

Kinetically Favored Adsorbate Ordering: Hydrogen and Iodine on the Si(100)-2 × 1 Surface

Kirill M. Bulanin, Ankit G. Shah, Danesha R. Fitzgerald, Douglas J. Doren, and Andrew V. Teplyakov*

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

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An equimolar mixture of hydrogen and iodine atoms adsorbed on the Si(100) surface is generated by adsorption of iodoethane and annealing to 570 K (which causes ethyl groups to undergo hydrogen elimination and ethylene to desorb). Multiple internal reflection–Fourier transform infrared spectroscopy (MIR–FTIR) shows that the adsorbed hydrogen is distributed among several configurations. After annealing to 700 K, the spectrum shows only a single configuration, which is assigned to surface dimers that are occupied by one hydrogen and one iodine atom. Density functional theory calculations indicate that these mixed-occupation dimers are not energetically favored over other doubly occupied configurations (two H atoms or two I atoms). This evidence indicates that, in contrast to other ordering phenomena in surface adlayers, the ordering in this case is a kinetic effect and is not driven by thermodynamics.

Introduction

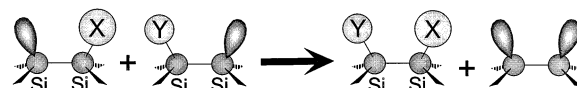
Adsorbate ordering on surfaces can be caused by several different kinds of interactions. For example, on metal surfaces, ordering is typically a consequence of interactions between adsorbates.¹ In the case of adsorbate atom pairing on Si(100), ordering is driven by interactions between unoccupied surface sites (dangling bonds).² In this latter case, a weak π interaction between dangling bonds on the same dimer favors the products of Scheme 1 by about 5 kcal/mol^{3–6} when X = Y = H, with similar values expected for other adsorbates. However, in all these cases, adsorbate ordering is determined by thermodynamic considerations. Here, we demonstrate a novel adsorbate ordering effect and show evidence that it is kinetic, and not thermodynamic, in origin.

Methods

Experimental Methods. Experiments were done in a fully equipped ultrahigh vacuum chamber (base pressure of 3×10^{-10} Torr) coupled to a Fourier transform infrared (FTIR) spectrometer with an external mercury cadmium telluride (MCT) detector configured to record the vibrational spectra in a multiple internal reflection mode. The Si(100)-2 × 1 crystal (25 mm × 20 mm × 1 mm, Harrick Scientific Corp.) with 45° beveled edges was mounted on a sample holder capable of heating the sample to 1150 K. The sample was prepared by sputtering with 0.5 kV Ar⁺ ions at room temperature followed by annealing to 1150 K. A clean well-ordered Si(100)-2 × 1 sample was obtained, as confirmed by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). Infrared spectra were recorded at room temperature with 4 cm⁻¹ resolution and at least 4096 scans per experiment.

Computational Methods. Electronic structure calculations were done using the B3LYP hybrid density functional^{7,8} as implemented in the Gaussian 98 suite of programs.⁹ The

SCHEME 1



Stevens–Basch–Krauss^{10,11} effective core potentials were employed, with a triple- ζ valence basis set (CEP-121G). Diffuse functions were added to all atoms except iodine; polarization functions were added to all atoms. Two models for the surface were used, a single-dimer cluster model (Si₉D₁₂) and a two-dimer cluster model (Si₁₅H₁₆). The single-dimer cluster model had C_s symmetry (C_{2v} for models doubly occupied by H or I). Calculated vibrational frequencies were scaled by 0.9695; this value gives the best fit of symmetric and antisymmetric Si–H stretch frequencies predicted with a single dimer cluster model (Si₉D₁₂H₂, representing species IV of Figure 1) to the corresponding literature values for a fully occupied monohydride surface.^{12–15} Zero-point energy (ZPE) corrections are included in the energies reported from the single-dimer models. Since these corrections are negligible (≤ 0.05 kcal/mol), they were not calculated for the two dimer models.

