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The local adsorption structure of benzene on Si(001)-(2x1): a photoelectron diffraction investigation

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Abstract

Scanned-energy mode C 1s photoelectron diffraction has been used to investigate the local adsorption geometry of benzene on Si(001) at saturation coverage and room temperature. The results show two different local bonding geometries co-exist, namely the 'standard butterfly' (SB) and 'tilted bridge' (TB) forms, with a composition of $58 \pm 29\%$ of the SB species. Detailed structural parameter values are presented for both species including Si-C bondlengths. Based on published measurements of the rate of conversion of the SB to the TB form on this surface we estimate that the timescale of our experiment is sufficient to achieve equilibrium, and in this case our results indicate that the difference in the Gibbs free energy of adsorption, ($\Delta G(\text{TB}) - \Delta G(\text{SB})$), is in the range -0.023 to $+0.049$ eV. We suggest, however, that the relative concentration of the two species may also be influenced by a combination of steric effects influencing the kinetics, and a sensitivity of the adsorption energies of the adsorbed SB and TB forms to the nature of the surrounding benzene molecules.

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1. Introduction

Since the early 1990's there has been considerable interest in the interaction of unsaturated hydrocarbons with semiconductor surfaces, as they offer a potential route to the manufacture of optoelectronic and bioanalytical devices. One such model system is that of benzene on Si(001)-(2x1). The clean Si(001) surface undergoes a reconstruction such that adjacent atoms pair together to form rows of dimers as illustrated in figure 1. Strictly, these dimers are asymmetric, but flip rapidly between the two opposite local asymmetry states to produce only the average (2x1) periodicity shown in figure 1; most adsorbates on this surface appear to remove or strongly suppress this asymmetry.

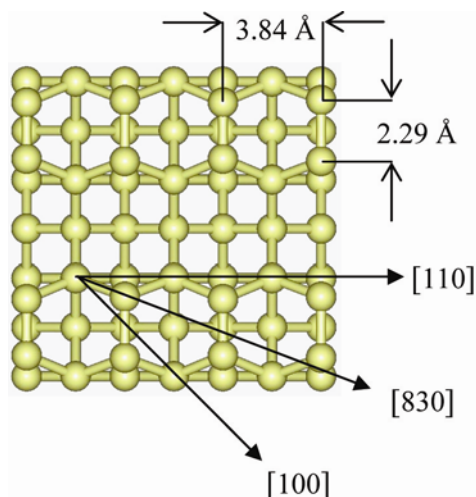


Figure 1. Clean Si(001) surface showing the arrangement of the dimers in the (2x1) reconstruction.

While there are no previous complete quantitative experimental determinations of the local chemisorption structure of benzene on Si(001), a number of different geometries have been proposed. These are illustrated in Figure 2. and can be categorised into two groups – those bonded to a single Si dimer and those bonded to two adjacent Si dimers (referred to in this paper as double-dimer configurations). In all cases the bonding between the C and Si atoms is believed to be of σ character such that the aromaticity of the benzene ring is removed. There are just two bonding configurations in the first category, referred to as the ‘standard butterfly’ (SB) and ‘tilted’ (T) species. In the SB form the interaction with the dimer is through the C_1 and C_4 atoms of the benzene ring. Two double bonds are retained and the molecule has C_{2v} symmetry. The T species is formed through the interaction of two adjacent C atoms in the benzene ring with the dimer and the plane of the molecule is tilted away from the surface. Four double-dimer species have been suggested. In the ‘pedestal’ (P) form the C_1 , C_2 , C_4 and C_5 atoms bond to adjacent Si dimers and the plane of the molecule is essentially flat and parallel to the surface. No double bonds remain, yet there is an unpaired electron at C_3 and C_6 , which may delocalise to some extent. The ‘tight bridge’ (TB) and ‘twisted bridge’ (TwB) species both involve bonding of the C_{1-4} atoms with Si dimers and they retain one C=C bond, the bond axis of which is parallel to the surface. They are azimuthally rotated through 90° with respect to one another and both species have C_s symmetry; the mirror plane is perpendicular to the dimers in the case of TB and parallel to them in the case of TwB. The final structure shown in Figure 2 is the

‘diagonal-bridge butterfly’ (DBB) species which is similar to the SB, in that only the C_1 and C_4 atoms of the benzene molecule are involved in the surface bonding, but the two Si atoms are in different dimers. Numerous studies have been carried out with a view to identifying the structure(s) of the chemisorbed benzene species and the main conclusions from these investigations are summarised below. There have also been a limited number of reports of structural parameters for benzene adsorbed in the different forms.

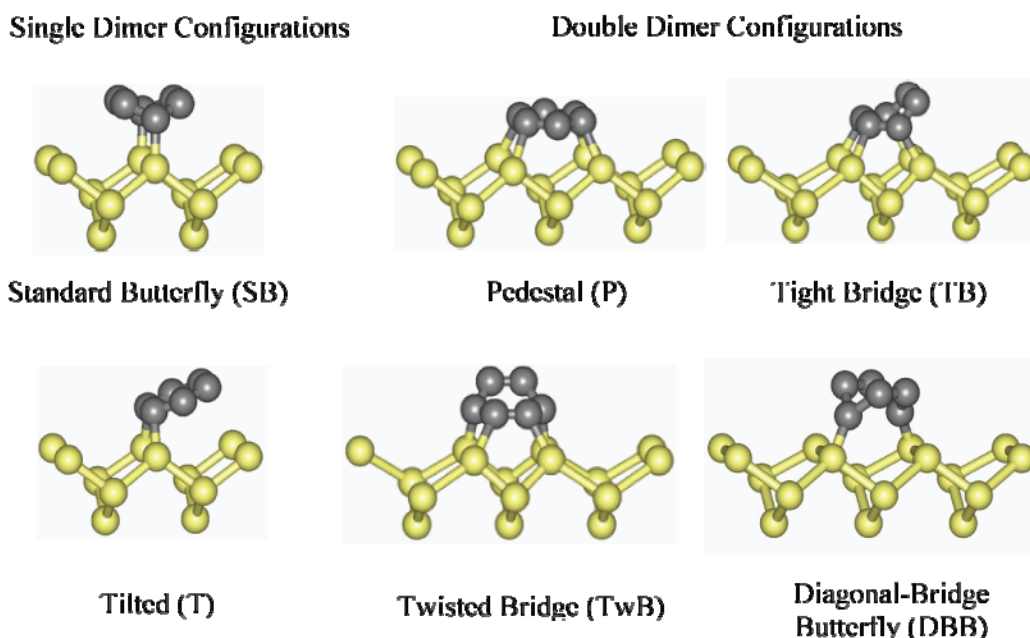


Figure 2. Structures of the possible configurations of benzene adsorbed on Si(001)-(2x1) considered in this paper.

