STM study of charge transfer and the role of rest-atoms in the binding of benzene to Si(111)7 × 7

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Abstract
Chemisorbed benzene was studied by room temperature STM at low coverage on Si(111)7 × 7. Images taken of both filled and unfilled states show effects on adatoms near the benzene molecules. Filled states imaging shows a significant amount of what we believe to be charge transfer throughout the involved half unit cell. For a benzene molecule bound to a middle adatom there is also significant charge transferred from the adjacent middle adatom of the neighbouring half unit cell. Symmetry considerations allow for the conclusion that benzene binds in a di-σ bridge configuration between an atom and rest-atom. Evidence has been obtained that charge transfers away from the involved rest-atom to adjacent adatoms. Empty states imaging of the π* state also provides evidence for the involvement of a rest-atom in the binding.
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1. Introduction
Future nanotechnologies are likely to require that atoms and molecules be located on surfaces with higher and higher precision in order to give the desired functionality. While getting the atoms and molecules to go where they are needed is a challenging task, so too is the task of precisely characterizing the system after (and perhaps during) the construction. Adsorption of molecules to Si(111)7 × 7 serves as good system for basic studies of nano-scaled characterization. In particular, STM-based techniques should be developed that easily and routinely image rest-atoms so that their role in chemical binding can be clearly ascertained.

Though benzene/Si(111)7 × 7 has been well studied both experimentally and theoretically, there still exists some doubt about the precise nature of the bonding in the chemisorbed state. When benzene reaches the surface of Si(111)7 × 7 from the gas phase it first enters a mobile precursor state and has a preference for residing over middle adatoms as compared to corner adatoms [1]. At room temperature, the molecule stays in this state for a time (too short to be observed with STM) before either desorbing or chemisorbing. The chemisorbed form of benzene has a preference for middle atoms over corner adatoms [2,3].

Early EELS and TPD studies pointed towards a π-bonded state for chemisorbed benzene with the benzene sitting directly above a silicon adatom with the ring approximately parallel to the surface [4]. Neighbouring rest-atoms are not involved in this configuration. The first STM studies of this system were consistent with this bonding picture [1,2]. Subsequent PES, EELS and TPD studies, however, resulted in the adoption of a considerably distinct di-σ bonding model that involves a 1,4 bridging between an adatom and a nearby rest-atom [5]. In this model, the molecule takes on a 1,4-cyclohexadiene-like bridge structure. Though the rest-atoms play an important role in this model, these studies provide no direct evidence for their involvement; rather the role of rest-atoms is deduced from geometric considerations i.e. no other bridging...
configuration seems plausible. This is likely the most important reason for why doubt still persists over which model is correct, the π-bonded state or the di-σ bonding state. Calculations seem to confirm that the di-σ state has the lowest energy [6,7]. The predicted binding energy from density functional calculations [6] is close to the value of 0.95 eV inferred from STM experiments [2]. Calculations at the B3LYP level also suggest that the on-top π-bonded state corresponds to the more weakly bound physisorbed form of benzene [7]. In the di-σ bonding configuration of benzene the aromaticity is lost, and it binds into a 1,4-cyclohexadiene-like butterfly structure. The loss of the aromatic ring structure helps explain why the benzene–silicon bond is relatively weak. When the Si(111)7 × 7 surface at room temperature is at or near saturation coverage, benzene desorbs quickly and numerous desorption events are observed over a timescale of a few minutes. At low coverage, intermolecular interactions diminish, and the desorption rate slows [2,3].

Though rest-atoms are now widely believed to play an important role in the binding, their role has yet to be clearly demonstrated. Indirect evidence comes from STM studies of unit cell crowding effects at high coverage [3]. STM can also be the ideal tool for direct demonstration. In this paper, we provide direct evidence that the rest-atoms are indeed involved in the chemisorption. This evidence comes from looking at shifts in apparent heights (also referred to as intensities) in regions around an adsorbate as compared to similar regions free of adsorbate. We also show that there are pronounced effects on nearby adatoms, most likely caused by charge transfer (CT). This CT seems necessary given the initial filled charge state of the rest-atoms. Comparisons to STM results on a similar system, i.e. chlorobenzene/Si(111)7 × 7 are made [8].

2. Experimental

This work was performed using a homemade STM in an ultra high vacuum (UHV) chamber with base pressure better than 4 × 10^{-11} Torr. During STM operation the chamber is continually pumped using a 300 L/s Varian StarCell ion pump as well as titanium sublimation. The STM operates at room temperature and has capabilities for both sample and tip transfer.

