PHYSICAL REVIEW B **69**, 235331 (2004)

Acetonitrile adsorption on Si(001)

R. Miotto,* M. C. Oliveira, and M. M. Pinto
Instituto de Física da Universidade de Brasília, Caixa Postal 04455, CEP 70919-970, Brasília, Distrito Federal, Brazil

F. de León-Pérez and A. C. Ferraz
Instituto de Física da Universidade de São Paulo, Caixa Postal 66318, CEP 05315-970, São Paulo, São Paulo, Brazil

(Received 8 July 2003; revised manuscript received 12 February 2004; published 30 June 2004)

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 acetonitrile on the silicon surface. Our first-principles calculations indicate that CH_3CN adsorb via a [2+2] cycloaddition reaction through the C≡N group (di-σ_{CN} model) with an adsorption energy around 37 kcal/mol. Although the di-σ_{CN} model is found to be the most probable adsorbed structure from the energetic point of view, we have also found that the adsorption via the Si-N dative bond (Si-N_{dat} model) is also possible. Based in our energetic analysis, and in the spectroscopy data by Bournel and co-workers, we suggest the existence of a mixed domain surface composed by both the di-σ_{CN} and Si-N_{dat} adsorbates, although the existence of the latter structure is disregarded by the core level shift analysis by Tao and co-workers. Possible reasons for the contrast between available data are addressed. We present theoretical scanning tunneling microscopy images of the possible adsorbed systems and suggest that this experimental procedure could possibly identify the existence of the proposed mixed domain structure. In addition, the electronic structure and surface states for both the di-σ_{CN} and Si-N_{dat} models are discussed in detail.

DOI: 10.1103/PhysRevB.69.235331 PACS number(s): 71.15.Dx, 68.43.Pq, 68.35.−p

I. INTRODUCTION

The increasing number of studies devoted to the chemistry of organic molecules on silicon surfaces is not only related to the understanding of its fundamental aspects, but also to its importance in various technological applications, such as insulator films, resistance of nanolithography, chemical and biological sensors, and molecular electronics. Each of these requires the development of a well defined organic layer on the semiconductor surface. As these organic layers are basically formed by exposing the semiconductor surface to organic compounds, the understanding of the first stages of the interaction between the surface and the organic structure is crucial in order to improve its quality. The majority of the reactions between semiconductor surface and hydrocarbon molecules occur at or near the dangling bonds of the reconstructed surface. In the case of silicon, the (001) surface reconstruction is based on dimers, where a strong σ bond between the two dimer atoms and a weak π bond is observed. It is now well established that the C═C double bonds in hydrocarbons break the dimer π bonds and lead to the formation of new surface bonds that are often energetically favorable.[1] Making use of this reaction, it is possible to produce well ordered organic films/Si structures with a stable and uniform interface. More importantly, the novel organic films on silicon introduce the possibility for an entirely new device physics based on utilization of their varieties of functional groups.

The majority of works so far focused on the interaction of simple alkenes with the silicon (001) surface. In particular, acetylene[2–4] and ethylene,[5–8] are among the most studied adsorbates on the silicon surface. Both molecules are adsorbed via a [2+2]-like cycloaddition reaction via the breaking of the weak π bond of the Si-Si surface dimer. Acetonitrile is isolectronic to acetylene. Therefore, it is expected that $CH_3-C\equiv N$ would also undergo a [2+2]-like cycloaddition reaction but via the cyano group, as there are no double carbon bonds in this molecule. Recent experimental works involving synchrotron radiation photoemission spectroscopy (PES) and near edge x-ray absorption fine structure spectroscopy (NEXAFS) (Refs. 9 and 10) and temperature programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS), and high-resolution electron energy-loss spectroscopy (HREELS) (Ref. 11) suggest that indeed this molecule is molecularly adsorbed on Si(001) through the C≡N group in a di-σ configuration, leaving a C═N functionality on the surface for further reaction and modification. Although both experimental studies point out to this similarity between acetylene and acetonitrile, the TPD, XPS, and HREELS measurements by Tao and co-workers and the PES and NEXAFS spectroscopy data by Bournel and co-workers indicated the possibility of multiple chemisorption states. While the former proposed interdimer and intradimer adsorption models, the latter clearly indicated the possibility of a N−Si dative bond configuration. In addition, Bournel and co-workers[9,10] observed that all Si-Si dimer states disappear upon adsorption of acetonitrile, indicating a saturation coverage around 1 monolayer (ML).

