or the number of special **k** points to 16 did not result in total-energy differences by more than 0.1%. The electronic and ionic degrees of freedom were relaxed by adopting the scheme described by Bockstedte *et al.*[37] 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 relaxed adsorption geometries were used to calculate the zone-center vibrational modes within the frozen-phonon scheme.[38] For setting up the dynamical problem we considered the adsorbed system (C_2H_2) and the Si dimer atoms.

III. RESULTS

A. Preliminary results

For bulk silicon our first-principles calculations produced 5.50 Å for the equilibrium lattice constant (a_o), 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. 39. The calculated theoretical lattice constant obtained for the bulk silicon is used in surface calculations. The clean Si(001)–(2×1) surface is characterized by a tilted Si–Si dimer, i.e., one dimer component is at a higher position than the other. 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 and hydrogen pseudopotentials, 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[39] values given in the parentheses. Furthermore, our calculated bond lengths for the C_2H_2 molecule are C–C$=1.24$ Å and C–H$=1.06$ Å, in good agreement with available experimental data.[39] For the free C_2H_2 molecule, our calculated vibrational frequencies are 3289 (symmetric C–H stretch), 3259 (asymmetric C–H stretch), 2090 (C–C stretch), 748 (asymmetric CH bend), and 621 (symmetric CH bend) cm^{-1}, in good agreement with the corresponding experimental values[40] of 3374, 3289, 1974, 730, and 612 cm^{-1}.

B. C_2H_2/Si(2×2)–(001) surface

Our total-energy calculations performed for the seven possible models for the C_2H_2 adsorption on the Si(001)–(2×2) surface (presented in Fig. 1) agree with all recent first-principles theoretical calculations, i.e., for low coverages (in the present study, 0.5 ML) the di-σ model corresponds to the minimum-energy structure, while for high coverages (in the present study, 1 ML) the end-bridge configuration corresponds to the minimum-energy structure. In Table I, we present the key structural parameters and the adsorption energies comparing our first-principles results with previous theoretical and experimental works. From the energetic point of view, for 0.5-ML coverage, we have found that the di-σ model is approximately 0.16, 0.79, 0.85, and 1.56 eV per (2×2) unit cell more favorable than the end-bridge, 1,2-hydrogen transfer, *r*-bridge, and tetra-σ models, respectively. However it should be emphasized that all the considered structures correspond to local minimum-energy configurations, i.e., they are energetically favorable when compared to the system composed of the free Si(001)–(2×2) surface and the C_2H_2 molecule. From Table I it is clear that the adsorption energies calculated using our first-principles pseudopo-

TABLE I. Comparison of the key structural parameters for ethylene adsorption on the Si(001)–(2×2) surface. The models are schematically shown in Fig. 1. All bond lengths (*d*) are in angstrom, bond angles in degrees, and the adsorption energy in electron volts. d_{Si-Si} represents the Si–Si dimer length for the adsorption site when the other dimer is unreacted.

	d_{C-C}	d_{Si-Si}	d_{C-Si}	d_{C-H}	∠Si–C–Si	∠C–C–H	∠Si–C–C	E_{ads}
di-σ (0.5 ML)								
present	1.37	2.34	1.89	1.10		124	106	3.45
[14]	1.36±0.19	2.44±0.58	1.83±0.09				107±9	
[18]	1.49	2.23	1.98	1.13		123	101	
[24]	1.40	2.40	1.94	1.11		123	105	
[29]	1.36	2.35	1.91	1.09		124	105	2.73
[31]	1.37	2.37	1.91					2.72
di-σ (1 ML)								
present	1.37	2.34	1.90	1.10		124	105	3.26
[27]	1.36	2.37	1.90	1.10		124	105	2.49
[29]	1.36	2.36	1.91	1.09		124	105	2.70
[31]	1.37	2.37	1.91					2.74
1,2-hydrogen transfer								
present	1.43	2.35	1.56	1.12	98			2.66
tetra-σ								
present	1.62	2.34	2.07	1.11	97	113		1.89
[27]	1.56	2.36	2.06	1.10	101	115		1.23
[29]	1.60	2.34	2.00	1.09	100	115		1.97
[31]	1.55	2.37	2.06					1.12
r bridge								
present	1.60	2.28	1.99	1.10	110	110		2.60
[27]	1.51	2.29	2.00	1.09	119	112		2.10
[29]	1.57	2.36	1.97	1.09	116	111		1.88
end bridge (0.5 ML)								
present	1.37	2.37	1.91	1.10	57	118		3.29
citeLu-00	1.36	2.40	1.90	1.09	62	120		2.89
end bridge (1 ML)								
present	1.62	2.34	1.97	1.10	55	120		3.32
citeSorescu-00	1.36	2.44	1.92	1.10	57	120		2.94
citeLu-00	1.36	2.41	1.91	1.09	69	119		3.21

