Local adsorption geometry of acetylene on Si(100)(2×1): Multiple sites and the role of substrate temperature

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Using C 1s scanned-energy mode photoelectron diffraction the local adsorption geometry of acetylene on the Si(100)(2×1) surface has been investigated at both low and room temperatures. Clear differences in the data at the two sample temperatures are attributed to the co-occupation of at least two distinct local sites. Quantitative modeling based on a two-site model indicates that the majority state at low temperature is bridge site adsorption with the C-C axis of the acetylene directly above, and parallel to, Si-Si surface dimers. At room temperature a second state accounts for more than 50% of the adsorbed acetylene molecules, and the favored model places these acetylene molecules midway between pairs of Si dimers, although the azimuthal orientation of the C-C axes is ambiguous. One possible geometry for this second species is the “pedestal site” tetra- σ species previously proposed by Xu *et al.* [Phys. Rev. Lett. **84**, 939 (2000)], although the specific geometry proposed by this group can be excluded. An alternative “rotated pedestal” site is comparably probable. There is no direct evidence for any occupation of a rotated bridge site across the ends of two adjacent Si dimers, but partial occupation of this site cannot be excluded.

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I. INTRODUCTION

In the last few years there has been growing interest in the adsorption of organic molecules onto Si surfaces with a view to developing a practical methodology to exploit molecular electronics and this has stimulated extensive studies of the interaction of small unsaturated hydrocarbon molecules on Si(100) as simple model systems to explore the relevant underlying physics and chemistry.¹ A key feature of the clean Si(100) surface is the presence of Si-Si dimers at the surface, nominally reducing the number of dangling bonds per surface Si atom from two on an ideally-terminated surface to one on a fully dimerised surface. At room temperature the apparent 2×1 reconstruction² is known to actually involve dynamically “flipping” asymmetric dimers³ arranged on a 2×1 mesh rather than a true long-range-ordered 2×1 phase; at low temperatures ordering of the asymmetric dimers results in a $c(4\times 2)$ phase.⁴

Using a range of experimental spectroscopies and real-space imaging with the scanning tunneling microscope^{5–19} as well as total energy calculations (both *ab initio*^{20–25} and semi-empirical^{26–32}) there has, until quite recently, been a general consensus that ethylene, $\text{H}_2\text{C}=\text{CH}_2$ and acetylene, $\text{HC}\equiv\text{CH}$, both bond to the Si(100) surface along the Si-Si dimers in a so-called di- σ configuration, the dimers being generally believed to remain intact. Indeed, in the case of ethylene adsorption two independent recent investigation based on the same technique of scanned-energy mode photoelectron diffraction (PhD) have provided direct evidence that this is the case. The PhD technique³³ exploits the coherent interference of the directly-emitted component of a core level photoelectron wavefield from an atom in an adsorbate with other components of the same wavefield elastically scattered from surrounding atoms. Modulations in the measured photoemission in specific directions as a function of

photoelectron energy (and thus wavelength) provide information on the location of the emitter atom relative to the neighboring substrate atoms. In one of these investigations³⁴ C 1s PhD spectra were modelled using multiple-scattering simulations to provide a detailed quantitative structure for this adsorption phase. In the other,³⁵ the experimental data were directly inverted using a photoelectron holography algorithm to provide an atomic-scale “image” of the structure which was interpreted as indicating this local adsorption geometry.

In the case of acetylene adsorption on Si(100), however, the same two groups, using the same methodology, reached quite different conclusions. Terborg *et al.*,³⁶ on the basis of quantitative modeling using multiple scattering simulations, concluded that acetylene does bond directly above intact Si dimers as previously anticipated. By contrast, Xu *et al.*³⁵ concluded, on the basis of holographic inversion of their C 1s PhD spectra, that while the C-C axis of the adsorbed acetylene is parallel to the Si-Si dimers of the Si(100) surface, the molecule is located midway between two dimers in a fourfold-coordinated “pedestal” site suggested to have “tetra- σ ” bonding. This second result has proved rather controversial, but has probably helped to encourage a number of new investigations which consider the possibility of other adsorption in geometries other than directly above the Si dimers, or indeed of multiple (co-occupied) adsorption geometries. The four different local adsorption geometries which have been considered most consistently in these new studies are shown schematically in Fig. 1. Unfortunately different authors have used quite different nomenclature to describe these different sites; here we adopt what seems to be the simplest names which are those used in Ref. 37. The bonding geometry placing the C-C axis parallel to, and directly above, a Si surface dimer (top left, Fig. 1) is referred to as the bridge site, while a second geometry bridging two

FIG. 1. Schematic diagram of the Si(100)(2×1) surface showing the alternative distinct acetylene adsorption sites considered here and in a number of previous investigations. The upper part of the figure shows a plan view of all four possible adsorption sites. The lower part shows side and perspective views, respectively, of the bridge and pedestal geometries, and shows the definition of the main structural parameters investigated in the present study.

Si atoms at the same end of two adjacent dimers (bottom left, Fig. 1) is referred to as rotated bridge. On the right-hand side of Fig. 1 are shown two alternative geometries in which the acetylene molecule lies midway between two dimers. We refer to these as pedestal sites, the geometry with the C-C axis being parallel to the Si dimers (top right, Fig. 1) being described as the pedestal geometry while adsorption with the C-C axis perpendicular to the Si dimers (bottom right, Fig. 1) is described as rotated pedestal. Insofar as the local geometry is a direct indication of the bonding character, both the bridge sites are compatible with di- σ bonding and both the pedestal sites are compatible with tetra- σ bonding. Using this nomenclature the two photoelectron diffraction studies mentioned above based on multiple-scattering modeling and holographic inversion concluded that the adsorption geometries were bridge and pedestal, respectively.

The main new experimental information since these structural studies arises from studies using scanning tunneling microscopy (STM). The first STM study of this adsorption system³⁸ (which predated the photoelectron diffraction work) concluded that the features seen in the images could be reconciled with adsorption only in the bridge (on-dimer) sites. Subsequently, however, Wolkow³⁹ suggested that the STM images shown in this publication showed evidence for occupation mainly of sites midway between two dimers (which are argued to be possibly tetra- σ bonded—i.e. pedestal or rotated pedestal) but also *minority* occupation of a single-dimer site, presumably the bridge site of Fig. 1. A more recent STM study⁴⁰ actually shows evidence for cooccupation of *three* different local geometries. Of course, an impor-

TABLE I. Comparison of the calculated adsorption energies in eV/molecule, *relative to that of the bridge site*, for the different geometries shown in Fig. 1 of acetylene on Si(100)(2×1). Positive values correspond to more strongly bound sites. In the case of the results of Sorescu and Jordan and of Morikawa the energies shown correspond to a coverage of 0.5 ML.