The first surface science study of this system, by Taguchi et al. [1], was a combined temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS) and Auger electron spectroscopy (AES) investigation which concluded that benzene physisorbs at low temperature and chemisorbs at room temperature. TPD showed two desorption peaks, at ~ 460 and ~ 505 K, which were attributed to benzene adsorbed on terrace and defect sites, respectively. From AES the saturation coverage of benzene was estimated to be 0.27 benzene molecules per surface Si atom (or approximately 1 benzene molecule per 4 surface Si atoms). This means that at saturation coverage one benzene molecule is adsorbed per pair of Si dimers. At saturation coverage it was estimated that $\sim 17\%$ of the benzene was adsorbed on the defect sites. HREELS results were found to be consistent with species with C_{2v} symmetry, and it was concluded that benzene adopted the SB configuration on the terrace sites.

Gokhale et al. [2] also detected two chemisorbed forms of benzene in TPD spectra, and having found evidence of C_{2v} symmetry in angle-resolved UV photoelectron spectroscopy (ARUPS) measurements, arrived at the same conclusion as Taguchi et al., although they detected a higher fraction of the saturated monolayer in the higher temperature desorption peak ($\sim 33\%$). Li et al. [3] observed a third peak in their

thermal desorption spectroscopy and concluded that in addition to the two adsorption states mentioned above, a double-dimer adsorbed species must also exist, although they did not specify its structure.

Several groups have reported mixed layers of SB and TB. On the theoretical side, both Silvestrelli et al. [4] and Lee et al. [5] (using density functional theory (DFT) total energy slab calculations) found that the TB is the most stable of the double-dimer species, while the SB is the most stable single dimer species. They also claimed that benzene was most likely to adsorb on the surface in the SB form, but that this was a metastable state, which would convert to the more stable TB form with time. The activation barrier for this process was estimated to be of the order of 1 eV. Kruse et al. [6] found evidence in STM images of the presence of both SB and TB species adsorbed on the surface at both low and high coverage. Kong et al. [7], employing a combination of near-edge X-ray absorption fine structure (NEXAFS), Fourier transform infrared spectroscopy (FTIR) and TPD, also concluded that two forms of adsorbed benzene were present in the saturated overlayer. One of these was the SB species, but they were unable to unambiguously assign the other species to either the TB or TwB form.

There have been a number of scanning tunnelling microscopy (STM) investigations that have been interpreted in terms of the presence of both TB and SB species, but in addition, a small amount of a third species was detected [8, 9, 10, 11, 12, 13]. The consensus was that this extra species is TwB benzene which is adsorbed at a 'type C defect' site, thought to consist of two dimers buckled in phase due to a vacancy or defect in the second layer [14]. Lopinski et al. [8] carried out their STM investigation at low coverage and observed a time dependent conversion of SB to TB, in agreement with the theoretical predictions. Borovsky et al. [9, 10] also observed conversion from SB to TB in their low coverage STM study. These experimental results were corroborated by Wolkow et al. [11] and Hofer et al. [12, 13] in a combination of semi-empirical Hartree-Fock and DFT calculations, as well as simulated STM images. The results of Borovsky et al. and Lopinski et al. differ, however, in the extent of the conversion of the SB to TB species. Borovsky et al. report complete conversion within the statistical limits of the experiment, while Lopinski et al. found that ~15 % of the benzene remained unconverted from the SB form after 150 mins.

In contrast, a significant number of studies have reached the conclusion that only the SB species is present on the surface. These include the STM investigation of Self et al. [15] at low coverages, as well as the angle-scan X-ray photoelectron diffraction (XPD) experiments of Shimomura et al. [16]. Nagao et al. [17] concluded from their high resolution Si 2p X-ray photoelectron spectroscopy (XPS) studies that at saturation coverage $50 \pm 10\%$ of the Si dimers were involved in bonding to benzene, consistent with SB adsorption. It should be noted, however, that this experiment was performed at 140 K. Witowski et al. [18, 19] recently reported that NEXAFS, reflectance anisotropy spectroscopy (RAS), and surface differential reflectivity spectroscopy (SDRS) studies indicated the presence of 0.47 benzene molecules per Si dimer.

DFT calculations by Birkenhauer et al. [20] led to the conclusion that the SB structure was the most stable. It should be noted, however, that they only considered the SB, T and P models. Kim et al. [21] recently carried out an XPS investigation of the structure of the surface species as a function of coverage and claimed that the TB species was preferred at low coverage while at high coverage benzene was exclusively in the SB form.

With the exception of a semi-empirical cluster calculation by Jeong et al. [22] which found the P form to be the most stable, there has been no support in the literature for the P, T and DBB forms of adsorbed benzene.

Turning now to quantitative structural aspects, almost all the information available comes from theoretical total energy calculations, rather than experiment. For the SB species Si-C bondlengths of 1.89 [8, 11, 13], 1.94 – 1.97 [20] and 1.98 Å [12] have been reported, all of which are slightly higher than those typically encountered in organo-silicon compounds (1.85 – 1.88 Å) [23]. The majority of C-C bondlengths lie in the range 1.47 - 1.51 Å, with one exception of 1.59 Å, while all theoretical models agree on a C=C bondlength of 1.35 Å [2, 4, 8, 12, 13, 20]. These values compare well with the average bondlengths in free hydrocarbon molecules of 1.54 Å for C-C and 1.34 Å for C=C [24]. The bondlength of the Si-Si dimer on which the benzene is adsorbed has been reported in the range 2.35 – 2.46 Å [8, 12, 20], which represents an increase from the dimer bondlength on the clean surface of 2.29 Å. Bond angles within the molecule correspond to the expected $\sim 120^\circ$ associated with sp^2 hybridisation and 109.9° expected for sp^3 C. Only two experimental structural studies have been carried out on this system. The ‘wings’ of the SB were found to be tilted upwards from the surface by 30° using NEXAFS [7]. XPD measurements (including some at low photoelectron kinetic energy) [16] gave bondlengths of 1.3 – 1.6 Å and 1.2 – 1.4 Å for the C-C and C=C bondlengths, respectively. These are in agreement with those predicted by theory, but the precision is rather low. Even less information is available about the structure of the TB species. The single experimental study (NEXAFS [7]) suggested that the wing of the molecule was tilted away from the surface plane by 43° . Theoretical calculations gave Si-C bondlengths of 1.87 – 1.89 Å [11, 13] and ~ 2.0 Å [12], C-C bondlengths in the range 1.47 – 1.59 Å, a C=C bondlength of 1.35 Å [4, 12, 13] and a wing tilt of 45° [4]. Only Hofer et al. [12] provide any structural data on the substrate in this adsorption structure; specifically their theoretical calculations led to the conclusion that the Si-Si dimer bondlength was increased to 2.35 Å, while the separation between the dimers involved in the bonding of a single benzene molecule was reduced from 3.84 Å on the clean surface to 3.36 Å.

As can be seen from the above summary, many aspects of the local structure of adsorbed benzene on Si(001)-(2x1) at saturation coverage remain unclear. There are a significant number of experimental studies indicating that benzene initially adsorbs in the SB state and that this converts rather quickly to the TB state, although there is very little quantitative experimental structural data. Taking into account the

reported activation energies for this conversion, together with the relative stabilities of the two states, one would expect that complete conversion to the TB state should occur within a relatively short time period. The experimental evidence for this, however, is inconclusive. Moreover, there are also a significant number of studies which conclude that only the SB form is present on the surface.