tential calculations within a GGA framework are consistently higher than the values obtained by Sorescu and Jordan[27] and Lu and Lin.[29] The differences between our work and that by Lu and Lin, who have used a hybrid density-functional *B3LYP* method, are probably related to the size of the cluster used in their work. With regards to the work by Sorescu and Jordan, on the other hand, one possible explanation for such differences is that all their calculations are done considering only the Γ point for the **k**-point sampling, while in our work we have used four special **k** points. The correct choice of **k**-point sampling is known to be crucial in the determination of the accuracy of the numerical integration formula (see, for example, Ref. 41). It is now well stablished[42] that any weighted sampling considering the high-symmetry points Γ, **X**, and **L** is inadequate in averaging over the Brillouin zone, specially when total energies of different systems are compared. Therefore we believe that the discrepancies between our work and the findings of Sorescu and Jordan are mainly due to a less accurate **k**-point sampling scheme used in their work. Besides the differences in the adsorption energies, in all the studies the di-σ model corresponds to the minimum-energy structure for low coverages, while for high coverages the end-bridge configuration corresponds to the minimum-energy structure. It is worth pointing out that the first-principles results for the adsorption energies presented in Table I for the most stable configuration both at 0.5- or 1-ML coverages are much higher than the 2 eV measured by Taylor *et al.*[5] Based only on energetic considerations, all first-principles theoretical works[27,29,30,32] conclude that, depending on growth conditions, all the models considered here might be observed in experiments carried out at low temperatures, explaining why apparently conflicting observations have been reported by different experimental groups. However, as we are going to see later, this is not true when the electronic structure, a key issue when the stability of different adsorbate reconstructions are studied, is also considered. It is also interesting to note that the above remark is consistent with the predicted formation of bridge adsorption sites between dimers within the same dimer row from the empirical molecular-dynamics simulations by Cramer and co-workers,[17] as none of the metastable configurations obtained here are found to occur between adjacent dimer rows.

While adjacent dimers in the same dimer row are around 3.8-Å apart for the free surface and for the di-σ (for both 0.5 and 1 ML) and 1,2-hydrogen transfer models, this value is much smaller for the tetra-σ (3.1 Å), *r*-bridge (3.4 Å), and end bridge (3.5 Å for 1-ML coverage, an asymmetric variation ranging from 3.4 Å, at the site of the C_2H_2 adsorption, to 3.9 Å at the other end of the Si–Si dimers for 0.5-ML coverage). The resultant stress is mainly responsible for the higher-energy state of the tetra-σ structure, when compared to the other studied models. In addition, according to our calculations the adsorption of the first acetylene molecule (corresponding to 0.5-ML coverage) is 0.19 eV per (2×2) unit cell more favorable than the adsorption of the second molecule (corresponding to 1-ML coverage) for the di-σ structure, but only 0.03 eV for the end-bridge configuration. This indicates that, at low temperatures when the dynamics of the system is less affected by details of the potential-energy surface such as precursor formation and lifetime, C_2H_2 adsorbs preferentially on the alternate dimer sites in the di-σ structure, in agreement with recent experimental observations.[15] Our work suggests that there is most certainly a critical coverage around 0.5 ML after which the adsorption rate decreases, but nothing forbids the completion of 1 ML of adsorbed acetylene if the silicon surface is exposed to a rich C_2H_2 environment or if the exposure occurs for a long period of time. This is consistent with the experimental observations by Cheng *et al.*[4] and by Taylor *et al.*[5] that the adsorption kinetics of C_2H_2 on Si(001) at 105 K is physically divided into two regions: one with a constant sticking coefficient which corresponds to a horizontal plateau of the initial uptake, followed by a region of decreasing sticking coefficient (see, for example, Fig. 3 in Ref. 4). Furthermore, our findings are also in agreement with the recent first-principles theoretical calculation by Cho and co-workers,[31] where coverage of 0.5 ML was found to correspond to the most stable configuration, but without the exclusion of a possible 1.0-ML coverage, but are in contrast with the theoretical estimation of 1-ML coverage by Tanida and Tsukada.[26] However, for the end-bridge configuration, the small difference between the adsorption energies for the 0.5- and 1-ML coverages [0.03 eV per (2×2) unit cell] indicates that both coverages can coexist, which is inconsistent with the experimental observations, as in this case the sticking coefficient should not decrease smoothly, as observed by Cheng *et al.*[4]