	Rotated bridge	Pedestal	Rotated pedestal
Silvestrelli <i>et al.</i> (Ref. 37)	−0.05	−1.98	−1.28
Mezhenny <i>et al.</i> (Ref. 40)	−0.6	−2.6	−1.7
Kim <i>et al.</i> (Ref. 42)	−0.20	−1.40	−0.65
Morikawa <i>et al.</i> (Ref. 43)	−0.10	−1.59	−0.92
Hofer <i>et al.</i> (Ref. 44)	−0.10	−1.77	−0.97
Sorescu and Jordan (Ref. 45)	0.02	−1.42	−0.56
Lu & Lin (Ref. 46)	0.20	−0.76	−0.85

tant issue here is the proper interpretation of the STM images in terms of local adsorption geometries; STM is intrinsically a spatially selective probe of electronic structure, and asperities in the images are not trivially related to atomic positions. For this reason this most recent STM study included the results of simulated images for different local geometries based on electronic structure calculations. Based on this methodology it was concluded that cooccupation of bridge, rotated-bridge, and rotated-pedestal sites occurred. The experiments were conducted at room temperature but the relative populations of the three sites were markedly dependent on coverage, the rotated-pedestal site occupation becoming increasingly occupied for coverage in excess of approximately 0.13 ML, but with the rotated-bridge site always being more populated than the simple bridge site. Very recently, however, a theoretical simulation of these STM images⁴¹ has concluded that the features previously interpreted as due to occupation of rotated-pedestal sites should be reassigned to the presence of two adjacent simple bridge-site acetylene molecules.

In addition to these STM-related studies, there have been several total-energy calculations^{37,40,42–47} to evaluate the relative bonding energy of the different adsorption geometries which have been proposed, and especially those illustrated in Fig. 1. These bonding energies, expressed relative to that for the bridge site, are summarized in Table I. All the calculations indicate that the pedestal sites are unfavorable, although there are large variations in the calculated relative bonding energies. All the calculations which quote the actual adsorption energies show all four geometries to be bonding. The relative bonding energies of the bridge and rotated bridge sites do differ in sign between some of the published results. In two cases the rotated bridge site is actually found to be slightly more strongly bonded than the simple bridge site at a nominal coverage of 0.5 ML; additionally, Sorescu and Jordan,⁴⁵ Morikawa,⁴³ and Miotto, Ferraz, and Srivastava⁴⁸ all found the relative stability of these two sites to be coverage dependent, the rotated bridge becoming more strongly favored at high coverage. In three of these theoretical studies^{43,46,47} the molecular vibrational frequencies were also calculated and compared with earlier published results

of high-resolution electron energy-loss spectroscopy^{5,13} in two cases good agreement was found for the simple bridge site adsorption, although Morikawa⁴³ argues that there is also clear evidence for co-occupation of the rotated bridge site and the authors of Ref. 47 suggest that the vibrational data are consistent with pedestal site occupation.

In view of the growing evidence that there may be co-occupation of more than one adsorption site for acetylene on Si(100), but significant controversy concerning *which* sites are occupied, we have extended our original C 1s PhD investigation with both new experiments and new data analysis. From the experimental standpoint, one key question is the role of sample temperature. In our original PhD investigation,³⁶ in which we found good agreement with the experimental spectra for bridge site occupation, our experiments were conducted entirely at low temperature (approximately 100 K), whereas the comparable investigation based on photoelectron holographic images by Xu *et al.*³⁵ appears to have been conducted at room temperature. Xu *et al.* show very few of their experimental PhD spectra, but comparison with those taken in our own study indicates significant differences in the raw data. Interestingly, there is no such obvious difference between the C 1s is PhD data for ethylene adsorption on Si(100) of Xu *et al.* and our own study.^{34,36} This suggests that the local adsorption structures in the two earlier experiments really are different. One possible reason is sample temperature. Another is the effects of radiation damage. Adsorbed hydrocarbon molecules are quite susceptible to photon-induced or (secondary) electron-induced desorption and dissociation, and collecting the large data sets required for a PhD structure analysis is quite time consuming, with significant attendant exposure to soft-x-ray synchrotron radiation. Our original studies were conducted using a bending magnet beamline on a second-generation synchrotron radiation source (BESSY), whereas those of Xu *et al.* exploited an undulator beamline on the third-generation ALS facility,⁴⁸ with very much (several orders of magnitude) higher photon flux density in the focussed X-ray spot on the sample. We have therefore looked carefully in our experiments (based on the third-generation BESSY II source) for any evidence of radiation-induced modification of the surface.

In addition to this extension of the experimental parameter space and *in situ* characterization, the possibility that there may be co-occupation of multiple adsorption sites also necessitates a reanalysis of the old PhD data as well as the results of the new measurements. Based on the usual scientific principle of concentrating on the simplest probable solutions (Occum's razor), the original analysis only considered the possibility of occupation of single adsorption sites, but this constraint should evidently now be relaxed.

In Sec. II of this paper we first describe the experimental details and the results of the basic characterization of the adsorption of acetylene on Si(100), the method of collection of the PhD data and the observed effects of differing surface temperature. In Sec. III we present the results of a quantitative analysis of these PhD data, including the possible effects of multiple coexisting adsorption sites. In Sec. IV we discuss

our findings in the light of the present state of understanding of this adsorption system.

II. EXPERIMENTAL DETAILS AND RESULTS OF SURFACE CHARACTERIZATION

As remarked in the Introduction, the original experiments (some of the data from which are re-analyzed here) were conducted at the BESSY I synchrotron radiation facility in Berlin on the HE-TGM-1 bending magnet beamline,⁴⁹ but our new data were measured using the UE56/2-PGM-2 beamline of BESSY II using a 56-mm period undulator, followed by a plane grating monochromator.⁵⁰ The ultrahigh-vacuum (UHV) end-station chamber is fitted with low-energy electron-diffraction (LEED) optics and an Omicron EA-125HR 125-mm mean radius hemispherical electrostatic electron energy analyzer equipped with seven-channeltron parallel detection which was mounted at a fixed angle of 60° to the incident X-radiation in the same horizontal plane as that of the polarization vector of the radiation. This analyser was used for soft-x-ray photoelectron spectroscopy (SXPS) to characterize the surface cleanliness and also to measure the photoelectron diffraction spectra. The 0.5-mm-thick Si(100) wafer (P doped, 10 Ω cm), cleaved to a rectangle of 12 $\times$ 7 mm³, was rinsed in methanol and ultrapure water prior to mounting on the UHV manipulator fitted with direct current heating together with cooling from a liquid helium reservoir connected by copper braid to one of the metal clips of the sample mounting. The sample was cleaned *in situ* by flashing to 1520 K, yielding a surface showing a well-ordered two-domain 2 $\times$ 1 LEED pattern at room temperature with no detectable contamination seen in SXPS.

Our previous studies of the Si(100)/acetylene system were conducted entirely with the sample cooled with liquid nitrogen at a temperature of approximately 100 K. In the present studies, measurements were made at room temperature, cooled to 120 K with liquid nitrogen, and also cooled with liquid helium; in this case the sample temperature was approximately 70 K. When cold the clean surface showed a two-domain *c*(4 $\times$ 2) LEED pattern as expected due to the ordering of the asymmetric dimers below about 200 K.⁴ A typical nominal saturation exposure of 2 $\times$ 10⁻⁵-mbar s acetylene at low temperature led to a LEED pattern characteristic of two orthogonal domains of a 2 $\times$ 1 unit mesh. As discussed by other authors previously, this is most probably due to removal of the dimer asymmetry. At room temperature the clean surface showed this 2 $\times$ 1 ordering, as expected due to the (dynamically) random ordering of the asymmetric dimers; in this case the translational symmetry was unchanged after acetylene exposure.

