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***p*-Benzoquinone on Si(111)-7×7: [6 + 2]-like Cycloaddition**Yue Sheng Ning,<sup>†,‡</sup> Yan Xia Shao,<sup>†</sup> and Guo Qin Xu<sup>\*,†</sup>*Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, The Dow Chemical (China) Company Limited, 936 Zhangheng Road, Zhangjiang Hi-Tech Park, Shanghai, China 201203**Received: December 6, 2009; Revised Manuscript Received: March 28, 2010*

The Covalent binding of *p*-benzoquinone ( $\text{O}=\text{C}_6\text{H}_4=\text{O}$ ) and the formation of an aromatic ring ( $-\text{O}-\text{C}_6\text{H}_4-\text{O}-$ ) on Si(111)-7×7 have been investigated by using high-resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) calculations. For chemisorbed *p*-benzoquinone, the absence of  $\nu(\text{C}=\text{O})$  at  $1659\text{ cm}^{-1}$ , the retention of  $\text{sp}^2$ - $\nu(\text{C}-\text{H})$  at  $3050\text{ cm}^{-1}$ , the appearance of  $\nu(\text{Si}-\text{O})$  at  $824\text{ cm}^{-1}$ , and aromatic  $\nu(\text{C}=\text{C})/\delta_{\text{ip}}(\text{C}-\text{H})$  at  $1600/1505\text{ cm}^{-1}$  demonstrate that the molecule reacts with the surface in a [6+2]-like cycloaddition mode, which is further confirmed by XPS and density functional theory (DFT) vibrational calculations. DFT calculations indicate that the [6+2]-like cycloadduct ( $-\text{O}-\text{C}_6\text{H}_4-\text{O}-$ ) bridging two nearest adatoms in neighboring half-unit cells is the most stable. This binding scheme may prove useful for chemical and electronic modification of the semiconductor surfaces.

**1. Introduction**

Recently, organic modification of silicon surfaces has been attracting continuous attention due to the great opportunities to tailor the surface electronic, optical, and biological properties by exploiting the organic reaction toolbox.<sup>1–3</sup> The binding of multifunctional organic molecules<sup>4–10</sup> is of particular interest since the intact functional groups may protrude from the surface, providing a molecular template to create more sophisticated and desirable structures. Specifically, considerable effort has been devoted to carbonyl-containing compounds, including simple carbonyls,<sup>11–14</sup> dicarbonyls,<sup>15,16</sup> and conjugated and unconjugated unsaturated carbonyls.<sup>17–19</sup> Reaction competition and selectivity have been discussed<sup>17,18</sup> between different binding modes such as  $\text{O}\cdots\text{Si}$  dative bonding, [2+2]  $\text{C}=\text{O}$ , [2+2]  $\text{C}=\text{C}$ , [4+2] cycloadditions, ene-like reactions, and tetra- $\sigma$  binding.

One interesting carbonyl-containing molecule is *p*-benzoquinone ( $\text{O}=\text{C}_6\text{H}_4=\text{O}$ ), a multifunctional molecule that bears ketonic, oxidant, and alkenic functionalities. As a highly conjugated compound, it is extensively employed for electron transport in biological systems.<sup>20</sup> However, despite its chemical versatility, there has been no report on its surface chemistry on any single crystalline substrate under ultrahigh vacuum (UHV) conditions. The main objective of this experiment is to explore its binding mechanism with silicon surfaces, particularly Si(111)-7×7.

As shown in Figure 1, the separation between the two terminal oxygen atoms in *p*-benzoquinone ( $5.34\text{ \AA}$ ) is comparable with those between neighboring dangling bonds on Si(111)-7×7,<sup>21,22</sup> which are  $4.57\text{ \AA}$  for the adjacent adatom and rest atom,  $6.65\text{ \AA}$  for the two adatoms across a dimer,  $7.68\text{ \AA}$  for the neighboring adatoms within the same half-unit cell, and  $7.85\text{ \AA}$  for the corner hole and its adjacent corner adatoms. This geometric matching suggests that a [6+2]-like cycloaddition (through binding both the terminal atoms of a conjugated triene to two dangling bonds on the surface) may be possible for

binding *p*-benzoquinone on Si(111)-7×7. This mechanism is indeed confirmed by our combined experimental (HREELS and XPS) and theoretical (DFT) studies presented in this work.

**2. Experimental Section**

The experiments were performed in two separate UHV chambers with a base pressure of  $\sim 2 \times 10^{-10}$  Torr. One system is equipped with a quadrupole mass spectrometer (UTI-100C) for gas analysis, and an HREELS (LK2000-14R). The HREELS spectrometer consists of a double pass  $127^\circ$  cylindrical deflector analyzer (CDA) as the monochromator and a single pass  $127^\circ$  CDA as the energy analyzer. For specular geometry experiments, an electron beam with  $6.9\text{ eV}$  kinetic energy impinges on Si(111)-7×7 at an incident angle of  $60^\circ$  with respect to the surface normal. A resolution of  $\sim 7\text{ meV}$  (fwhm:  $50\text{--}60\text{ cm}^{-1}$ ) was routinely achieved. XPS experiments were carried out in another UHV chamber equipped with a dual-anode X-ray source and a concentric hemispherical energy analyzer (CLAM2, VG). The spectra were acquired with Al K $\alpha$  radiation ( $h\nu = 1486.6\text{ eV}$ ) and  $20\text{ eV}$  pass energy. The binding energy (BE) scale is referenced to the peak maximum of Si(2p) line ( $99.3\text{ eV}^{23}$ ) of a clean Si(111)-7×7 substrate.