Considering the phenomenological approach in the form of the Arrhenius equation, with the choice for the *A* factor between $10^{13}-10^{15}\ \mathrm{s}^{-1}$,[43] we have estimated that complete desorption of the C_2H_2 molecule is unlikely, as it will occur only at very high temperatures (around 1600 K). This is in agreement with an estimated value of ~1450 K in the temperature-programmed desorption experiments by Taylor *et al.*,[5] and the experimental observations of a small acetylene desorption around 750 K followed by the decomposition of the molecule on SiH and CH species and the subsequent formation of SiC around 900 K.[2,6,15] The predicted energetics for the transition from the di-σ structure to the 1,2-hydrogen transfer structure suggest that the coexistence of these models is possible, as the transition between these models will occur after an energy activation corresponding to ~300 K, in agreement with the experimental observations of Liu and Hamers.[11] This is consistent with the NEXAFS observations by Matsui *et al.*[15] of the coexistence of physisorbatelike species with the chemisorbates at 0.5-ML coverage. However, the transition between the di-σ and the tetra-σ, end-bridge, or *r*-bridge structures is very unlikely to be observed, as our calculations suggest that the energy necessary for these processes corresponds to a thermal activation of the order of 3000 K, which is much higher than the temperature necessary for the decomposition of the C_2H_2 molecule. This is in agreement with the lack of experimental observation of a mixed domain containing the di-σ and the tetra-σ, end-bridge, or *r*-bridge structures, but is in disagreement with the theoretical findings of Sorescu and Jordan.[27] In their work, Sorescu and Jordan estimated an energy barrier corresponding to ~800 K for the translation of a C_2H_2 molecule between the di-σ and the tetra-σ models. If this was the case, a mixed domain containing both structures should be observed. Therefore we believe that the energy barrier height obtained by Sorescu and Jordan for this translation is somehow underestimated.

Table I contains the structural parameters for the acetylene adsorption geometries within the di-σ, 1,2-hydrogen transfer, tetra-σ, *r*-bridge, and end-bridge structures. Structural data for the Si–Si dimers that do not correspond to an adsorption site are not presented, as they are very similar to the values found for the free surface, i.e., Si–Si dimer bond length is 2.31 Å while the tilt angle is 17.9°, indicating that the interaction between the adsorbate and the neighboring free dimer is not very strong. Upon the adsorption of acetylene, the Si–Si dimer gets elongated by approximately 2%, for all the considered models (except for the *r*-bridge structure, where a small contraction is verified), and becomes symmetric. This finding is in agreement with the experimental value[14] of 2.44 ± 0.58 Å and with the theoretical estimations by Meng and co-workers,[24] Sorescu and Jordan,[27] and Hofer and co-workers,[32] but is slightly bigger than the value of 2.23 Å calculated by Zhou *et al.*[18] The calculated C–H bond length of ~1.11 Å for all the considered models is also in good agreement with early theoretical estimates. Our calculations also indicate that the C–Si bond length is approximately 1.90 Å for all considered models, except for the 1,2-hydrogen transfer structure for which it is 1.56 Å. Therefore we believe that the nature of the Si–Si and C–H bonds is not decisively affected by the choice of the adsorption site for C_2H_2, except maybe for the *r*-bridge model.