While the photoelectron diffraction measurements concentrated on nominal saturation first-layer coverages of acetylene, SXPS was first used to characterize the uptake on the surface. Relative to our earlier bending-magnet beamline studies at BESSY the new BESSY II undulator beamline allowed us to collect spectra a significantly higher spectral resolution, offering some potential to detect the effects of any surface reaction, radiation damage or even, perhaps,

FIG. 2. C 1s photoemission spectra, recorded at a photon energy of 350 eV, from Si(100) as a function of exposure to acetylene at a sample temperature of 70 K. Note that we define 1 L (Langmuir) as 10^{-6} mbar s using SI nomenclature rather than in terms of the pressure in torr.

multiple local adsorption sites. Previous XPS (Ref. 51) and high-resolution SXPS (Ref. 52) characterization of a range of different hydrocarbon species on Si(100) at saturation coverages has shown significant (up to >1 eV) variation in the C 1s photoelectron binding energy associated with different C coordinations, while there are also many XPS measurements related to SiC growth on Si surfaces which provide reference energies characteristic of complete molecular dissociation. Figure 2 shows the results of our own measurements of the C 1s region of the photoemission spectrum using a photon energy of 350 eV for increasing exposures of acetylene at a surface temperature of 70 K. (Notice that in this paper we use an SI definition of the unit of exposure of the Langmuir as $1 \text{ L} = 10^{-6}$ mbar s). A single peak at a binding energy of approximately 283.8 eV grows and shifts 0.25 eV to higher binding energy, with a slight increase in width, as the coverage increases. The narrowest width is approximately 0.5 eV, similar to that seen in the earlier SXPS study conducted with an estimated total instrumental resolution of 120 meV.⁵² Our own spectral resolution is similar, and the observed width is clearly related to intrinsic rather than instrumental broadening. The small shift and increase in width with increasing coverage is consistent with intermolecular interactions (either in the initial or final state or both) and associated inhomogeneous broadening. A similar observation involving a shift of two C 1s components in 1,5-cyclooctadiene on Si(100) has been attributed to the same effect.⁵³ These spectra show no evidence of two distinct adsorption states, caused either by surface reaction or due to the existence of multiple adsorption sites. On the other hand, of course, the existence of such sites cannot be excluded, because there is no simple way, *a priori*, of knowing whether the shifts in the C 1s photoelectron binding energy associated with these different sites are sufficiently large to be observed. Our results are thus necessary, but not sufficient, evidence of a single site.

FIG. 3. C 1s photoemission spectra (photon energy 350 eV) recorded from a Si(100) surface first exposed to 40-L acetylene at 70 K, after collecting photoemission spectra and subsequently heating to 123 K, and after moving the incident photon beam to a different part of sample.

At a surface temperature of 70 K, it is also possible to form multilayers of condensed acetylene on the surface by increased exposure. Figure 3 shows the resulting C 1s SXP spectrum, with a large component at an increased binding energy of approximately 286.1 eV which we associate with these multilayers. Figure 3 also shows, however, the spectrum recorded after heating this surface to 120 K to desorb the multilayer; while the peak at 286.1 eV is lost, a peak at 285.4 eV appears. However, when a similar spectrum is recorded from a slightly different position on the same surface, this feature is lost, and only the peak around 284 eV is seen. We take these spectra as clear evidence that the incident photon beam is producing some modification of the adsorbed molecules, but this effect *was only seen with multilayer adsorption*. The nature of the radiation-modified surface species is unclear. Liu and Hamers noted a similar (weaker) feature in their XPS data from acetylene on Si(100) at room temperature, and tentatively attributed it to a $\text{H}_2\text{C}=\text{C}=\text{}$ surface species.⁵¹ What seems clear is that this modified species is not atomic C in the form of SiC, as the complete dehydrogenation of acetylene to grow SiC leads to a decrease in the C 1s photoelectron binding energy relative to that of the intact adsorbed acetylene. In bulk SiC this binding energy appears to be close to 283.2 eV (e.g., Refs. 54–56) although in the early stages of growth of SiC on Si(100) achieved by high-temperature interaction with acetylene even lower binding energies around 282.6 eV are seen.⁵⁵

Figure 4 shows the effects of increasing acetylene exposure on the C 1s SXP spectra when the sample is dosed at a temperature of 120 K. Clearly there is no evidence of any multilayer or other second species formation. There was also no evidence of radiation-induced modification of this chemisorbed layer at 120 K or after dosing at room temperature. In this regard we should stress that our data show no evidence

FIG. 4. C 1s photoemission spectra, recorded at a photon energy of 350 eV, from Si(100) after several high exposures to acetylene at a sample temperature of 120 K.

of the C 1s feature at approximately 285 eV seen by Liu and Hamers in conventional XPS following exposure at room temperature.⁵¹ An independent SXPS study of acetylene adsorption at room temperature by Xu *et al.*⁵⁷ also found no evidence for this second species.

A final objective of our investigation of the uptake of acetylene on Si(100) at different sample temperatures was to use the SXPS to estimate the actual saturation coverages, as the coverage appears to play a significant role in the predicted relative stability of different adsorption sites, and particularly the bridge and rotated bridge sites, according to the theoretical calculations described in the Introduction. The resulting measurements of the C 1s peak intensity as a function of exposure showed that the rapid uptake at 70 K, 120 K and room temperature occurred in the first 2 L, with a further increase of little more than 10% in the coverage with exposures of 20 L. At 70 K the saturation coverage was approximately 40% higher than at 120 K, while at room temperature this coverage was approximately 10% lower than at 120 K, although this difference is within our estimated precision. Determining the absolute coverage is potentially subject to quite large systematic errors, but in the present case these were minimized by comparing our data with similar spectra, from the same monochromator, from bulk SiC (Ref. 58); although the stoichiometry of this sample was well known, ambiguities in the layer termination still introduce systematic errors which we estimate could be up to 20%. The saturation coverages calculated in this way were found to be 0.6 ML at 70 K and 0.4 ML at the two higher temperatures. This strongly suggests that the coverages were much closer to 0.5 ML than 1.0 ML, an important distinction in some of the published theoretical (total energy) calculations referred to earlier.

