

Benzene adsorbed on Si(001): The role of electron correlation and finite temperature

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van der Waals energy-corrected density functional theory (DFT + vdW) as well as the exact exchange with electron correlation in the random-phase approximation are used to study the adsorption of benzene on the Si(001) surface with respect to two controversial adsorption structures (termed “butterfly” and “tight bridge”). Our finding that the tight-bridge structure is energetically favored over the butterfly structure agrees with standard DFT but conflicts with previous vdW-inclusive calculations. However, the inclusion of zero-point energy and thermal vibrations reverses the stability of the two structures with increasing temperature. Our results provide an explanation for the recent experimental observation that both structures coexist at room temperature.

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The interaction of aromatic hydrocarbon molecules with the Si(001) surface is of considerable interest because of the functionalization of the silicon surface toward molecular control of electronic devices.^{1–5} Especially, the adsorption of benzene on the Si(001) surface has become a prototype system to study and understand the interaction of π -conjugated aromatic rings with the dangling bonds of the Si surface dimers.^{4–19} Despite its apparent simplicity, the structure and dynamics of benzene on Si(001) have been controversial between experiment^{6–14} and theory.^{15–19}

Many experimental studies on the adsorption of benzene on Si(001) have been performed at room temperature, using high-resolution electron-energy-loss spectroscopy,⁶ thermal-desorption spectroscopy,^{6,7} Auger electron spectroscopy,⁶ near-edge x-ray-absorption fine structure,^{8,9} and optical spectroscopy.¹⁰ All of them supported the so-called butterfly (BF) structure, where benzene adsorbs on top of a single Si dimer [see Fig. 1(a)]. However, scanning tunneling microscopy (STM) experiments at room temperature observed both the BF structure and the tight-bridge (TB) structure, where benzene adsorbs across two adjacent Si dimers [see Fig. 1(b)].^{11–13} It was also observed by STM that the BF structure was initially formed but was gradually converted to the TB structure,^{12,13} implying that the BF structure is an intermediate state. Recently, a room-temperature photoelectron diffraction study concluded that the saturated monolayer (ML) of benzene on Si(001) contains both structures with $58 \pm 29\%$ of molecules having the BF structure.¹⁴

To date, theoretical works remain divided on the issue of the adsorption structure of benzene on Si(001).^{15–19} Standard density functional theory (DFT) calculations using the slab geometry predicted that the TB structure is more stable than the BF structure by 0.07–0.27 eV depending on the coverage,^{15–19} and that the initially formed BF structure undergoes a conversion into the more stable TB structure with an activation barrier of ~ 1 eV,¹⁷ which seemed to be consistent with STM experiments.^{12,13} On the other hand, a MP2 cluster calculation (Møller-Plesset second-order perturbation theory)¹⁸ and a van der Waals density functional (vdW-DF) calculation¹⁹ found the BF structure to have lower energy than the TB structure. Thus, it appeared that more

rigorous treatments of electronic correlation stabilize the BF structure over the TB structure. This apparent influence of vdW forces for the adsorption structure of benzene on Si(001) has significant implications for the reliability of previous DFT studies with local or semilocal treatment of exchange and correlation (DFT-LDA/GGA)^{4,5,15–17} that have been widely used for studying hybrid organic-silicon systems.

In this Rapid Communication, we present a theoretical study of benzene on Si(001) by using vdW energy-corrected density-functional theory (DFT + vdW scheme²⁰) as well as the exact exchange with electron correlation in the random-phase approximation (EX + cRPA).^{21–23} In a second step, we also evaluate the free energy in order to study the temperature dependence. Unlike the above-mentioned MP2¹⁸ and vdW-DF¹⁹ calculations, we find that the TB structure is more stable than the BF structure at zero temperature, in accordance with previous DFT-LDA/GGA calculations.^{15–17} However, when the free energy is considered, the stability of the two structures is reversed with increasing temperature, giving rise to a transition from the TB to the BF structures. This transition is caused by a subtle interplay of the lower total energy of the TB structure and the larger vibrational entropy of the less tightly bound BF structure at finite temperatures.