However, as expected, the C–C bond length is directly dependent on the choice of the adsorption site. Our calculated values of d_{C-C} for the models di-σ (1.37 Å), 1,2-

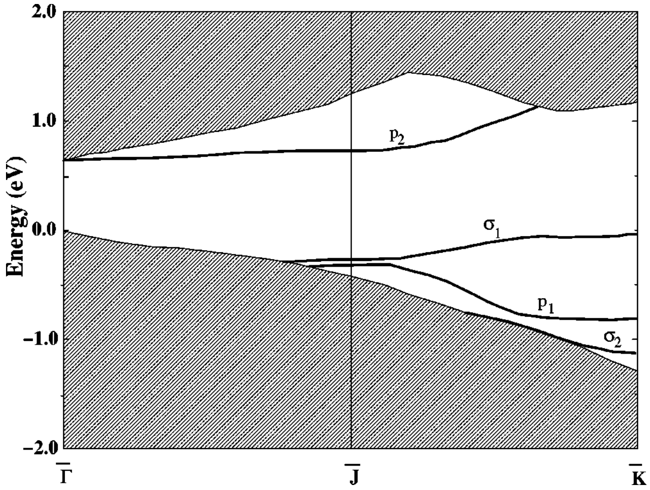

FIG. 2. Surface band structure for the di-σ model for the adsorption of C_2H_2 on the Si(001)–(2×2) surface. The shaded areas represent the projected bulk band structures.

hydrogen transfer (1.43 Å), and end-bridge 0.5 ML (1.37 Å) are close to the double bond length observed experimentally for ethylene (1.34 Å),[39] while for the tetra-σ, *r*-bridge, and end-bridge 1-ML structures our calculated values (1.62, 1.60, and 1.62 Å, respectively) are comparable to the single carbon-carbon bond in the ethane molecule (1.54 Å).[39] In general our calculated values for the di-σ, tetra-σ, *r*-bridge, and end-bridge (0.5-ML) models are in very good agreement with the experimental values obtained by Terborg *et al.*[14] and the various other theoretical values presented in Table I. However, for the end-bridge (1-ML) structure, our first-principles pseudopotential calculations result in a different structure, with the carbon atoms forming a squared ring, as shown in Fig. 1. This is probably due to the fact that we have not considered any symmetry constraint in our calculations.

The surface band structure resulting from our calculation for the di-σ model considering a 0.5-ML coverage is shown in Fig. 2. We have identified four surface states within the fundamental band gap of silicon: these are labeled σ_1, σ_2, p_1, and p_2. As seen in Fig. 3, the σ_1 and σ_2 states with binding energies of approximately 0.1 eV and 1.0 eV are mainly localized on the Si–Si dimer underneath the adsorbate, and represent the interaction between Si–Si $pp\sigma$ and different CH orbital components of the C_2H_2 molecule. The p_1 and p_2 states correspond to the occupied and unoccupied surface states of the free silicon surface and are localized at the "up" and "down" atoms, respectively, of the Si–Si dimer not bonded to the acetylene molecule. The main structural difference between the 1.0- and 0.5-ML acetylene coverages of the di-σ configuration is the absence of the "free" Si dimer atoms in the former. This will lead to a surface band structure very similar to that observed for 0.5-ML coverage, where the p_1 and p_2 surface states are not observed, as they are related to the "free" Si–Si dimer. In other words, for the 1.0-ML acetylene coverage, the binding energies and the (σ) surface-states dispersion are very similar to that observed for the 0.5-ML coverage. In fact, the diferences in the binding energies of these states for the two coverages are always smaller than 0.06 eV. These small changes in the surface states observed upon the adsorption of a second acetylene molecule indicate that adjacent dimer interactions are minimal, which is consistent with the small energy difference observed for both structures. As far as we are aware, the only other electronic band structure for the adsorption of acetylene on the silicon surface was obtained by Tanida and Tsukada[26] for the dimer-cleaved geometry. Although they have not calculated the same structure, it is interesting to note that their surface band structure resembles the results obtained here, i.e., the number of surface states and their positions are similar. However, as expected, the origin of the surface states obtained in their work is very different than presented here.

