

## Formation of Di- $\sigma$ Bond in Benzene Chemisorption on Si(111)-7 $\times$ 7

Y. Cao,<sup>†,‡</sup> X. M. Wei,<sup>†</sup> W. S. Chin,<sup>†</sup> Y. H. Lai,<sup>†</sup> J. F. Deng,<sup>‡</sup> S. L. Bernasek,<sup>§</sup> and G. Q. Xu<sup>\*,†</sup>

Department of Chemistry, National University of Singapore, 10 Kent Ridge, Singapore 119260; Department of Chemistry, Fudan University, Shanghai, 200433, P.R.C.; and Department of Chemistry, Princeton University, Princeton, New Jersey 08544-1009

Received: February 9, 1999; In Final Form: May 4, 1999

The adsorption of benzene on Si(111)-7 $\times$ 7 has been studied using high-resolution electron energy loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS). Both chemisorbed and physisorbed benzene were observed at an adsorption temperature of 110 K. Chemisorbed benzene desorbs molecularly at 350 and 364 K while physisorbed molecules desorb at 180 K. In the HREELS studies, two separate energy losses at 2920 and 3025  $\text{cm}^{-1}$  were observed for chemisorbed benzene, attributable to the C–H stretching vibrations of  $\text{sp}^3$  and  $\text{sp}^2$  carbon atoms, respectively. In addition, the formation of Si–C bond is also evidenced at a vibrational frequency of 540  $\text{cm}^{-1}$ . Our results clearly demonstrate that benzene is di- $\sigma$  bonded to the adjacent adatom and rest atom on Si(111)-7 $\times$ 7, forming a 1,4-cyclohexadiene-like structure.

### 1. Introduction

The adsorption of benzene on silicon surfaces has attracted much attention recently.<sup>1–14</sup> Benzene is considered to be a promising precursor for the growth of Si–C<sup>15</sup> and CVD diamond<sup>16,17</sup> thin films on silicon surfaces. The scientific interest in these studies arises from the challenge of determining the electronic and geometric structures of benzene on reconstructed semiconductor surfaces, expected to be intrinsically different from those on transition metal surfaces.<sup>18–20</sup>

On transition metals surfaces,<sup>18–20</sup> benzene bonds to the substrates by partially transferring part of its  $\pi$ -electrons to the d-bands of transition metals. However, the adsorption of benzene on silicon surfaces is strongly dependent on the surface structures. Different adsorption mechanisms were observed for different surface orientations, even for different reconstructions of the same surface orientation.<sup>1–4</sup> The adsorption of benzene on a well-defined Si(100)-2 $\times$ 1 surface has been extensively studied. In their HREELS work, Taguchi et al.<sup>4</sup> observed the vibrational features of 2935 and 3065  $\text{cm}^{-1}$ , which indicates the rehybridization of carbon atoms from  $\text{sp}^2$  to  $\text{sp}^3$  in benzene upon adsorption. On the basis of the observation, they proposed two di- $\sigma$  bonded adsorbate structures corresponding to 1,4- and 1,3-cyclohexadiene. In STM studies,<sup>5–7</sup> two adsorption states of benzene were observed and the transformation between the two can be induced by the STM tip. Using combined techniques of TPR/D, IR, and NEXAFS, Kong et al.<sup>8</sup> detected the primary 1,4-cyclohexadiene-like intermediate as well as an adduct of tetra- $\sigma$ -bonded structure. Recent angle-resolved UPS (ARUPS) studies coupled with first-principle density function cluster calculations<sup>9</sup> also revealed a 1,4-cyclohexadiene-like adsorption complex, that is, a flat-lying benzene molecule di- $\sigma$  bonded to the two dangling bonds of a single Si–Si surface dimer. This notion of rehybridization in chemisorbed benzene on Si(100)-2 $\times$ 1 is further supported by theoretical calculations.<sup>10–12</sup>