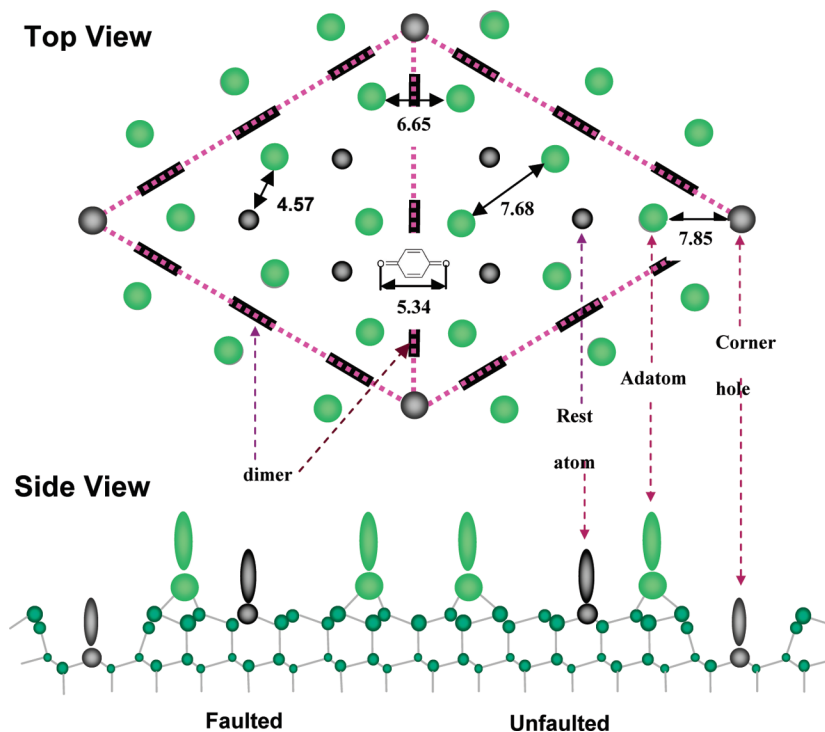
The silicon samples with a dimension of  $8 \times 18 \times 0.38\text{ mm}^3$  were cut from p-type boron-doped silicon wafers (99.999%,  $1\text{--}30\text{ }\Omega\cdot\text{cm}$ , Goodfellow). A piece of tantalum (Ta) foil ( $0.025\text{ mm}$  thick, Goodfellow) was sandwiched between two Si(111) crystals held together by two Ta clips, and in turn spot-welded to two Ta posts at the bottom of a sample holder. The samples can be resistively heated to  $1400\text{ K}$  by passing a current through the Ta foil and cooled to  $110\text{ K}$  with liquid  $\text{N}_2$ . They were degassed at  $900\text{ K}$  for  $12\text{ h}$ , and cleaned by several cycles of  $\text{Ar}^+$  bombardment ( $500\text{ eV}$ , sample current  $5\text{ }\mu\text{A}\cdot\text{cm}^{-2}$ ,  $30\text{ min}$ ) and annealing ( $1200\text{ K}$ ,  $10\text{ min}$ ). The cleanliness was verified with XPS and HREELS. The surface structure was examined by using scanning tunneling microscopy (STM) in a separate system.

*p*-Benzoquinone (99.5%, Aldrich) and *p*-benzoquinone- $d_4$  (98 atom % D, Aldrich) powders were placed in a glass bulb. Prior to experiments, the stainless steel manifold was cleaned by

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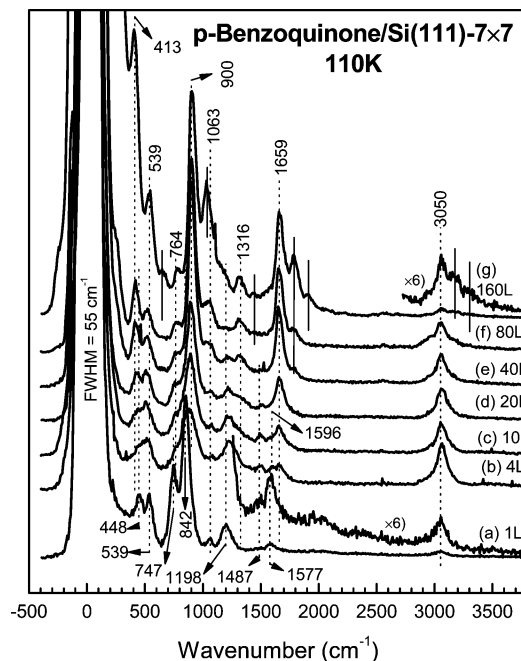
**Figure 1.** Structure of Si(111)-7 $\times$ 7 based on the Dimer-atom-stacking (DAS) faulted model. The top view shows adatoms, rest atoms, corner holes, and dimers. Adatoms, rest atoms, and corner holes are distinguished by different size and color. The side view marks the dangling bonds with “flame”. The distances (in Å) between different dangling bonds and the molecular size of a *p*-benzoquinone molecule are depicted in the top view.

acetone and heated at >400 K and pumped to  $<1 \times 10^{-3}$  Torr. The chemicals were purified in situ by pump–sublime (heated to  $\sim 370$  K)—crystallize (cooled to  $\sim 300$  K) cycles. Maintaining the glass bulb and the manifold at  $\sim 370$  K, the chemicals were dosed onto the front surface of Si(111)-7 $\times$ 7 through a dosing tube attached to a variable leak valve without the calibration of ion gauge sensitivity. The distance between the dosing tube and the front surface was about 1 cm. Since XPS and HREELS experiments were performed in two separate systems, the absolute exposure may not be directly compared.

### 3. Results and Discussion

#### 3.1. High-Resolution Electron Energy Loss Spectroscopy.

Figure 2 shows the HREELS spectra of Si(111)-7 $\times$ 7 exposed to *p*-benzoquinone at 110 K as a function of exposure. The vibrational frequencies and their assignments for physisorbed and chemisorbed *p*-benzoquinone are listed in Table 1. Figure 2a (1 L) could originate from purely chemisorbed species, as the peaks positions and intensities differ significantly from those of the physisorption (Figure 2f,g) spectra. Physisorbed species appear at an exposure of 4 L (Figure 2b). The small peak shift from 1577  $\text{cm}^{-1}$  (Figure 2a) to 1596  $\text{cm}^{-1}$  (Figure 2b) is possibly due to the peak overlapping of coexisting physisorption and chemisorption states. Spectra f and g in Figure 2 display the vibrational features for a physisorbed multilayer after exposing 80 and 160 L ( $1 \text{ L} = 1 \times 10^{-6} \text{ Torr}\cdot\text{s}$ ) onto the Si(111) surface, respectively. The energy-loss peaks at 413, 539, 764, 900, 1063, 1316, 1659, and 3050  $\text{cm}^{-1}$  are readily resolved, which are in good agreement with the vibrational energies of solid-phase *p*-benzoquinone as included in Table 1.<sup>24,25</sup> Among these vibrational signatures, the peaks at 3050, 1659, and 1316  $\text{cm}^{-1}$  are assigned to the ethylenic C–H stretching, C=O stretching, and quinoid ring stretching/C–H in-plane bending modes, respectively. Notably, in our physisorption spectra (Figure 3a,



