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Bonding configurations of acetylene adsorbed on the Si(100)-2 × 1 surface predicted by density functional cluster model calculations

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We have used the hybrid density functional B3LYP method in combination with cluster surface models to study the adsorption of C_2H_2 on the Si(100)-2 × 1 surface. Four bonding configurations of C_2H_2 adsorption on a single Si dimer and on two neighboring dimers have been found. Two bonding configurations with C_2H_2 di-σ bonds result in high and comparable adsorption energies (> 60 kcal mol^{-1}), whereas the two bonding configurations with C_2H_2 tetra-σ bonded over two neighboring Si dimers give lower, but substantial, adsorption energies centering around 44 kcal mol^{-1}. The calculated vibrational frequencies for the bonding configurations with C_2H_2 di-σ bonded structures are found to be in reasonable agreement with the experimental HREELS spectra reported in the literature (M. Nishijima, J. Yoshinobu, H. Tsuda and M. Onchi, *Surf. Sci.*, 1987, **192**, 383; C. Huang, W. Widdra, X. S. Wang and W. H. Weinberg, *J. Vac. Sci. Technol. A*, 1993, **11**, 2250).

Introduction

The adsorption of acetylene (C_2H_2) on Si single crystal surfaces has received considerable attention in both experiment[1–8] and theory[9–15] over the past decades. Acetylene is considered to be a promising precursor for chemical vapor deposition (CVD) of silicon-carbide and diamond-like films on silicon surfaces. The interest in these studies arises from the challenge in determining the electronic and geometric structures of C_2H_2 on reconstructed Si surfaces. Despite the extensive efforts that have been devoted to this seemingly simple chemisorption system, several fundamental issues still remain controversial regarding the structure and bonding between the C_2H_2 molecule and the Si surface. The controversy lies in the nature of C–C bonding (*i.e.* the C atoms in acetylene rehybridized either to the sp^2 state or to the sp^3 state) and the configuration of Si dimers beneath them (*i.e.*, the dimer bonds either cleaved or preserved upon chemisorption).

On the experimental side, Nishijima *et al.*[1] investigated the C_2H_2/Si(100)-2 × 1 chemisorption system using HREELS (high resolution electron energy loss spectroscopy) and LEED (low energy electron diffraction), and inferred that C_2H_2 was di-σ bonded to the dangling bonds of a Si dimer with the dimer bond preserved and the C molecular orbitals rehybridized from the sp to the sp^3 state. Also using HREELS, Huang *et al.*[2] observed a new peak at 1450 cm^{-1}, which had not been detected by Nishijima *et al.*,[1] and argued that the adsorbed C_2H_2 should possess an sp^2 hybridization state with a C=C double bond length of ∼1.4 Å, and the substrate Si dimer should be cleaved to make an appropriate bond angle between the C=C and the Si–C bonds. This is consistent with the model proposed earlier by Taylor *et al.*[3] In their TPD (temperature-programmed desorption) and AES

(Auger electron spectroscopy) experiments, Taylor *et al.*[3] found that C_2H_2 chemisorbed onto the Si(100)-2 × 1 surface *via* a mobile precursor and the saturation coverage was 1 ML (monolayer). Recent STM (scanning tunneling microscope),[4] XPS (X-ray photoelectron spectroscopy),[5] NEXAFS (near edge X-ray absorption fine structure)[6] and UPS (ultraviolet photoemission spectroscopy)[6] studies confirm that the Si dimer remains uncleaved upon C_2H_2 chemisorption.

On the theoretical side, Liu and Hoffmann, using EH (extended Hückel), HF (Hartree–Fock) and DFT (density functional theory) methods, predicted the presence of a precursor state, a π-complex formed between C_2H_2 and a Si dimer, and the formation of a chemisorbed state with a di-σ bonded C_2H_2 adsorbed on an unbroken Si dimer.[9] This prediction has been confirmed in some other theoretical studies using empirical, semi-empirical and other first-principles methods.[10–15]

Based on those aforementioned experimental and theoretical studies reported before 1999, a consensus can seemingly be reached that acetylene is di-σ bonded over a Si dimer on the Si(100)-2 × 1 surface. However, a new point of view,[7,8] which was contradictory to this consensus appeared very recently. In 1999, Su and co-workers performed HRPES (high-resolution photo-emission spectroscopy)[7] and photoelectron diffraction imaging[8] experiments on the C_2H_2/Si(100)-2 × 1 chemisorption system; they concluded that C_2H_2, instead of being di-σ bonded on a Si dimer, was tetra-σ bonded onto two neighboring Si dimers, and consequently the C atoms are rehybridized from the sp state to the sp^3 state. They further pointed out that this new bonding scenario was in accord with the previous STM observation[4] of an adsorbate overlayer with either local 2 × 2 or c(4 × 2) order that led to a saturation coverage of 0.5 ML.

