

# The binding of benzene on Si(1 1 1)-(7 × 7): a theoretical modelling approach

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## Abstract

The molecular adsorption of benzene on the Si(1 1 1)-(7 × 7) surface has been studied using a combination of semi-empirical (PM3) and density functional theory (DFT) (pBP86/DN\*\*) methods with cluster models. Two di-σ bonded adsorption configurations corresponding to the 1,2 and 1,4 states are considered. Energy calculations by both theoretical methods have revealed that the 1,4 state is thermodynamically favoured over the 1,2 state. In particular, the adsorption energy and vibrational frequencies of the 1,4 state predicted by the DFT method are in excellent agreement with the experimental observations, which further confirms the 1,4-cyclohexadiene-like binding state of benzene on Si(1 1 1)-(7 × 7). © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Motivated primarily by the potential applications in the formation of silicon carbide and diamond thin films on silicon surfaces via chemical vapor deposition (CVD) [1,2], adsorption of unsaturated hydrocarbons on silicon surfaces has attracted increasing attention in recent years [3–5]. As a prototypical aromatics/silicon surface system, adsorption of benzene on the industrially important Si(1 0 0)-(2 × 1) surface has been intensively investigated [5–10]. With numerous experimental and theoretical studies performed, it is now understood that benzene reacts readily with the surface, leading to the formation of a 1,4-cyclohexadiene-like adsorption complex

di-σ bonded to a single Si dimer on the surface [8–10].

In contrast, the adsorption state of benzene on the Si(1 1 1)-(7 × 7) surface has not been fully established [11–14]. Early understanding of the π-type of interaction, based on the thermal desorption spectroscopy (TDS) results by MacPherson et al. [11] and the high resolution electron energy loss spectroscopic (HREELS) studies of Taguchi et al. [12], was challenged by a recent synchrotron photoemission study [13], where a significant loss of molecular symmetry in the adsorption state was observed. More recently, this system was revisited by our group using HREELS at a higher instrumental resolution [14]. Our results have clearly unveiled the presence of rehybridisation of carbon atoms within chemisorbed benzene, which strongly suggests the σ-attachment of benzene to the Si(1 1 1)-(7 × 7) surface. A 1,4-cyclohexadiene-like adsorption configuration with benzene di-σ

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bonded to a pair of neighbouring adatom and rest atom was proposed [14].

Microscopic geometrical details of the adsorption state of benzene on Si(1 1 1)-(7 × 7) cannot be fully obtained with experimental efforts alone. On the other hand, the large dimensions and complex nature of the (7 × 7) reconstruction make theoretical modelling intrinsically difficult. There is a noticeable lack of theoretical studies concerning this system to our knowledge, in sharp contrast to the numerous calculations conducted on the benzene/Si(100) system [8–10]. In the present work, we attempt to develop ways to theoretically study the benzene Si(1 1 1)-(7 × 7) adsorption system using cluster models with molecular orbital methods.

Clusters of suitable sizes representing only a fraction of the (7 × 7) unit cell have been constructed to perform the modelling and calculations. Two di- $\sigma$  bonded adsorption configurations corresponding to the 1,4 and 1,2 di- $\sigma$  state have been investigated at both semi-empirical (PM3) [15] and density functional theory (DFT) (pBP86/DN\*\*) [16] levels. The more strained 1,2 di- $\sigma$  binding state with two neighbouring carbon atoms bonded to an adatom and a neighbouring rest atom is also considered here since the previous photoemission study [13] as well as the HREELS investigation [14] do not obviously exclude this configuration. In addition, this type of geometry closely resembles the adsorption configuration of ethylene on Si(1 1 1)-(7 × 7) [17]. Energy calculations were conducted to study the adsorption energy of benzene on the surface. Vibrational features of the energetically favoured state were calculated for direct comparisons with the HREELS observations [14].

## 2. Models and methods

As shown in Fig. 1, cluster model II (Si<sub>30</sub>H<sub>28</sub>) was cut from the central part of MMFF94 [18] optimised Cluster I, where the precision of atomic positions least suffers boundary effects. It contains a corner adatom and a neighbouring rest atom from an unfaulted half of the unit cell, which serves as a single ‘di-radical’ binding site for the

attachment of one benzene molecule. Capping H atoms at the cluster boundaries were kept frozen. Silicon atoms in the bottom double layer were placed at bulk lattice positions prior to the geometry optimisation process, with each Si–Si bond length set to 2.3517 Å and all bond angles adjusted to 109.4712°. Cluster III (Si<sub>9</sub>H<sub>12</sub>) was obtained from further reduction of Cluster II. Again, all capping H atoms were frozen during geometry optimisation. Clusters IV to VII in Fig. 2 were constructed by addition of C<sub>6</sub>H<sub>6</sub> onto respective mother clusters.