Having established that, within the limits of our ability to distinguish different surface species by SXPS, there is only a single sub-monolayer species present in the temperature range 70–300 K we recorded a series of PhD modulation spectra from the C 1s photoemission taken from nominal (single layer) saturation coverages of acetylene on Si(100)

FIG. 5. Comparison of the experimental C 1s PhD modulation spectra from acetylene adsorbed on Si(100)(2×1) at 100 K (bold curves) and at room temperature (gray curves).

prepared and measured at 70 K, 120 K and room temperature. C 1s photoelectron diffraction data were measured in the kinetic-energy range 80–470 eV in the two main azimuthal directions $\langle 100 \rangle$ and $\langle 110 \rangle$ for polar emission angles between 0° and 60° in steps of 10°. The photon energy was incremented in steps of 2 eV to cover the necessary kinetic energy range for the C 1s photoelectrons and at each photon energy the emitted electron signal was recorded, in the kinetic energy range of ± 25 eV around the C 1s core level peak, to give a series of energy distribution curves (EDCs). The intensity of the peak in each EDC was then determined by background subtraction and integration, and the resulting intensity-energy spectra were normalized to give the photoelectron diffraction modulation functions.³³ The modulation function is defined by

$$\chi_{\text{ex}}(\theta, \phi, k) = [I(k) - I_0(k)] / I_0(k),$$

where $I(k)$ and $I_0(k)$ are the diffractive and nondiffractive intensities, θ and ϕ are the polar and azimuthal emission angles, and k is the modulus of the photoelectron wave vector. $I_0(k)$ also includes the influence of smoothly varying instrumental effects and is obtained by performing a smooth fit to $I(k)$ with a spline function. The main conclusion of a survey of these data is that the PhD modulation spectra recorded after exposure at 70 and 120 K were essentially identical to one another, and to the original data set³⁶ recorded with a sample temperature estimated at 100 K. These data, however, show a few rather distinct differences from those recorded after room temperature exposure. A comparison of a set of five PhD modulation spectra which showed the strongest modulations, recorded for these two preparation temperatures (100 K in bold, room temperature in gray), is shown in Fig. 5. Clearly most of the modulations in the two sets of spectra are similar, but an important difference is in the energy range 120–180 eV, especially at normal emission. In this region the room-temperature data show a strong modulation which in the low-temperature data is much

weaker at normal emission, and is almost completely absent in the spectra recorded at 10° polar emission angle.

In view of these findings, we have undertaken a full structural analysis based on the PhD data sets recorded at 100 K and room temperature. This is described in Sec. III.

III. PhD STRUCTURAL ANALYSIS

A. Methodology and preliminary data evaluation

Our general methodology for extracting quantitative structural information from PhD has been described in detail elsewhere [e.g. Refs. 33 and 59] but the most important step is the use of multiple scattering simulations of the experimental data based on a series of trial structures. We have also made use of an approximate method of direct data inversion, the so-called projection method,^{60,61} to obtain an “image” of the real-space structure. This approach, however, is only of real value in identifying the single or dominant adsorption site, especially when this places the emitter atoms in locations of high symmetry.⁶² As such this method is unlikely to be of real value in the present case in which co-occupation of several sites, none of which place the C emitter atoms in high-symmetry sites, is considered likely.

The multiple scattering simulations in the present analysis used computer codes developed by Fritzsché^{63–65} based on the expansion of the final-state wave function into a sum over all electron scattering pathways from the emitter atom to the detector outside the sample. A magnetic quantum number expansion of the free electron propagator is used to calculate the scattering contribution of an individual scattering path. Double and higher-order scattering events are treated by means of the reduced angular momentum expansion. The influence of the finite energy resolution and angular acceptance of the electron analyser, both of which reduce the importance of longer scattering paths and thus improve convergence in the cluster scattering calculation, are included. In order to quantify the level of agreement between theory and experiment, a reliability factor or *R* factor is defined as⁶⁶

$$R_m = \sum (\chi_{th} - \chi_{ex})^2 / \sum (\chi_{th}^2 + \chi_{ex}^2)$$

where a value of 0 corresponds to perfect agreement, a value of 1 to uncorrelated data, and a value of 2 to anticorrelated data. In order to establish the significance of best-fits to different structural models and to estimate the precision associated with the individual structural parameters we use an approach based on that of Pendry which was derived for LEED.⁶⁷ This involves defining a variance in the minimum of the *R* factor, R_{min} as

$$V = R_{min} \sqrt{2/N}$$

where *N* is the number of independent pieces of structural information contained in the set of modulation functions used in the analysis. Structures and parameter values leading to *R* factors less than $R_{min} + V(R_{min})$ are regarded as falling

FIG. 6. Comparison of the C 1s PhD spectra recorded from Si(100) with adsorbed acetylene and ethylene (at low temperature) with the best-fit simulations obtained in the original analyses (Refs. 34 and 36). The bold curves are the experimental data, the gray curves are the results of the theoretical calculations.

within one standard deviation of the “best-fit” structure. More details of this approach and the definition of *N* can be found elsewhere.⁶⁸ As we shall be presenting the results of calculations modelling surfaces in which the adsorbate coverage is quite high we should stress that while it is important in the multiple scattering calculations to include the scattering contribution of quite a large number of substrate atoms, intermolecular scattering (notably scattering from C atoms of molecules adjacent to the emitter atom) have almost no influence on the PhD spectra due to the combination of weak scattering cross section and unfavorable scattering angles. Modeling based on isolated molecules adsorbed on the surface, with no regard to the adsorption geometry of neighboring molecules, therefore provides an accurate description of the PhD data.

Before considering the results of all the calculations it is helpful to review, very briefly, the results of the original analysis of the low-temperature data.³⁶ Figure 6 shows a comparison of this experimental data set with the calculated spectra for the best-fit bridge site structure, together with a similar comparison for the C 1s PhD data for ethylene adsorbed on Si(100). In both cases the (bridge) adsorption geometry is similar, with the C-C axis parallel to, and directly above the symmetric Si dimer, placing the C emitter atoms a little off the atop sites of the Si dimer atoms. Atop sites typically give rise to strong PhD modulations in emission directions near the surface normal (and thus in the favored 180° backscattering geometry for the nearest-neighbor substrate atom), while the modulations fall off as one moves away from normal emission, an effect exaggerated by the large vibrational amplitudes parallel to the surface which typify atop adsorption sites. A striking feature of Fig. 6 is the much larger modulation amplitudes seen for the ethylene

data. In part this is attributable to the fact that the C-C bond length in acetylene is shorter than in ethylene, so as both of these bond lengths are significantly shorter than that of the Si-Si dimer, the C emitter atoms are further from the true atop sites for adsorbed acetylene, leading to weaker PhD modulations. In optimizing the fit of the theoretical simulations to the experimental data, however, the vibrational amplitudes of the emitter and scatterer atoms are adjusted, and these have a marked effect on the modulation amplitudes. This optimization led to very substantially larger vibrational amplitudes of the adsorbed acetylene than the adsorbed ethylene. Specifically, the optimized values of the mean-square vibrational amplitudes of the C emitter atoms perpendicular to the surface were found to be $0.003 \pm 0.002 \text{ \AA}^2$ for ethylene and $0.010 \pm 0.007 \text{ \AA}^2$ for acetylene. A small contribution to this difference could be due to the higher temperature (100 K) at which the acetylene data were recorded relative to that used for the ethylene (60 K), but the conclusion is still surprising. In view of the possibility of cooccupation of multiple adsorption sites which has now been raised, we may consider an alternative explanation for the very weak PhD modulation amplitudes. In particular, if a second adsorption site is occupied which places the C emitters rather far from atop near-neighbor Si atoms, the PhD modulations from this site are likely to be weak near normal emission. Adding (incoherently) the (absence of) PhD modulations from this site to those from the bridge site will then lead to an attenuation of the normal emission modulations from the bridge site acetylene. In this case a comparably good fit to the experimental data may be obtained without the need for anomalously large emitter vibrational amplitudes.