From the theoretical point of view, two cluster calculations were carried out by Tao and co-workers[11] and Lu *et al.*[12] In these two studies the theoretical findings are in agreement with the experimental observation of a [2+2]-like cycloaddition reaction via the cyano group, but in both cases, only a small number of possible adsorption sites were considered. It is worthy pointing out that in Tao's work a possible N−Si dative bond configuration was not under investigation, while in Lu's investigation, this structure was only considered as a possible transition state for the $[2+2]$-like cycloaddition reaction via the cyano group structure. 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 acetonitrile on the silicon surface. A detailed analysis of the structural, electronic, and vibrational structures of possible adsorbed systems are discussed and compared to available experimental results. In addition, theoretically scanning tunneling microscopy (STM) images are presented, 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 (2×2) 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 CH_3CN 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 CH_3CN molecule placed in a cubic box of 22 atomic units (a.u.) side. The pseudopotentials for Si, C, N, and H were derived by using the scheme of Troullier and Martins[13] and the electron-electron exchange-correlation interactions were considered by using a generalized gradient approximation[14] 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 $\mathbf{k}$ points were used for surface calculations while for the isolated molecule we considered eight special $\mathbf{k}$ points. Increasing the energy cutoff to 50 Ry or the number of special $\mathbf{k}$ 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.*[15] 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.[16] For setting up the dynamical problem we considered the adsorbed system (CH_3CN) and the Si dimer atoms. In order to obtain STM images from the calculated eigensolutions, we employed the Tersoff-Hamann formalism, as described in a previous work.[17] The most probable pathways and predicted energies from the gas-phase molecule to the adsorbed states were obtained by using a constraint dynamics scheme in which atomic movement along the pathway is a response to forces in a local region around it. The constraint is set only for the carbon (or hydrogen) atoms during the adsorption and dissociation processes. The energetic barriers are estimated following the phenomenological approach in the form of the Arrhenius equation[18] (for a more complete description see Ref. 19). The adsorption energy for the CH_3CN molecule was calculated as $E^{ads}_{conf} = -[E_{conf} - (E_{ref} + E^{ads})]$, where E_{conf} is the total energy for the considered configuration, E_{ref} is the total energy for the free $Si(001)-(2\times 2)$ surface and $E^{ads} = aE^{CH_3CN}_{chem} + bE^{CH_3CN}_{free}$, where $E^{CH_3CN}_{free}$ is the total energy for a CH_3CN molecule in a box of side 22 a.u., and $E^{CH_3CN}_{chem}$ is the chemisorption energy of a CH_3CN molecule on the Si(001) surface. The coefficients a and b are appropriately chosen for a given configuration.[19]

III. RESULTS

A. Preliminary results

For bulk silicon our first-principles calculations produced 5.42 Å for the equilibrium lattice constant (a_o), 0.86 GPa for the bulk modulus (BM), and 4.39 eV for the cohesive energy, all in good agreement with the experimental values presented in Ref. 20. 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 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[20] values given in the parenthesis. Furthermore, our calculated bond lengths for the CH_3—CN molecule are C—C $=1.44$ Å, C—N $=1.59$ Å, and C—H $=1.11$ Å, in good agreement with available experimental data.[20]

B. $CH_3-CN:Si(2\times 2)-(001)$ surface

In order to investigate the interaction of acetonitrile with the silicon (001) surface, we have considered 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 in selected adsorbed structures obtained via an exothermic process, i.e., the adsorbed system is lower in energy when compared to the products: the free molecule and the bare silicon (001) surface. In Fig. 1, we present the schematic views of four possible models for the adsorption of a single CH_3CN on the $Si(001):(2\times 2)$ surface (corresponding to 0.5 ML coverage): (a) $[2+2]$ cycloaddition via the $C\equiv N$ group (di-σ_{CN}); (b) Si−N dative bond (Si-N_{dat}); (c) cyano+methyl dissociative model (cyan-met_{dis}); and (d) $[2+2]$ cycloaddition via the C−C group (di$-\sigma_{CC}$) with hydrogen dissociation. We have further considered the possibility of end-bridge adsorbed structures, i.e., the CH_3CN molecule bonded to the silicon atoms from two adjacent dimers in the dimer row direction and oriented perpendicular to the dimer