Stimulated by this new report, we have performed a detailed theoretical investigation on the chemisorption process of acetylene over the Si(100)-2 × 1 surface by means of density-functional cluster model calculations. Upon completion of the

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present study, we have learned that Sorescu and Jordan[16] had carried out a similar study with a slab model. Their results will be compared with our cluster model calculations.

Computational procedure

We have employed the $Si_{15}H_{16}$ cluster model to represent the reconstructed Si(100)-2 × 1 surface. Two dimers consisting of 4 Si atoms, each with one dangling bond, are considered as the top layer of this surface model with all other dangling bonds terminated with H atoms.[17,18] All calculations were performed with the GAUSSIAN 98 package.[19] Analytical gradients and the hybrid density functional theory method, including Becke's 3-parameter nonlocal-exchange functional[20] with the correlation functional of Lee–Yang–Parr[21] (B3LYP), were used for geometry optimizations with no constrained degrees of freedom. The basis set used in this paper is the standard all-electron split-valence basis set 6-31G(d)[22] including the polarization d-function on non-hydrogen atoms. Final energy parameters for the $Si_{15}H_{16}$ cluster models include the unscaled zero-point-energy corrections (ZPC) calculated at the B3LYP/6-31G(d) level.

Results and discussion

A. Single C_2H_2 chemisorption

We have considered several possible bonding configurations for a single C_2H_2 chemisorption onto the double Si-dimer $Si_{15}H_{16}$ cluster and have obtained 4 local minima. They are depicted in Fig. 1((a), (b), (c) and (d)), and denoted as $C_2H_2 \cdot d$, $C_2H_2 \cdot eb$, $C_2H_2 \cdot tb$ and $C_2H_2 \cdot pb$, respectively. The optimized geometric parameters and the corresponding chemisorption energies are given in Table 1.

In the $C_2H_2 \cdot d$ configuration, the optimal C–Si bond length is 1.91 Å; the Si–Si bond in the Si dimer beneath the adsorbed acetylene is elongated by 0.13 Å (from 2.22 to 2.35 Å) upon chemisorption; the C–C bond length increases substantially, from 1.21 Å in the free C_2H_2 to 1.36 Å in the adsorbed state. These structural features indicate that the adsorbed C_2H_2 is di-σ bonded onto an unbroken Si dimer, forming a closed, 4-member –C–C–Si–Si– ring and the C–C triple bond in free acetylene molecule degrades to a double bond upon the [2 + 2] cycloaddition. The calculated energy for this chemisorption process is −62.9/−66.7 kcal mol⁻¹ with/without zero-point energy corrections, in good agreement with the B3LYP/6-31G(d) prediction of −66.1 kcal mol⁻¹ by Konecný and Doren,[15] who used the smaller Si_9H_{12} cluster to simulate the Si dimer. Our value also agrees with the theoretical prediction of −64.8 kcal mol⁻¹ from first-principles molecular dynamics calculations by Imamura et al.[13] A smaller adsorption energy of −54.9 kcal mol⁻¹ was predicted by Fisher et al.[14] for the same process using the LDA-PAW method.
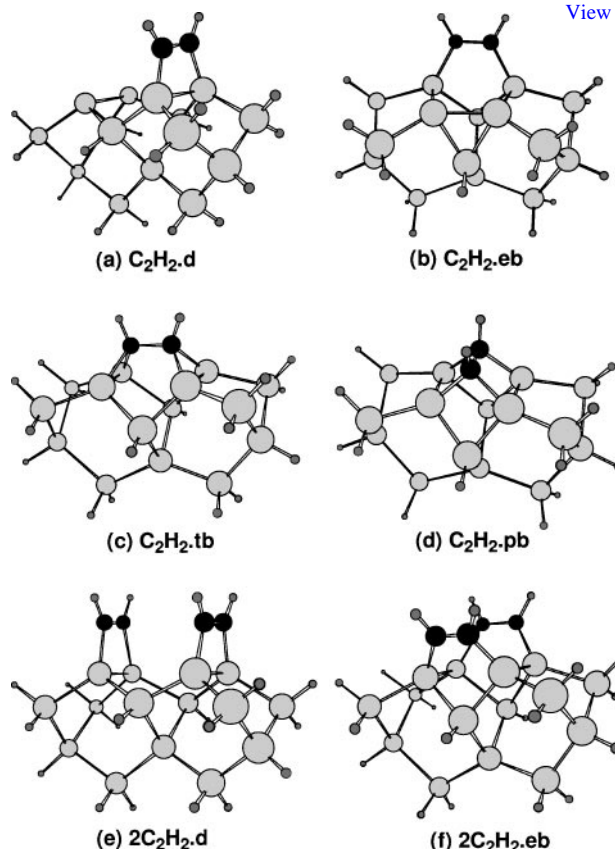

