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Adsorption geometries and vibrational modes of C_2H_2 on the Si(001) surface

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Adsorption geometries and vibrational modes of C_2H_2 on the Si(001) surface are studied by means of density-functional theory within the generalized gradient approximation. By comparing theoretically calculated high-resolution electron-energy-loss spectra with experimentally reported spectra, it is clearly shown that at least two energetically most stable adsorption states coexist.

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Adsorption of hydrocarbons on Si surfaces has been intensively studied because of fundamental as well as technological importance.[1,2] Among them, C_2H_2 and C_2H_4 adsorption on the Si(001) surface are the simplest cases and have been studied using various experimental and theoretical techniques. Nishijima and co-workers[3,4] proposed a structural model in which C_2H_2 and C_2H_4 are adsorbed on a substrate Si dimer with their C-C axis parallel to the dimer bond [shown in Fig. 1(a), denoted by $\mathrm{HB}_\parallel$ model hereafter[5]]. As for the adsorption of C_2H_4, the $\mathrm{HB}_\parallel$ model has been supported by many studies and has been well established.[6–8] On the other hand, for C_2H_2 adsorption, although the model has been supported by several studies,[8–15] several problems have been raised and the subject is now in intense debate. From high-resolution electron-energy-loss spectroscopy (HREELS) experiments, Widdra *et al.*[16] inferred that the symmetric out-of-plane CH bending [$\rho_s(\mathrm{CH})$] mode has a significantly large dynamic dipole moment perpendicular to the surface, which cannot be explained by the $\mathrm{HB}_\parallel$ model. By using scanning tunneling microscopy (STM), Li *et al.*[17] observed that the C_2H_2-adsorbed Si(001) surface has $p(2\times2)$ or $c(4\times2)$ periodicity and suggested that C_2H_2 molecules occupy the Si dimers alternately along the dimer row. In contrast to the STM results, the saturation coverage of C_2H_2 on the Si(001) surface was reported to be nearly one molecule per one Si dimer site on the basis of thermal desorption spectroscopy (TDS) outcomes.[16,18] Furthermore, a recent photoemission study[19] showed that upon saturation of C_2H_2, all the Si dangling bonds are saturated and only one surface component exists in the Si $2p$ core level. Xu *et al.*[7] proposed a new structural model in which C_2H_2 is adsorbed between the two Si dimers along the dimer row with its C-C axis parallel to the Si dimer bond [shown in Fig. 1(c), denoted by $\mathrm{HH}_\parallel$ model hereafter]. Very recently, Sorescu and Jordan[20] carried out density-functional calculations with slab models and examined several possible adsorption structures. They found that although the $\mathrm{HB}_\parallel$ model is the most stable structure at low-coverage regime, the bridge site between the two neighboring dimers along the dimer row [shown in Figs. 1(g) and 1(h), denoted by $\mathrm{B2}_\perp$ model hereafter] becomes the most stable adsorption site above ~0.5 monolayer (ML).

In this study, adsorption geometries and vibrational modes are examined for C_2H_2 on the Si(001) surface by means of density-functional theory[21,22] (DFT) within the generalized gradient approximation (GGA). Briefly, the results of the present work are as follows: At 0.5 ML, the $\mathrm{HB}_\parallel$ structure is the most stable configuration while at 1.0 ML, in turn the $\mathrm{B2}_\perp$ structure becomes the most stable configuration, in agreement with the work of Sorescu and Jordan. Comparison of theoretically calculated HREEL spectra with experimental spectra allows one to clearly conclude that both the $\mathrm{B2}_\perp$ 1 ML configuration and the $\mathrm{HB}_\parallel$ configuration coexist.

All DFT calculations are carried out using the program package called STATE (simulation tool for atom technology), which has been successfully applied for molecular adsorption problems on Si surfaces[9,23–25] as well as metal surfaces.[26,27] We adopted the Perdew, Burke, and Ernzerhof exchange and correlation functional.[28] Vanderbilt's ultrasoft pseudopotentials[29] are used for C $2p$ and H $1s$ components, while other components are described by the Troullier-Martins norm-conserving pseudopotentials.[30] Wave functions are expanded in a plane wave basis set and the cutoff energies for wave functions and augmentation charges are 25 Ry and 225 Ry, respectively. We used a repeated slab model, in which one slab consists of eight Si atomic layers and a vacuum region of 13.8 Å separates the periodically repeated slabs. Adsorbates are introduced only on one side of the slab, while the atoms of the other side are kept fixed to the ideal