The silicon samples were cut from a (111)-oriented wafer (n-type antimony doped, 0.03 Ω cm, 0.35 mm thick) that was purchased from Montco Silicon Technologies Inc. To remove carbon contaminants, the sample pieces were cleaned using a simplified RCA process [9] as follows: The samples were immersed in a 1:1:4 solution of hydrogen peroxide, ammonium hydroxide, and purified water, respectively. Chemicals used were either reagent or electronic grade. The beaker holding the samples and solution was held in a 75 °C water bath for a period of 10 min. Following this treatment, the solution was diluted with purified water, after which samples were loaded into a sample holder and transferred, via a load-lock, to the vacuum chamber. The sample holder was designed so that when fixed into the sample holder the silicon sample makes direct contact only to pieces machined from tantalum [10].

Inside the chamber the samples were heated resistively and degassed ~12 h at 640 °C before flashing at high temperatures. Sample temperatures were measured using an optical pyrometer positioned outside the vacuum chamber. The samples were flashed at 1235 °C for 10 s, while ensuring that the chamber pressure stayed lower than 2 × 10^{-10} Torr, followed by a quick cool-down. Shortly after, they were again heated to 920 °C and then slowly cooled down at the rate of 0.5 °C/s, before transfer to the STM. The cleanliness and quality of the reconstruction and terrace structure of the surface produced by this procedure is sufficient for conducting basic studies of adsorbates with STM.

Tips were made from 0.375 mm diameter polycrystalline tungsten wire, prepared by electrochemical etching in 2.5 M, NaOH solution. The drop-off technique was used. Before using the tips for scanning, the tips were cleaned under UHV conditions by electron bombardment from a nearby tantalum filament. A schematic of this circuit used for this procedure is shown in Fig. 1. The distance between tip and filament was typically 0.5–1.0 mm. The filament was heated resistively until white hot, while the tip was held at +450 V. The bombardment current was 5 mA with one treatment lasting for 5–10 s. These treatments were typically repeated 4–6 times to remove the tungsten oxide surface layer from the tip. After each electron bombardment treatment the cleanliness and sharpness of the tip was characterized by monitoring the stability and magnitude of the field emission current from the tip. Field emission was performed using the same apparatus with the bias polarity reversed and the filament grounded and at room temperature. Tips suitable for STM studies typically field emit 1 nA of current at ~300–500 V bias.

Benzene with purity of 99.5% was used for dosing the sample, after it was repeatedly degassed by three or more freeze–pump–thaw cycles. The clean silicon sample was exposed to benzene using a variable leak valve and back-filling of the chamber typically to ~2 × 10^{-5} Torr for 80 s. The pressure was measured with a nude ion gauge and was not corrected for benzene. In the work presented here all doses resulted in very low coverage surfaces so that inter-adsorbate interactions were minimal.

Fig. 1. Schematic of electron-beam apparatus used to clean tips. This apparatus is located inside the vacuum chamber separate from the STM head used for imaging. A wobble-stick mechanism is used to transfer tips between this apparatus and the STM head.
Images taken shortly after very low doses of benzene show very few desorption events during a typical scan and studies can usually be carried out for several hours. In previous STM reports the tell-tale signature of chemisorbed benzene is a feature that resembles a missing adatom i.e. saturation of an adatom dangling bond. Fig. 2a shows an STM image taken at +2.0 V sample bias and after exposure to a low dose of benzene. Examples are indicated for saturated adatoms of all four varieties, i.e. faulted middle (FM), faulted corner (FC), unfaulted middle (UM), and unfaulted corner (UC). For example, a benzene molecule bound to a corner adatom in the faulted half of the unit cell is labeled FC-Bz. Distinct examples are labeled with Greek letters starting with $\alpha$. At this bias there is no easily discernable effect on nearby adatoms. Rest-atoms are not visible, making it difficult to say what role they play in the binding. Fig. 2b shows the area around a FM-Bz feature at +1.6 V bias. We observe several subtle effects of adsorption on this neighbouring area. The most significant effect on neighbours, indicated with a solid arrow, is that a nearest-neighbour middle adatom is brightened considerably. Though not obvious in Fig. 2b the nearest-neighbour corner adatom, adjacent to the brightened middle adatom (dashed arrow), is sometimes brighter as well (in unoccupied states imaging), though the degree of brightening is small.