Fig. 1 Bonding configurations of one and two C_2H_2 molecules adsorbed on the $Si_{15}H_{16}$ cluster: (a) $C_2H_2 \cdot d$—C_2H_2 lies on top of a single (Si–Si) dimer; (b) $C_2H_2 \cdot eb$—C_2H_2 bridges over the ends of two (Si–Si) dimers; (c) $C_2H_2 \cdot tb$—C_2H_2 bridges over the two (Si–Si) dimers with the C–C bond perpendicular to the dimer bonds; (d) $C_2H_2 \cdot pb$—C_2H_2 adsorbs between the two neighboring dimers with the C–C bond parallel with the dimers; (e) parallel adsorption of two C_2H_2 molecules in the $C_2H_2 \cdot d$ configuration; (f) parallel adsorption of two C_2H_2 molecules in the $C_2H_2 \cdot eb$ configuration.

Experimentally Taylor et al.[3] estimated an activation energy of 46.1 kcal mol⁻¹ for the desorption of chemisorbed C_2H_2 on the Si(100)-2 × 1 surface in their TPD study.

In the $C_2H_2 \cdot eb$ configuration, the in-coming C_2H_2 molecule bridges over the ends of two neighboring dimers, giving rise to a closed, 6-member –C–C–Si–Si–Si–Si– ring. The Si–C bond length is 1.90 Å; the C–C bond length is 1.36 Å. The structural feature is indicative of the di-σ bonding of C_2H_2 with the two Si dimers, i.e., each dimer contributing one Si atom and one dangling bond for the formation of di-σ bonded complex. The C atoms in $C_2H_2 \cdot eb$ become sp²-rehybridized upon chemisorption. The calculated chemisorption energy for

Table 1 Adsorption energies[a] and selected geometric parameters of the $C_2H_2/Si_{15}H_{16}$ model systems from B3LYP/6-31G(d) calculations

	$C_2H_2 \cdot d$	$C_2H_2 \cdot eb$	$C_2H_2 \cdot tb$	$C_2H_2 \cdot pb$	$2C_2H_2 \cdot d$[b]	$2C_2H_2 \cdot eb$[b]
Si–Si/Å	2.352	2.397	2.364	2.341	2.356	2.410
C–Si/Å	1.911	1.904	1.966	1.996	1.911	1.908
C–C/Å	1.357	1.359	1.566	1.599	1.356	1.355
C–H/Å	1.092	1.093	1.090	1.094	1.092	1.092
H–C–C/°	123.6	120.5	111.4	114.9	123.5	119.2
H–C–Si/°	131.3	122.8	117.5	121.4	131.3	121.5
C–C–Si/°	105.1	117.8	116.0	100.7	105.2	119.2
Si–Si–C/°	74.9	107.1	53.0	79.3	74.8	110.8
ΔE/kcal mol⁻¹	−66.7	−71.0	−47.1	−49.1	−131.9	−156.8
	(−62.9)	(−66.6)	(−43.4)	(−45.4)	(−124.5)	(−148.5)

[a] Adsorption energy $\Delta E = E(C_2H_2/Si_{15}H_{16}) - E(Si_{15}H_{16}) - E(C_2H_2)$. Energies after zero-point energy corrections are given in parentheses.
[b] Parallel adsorption of 2 C_2H_2 molecules. Adsorption energy $\Delta E = E(2C_2H_2/Si_{15}H_{16}) - E(Si_{15}H_{16}) - 2E(C_2H_2)$. The zero-point energy corrected value is given in parentheses.