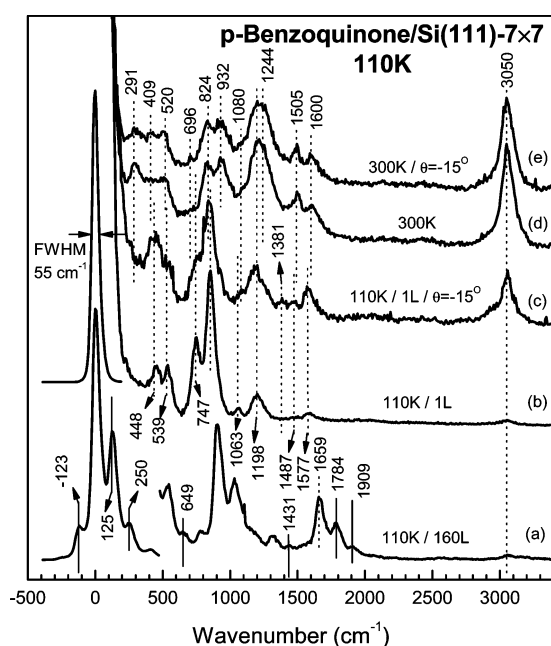
**Figure 2.** HREELS spectra of *p*-benzoquinone adsorbed on Si(111)-7 $\times$ 7 at 110 K as a function of exposure.

reproduced from Figure 2g), a series of peaks, which are indicated by vertical solid lines, were not reported in previous vibrational studies.<sup>24,25</sup> Detailed analysis indicates that these “additional peaks” are either ca.  $\pm 125N \text{ cm}^{-1}$  ( $N = 1, 2, \dots$ ) or the combination of the  $125N \text{ cm}^{-1}$  peak and a fundamental IR peak of *p*-benzoquinone. They are possibly attributable to the crystallization of *p*-benzoquinone molecules on the surfaces, causing the coupling between the molecular and lattice vibrational modes.<sup>26</sup>

**TABLE 1: Vibrational Modes Assignment for Physisorbed and Chemisorbed *p*-Benzoquinone on Si(111)-7×7<sup>a</sup>**

| mode                  | IR <sup>24,25</sup> solid | physisorption <sup>b</sup> | mode                      | [6+2]-DFT <sup>b</sup> | chemisorption <sup>b</sup> |
|-----------------------|---------------------------|----------------------------|---------------------------|------------------------|----------------------------|
| CH str                | 3062                      | 3050                       | CH str                    | 3091, 3078             | 3050                       |
| C=O str               | 1666                      | 1659                       | ring str                  | 1578, 1556             | 1600                       |
| ring str              | 1592                      | 1596                       | ring str + CH ip bend     | 1466                   | 1505                       |
| CH ip bend            | 1354                      | 1316                       | ring str                  | 1272                   | 1244                       |
| ring str              | 1299                      | 1316                       | C–H ip bend               | 1256                   | 1244                       |
| CH ip bend + ring str | 1066                      | 1063                       | C–O str                   | 1191, 1153             | 1198                       |
| ring ip def           | 944                       | 900                        | CH ip bend                | 1085                   | 1080                       |
| CH wag + C=O wag      | 882                       | 900                        | CH ip bend                | 993                    | 932                        |
| C–C str               | 728                       | 764                        | CH oop bend               | 922, 911               | 932                        |
| C=O wag + CH wag      | 505                       | 539                        | Si–O str                  | 843, 809               | 824                        |
| C=O ip bend           | 409                       | 413                        | CH oop bend               | 825                    | 824                        |
| ring tors             | 89                        | 125                        | CH oop bend               | 782                    |                            |
| lattice mode          |                           | 125                        | ring oop def.             | 695                    | 696                        |
|                       |                           |                            | CH oop bend               | 542                    | 520                        |
|                       |                           |                            | ring ip def + Si–O–C bend | 457                    | 409                        |
|                       |                           |                            | adatom vib                | 313, 294               | 291                        |

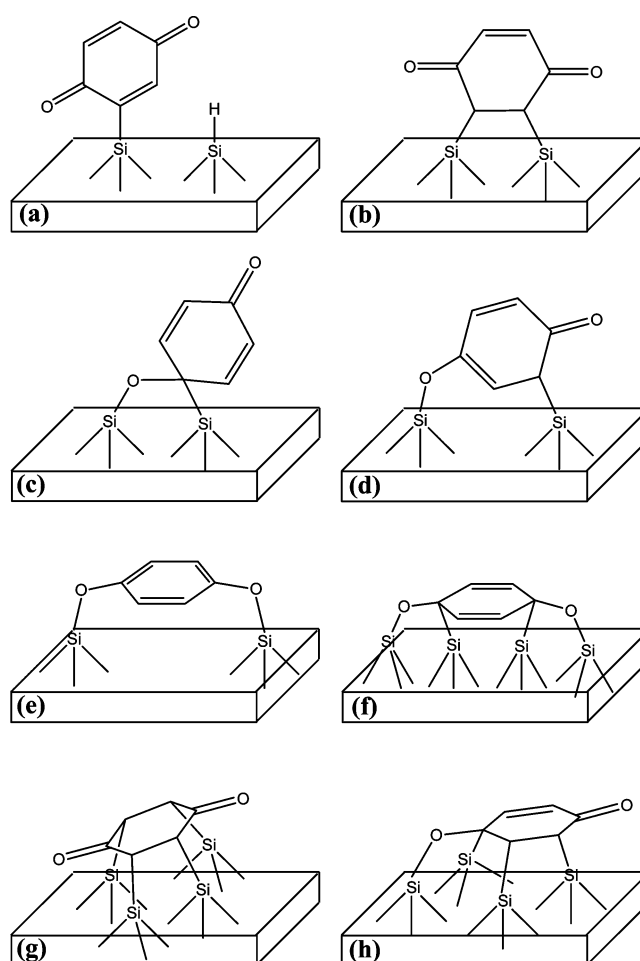
<sup>a</sup> All frequencies are in cm<sup>−1</sup>. <sup>b</sup> This work; assignments from DFT calculations are based on Mode V, Figure 9.