We also note from Fig. 2b that the saturated adatom feature itself is no longer symmetric. Instead the feature has more intensity in the area closer to the brightened adatoms. We refer to this as a “grey” feature and denote the center of it with a cross. This asymmetry is the first piece of direct evidence that the chemisorption is not a $\pi$-bonded feature involving only an adatom, but rather the di-$\sigma$ bridge structure. The two possible di-$\sigma$ configurations are shown schematically in Fig. 2c and d. The first option (c) is more sensible since the grey feature imaged at the site of the saturated middle adatom is most likely caused not by the silicon rest-atom but rather by the two C=C double bonds left over after chemisorption. On the Si(100)2 × 1 surface these double bonds are believed to be responsible for the brightness of a particular form of chemisorbed benzene (also in a butterfly configuration) at bias values near +2.0 V [11]. The LUMO of this structure is located around +2.5 eV so the tunneling is of a near-resonant nature [12]. This enhancement of the tunnel current seems to be not significant enough to make the C=C bonds brighter than unreacted adatoms on Si(111)7 × 7. On Si(111)7 × 7 the adatom bands have substantial DOS at the Fermi level, unlike the case for clean Si(100)2 × 1 silicon dimer surface bands which have an energy gap. It is therefore not surprising that the C=C double bonds of the di-$\sigma$ structure appear to be brighter than clean Si dimers on Si(100)2 × 1 but dimmer than clean adatoms on Si(111)7 × 7.

Fig. 2. (a) Empty states STM images at (+2.0 V, (b) +1.6 V, (c) +1.3 V of benzene/Si(111)7 × 7. Image (b) shows in high detail a benzene molecule bound to a faulted middle (FM) adatom while (e) shows the UM case. Schematic diagrams for the di-$\sigma$ bonding between a middle adatom and the two nearest-neighbour rest-atoms are shown in (c) and (d). These schematic diagrams have the same half unit cell orientation as the image shown in (b).
The situation is much the same for the UM case of benzene bound to a middle adatom of an unfaulted half unit cell and imaged at $+1.3 \text{ V}$. Fig. 2e shows that for this UM case the grey feature associated with the $\pi^*$ state is even more prominent than for the FM case. For the case of chlorobenzene, Sloan and Palmer have reported very similar results i.e. an asymmetric grey feature located closer to brightened adatom neighbours [8]. The brightness of the chlorobenzene grey feature increases with higher bias becoming almost as bright as adatoms at $+3.0 \text{ V}$. This is consistent with resonant and near-resonant electron tunneling through the $\pi^*$ state of the molecule.

More information about the role that rest-atoms play in benzene chemisorption is gained from measurements made of occupied states. Fig. 3a shows a portion of the same area of the surface shown in Fig. 2a, imaged about 10 min later and at $-0.7 \text{ V}$ bias. In Fig. 2a, the arrow labeled UM-Bz points to a benzene molecule chemisorbed to a middle adatom of an unfaulted half unit cell. That same adatom is also dark at $-0.7 \text{ V}$. Further inspection of Fig. 3a reveals that nearby adatoms are also very much affected, more so than is indicated in Fig. 2a. Some of these local effects are large and significant while others are more subtle. Also the binding configuration of the benzene molecule has less symmetry than the empty states image suggests. In order to better emphasize the effect on neighbouring adatoms, the same feature is presented, in enlarged format, in Fig. 3b. Also, to aid in a detailed discussion of this feature, neighbouring adatoms have been labeled 1–9 starting with the binding site itself. A dashed line is displayed as well. This line would represent a $\sigma^*$ mirror plane if the benzene were not present. Large effects caused by the adsorption are (i) adatoms 5 and 6 are considerably brighter than adatoms 3 and 2, respectively and (ii) one is also struck by the considerable dimming of adatom 8 in the faulted half unit cell. More subtle effects observed include: (i) adatom 7 is slightly brighter than adatom 9 and (ii) adatom 4 is slightly dimmer than normal UC adatoms.

Since adatom 5, for example, is equivalent on the clean surface to adatom 3, we conclude that the benzene breaks the mirror symmetry. As in the case of the empty states image, at least for the case of middle adatoms, this observation rules out the possibility of a $\pi$-bonded structure in which the benzene sits directly above an adatom. The lack of symmetry is very much consistent with the di-$\sigma$ structure which involves a neighbouring rest-atom. When the benzene molecule binds to site 1, it has two equivalent rest-atoms to bind with. After binding with one of them, the $\sigma^*$ symmetry is lost.