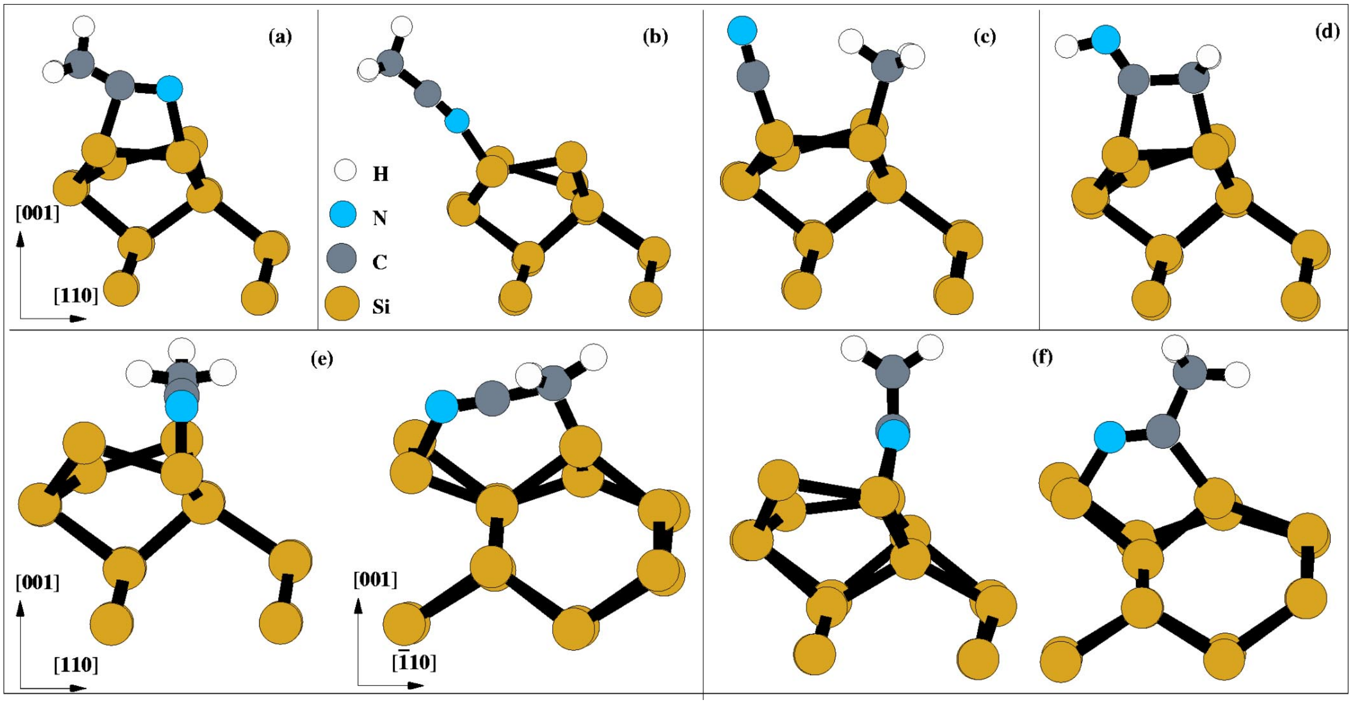

FIG. 1. Schematic views of possible models for the adsorption of a single CH_3CN molecule on the Si(001):(2×2) surface (corresponding to a 0.5 ML coverage): (a) [2+2] cycloaddition via the C≡N group (di-σ_{CN}); (b) Si—N dative bond (Si—N_{dat}); (c) cyano +methyl dissociative model (cyan-met$_{dis}$); (d) [2+2] cycloaddition via the C—C group (di-σ_{CC}); (e) end-bridge adsorption via the C—C bond (end bridge$_{CC}$); and (f) end-bridge adsorption via the C≡N group (end bridge$_{CN}$).

row, first proposed by Dyson and Smith[21] for the adsorption of acetylene on the silicon (001) surface. For the CH_3CN molecule, there are two possible end-bridge adsorption structures: via the C—C bond (end bridge$_{CC}$) as in Fig. 1(e), or via the C≡N group (end bridge$_{CN}$) as in Fig. 1(f). At this point, it is also worth emphasizing that a possible dissociative adsorption model whose final configuration would result in a isocyano and a methyl group bonded to the silicon atoms of the Si-Si surface dimer, as suggested by Bournel and co-workers,[9,10] was found to be unstable, i.e., our molecular dynamics simulations indicate that all possible precursor states for this configuration always ended up in the di-σ_{CN} adsorption model. Therefore, we are not going to address such dissociative adsorption structure.

Our total-energy calculations performed for the selected models for the acetonitrile adsorption on the Si(001)-(2×2) surface indicates that the cyan-met$_{dis}$ configuration corresponds to the most probable structure from the energetic point of view, with an adsorption energy around 48 kcal/mol (against 37 kcal/mol for the di-σ_{CN} configuration). This is in contrast with the experimental findings by Bournel and co-workers[9,10] and Tao and co-workers,[11] indicating the di-σ_{CN} as the most probable adsorbed structure. In order to elucidate this point, we have estimated possible adsorption and dissociation paths for all considered structures. According to our calculations, the dissociative adsorption leading to the cyan-met$_{dis}$ model would involve the formation of a precursor state whose adsorption reaction presents an activation barrier of 42 kcal/mol (Fig. 2). Considering the phenomenological approach in the form of the Arrhenius equation, with the choice for the *A* factor between 10^{13} and 10^{15} s^{-1}[19], we have estimated that, for complete adsorption and with no zero-point correction, an activation barrier of 42 kcal/mol corresponds to a thermal activation in the range of 603–696 K. As in all experimental works the adsorption process occurred at room temperature and the calculated energy barrier corresponds to a thermal activation much higher than that, we understand that the cyan-met$_{dis}$ configuration is unlikely to be observed. For the di-σ_{CN} adsorbed model, on the other hand, our calculations suggest a

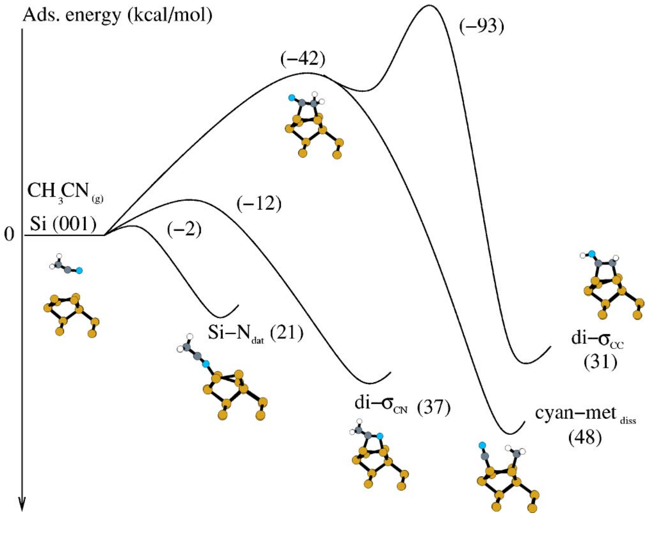

FIG. 2. Profile of the energy surface diagram for possible adsorption models of a single CH_3CN molecule on the Si(001):(2×2) surface. The values in parentheses correspond to the adsorption energies in kcal/mol (without zero-point corrections).