**Figure 3.** HREELS spectra of chemisorbed *p*-benzoquinone on Si(111)-7×7. (a) 110 K, physisorption; (b) low exposure at 110 K; (c) same as (b), but HREELS in off-specular mode; (d) obtained by annealing the physisorbed sample (a) to 300 K and then cooling down to 110 K; (e) same as (d), but HREELS in off-specular mode.

The vibrational features of chemisorbed *p*-benzoquinone can be obtained at low exposures at 110 K (Figure 3b, reproduced from Figure 2a), or upon annealing the physisorbed sample to 300 K to drive away the multilayer molecules and only retain the chemisorbed monolayer (Figure 3d). The difference in HREELS spectra between these two conditions will be discussed later in this paper. In Figure 3d, peaks at 291, 409, 520, 696, 824, 932, 1080, 1198, 1244, 1505, 1600, and 3050 cm<sup>−1</sup> can be identified. Compared to physisorbed features, several spectroscopic changes can be identified. All the lattice combination modes (indicated by solid vertical lines in Figure 3a) resulting from *p*-benzoquinone crystallization disappear in the chemisorbed state. The disappearance of the C=O stretching peak indicates the participation of both the carbonyl groups in surface reactions. However, the change in C–H stretching (3050 cm<sup>−1</sup>) is negligible, suggesting that the ethylenic C=C groups in the six-membered ring are not linked to the surface.

Considering its functionalities, the possible reaction modes of *p*-benzoquinone on Si(111)-7×7 (Figure 4) are C–H dis-



**Figure 4.** Schematic diagrams for the possible reaction modes of *p*-benzoquinone on Si(111)-7×7: (a) dissociation; (b) [2+2] C=C cycloaddition; (c) [2+2] C=O cycloaddition; (d) [4+2] cycloaddition; (e) [6+2] cycloaddition; (f) tetra-σ C=O cycloaddition; (g) tetra-σ C=C cycloaddition; (h) tetra-σ C=O/C=C cycloaddition.

sociation reaction (a), [2+2]-like cycloaddition through the C=C (b) or C=O (c), [4+2]-like cycloaddition (d), [6+2]-like cycloaddition (e), and tetra-σ binding through two C=O groups (f), two C=C bonds (g), or C=O/C=C (h). On the basis of the results mentioned above, reaction models a–d, g, and h can be readily ruled out, since in all these modes at least one C=O group is retained, which is inconsistent with our HREELS

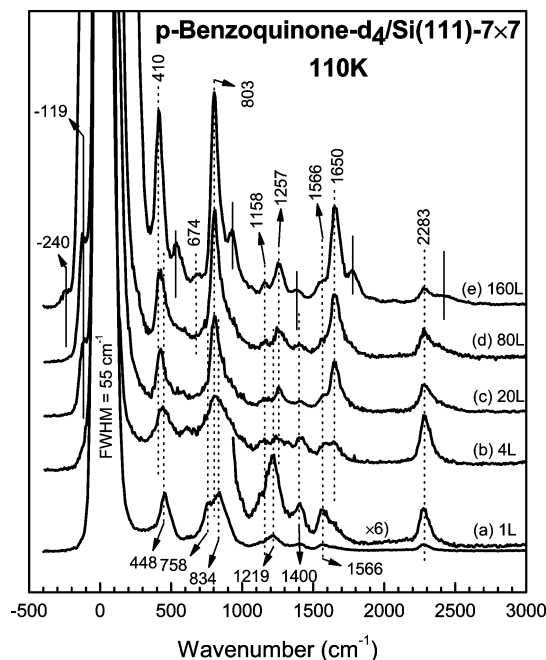
results. Detailed analysis of the HREELS results of chemisorbed *p*-benzoquinone indicates the existence of an aromatic ring, in agreement with the [6+2] cycloaddition mode (e). Two C=C stretching modes at 1600 and 1505  $\text{cm}^{-1}$  (Figure 3d) are consistent with HREELS results of benzene physisorbed on Si(111)-7 $\times$ 7 (1587 and 1483  $\text{cm}^{-1}$ <sup>27</sup>). On the other hand, the tetra- $\sigma$  binding mode through two terminal C=O groups (f) would result in the formation of a six-membered ring with two unconjugated C=C bonds, a 1,4-cyclohexadiene-like structure. Previous investigation of benzene chemisorption<sup>15</sup> and 1,4-cyclohexadiene physisorption<sup>28</sup> on Si(111)-7 $\times$ 7 reported that the 1,4-cyclohexadiene-like structure has unconjugated C=C stretching modes at 1635–1660  $\text{cm}^{-1}$ , which is significantly higher than the frequency observed for the conjugated C=C stretching modes in this study. This comparison further confirms the occurrence of the [6+2]-like cycloaddition. Other peaks characterizing the [6+2]-like cycloaddition binding modes are ( $\text{sp}^2$ ) C–H stretching at 3050  $\text{cm}^{-1}$ , and Si–O stretching at 824  $\text{cm}^{-1}$ , as listed in Table 1.

HREELS spectra of low-dose *p*-benzoquinone at 110 K (Figures 2a and 3b), especially that in the off-specular HREELS mode (Figure 3c), agree well with that of the chemisorbed monolayer (Figure 3d,e). The absence of C=O stretching (1659  $\text{cm}^{-1}$ ) and  $\text{sp}^3$  C–H stretching (2800–3000  $\text{cm}^{-1}$ ) and the appearance of aromatic ring stretching (1577, 1487, and 1381  $\text{cm}^{-1}$ ) and Si–O stretching (841  $\text{cm}^{-1}$ ) are all in good agreement with the formation of the Si–O–C<sub>6</sub>H<sub>4</sub>–O–Si structure, suggesting a high selectivity toward [6+2]-like cycloaddition.