The present DFT + vdW²⁰ and EX + cRPA^{21–23} calculations were performed using the FHI-AIMS²⁴ code for an accurate, all-electron description based on numeric atom-centered orbitals, with “tight” computational settings and accurate tier-2 basis sets.²⁴ Calculations with a larger tier-3 basis set show that our DFT + vdW adsorption energies are converged to 0.01 eV and EX + cRPA values are converged to 0.05 eV, with even better convergence for adsorption energy differences. These calculation schemes combined with the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)²⁵ are required since GGA functionals tend to underestimate the binding energy at organic/inorganic interfaces.²⁶ For the periodic slab geometry, the \mathbf{k} -space integration was done with 16, 8, and four points in the surface Brillouin zone of the 2×2 , 2×4 , and 4×4 unit cells, respectively. All the atoms except the bottom Si layer were allowed to relax along the calculated forces until all the residual force components are less than 0.02 eV/Å.

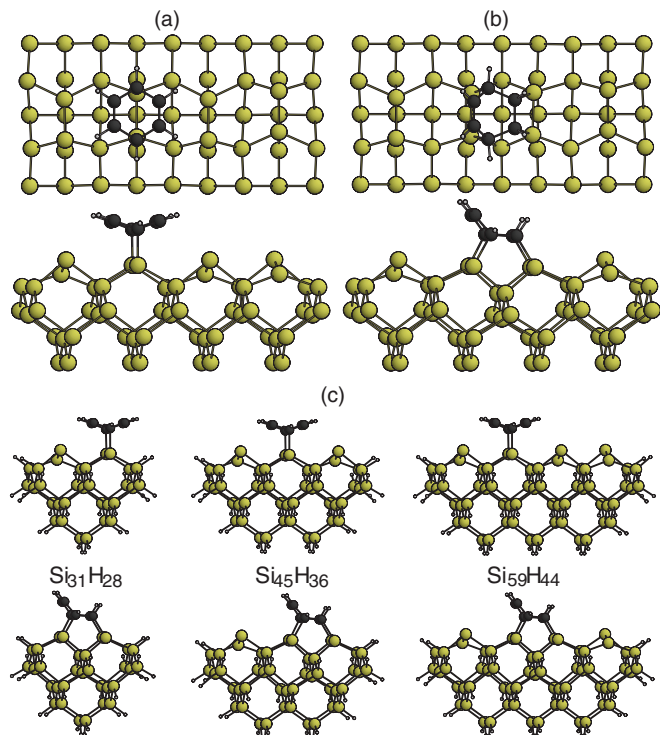


FIG. 1. (Color online) Top and side views of the structure of adsorbed benzene on Si(001), obtained using PBE for the slab geometry: (a) the BF structure and (b) the TB structure. Cluster models of the BF and TB structures containing two, three, and four Si dimers are also given in (c). The large, medium, and small circles represent Si, C, and H atoms, respectively.

We first employ the PBE functional to optimize the BF and TB structures modeled with clusters and the periodic slab geometry. Cluster models contain a single row of dimers with two (Si₃₁H₂₈), three (Si₄₅H₃₆), and four (Si₅₉H₄₄) dimers [see Fig. 1(c)]. The slab geometry consists of five Si atomic layers including four dimers within a 2×4 unit cell, and the bottom Si layer is passivated by two H atoms per Si atom (with a Si-H bond length of 1.48 Å, optimized at the clean Si(001)-2×2 surface). The calculated adsorption energies (E_{ads}) of the BF and TB structures are listed in Table I of the Supplemental Material.²⁷ We find that the adsorption energy of the BF (TB) structure varies depending on the cluster size as $E_{\text{ads}} = 1.09$, 0.91, and 0.95 (1.50, 1.29, and 1.13) eV for Si₃₁H₂₈, Si₄₅H₃₆, and Si₅₉H₄₄, respectively, yielding $E_{\text{ads}} = 0.92$ (1.01) eV for the fully periodic slab geometry. The larger adsorption energies in the small clusters are possibly caused by artificial localization of dangling-bond electrons, which enhances a hybridization with π orbitals of benzene. This cluster size effect is seen to be more significant in TB compared to BF. As a result, our PBE calculations show that TB is more stable than BF by $\Delta E_{\text{ads}} = 0.41$, 0.38, 0.18, and 0.09 eV for Si₃₁H₂₈, Si₄₅H₃₆, Si₅₉H₄₄, and the slab geometry, respectively (see Fig. 2).²⁸ We note that our PBE results for the slab geometry agree well with previous DFT calculations (see the Supplemental Material²⁷).