much lower activation barrier (12 kcal/mol, corresponding to a thermal activation barrier in the range of 175–201 K). As the energy barrier for the di-σ_{CN} adsorbed model corresponds to a thermal activation of the same order of the temperature in which the experiments by Bournel and co-workers[9,10] and Tao and co-workers[11] were carried out, we understand that our first-principles calculations are consistent with the experimental observations. It is interesting to note that our calculated adsorption energy for the di-σ_{CN} adsorbed model (37 kcal/mol) is larger than the adsorption energy of 29.6 kcal/mol predicted by Lu *et al.*,[12] and the estimated value of 31.6 kcal/mol obtained by Tao and co-workers. However, the present value is considerably larger then the activation energy for the desorption of the β1 state $E_{des}=29.8$ kcal/mol (attributed to a di-σ_{CN} adsorbed structure) obtained in the TPD experiment by Tao and co-workers[11] if we consider that activation energies for desorption should be compared with the sum of the binding energy and the activation energy. In the present case our data indicates a desorption energy around 47 kcal/mol, which is larger than the 30 kcal/mol measured by Tao and co-workers.[11] Lu *et al.*,[12] cluster calculations predicted that the formation of the di-σ_{CN} adsorbate would happen via the distortion of a Si-N$_{dat}$ structure with an energy barrier close to 7 kcal/mol. We could not follow this energy path using our present constrain dynamics scheme, as all tentative paths for the distortion of the C$\equiv$N bond of the Si-N$_{dat}$ adsorbate lead to its desorption. We understand that the difference between our results and the predictions by Lu *et al.*[12] are probably related to the fact that their cluster calculations do not correctly describe some aspects of the free silicon surface (such as, the buckling of the Si-Si dimers) and the limitations in their cluster size (dimer-dimer interactions, for example, are not considered in their calculations due to the small cluster—Si_9H_{12}—used by the authors). At this point, it is worth emphasizing that it is well known that the use of pseudopotentials in nonlocal density-functional theory calculations is responsible for an underestimation of the calculated activation energies. The degree of underestimation is system dependent and it was found to be around 10 kcal/mol for a Si_2H_6 model of H_2 desorption form Si(001).[22] One must also have in mind that our predicted dissociation pathway should be considered only as a general description of the reaction. This is because it does not correspond necessarily to the experimentally observed reaction, as local conditions might play a decisive role in this process. For this reason, we understand that we cannot completely rule out a possible Si—N$_{data}\rightarrow$di-σ_{CN} reaction pathway.

We also present in Fig. 2 the energetics for the adsorption of CH_3CN on the Si-N$_{dat}$ and di$-\sigma_{\mathrm{CC}}$ configurations. The Si-N$_{dat}$ structure is also found to be energetically favorable, with an adsorption energy close to 21 kcal/mol. By adding to this chemisorption energy our estimated energy barrier for the adsorption process, we get 23 kcal/mol, which is close to the TPD desorption energy of 24.6 kcal/mol experimentally observed by Tao and co-workers[11] for the β2 structure attributed by them to a di-σ-like configuration. The existence of a Si-N$_{dat}$ structure is consistent with the photoemission and NEXAFS data by Bournel and co-workers[10] indicating a N−Si dative configuration, but was entirely disregarded by Tao and co-workers.[11] The absence of vibrational mode around 2200 cm^{-1} and the large chemical shifts observed after annealing at 250 K are the main reasons gaven by Tao and co-workers for the impossibility of the existence of a Si-N$_{dat}$ like structure. This is in clear disagreement with the NEXAFS $\pi^{\star}(2)$ core level state attributed by Bournel and co-workers[10] to cyano or isocyano groups bonded to silicon dangling bonds after the dissociation of the molecule or to a N-Si dative bond configuration with a down Si dimer atom. As discused above, the dissociation reaction is unlikely to be observed. Therefore we understand that the NEXAFS and PES data from Bournel and co-workers[9,10] are probably related to a Si-N$_{dat}$ species. The adsorption of the acetonitrile molecule in the Si-N$_{dat}$ configuration is found to be almost barrierless, with a thermal activation barrier around 30 K. For the di-σ_{CC} adsorption model, although we have found a higher adsorption energy (31 kcal/mol), our first-principles calculations suggest that the adsorption in such configuration will take place via the same precursor state observed for the cyan-met$_{dis}$ model. As this precursor state adsorption reaction presents an activation barrier of 42 kcal/mol the di-σ_{CC} adsorption model is unlikely to be observed. Indeed we have found that the dissociation pathway leading from the precursor state to the di $-\sigma_{\mathrm{CC}}$ model involves a further activation barrier (this time close to 93 kcal/mol, corresponding to a thermal activation energy of 1355 K) which will make the probability of observation of such structure almost null.

Our first-principles calculations suggest that, for both considered end-bridge configurations (i.e., end-bridge$_{\mathrm{CC}}$ and end-bridge$_{\mathrm{CN}}$), the nitrogen atom is more likely to be adsorbed over the down silicon atom of the Si-Si dimer, as schematically indicated in Figs. 1(e) and 1(f). This is consistent with the fact that the adsorption of electron-rich species, such as NH_3, with the silicon surface are initiated by the interaction with the electrophilic surface atom. Our calculated adsorption energies are found to be 29.5 and 36.1 kcal/mol for the end-bridge$_{\mathrm{CC}}$ and end-bridge$_{\mathrm{CN}}$ adsorbed species, respectively. As the presented calculated adsorption energies are of the same order as those observed for the di$-\sigma$ and Si-N$_{dat}$ adsorbed structures, we have estimated the activation barriers for the adsorption of CH_3CN on such configurations. Our phenomenological approach indicates an activation barrier of 375 kcal/mol (corresponding to a thermal activation much higher than the system melting point) for the end-bridge$_{\mathrm{CC}}$ structure. For the end-bridge$_{\mathrm{CN}}$ adsorbed structure, on the other hand, this activation energy is much smaller (36 kcal/mol) and corresponds to a thermal activation energy around 600 K. Still this value is considerably higher than those found for the Si-N$_{dat}$ and di$-\sigma$ adsorption models, suggesting that end-bridge adsorbed structures are not likely to be observed in the experimental conditions reported in all addressed investigations, although its existence cannot be completely ruled out.