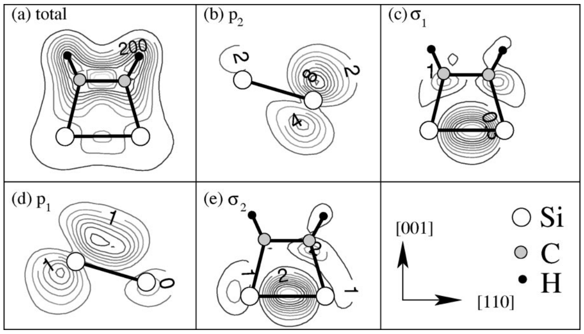

FIG. 3. Charge-density plot for the di-σ model for the adsorption of C_2H_2 on the Si(001)–(2×2) surface. All charge-density contour plots were obtained at the **K** point, except for the p_2 surface state that was obtained at the **J** point. All drawings are in the [001]-[110] plane, unless indicated. Bonds in the drawing plane are shown as solid lines. The contour values are in units of 10^{-3} electrons per unit-cell volume.

In Fig. 4 we present the surface band structure resulting from our calculation for the end-bridge model considering 0.5-ML coverage of C_2H_2. For this model we obtain two surface states along the dimer direction (along $\overline{\Gamma}$–$\overline{J}$) lying

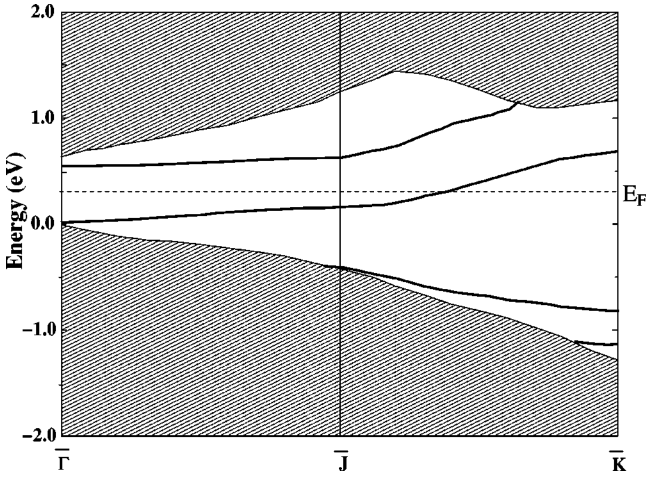

FIG. 4. Surface band structure for the end-bridge model for the adsorption of C_2H_2 on the Si(001)–(2×2) surface. The shaded areas represent the projected bulk band structures.

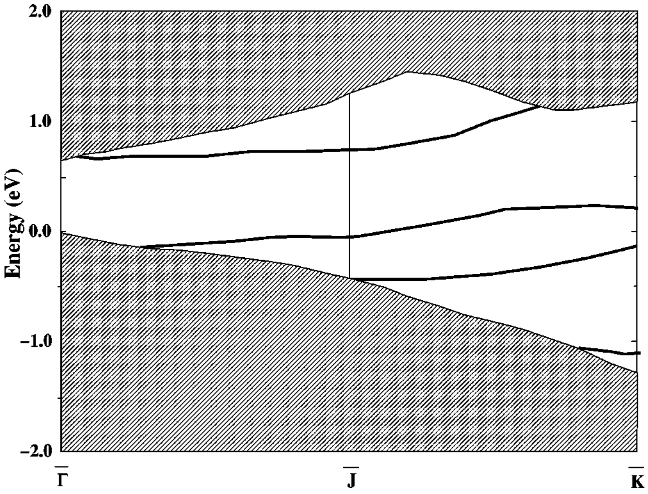

FIG. 5. Surface band structure for the 1,2-hydrogen transfer model for the adsorption of C_2H_2 on the Si(001)–(2×2) surface. The shaded areas represent the projected bulk band structures.