One possible explanation for the shifts in apparent heights of the nearby adatoms is that they are in fact vertical shifts of the actual atomic positions. Density functional calculations show however that on the clean Si(111) $7 \times 7$ surface the adatoms on the faulted half of the unit cell are on average only about 4 pm higher than the unfaulted adatoms [13]. Electronic structure effects are usually the more prominent in STM images. In empty states images both halves of the unit cell appear to have the same height i.e. there is near cancellation of atomic structure and electronic structure differences. In filled states images though, at $-0.7 \text{ V}$ bias, we measure 37 pm on average for the contrast between half unit cells. Roughly 90% of this contrast is attributed to electronic structure. Contrast between adatoms, caused by density of states effects, is more pronounced in filled states than for empty states. The situation with adatoms near chemisorbed benzene is similar. We therefore conclude that the real shifts in adatom heights are relatively small and that the strong contrast observed between neighbouring adatoms at $-0.7 \text{ V}$ is mainly due to electronic structure.

It has been understood since about 1985 that CT plays a key role in determining the electronic structure of the clean unit cell [14]. Since then further theoretical work has supported this understanding [13] and CT effects have been directly verified using STM on a variety of clean semiconductor surfaces including Si(100), GaAs(110), Ge(111) as well as Si(111) [15]. Adatoms transfer charge to rest-atoms so that rest-atom dangling bonds are filled with two electrons and are located $-0.8 \text{ eV}$ below the Fermi level. Middle adatoms lose more charge than corner adatoms and overall, the unfaulted half unit cell transfers charge to the faulted half unit cell. Theoretical DFT studies predict that significant CT occurs around atomic adsorbates such as hydrogen [13,16]. It is reasonable to suppose that significant CT also occurs around chemisorbed benzene. In order to form a covalent Si–C bond the rest-atom must change from a charge state of two electrons to close to one. Some of this charge may end up located in the other Si–C bond at the adatom, since the unreacted adatoms have less than one electron of charge. However, this still leaves some electron charge that must transfer to neighbouring adatoms. One is led to the logical conclusion that the brightening of adatoms 5 and 6 in Fig. 3b is due to CT from the adjacent rest-atom. This provides further support for the di-$\sigma$ bridging model. The benzene bridges between anadatom 1 and the rest-atom located between adatoms 1, 5 and 6.

Though this model explains several of the observed features, new questions are raised. Two such questions have to do with why adatoms 2, 3 and 4 become dimmer, and why adatom 8 almost disappears at $-0.7 \text{ V}$. The answers may have to do with why the other adatom 1 and its depleted charge state before bonding. From density functional calculations an unfaulted middle adatom has a charge of about 0.6 in units of electron charge [13]. Since the covalent bond formed at adatom 1 prefers to have a full two electrons in it some charge must be transferred from elsewhere. Why this charge does not come directly from the adjacent rest-atom is not known. It appears that while the rest-atom charge goes to adatoms 5 and 6, electric charge moves towards the bond at adatom 1 and away from adatoms 2, 3, 4 and 8.

That adatom 8 is a major contributor to this CT process is perhaps not surprising. Quantum ground state calcula-
tions predict that at low temperature the conduction band for the ground state of the Si(111)7/C27 surface is dominated by “dimer” states which can be described as pairs of closely-linked middle atoms interacting across the dimer rows [17]. These dimer states are decoupled from the “corner ring” states which are localized on corner adatoms and make up the valence band. An important reason for why the ground state is predicted to have this structure has to do with the distances between adatoms. The closest adatom to a given middle adatom is the middle adatom across the dimer row from it in another half unit cell i.e. in Fig. 3b adatom 8 is geometrically the closest to adatom 1.

In discussing the first report of such a cross-half cell effect for the case of chlorobenzene/Si(111)7 × 7, Sloan and
Palmer considered the possibility that charge redistribution could be caused by the C–Cl dipole moment [8]. Both benzene and chlorobenzene chemisorption result in the darkening of an adjacent adatom from a neighbouring half unit cell. This indicates that the Cl atom is not the major factor in producing this darkening effect. Apart from benzene and chlorobenzene, to our knowledge, no other report of such a CT effect exists, so it remains to be seen how general this type of adsorbate-induced CT is.

The case of a benzene molecule chemisorbed to a middle adatom of a faulted half unit cell (FM-Bz) is shown in Fig. 3c. Note that the adatom numbering system used here is case-specific. For the most part the results are qualitatively similar to those of the UM case. Adatoms 5 and 6 brighten considerably while their counterparts 2 and 3 darken. After adatom 1, adatom 8 is affected the most, almost disappearing completely. The most notable distinction is that adatom 4 brightens slightly in this case, in contrast to a slight darkening for the UM-Bz case.