We report here on the results of experiments conducted with the objective of determining unambiguously the local adsorption structure(s) in the saturated layer; i.e. to determine which local bonding configurations are occupied by benzene (SB, TB or other species), and whether at this coverage one or more of these states coexist on the surface. To achieve this goal, we present here the results of a scanned-energy mode photoelectron diffraction (PhD) [25, 26] study of C 1s photoemission from a saturated layer of benzene on Si(001)-(2x1) at room temperature. The PhD technique exploits the coherent interference of the directly-emitted component of the outgoing photoelectron wavefield from a core level of an adsorbate atom with components of the same wavefield which are elastically backscattered by the nearby substrate atoms. By measuring the photoemission intensity in specific directions as a function of photon energy, the resulting changes in photoelectron energy, and thus photoelectron wavelength, cause specific scattering paths to switch in and out of phase with the directly-emitted component, leading to modulations in the intensity which depend on the relative emitter-scatterer location. Simulations of these PhD modulation spectra, including multiple scattering for the surrounding atoms in ‘guessed’ model structures, allow one to determine the local adsorption geometry around the emitter atom. In the present case our C 1s PhD data provides detailed information on the local scattering environment of the adsorbed benzene molecules, thus providing the first complete set of experimental structural parameters for this system.

2. Experimental details

The experiments were performed in a UHV surface science end-station operating at a base pressure of 10^{-10} mbar. The Si(001) wafer (P doped, 10 Ω cm) was cleaned *ex situ* by rinsing in methanol and ultra pure water prior to mounting on the end of a manipulator which was designed to allow both azimuthal and polar rotation of the sample. The crystal surface was cleaned *in situ* by flashing the sample to 1550 K which, on cooling to room temperature, produced a well ordered two-domain (2x1) LEED pattern, characteristic of the clean Si(001)-(2x1) surface. Surface cleanliness was also confirmed by XPS. Benzene was purified by freeze-pump-thaw cycles prior to dosing, and the purity of the vapour in the UHV chamber confirmed using a quadrupole mass spectrometer. A series of XPS spectra of the C 1s and Si 2p regions were recorded as a function of benzene exposure to the surface at room temperature (figure 3). It can be seen that there is a shift in the kinetic energy of the C 1s peak maximum of ~ 0.4 eV as the coverage increases, and that a dose of 5 L is sufficient to produce a saturated monolayer of adsorbed benzene. This exposure was used to create the overlayers which were subsequently measured by PhD. The UE56/2-PGM1 beamline at the BESSY II synchrotron radiation facility in Berlin was used as the photon source for these experiments. The analyser chamber contains an Omicron EA-125HR, 125 mm mean

radius hemispherical electrostatic analyser, equipped with seven-channeltron parallel detection used to detect the emitted photoelectrons. Scanned-energy mode PhD data were collected by recording energy distribution curves (EDCs) covering an energy window of 10.8 eV width centred around the C 1s peak at 3 eV intervals in photon energy. Measurements were made on the C 1s photoemission peak in the kinetic energy range of 60 – 221 eV at polar emission angles of between 0° and 60°. Most measurements were made in the two high-symmetry azimuths, [100] and [110], but a few measurements were also made in an intermediate [830] azimuth corresponding approximately to the average direction of the bonds between Si dimer atoms and the Si atoms in the underlying unreconstructed layer (see figure 1). These data were processed following our general PhD methodology (e.g. [25, 26]) in which the individual EDCs are fitted by a Gaussian peak, a step and a template background. The integrated areas of the C 1s peaks were then plotted as a function of photoelectron energy and each final PhD modulation spectrum was obtained by subtraction of, and normalisation by, a smooth spline function representing the non-diffractive intensity and instrumental factors. These PhD modulation spectra were used in the structure analysis described in the following section.

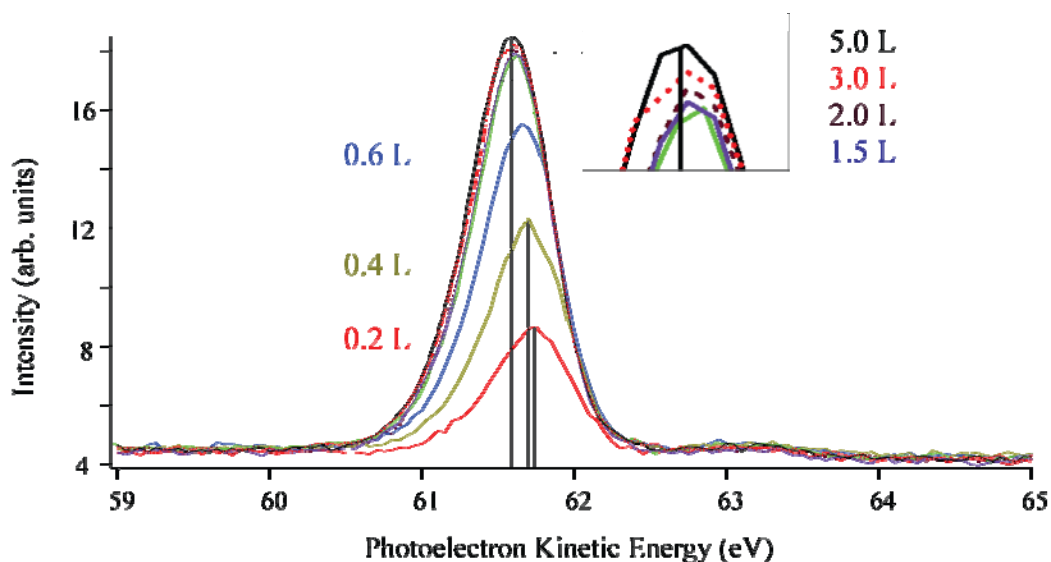


Figure 3. C 1s spectra recorded with a photon energy of 350 eV as a function of benzene exposure to the clean Si(001)-(2x1) surface.

3. Structure analysis

A subset of the C 1s PhD modulation functions obtained in these experiments and used in the structural analysis are shown in Figure 4. A characteristic feature of the data is the very weak modulations; the data shown in Figure 4, which were all recorded at relatively small polar emission angles, were selected as showing the strongest (and thus most reliable) modulations, yet even these spectra show a modulation of amplitude of only about $\pm 10\%$. In general one sees the strongest modulations in PhD when making a measurement in a geometry corresponding to 180° backscattering from a nearest-neighbour substrate scattering atom. For benzene on Si(001) such a situation is impossible for two reasons. Firstly, the molecule contains six C atoms which, on this surface, must occupy at least two symmetrically

inequivalent sites, so as the C 1s photoemission peak is a composite of emission from all of these six C atoms, not all of them can be in this favourable backscattering geometry for any emission direction. Secondly, because there is a mismatch of the C-C and Si-Si distances on the surface, not all these C atoms can occupy high-symmetry sites on the surface, so in any PhD measurements recorded at angles away from normal emission there is further averaging of inequivalent geometries, for the different emitter atoms, and in the different symmetrically-equivalent surface domains. Both effects mean that the measured C 1s PhD spectra comprise an incoherent sum of the individual diffraction spectra from a multiplicity of different scattering geometries, strongly attenuating the resultant modulations. These weak modulations represent a significant challenge to the structure determination in that both experimental noise and possible defects in the theoretical modelling have an enhanced significance. Nevertheless, the data do prove to form the basis of a surprisingly incisive structure determination.