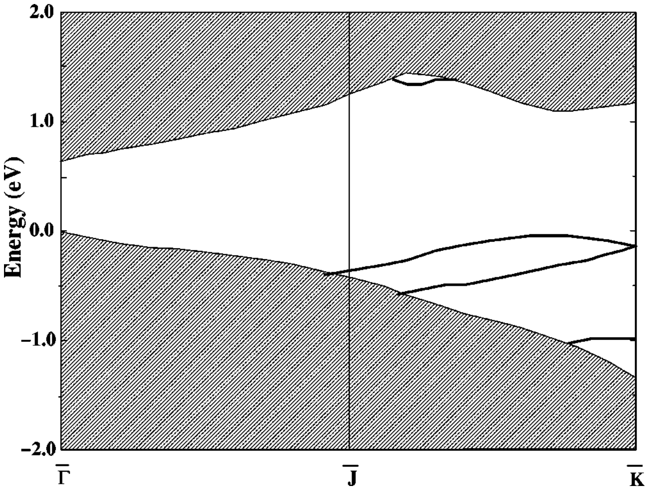

FIG. 6. Surface band structure for the *r*-bridge model for the adsorption of C_2H_2 on the Si(001)–(2×2) surface. The shaded areas represent the projected bulk band structures.

totally within the silicon band gap. The metallic character of this surface band structure is very clear: first, the highest occupied state crosses the Fermi level, and second the partially occupied band around the $\bar{K}$ point has an energy that is higher than the first unoccupied state around the $\bar{\Gamma}$ point. The surface band structure for 1-ML acetylene coverage is not presented here, as the main difference is the absence of the first fully unoccupied state, mainly due to the Si–Si dimer dangling bonds. However, it still presents a metallic character, as the highest occupied state crosses the Fermi level. This metallic behavior, sometimes called Peierls instability, is a clear indication that this structure does not correspond to a stable configuration. We have merely considered this model to compare its relative stability against the other models. We also believe that these findings are consistent with the lack of experimental observations of this structure, i.e., if the end-bridge configuration is the most stable structure, it should be observed experimentally as many different techniques have been employed in the analysis of this system. It should also be emphasized that even experimental STM image features were never interpreted as having signatures indicating the existence of the end-bridge model. The experimental STM images obtained by Li *et al.*,[9] for example, strongly support the di-σ model. Hofer *et al.*,[32] on the other hand, found that their STM theoretical simulations for the tetra-σ model agree better with the experimental STM images, and attribute this difference to the absence of the unreacted dimers. However, the interpretation by Hofer *et al.* is inconsistent with the site-occupation probability experimentally obtained by Li *et al.*, as the latter group has shown that only a very small number of sites near adsorbates are occupied. Furthermore, for 0.5-ML coverage, the tetra-σ configuration corresponds to a stressed system where the distance between adjacent Si–Si dimers in the same dimer row is not constant, as discussed earlier in this section.

The surface band structures for the 1,2-hydrogen transfer, *r*-bridge, and tetra-σ models are presented in Figs. 5–7, respectively. An inspection of these clearly shows that they have a semiconducting nature, and therefore the structural models considered indeed represent metastable configurations for the adsorption of acetylene on the silicon surface, as observed in our total-energy calculations. This is consistent with the experimental observations of these systems by different groups under different exposure conditions, and confirms the suggestions from Hamers *et al.*[33] that the irreversible binding of simple organic molecules to the surface is characterized by the formation of strong covalent bonds in various metastable configurations. It is interesting to note that all the models considered here present occupied surface states, at least along $\bar{J}$–$\bar{K}$, in clear opposition to the absence of surface states indicated by the valence-band spectra by Xu *et al.*[12] In their paper, Xu *et al.* observed a decrease of the surface-state signal in the valence-band spectrum with an increase in the coverage of acetylene, with the complete disappearance after the saturation adsorption of 0.5 ML, showing that the Si dangling bonds are quenched by the adsorp-