The case of chemisorption to a corner adatom is quite different. Here there is only one rest-atom available for binding. Since the rest-atom lies in the mirror plane the symmetry should be preserved. In the UC case, as shown in Fig. 3d, there is considerable darkening of the two nearest middle atoms, 2 and 6. Outside the half unit cell there is noticeable brightening of the middle adatoms 7 and 7’ adjacent to 2 and 6, respectively. After careful inspection one notes that adatom 7 appears to be slightly brighter than adatom 7’ i.e. the mirror symmetry appears to be broken. This apparent symmetry breaking is believed to be mainly an experimental artefact associated with the tip scanning motion and perhaps partly due to artefacts arising from tip asymmetry. In Fig. 3d, the tip scan motion (backscan) was from left to right across the image. Fig. 3e shows the image generated from data collected while the tip motion was from right to left i.e. the forward scan. In this case one can see that adatom 7’ now appears to be slightly brighter than adatom 7. Though mirror symmetry about the dashed line is completely consistent with the data shown in (d) and (e) we do acknowledge that experimental details associated with the tip symmetry and the scanning procedure do tend to produce noticeable effects in occupied states images i.e. more noticeable than in unoccupied states. Even though our measurements of the larger shifts in intensities are almost certainly real and not due to experimental artefacts, we realize that some of the more subtle shifts noted here may actually be artefacts. Currently the level of experimental artefact for our images of occupied states is estimated to be around 10–20 pm. To put this in perspective adatom 8 in Fig. 3e is imaged 140 pm lower than equivalent adatoms at clean areas i.e. this observed dimming is not an artefact. Future studies on this and similar systems may indeed discover interesting physics behind these subtle shifts if techniques can be found to eliminate or at least reduce these artefacts.

As expected, adatom 1 is considerably darkened after the saturation of its dangling bond. A dark grey feature, denoted by a cross, does persist in the image at −0.7 V. The most striking aspect of this grey feature is that it is not centered at the position of the adatom. Instead, it is located about 30% of the way between adatom 1 and the nearest corner hole. This suggests that the grey feature may actually be an image of one of the three backbonds of adatom 1 i.e. the one directed towards the corner hole. The backbond energy level lies at −1.7 eV and should not normally be visible at −0.7 V [18]. If however the bond is highly strained then the energy level should move towards the Fermi level considerably. The presence of strain is reasonable since the adatom is involved in accommodating the benzene chemisorption. Also, the energy level should be very broad as it is very well coupled to the bulk silicon. These considerations make it reasonable to suppose that the backbond would be visible in STM at −0.7 V. Another intriguing possibility is that this grey feature is actually a state arising directly from strong interaction between the molecule and the tip. Such a state has been both predicted theoretically and observed using STM at 5 K for the 1,3-cyclohexadiene/Si(100) system [19]. In this case Naydenov et al. found that when the tip is brought to within a distance of ~250 pm from the molecule that a new electronic state forms at 0.35 eV above the Fermi level. This state involves a rehybridization between tip states and a C=C double bond. While the grey feature seems to be too distant from where we would expect the C=C bonds to be and it is doubtful that the tip is so close to the benzene molecule under our tunneling conditions, this possible explanation for the observed grey feature cannot be ruled out. The same reasoning applies to the grey features indicated in Fig. 2b and e taken at positive bias.

The case of a benzene molecule bound to a corner adatom of a faulted half unit cell is shown in Fig. 3f. The binding site is darkened as expected but the nearest-neighbour middle adatoms 2 and 3 are brightened now. This is consistent with the model of CT from the adjacent rest-atom. The reason for the substantial darkening of cross-dimer adatoms 7 and 7’ is not known. A very similar result was found by Sloan and Palmer at −0.5 V for the chlorobenzene case [8]. We note that our observed adatom contrast is opposite to what was observed for the UC-Bz case.

We have studied all four possibilities, UM, FM, UC and FC, for benzene chemisorption sites. In all cases the effect on nearby adatom electronic structure is extensive. One clear implication is that one must be very careful when considering adsorbate–adsorbate interactions. It is often desirable to ignore such effects: increasing coverage will increase signal to noise for traditional techniques such as PES, TDS and EELS. However, in this case it is probably safe to ignore inter-adsorbate interactions only when there is less than about one molecule per unit cell of coverage. At higher coverage such interactions may become important. For example, the binding energy does get measurably smaller as the benzene molecules get more crowded [2,3]. Any future theoretical modeling of such interactions should incorporate CT effects. In particular such modeling, if
successful, should also be capable of predicting the observed CT around a single adsorbate, consistent with the measurements presented here.