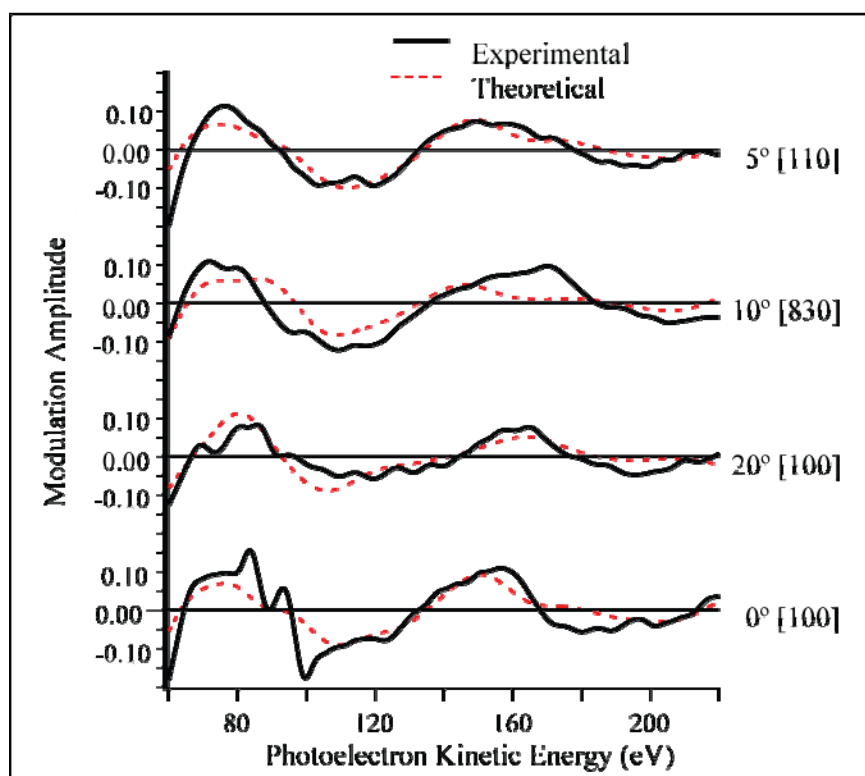


Figure 4. Comparison of the experimental and theoretical C 1s PhD modulation functions giving the best fit structural model for the saturated monolayer of benzene on Si(001)-(2x1).

In order to extract the structure from these measurements, multiple scattering curved-wave calculations must be performed for a range of trial structures, using a computer code developed by Fritzsche [27, 28]. This theoretical formulation is based on a magnetic quantum number expansion and takes into account the finite acceptance angle of the detector and the energy resolution of the experiment. These factors help to reduce the importance of longer scattering pathways, and ensure that fourth and higher order scattering events can largely be ignored. Calculations are then performed for a range of trial structures until optimal agreement is achieved between theory and experiment; if the result satisfies certain criteria of structural sensitivity, goodness-of-fit and uniqueness, the best model structure is then believed to be an accurate

description of the true structure. To quantify the agreement between the theoretical and experimental modulation functions a reliability factor, R_m is calculated using the equation:

$$R_m = \frac{\sum_{i=1}^m (\chi_{th}^i - \chi_{exp}^i)^2}{\sum_{i=1}^m (\chi_{th}^i{}^2 + \chi_{exp}^i{}^2)} \quad (1)$$

χ_{exp} is the experimental modulation amplitude, while χ_{th} is the theoretical modulation amplitude, and the summations are over all different energies and emission directions in the set of PhD modulation spectra used in the analysis. R_m is the normalised sum of the squares of the differences between χ_{exp} and χ_{th} and should be as close to zero as possible. Typically, in a range of structural studies using this approach, values in the range $\sim 0.1 - 0.3$ have been found to be achievable. In general, it is easier to get a low R-factor when the modulation functions have a high amplitude, but good agreement may also be achieved even with modulations comparably weak to those seen here [29].

Once a minimum R-factor is found (R_{min}), there is also an objective criterion to discriminate between acceptable and unacceptable structural models, as well as to determine the error limits of the structural parameters in the preferred model. This involves a calculation of the variance in R_{min} , which is defined as $var(R_{min}) = R_{min} \sqrt{2/N}$, where N is a measure of the number of independent pieces of information in the experimental data (see reference [30] for more detail). Any structural model that has an R-factor value greater than $R_{min} + var(R_{min})$ can be excluded. The relatively short data range of the experimental PhD spectra used in the present analysis lead to a value of $var(R_{min}) = 0.30 R_{min}$.

The analysis was first conducted on the assumption that only one structural species was present on the surface. Multiple scattering simulations were therefore conducted starting from each of the structures depicted in figure 2. Calculations were conducted assuming an ordered (2x2) overlayer structure such that each unit mesh contained one benzene molecule per pair of Si dimers. As intermolecular scattering of photoelectrons is relatively unimportant, particularly for near-normal emission geometries, the results are very insensitive to the long-range ordering of the overlayer. For each structural model, optimisation of the agreement between theory and experiment was achieved by adjusting the C-C, C=C, Si-C and Si-Si dimer bondlengths, together with intramolecular bond angles, to achieve a minimum R-factor. The results are summarised in Table 1, which clearly shows that R_{min} is lowest for the SB species (0.23). Next lowest is the TB species with an R-factor of 0.26, which lies within the $R_{min} + var(R_{min})$ value of 0.30, and consequently must also be considered as a possible structural model. The R-factors of the remaining species are above this limit, which permits us to exclude overlayers of the TwB, T, P and DBB species as possible adsorption configurations of benzene on Si(001)-(2x1). Thus the preliminary analysis would indicate that if we have a single form of benzene adsorbed in the saturated monolayer, then it is most

likely to be the SB species, although we cannot exclude at this point the possibility that the TB configuration is adopted instead. These findings are consistent with the conclusions of many of the previous studies on this system.

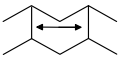
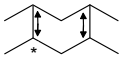
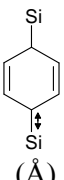
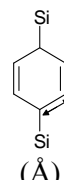
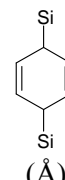
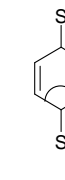
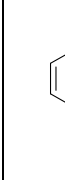
Table 1. Summary of the best-fit R-factor values achieved through fits to the experimental PhD modulations spectra of figure 4, assuming all adsorbed benzene molecules occupy one of the geometries shown in figure 2.