In contrast, the adsorption of benzene on Si(111), especially on Si(111)-7 $\times$ 7, is still not well understood. There remain some unresolved issues regarding the geometric configuration and adsorption mechanism of benzene on Si(111)-7 $\times$ 7. Piancastelli et al.<sup>1,2</sup> reported the dissociative adsorption of benzene on a cleaved Si(111)-2 $\times$ 1 surface at room temperature. The observation of Si–H stretching vibration at 2055  $\text{cm}^{-1}$  in HREELS suggests the formation of phenyl and hydride surface species. MacPherson and co-workers<sup>13</sup> studied the adsorption of benzene on Si(111)-7 $\times$ 7 at room temperature. On the basis of the TDS results, they hypothesized the  $\pi$ -bonded configuration of benzene chemisorbed on Si(111)-7 $\times$ 7. A similar conclusion was reached by Taguchi et al.<sup>3</sup> using HREELS and TDS. However, in a recent photoemission study,<sup>14</sup> the removal of the degeneracy of “e” orbitals in chemisorbed benzene was evidenced, which strongly suggests a loss of symmetry of benzene upon adsorption. The chemisorption of benzene is thus proposed to involve simultaneously an adatom and a rest atom of the Si(111)-7 $\times$ 7 surface in the adsorption process. The adsorbate intermediate is suggested to have a structure between benzene and 1,4-cyclohexadiene. This work challenges the previous  $\pi$ -bonded model of chemisorbed benzene on Si(111)-7 $\times$ 7. For better understanding of this adsorbate system, information about C–H vibrations in chemisorbed benzene and the formation of C–Si bond becomes necessary and essential.

We present here an investigation of chemisorption of benzene on Si(111)-7 $\times$ 7 using high-resolution electron energy-loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS). Two separate vibrational features at 2920 and 3025  $\text{cm}^{-1}$  were observed, corresponding to the C–H vibrations with  $\text{sp}^3$ - and  $\text{sp}^2$ -hybridized carbon atoms, respectively. The formation of C–Si bond is clearly demonstrated at a vibrational frequency of 540  $\text{cm}^{-1}$ . Our results are consistent with the di- $\sigma$  adsorption model, in which the adsorbate complex is 1,4-cyclohexadiene-like.

### 2. Experimental Section

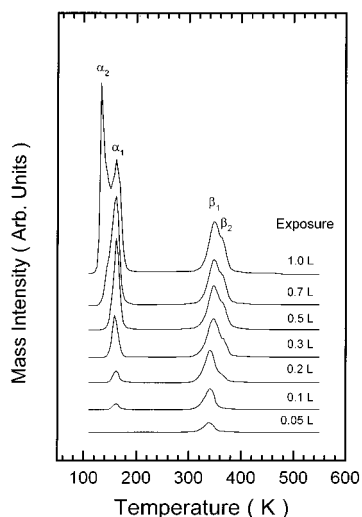
The experiments were conducted in a UHV system with a base pressure of  $<3 \times 10^{-10}$  Torr.<sup>21</sup> The vacuum chamber is equipped with a high-resolution electron spectrometer (LK-

\* Corresponding author. Fax: +65 779 1691. E-mail: chmxuq@nus.edu.sg.

<sup>†</sup> National University of Singapore.

<sup>‡</sup> Fudan University.

<sup>§</sup> Princeton University.



**Figure 1.** Thermal desorption spectra of benzene,  $C_6H_6$ , from Si(111)-7×7, obtained after various exposures at 110 K and at a heating rate of 2 K/s.

2000-14R) for HREELS and a quadrupole mass spectrometer (UTI-100) for TDS and gas analysis. The HREELS spectrometer consists of a double-pass 127° cylindrical deflector analyzer (CDA) for the monochromator and a single-pass 127° CDA for the detector. For HREELS measurements, an electron beam with a primary energy ( $E_p$ ) of 5.0 eV collides on the surface at an incident angle ( $\theta_i$ ) of 60° from the surface normal. The energy resolution of the spectrometer (full width at half-maximum, fwhm) was determined to be ~5 meV. The off-specular spectra were taken at -10° off-specular directions, where the -10° refers to the angle of  $\theta(\text{analyzer}) - \theta(\text{specular})$ . For TDS measurements, the ionizer was enclosed in a glass envelope with a 4 mm diameter aperture located about 2 mm from the sample surface. The linear heating rate of 2  $K \cdot s^{-1}$  was achieved using a RHK temperature controller.