To assess the influence of vdW forces on the binding, we use the PBE + vdW scheme by Tkatchenko and Scheffler.²⁰ In this method, the vdW coefficients and radii are determined

using the self-consistent electron density. We also assessed the influence of screening effects inside the Si bulk on the vdW energy by using the recently determined screened vdW parameters²⁹ and found these effects to be small for the energy difference between the TB and BF structures. The calculated adsorption energies of the BF and TB structures with fully relaxed PBE + vdW geometries are also listed in Table I of the Supplemental Material.²⁷ We find that all the optimized geometries obtained using PBE and PBE + vdW showed little changes in the bond lengths, differing by less than 0.005 Å.³⁰ In the BF (TB) structure, we find $E_{\text{ads}} = 1.67$, 1.62, 1.70, and 1.47 (2.11, 1.98, 1.88, and 1.54) eV for Si₃₁H₂₈, Si₄₅H₃₆, Si₅₉H₄₄, and the slab geometry, respectively. Therefore, the TB structure is energetically favored over the BF structure by $\Delta E_{\text{ads}} = 0.44$, 0.36, 0.18, and 0.07 eV for Si₃₁H₂₈, Si₄₅H₃₆, Si₅₉H₄₄, and the slab geometry, respectively. Thus, the inclusion of vdW interactions does not significantly alter the energy gap between TB and BF as shown in Fig. 2, indicating that the magnitude of vdW energy is insensitive to the adsorption geometry of benzene.

In the Supplemental Material,²⁷ we compare the present PBE and PBE + vdW results for the adsorption energies of the BF and TB structures with previous PBE, vdW-DF,¹⁹ and MP2¹⁸ calculations. All PBE calculations support the larger stability of the TB structure. The present PBE + vdW calculation also predicts the preference of the TB structure, in contrast with previous vdW-DF¹⁹ and MP2¹⁸ calculations, which predict the BF structure to be more stable. As the coverage increases from 0.125 to 0.5 ML, our PBE + vdW calculations for the BF (TB) structure show an increase of 0.17 (0.25) eV in adsorption energy, representing an intermolecular attractive interaction owing to vdW forces. On the other hand, the previous vdW-DF¹⁹ calculation obtained a slight decrease of 0.02 (0.05) eV for the BF (TB) structure, indicating a repulsive interaction between benzene molecules as the separation decreases. This different aspect in molecule-molecule interaction between the present PBE + vdW and previous vdW-DF¹⁹ results needs to be examined by future experiments and calculations. However, the prediction of previous vdW-DF¹⁹ and MP2¹⁸ calculations supporting the BF structure cannot account for the conversion from the BF to the TB structure, as observed in STM experiments.^{12,13} We note that a MP2 cluster calculation

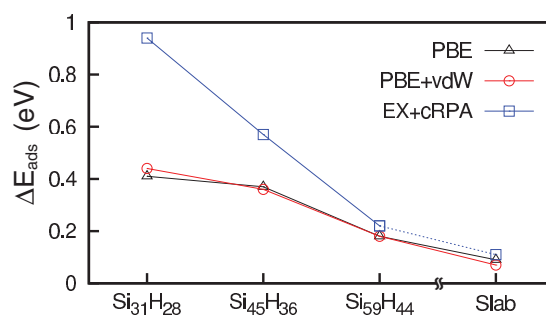


FIG. 2. (Color online) Calculated adsorption energy difference between the TB and BF structures, defined as $\Delta E_{\text{ads}} = E_{\text{ads}}(\text{TB}) - E_{\text{ads}}(\text{BF})$, for Si₃₁H₂₈, Si₄₅H₃₆, Si₅₉H₄₄, and the slab geometry. The EX + cRPA values are extrapolated as the difference between EX + cRPA and PBE + vdW using the method of Ref. 32.

employing the two-dimer $\text{Si}_{31}\text{H}_{28}$ cluster missed obtaining the tilted Si-dimer structure,^{18,31} thereby being unclear whether it can predict the accurate adsorption energies of the BF and TB structures.