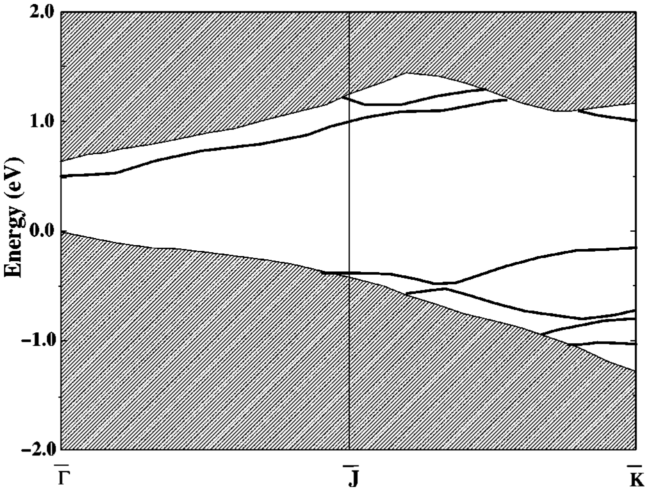

FIG. 7. Surface band structure for the tetra-σ model for the adsorption of C_2H_2 on the Si(001)–(2×2) surface. The shaded areas represent the projected bulk band structures.

TABLE II. Calculated vibrational modes for models *A*, *C*, and *D* for the adsorption of C_2H_2 on the Si(001)–(2×2). All values are in cm^{-1}.

	C–H (stretch)	C–C (stretch)	C–H (in-plane bend)	C–H (out-of-plane bend)	C–Si (stretch)
di-σ					
present	3091	1376	1192	1037	690
[18]	2958	1383		1047	653
[19]	2990	1479	1193	939	688
[29]	3154	1523	1277	1001	732
1,2-hydrogen transfer					
present	3048	1183	1069	1129	592
tetra-σ					
present	3060	1102	975	985	553
[29]	3122	824	1195	916	610
r bridge					
present	3090	1099	806	971	
[29]	3150	894	1230	909	722
Experimental (HREELS)					
[2]	3000	1090	1255		690
[6]	2980	1450	1240	1065	680
[7]	2980	1450	1240–1065		680

tion of acetylene.[12] However, while our work indicates the local saturation of the Si–Si dimer dangling bonds by the adsorbed molecules (i.e., only the adsorption sites dangling bonds are saturated by the C_2H_4 molecule), the existence of occupied surface states is clearly seen in Figs. 2 and 5–7. Furthermore, it is interesting to point out that even for the 1,2-hydrogen transfer, *r*-bridge, and tetra-σ models, the wave function for the highest occupied surface state is mainly localized around the adsorbate. Furthermore, recent NEXAFS and UPS experiments by Matsui *et al.*[15] corroborate our theoretically predicted band structure, as they clearly show the presence of adsorbate surface states by identifying features in those states that are not related to any bulk or surface states of the Si(001) substrate.

For calculating the zone-center optical-phonon modes we set up a 36×36 eigenvalue problem, and identified selected modes that describe pronounced surface character. The results of our calculations as well as available experimental and other theoretical data, for stretch and bend modes for the di-σ, 1,2-hydrogen transfer, tetra-σ, and *r*-bridge adsorption models, are presented in Table II. The vibrational modes of the adsorbates obtained for the di-σ structure when acetylene coverage of 1 ML is considered are identical to the values calculated for the 0.5-ML coverage, following the same pattern observed for the structural parameters determined for these two models. This is another clear indication that the interaction between neighboring dimers is not very strong. Therefore we will not explicitly discuss the results for 1-ML acetylene coverage and present only the results for the 0.5-ML coverage.