We have further extend our study in order to investigate the possibility of the adsorption of a second acetonitrile molecule (corresponding to 1.0 ML CH_3CN coverage, i.e., one molecule per Si-Si dimer). For both the di-σ_{CN} and Si-N$_{dat}$ models, the calculated adsorption energy are slightly smaller (35 kcal/mol and 18 kcal/mol, respectively) than those found for a 0.5 ML coverage. This indicates 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 acetonitrile if the silicon surface is exposed to a rich CH_3CN environment or if the exposure occurs for a long period of time. This is consistent with the experimental observations by Bournel and co-workers[9,10] whose findings indicate that Si-Si dimer states disappear upon adsorption of acetonitrile, suggesting a saturation coverage around 1 ML. This was also observed for the adsorption of other hydrocarbons, such as acetylene.[4] Although we have found that the adsorption of a single acetonitrile molecule in an end-bridge$_{CN}$ configuration is unlikely to be observed, we have investigated the possibility of the adsorption of a second molecule in such structure, considering neighboring acetonitriles aligned in the same and opposite directions. While the adsorption energy decreases considerably for acetonitriles adsorbed in the same direction, only a small decrease is observed for acetonitriles adsorbed in opposite directions, as is the case for the di-σ and Si-N$_{dat}$ models. However, the energy barrier for the adsorption of a second molecule in opposition to the first adsorbed molecule is slightly larger than that observed for the 0.5 ML coverage case. Therefore we understand that our calculations clearly indicate that single or paired end bridge structures are not likely to be observed for this system. Our total energy calculations suggest that the interaction of CH_3CN with the silicon surface will most likely result in the formation of the di-σ_{CN} and Si-N$_{dat}$ structures (with adsorption energies of 37 and 21 kcal/mol, respectively, for a 0.5 ML acetonitrile coverage). This is consistent with the overall experimental picture indicated by Bournel and co-workers,[9,10] but while the di-σ_{CN} was also predicted by Tao and co-workers[11] the existence of a possible Si-N dative bond configuration is in clear contrast to their conclusions. With a view to explore this apparent contradiction, we are going to refrain our analysis from now on to these two adsorbed species.

In Table I, we present the key structural parameters obtained in our first-principles calculations for the di-σ_{CN} and Si-N$_{dat}$ structures. Upon the adsorption of CH_3—CN, the Si-Si dimer gets elongated by ≈2%, for both adsorption models, and becomes symmetric. This finding is in agreement with experimental[23] as well as theoretical[4,8] findings for other small hydrocarbon molecules, such as acetylene and ethylene. It is worth pointing out that the structural data presented here correspond to the 0.5 ML coverage adsorbed system. For simplicity, the structural data for the Si-Si dimers that do not correspond to an adsorption site are not discussed, 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 17.9°, indicating that the interaction between the adsorbate and the neighboring free dimer is not very strong. The calculated C−H bond length of ~1.11 Å for both the di-σ_{CN} and Si-N$_{dat}$ models is also in good agreement with early theoretical estimates for other small hydrocarbon molecules and is close to that observed for the free CH_3—CN molecule. Our calculations also indicate that the C-Si bond length is approximately 1.90 Å for the di-σ_{CN} model, which is again comparable to the C-Si bond length observed for other hydrocarbons. This indicates that the nature of the Si-Si and C−H bonds is not decisively affected by the small hydrocarbon molecule considered or by the choice of the adsorption site. While our structural data is comparable to the findings by Lu *et al.*[12] for the Si-N$_{dat}$ adsorbed structure, the same is not observed for the bond length and bond angles calculated for the di-σ_{CN} structure. We believe that the difference between our results and the predictions by Lu *et al.*[12] are probably related to the limitations on their cluster calculations, as discussed above.

TABLE I. Comparison of the key structural parameters for acetonitrile adsorption on the Si(001)-(2×2) surface. The models are schematically shown in Fig. 1. All bond lengths (d) are in angstorm, bond angles in degrees. $d_{Si\text{-}Si}$ represents the Si-Si dimer length for the adsorption site when the other dimer is unreacted.

	di-σ_{CN}		Si-N$_{dat}$	
	pres	cluster (Ref. 12)	pres	cluster (Ref. 12)
$d_{\text{Si-Si}}$	2.33	2.25	2.36	2.39
$d_{\text{C-N}}$	1.37	1.29	1.16	1.16
$d_{\text{C-C}}$	1.27	1.50	1.43	1.45
$d_{\text{Si-C}}$	1.89	1.98		
$d_{\text{Si-N}}$	1.90	1.82	1.83	1.89
$d_{\text{C-H}}$	1.11		1.10	
∠C-C-N	156	122	176	180
∠Si-N-C	106		170	173
∠Si-Si-N	74	79	114	108
∠H-C-H	105		106	

The surface band structure resulting from our calculation for the di-σ model considering a 0.5 ML coverage is shown in Fig. 3. We have identified five surface states within the fundamental band gap of silicon: these are labeled σ, p_1, p_{do}, p_{du}, and p_2. The p_{do} and p_{du} states correspond to the occupied and unoccupied surface states of the free silicon