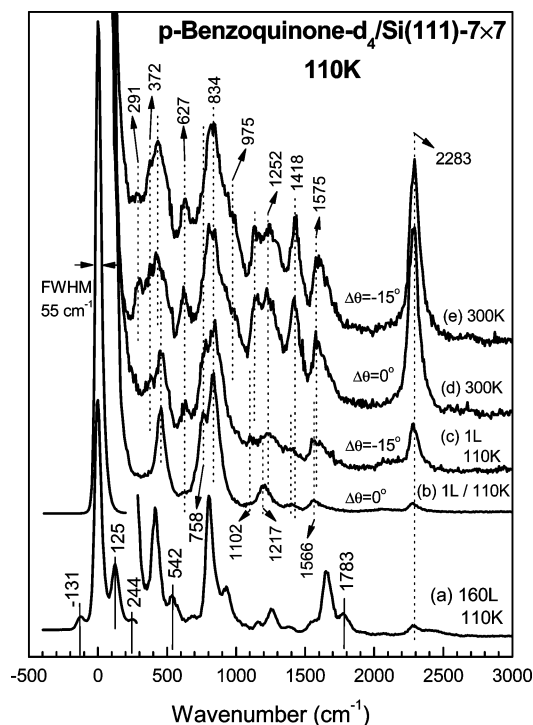
However, there are also some differences between the 110 K low-dose (Figure 3b,c) and the 300 K monolayer spectra (Figure 3d,e). First, the 110 K low-dose in-specular spectra (Figure 3b) show much lower intensities for the CH stretching (3050  $\text{cm}^{-1}$ ), ring stretching and CH in plane bending (1577, 1487  $\text{cm}^{-1}$ ), and C–O stretching (1198  $\text{cm}^{-1}$ ) than the Si–O stretching (841  $\text{cm}^{-1}$ ) and CH out-of-plane bending (747  $\text{cm}^{-1}$ ) modes. In the off-specular mode (Figure 3c), the relative intensity for former peaks increased significantly. This indicates that the [6+2]-like cycloadducts thus obtained have their aromatic rings parallel to the surface. On the other hand, the 300 K monolayer off-specular HREELS spectra (Figure 3e) are quite similar to the in-specular spectra (Figure 3d). This suggests that the annealed chemisorption species may not be flat, but probably tilted.

The second difference is that in the 300 K monolayer spectra (Figure 3d,e), two peaks at 932 and 291  $\text{cm}^{-1}$  cannot find their corresponding peaks in the 110 K low-dose spectra (Figure 3b,c). According to our DFT calculation (Table 1), the 932  $\text{cm}^{-1}$  is attributable to CH bending (including both in-plane and out-of-plane components), whose infrared activity is calculated to be quite small. The 291  $\text{cm}^{-1}$  peak is assigned to the silicon adatom vibration against the underlying layers, which may be intensified by the accumulation of the chemisorbed molecules.

Currently, there is no clear explanation for these differences. It is possible that at higher exposures, because of molecular crowding, the aromatic ring plane is not parallel to the surface, leading to the tilted orientation of the adspecies. Moreover, because of the structural heterogeneity of Si(111)-7 $\times$ 7, different active site pairs can participate in forming cycloadducts with the incident molecules, resulting in chemisorbed species with different structural strain and orientation. This further contributes to the difference between the 110 K low-dose (Figure 3b,c) and the 300 K annealed monolayer spectra (Figure 3d,e). However, the most important observation in our experiments is that in



**Figure 5.** HREELS spectra of *p*-benzoquinone-*d*<sub>4</sub> adsorbed on Si(111)-7 $\times$ 7 at 110 K as a function of exposure.



**Figure 6.** HREELS spectra of chemisorbed *p*-benzoquinone-*d*<sub>4</sub> on Si(111)-7 $\times$ 7: (a) 110 K, physisorption; (b) low exposure at 110 K; (c) same as (b), but HREELS in off-specular mode; (d) obtained by annealing the physisorbed sample (a) to 300 K and then cooling down to 110 K; (e) same as (d), but HREELS in off-specular mode.

either conditions, the majority of adsorbed species can be attributed to [6+2]-like cycloadducts.

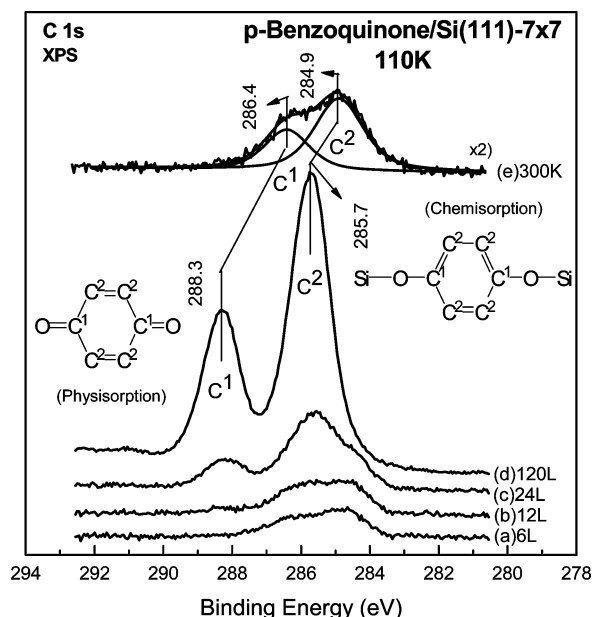
For further clarifying the binding structure of *p*-benzoquinone on Si(111)-7 $\times$ 7, *p*-benzoquinone-*d*<sub>4</sub> was also employed in our HREELS experiment. The spectra as a function of exposure at 110 K are displayed in Figure 5, and the chemisorption spectrum, obtained at low exposure at 110 K or upon heating the physisorbed sample to 300 K to drive away the multilayers,