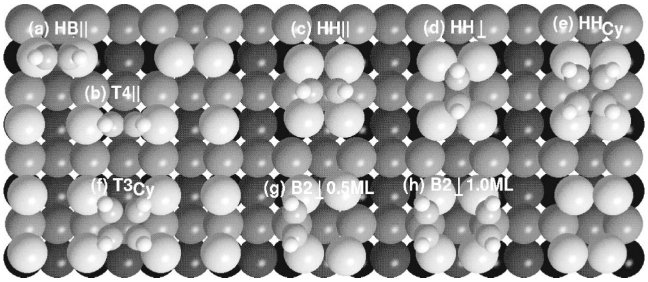

FIG. 1. Top view of the adsorption geometries of C_2H_2 on the Si(001) surface. (a) $\mathrm{HB}_\parallel$, (b) $\mathrm{T4}_\parallel$, (c) $\mathrm{HH}_\parallel$, (d) $\mathrm{HH}_\perp$, (e) $\mathrm{HH}_{\mathrm{Cy}}$, (f) $\mathrm{T3}_{\mathrm{Cy}}$, (g) $\mathrm{B2}_\perp$ (0.5 ML), and (h) $\mathrm{B2}_\perp$ (1.0 ML) configurations. Small, medium, and bright large circles indicate H, C, and the first-layer Si atoms, respectively, while darker large circles indicate Si atoms deeper than the first layer.

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bulk positions and the dangling bonds are terminated by H atoms. The work function difference between the two surfaces is compensated by a scheme proposed by Neugebauer and Scheffler.[31] Since the effect of the correction is very small, the geometry optimizations could be carried out neglecting this correction, which is instead, included in the calculation of the dynamic dipole moments of surface vibrational modes. A $p(2\times2)$ supercell is used for all calculations and the surface Brillouin zone was sampled with 16 k points. Adsorbates and the six surface Si layers are allowed to relax, while the bottom two Si layers and the terminating H atoms are kept fixed. The vibrational normal mode frequencies ω_k and normal coordinates Q_k of adsorbates are calculated by diagonalizing the Hessian matrices which are numerically estimated by displacing the adsorbate atoms and the top three Si layers by 0.015 to 0.1 Å. The dynamic dipole moments of the vibrational modes $d\mu/dQ_k$ are then calculated to estimate the intensity of HREEL spectra. The absolute intensity of energy loss peaks from the dipole scattering mechanism is expressed as[32]

$$\frac{I_{\mathrm{loss}}}{I_{\mathrm{elastic}}}=\frac{\hbar(1-2\theta_E)^{1/2}}{8a_0\epsilon_0E_I\cos\theta_I}\left(\frac{d\mu}{dQ_k}\right)^2\frac{1}{\omega_k}F_s(\hat{\theta}_c)n_s\,, \tag{1}$$

where a_0 is the Bohr radius, ϵ_0 is the vacuum permittivity, E_I is the primary energy of electron beam, and θ_I is the incident angle of electron beam. $\theta_E=h\omega_k/2E_I$ and $\hat{\theta}_c=\theta_c/\theta_E$, where θ_c is the acceptance angle of the spectrometer. We assumed E_I and θ_c to be 5.0 eV and 3.0°, respectively. These assumed experimental parameters affect the calculated intensity of HREEL spectra to some extent, but they do not alter the main conclusion of the present work. n_s is the coverage of adsorbates. $F_s(\hat{\theta}_c)$ is given by

$$F_s(\hat{\theta}_c)=(\sin^2\theta_I-2\cos^2\theta_I)\frac{\hat{\theta}_c^2}{1+\hat{\theta}_c^2}+(1+\cos^2\theta_I)\ln(1+\hat{\theta}_c^2). \tag{2}$$