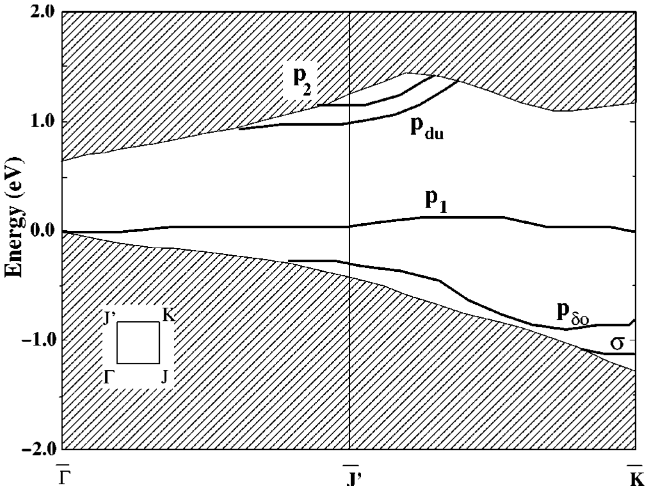

FIG. 3. Surface band structure for the di-σ_{CN} model for the adsorption of CH_3CN on the Si(001)-(2×2) surface. The shaded area corresponds to the projected bulk band structure, while surface states are denoted as solid lines.

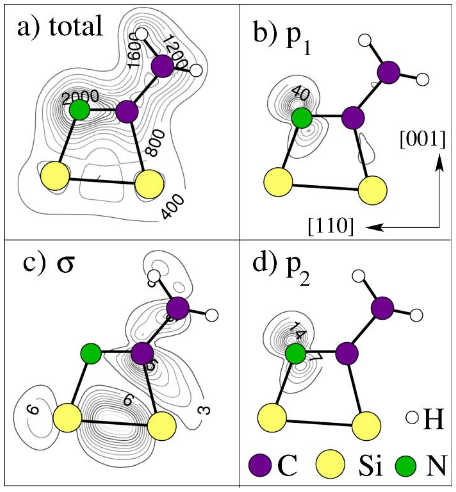

FIG. 4. Charge density plot for the di-σ_{CN} model for the adsorption of CH_3CN on the Si(001)-(2×2) surface. All charge density contour plots were obtained at the **K** point, except for the p_2 surface state that was obtained at the **J** point. All drawings are in the [001]-[110] plane. Bonds in the drawing plane are shown as solid lines. The contour values are in units of 10^{-3} electrons per unit-cell volume.

surface and are localized at the up and down atoms, respectively, of the Si-Si dimer not bonded to the acetonitrile molecule, and therefore are not discussed here. As seen in Fig. 4, the occupied p_1 state (with binding energy around 0.1 eV) and the unoccupied p_2 state are mainly localized on the nitrogen atom. The σ state with binding energies around 0.5 eV is mainly localized on the Si-Si dimer underneath the adsorbate, and represent the interaction between Si-Si $pp\sigma$ and different CN orbital components of the CH_3CN molecule. The main structural difference between the 1.0 and 0.5 ML acetonitrile coverages of the di-σ_{CN} 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_{do} and p_{du} surface states are not observed, as they are related to the free Si-Si dimer. In other words, for the 1.0 ML acetonitrile coverage, the binding energies and the surface states dispersion are very similar to that observed for the 0.5 ML coverage. In fact, the differences in the binding energies of these states for the two coverages are always smaller than 0.05 eV. These small changes in the surface states observed upon the adsorption of a second acetonitrile molecule indicate that adjacent dimer interactions are minimal, which is consistent with the small energy difference observed for both structures. Comparing the present calculated band structure to that obtained for the acetylene adsorption on silicon surface,[4] we note that while for acetylene there are no occupied states due to the adsorbate, the presence of a Si-N bonding induced the presence of the p_2 state. An occupied p-like state, such as p_{do} is also not observed for the acetylene covered system. This could indicate that acetonitrile electronic interaction with the silicon substrate is stronger than that observed for acetylene.

The surface band structure for the Si-N$_{dat}$ model is presented in Fig. 5. An inspection of this figure clearly shows that this model has a semiconducting nature, and therefore indeed represents a metastable configuration for the adsorption of acetonitrile on the silicon surface, as observed in our total-energy calculations. This is consistent with the experimental observations of this system by the TPD measurements by Tao and co-workers,[11] and confirms the suggestions from Hamers *et al.*[1] that the irreversible binding of simple organic molecules to the surface is characterized by the formation of strong covalent bonds in various metastable configurations. For this adsorption model we have identified only three surface states, namely, p, p_{do}, and p_{du} (shown in Fig. 6). From those, only the p state is related to the adsorbate, and is mainly localized on the silicon atom not forming

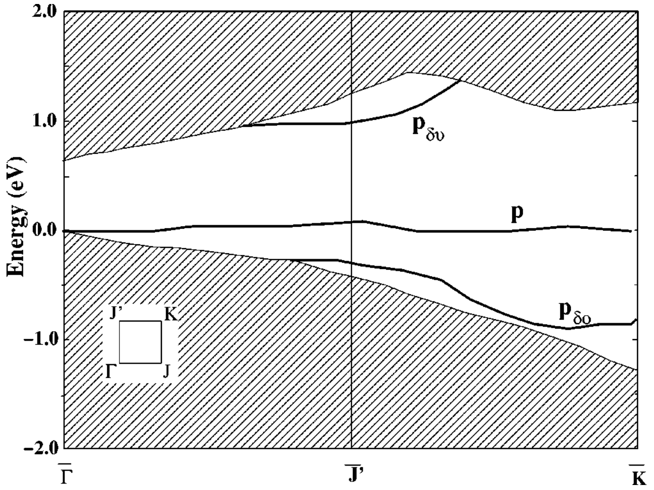

FIG. 5. Surface band structure for the Si-N$_{dat}$ model for the adsorption of CH_3CN on the Si(001)-(2×2) surface. The shaded areas represent the projected bulk band structure, while surface states are denoted as solid lines.