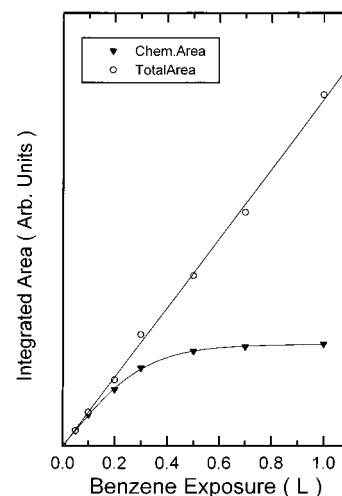
The Si(111) wafer commercially obtained from Goodfellow Cambridge is P-doped n-type and has a resistivity of 1–5  $\Omega \cdot \text{cm}$ . The sample (9 mm × 14 mm × 0.38 mm) was carefully cleaned by several cycles of Ar ion bombardment (500 eV, 30 min, 20  $\mu\text{A} \cdot \text{cm}^{-2}$ ) and annealing at 1150 K for 10 min. Surface cleanliness was checked using HREELS. The structure of Si(111)-7×7 was confirmed by LEED and STM in a separate UHV system.

The sample can be cooled to 110 K using a liquid- $N_2$  reservoir and annealed to 1200 K by resistively heating a Ta foil clamped to the back of the sample. The temperature was measured by a W/Re(5%)–W/Re(26%) thermocouple attached to the edge of the sample using a high-temperature ceramic adhesive (Aremco 516), and calibrated with an optical pyrometer (Minolta,  $\epsilon = 0.74$ ).

Benzene (Aldrich, 99.8%) was introduced into the chamber via a 6 mm diameter doser located 2 mm from the sample surface. Benzene exposures of the doser were calibrated by background dosing.

### 3. Results and Discussion

Figure 1 shows the changes in thermal desorption spectra of benzene from the Si(111)-7×7 surface as a function of exposure at 110 K. An initial exposure of 0.05 langmuir results in a single desorption peak at 342 K ( $\beta_1$ ). With increasing exposure, the 342 K peak shifts up to 349 K and a shoulder at 363 K ( $\beta_2$ ) appears. The peak at 160 K ( $\alpha_1$ ) becomes noticeable even at a



**Figure 2.** Plot of total and chemisorbed benzene as a function of exposure, based on the spectra in Figure 1.

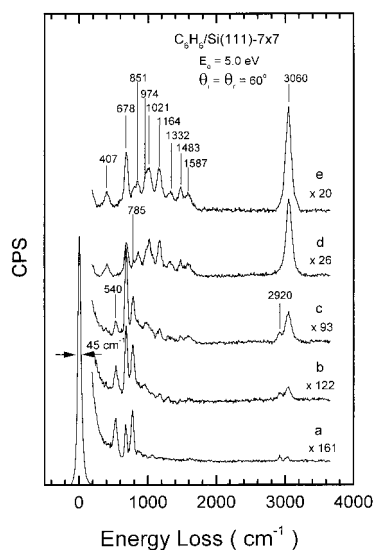
low exposure of 0.1 langmuir. Upon saturation of the  $\alpha_1$  peak at ~0.7 langmuir, a new feature ( $\alpha_2$ ) at 130 K can be identified.

The  $\beta_1$  and  $\beta_2$  peaks are attributed to the chemisorption states of benzene on Si(111)-7×7. Their desorption energies are estimated to be 92 and 96 kJ/mol, respectively, assuming a first-order desorption and a preexponential factor of  $10^{13} \text{ s}^{-1}$ .<sup>22</sup> The  $\alpha_2$  (130 K) and  $\alpha_1$  (160 K) peaks are related to the physisorbed benzene. The fact that the intensity of the 130 K peak grows almost linearly with the benzene exposure without saturation indicates the “bulklike” multilayer adsorption.

In a previous STM study, Wolkow and Moffat<sup>23</sup> studied the adsorption sites of benzene on Si(111)-7×7 at room temperature. Specific desorption energies of  $0.94 \pm 0.01 \text{ eV}$  (~91 kJ/mol) and  $0.95 \pm 0.01 \text{ eV}$  (~92 kJ/mol) were extracted for the center and corner faulted adatom sites, respectively, in excellent agreement with the desorption heat of the  $\beta_1$  peak observed in our TDS. Their work also showed that benzene desorption from the adatom sites on the unfaulted side has a similar desorption energy to that of the faulted side, but at a smaller desorption rate was noticed. We suggest that the  $\beta_2$  state observed in our TDS spectra is related to benzene desorption from the unfaulted subunit cell of Si(111)-7×7.