this end-bridge configuration is $-66.6/-71.0$ kcal mol^{-1} with/without zero-point energy corrections. It is interesting to find that this end-bridge mode is slightly more favorable (by 3.7 kcal mol^{-1}) over the $C_2H_2 \cdot d$ mode that has been intensively studied previously.[9–15] Dyson and Smith once considered this end-bridge mode in their MD study with the extended Brenner potential and predicted that the end-bridge mode is favored by 2.8 kcal mol^{-1} over the $C_2H_2 \cdot d$ mode.[11] Furthermore, they performed B3LYP/3-21G* calculations on the $C_2H_2/Si_{15}H_{16}$ model system and obtained an adsorption energy of -59.3 kcal mol^{-1}, which is about 12 kcal mol^{-1} less exothermic than the our prediction.

In the $C_2H_2 \cdot tb$ configuration, the acetylene molecule lies above the two neighboring dimers with the C–C bond parallel to the dimer row (but perpendicular to the two Si-dimer bonds, see Fig. 1(c)). Each C atom in C_2H_2 is thus di-σ bonded with a Si dimer, giving rise to a tetra-σ bonded C_2H_2. The optimal Si–C bond length is 1.97 Å. The C–C bond length is 1.57 Å, significantly elongated by 0.36 Å with respect to the free C_2H_2. The Si–Si bond length increases by 0.18 Å after C_2H_2 adsorption. In such a tetra-σ bonding configuration, all the dangling bonds available on the two neighboring Si dimers are fully used, the C–C triple bond in free acetylene degrades to a C–C single bond, with the C–C sp^3 rehybridization from the original sp state. The adsorption energy ($-43.4/-47.1$ kcal mol^{-1} with/without zero-point energy corrections) for this $C_2H_2 \cdot tb$ mode of adsorption, however, is lower than those di-σ bonding configurations ($C_2H_2 \cdot d$ and $C_2H_2 \cdot eb$) by about 20 kcal mol^{-1}. Hence, the formation of such a tetra-σ bonded surface complex is energetically less favorable than the formation of the di-σ bonded surface complexes. Furthermore, the Si–Si–C angle is only 53.0° in this configuration, implying that the steric repulsion between the Si–C bonds and the Si-dimer bonds may be substantial.

In the $C_2H_2 \cdot pb$ configuration given by Fig. 1(d), C_2H_2 lies above the pedestal site between two neighboring Si dimers with the C–C bond parallel to the Si dimers. This is the very bonding configuration that was concluded by Su *et al.* based on their recent HRPES and photoelectron diffraction imaging results,[7,8] although this bonding configuration had been predicted to be unstable by Dyson and Smith in their MD study.[11] We did obtain an equilibrium geometry for this bonding configuration in our B3LYP/6-31G(d) cluster model calculations. The adsorbed acetylene is tetra-σ bonded over the two neighboring dimers with the optimal Si–C bond length being 2.00 Å. Upon chemisorption, the C–C triple bond degrades to a C–C single bond, and the C–C molecular orbitals undergo rehybridization from the original sp to the final sp^3 state. As a result, the C–C bond is considerably elongated from 1.22 to 1.60 Å (in the adsorbed one). The Si–Si bond length increases by 0.12 Å because the dangling bonds of the 4 first-layer Si atoms are fully used to form the tetra-σ bonded surface complex. The calculated adsorption energy is $-45.4/-49.1$ kcal mol^{-1} with/without zero-point energy cor-

rections; this value is comparable to that of the $C_2H_2 \cdot tb$ mode of adsorption.

B. Parallel adsorption of two C_2H_2 molecules

We have also considered the parallel adsorption of two C_2H_2 molecules over the two Si dimers both in the $C_2H_2 \cdot d$ mode (see Fig. 1(e)). The optimized geometric parameters and adsorption energy are included in Table 1. The calculated energy for the adsorption of the second acetylene molecule is $-61.6/-65.2$ kcal mol^{-1} with/without zero-point energy corrections; it is only 1.4 kcal mol^{-1} lower than the predicted value for the adsorption of the first molecule. The optimized geometry is almost the same as the single molecular adsorption case. These results indicate that the repulsive interaction between the two adsorbed acetylene molecules is small. Accordingly, it is unlikely to be the cause of the preferential local 2×2 or $c(4 \times 2)$ ordering of adsorbate overlayers as observed by Li *et al.* in their STM experiment;[4] they considered this to be a major cause of their observed ordering.