**TABLE 2: Vibrational Modes Assignment for Physisorbed and Chemisorbed *p*-Benzoquinone-*d*<sub>4</sub> on Si(111)-7×7<sup>a</sup>**

| mode                  | IR <sup>24,25</sup> solid | physisorption <sup>b</sup> | mode                        | [6+2]-DFT <sup>b</sup> | chemisorption <sup>b</sup> |
|-----------------------|---------------------------|----------------------------|-----------------------------|------------------------|----------------------------|
| CD str                | 2277                      | 2283                       | CD str                      | 2289, 2271             | 2283                       |
| C=O str               | 1660                      | 1650                       | ring str                    | 1552                   | 1575                       |
| ring str              | 1560                      | 1566                       | ring str                    | 1373                   | 1418                       |
| CD ip bend            | 1160                      | 1158                       | ring str                    | 1266                   | 1252                       |
| ring str              | 1248                      | 1257                       | C–O sym str                 | 1179                   | 1134                       |
| CD ip bend + ring str | 793                       | 803                        | C–O asym str                | 1077                   |                            |
| ring ip def           | 873                       | n.r.                       | CD ip bend                  | 984                    | 975                        |
| CD wag + C=O wag      | 793                       | 803                        | Si–O–C str + CD ip bend     | 847, 840               | 834                        |
| C–C str               | 635                       | 674                        | Si–O str.                   | 812                    | 834                        |
| C=O wag + CD wag      | 418                       | 410                        | ring oop bend + Si–O–C bend | 762, 755               | 758                        |
| C=O ip bend           | 402                       | 410                        | Si–O–C bend                 | 640                    | 627                        |
| ring tors             | 106                       | 124                        | CD oop bend                 | 454                    | 448                        |
| lattice mode          |                           | 124                        | Si–O–C bend + ring bend     | 390                    | 372                        |
|                       |                           |                            | adatom vib                  | 313, 294               | 291                        |

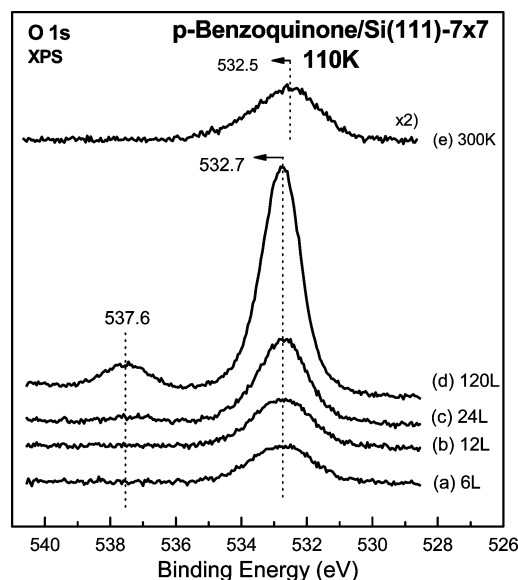
<sup>a</sup> All frequencies are in cm<sup>−1</sup>. <sup>b</sup> This work; assignments from DFT calculations are based on Mode V, Figure 9.



**Figure 7.** C 1s XPS spectra for *p*-benzoquinone adsorbed on Si(111)-7×7: (a–d) at 110 K as a function of exposure; (e) obtained by annealing sample (d) to 300 K.

is presented in Figure 6. Vibrational assignments for physisorbed and chemisorbed *p*-benzoquinone-*d*<sub>4</sub>, along with DFT calculated vibrations for [6+2]-like cycloadduct are listed in Table 2. For the chemisorption spectrum (Figure 6d), the absence of (sp<sup>3</sup>) C–D and C=O stretching (1650 cm<sup>−1</sup>, Figure 6a) and the appearance of aromatic ring stretching (1575 and 1418 cm<sup>−1</sup>) and Si–O stretching (834 cm<sup>−1</sup>) are similar to the HREELS results of chemisorbed *p*-benzoquinone mentioned above, confirming the predominance of [6+2]-like cycloaddition (Figure 4e). The similarity and difference between the 110 K low-dose and 300 K annealed monolayer spectra (Figure 6) can also be found for the *p*-benzoquinone-*d*<sub>4</sub>, suggesting different molecular orientations and binding sites.

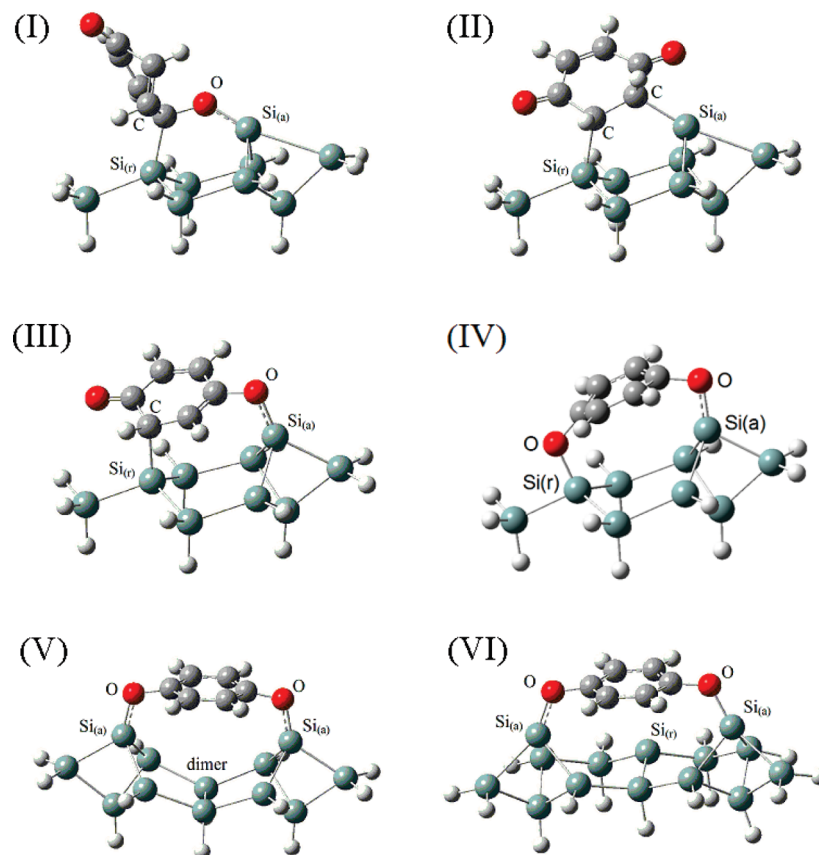
**3.2. X-ray Photoelectron Spectroscopy.** The C(1s) and O(1s) spectra of *p*-benzoquinone following a sequence of exposure at 110 K are shown in Figures 7 and 8, respectively. At low exposures of <12 L (Figure 7a,b), The C(1s) spectra display a main peak at 284.9 eV, with a shoulder at the higher binding energy side. With increasing the exposure from 12 to 120 L (Figure 7c,d), two new peaks at 285.7 and 288.3 eV appear and grow in intensity without saturation, suggesting their physisorption nature. The C<sup>1</sup>(1s) at 288.3 eV can be assigned