Species	SB	T	P	TwB	TB	DBB
R_{\min}	0.23	0.63	0.47	0.45	0.26	0.35

As described in the introduction, however, there have also been a number of reports which suggest that the overlayer contains more than one form of adsorbed benzene. The second step in our structural analysis was therefore to run similar simulations of mixed overlayers comprising coadsorption of two structural components. As a starting point, these calculations used the structural parameter values obtained in the analysis based on the presence of a single species described above. In these simulations the relative amounts of each coadsorbed species on the surface was systematically varied over the whole composition range to find the mixture which gave the best R-factor. The structural parameters of each species were then re-optimised at that composition. The first mixture chosen was SB and TB, based primarily on the observation that these two species gave the lowest R-factors in the single-site analysis, although we also note that this is the most common mixture reported in the literature [4-13]. The significantly higher R-factor values for the other single-site structures makes it improbable that some other two-site model will provide an improved description of the PhD data. A striking result of these calculations was that the inclusion of even a small amount of the second species in the overlayer led to a significant decrease in R-factor, even before re-optimising the individual structures. The lowest value of 0.14 corresponded to an SB;TB mixture in the proportions 58%;42%. The re-optimisation of the SB structure at this composition resulted in a decrease in the Si-Si dimer bondlength from 2.75 Å to a more reasonable value of 2.45 Å, and a decrease in the wing tilt from 42° to 15°. Other parameters were unchanged and are listed in Table 2. Re-optimisation of the TB structure in the coadsorption model caused the bondlength of the Si-Si dimer bonded to C_{2,3} to decrease from 2.24 Å to 2.06 Å, while that bonded to C₁ and C₄ increased from 2.34 Å to 2.65 Å. The C₂-C₃ bondlength was increased from 1.45 Å to 1.76 Å while that of C₁-C₂ was reduced from 1.59 Å to 1.38 Å. The C=C bondlength was also reduced from 1.52 Å to 1.41 Å (see Table 3). These values will be discussed later. This re-optimised mixed SB/TB model yielded a further reduction of the R-factor to 0.12, which was markedly lower than that for either of the single species overlayers. Indeed, based on the variance, we can exclude compositions which give rise to an R-factor above 0.16, which allows us to discount the possibility that the overlayer consists of a single species. Simulations run on TB/DBB and SB/DBB mixtures also gave minimum R-factors significantly larger than this (0.24 at 71% TB and 0.23 at 62% SB, respectively). Therefore we can conclude that the saturated monolayer of benzene

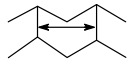
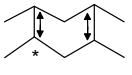
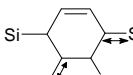
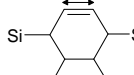
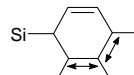
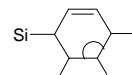
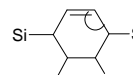
adsorbed on Si(001)-(2x1) at room temperature must contain a mixture of at least SB and TB. Figure 5 shows the variation in R-factor as a function of the percentage of SB in an overlayer containing both SB and TB using the structural parameters obtained for the optimum composition and listed in Tables 2 and 3. This shows that after structural re-optimisation the composition yielding the minimum R-factor is unchanged, indicating a stable solution. The horizontal dashed line in figure 5 at an R-factor value corresponding to $R_{\min} + \text{var}(R_{\min})$ shows that the range of acceptable solutions (with R-factor values below this line) corresponds to an SB fractional occupation of $58 \pm 29\%$. The structural parameters for both the SB and TB species in this saturated layer are listed in figure 6.

Table 2. Structural parameter values for the 'standard butterfly' (SB) adsorption site of benzene on Si(001) – (2x1). * denotes the Si dimer on which benzene is adsorbed.

Ref.	 Si-Si dimer separation (Å)	 Si-Si dimer (Å)	 Si (Å)	 Si (Å)	 Si (Å)	 Si	 Si
DFT STM [12]	3.36Å	2.39*	1.98	1.50	1.35		
DFT STM [13]		2.38*	1.89	1.47-1.49	1.35		
TPD ARUPS [2]				1.51	1.35	close to the ideal tetrahedron angle (109.5)	
Theory STM [4]				1.49-1.59	1.34-1.36	103° – 113°	119° – 122°
STM FTIR SQCC [8]		2.44*	1.89	1.49	1.35		
NEXAFS [7]						wing tilted ~30° from surface plane	
XPD [16]				1.3-1.6	1.3	85°– 115°	
DFT MNDO/d LCGTO-DF [20]		2.46* 2.35	1.97 1.94	1.51 1.53	1.35 1.36	109.9° 109.6°	119.2° 118.8°
Current Study	3.59 ± 0.70	2.45* ± 0.40 2.30 +4.00/-1.00	1.93 ± 0.03	1.47 +0.36/-0.11	1.35 +0.15/-0.45	120.5° wing tilted 15±4° from surface plane	115.9°

In the analysis described above, the surface was assumed to contain independent domains of either SB or TB. For completeness, further simulations were conducted on a selection of long-range ordered phases containing both species. Since the minimum R-factor corresponded to a composition close to a 1:1 ratio of SB:TB, these phases were defined to have 1 SB and 1 TB molecule per surface unit mesh. Figure 7 shows the arrangement of the benzene molecules in these models; while other possible long-range ordered arrangements of equal occupation of the SB and TB species on the surface clearly exist, these models serve to test the sensitivity of the measurements to the effects of intermolecular scattering. As anticipated, the simulations showed only very small differences in individual R-factors, all values falling within a range of 0.007. A consequence of this insensitivity, of course, is that it is not possible, on the basis of PhD measurements alone, to determine whether the co-adsorbed SB and TB structures are locally mixed or occur in separated domains.

Table 3. Structural parameter values for the 'tight bridge' (TB) adsorption site of benzene on Si(001)-(2x1). * denotes the Si dimer which interacts with the C₂ and C₃ atoms of the benzene ring.

Ref.	 (Å)	 (Å)	 (Å)	 (Å)	 (Å)		
DFT STM [12]	3.36	2.35*	2.0	1.35	1.57		
DFT STM [13]			1.87-1.89	1.35	1.47-1.53		
Theory STM [4]				1.34-1.36	1.49-1.59	119 –122°	103 –113° wing tilted 45° from the surface plane
NEXAFS [7]							wing tilted 43° from the surface plane
Current Study	2.71 +0.31/-0.40	2.06* +0.44/-0.76 2.65 ± 0.35	1.85 +0.10/-0.15	1.41 +0.62/-0.55	1.76 +1.06/-1.72 1.38 +0.47/-0.29	116.0°	105.5° wing tilted 47+7/-15° from the surface plane

So far we have presented the results of an analysis of the PhD data based on either a single local benzene adsorption geometry or the coexistence of two different local species. The results show a clear and significant preference for the coexistence of the SB and TB species. We might therefore ask whether a similar improvement might be achieved by a model involving the coexistence of three distinct species; indeed, some occupation of a third species has been reported in several STM studies [8, 9, 10, 11, 12, 13].