For the end-bridge case, the adsorption of a second acetylene onto the end-bridge $C_2H_2 \cdot eb$ structure may be kinetically unlikely at low temperature due to the lack of free dangling bonds, as the two free dangling bonds located at the other ends of the two dimers are already coupled by the formation of an inter-dimer Si–Si σ-bond (2.41 Å) (see Fig. 1(b)) upon the adsorption of the first acetylene. However, it may be possible to undergo the simultaneous adsorption of two acetylene molecules both in the end-bridge mode over two neighboring Si dimers. This process requires the simultaneous breaking of the two Si–Si bonds; such a third-order adsorption process is probably kinetically prohibitive at low temperatures. The geometry of the two end-bridge adsorption is shown in Fig. 1(f). The optimized geometric parameters are also listed in Table 1. Interestingly, the calculated total adsorption energies, $-148.5/-156.8$ kcal mol^{-1} with/without zero-point energy corrections are, unexpectedly, more than two times higher than the predicted values for the single molecular adsorption case ($-66.6/-71.0$ kcal mol^{-1} with/without zero-point energy corrections). The high exothermicity suggests that this type of adsorption process may be relevant to our understanding of the CVD process; it may possibly occur at high temperatures.

C. Vibrational frequencies of the adsorbed C_2H_2

The calculated vibrational frequencies for the different modes of C_2H_2 chemisorption on the $Si_{15}H_{16}$ cluster are listed in Table 2, together with the experimental data from HREELS experiments.[1,2] For the free C_2H_2 molecule, the B3LYP/6-31G(d) calculation predicted frequencies are 3542 (sym. C–H str.), 3443 (asym. C–H str.), 2087 (C–C str.), 776 (asym. CH bend) and 538 (sym. CH bend) cm^{-1}. The corresponding experimental values are 3374, 3289, 1974, 730 and 612 cm^{-1}.[23] Obviously, the C–H, C–C stretch mode frequencies are overestimated by about 5% at the B3LYP/6-31G(d) level

Table 2 Some selected vibrational frequencies (cm^{-1}) of the $C_2H_2/Si_{15}H_{16}$ model system (B3LYP/6-31G(d)^a and of the $C_2H_2/Si(100)$-2×1 system (experiments)

Mode	EELS^b	EELS^c	$C_2H_2 \cdot d$	$C_2H_2 \cdot eb$	$C_2H_2 \cdot tb$	$C_2H_2 \cdot pb$
C–H str.(sym.)	3000	2980	3154(2996)	3141(2984)	3150(2993)	3122(2967)
C–H str.(asym.)			3132(2975)	3118(2962)	3134(2986)	3108(2953)
C–C str.	1090	1450	1523(1447)	1528(1452)	894(849)	824(783)
C–Si str.(asym.)	(820)^d		732	730	722	610
C–Si str.(sym.)	690	680	712	680	653	635
C–H bend.(in-plane, asym.)	1255	1240	1277	1300	1230	1195
C–H bend.(in-plane, sym.)	(1090)^d		1078	1116	1119	1041
C–H bend.(out-of-plane, asym.)	970	1065	1001	989	909	916
C–H bend.(out-of-plane, sym.)		680	735	645	905	917

^{a} The calculated values given in parentheses are scaled by 0.95. ^{b} Ref. 1. ^{c} Ref. 2. ^{d} Not explicitly assigned.

of theory. Employing a scale factor of 0.95 on those C–H, C–C stretch mode frequencies gives the values of 3365, 3271 and 1983 cm^{-1}, fitting better to the experimental data. Thus for the chemisorption systems, the scaled factor of 0.95 is also employed for the B3LYP/6-31G(d) calculated C–H and C–C stretch frequencies. The scaled values are given in parentheses in Table 2.