Calculations were performed using the SPARTAN package [19]. The formation heat of Clusters II (Si<sub>30</sub>H<sub>28</sub>), IV and VI were calculated at semi-empirical level using the PM3 method [15]. Total energies of Clusters III (Si<sub>9</sub>H<sub>12</sub>), V and VII as well as the vibrational frequencies of normal modes were obtained at the DFT level using perturbative Becke–Perdew functional (pBP86) in conjunction with a basis set DN\*\* (comparable to 6-31G\*\*) [19]. Geometric optimisations were conducted under SPARTAN default criteria. Binding energy (BE) (synonymous to adsorption heat or adsorption energy) is quoted here as the energy of the adsorbate/substrate complex minus the energy of the substrate, minus the energy of the adsorbate.

## 3. Results and discussion

From MMFF94 optimised cluster model I (Fig. 1) the average spacing between an adatom and a neighbouring rest atom is found to be around 4.5 Å, which is in good consistency with the literature value of 4.5 Å [20]. As shown in Table 1, the binding energies for the 1,4 and 1,2 adsorption states obtained by PM3 calculations, as modelled by Clusters IV and VI (Fig. 2), are –41.1 and –17.4 kcal/mol, respectively. This indicates that adsorption into the 1,4 di- $\sigma$  state is thermodynamically much more favourable compared to the 1,2 state. Although semi-empirical calculation may not be capable of providing very accurate energy values [15,19], the energy difference here is large enough to state the energetic preference.

To obtain more accurate binding energy, calculations were also performed at a DFT level.