Figure 2 shows the changes in the total adsorption and chemisorbed benzene as a function of exposure. Our result indicates that chemisorbed benzene saturates at an exposure of 0.5 langmuir. However, the first physisorbed layer appears on top of chemisorbed benzene at exposures  $\geq 0.1$  langmuir, indicating the formation of islands. A similar observation was made in the case of  $H_2S$  adsorption on Si(111)-7×7.<sup>24</sup> The linear dependence of the total integrated peak area as a function of exposure suggests the unitary sticking coefficient for benzene adsorption on Si(111)-7×7 at 110 K.

Figure 3 presents the HREELS spectra as a function of benzene coverage on Si(111)-7×7 at 110 K. Upon 1.0 langmuir exposure, the formation of multilayer benzene is clearly demonstrated in Figure 3e. Loss features at 407, 678, 851, 974, 1021, 1164, 1332, 1483, 1587, and 3060  $\text{cm}^{-1}$  can be readily identified. The corresponding loss energies compare well with the vibrational energies of liquid-phase benzene<sup>25</sup> within ~20  $\text{cm}^{-1}$ . The detailed assignments for physisorbed benzene are summarized in Table 1. For exposures of ~0.2 langmuir benzene (Figure 3b), three additional losses at 540, 785, and 2920  $\text{cm}^{-1}$  can be unambiguously resolved, which are associated with chemisorbed benzene on the surface. These characteristic features of chemisorbed benzene are gradually screened by the



**Figure 3.** HREELS spectra obtained after exposing the Si(111)-7 $\times$ 7 surface to various exposures of benzene at 110 K: (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.7 and (e) 1.0 langmuir.

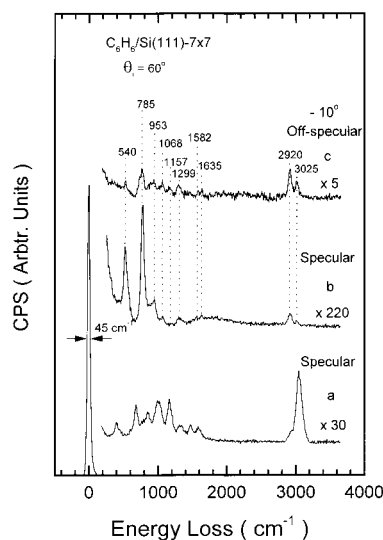
**TABLE 1: Comparison of Vibrational Structures of Physisorbed Benzene on Si(111)-7 $\times$ 7 at  $T = 110$  K with That of Liquid Phase Benzene (Ref 25)**

mode no. <sup>a</sup>	rep	mode	benzene (liquid phase)	physisorbed benzene/Si(111)-7 $\times$ 7
$\nu_{20}$	E <sub>2u</sub>	ring deform	404	407
$\nu_4$	A <sub>2u</sub>	CH bend ( $\gamma$ (CH))	673	678
$\nu_{11}$	E <sub>1g</sub>	CH bend ( $\delta$ (CH))	846	851
$\nu_7$	B <sub>2g</sub>	CH bend ( $\delta$ (CH))	992	974
$\nu_{14}$	E <sub>1u</sub>	CH bend ( $\delta$ (CH))	1037	1021
$\nu_{10}$	B <sub>2u</sub>	CH bend ( $\delta$ (CH))	1150	1164
$\nu_{17}$	E <sub>2g</sub>	Ring str ( $n$ (CC))	1320	1332
$\nu_3$	A <sub>2g</sub>	ring str ( $\delta$ (CC)) and deform	1482	1483
$\nu_{16}$	E <sub>1u</sub>	ring str ( $\delta$ (CC))	1596	1587
$\nu_{15}$	E <sub>2g</sub>	CH str ( $\nu$ (CH))	3047	3060
$\nu_1$	A <sub>1g</sub>	CH str ( $\nu$ (CH))	3062	
$\nu_{12}$	E <sub>1u</sub>	CH str ( $\nu$ (CH))	3063	
$\nu_5$	B <sub>1u</sub>	CH str ( $\nu$ (CH))	3068	

<sup>a</sup> Herzberg Numbering System (ref 36).