To treat electronic correlation more rigorously, we employ the EX + cRPA^{21–23} method to calculate the adsorption energies of the TB and BF structures. The EX + cRPA energy is computed using the PBE determined adsorption structure, orbitals, and orbital energies. Using the method of Hu, Reuter, and Scheffler,³² we extrapolate the adsorption energy to the slab limit. In Fig. 2, we plot the adsorption energy difference ΔE_{ads} between TB and BF obtained using EX + cRPA for finite clusters and extrapolated to the slab limit.³³ It can be seen that EX + cRPA predicts essentially the same energy difference between TB and BF as PBE(+vdW), with the TB structure being more stable than BF by 0.11 eV. However, for a small $\text{Si}_{31}\text{H}_{28}$ cluster, ΔE_{ads} of EX + cRPA shows a large difference compared with those of PBE and PBE + vdW because of the incorrect description of correlation due to artificial localization of electrons. We conclude that the TB structure is more stable energetically than the BF structure for benzene adsorption on Si(100).³⁴

Next, we evaluate the vibrational free energy. In the harmonic approximation,³⁵ this is given by

$$F(T) = E + k_{\text{B}}T \sum_i \left[\frac{\hbar\omega_i}{2k_{\text{B}}T} + \ln \left(1 - \exp \frac{-\hbar\omega_i}{k_{\text{B}}T} \right) \right]. \quad (1)$$

The vibrational frequencies ω_i are obtained from the force constant matrix on the $\text{Si}_{59}\text{H}_{44}$ cluster using numerical derivatives of the PBE + vdW energies.³⁶ The first term in Eq. (1) is the total energy at 0 K and the second term is the vibrational energy and entropy including zero-point vibration. We note that the TB structure with four sp^3 hybridized Si-C bonds are more tightly bound to the surface compared to the BF structure with two sp^3 hybridized Si-C bonds, resulting in larger force constants at the interface. Figure 3 shows the vibrational density of states calculated for the BF and TB structures, where the vibrational frequencies are sufficiently converged enough to be free of any residual numerical noise in the employed finite difference method.³⁶ It is seen that the vibrational frequencies of TB are overall blueshifted compared with those of BF. Using Eq. (1), we calculate the free energies

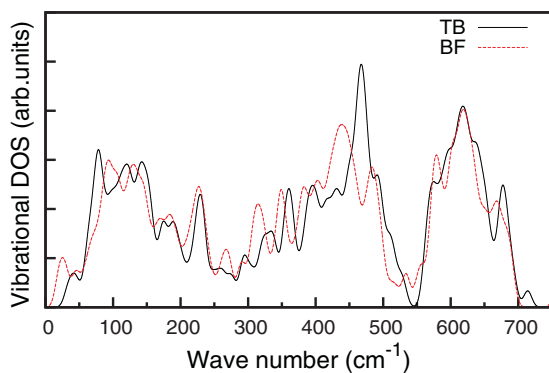


FIG. 3. (Color online) Vibrational density of states (DOS) calculated for the BF and TB structures on the $\text{Si}_{59}\text{H}_{44}$ cluster. Both are convoluted with a Gaussian broadening function with 6 cm^{-1} width.

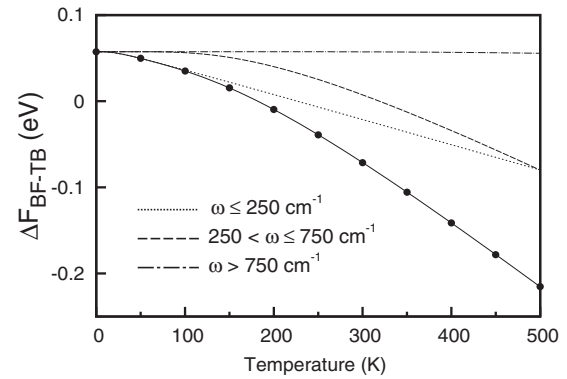


FIG. 4. Calculated free-energy difference $\Delta F_{\text{BF-TB}}$ between the BF and TB structures. The components of $\Delta F_{\text{BF-TB}}$ contributed by three frequency ranges $\omega \leq 250 \text{ cm}^{-1}$, $250 < \omega \leq 750 \text{ cm}^{-1}$, and $\omega > 750 \text{ cm}^{-1}$ are also plotted.

for the BF and TB structures as a function of temperature. The free-energy difference ($\Delta F_{\text{BF-TB}}$) between the BF and TB structures is given in Fig. 4. It is obvious that thermal vibrations have a noticeable effect. We find that the zero-point vibrations give rise to a significant reduction of $\Delta F_{\text{BF-TB}} = 0.05 \text{ eV}$, compared with $\Delta E_{\text{BF-TB}} = 0.18 \text{ eV}$ for the $\text{Si}_{59}\text{H}_{44}$ cluster. As the temperature increases, $\Delta F_{\text{BF-TB}}$ further decreases, finally vanishing at 182 K. At this critical temperature (T_c), the vibrational entropy of the BF structure is greater in magnitude than that of the TB structure, being enough to compensate for the lower total energy of TB compared to BF.