Inspection of the acetylene data of Figs. 5 and 6 reveals another significant factor. Clearly in Fig. 6 the theoretical fits to the experimental PhD data are very significantly better for the ethylene than the acetylene, a qualitative judgement reinforced by the *R*-factor values which are an unusually low value of 0.057 for the ethylene data set and a relatively poor value of 0.40 for the acetylene. In part this reflects the weak modulation amplitudes which make the statistical noise in the experimental data as well as any defects in the modelling more important. What is clear in Fig. 6, however, is that the parts of the spectra where the experiment-theory agreement is worst is in the same 120–180-eV energy range in which the room temperature data differ most strongly from the low-temperature data (Fig. 5). In particular, the weak feature of the low-temperature data which appears much stronger in the room temperature data is almost completely absent from the bridge-site calculations. This leads to a further consideration: is there a second adsorption site which is responsible for this feature in the PhD spectra which is co-occupied at both temperatures, but is more populated at room temperature?

Before explicitly considering the consequences of two-site models, however, we have first considered the extent to which single site models can provide an adequate description of the new room temperature PhD spectra. This also allows us to address the question of the completely different conclusions arising from our original analysis and that of Xu *et al.*, apparently performing a very similar experiment although using quite different methods of data analysis. We remarked

FIG. 7. Comparison of C 1s PhD spectra obtained at normal emission at 100 K (LT) and room temperature (RT) (bold curves) with a normalized spectrum taken from Ref. 35 (gray curves).

earlier that a comparison of the raw experimental data from the two original analyses indicated pronounced differences. These differences appear to be much less acute if we compare the two room-temperature data sets. Unfortunately, in their original paper Xu *et al.*³⁵ show only two raw (unnormalized) PhD spectra, recorded at normal emission and at 60° polar angle in an unspecified azimuth. Our own measurements at these large polar angles all show very weak modulations which consequently have poor signal-to-noise ratios, but without information on the normalization and smoothing procedures (see below) used by Xu *et al.* it is difficult to know if this apparent difference is significant. A more direct comparison of the normal-emission data is possible, however, and is shown in Fig. 7, normalizing the spectrum of Xu *et al.* to have the same average amplitude as our own room temperature spectrum. The spectrum of Xu *et al.* is much smoother than our own data, perhaps the result of some processing of the data, and there seems to be a slight energy offset which may arise from the fact that we have had to convert the abscissa from electron wave vector in their original paper to energy, with no knowledge of the inner potential used in the original conversion from the experimental energy scale. Nevertheless, the agreement with our room-temperature spectrum is clearly quite good, whereas the agreement with our original low temperature data, as noted earlier, is poor. Of course, we are not able to compare other spectra from the much larger data set recorded at many different emission directions, but Fig. 7 does suggest that the surfaces studied in the two independent investigations of acetylene on Si(100) at room temperature may well be quite similar.

B. Single-site models and the room-temperature data

We have therefore first performed calculations to compare the room-temperature PhD data set with the results of multiple-scattering simulations for the four different basic adsorption site models of Fig. 1. The results are summarized in Table II. The first row of the table shows the structural parameters (and their associated precision) taken from the original analysis of the low-temperature (LT) data set³⁶ but

TABLE II. Summary of results for single-site fits to the PhD data. The first row shows the structural parameters associated with the original bridge site model derived from fitting the low-temperature data alone. $R(\text{LT})$ and $R(\text{RT})$ are the R -factor values obtained when comparing the experimental LT and RT data sets with the calculated spectra for this structure. R is the combined R -factor value for both experimental data sets. For the rotated bridge, rotated pedestal, and pedestal models there are then two rows: the first gives the structural parameters which gave the best fit to the new room temperature data alone, while the second line shows the structural parameter range given by recent total energy calculations (Refs. 37 and 44–47) for these structures, and the R -factor values obtained if one specific set of these parameters (not in parentheses) is used to calculate a set of PhD spectra with no adjustable parameters. In the final row the results of fitting the room temperature data to the pedestal model, constrained to include the specific parameter values given by Xu *et al.* (Ref. 35) ($z_{(\text{C-Si}, 2\text{nd layer})} = 1.6 \text{ \AA}$, $z_{(\text{C-Si}, 3\text{rd layer})} = 2.8 \text{ \AA}$, $d_{\text{C-C}} = 1.20 \text{ \AA}$) are shown. Notice that an R -factor value of 1.0 indicates there is no correlation between experimental and theoretical spectra.

	$d_{\text{C-C}}$ ($\text{\AA}$)	$d_{(\text{C-Si,D})}$ ($\text{\AA}$)	$d_{(\text{Si,D-Si,D})}$ ($\text{\AA}$)	$\langle u^2(c,z) \rangle$ ($\times 10^{-3} \text{ \AA}^2$)	R	$R(\text{LT})$	$R(\text{RT})$
bridge [LT fit (Ref. 36)]	1.36 ± 0.19	1.83 ± 0.04	2.44 ± 0.58	10 ± 7	0.51	0.40	0.64
bridge (RT fit)	1.26 ± 0.18	1.84 ± 0.08	2.09 ± 0.59	1.3 ± 10			0.57
bridge-theory (range)	1.36 (1.35–1.37)	1.89 (1.89–1.91)	2.37 (2.34–2.37)	4	0.64	0.57	0.72
rotated bridge (RT fit)	1.25 ± 0.21	2.49 ± 0.13	3.00 ± 0.54	$5 (+7/-5)$			0.45
rotated bridge- theory (range)	1.37 (1.36–1.37)	1.92 (1.90–1.92)	2.43 (2.37–2.44)	2	1.13	1.23	1.07
rotated pedestal (RT fit)	1.11 ± 0.35	1.82 ± 0.13	1.84 ± 0.76	$5 (+13/-5)$			0.61
rotated pedestal –theory (range)	1.57 (1.54–1.60)	2.01 (1.97–2.01)	2.32 (2.28–2.36)	1	1.01	0.96	1.08
pedestal (RT fit)	1.20 ± 0.42	2.17 ± 0.05	2.80 ± 0.56	10 ± 10			0.57
pedestal–theory (range)	1.58 (1.58–1.62)	2.07 (2.00–2.07)	2.32 (2.34–2.37)	2	0.99	0.97	1.00
pedestal [Xu <i>et al.</i> (Ref. 35)]	1.2	fitted (2.13)	fitted (2.44)	fitted (10)			0.98

includes not only the value of the R -factor obtained in this original analysis, $R(\text{LT})$, but also the value, $R(\text{RT})$ obtained when spectra calculated with these structural parameters are compared with the room-temperature (RT) data set. The value of $R(\text{RT})$ is large, entirely reasonable if we note that these theoretical spectra (Fig. 6) completely fail to show the strong peak around 140 eV seen in the normal-emission room-temperature spectrum (Fig. 5). Also shown in this row is the value of the R factor, R , obtained when summed over both the low and room temperature data sets. The value of 0.51 is clearly not very low, but will prove a useful reference value in the discussion which follows later.