We have not investigated this possibility, in part because optimisation of a three-site model presents a formidable (and probably unrealistic) computational task, but also because the results obtained so far indicate that such an investigation is unlikely to be fruitful. In particular, the R-factor obtained for the two-site model is already very low, while the R-factors for the single-site models based on all the other structures are high, so a substantial occupation of any of these sites is most unlikely to reduce the overall R-factor. It is certainly possible that a very small fractional occupation (e.g. $\sim 5\%$ or less) of a third site could lead to further improvement we have obtained, but it is unlikely that the improvement in the R-factor would prove to be sufficient to be formally significant in view of the relatively large value of the variance associated with the modest size of the useable PhD data set. The implication, of course, is that such a low fractional occupation of a third site may occur, but we would be unable to confirm or refute this in a definitive way.

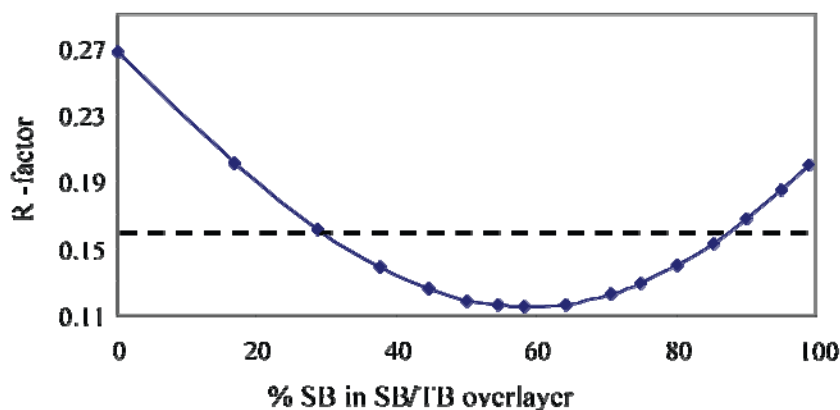


Figure 5. Plot of R-factor as a function of the percentage of SB in a mixed SB/TB monolayer. The horizontal line represents the upper limit of the variance.

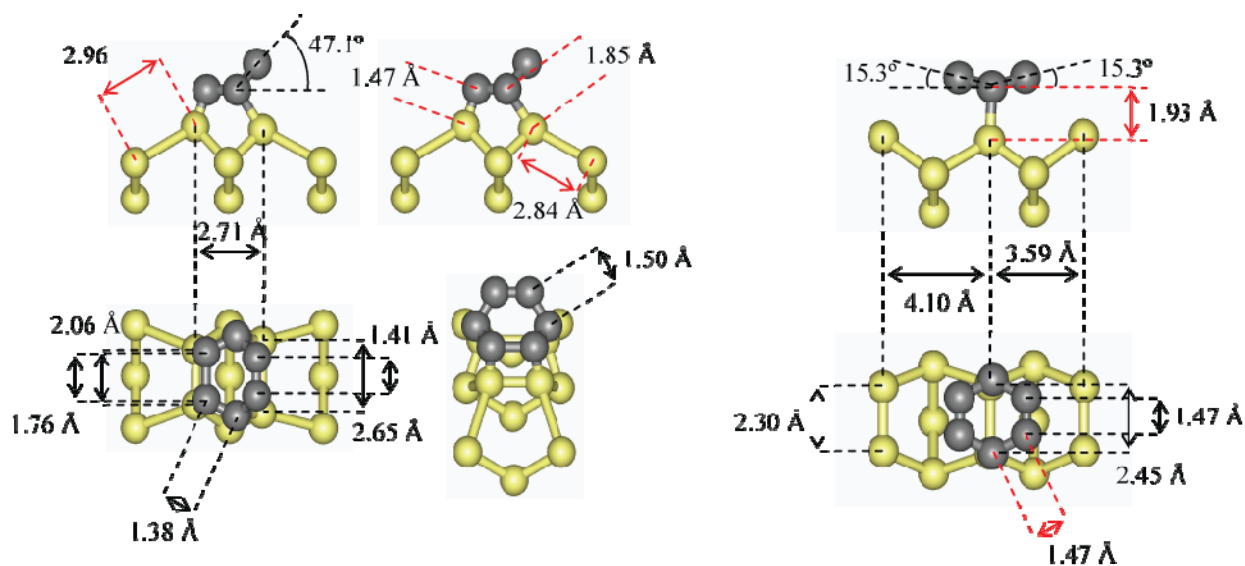


Figure 6. Structural models of the TB (left hand side) and SB (right hand side) determined from our PhD analysis.

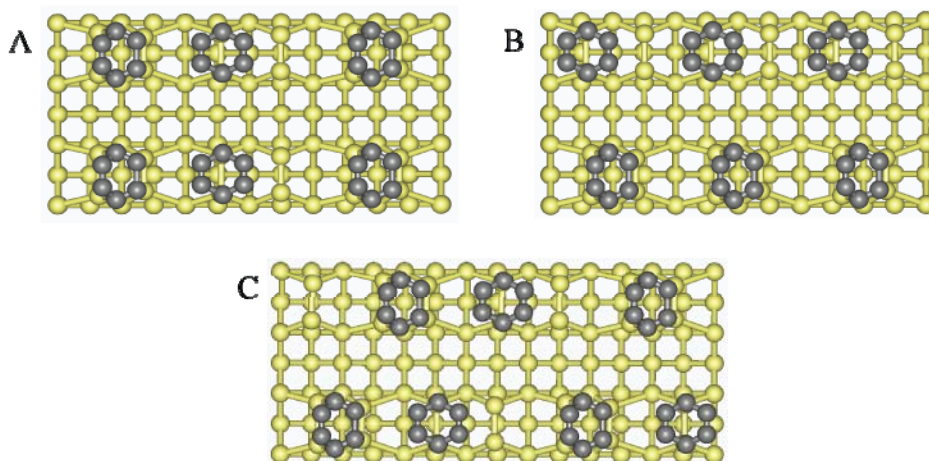


Figure 7. Diagrams of the arrangement of benzene molecules in mixed SB/TB domains which were simulated to test the sensitivity of PhD to the nearest neighbour molecules.

4. Discussion

Using C 1s PhD we have been able to determine unambiguously that the saturated benzene overlayer on Si(001)-(2x1) contains both SB and TB species with a composition of $58 \pm 29\%$ of the SB species. This conclusion is consistent with the results of earlier STM studies, but in the present case the structural conclusions in identifying the bonding sites and their detailed geometries is quantitative rather than qualitative. Despite the weak PhD modulations and the complexity of the system, we have been able to achieve an extremely good R-factor of 0.12.