Results and Discussion

Spectral Assignments. As shown elsewhere,¹⁶ adsorption of iodoethane on Si(100)-2 × 1 at room temperature produces surface-bound iodine and ethyl groups (e.g., I; see Figure 1). IR spectra show no Si–H species after dosing at room temperature. β -Hydrogen elimination to produce ethylene is the dominant reaction pathway for silicon surface-bound ethyl groups.^{17–20} Ethylene desorbs upon heating the surface, leaving iodine (as confirmed by AES) and hydrogen in equal numbers, forming structures such as II–V. The characteristic vibrational features of the C–H stretch region disappear on annealing to 570 K, and the Si–H stretch intensity increases concurrently, as expected. The integrated intensity of the ν (Si–H) bands is plotted in Figure 2 as a function of the annealing temperature. Above 700 K, the integrated ν (Si–H) peak intensity decreases

* Corresponding author: Tel (302) 831-1969; fax (302) 831-6335; e-mail andrewt@udel.edu.

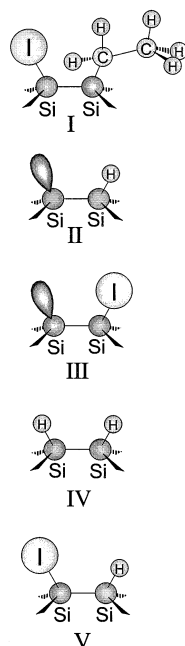


Figure 1. Schematic diagram of typical species present in these experiments. **I**, iodine and ethyl after adsorption of ethyl iodide (this example is for illustration only; the two species need not be bound to the same dimer); **II**, singly occupied dimer with hydrogen; **III**, singly occupied dimer with iodine; **IV**, doubly occupied dimer with hydrogen; **V**, mixed occupation dimer, i.e., doubly occupied dimer with hydrogen and iodine.

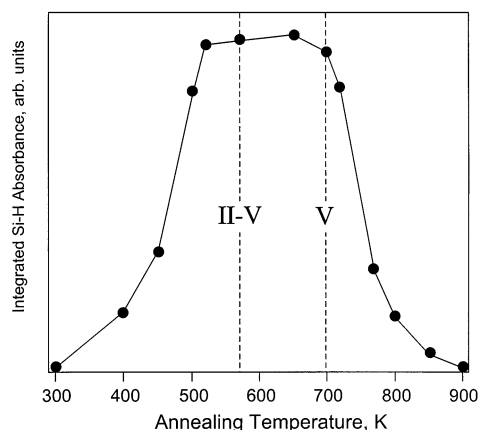


Figure 2. Integrated intensities of Si-H stretch absorption (measured at room temperature without a polarizer) as a function of annealing temperature. The vertical dashed lines indicate the temperatures at which the spectra in Figure 3 were taken. The roman numerals refer to the species in Figure 1 that are present at these temperatures.

due to recombinative hydrogen desorption. However, the total amount of adsorbed hydrogen is practically unchanged between 570 and 700 K.

There are clear changes in the distribution of hydrogen on the surface between 570 and 700 K, as indicated by polarization-dependent multiple internal reflection-Fourier transform infrared (MIR-FTIR) studies. The spectra in Figure 3 show differences in the shape and peak position of the $\nu(\text{Si-H})$ features as a function of annealing temperature. The polarization-dependent IR studies shown here all began with a saturation exposure of iodoethane, but we have confirmed the same behavior for exposures of less than half the saturation value.¹⁶ The solid curves in Figure 3 compare s- and p-polarization MIR-FTIR spectra in the Si-H stretch region after briefly annealing to 570 K. At least three different species are present.