In the following rows of Table II are shown the results of optimizing the fits of the multiple-scattering calculations to the room-temperature data based on all four models, initially adjusting the structural parameters to optimize the fit in each case. The key parameters varied are the C-C bond length, $d_{\text{C-C}}$ within the adsorbed acetylene, the distance of each C atom to the nearest-neighbor Si atom at one end of the Si dimer, $d_{(\text{C-Si,D})}$, and the Si-Si dimer bond length $d_{(\text{Si,D-Si,D})}$. The principle vibrational parameter adjusted was $\langle u^2(c,z) \rangle$, the mean-square vibrational amplitude of the C emitter atom perpendicular to the surface. This table also shows the structural parameter values obtained from several recent total energy calculations of these different structural models; the ranges of values from five recent independent

calculations^{37,44–47} are shown, but in general these ranges are very small, reflecting the excellent agreement of the different calculations in terms of optimised geometries. For reference, the R -factor values obtained when calculations are performed using these theoretically derived structural parameter values are also shown, although with the exception of the bridge site all the resulting values are close to unity and indicate no meaningful description of the experimental data. Clearly, even for the geometries optimised to fit the PhD data, none of the R -factor values associated with these single-site fits are very low, but the actual spectra do show that the two pedestal geometries are able to reproduce the normal-emission PhD modulation around 140 eV which we have identified as a kind of spectral fingerprint of the room-temperature data. Figure 8 shows the comparison of the room-temperature data set and the best-fit simulated spectra for these two cases. Model calculations show that the origin of this spectral feature is scattering from the third-layer Si atoms directly below the midpoint of the C-C axis in these two adsorption sites. There are, of course, detailed differences between the simulated spectra; in particular, the pedestal site gives a superior fit to the normal emission spectrum (as reflected in a single-spectrum R factor of 0.41 compared with 0.52 for the rotated pedestal site), but provides a much worse fit to the 30° spectrum (single-spectrum R factor of 0.84 compared with 0.41 for the rotated pedestal site). The

FIG. 8. Comparison of the C 1s PhD modulation spectra obtained from acetylene adsorbed at room temperature with the results of calculations for the best-fit single site pedestal and rotated pedestal adsorption geometries (see Table II).

bridge site fails to provide a reasonable fit to the 140-eV normal-emission feature at any realistic bond lengths. The same is true for the rotated bridge site. For this geometry, an unconstrained fit actually gives the lowest R -factor value in Table II, but the C-Si bond length has an unrealistically large value of 2.49 Å. In this situation the acetylene molecule is raised high above the surface, and in the rotated bridge site scattering from the second-layer Si atoms almost directly below the center of the C-C axis (in this case there is an additional lateral offset due to the dimerisation of the outer-layer Si atoms to which the C atoms are bonded) can then produce the characteristic PhD spectral feature. However, in this geometry the acetylene molecule is far too high above the surface for the resulting (bonding) distance between the Si dimer atom and the acetylenic C atom to represent a physical bond.

The final row of Table II shows the result of comparing the room-temperature PhD data with the results of simulations based on the structural model proposed by Xu *et al.* These authors identified the pedestal site as fitting their data, but also gave values for the C-C distance and the layer spacing of the C emitter atoms to the second and third-layer Si

FIG. 9. Comparison of the C 1s PhD modulation spectra obtained from acetylene adsorbed at room temperature with the results of calculations for the pedestal site using the structural parameters given by Xu *et al.* (Ref. 35).

atoms. We have therefore conducted calculations based on this model in which the only unknown structural parameter is the Si-Si dimer distance (which also changes the C-Si dimer bonding distance for a fixed layer spacing). The result of this calculation is a very poor fit to the data (Fig. 9), with the low energy modulations in antiphase, and an R -factor value of 0.98, indicating no meaningful correlation of theory and experiment. Notice that the Si-Si dimer distance in this fit is actually much closer to the expected value than the comparable distance found in the optimized pedestal-site fit. It is certainly possible that in interpreting the “holographic images” obtained from the PhD data by Xu *et al.*, these authors were influenced by the expected values of bond lengths in relating apparent scatterer positions to an actual adsorption geometry. Of course, despite the comparison of Fig. 7, we cannot be sure that their data were collected from an identical surface to our own. What we can conclude is that the detailed model of Xu *et al.* is wholly incompatible with our experimental data.

C. Multiple-site models

The preliminary results of our attempts to fit new-room temperature PhD data by a single-site model can therefore be summarized as follows. First, none of these models provides an adequate description of the data (all the R -factor values are unacceptably large). Second, however, some of these sites can provide an explanation for the strong PhD modulation seen around 140 eV in normal and near-normal emission which is especially strong in the room-temperature data set and is not reproduced by the bridge site calculations. This leads us to explore models involving a mixture of bridge site adsorption (which clearly provides quite a good description of the low-temperature data in terms of the main modulation features) and the other models each of which, to some extent, is able to reproduce the characteristic features of the room

TABLE III. Summary of results for fits to the PhD data involving co-occupation of the bridge site and one of the three other sites illustrated in Fig. 1. In all cases the structural parameters for the bridge site were fixed at the values previously found to give the best fit to the low-temperature data which are also in good agreement with the theoretical values (see Table II) while the vibrational amplitude of the C emitters was set to a value close to that found in the previous PhD study of ethylene adsorbed on Si(100). These parameter values are shown in the first row of the table. The following rows show information relating to the different two-site models. For each two-site model the structural parameters were adjusted to optimize the fit to both the low and room temperature PhD data, allowing only the fractional population of the bridge site to be dependent on temperature. For each model there are three rows. The first row shows the structural parameter values leading to the lowest value of the R -factor, giving first the optimum fraction of bridge site occupation at each temperature and then the values of the structural parameters associated with the second site of the two-site model. The second row for each site shows the results of a similar fit in which some structural parameters were constrained to be closer to the theoretical (total energy calculation) parameter values (Refs. 37 and 44–47) which are shown in the third row.

	% bridge LT/RT	$d_{\text{C-C}}$ (Å)	$d_{(\text{C-Si,D})}$ (Å)	$d_{(\text{Si,D-Si,D})}$ (Å)	$\langle u^2(c,z) \rangle$ ($\times 10^{-3} \text{ Å}^2$)	R
bridge parameters: all combined models		1.36	1.83	2.44	4	
bridge+rotated pedestal						0.45
rotated pedestal	69/37	1.28 ± 0.42	1.74 ± 0.12	2.05 ± 1.00	1 (+74/−1)	
bridge+rotated pedestal						0.46
rotated pedestal (constrained)	69/37	1.40	1.81 ± 0.08	2.40	1 (+28/−1)	
rotated pedestal theory		1.54–1.60	1.97–2.01	2.28–2.36		
bridge+pedestal						0.40
pedestal	65/37	1.19 ± 0.40	2.17 ± 0.07	2.82 ± 0.93	2 (+20/−2)	
bridge+pedestal						0.44
pedestal (constrained)	65/37	1.40	2.07 ± 0.07	2.40	2 (+30/−2)	
pedestal theory		1.58–1.62	2.00–2.07	2.34–2.37		
bridge+rotated bridge						0.39
rotated bridge	55/19	1.31 ± 0.37	2.46 ± 0.17	3.09 ± 0.98	5 (+19/−5)	
bridge+rotated bridge						0.48
rotated bridge (constrained)	68/49	1.40	1.84 ± 0.21	2.40	10 (+64/−10)	
rotated bridge theory		1.36–1.37	1.90–1.92	2.37–2.44		