subsequent coverage of the physisorbed benzene. The direct formation of chemisorbed benzene at a cryogenic temperature of 110 K on the Si(111)-7 $\times$ 7 surface is somewhat different from the case of benzene adsorption on Si(100)-2 $\times$ 1 surface,<sup>8</sup> where only physisorbed state is formed at a low adsorption temperature. The observation of the 678 and 3060 cm<sup>-1</sup> losses from Figure 3a to Figure 3c strongly suggests the existence of physisorbed benzene at exposures  $\geq 0.1$  langmuir, which agrees well with the above TDS studies. The physisorbed  $\alpha_1$  state on top of the chemisorbed layer may be slightly tilted away from the surface plane, based on the observed intensity ratio of the out-of-plane C-H bending to C-H stretching vibrations for the physisorbed benzene.<sup>4</sup>

To study the chemisorbed benzene, Si(111)-7 $\times$ 7 was preexposed to 0.5 langmuir C<sub>6</sub>H<sub>6</sub> at 110 K, and then annealed to 300 K. This procedure allows us to drive all the physisorbed benzene away, leaving only chemisorbed benzene on the surface. Figure 4b presents the HREELS spectrum for the chemisorbed benzene. Losses at 540, 785, 877, 951, 1068, 1157, 1299, 1582, 1635, 2920, and 3025 cm<sup>-1</sup> can be resolved. The assignments for the peaks present in the spectrum of Figure 4b are summarized in Table 2. The two separate vibrational features at 2920 and 3025 cm<sup>-1</sup> corresponding to the C-H stretching modes for sp<sup>3</sup> and



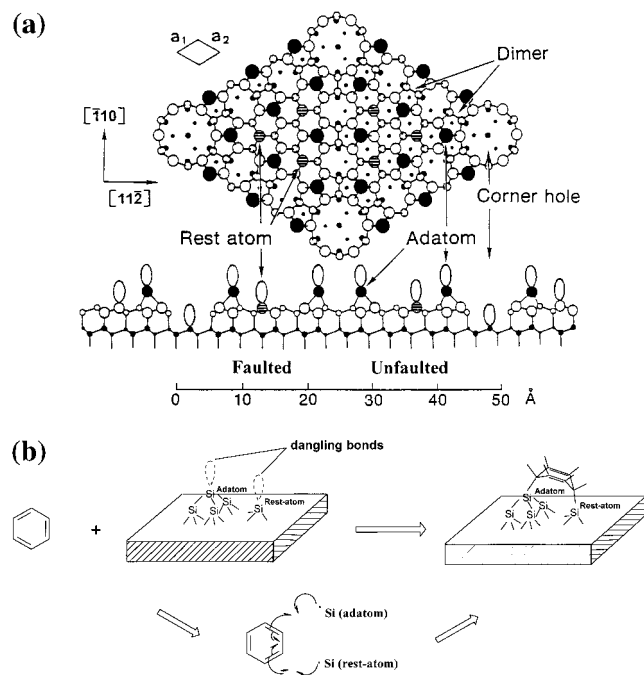
**Figure 4.** HREELS spectra obtained after: (a) exposing the Si(111)-7 $\times$ 7 surface to 0.5 langmuir benzene at 110 K; (b) annealing (a) to 300 K; (c) off-specular spectra of (b) with  $\Delta\theta = -10^\circ$ .

**TABLE 2: Comparison of Vibrational Structures of Chemisorbed Benzene on Si(111)-7 $\times$ 7 at  $T = 110$  K with That of Liquid Phase Benzene (Ref 25) and 1,4-Cyclohexadiene (Ref 27), and the Dominant Electron Scattering Mechanism**

mode description	benzene (liquid phase)	1,4-cyclohexadiene (liquid phase)	chemisorbed benzene/Si(111)-7 $\times$ 7	dominant mechanism
SiC str			540	dipole
CH bend	673	887	785	dipole
CH bend	849		877	impact
CH bend	995	956	951	impact
CH bend	1038		1068	impact
CH bend	1150	1159	1157	impact
CH bend		1197	1299	impact
CC stretch	1326	1430	1582	impact
CC stretch	1596	1639	1635	impact
CH stretch	3047	2877	2920	impact
CH stretch	3062	3032	3025	impact