It is interesting to note that the assignment of the key carbon-carbon vibrational frequencies are somewhat different in two of the experimental works (Refs. 2 and 6). While Nishijima *et al.*[2] have assigned the peak appearing at 1090 cm^{-1} to a C–C σ-bond vibrational mode, Huang and co-workers[6] have assigned to a 1450 cm^{-1} loss feature the same vibrational mode, as listed in Table II. When the experimental deuterated spectra (C_2D_2) is considered (not shown in Table II), the same pattern is observed: Nishijima *et al.*[2] assigned a peak at 1040 cm^{-1} to the C–C σ bond in contrast to the 1420 cm^{-1} assigned by Huang and co-workers.[6] As the frequency ratio for the hydrogenated molecule and the deuterated molecule is close to unity in both experiments, it is very difficult to rule out any one of the assignments. This apparent contradiction can be resolved if we consider different models for the adsorption of acetylene on the silicon surface, as discussed below. Our calculated values of the various stretch and bend mode frequencies for the di-σ model reliably reproduce the experimental HREELS measurements by Huang *et al.*[6] and are in very good agreement with previous theoretical estimates.[18,19,29] The similarity between our calculated values for the di-σ model and the available experimental and previous theoretical data gives us a clear indication that indeed the di-σ model corresponds to the structure experimentally observed by Huang *et al.* However, although in their paper Nishijima *et al.*[2] suggested a structural model similar to the di-σ for the adsorption of acetylene on the silicon surface, their experimental findings for the C–$H_{stretch}$ and C–$C_{stretch}$ modes are much closer to our calculated values for the tetra-σ model than for the di-σ one, except maybe for the C–H in-plane bending mode.

Our calculations strongly suggest that the vibrational modes due to the C–C bonds are decisively affected by the choice of the adsorption site in contrast to the Si–Si and C–H bonds. This is directly reflected by the fact that the largest differences in the computed frequencies (up to 28%) are found for the C–C stretch mode. Therefore we suggest that the characterization of the C–C bond is very important in determining the adsorption site of the C_2H_2 molecule. As HREELS is one of the most accurate surface science techniques for the identification of bonding nature, we believe that the observations of Nishijima *et al.*[2] and Huang and co-workers[6] are not in conflict with each other, as they could be the signature of two different systems. In light of the evidence provided by the direct observation of the tetra-σ-bond structure by Xu *et al.*[13] in a recent PhD experiment and the vibrational modes obtained in our total-energy calculations, we suggest that the results obtained in the experiments by Nishijima *et al.*[2] could be reinterpreted to reflect the data for the metastable structure represented by the tetra-σ model. The same kind of analysis can be extended to the *r*-bridge structure. In fact, both the *r*-bridge and the tetra-σ structures present a single C–C bond, and therefore all C–C and C–H vibrational modes should be similar, as observed in our first-principles calculations. We do not rule out the possibility that the results obtained in the experiments by Nishijima *et al.*[2] could be associated with the *r*-bridge structure, as this structure is energetically more favorable than the tetra-σ one. However, as the *r*-bridge structure was not observed experimentally, and both in the experiment of Nishijima *et al.* and Xu *et al.* a vicinal Si(001) surface (9° and 4°, respectively) is exposed to acetylene and then annealed, we suggest that the tetra-σ structure is more likely to be responsible for the experimental data by Nishijima *et al.*

IV. SUMMARY

In conclusion, using a first-principles pseudopotential technique, we have investigated seven possible structural models for the adsorption of C_2H_2 on the Si(001) surface. At low temperatures, the di-σ-bond structure is found to be the most stable structure. The relative stability of this model is 0.8, 0.85, and 1.6 eV per (2×2) unit cell when compared to the 1,2-hydrogen transfer, the *r*-bridge, and the tetra-σ-bond structures, respectively. The end-bridge adsorption model, first proposed by Dyson and Smith,[23] and recently found by Sorescu and Jordan[27] to be the most stable configuration for the adsorption of C_2H_2 on the silicon surface, is found to present a metallic surface band structure and thus to be Peierls unstable. According to our calculations C_2H_2 adsorbs preferentially on the alternate dimer sites, corresponding to coverage of 0.5 ML, in agreement with recent experimental observations.[15] The di-σ adsorbed system is locally (i.e., at the adsorbed site) characterized by symmetric and slightly elongated Si–Si dimers, and by C–C bonds with $d_{C-C} = 1.37$ Å, close to the double carbon bond for the acetylene molecule. Our total-energy calculations further suggest that other metastable configurations, like the tetra-σ model recently proposed by Xu *et al.*,[13] are also possible. The HREELS experimental data obtained by Nishijima *et al.*[2] are reinterpreted to support the existence of the tetra-σ model.

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