temperature data. Clearly, a two-site model potentially introduces a large number of additional fitting parameter, and with too many such parameters there is likely to be a major problem of uniqueness. One may also question whether a fit based on too many parameters is fundamentally meaningful. Our starting point was therefore to assume that the *same* two models (with identical structural parameter values) should fit both the low- and room-temperature data, the only difference between the two temperatures being the relative occupation of these two sites. We have also assumed that the structural parameters of the bridge site are those which we have already found to provide a good description of the low-temperature data. Notice that these structural parameter values are in quite good agreement with the values predicted by theoretical total-energy calculations. In the two-site fitting, however, we have reduced the amplitude of the C emitter

atom vibrations from the value found in the original optimised fit to the low temperature data alone; we have already noted that this seemed to be unusually large, and in our calculations a value of 0.004 Å^2 was used, similar to that used in fitting the ethylene PhD data which is widely believed to occupy only bridge sites.

The results of this two-site fitting of the complete (low and room temperature) C 1s PhD data set are summarized in Table III. For each alternative second site we show results for fits only constrained in the way we have just described, and for a second set of calculations in which some of the structural parameters of the second sites were additionally constrained to values more in keeping with the predictions of the total-energy calculations (the results of which are included for comparison). While none of the global R factors in this table are especially low (a consequence, at least in

FIG. 10. Comparison of C 1s PhD modulation spectra obtained from acetylene adsorbed at both 100 K (upper set of spectra) and room temperature (lower set of spectra) with the results of calculations for the constrained bridge plus pedestal and bridge plus rotated pedestal models.

part, of the rather weak experimental modulations and the associated degraded signal-to-noise ratio), the values are lower than the pure bridge site R -factor value for fitting both data sets of 0.51, and are probably acceptable for this data set. The lowest R factors correspond, of course, to the fits with the fewest constraints, but the associated structural parameter values are of variable acceptability. In particular, the lowest R -factor of Table III, 0.39, corresponds to the optimized bridge plus rotated bridge site solution, but the C-Si nearest-neighbor bonding distance for the rotated bridge site in this solution is even longer than in the optimized single-site fit to the room-temperature data; the value of 2.49 Å is clearly far too long to represent a chemical bond. For the two pedestal site combinations, the optimized structural parameter values are somewhat closer to theoretical expectations, but still show significant deviations. In the more constrained fits some of the values of the constrained parameters were chosen as a compromise between the values expected on the basis of theory (which gave poor fits to the PhD data—see Table II) and the values which gave optimal fits to the PhD data. A clear conclusion from these constrained fits is that mixtures of the simple bridge site with either of the pedestal sites offer acceptable descriptions of our complete PhD data set. Figure 10 shows comparison of the experimental and calculated PhD spectra for these two alternative solutions. Moreover, a rather consistent feature of all of these two-site fits is that at low temperature the bridge site dominates with some 65% of the population, whereas at room temperature the population is inverted with the second site reaching a similar fractional occupation.

Finally, in view of earlier suggestions that there may be at least *three* different sites cooccupied, we have considered the possibility of a mix of all four of the local sites of Fig. 1.

Clearly in this case a simultaneous optimization of the many structural parameters is impossible, and indeed with so many parameters the value of the solution would also be questionable. We have therefore fixed all the structural parameter values at those given by the total-energy calculations given in Table II. While these structures led to poor R -factor values for the single-site fits, the same is not necessarily true for the mixed site picture. The result of this procedure, in which only the relative occupations of the four sites could be varied to optimize the fit with experiment gave for the bridge:rotated bridge:pedestal:rotated pedestal occupations the values of 62%:7%:0%:31% for the low-temperature data, with $R(\text{LT})=0.45$, and 63%:34%:0%:3% for the room-temperature data, but with $R(\text{RT})=0.66$. For the low-temperature data this model thus favors a mixture of essentially bridge and rotated pedestal with site occupations similar to those of the partially constrained two-site model. More surprisingly, this model favors a combination of bridge and rotated bridge, the majority state being bridge; this differs fundamentally from the constrained two-site optimization of Table II, but the R -factor value in the present case is very much larger and so not obviously in conflict with the earlier conclusions.

IV. DISCUSSION AND CONCLUSIONS

Our starting point in this PhD study of acetylene adsorbed on Si(100) was the conflict in conclusions between our own earlier investigation conducted at low temperature³⁶ and the results of Xu *et al.*³⁵ conducted at room temperature using essentially the same experimental technique but a different method of data evaluation. Combined with the results of STM studies at room temperature which appeared to identify

cooccupation of two or three distinctly different sites (notably in Ref. 40) this raised the question of whether the apparent conflict of the two PhD investigations may be reconciled by multiple-site occupation, a possibility involving different dominant sites at different temperatures.

Our experimental results, measured at low and room temperature, provide clear evidence that the sample temperature *does* lead to surfaces which are structurally different, at least to some degree. Moreover, careful characterization of these surfaces by high-resolution SXPS indicates that these differences are unlikely to arise from the creation of fundamentally different C-containing surface species, caused either by thermally activated surface reactions or radiation-induced processes. A constrained fitting of the complete PhD data set based on cooccupation of the bridge site and a second site provides a reasonable description of the data with the second site being either the pedestal or rotated pedestal. In neither case are the structural parameters values exactly those one would expect on the basis of the published total-energy calculations, but both are quite close and it is difficult to regard either model as clearly preferable. Of course, based on the STM evidence, even a two-site model be an overly simplified description of the true surface structure.

In considering multiple-site models, we should also point out some intrinsic limitations of the PhD technique to provide a unique structural solution for such a complicated situation. As with all structural techniques, PhD works best when the emitter atoms occupy single highly symmetric sites. In such situations, one generally observes very strong (typically $\pm 40\%$ but sometimes significantly larger) modulations in emission directions corresponding to 180° backscattering by the nearest-neighbor substrate atoms. Indeed, in such cases identifying these directions alone by the strong long-period modulations provides the basis of a first-order adsorption site identification.⁶⁹ In the case of emitters which occupy lower symmetry sites some of this simplicity is lost, because averaging over symmetrically equivalent directions (or equivalently adsorption domains) relative to the substrate causes an attenuation of the modulation amplitudes and no longer guarantees that the strongest modulations will be seen in directions corresponding to the nearest-neighbor backscattering directions. For molecular adsorbates such low-symmetry emitter sites are common; in the case of acetylene adsorbed on Si(100) with its C-C axis parallel to the surface, low-symmetry emitter sites are inevitable, due to the mismatch of the C-C distance to any lateral periodicity of the Si(100) substrate. Notice, incidentally, that near atop emitter sites remain most favorable, because averaging over azimuthally equivalent directions of domains has no attenuating effect at normal emission, the direction close to the favored backscattering direction. In the case of multiple (co-occupied) adsorption sites, the incoherent summation of the PhD spectra from each site clearly makes these problems even more severe. Emission directions which lead to the largest modulation amplitudes for one site will involve the addition of more weakly modulated spectra from other sites, causing attenuation of modulation amplitudes in even these “signature” directions for one of the sites. Cooccupied low-symmetry emitter sites, the scenario now proposed for