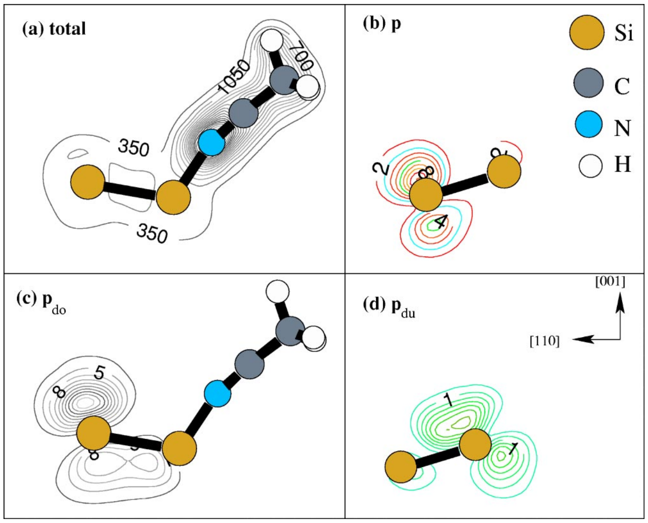

FIG. 6. Charge density plot for the Si-N$_{dat}$ model for the adsorption of CH_3CN on the Si(001)-(2×2) surface. All charge density contour plots were obtained at the **K** point, except for the p_{du} surface state that was obtained at the **J** point. All drawings are in the [001]-[110] plane. Bonds in the drawing plane are shown as solid lines. The contour values are in units of 10^{-3} electrons per-unit-cell volume.

TABLE II. Calculated vibrational modes for the di-σ_{CN} and Si-N$_{dat}$ adsorption models of CH_3CN on the Si(001)-(2×2). The gas phase CH_3CN molecule is also presented. All values are in cm^{-1}.

	CH_3CN on Si(001)				CH_3CN (gas)	
mode	Present		Expt. (Ref. 11)		Present	Expt. (Ref. 11)
	di-σ_{CN}	Si—N$_{dat}$	Chem	Phys		
CH_3sym str	3186	3261	3012	3005	3044	3009
CH_3asym str	2969	3056	2970		2988	2954
C≡Nstr		2317		2218	2214	2268
C=Nstr	1725		1603			
CH_3rock	1081	1057	1065	1026	991	1041
C-Cstr	855	913	952	915	883	920
Si-Nstr	793	620	835			
Si-Cstr	618		695			
CCNbend	403	542	412		486	361

the Si-N dative bond. As for the di-σ_{CN} structure, the occupied p_{do} and unoccupied p_{du} states are due to the free Si-Si dimer.

For calculating the zone-center optical phonon modes we set up a 48×48 eigenvalue problem, and identified selected modes that describe pronounced surface character. The results of our calculations, available experimental data, for stretch and bend modes for the di-σ_{CN} and Si-N$_{dat}$ adsorption models, as well the data for the CH_3CN molecule in its gas phase, are presented in Table I. As for the acetylene case,[4] the vibrational modes of the adsorbates obtained for both structures when an acetonitrile 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. Considering the error bars for both the experimental and theoretical procedure, our calculated vibrational modes (presented in Table I) for the di-σ_{CN} structure are close to the experimental observations by Tao and co-workers,[11] when they are compared to the experimentally proposed chemisorbed specie. Surprisingly, the same is observed when the Si-N$_{dat}$ structure vibrational modes are compared to the experimental observations by Tao and co-workers' for the physisorbed specie. It is interesting to note that Tao and co-workers analysis of their core level shift data suggests that the physisorbed adsorbate is mainly related to van der Waals bonded species, disregarding the existence of a possible Si-N$_{dat}$ structure. However, this analysis is in contrast to the core level transitions observed and discussed by Bournel and co-workers[9,10] and the theoretical analysis by Lu *et al.*[12] We can only speculate that the annealing process carried out by Tao and co-workers[11] before the core level shift analysis might have led to the desorption of a considerable amount of the Si-N$_{dat}$ adsorbate, reducing its signal accordingly. If this is the case, the vibrational modes experimentally observed and attributed to a physisorbed specie by Tao and co-workers might be reinterpreted as the signature of the Si-N$_{dat}$ adsorbate. The agreement between calculated and experimental vibrational modes data combined to the experimental observations via photoemission and NEXAFS of a state possibly originated from a Si-N dative bond configuration[10] suggests that the physisorbed and chemisorbed species could possibly represent our di-σ_{CN} and Si-N$_{dat}$ models. In other words, our theoretical results, combined with the photoemission and NEXAFS data, suggest the possibility of another interpretation for the HREEL spectra obtained by Tao and co-workers.[11] We propose that Tao and co-workers have actually observed a mixed domain of the di-σ_{CN} and Si-N$_{dat}$ adsorbed species, instead of a physisorbed and a chemisorbed structure. Our mixed domain model would explain not only the vibrational results by Tao and co-workers,[11] but also their TPD spectra. This is because they have suggested the existence of two chemisorbed species: $\beta1$ (with binding energy of 29.8 kcal/mol) and $\beta2$ (with binding energy of 24.6 kcal/mol), whose binding energies could not possibly represent a physisorbed system. We would like to emphasize that our proposed mixed domain structure is also consistent with the photoemission and NEXAFS transitions for acetonitrile obtained by Bournel and co-workers[10] suggesting a possible Si—N dative bond configuration. It is worth pointing out that both the experimental works by Bournel and co-workers[9,10] and by Tao and co-workers[11] clearly indicate the possibility of the existence of a mixed domain structure, supporting our theoretical proposal.