sp<sup>2</sup> carbons, respectively, clearly suggest the presence of rehybridization of carbon atoms in chemisorbed benzene on Si(111)-7 $\times$ 7. Similar HREELS results were reported for chemisorbed benzene on the Si(100)-2 $\times$ 1 surface.<sup>4</sup> The 1582 and 1635 cm<sup>-1</sup> losses are attributed to the C=C stretching vibrations. The 1157, 1068, and 951 cm<sup>-1</sup> peaks can be assigned to the C-H in-plane bending modes. The C-H out-of-plane bending and Si-C stretching modes can account for the intensities at 785 and 540 cm<sup>-1</sup>, respectively. The broad loss around 1900 cm<sup>-1</sup> is known to be caused by electronic transitions associated with the residual surface states of the Si(111)-7 $\times$ 7 surface.<sup>3,26</sup> We did not observe any peak at  $\sim 2055$  cm<sup>-1</sup> associated with the Si-H stretching mode, indicating the molecular nature of chemisorbed benzene on the Si(111)-7 $\times$ 7 surface. Upon thermal desorption of chemisorbed benzene, no deposition of carbon species can be detected in HREELS, which further confirms the molecular desorption.

The off-specular spectra were taken at a  $-10^\circ$  off-specular direction, shown in Figure 4c. Only the 540 and 785 cm<sup>-1</sup> losses associated with the Si-C stretch and C-H out-of-plane bending modes are mainly dipole-active, while other losses have large contributions of impact scattering (Table 2). The involvement of impact excitation mechanism makes it impossible to deduce the adsorbate orientation by simply checking the intensity ratio of the C-H out-of-plane bending and stretching modes.



**Figure 5.** (a) Dimer adatom stacking fault (DAS) model of the Si(111)-7×7 unit cell proposed by Takayanagi et al. (ref 28). Only adatoms, rest atoms, and corner hole atoms have dangling bonds. Faulted (F) and unfaulted (U) halves of the 7 × 7 unit cell are also marked. (b) Schematic model (side view) of C<sub>6</sub>H<sub>6</sub> adsorbed on Si(111)-7×7 (the adatom/rest-atom bridging model).

The present HREELS results are markedly different from the previous work on the same surface by Taguchi et al.<sup>3</sup> The coexistence of two hybridization states of carbon atoms is clearly resolved, as evidenced by the observation of two separate vibrational losses of 2920 and 3025 cm<sup>-1</sup> for chemisorbed benzene on Si(111)-7 × 7. The failure to observe this splitting in their work<sup>3</sup> may partly be attributable to the lower instrumental resolution (fwhm ~ 80 cm<sup>-1</sup>) compared to an energy resolution of ~45 cm<sup>-1</sup> in this experiment. Our observation rules out the π-bonding model, where benzene is suggested to be bonded to a single dangling bond (an “on-top” site), as well as the possibility of benzene adsorption to a single dangling bond of adatom, rest atom, or corner hole on Si(111)-7 × 7 (Figure 5a).

The present experimental findings suggest the formation of chemical bonds between two carbon atoms in benzene and two adjacent Si atoms with dangling bonds. Benzene is therefore di-σ-bonded to a pair of neighboring adatom and rest atom on Si(111)-7 × 7, forming a 1,4-cyclohexadiene-like structure. A schematic structure of chemisorbed benzene is shown in Figure 5b. Table 2 compares the vibrational frequencies of liquid phase 1,4-cyclohexadiene<sup>27</sup> and the chemisorbed benzene. Indeed, the well-correlated vibrational structures between the two suggest the similarities in their molecular structures. Our result provides complementary information and is consistent with the photoemission study.<sup>14</sup> In their work, the evidence of removal of degeneracy of the “e” orbitals in chemisorbed benzene strongly suggests a loss of symmetry of benzene upon adsorption.

Previous HREELS studies<sup>30,31</sup> of acetylene and ethylene on Si(111)-7 × 7 surfaces demonstrated that acetylene and ethylene are both di-σ-bonded to two adjacent adatom and rest atom, yielding “ethylenic”- or “ethanic”-like adsorbates, respectively. In these two cases, only one C–C bond is involved in the di-σ bonding configuration. Considering the direct distance (~4.5 Å) between two adjacent adatom and rest atom based on the

DAS (dimer adatom stacking fault) model (Figure 5a) of Si(111)-7×7<sup>28</sup> and a typical bond length of Si–C (1.8–2.1 Å),<sup>29</sup> the C–C bond is expected to be much stretched in the adsorption intermediate. In the present case of benzene adsorption on Si(111)-7×7, the bonding of benzene to the silicon surface through two adjacent carbon atoms would yield a 1,3-cyclohexadiene-like complex. However, this structure may have greater strain due to the short distance of C–C bond in benzene (1.39 Å). Since the separation between 1,4-carbon atoms is 2.78 Å, nearly twice that of a single C–C bond, the formation of 1,4-cyclohexadiene-like complex is expected to be more favorable. In addition, the bridging geometry of chemisorbed benzene would be tilted by ~13° with respect to the surface plane of Si(111)-7×7 since the adatoms are about 1 Å above the rest atoms.<sup>34</sup>