FIG. 11. Variation of relative site populations and R -factor value for optimized fits to the complete set of low and room-temperature PhD spectra for the model based on cooccupation of the bridge and rotated pedestal sites in which the mean-square vibrational amplitude of the C emitter in the bridge site was set to different values and the R -factor minimized by adjusting the relative population of the two sites. The variation in the R factor is shown in gray with ordinate labeling on the left. The pedestal site fractional populations are shown in bold with ordinate labeling on the right.

acetylene on Si(100), clearly comprise a particularly unfavorable situation. One way out of this problem in general is to exploit the shifts in the photoelectron binding energies which accompany adsorption of the same species in different sites, or different species containing the same emitter atoms, to obtain chemical-state specific PhD spectra from each component (e.g., Ref. 70). Unfortunately, as we have shown here, there are no detectable changes in the C $1s$ photoelectron binding energy between the two (or more) coadsorbed acetylene species on Si(100), and the ability to resolve any such differences appears to be limited by intrinsic, rather than instrumental, broadening mechanisms.

Bearing in mind these limitations, what are we able to conclude from our measurements concerning the structure of acetylene adsorbed on Si(100)? Our low-temperature data, in particular, show that there must be a significant fraction of the adsorbed molecules in bridge sites, with structural parameter values close to those found in our original optimised fit to the data. Second, we see a clear difference in the PhD spectra around normal emission for room-temperature adsorption which cannot be accounted for by bridge site adsorption. Some occupation of pedestal or rotated pedestal sites can account for these effects, and indeed one (or both) of these sites is apparently the majority state at room temperature, although not with the structural parameter values deduced by Xu *et al.* One aspect of our analysis concerns the true value of the vibrational amplitudes of the C emitter atoms (or more strictly the true *relative* amplitudes of vibration relative to the Si scatterer atoms, because vibrational correlations can be important in PhD). As we have already described, the low-temperature PhD data can be described essentially equally well by bridge site adsorption alone with large vibrational amplitudes to attenuate the PhD modulations, or cooccupation of these bridge sites with smaller vibrational amplitudes, the modulation amplitudes being suppressed by emission from C atoms in other sites which do not lead to strong PhD modulations near normal emission. In this sense it is clear that the relative occupation of the two

sites in a model involving a bridge site and a second site will be influenced by the choice of the bridge-site vibrational amplitude. To illustrate this point, Fig. 11 shows the results of some calculations for the bridge plus rotated pedestal site model, in which the bridge-site C emitter vibrational amplitude has been set to several different values, and the relative populations of the two sites adjusted (for identical geometries for the two sites) to minimize the R factor comparing the calculated spectra with the complete set of PhD spectra at both sample temperatures. As might be expected from the above qualitative description, the optimal fractional occupation of the rotated pedestal site increases (and thus that of the bridge site falls) as the vibrational amplitude of the C emitter in this site is reduced, although even if we assume there is no vibrational amplitude at all, the bridge site remains the majority species at low temperature. Interestingly the lowest R -factor actually corresponds to the large vibrational amplitude used for the original fit of the low temperature alone, a solution corresponding to 90% bridge sites at low temperature. Figure 11 should not, however, be taken as an indication of the true vibrational amplitude nor the true relative populations, but rather as an indication of the underlying coupling of these parameters which limits our ability to complete a precise structure determination.

One potentially surprising feature of our analysis is that the rotated bridge site appears not to be favored in our models. The STM study of Mezheny *et al.*⁴⁰ has been interpreted as indicating this is the majority state on the surface, and several of the total-energy calculations suggest that this may be the lowest energy configuration at high coverages (though our own coverage estimate suggests we do not typically exceed 0.5 ML). We should stress, however, that the rotated bridge site is not wholly excluded by our analysis. What our modeling indicates is that the rotated bridge site cannot account for the dominant PhD modulations seen at low temperature and cannot (at realistic bond lengths) account for the main new features seen in the room-temperature data. In fact the rotated bridge site with interatomic distances compatible with theoretical expectations does not lead to any strong modulations near normal incidence which correlate with the measured PhD spectra. However, a partial occupation of this site may also provide an alternative explanation for the apparent need for large vibrational amplitudes for the bridge site. We can therefore state that while our PhD data provide no specific evidence to support the presence of rotated bridge sites, the fact that such sites would not lead to strong effects in our measurements means that we cannot discount possible partial occupation of these sites. Unfortunately, this possibility would imply a three-site model, and we do not feel a quantitative evaluation of such a complex model is realistic. In this regard, the highly constrained four-site model we have tested fails to lead to an acceptable R -factor value for the room-temperature data.

One further question which we are regrettably unable to answer is whether the change in relative site occupation at low and room temperatures is due to a change in equilibrium concentrations or to (at least) one of these situations being metastable. Varying the Si sample temperature in a reason-

ably rapid and well-characterized fashion in our experiments is difficult. Initial cooling from a room-temperature stage is slow, and while it is straightforward to heat a sample held at low temperature and recool quite rapidly, it is difficult to know to what temperature the sample has been heated. Measuring the Si sample temperature accurately has proved difficult because of its poor thermal conductivity, and we have relied on measurements of the temperature at the metallic clips holding the Si sample in place, which provides the heat path to the liquid-gas filled cooling tank via a copper braid. This clip temperature is likely to be a good measure of the sample temperature after long-term thermal equilibration, but not during rapid thermal cycling.

In view of our comments on the limitations of the PhD technique to provide a unique solution to this complex multiple site adsorption system, we should comment briefly on the potential of other techniques. In truth, for a system lacking long-range order in the adsorbate, and having no detectable photoelectron binding-energy chemical shift between the different adsorption sites, it is doubtful that any other quantitative surface structural method can even provide as much information as PhD. Notice that further PhD data could, in principle, be gained from the Si 2*p* photoemission signal, since there appear to be small shifts in the associated photoelectron binding energy associated with the surface Si atoms bonded to the adsorbed acetylene.⁵² However, the associated chemical shifts are too small to be likely to provide useful PhD data over a significant electron energy range, and there is no evidence that different shifts are associated with the different coexistent bonding sites. Vibrational spectroscopy is expected to show some significant differences in the spectral fingerprints of the different sites, and insofar as the theoretical calculations can predict these frequencies sufficiently accurately, this ought to help to characterize the different states present, even if there is no direct way of determining the exact local geometries. STM clearly offers the important advantage of detecting the spatial inhomogeneity directly and identifying distinct local features; combined with a theoretical modeling of the STM images expected for different geometries this is potentially a powerful method, although recent publications suggest that this modeling, and matching the model calculations to the observed images, is not without controversy. Perhaps the most conclusive approach would be the combination of atomic-scale imaging and vibrational spectroscopy achieved in some recent scanning tunneling spectroscopy investigations (e.g. Ref. 71). Even in this case, quantitative structural information would not be obtained directly from the experiments, but positive site identification ought to be achieved.

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