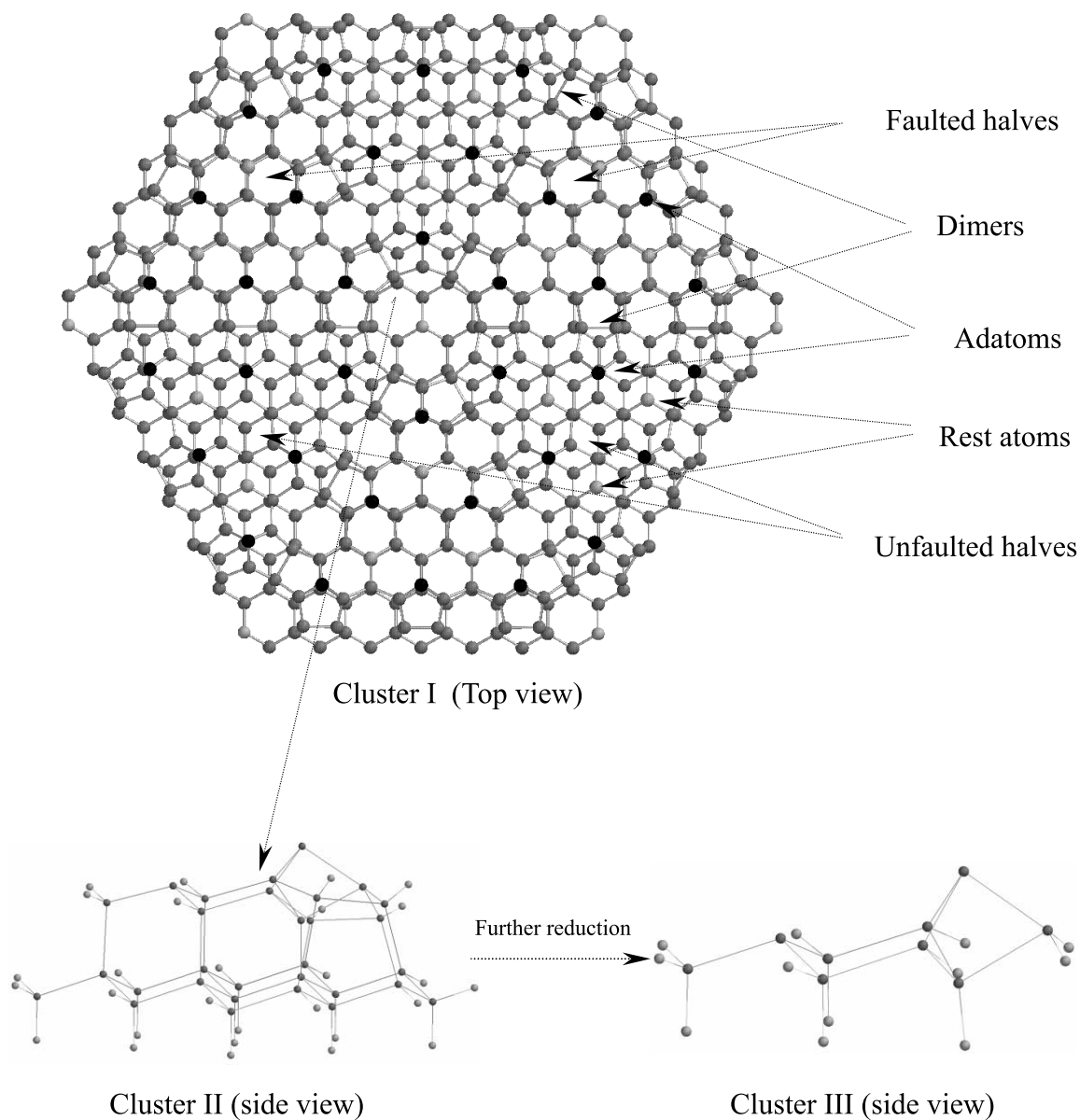


Fig. 1. A large cluster of the top five silicon layers constructed based on the DAS model [20] to represent three Si(1 1 1)-(7 × 7) surface unit cells surrounding a corner hole. It (Cluster I) has 973 atoms including the capping H-atoms (not displayed for clarity). Clusters II ( $\text{Si}_{30}\text{H}_{28}$ ) and III ( $\text{Si}_9\text{H}_{12}$ ) are reduced from Cluster I.

Based on cluster model V, a binding energy of  $-24.1$  kcal/mol for the 1,4 di- $\sigma$  state is obtained by pBP86/DN\*\* calculations. This value is very consistent with the TDS result of a 22.0 kcal/mol desorption energy for benzene from the Si(1 1 1)-(7 × 7) surface [14]. Strictly speaking, TDS studies

only reveal the kinetic information (the activation barrier of desorption), which may not be directly comparable to the thermodynamic information (binding energy). However, in the case of adsorption without an appreciable potential energy barrier, the value of activation of desorption is