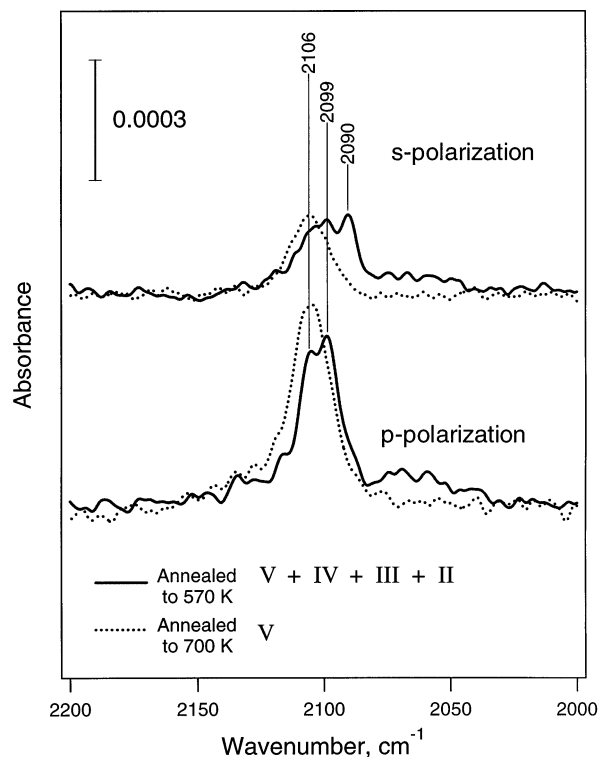


Figure 3. MIR-FTIR spectra in the Si-H stretch region with s-polarized (upper curves) and p-polarized (lower curves) light. The solid curves show spectra after annealing to 570 K, where all ethyl groups have been removed from the surface, so that only I and H remain. Dotted curves show spectra after annealing to 700 K.

The peaks at 2099 and 2090 cm^{-1} correspond, respectively, to the well-known symmetric and antisymmetric stretches of a dimer occupied by two hydrogen atoms, **IV**.¹²⁻¹⁵ This assignment is supported by the polarization dependence of the two peaks: In s-polarization, the 2090 cm^{-1} antisymmetric stretch peak dominates, while only the 2099 cm^{-1} symmetric stretch peak is present in p-polarization. It is not clear how to assign the peak at 2099 cm^{-1} in s-polarization. On an ideal surface completely covered with the monohydride, a peak at this frequency should appear only in p-polarization. The presence of this peak in s-polarization and the broad feature near 2065 cm^{-1} in s- and p-polarization (which has previously been assigned to defect sites¹⁴) may indicate the presence of steps or defects. For our purposes, definitive assignment of these peaks is not necessary, since there are no features distinguishable at these frequencies after annealing to 700 K.

To assign the spectral feature at 2106 cm^{-1} , we have calculated vibrational frequencies for some cluster models of candidate species, using density functional theory (DFT). We have also considered models with a singly occupied dimer, **II** (one H atom and one dangling bond), and a mixed-occupation dimer, **V** (one I atom and one H atom), using the same scaling factor. The predicted Si-H stretch frequency on the singly occupied dimer is 2092 cm^{-1} (Table 1), and this species may contribute to the observed spectra. STM investigations of hydrogen on $\text{Si}(100)-2 \times 1$ show that such singly occupied dimers exist on the surface even after annealing to 600 K.^{2,21} The predicted frequency for mixed-occupation dimers is 2108 cm^{-1} (Table 1), and we have assigned the feature at 2106 cm^{-1} to this species.

The IR spectra change significantly after annealing to 700 K, showing only a single peak at 2106 cm^{-1} . This is the peak that we have assigned to mixed-occupation dimers. The peak

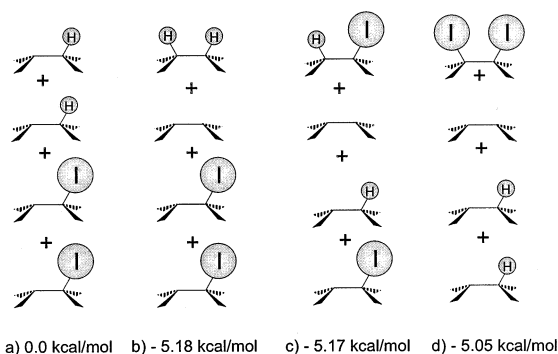


Figure 4. Pairing energies of adsorbed H and I atoms in several configurations, relative to independent, singly occupied dimers (a). Energies are calculated, with the single-dimer model of the surface, at the B3LYP/CEP-121G level and include corrections for zero-point energy. Note that the energies of each dimer are calculated independently, with no interactions between dimers.

TABLE 1: Comparison of Predicted Vibrational Frequencies of Possible Si–H-Containing Surface Species with Experimentally Measured Values

surface species	vibrational frequencies (cm ⁻¹)	
	predicted	measured
SiH–SiH (asym) (IV)	2090	2090
SiH–SiH (sym) (IV)	2096	2099
Si(•)–SiH (II)	2092	
SiI–SiH (V)	2108	2106

position and shape are independent of polarization, consistent with this assignment. Furthermore, the peaks at 2090 and 2099 cm⁻¹, characteristic of dimers that are doubly occupied by hydrogen atoms, are gone. Thus, annealing drives the surface hydrogen to pair with iodine, rather than with other hydrogen atoms.