Figure 1 shows various adsorption geometries examined in this study. Figure 1(b) shows a model in which C_2H_2 is absorbed just above a fourth layer Si atom in the trough between the dimer rows with its C-C axis parallel to the Si dimer bond (denoted by $T4_{\parallel}$ model hereafter). The $T4_{\parallel}$ model corresponds to the dimer creaved model examined in our previous study.[9] The $HH_{\parallel}$ [Fig. 1(c)] model was proposed by Xu *et al.*[7] In Figs. 1(e) and 1(f), two C_2H_2 molecules are assumed to form cycrobutadiene and they are absorbed on the hill of the dimer row at the hollow site (denoted by HH_{Cy} model) and in the trough just above a third layer Si atom (denoted by $T3_{\mathrm{Cy}}$ model), respectively. The $B2_{\perp}$ [Figs. 1(g) and 1(h)] models were studied in previous works.[20,33] The adsorption energies of these adsorption models are summarized in Table I. The adsorption energies of the $HB_{\parallel}$ and the $T4_{\parallel}$ configurations in the present study turn out to be 4–5 kcal/mol smaller than those of our previous study.[9] In our previous study, a $p(2\times1)$ buckled dimer configuration was used for the clean Si(001) surface, while a $p(2\times2)$ buckled dimer configuration is used in the present study. Considering that the $p(2\times2)$ geometry is more stable than the $p(2\times1)$ geometry by 2.1 kcal/mol,[34] the adsorption energies agree within 3 kcal/mol in both studies. The present study suggests little dependence of the adsorption energy on the coverage for the $HB_{\parallel}$ configuration, in contradiction to the results by Sorescu and Jordan,[20] where they reported that the adsorption energy changes from 63.15 kcal/mol ($\theta=0.125$) to 57.45 kcal/mol ($\theta=1.0$). Although the reason for the discrepancy is not clear to us, this point does not affect the conclusion of the present work, thus we shall not discuss it any further. A remarkable feature of Table I is the large dependence of the adsorption energy of the $B2_{\perp}$ configuration on the coverage and the fact that it becomes the most stable configuration at $\theta=1.0$, in good agreement with Sorescu and Jordan.[20] At $\theta=0.5$, two isolated dangling bonds are created by adsorption of C_2H_2 as shown in Fig. 1(g), while they are saturated at $\theta=1.0$ as shown in Fig. 1(h). Therefore, we should ascribe the adsorption energy difference between the two coverages (6.0 kcal/mol) mainly to the pairing energy of two isolated dangling bonds, which is estimated to be 7.4 kcal/mol.[35]

TABLE I. The adsorption energies (E_{ad}) of various adsorption structures given in Fig. 1.

Site	θ (ML)	Structure in Fig. 1	E_{ad} (kcal/mol)
$HB_{\parallel}$	0.5	(a)	60.67
	1.0		60.72
$T4_{\parallel}$	0.5	(b)	35.16
	1.0		36.03
$HH_{\parallel}$	0.5	(c)	24.01
$HH_{\perp}$	0.5	(d)	39.51
HH_{Cy}	1.0	(e)	58.31
$T3_{\mathrm{Cy}}$	1.0	(f)	31.85
$B2_{\perp}$	0.5	(g)	58.34
	1.0	(h)	64.36

To provide support to the existence of the $B2_{\perp}$ configuration, vibrational modes and their dynamical dipole moments have been computed and the intensity of loss peaks in HREELS has been estimated on the basis of the dipole scattering mechanism. As mentioned above, our main concern is the strongest peak due to the ρ_s(CH) mode observed at 680 (530–540) cm^{-1} for C_2H_2 (C_2D_2) absorbed Si(001).[3,16] We have calculated HREEL spectra of C_2D_2 adsorbed system instead of C_2H_2 because the ρ_s(CH) mode is close in frequency to the symmetric Si-C stretching [ν_s(Si-C)] mode and it cannot be resolved clearly, while the ρ_s(CD) mode is isotope shifted and is well separated from the ν_s(Si-C) mode. Figure 2 shows the theoretically calculated HREEL spectra for various adsorption models. The intensity calculated from Eq. (1) is broadened by Gaussians the full width at half maximum (FWHM) of which is 80 cm^{-1}. As reported in our previous study,[9] experimentally observed vibrational frequencies can be well reproduced by the $HB_{\parallel}$ model, and this fact led us to the conclusion that the $HB_{\parallel}$ configuration should be the correct adsorption geometry.[9] Figures 2(a) and