The calculations show that the stability of the BF and TB structures is inverted at $T_c = 182 \text{ K}$. This temperature-induced transition is driven by the different features of bond formation and vibrational entropy between the BF and TB structures. Compared with BF, TB has a greater bond energy because of its increased bond number (four Si-C bonds), but has a smaller vibrational entropy caused by its enhanced vibrational frequencies. In Fig. 4, the components of $\Delta F_{\text{BF-TB}}$ arising from three frequency ranges are also plotted. It is seen that the vibration modes with $\omega \leq 250 \text{ cm}^{-1}$ and $250 < \omega \leq 750 \text{ cm}^{-1}$ mostly contribute to $\Delta F_{\text{BF-TB}}$, while the contribution from $\omega > 750 \text{ cm}^{-1}$ is negligible. Noting that the vibrational modes originating from benzene molecule (i.e., C-C and C-H stretching modes) are located above 750 cm^{-1} ,^{6,8} we can say that such molecular modes hardly contribute to $\Delta F_{\text{BF-TB}}$. On the other hand, low-frequency modes below 750 cm^{-1} in the TB structure are overall blueshifted relative to the BF spectrum (see Fig. 3), resulting in a decrease of $\Delta F_{\text{BF-TB}}$ with increasing temperature. Since the vibrational modes associated with the Si-C bonds are located below 750 cm^{-1} ,³⁷ the overall blueshift reflects the difference in the bonding nature between the BF and TB structures.

Using the calculated free energies and the law of mass action, we estimate that at room temperature the BF structure is ~ 15 times more likely populated than the TB structure. Although the precise values of the population will depend on the coverage and the structure of benzene on Si(100), such a prediction about the coexistence of the two adsorption structures is consistent with a recent photoelectron diffraction analysis,¹⁴ where the BF and TB structures coexist at saturation coverage with $58 \pm 29\%$ of molecules having

the BF structure. Below room temperature, the population ratio of the BF and TB structures is determined by the free-energy difference as well as by kinetics. We note that the conversion from BF to TB becomes reduced with decreasing temperature because it is a thermally activated process. As a matter of fact, the STM experiment at 200 K showed exclusive population of the BF structure with no evidence of conversion.¹³ Thus, in order to explore vibrational effects of the BF and TB structures, it is necessary to investigate their population changes at temperatures above 200 K. We note that a recent photoelectron diffraction experiment¹⁴ at room temperature observed the composition of 71% of the TB structure at one extreme composition range, implying that the free energy of TB is lower than that of BF. Therefore, it is likely that T_c might be influenced by the real circumstances such as intermolecular interactions as well as steric effects of the two competing structures, as pointed out by Nisbet *et al.*¹⁴

In summary, we have investigated the influence of the treatment of electronic correlation on the adsorption structure of benzene on Si(001) by using the DFT + vdW scheme as well as EX + cRPA, and found that vdW forces do not switch the

stability of the BF and TB structure, in contrast with previous MP2¹⁸ and vdW-DF¹⁹ calculations. However, we found that when zero-point and thermal vibrations are taken into account, the stability of the two structures is reversed with increasing temperature, giving rise to a temperature-induced transition from the TB to the BF structures. The present work sheds light on the controversial issue of the adsorption structure of benzene on Si(001) between theory and experiment. We anticipate the vibrational effects presented here to be relevant for the adsorption of other organic molecules on inorganic surfaces.

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²⁷See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.85.041403> for the calculated adsorption energies, bond lengths, energy gap, and energy decomposition for benzene adsorption on Si(001).

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³³If the extrapolation method of Hu, Reuter, and Scheffler (Ref. 32) is applied to the PBE + vdW results, we obtain a slab-extrapolated adsorption energy of 1.67 (1.76) eV for the BF (TB) structure, yielding an adsorption energy difference of 0.09 eV between TB and BF. This adsorption energy difference agrees well with that (0.07 eV) obtained from the directly calculated adsorption energies.

³⁴Our PBE calculations for the 2×4 slab geometry show that the TB structure has a larger band gap of 0.78 eV compared with that (0.67 eV) of the BF structure, indicating that the electronic energy gain due to the formation of sp^3 hybridized Si-C bonds is

more significant in TB compared to BF. As shown in Table IV in the Supplemental Material (Ref. 27), the energy gain arising from bond formation is found to be greater than the energy cost due to molecular and surface deformations.

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