Energetics of Pairing. To understand the origin of this ordering, we have used density functional theory to compare the energy of various arrangements of H and I on Si(100). Calculations with a single-dimer cluster model were first used to compare the relative energies of various arrangements of adsorbed H and I atoms, as shown in Figure 4 for several examples. For a fixed number of H and I atoms, arrangements with the same number of doubly occupied dimers have essentially the same energy, whether the occupying atoms are both H atoms, both I atoms, or one I and one H. Just as for pairing of hydrogen atoms, the energy difference between configurations with singly and doubly occupied dimers is best understood as a consequence of the difference in dangling bond interactions on unoccupied dimers, rather than a direct interaction between adsorbed atoms. In other words, doubly occupied

configurations are lower in energy than configurations with singly occupied dimers because double occupation disrupts the pairing interaction between dangling bonds in the fewest possible dimers. While there is a driving force to form doubly occupied dimers, these calculations show no energetic preference for the particular arrangement with occupation by I and H.

If the adsorbate ordering after annealing were determined by thermodynamics, these calculations imply that the vast majority of occupied dimers would be doubly occupied. If we assume, as the calculations indicate, that all doubly occupied configurations have essentially the same energy, then a quarter would have two H atoms, a quarter would have two I atoms, and half would have mixed occupation (one H and one I). In other words, at equilibrium half of the adsorbed H should be on dimers that are doubly occupied by H atoms. This conclusion is clearly inconsistent with the observed spectra, in which the peak at 2090 cm⁻¹ in s-polarization, characteristic of doubly H-occupied dimers, is absent after annealing to 700 K. The calculated energies for these species cannot explain the observed distribution of hydrogen as an equilibrium distribution. Even a conservative interpretation of the spectrum suggests that at least 80% of the H atoms are in mixed-occupation configurations. To explain this as the result of a thermodynamic distribution at 700 K, an energy difference of nearly 6 kcal/mol would be required between configurations with mixed and unmixed occupations.

Before we consider the possible origins of a nonequilibrium distribution, it is worth evaluating the possible sources of error in the calculated energies. In this analysis, we regard energy differences as insignificant unless they are greater than $k_B T$, the typical thermal energy. At 700 K, the annealing temperature, this energy is 1.4 kcal/mol.

The first possible source of error may be the density functional or basis set used. However, the arrangements in Figure 4 that include a doubly occupied dimer are all homodesmic; that is, they have the same number of each type of covalent bond, and the same number of each type of atom with a given hybridization. This cancels most of the errors due to the electronic structure method when energy differences are calculated between these arrangements, so we do not expect substantial errors from this source.

Next, we consider errors due to the cluster model of the surface. It is possible that an extended surface would not allow the same geometry relaxation that occurs on the cluster. Our cluster calculations show that the degree of intradimer relaxation is similar for all the adsorbate arrangements. For each doubly occupied dimer, the Si–Si distance is 2.41–2.43 Å, and the Si–Si–X (X = H or I) angles are all 113–115°, regardless of the identity of the adsorbed atoms. Thus, there is no indication

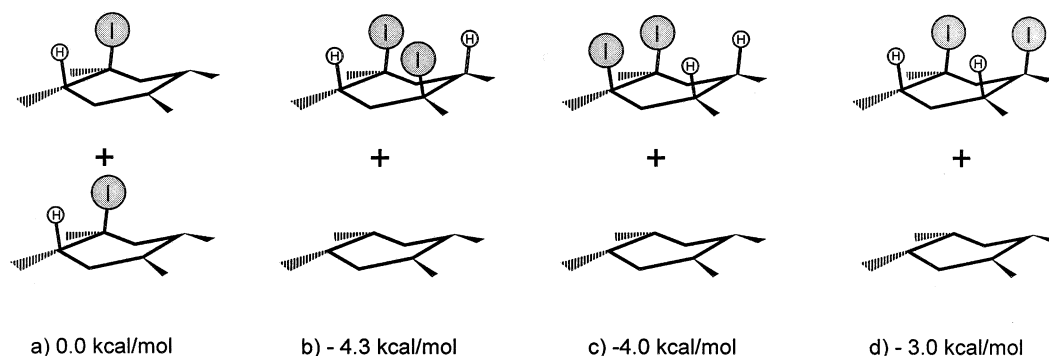


Figure 5. Pairing energies of adsorbed H and I atoms on two-dimer models of the surface, relative to the lowest energy configuration of HI molecules adsorbed on separate two-dimer models (a). Energies are calculated at the B3LYP/CEP-121G level and do not include corrections for zero-point energy (see text).