In the next step of our study, we simulated the STM images for our most probable structures, i.e., CH_3—CN adsorbed via a CN:[2+2] cycloaddition (di-σ_{CN}) and via the Si-N dative bond (Si-N$_{dat}$). STM images were obtained from the calculated electronic eigensolutions, following the Tersoff-Hamann formalism, as described in Ref. 17. Figure 7 shows the theoretical STM image for the filled states of the CH_3—CN:Si(001)-(2×2) system, considering the (a) di-σ_{CN} and (b) Si-N$_{dat}$ adsorption models. The (2×2) reconstruction is easily identified in both images and is indicated by the dashed rectangles. 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 all tunneling currents are considered and represented by

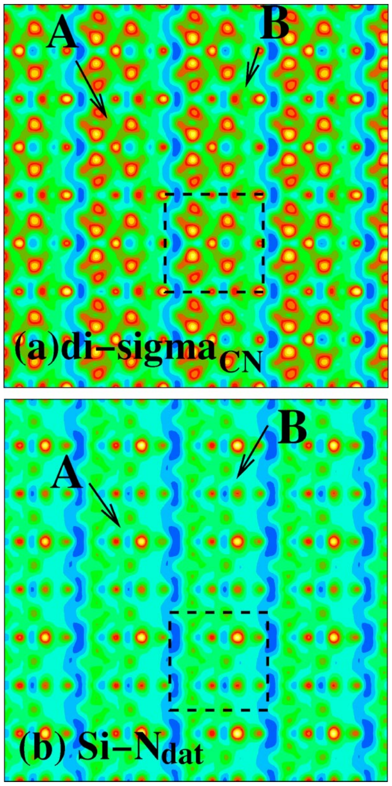

FIG. 7. Theoretical STM image obtained for a bias voltage of −2.0 V for the (a) [2+2] cycloaddition adsorption via the C-N group (di-σ_{CN}) and (b) Si−N dative (Si-N$_{dat}$) adsorption models for the interaction of a single CH_3CN molecule with the Si(001)-(2 ×2) surface (corresponding to a 0.5 ML coverage). The dashed rectangle indicates the unit cell, while *A* and *B* indicate the adsorbed molecule and the Si-Si dimer features, respectively.

different brightness. If only the brighter regions are considered, only the adsorbate (depicted by *B* in Fig. 7) and the Si-Si dimer (*A* in Fig. 7) can be identified. Note that our free Si-Si dimer signature is not as strong as in a STM experiment as our electronic eigensolutions represents a tilted dimer. This is not the case in a STM experiment, where the image is taken in a time scale that is bigger than the dimers flip-flop movement, and so the image has contributions from both sides of the dimer.[24] Even considering the differences between theoretical and experimental STM images, it is clear from Fig. 7 that the image pattern obtained for the di-σ_{CN} adsorbate is completely different from the pattern obtained for the Si-N$_{dat}$ adsorbed structure. While for the Si-N$_{dat}$ our calculations suggest that the final image will be characterized by a sharp peak, for the di-σ_{CN} structure the resulting image will be more diffused and spread over the Si-Si dimer. Therefore, we understand that a simple STM experiment could possibly prove the existence of a mixed domain surface for the adsorption of acetonitrile on the silicon (001) surface.

IV. SUMMARY

We have performed first-principles calculations for the atomic structure and dynamical properties of the adsorption of acetonitrile on the silicon surface. Our first-principles calculations indicate that CH_3CN adsorb via a [2+2] cycloaddition reaction through the C≡N group (di-σ_{CN}) with an adsorption energy around 37 kcal/mol, close to the 30 kcal/mol estimated by Tao and co-workers.[11] The agreement between our calculated vibrational modes and the experimental HREELS data obtained by Tao and co-workers further support the existence of a di-σ_{CN} adsorbate. We have further explored the existence of multiple adsorption species and found that a Si-N$_{dat}$ model is also possible, with an adsorption energy close to 21 kcal/mol. While the existence of a di-σ_{CN} structure is in agreement with all available experimental and theoretical data, a possible Si-N$_{dat}$ model is supported by the theoretical work by Lu *et al.*[12] and the photoemission and NEXAFS experimental data by Bournel and co-workers,[9,10] but is clearly disregarded by the TPD and XPS analysis by Tao and co-workers.[11] As our estimated desorption energies for both structures are considerably different (23 kcal/mol for the Si-N$_{dat}$ species against 49 kcal/mol for the di-σ_{CN} structure) we suggest that the annealing process performed by Tao and co-workers might have led to the desorption of a considerably amount of Si-N$_{dat}$ adsorbates, reducing its signal accordingly. If this is correct and based on our energetic analysis and our calculated vibrational modes we propose that the contrast between the photoemission and NEXAFS data obtained by Bournel and co-workers[9,10] and the HREEL, TPD and XPS analysis by Tao and co-workers[11] could be explained by the existence of a mixed domain surface composed by both the di-σ_{CN} and Si-N$_{dat}$ models. We present theoretical STM images of the possible adsorbed systems and suggest that this experimental procedure could possibly identify the existence of the mixed domain structure, as the di-σ_{CN} presents a scattered pattern in contrast to the sharp image pattern observed for the Si-N$_{dat}$ adsorbed species. In addition, the electronic structure and surface states for both the di-σ_{CN} and Si-N$_{dat}$ models are discussed in detail.

ACKNOWLEDGMENTS

The authors acknowledge financial support from the Brazilian agencies CNPq, DPP-UnB, Finatec, and Fapesp.

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*Electronic address: romiotto@fis.unb.br

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