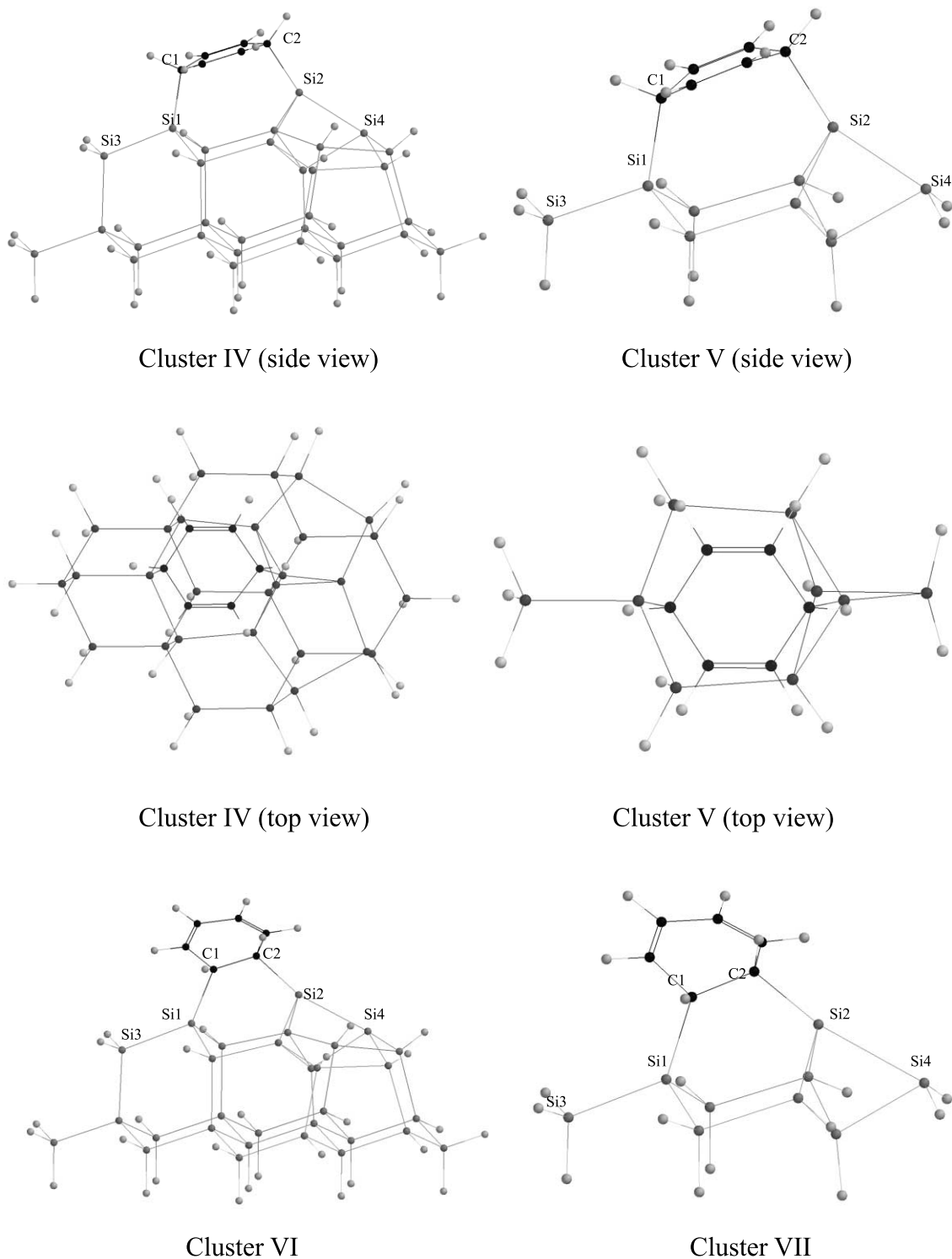


Fig. 2. Four molecular clusters modelling benzene adsorption into respective 1,4 and 1,2 di- $\sigma$  states.

Table 1

The binding energies and essential geometrical details of structures optimised by both PM3 and DFT (pBP/DN\*\*) methods<sup>a</sup>

	PM3 results (Energy in kcal/mol)	DFT results (Energy in kcal/mol)
<i>Binding energies of respective states</i>		
Modelled 1,4 di- $\sigma$ state	-41.1	-24.1
Modelled 1,2 di- $\sigma$ state	-17.4	6.0
Energy difference between 1,4 and 1,2 states	23.7	30.1
<i>Essential geometrical parameters of the 1,4 state</i>		
D(Si <sub>1</sub> Si <sub>2</sub> )	4.08 Å	4.24 Å
D(Si <sub>1</sub> -C <sub>1</sub> )	1.94 Å	2.02 Å
D(Si <sub>2</sub> -C <sub>2</sub> )	1.91 Å	1.99 Å
$\angle$ (C <sub>1</sub> Si <sub>1</sub> Si <sub>3</sub> )	118.45°	112.46°
$\angle$ (C <sub>2</sub> Si <sub>2</sub> Si <sub>4</sub> )	149.66°	152.32°
<i>Essential geometrical parameters of the 1,2 state</i>		
D(Si <sub>1</sub> Si <sub>2</sub> )	3.39 Å	3.71 Å
D(Si <sub>1</sub> -C <sub>1</sub> )	1.98 Å	2.03 Å
D(Si <sub>2</sub> -C <sub>2</sub> )	1.92 Å	2.04 Å
$\angle$ (C <sub>1</sub> Si <sub>1</sub> Si <sub>3</sub> )	127.12°	121.93°
$\angle$ (C <sub>2</sub> Si <sub>2</sub> Si <sub>4</sub> )	152.99°	163.07°

<sup>a</sup> DFT energies have been corrected for zero-point energies.

approximately equal to the binding energy [10,21]. Therefore, the 1,4 di- $\sigma$  state is the true and energetically favoured chemisorption state of benzene on Si(111)-(7 × 7) based on the consistency between the above theoretical binding energy prediction and experimental TDS results. In contrast, the positive heat of adsorption of 6.0 kcal/mol suggests high instability of the 1,2 di- $\sigma$  state (Cluster VII).