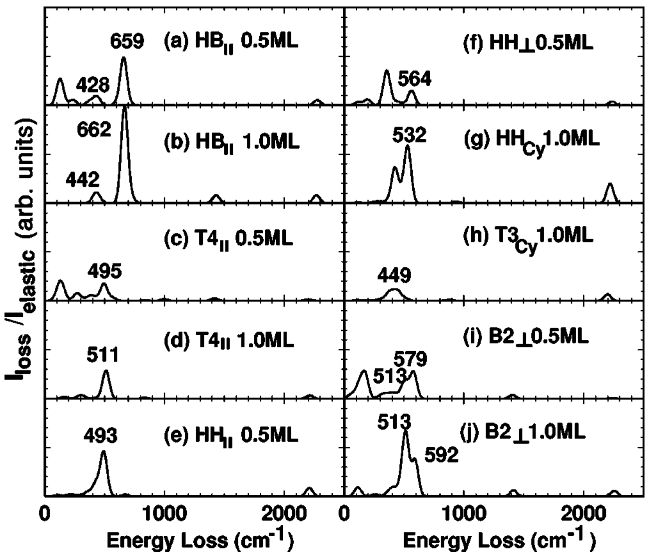

FIG. 2. Theoretically calculated HREEL spectra due to the dipole scattering mechanism for various structural models.

2(b), however, clearly demonstrate that the experimentally observed strongest loss peak due to the ρ_s(CD) mode cannot be reproduced at all because it is dipole forbidden by symmetry reasons. Although the T4$_\parallel$ (511 cm^{-1}), the HH$_\parallel$ (493 cm^{-1}), the HH$_{Cy}$ (532 cm^{-1}), and the B2$_\perp$ (1.0 ML) (513 cm^{-1}) models give sharp peaks near 530 cm^{-1}, the B2$_\perp$ (1.0 ML) model can be unequivocably identified by looking at the nature of the modes. In the T4$_\parallel$, the HH$_\parallel$, and the HH$_{Cy}$ models, strong peaks near 500 cm^{-1} are not ascribed to the ρ_s(CD) mode but to the ν_s(Si-C) mode, and therefore, they do not show large isotope shift between C_2H_2 and C_2D_2 adsorption, in disagreement with the experimental results. Thus, we can conclude that the B2$_\perp$ (1.0 ML) model is the only model that can reproduce the ρ_s(CD) mode.[36] We now turn to the second strongest peak, the ν_s(Si-C) mode observed at 670–675 cm^{-1}.[3,16] In the B2$_\perp$ (1.0 ML) model, the ν_s(Si-C) mode appears at 592 cm^{-1}, which is about 80 cm^{-1} smaller than the experimental value. Considering that GGA functionals reproduce the experimentally observed fundamental frequencies remarkably well,[37] this discrepancy seems to be too large to be explained on the basis of the DFT level adopted. We propose an alternative interpretation for this mode. As discussed in our previous study and as clearly demonstrated in Figs. 2(a) and 2(b), the HB$_\parallel$ model reproduces the ν_s(Si-C) mode quite well. Furthermore, the HB$_\parallel$ configuration gives a loss peak more than a factor of two stronger than the B2$_\perp$ (1.0 ML) configuration. Hence, we believe that the B2$_\perp$ (1.0 ML) configuration and the HB$_\parallel$ configuration coexist and the strongest loss peak observed at $\sim$530 cm^{-1} should be ascribed to the ρ_s(CD) mode of the B2$_\perp$ (1.0 ML) configuration, while the second strongest loss peak observed at $\sim$670 cm^{-1} should be ascribed to the ν_s(Si-C) mode of the HB$_\parallel$ configuration. We can actually observe a weak shoulder in the lower side of the 670 cm^{-1} peak in both the Nishijima *et al.* and Widdra *et al.* experimental HREEL spectra.[3,16] This shoulder is presumably due to the ν_s(Si-C) mode of the B2$_\perp$ (1.0 ML) configuration.

In conclusion, we have studied adsorption geometries of C_2H_2 on the Si(001) surface using a generalized gradient approximation in the framework of the density-functional theory. In the low-coverage regime, the HB$_\parallel$ model in which C_2H_2 is di-σ-bonded on a Si dimer with its C-C axis parallel to the dimer bond is the most stable structure, while in the high-coverage regime, the B2$_\perp$ (1.0 ML) model in which C_2H_2 is di-σ-bonded to two neighboring Si dimers along the dimer row becomes the most stable adsorption geometry. By comparing the theoretically calculated HREEL spectra with experimental spectra, it is clearly demonstrated that these two most energetically stable adsorption states coexist.

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