4.1 SB/TB co-occupation and interconversion

While our PhD study provides fundamentally new quantitative structural information on the local structures of benzene adsorbed on Si(001), we also find quantitative information on the co-occupation of two sites that may help to illuminate questions concerning the relative stability of these two adsorption states and the rate of conversion between these states. Our results are in general agreement with those groups who reported that both SB and TB exist on the surface, but who also identified inter-site conversion from SB to TB [4, 5, 6, 7]. Underlying this observation of inter-site conversion is that of the possible conditions for equilibrium between occupation of the two sites.

Before considering this issue in more detail we first comment on those studies which reported the presence of only SB species; do these results really conflict with other experiments identifying co-occupation of two sites? In some of these studies the failure to identify two sites can clearly be attributed to the limited range of adsorbate species considered (for example, only the SB, T and P in refs [15] and [20]). In some other cases, such as the XPD study of Shimamouro et al. [16], the possibility of a mixed SB/TB overlayer was simply not considered, and it is certainly possible that including co-occupation of the TB geometry may produce improved theory/experiment agreement. Witowski et al. [18] based their identification of the SB site occupation on their measured coverage of 0.47 benzene molecules per Si dimer, but this only

really explains that there is one benzene molecule per two dimers, not whether the benzene molecule is bonded to one or two of these dimers. Perhaps the most convincing argument for the presence of only the SB species is the XPS study by Nagao et al. [17], in which they found that $50 \pm 10\%$ of the Si dimers were involved in bonding to benzene. However these measurements were carried out at 140 K. If adsorption is initially into the SB site and then converts to TB sites by a thermally-activated process, the measured activation barrier (see below) implies a half life for the conversion at 140 K of $\sim 10^{14}$ years! Thus, the results of Nagao et al. may be regarded as demonstrating that the SB state is the one adopted on initial benzene adsorption, and that conversion to the TB species is highly activated. Finally we turn to the XPS measurements of Kim et al. [20]. We have, reproduced the qualitative trend of results in our coverage uptake measurements, in that we detect an increase of 0.4 eV in binding energy of the C 1s peak on going from low coverage to high coverage, but they detect only an increase of about 0.2 eV (figure 3). These shifts can be rationalised in terms of the two chemically distinct C atom environments, i.e. the sp^3 type C which is σ -bonded to Si and the sp^2 type C in the double bonds. In the SB species the ratio of the σ -bonded C to the doubly bonded C is 1:2. This ratio is reversed to 2:1 for TB. Since the photoelectron binding energies of the C 1s will be different for these two chemically distinct species, a shift in energy of the peak maximum is consistent with a change in the relative concentrations of adsorbed SB and TB species. Assuming a BE of 238.9 eV for the σ -bonded C and 284.2 eV for the doubly bonded C, Kim et al. concluded that at low coverage the molecules were all in the TB state while at high coverage they were all in the SB state. However, the binding energy assigned to the doubly bonded C is inconsistent with earlier work by Tao et al. [31], who measured XPS spectra of a series of unsaturated C_6 rings on Si(111)-(7x7), and were able to attribute binding energies of 283.8 – 283.9 eV to σ -bonded C and 285.0 – 285.1 eV to doubly bonded C. Using these binding energies, we estimate that a shift of 0.4 eV would be expected for an SB/TB overlayer which was approximately 50 % SB at high coverage, if initial adsorption at low coverage is predominantly in the TB configuration. This composition of the saturated monolayer is consistent with that obtained from our PhD results.

Both Taguchi et al. [1] and Gokhale et al. [2] found evidence from TPD for two species adsorbed on the surface. In the light of the results of subsequent studies it may now be appropriate to reinterpret their data in terms of co-occupation of SB and TB states, rather than SB and step-edge adsorption; the peak at ~ 465 K would thus correspond to desorption of the SB species, while that at ~ 505 K is due to TB. The HREELS spectra of Taguchi et al. contain many peaks which are excited both by impact scattering as well as dipole scattering, which would be consistent with the presence of both the TB species and the highly symmetric SB species. Gokhale et al. observed some features in their ARUPS spectra which did not conform with the C_{2v} symmetry of the SB species. In particular there was a breakdown of the symmetry in the vertical plane perpendicular to the Si dimers. They suggested that this was due to the miscut of the crystal required to suppress one of the two rotational domains of the (2x1) reconstruction on the surface,

but an alternative explanation would be that these features arise from a molecule adsorbed with the symmetry of the TB species.

The results of our structure determination show that a significant range of compositions of SB and TB give an acceptable fit between theory and experimental data, a consequence of the limited precision of this parameter. However, previous studies in the literature report an even wider range of compositions, implying a significant variation in this quantity for different experiments. The probable reason for this is that not all experiments measure the equilibrium composition (indeed, some studies show the composition changes with time), and that the nature of the non-equilibrium states studied depend on the kinetics of the conversion between the TB state and SB states. Time-dependent STM measurements at room temperature have shown a gradual conversion from SB to TB states with an estimated activation barrier of 0.94 – 1.0 eV [8, 9, 11], assuming a pre-exponential factor of 10^{13} sec^{-1} ; the value of 0.87 eV obtained in the calculations of Lee and Cho [5] is in good agreement with this value. On this basis, experiments which are performed quickly are likely to show the presence of more SB than TB [19, 32], as the molecules will not have had sufficient time to convert, but at room temperature one would expect conversion of > 90 % of the SB to the TB form within an hour. As our PhD data are collected on timescales longer than one hour, this argument might lead us to expect that our surface should contain only the TB species. Such a conclusion, however, is based on the implicit assumption that the equilibrium state is essentially 100% TB occupation, (and that the rate of the reverse TB-to-SB conversion process is negligible), which in turn implies that the adsorption energy of the TB state is very much larger than that of the SB state.

Theoretical total energy calculations have produced a wide range of relative adsorption energies for these two structures, the majority predicting that the TB species is more stable by 0.3 – 0.65 eV [4, 8, 11, 12, 13]. These values would give an equilibrium constant (defined here as the ratio of TB/SB in the monolayer) of between 1×10^5 and 8×10^{10} , so the equilibrium state is, essentially, pure TB state adsorption. Since we did not observe this, and our experimental timescale is long compared with the rate constant measured in the STM experiments, we may infer that the adsorption energy difference must be much smaller than these values. Indeed, our experimental result indicates that the equilibrium constant is 0.72, implying that the SB state is actually energetically favoured, but by only 0.009 eV. Using the range of compositions consistent with our data we may conclude that at one extreme the TB species is more stable by 0.023 eV, while using the opposite end of the composition range leads to the conclusion that the SB species is more stable by 0.049 eV. These values are consistent with the much smaller energy differences calculated by Lee et al. [5] (TB more stable by 0.07 eV), Lopinski et al. [33] (TB more stable by 0.04 eV) and Jung et al. [34] (SB more stable by 0.1 eV).