In fact, the loss in bond energy for forming the 1,4-cyclohexadiene structure can be sufficiently compensated by the formation of two Si–C bonds. In organosilicon chemistry, the typical bond energy for Si–C ( $D_{\text{Si-C}}$ ) is 75.95 kcal/mol,<sup>32</sup> much greater than 48 kcal/mol = (resonance energy + 1 double bond)/2 = (36 + 60)/2 kcal/mol.<sup>33</sup> Therefore, the di-σ bonding of benzene molecule to two adjacent adatom and rest atom is energetically favorable.

Hu et al.<sup>35</sup> studied the thermal reactions of cyclohexene and 1,3- and 1,4-cyclohexadiene on Si(111)-7×7. The observed dominant desorption feature at mass 78 showed the formation of benzene through a dehydrogenation surface reaction. The catalytic conversion of 1,4-cyclohexadiene to benzene on Si(111)-7×7 suggests the presence of a reaction intermediate which is structurally correlated with these two molecules. Indeed, our observation of a 1,4-cyclohexadiene-like structure for chemisorbed benzene on Si(111)-7×7 is consistent with their experiment.

We have shown that benzene binds to a pair of adatom and rest atom through a di-σ bond. However, there are two types of adatoms in one unit cell, that is, center and corner adatoms. Our result does not allow us to determine the preferential adatom sites for benzene adsorption. In a STM study, Moffatt and Wolkow<sup>23</sup> observed the adsorption of benzene on corner adatoms of Si(111)-7×7 surface at room temperature, although the number of neighboring pairs of center adatoms and rest atoms is twice of that of corner adatoms and rest atoms. In a 7 × 7 unit cell, no more than six adatoms can be involved in the di-σ bonding reaction, limited by the available six rest atoms with dangling bonds. Thus, the predicted saturation coverage of di-σ bonded benzene on Si(111)-7×7 is ~0.12 (~6/49), which agrees well with the saturation coverage of 0.1 monolayer determined using combined techniques of AES and TDS.<sup>3</sup>

#### 4. Conclusions

The adsorption of benzene on a Si(111)-7×7 surface has been investigated using high-resolution electron energy-loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS). Both physisorption and chemisorption of benzene occur at 110 K. The chemisorbed benzene desorbs molecularly at 349 and 363 K, possibly attributed to benzene desorption from faulted and unfaulted sides of the unit cell, respectively. The HREEL results clearly demonstrate the presence of both sp<sup>2</sup> and sp<sup>3</sup> carbon atoms in chemisorbed benzene as well as the formation of C–Si bond. Our observation is consistent with the di-σ bonding of benzene to two adjacent adatom and rest atom on Si(111)-7×7, yielding a 1,4-cyclohexadiene-like structure.