Compared to the TDS results (22 kcal/mol [14]), our PM3 calculations (Table 1) have apparently overestimated the binding energy. PM3 method is known to be not very reliable when dealing with highly strained and/or unsaturated systems [15]. In our case, the higher binding energies predicted by PM3 method may be attributable to the overestimation of the instability of Cluster II, which represents the unsaturated free surface. Besides, the PM3 calculation gives a lower energy difference (23.7 kcal/mol) between the 1,4 and 1,2 states compared to DFT results (30.1 kcal/mol).

The calculated binding energies for the 1,4 state at both PM3 and DFT levels are large negative values, indicating the thermodynamic feasibility of the adsorption of benzene into such a 1,4-cyclohexadiene-like state. Destabilisation factors such as ring strains as well as loss of aromaticity and

one C=C double bond have been well compensated by the formation of two Si-C  $\sigma$  bonds upon adsorption. At a closer look, however, the average Si-C bond energy of 60 kcal/mol (taken aromatic stabilization as 36 kcal/mol and a C=C bond energy as 60 kcal/mol) suggested from the DFT binding energy is substantially lower than a typical Si-C bond energy of 76 kcal/mol [22]. The weakening of Si-C bonds could be mainly attributed to the presence of a dimensional mismatch between the adsorbate (a benzene molecule with furthest carbon to carbon distance of 2.8 Å) and the substrate (a di-radical binding site, with adatom to rest atom separation of 4.5 Å). This mismatch induces significant steric strains upon adsorption. As shown in DFT geometries (Table 1), two Si-C bond lengths in the 1,4 state are significantly stretched to 2.02 and 1.99 Å from a typical Si-C bond length of 1.89 Å (obtained in a DFT pBP/DN\*\* optimised structure CH<sub>3</sub>-SiH<sub>3</sub>); and the C-Si-Si bond angles are severely bent from the ideal tetrahedral 109.5°. In the 1,2 state, a greater extent of the elongation of Si-C bonds and bending of respective C-Si-Si bond angles is clearly evidenced in response to the greater dimensional mismatches and substantial reduction of binding energies. The geometrical trend in the PM3

Table 2

Comparisons of the vibrational features (in  $\text{cm}^{-1}$ ) between HREELS data and present DFT (pBP/DN\*\*) predictions

Normal mode description	HREELS results of $\text{C}_6\text{H}_6/\text{Si}(111)-(7 \times 7)^a$	DFT results based on Cluster V <sup>b</sup>
Si–C stretching	540	549.3
Si–C stretching	–	683.1
Si–C stretching	–	695.3
C=C stretching	1582	1574
C=C stretching	1635	1626
C–H stretching ( $\text{sp}^3$ )	2920	2912
C–H stretching ( $\text{sp}^3$ )	–	2975
C–H stretching ( $\text{sp}^2$ )	3025	3030
C–H stretching ( $\text{sp}^2$ )	–	3051
C–H stretching ( $\text{sp}^2$ )	–	3056
C–H stretching ( $\text{sp}^2$ )	–	3073

<sup>a</sup> Ref. [14].<sup>b</sup> The present work.

optimised structures is reproduced by the DFT calculations.

The applicability of our theoretical modelling approach is further demonstrated by frequency calculations on the thermodynamically favoured 1,4 di- $\sigma$  state. From Table 2, DFT results are found to agree very well with the experimental results (HREELS data) with average discrepancies less than of  $10 \text{ cm}^{-1}$ . Among the listed frequencies, consistency in the Si–C stretching region is of particular significance. This is because the Si–C stretching information provides direct evidence for the existence of  $\sigma$  bonding between benzene and Si(111)-(7  $\times$  7) as well as the strength of such bonding. The excellent consistency between calculated frequencies in the C–H and C=C stretching region further confirms the 1,4-cyclohexadiene-like binding state for benzene adsorption.

It should be noted that due to the limited size of our clusters, the subtle differences in reactivity among various surface sites cannot be provided, which could be an interesting topic for future study.

#### 4. Conclusion

A theoretical modelling approach using small silicon clusters has been employed in the investigation of the chemisorption state of benzene on the Si(111)-(7  $\times$  7) surface. Two possible binding

states, the 1,2 and 1,4 di- $\sigma$  states, were investigated at both PM3 semi-empirical and DFT levels. The 1,4 di- $\sigma$  state is found to be the energetically preferred state. Frequency calculation results, matching very well with HREELS observations, further confirm the 1,4 binding state for benzene chemisorption.

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