From Table 2, it can be seen that the bonding configurations ($C_2H_2 \cdot d$ and $C_2H_2 \cdot eb$) with the C_2H_2 di-σ bonded give rise to frequencies fitting better with the experimental HREELS data than do the bonding configurations ($C_2H_2 \cdot tb$ and $C_2H_2 \cdot pb$) with the C_2H_2 tetra-σ bonded. This suggests that the adsorbed species experimentally detected by HREELS could be better assigned to those di-σ bonded C_2H_2. The C–C stretching frequency of the adsorbed acetylene can be normally used as a key criterion for the C–C bonding characteristic, i.e. the frequency of a C–C triple bond is always around 1980 cm^{-1}, C–C double bond around 1600 cm^{-1} and C–C single bond around 1000 cm^{-1}. In their HREELS study, Nishijima et al. assigned the peak at 1090 cm^{-1} to C–C single bond stretch and, accordingly, inferred that the C molecular orbitals were rehybridized to the sp^3 state.[1] Our calculations, however, showed that it is better to assign the 1090 cm^{-1} peak to the C–H in-plane bend mode (symmetric) of the di-σ bonded C_2H_2 molecule, whereas the C–C single bond stretch in the tetra-σ bonded C_2H_2 adspecies (with the scaled B3LYP/6-31G(d) value <850 cm^{-1}) is much softer than the ordinary C–C single bond stretch; e.g., that in the free C_2H_6 (with the experimental value of 995 cm^{-1} [23] and the scaled B3LYP/6-31G(d) value of 960 cm^{-1}).

D. Comparison of the results from cluster model and slab model calculations

While we were preparing this paper, Sorescu and Jordan's result obtained from their DFT slab model calculations for the same chemisoprtion system[16] was brought to our attention. Their result revealed the presence of the same 4 bonding configurations in the chemisorption system as we had found in our cluster model calculations, with a similar trend that the two configurations with di-σ bonded C_2H_2 have comparable adsorption energies and are thermodynamically favorable over the other configurations. The coverage-dependence of the binding energy has been taken into account in their calculations. Interestingly, for the two most favorable configurations, they found that the adsorption energy for the $C_2H_2 \cdot d$ configuration decreases with increasing coverage (from 63 kcal mol^{-1} at 0.125 to 57 kcal mol^{-1} at 1.0), whereas for the $C_2H_2 \cdot eb$ configuration the adsorption energy increases with increasing coverage (from 56 kcal mol^{-1} at 0.125 to 68 kcal mol^{-1} at 1.0). These values are comparable to ours predicted for the two most favorable configurations. On the other hand, they have predicted the presence of three more bonding configurations, a $C_2H_2 \cdot d$ configuration with the substrate Si dimer bond broken, a cross-dimer configuration with C_2H_2 bridging over two neighboring Si-dimers diagonally and a cross row configuration with C_2H_2 bridging over two dimer rows. We have considered the former two configurations in our cluster model calculations, but they were found to converge to the $C_2H_2 \cdot d$ configuration with the Si-dimer bond retained and to the $C_2H_2 \cdot tb$ configuration, respectively, upon geometry optimization. We did not consider the cross-row configuration in our cluster model calculations, because a much larger cluster model exceeding the capability of our computational facility is required in order to simulate such an adsorption properly.

Concluding remarks

We have performed hybrid density-functional/cluster model calculations to investigate the bonding configurations of C_2H_2

chemisorption on the Si(100)-2×1 surface. Four types of stable bonding configurations have been found, namely the $C_2H_2 \cdot d$ configuration with C_2H_2 di-σ bonded onto a single Si dimer, the $C_2H_2 \cdot eb$ configuration with C_2H_2 di-σ bonded with the two neighboring end-Si atoms, the $C_2H_2 \cdot tb$ configurations with the tetra-σ bonded C_2H_2 bridging over two neighboring Si dimers and parallel to the dimer row and the $C_2H_2 \cdot pb$ configuration with the tetra-σ bonded C_2H_2 bridging over and parallel to two neighboring Si dimers. We found that the chemisorptions with di-σ bonded C_2H_2 in the $C_2H_2 \cdot d$ configuration and in the $C_2H_2 \cdot eb$ configuration have comparable adsorption energies (-66.6 kcal mol^{-1} for $C_2H_2 \cdot eb$ and -62.9 kcal mol^{-1} for $C_2H_2 \cdot d$), and both are highly exothermic. The two bonding configurations with tetra-σ bonded C_2H_2 over two neighboring Si dimers also show a substantial stability (with a chemisorption energy of -43.4 kcal mol^{-1} for the $C_2H_2 \cdot tb$ configuration and a chemisorption energy of -45.4 kcal mol^{-1} for the $C_2H_2 \cdot pb$ configuration) and thus can not be excluded from the chemisorption system. The reasonable agreement in the calculated vibrational frequencies for the former two bonding configurations with the experimental HREELS spectra favors these two bonding configurations. A detailed kinetic modeling study on the adsorption process based on predicted transition-state parameters may be needed in order to identify the rate-limiting factor which controls the appearance of a certain adsorption configuration.

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