**Figure 8.** O 1s XPS spectra for *p*-benzoquinone adsorbed on Si(111)-7×7: (a–d) at 110 K as a function of exposure; (e) obtained by annealing sample (d) to 300 K.

to two carbonyl C atoms, similar to the value (287.7–289.3 eV) obtained for molecules containing intact carbonyl groups on Si(111) surfaces.<sup>12,17</sup> The C<sup>2</sup>(1s) at 285.7 eV is associated with the four ethylenic C atoms. For chemisorbed *p*-benzoquinone (Figure 7e), the C 1s spectrum can be deconvoluted into two peaks at 284.9 and 286.4 eV, with an area ratio of ~2:1. Compared to the physisorbed molecules, the C<sup>1</sup>(1s) core level experiences an obvious down-shift of 1.9 eV, which indicates the disruption of the C=O groups in molecular binding with silicon surfaces. Besides, the C<sup>2</sup>(1s) core level displays a down-shift of 0.8 eV upon chemisorption, possibly suggesting an increase of electron density on the ethylenic C<sup>2</sup> atoms due to the formation of the Si–O–C<sup>1</sup>-linkages.

For O(1s) (Figure 8), the main peak at 532.7 eV does not change much with increasing exposures. At high exposures, a shakeup peak appears at 537.6 eV (Figure 8d, 120 L), which is indicative of the physisorbed multilayers.<sup>29</sup> For chemisorbed molecules (Figure 8e), the O(1s) BE at 532.5 eV is similar to the values (532.4 eV) of Si–O–C linkage reported previously.<sup>11,31,32</sup> Thus, our XPS results support that the two O atoms are directly attached to the surface, while the four ethylenic C atoms are not, in agreement with the [6+2]-like cycloaddition model proposed above.



**Figure 9.** Adsorption structures of *p*-benzoquinone on Si(111)-7×7 optimized with B3LYP/6-31G(d,p): (I) [2+2]-like C=O cycloaddition; (II) [2+2]-like C=C cycloaddition; (III) [4+2]-like cycloaddition; (IV–VI) [6+2]-like cycloaddition. For structures I–IV, the surface clusters are Si<sub>9</sub>H<sub>12</sub> containing one adatom and its adjacent rest atom. For structure V, the surface cluster is Si<sub>12</sub>H<sub>12</sub> containing two adatoms in neighboring half-unit cells. For structure VI, it is Si<sub>14</sub>H<sub>15</sub> containing two adatoms and one rest atom within a half-unit cell.

**TABLE 3: Summary of 1s Core Level Binding Energies for *p*-Benzoquinone Physisorption and Chemisorption on Si(111)-7×7<sup>d</sup>**

|                                     | O     | C <sup>1 a</sup> | C <sup>2 a</sup> | $\Delta O_{\text{shakeup}}/I^b$ | O–C <sup>1</sup> | C <sup>1</sup> –C <sup>2</sup> |
|-------------------------------------|-------|------------------|------------------|---------------------------------|------------------|--------------------------------|
| <i>p</i> -benzoquinone <sup>c</sup> | 537.5 | 293.0            | 290.3            | 4.9/11%                         | 244.5            | 2.7                            |
| physisorbed                         | 532.7 | 288.3            | 285.7            | 4.8/10.3%                       | 244.4            | 2.6                            |
| hydroquinone <sup>c</sup>           | 538.9 | 291.9            | 290.3            |                                 | 247.0            | 1.6                            |
| chemisorbed                         | 532.5 | 286.3            | 284.7            |                                 | 246.2            | 1.6                            |

<sup>a</sup> C<sup>1</sup> refers to the C attached to oxygen; C<sup>2</sup> refers to the C attached to H. <sup>b</sup> Reference 29; “ $\Delta O_{\text{shakeup}}$ ” is the binding energy difference between the O shakeup and the main peak. “*I*” is the shakeup intensity normalized to the main O 1s peak; <sup>c</sup>. Reference 30. <sup>d</sup> The referenced values of pure *p*-benzoquinone and hydroquinone are included for comparison.

Table 3 lists the major components of C(1s) and O(1s) for both the physisorbed and chemisorbed molecules, along with the literature values for *p*-benzoquinone and hydroquinone.<sup>29,30</sup> Regarding both the binding energy differences and relative intensities between one O(1s) and two C(1s) components, our physisorption values agree well with the literature values. The O(1s) shakeup peak observed at 537.6 eV (Figure 8d) is ascribed to the provocation of  $\pi_4 \rightarrow \pi_5^*$  transition accompanying the photoelectron event.<sup>29</sup> For the chemisorption species, the differences between one O(1s) and two C(1s) components are similar to those of hydroquinone,<sup>30</sup> which suggests that chemisorbed molecules have a hydroquinone-like structure, i.e. [6+2]-like cycloadduct as depicted in Figure 4e.

**3.3. Density Functional Theory (DFT) Calculations.** Due to the “sparse” distribution of dangling bonds on Si(111)-7×7

(Figure 1), all the tetra- $\sigma$  binding modes (sketched in Figure 4f,g) with the formation of four Si–C/Si–O bonds are unconvivable. Therefore, only the di- $\sigma$  (Figure 4b–f) modes have been optimized. For [2+2]- and [4+2]-like cycloadditions, the molecular size is always smaller than 4.57 Å, the length of an adatom–rest atom pair.<sup>22</sup> In these reactions, only an adatom and its adjacent rest atom are concurrently and covalently bonded to a molecular entity. In our calculation, a Si<sub>9</sub>H<sub>12</sub> cluster containing an adatom–rest atom pair is used to optimize the possible [2+2]-, [4+2]-, and [6+2]-like cycloadducts of *p*-benzoquinone, as shown in Figure 9, models I–IV. This cluster has been successfully employed to predict the most stable chemisorption configurations for a number of chemisorbed molecules.<sup>8,33–35</sup> For [6+2]-like cycloaddition, because the separation between the two terminal oxygen atoms (5.34 Å) is slightly larger than that between an adatom and its adjacent rest atom (4.57 Å), larger clusters containing two adatoms, either across a dimer (6.65 Å, Figure 1, also in model V, Figure 9) or within a half-unit cell (7.68 Å, Figure 1, also in model VI, Figure 9) were also employed.