While this discussion provides a rationale for many aspects of the experimental results for the Si(001)/benzene adsorption system, several aspects are significantly simplified. In particular, no account is

taken on intermolecular effects on the adsorption energies and in steric effects that may influence the ability of the surface to achieve equilibrium. In general all theoretical calculations of these adsorption energies are based on isolated molecules in either the SB or TB geometry, or ordered arrays of these single species. However, Lee and Cho [5] extended their calculations to include the energies for small linear clusters consisting of three adsorbed benzene species containing SB and TB species arranged in different configurations. Their results show variations in the energies of up to 0.1 eV depending on the configuration, and we believe that these effects may be a key to understanding the composition of the equilibrium layer. Another factor which must be considered is steric effects. To understand this, we start by picturing a saturated overlayer of benzene on Si(001)-(2x1) in which all of the benzene molecules are adsorbed in the SB configuration, and are equally spaced on the surface, i.e. there is a vacant dimer on either side of each SB. To convert from the SB to the TB form, the SB molecule simply has to tilt over to either the right or left hand side and interact with the free dimer. If we assume that the direction of this tilt is completely random, then there can arise a situation where the molecules on either side of an SB both tilt towards it. As a result, this SB species is unable to convert to the TB form as it does not have an adjacent free dimer. This could provide an alternative explanation of why conversion to the TB species is not complete at saturation coverage: that the conversion process is sterically hindered, rather than limited by equilibrium between two states of very similar adsorption energy. A very simple Monte Carlo-like calculation based on these assumptions led to an estimate that around 20% of the SB may remain, which is slightly lower than our experimental values. In reality, though, it is likely that once one molecule has tilted in one particular direction it will influence the kinetics of the surrounding molecules, so a more sophisticated Monte Carlo simulation taking these factors into account may result in a surface composition which is closer to our experimentally determined values.

4.2 Structural parameters

The PhD technique provides us with two key pieces of information: the adsorption sites, and the detailed structural parameters of these sites. In the present case the identification of two distinct co-occupied sites, and their relative occupation, provides an unusual degree of insight into the energetics and kinetics of the surface species not generally available for a structural technique, as discussed above. More typical of such measurements are quantitative details of the adsorption geometries. The structural parameter values associated with the two adsorption states are listed in Tables 2 and 3 and show good agreement with theoretical total-energy calculations. The Si-C bondlengths have been determined with a high degree of precision, and did not change on re-optimisation of the species in the mixed overlayer. Good precision for the bondlengths from the emitter atoms (in this case C) and the nearest-neighbour substrate scatterer atoms (Si) is characteristic of the PhD technique, particularly when the experimental data set involves emission angles reasonably close to these bond directions, as in the present case. The precision of the C-C and C=C bondlengths is much lower. This arises because this information comes primarily from scattering off neighbouring, weakly-scattering, C atoms and also because many of the C-C and C=C bonds are oriented

close to parallel to the surface and so will not lead to strong scattering modulations in emission directions close to the surface normal. The precision is also limited in the present case by the use of only four PhD spectra in the analysis, leading to a higher variance. Better precision can generally be obtained by including more spectra in the simulations; for example using eight spectra would have reduced the variance from 30% to 20% of R_{\min} , but because the intensity of the modulations at emission angles further away from normal were extremely weak, a higher value of R_{\min} is to be expected, resulting in no overall improvement in the absolute variance.

Considering firstly the SB structure, our Si-C bondlength of 1.93 ± 0.03 Å is extremely close to that of Birkenheuer et al. [20], and within the overall range of $1.89 - 1.98$ Å [8, 11, 12, 13] reported in the literature. Similarly the C=C bondlength of $1.35 (+0.15/-0.45)$ Å, while less precise, shows excellent agreement with previous studies as does our C-C bondlength of $1.47 (+0.36/-0.11)$ Å [2, 4, 8, 12,13, 20]. The bondlength of the Si-Si dimer to which the benzene was bonded was determined with reasonable precision (2.45 ± 0.40 Å), unlike that of the free dimer ($2.30 (+4.00/-1.00)$ Å). The latter is unsurprising as the scattering of the C 1s photoelectron waveform from these atoms is expected to be minimal. Perhaps the most interesting structural parameter is the wing tilt, which was determined quite precisely to be $15 \pm 4^\circ$, a smaller degree of distortion than the 30° previously found by NEXAFS [7], but within the limits of $10.4^\circ - 26.5^\circ$ derived from the structural parameters of Silvestrelli et al. [4].

There are fewer structural parameters available for comparison for the TB species. The results presented here are those which have given the optimum R-factor. Those which we were able to determine with reasonable precision, namely the Si-C bondlength of $1.85 (+0.10/-0.15)$ Å and the wing tilt of $47 (+7/-15)^\circ$ agree well with previously reported values (references [13] and [4, 7], respectively). In contrast, the intramolecular bondlengths are somewhat surprising. For example, the C=C bondlength of 1.41 Å is 0.07 Å longer than the standard value, and the C-C bondlengths of 1.76 and 1.38 Å are 0.22 Å longer and 0.16 Å shorter, respectively, than the standard C-C bondlength [24]. It should be noted, however, that the error bars on these parameters are rather large (see Table 3), and that they encompass more typical values. The substrate parameters also show some variation compared to previous results. The two Si dimers were found to move approximately $1.00 (+0.40/-0.31)$ Å closer together, relative to their spacing on the clean surface, and the dimer which interacts with the C₂-C₃ bond is shortened to $2.06 (+0.44/-0.76)$ Å while that interacting with the C₁ and C₄ atoms is lengthened to 2.65 ± 0.35 Å. Overall, our structural parameters for the TB species tend to suggest that both the benzene molecule and the substrate are more distorted in this configuration than in the SB form, although the magnitude of the error bars precludes us making a definitive statement. Bearing in mind that when the benzene molecule tilts over from the SB form, to produce the TB species, there is considerable mismatch between the positions of the Si and C atoms in the unrelaxed species, some distortion is to be expected.

5. Conclusions

Using scanned-energy mode photoelectron diffraction we have shown that the saturated monolayer of benzene on Si(001)-(2x1) contains both 'standard butterfly' and 'tilted bridge' forms of benzene, with a composition of $58 \pm 29\%$ of the SB species. Detailed structural parameter values have been obtained for both species, including Si-C bondlengths and out of plane tilt angles of the benzene molecules, both with quite a high degree of precision. Intramolecular bondlengths and Si dimer bondlengths and separations have also been determined, but with less precision. The results for the SB species agree well with previous theoretical studies. The structural parameters for the TB species suggest considerable distortion of both the benzene molecule and the Si substrate. Our conclusion regarding the co-occupation of the SB and TB adsorbed species is consistent with the results of several previous studies by other methods, suggesting that at high coverage benzene initially adsorbs on this surface in the SB form at room temperature, but then partially converts to the TB form with time. If the extent of this conversion is based purely on the relative adsorption energies of these two forms, our results indicate that the difference in the Gibbs free energy of adsorption, $(\Delta G(\text{TB}) - \Delta G(\text{SB}))$, is in the range -0.023 to $+0.049$ eV. We suggest, however, that the reason that the conversion is not complete may also be due to a combination of steric effects and a sensitivity of the adsorption energies of the adsorbed SB and TB forms to the nature of the surrounding benzene molecules.

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