**Acknowledgment.** This work was supported by National University of Singapore under Grant No. RP 3970612.

## References and Notes

- (1) Piancastelli, M. N.; Margaritondo, G.; Anderson, J.; Frankel, D. J.; Lapeyre G. J. *Phys. Rev. B* **1984**, *30*, 1945.
- (2) Piancastelli, M. N.; Kelly, M. K.; Margaritondo G.; Frankel D. J.; Lapeyre G. J. *Phys. Rev. B* **1986**, *34*, 2511.
- (3) Taguchi, Y.; Fujisawa, M.; Nishijima, M. *Chem. Phys. Lett.* **1991**, *178*, 363.
- (4) Taguchi, Y.; Fujisawa, M.; Takaoka, T.; Okada, T.; Nishijima, M. *J. Chem. Phys.* **1991**, *95*, 6870.
- (5) Self, K. W.; Pelzel, R. L.; Owen, J. H. G.; Yan C.; Widdra W.; Weinberg W. H. *J. Vac. Sci. Technol. A* **1998**, *16*, 1031.
- (6) Lopinski, G. P.; Fortier, T. M.; Moffat, D. J.; Wolkow, R. A. *J. Vac. Sci. Technol. A* **1998**, *16*, 1037.
- (7) Lopinski, G. P.; Moffat, D. J.; Wolkow, R. A. *Chem. Phys. Lett.* **1998**, *282*, 305.
- (8) Kong, M. J.; Teplyakov A. V.; Lyubovitsky J. G.; Bent, S. F. *Surf. Sci.* **1998**, *411*, 286.
- (9) Gokhale, S.; Trischberger, P.; Menzel, D.; Widdra, W.; Dröge, H.; Steinrück, H.-P.; Gutdeutsch, U.; Rösch, N. J. *Chem. Phys.* **1998**, *108*, 5554.
- (10) Craig, B. I. *Surf. Sci. Lett.* **1993**, *280*, L279.
- (11) Jeong, H. D.; Ryu, S.; Lee, Y. S.; Kim S. *Surf. Sci.* **1995**, *344*, L1226.
- (12) Birkenheuer, U.; Gutdeutsch, U.; Rösch, N. *Surf. Sci.* **1998**, *409*, 213.
- (13) MacPherson, C. D.; Hu, D. Q.; Leung, K. T. *Solid State Commun.* **1991**, *80*, 217.
- (14) Carbone, M. C.; Piancastelli, M. N.; Zaroni, R.; Comtet, G.; Dujaralin, G.; Hellner, L. *Surf. Sci.* **1998**, *407*, 275.
- (15) Yi, J. W.; Lee, Y. H.; Farouk, B. *Thin Solid Films* **1998**, *326*, 154.
- (16) Singh, J.J. *Mater. Eng. Perform.* **1994**, *3*, 378.
- (17) Kotaki, T.; Horii, N.; Isono, H.; Matsumoto, O. *J. Electrochem. Soc.* **1996**, *143*, 2003.
- (18) Grassian, V. G.; Muetterties, E. L. *J Phys. Chem.* **1987**, *91*, 389.
- (19) Koel, B. E.; Crowell, J. E.; Mate, C. M.; Somorjai, G. A. *J. Phys. Chem.* **1984**, *88*, 1988.
- (20) Surman, M.; Bare, S. R.; Hoffman, P.; King D. A. *Surf. Sci.* **1983**, *126*, 349.
- (21) Huang, H. H.; Zhou Z.; Jiang X.; Xu, G. Q. *Surf. Sci.* **1998**, *396*, 304.
- (22) Redhead, P. A. *Vacuum* **1962**, *12*, 203.
- (23) Wolkow, R. A.; Moffatt, D. J. *J. Chem. Phys.* **1995**, *103*, 10696.
- (24) Chakarov, D. V.; Ho, W. *Surf. Sci.* **1995**, *323*, 57.
- (25) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated*, NSRDS-NBS 39.
- (26) Demuth, J. E.; Person, B. N. J.; Schell-Sorokin, A. *J. Phys. Rev. Lett.* **1983**, *51*, 2214.
- (27) Slidham, H. D. *Spectrochim. Acta* **1965**, *21*, 23.
- (28) Takayanagi, K.; Tanishiro, T.; Takahashi, S.; Takahashi, M. *J. Vac. Sci. Technol. A* **1985**, *3*, 1502.
- (29) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983.
- (30) Yoshinobu, J.; Tasuda H.; Onchi, M.; Nishijima, M. *Chem. Phys. Lett.* **1986**, *130*, 170.
- (31) Yoshinobu, J.; Tasuda, H.; Onchi, M.; Nishijima, M. *Solid State Commun.* **1986**, *60*, 801.
- (32) E. W. Colvin, *Silicon Reagents in Organic Synthesis*; Academic Press: New York, 1988; p 2.
- (33) Morrison, R. T.; Boyd R. N. *Organic Chemistry*, 3rd ed.; Allyn and Bacon: Boston, 1973.
- (34) Tong S. Y.; Huang, H.; Wei, C. M.; Packard, W. E.; Men, F. K.; Glander, G.; Webb, M. B. *J. Vac. Sci. Technol. A* **1986**, *6*, 615.
- (35) Hu, D. Q.; MacPherson, C. D.; Leung, K. T. *Surf. Sci.* **1992**, *273*, 21.
- (36) Hertzberg, G. *Infrared and Raman Spectrum of Polyatomic Molecules*; Van Nostrand: New York, 1945.