that differences in the intradimer interactions for the different arrangements have a substantial effect on structures. This leaves the possibility that interactions between atoms adsorbed on different dimers may alter the energies of different adsorbate arrangements. We have done a series of calculations on two-dimer cluster models to explore such effects. As indicated in Figure 5, interdimer interactions favor adsorption on adjacent dimers and they make small differences in the energies of various arrangements (e.g., the structure of Figure 5d is disfavored due to steric repulsion between the I atoms). However, the lowest energy configuration with mixed-occupation dimers (Figure 5b) has essentially the same energy as the configuration with two H atoms on the same dimer (Figure 5c). Thus, interdimer interactions within a dimer row do not appear to confer a significant energetic advantage on the mixed-occupation dimers. Our cluster models also neglect interactions between different dimer rows. It has been observed that iodine atoms are bulky enough to cause steric repulsion when they are adsorbed on adjacent sites in different dimer rows.²² However, under the conditions of our experiments, iodine coverage is less than 0.25 monolayer,¹⁶ so that high-energy configurations with inter-row repulsion can easily be avoided. We cannot rigorously rule out the possibility that (with some particular adsorbate ordering) collective interactions among several dimers may lower the energy of mixed-occupation dimers. However, given the lack of significant energy differences in the models examined here, it seems unlikely that more subtle interactions will be large enough to account for the hydrogen distribution at the low coverage and high-temperature conditions of these experiments.

Kinetically Favored Adsorbate Ordering. If the observed ordering is not driven by energetics, it must instead be driven by kinetic competition. That is, even though all configurations with doubly occupied dimers are energetically equivalent, we propose that only one such configuration can be reached by a kinetically accessible pathway. One plausible mechanism assumes that I atoms are initially unpaired (as expected from the dissociative adsorption mechanism) and that I diffusion is slower than H diffusion. Annealing would allow paired H atoms on a single dimer to break up and explore configurations with mixed-occupation dimers. Since configurations with dimers occupied by a single I atom are higher in energy than configurations with doubly occupied dimers of any kind, forming mixed-occupation dimers would lower the total energy of the system by allowing H atoms to reach the I-occupied dimers. With iodine diffusion being slow, the formation of dimers doubly occupied by iodine would not occur on the same time scale. Other mechanisms for forming mixed dimers are possible that do not require slow iodine diffusion. As long as the formation of dimers that are doubly occupied by I atoms ($X=Y=I$ in Scheme 1) is slower than the formation of mixed-occupation dimers ($X=I$, $Y=H$), kinetics will favor mixed dimers.

Previous observations of adatom mobility in related systems are consistent with this picture. STM studies of Si(100) partially covered by H show that H atoms are immobile up to 570 K,^{2,21} so the lower-temperature spectrum in Figure 3 reflects the distribution before significant H migration. Annealing to 700 K allows rapid H migration,^{2,21} as reflected in the higher-

temperature spectrum of Figure 3. Our findings are also consistent with the presence of singly occupied dimers observed by STM for a Si(100) surface exposed to I₂ at room temperature.²²

Conclusions

MIR–FTIR spectra show that a mixture of adsorbed H and I on Si(100)- 2×1 spontaneously forms mixed-occupation dimers as the dominant species at elevated temperatures. Density functional theory calculations provide evidence that this ordering is not driven by the relative energetics of the product configurations. Instead, the observed ordering appears to be a novel consequence of the slow kinetics of iodine pairing. Since this effect does not depend on details of the interactions between adsorbates, it should be expected for other systems in which one adsorbate forms pairs more rapidly than the other. This effect may be useful in altering the kinetics of surface processes. For example, a slowly diffusing species that acts as a trap for surface hydrogen can reduce the concentrations of surface H available for reaction, even at temperatures too low for H desorption.

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