The system studied here emphasizes the wisdom that any attempt to extract kinetic parameters such as binding energy, prefactors and iso-kinetic temperatures must carefully account for the adsorbate binding energy varying with coverage [20]. Indeed the studies listed in [20] provide discussion of the extraction of both binding energies and prefactors which depend on coverage, for several example systems with first-order desorption kinetics and on metal surfaces. This extraction typically utilizes a differential TDS method. Though TDS studies have been conducted on Si(111)7 × 7 (see [4,21] for some examples) we know of no such studies that employ a differential TDS approach to extract information on how the kinetic parameters depend on coverage. Presumably if such an extraction were to be made in future study then the long range CT observed here may help to explain any such dependences on coverage.

Semiconductor surfaces have a higher corrugation than metal surfaces, mainly because of the highly directional nature of the covalent bonding. For example, diffusion of adsorbates on semiconductor surfaces is very distinct (hindered) as compared to diffusion on metals: the ratio of the energy barrier to diffusion to the barrier to desorption is significantly higher in semiconductor systems [2]. The directional nature of the covalent bonding may also hinder CT as the charge flow is channeled. Further bottlenecks can be caused by narrow energy bands, especially in a rich system with several bands at various energies. This is indeed the case for Si(111)7 × 7 where an adatom band is located at −0.2 eV, with FWHM width of 0.2 eV, a rest-atom band located at −0.8 eV with width 0.35 eV and adatom backbond band at −1.7 eV with width of 0.7 eV, are all well separated in energy [18]. These energetic bottlenecks are not likely to arise in wideband metallic systems on coverage.

Thus we are led to speculate that long range inter-adsorbate interactions may in general be stronger and of longer range on the surfaces of semiconductors as compared to metals. Charge transfer for the case of benzene/Si(111)7 × 7 extends visibly out to a relatively large distance of ~1.4 nm. Presumably this length scale is also the scale for adsorbate–adsorbate interaction. Chlorine/Si(100)2 × 1 offers another example. Chlorine atoms adsorbed at room temperature to Si(100)2 × 1 dimers causes buckling of dimers on the same dimer row as far out as 4 dimers i.e. 1.5 nm to either side [22]. This effect on the buckling of nearby dimers is likely caused by CT induced by the high electronegativity of chlorine [23].

For the case of benzene chemisorption to a middle adatom we summarize what we have learned in the schematic diagram shown in Fig. 4. The bridging of the benzene molecule is illustrated along with arrows showing the adatoms with the most significant inferred direction of electronic CT. We note that the arrows merely indicate CT in a qualitative way. Further experimental and theoretical study is required for quantification of these interesting redistributions of electrical charge.

4. Conclusions

We have used filled states STM imaging of chemisorbed benzene/Si(111)7 × 7 at room temperature to show that there are significant effects throughout the involved half unit cell. Every adatom in the unfaulted half unit cell is noticeably affected by the presence of a chemisorbed benzene molecule. These effects are mainly attributed to changes in electronic structure caused by CT. For benzene bound to a middle adatom there is also significant charge transferred from the adjacent middle adatom of the neighbouring half unit cell. In fact, this adatom is the most affected, of all adatoms affected by the adsorption. This is the case whether the benzene is bound to either the faulted or the unfaulted half of the unit cell.

Symmetry considerations allow for the conclusion that benzene binds in a bridge configuration between an adatom and a rest-atom. Evidence has been obtained that charge transfers away from the involved rest-atom to adjacent adatoms.

Empty states imaging of what we believe are the π* states associated with C=C double bonds, also provides further evidence for the involvement of a rest-atom in the binding, since π symmetry is broken.

Similar results for the case of chlorobenzene [8] suggest that the chlorine atom attached to the benzene molecule has no qualitative effect in both occupied and unoccupied states STM imaging. It remains to be seen whether or not there are small differences in CT between benzene and chlorobenzene. As it stands, the only significant difference between the two systems is that imaging at bias values above +3.0 V will induce chlorine dissociation [24].

From the results presented here, combined with consideration of previous theoretical and experimental results, we are led to the conclusion that the bridge bonding of benzene to Si(111)7 × 7 is most likely the di-σ 1,4-cyclohexadiene-like butterfly configuration.
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