Calculations were performed with Gaussian 03 package,<sup>36</sup> at the B3LYP/6-31G(d,p) level. Adsorption energy was obtained by subtracting the energy of the adsorbate/substrate complex from the total sum of the energies of the substrate and *p*-benzoquinone molecule. Figure 9 presents the six optimized structures. Their adsorption energies are given in Table 4. It was found that [6+2]-like cycloaddition across a dimer (mode V) is the most exothermic. In addition, vibrational calculations for all models were performed with a scaling factor of 0.9608.<sup>37</sup>

**TABLE 4: Adsorption Energies of p-Benzoquinone on Si(111)-7×7 for Different Reaction Modes from B3LYP/6-31G(d,p)**

| binding mode                   | I         | II        | III   | VI                     | V                          | VI                         |
|--------------------------------|-----------|-----------|-------|------------------------|----------------------------|----------------------------|
| reaction mode                  | [2+2]-C=O | [2+2]-C=C | [4+2] | [6+2]-adatom—rest atom | [6+2]-inter half-unit cell | [6+2]-intra half-unit cell |
| adsorption energy <sup>a</sup> | −39.5     | 27.5      | 69.6  | 84.0                   | 105.6                      | 91.2                       |

<sup>a</sup> Adsorption energy:  $\Delta E = [E(\text{surface cluster}) + E(p\text{-benzoquinone}) - E(\text{adsorption complex})]$ . All energies are in kcal·mol<sup>−1</sup>.

The calculated vibrational energies of [6+2]-like cycloaddition models (models IV, V, and VI, assignments listed in Tables 1 and 2) are consistent with the HREELS results obtained for chemisorbed molecules, especially the 110 K low-dose spectra (Figures 3b,c and 6b,c).

**3.4. p-Benzoquinone on Si(111)-7×7: Reaction Mechanism of the [6+2]-like Cycloaddition.** The combined experimental and theoretical results demonstrated a [6+2]-like cycloaddition of p-benzoquinone on Si(111)-7×7. The reactivity can be rationalized considering both the molecular conjugation structure and surface dangling bonds arrangement. For the three [6+2]-like cycloadducts (modes IV–VI, Figure 9), the generation of an aromatic ring (with a resonance energy of ~36 kcal/mol) stabilizes the products significantly. In addition, for all the optimized structures, mode V experiences the smallest geometric strain, as concluded upon examining the changes in molecular and substrate structures. DFT calculation also confirmed that mode V is the most thermodynamically favorable. In fact, the parallel molecular plane at low exposures at 110 K (Figures 3b,c and 6b,c) suggests that mode V is the predominant species. However, for the chemisorbed monolayer obtained by annealing the physisorbed multilayer at 300 K (Figures 3d,e and 6d, e), mode V may not be predominant, as the cycloadducts lack significant preferential orientation. It is suggested that mode III, where the [6+2]-like cycloadducts formed across an adatom—rest atom pair, is more abundant on the surface. This suggest to us that reaction kinetics play important roles in governing the surface reactions.

Detailed analysis on the [6+2]-like cycloaddition mechanism based on theoretical calculation is out of the scope of this paper. To facilitate the understanding, it is useful to mention some theoretical works in the field of silicon surface chemistry. One of the most important differences between the organic cycloaddition and its surface analogue is that in surface cycloaddition, the  $(4n + 2)\pi$  electron rule<sup>38</sup> is not a necessary requirement. The reason has been extensively discussed in the [2+2]-like cycloaddition of ethylene on Si(100)-2×1 dimers.<sup>39–41</sup> In organic chemistry, thermal [2+2] cycloaddition is either symmetry-forbidden in the suprafacial–suprafacial pathway, or sterically hindered in the antarafacial–suprafacial pathway. On the other hand, on Si(100)-2×1, due to the buckling of the Si(100) dimer and concomitant charge transfer from the buckled-down atom to the buckled-up atom,<sup>42,43</sup> ethylene can first donate its  $\pi$  electrons to the buckled-down atom, forming a  $\pi$ -complex intermediate. Through this low symmetry precursor state, the [2+2]-like cycloaddition is allowed to proceed, which circumvents both the orbital-symmetry prohibition and the steric hindrance problems.<sup>39–41</sup>

The [6+2]-like cycloaddition, as has been discussed in this work, also violates the  $(4n + 2)\pi$  electron rule in organic chemistry. However, on Si(111)-7×7, there is no direct  $\sigma$  bonding between any two dangling bonds. The “diradicals”<sup>27,44</sup> used to simulate the surface have very different chemical reactivity from alkenes. In fact, the stepwise, diradical reaction mechanism has been proposed for [2+2]- and [4+2]-like cycloadditions for a large array of organic molecules based on DFT cluster model calculations.<sup>44</sup> Probably, [6+2]-like cycloaddition

reaction on Si(111)-7×7 can also proceed in the stepwise, diradical reaction pathway, and the  $(4n + 2)\pi$  electron rule is not required.

Furthermore, the selective attachment of oxygen to the surface is possibly attributable to a barrierless pathway passing through a dative-bonded precursor, as proposed in the concept of “heteroatom cycloaddition” on Si(100)-2×1.<sup>16</sup> The oxygen atoms with lone-pair electrons may act as donors to provide electrons to form an O→Si dative-bonded precursor with electron-deficient Si dangling bonds on adatoms, lowering the energy barrier of the surface reaction.

#### 4. Conclusions

p-Benzoquinone was found to undergo a new surface reaction, namely, [6+2]-like cycloaddition, on Si(111)-7×7, as identified using HREELS, XPS, and DFT calculations. The resulting Si–O–C<sub>6</sub>H<sub>4</sub>–O–Si intermediates can serve as precursors (or templates) for further construction of bilayer organic films on the semiconductor surfaces.

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**Supporting Information Available:** Figure S1 showing the HREELS spectra by exposing Si(111)-7×7 to 160 L of p-benzoquinone at different temperatures, and Table S1 giving the vibrational modes assignment for p-benzoquinone chemisorbed on Si(111)-7×7 at room and higher temperatures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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