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Adsorption and surface penetration of atomic hydrogen at the open site of Si(111): An *ab initio* cluster-model study

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The interaction of a hydrogen atom with the Si(111) surface is studied using clusters with up to ten silicon atoms in order to model the threefold open site. On the basis of *ab initio* Hartree-Fock linear-combination-of-atomic-orbital theory the potential curve is calculated as a function of distance of the hydrogen atom from the surface. Using a two-configuration multiconfigurational self-consistent-field (MCSCF) wave function, which allows for both ionic and covalent structures, leads not only to the proper dissociation behavior at infinite separation but also shifts down the SCF ground-state energy curve by about 1 eV. This effect leads to a well with a minimum at 1.4 Å above the surface and a depth of about 1 eV. The SCF barrier height for penetration of the surface of 2.7 eV is reduced to 1.8 eV. We compute a vibrational frequency for motion normal to the surface of about 100 meV, considerably smaller than the vibrational energy for the head-on adsorption site. The study shows that SCF cluster calculations of this type give qualitatively correct potential curves with minima and barriers at about the right distances but binding energy errors of about 1 eV due to the neglect of the main correlation contributions. The possible role of the interaction of hydrogen at the open site in the formation of the trihydride phase is discussed.

I. INTRODUCTION

In the cluster-model approach to a quantitative description of the interaction between atoms or molecules and a solid surface a small number of atoms representing the surface plus a chemisorbed atom (molecule) are considered as a fictive molecule (cluster). Wave functions are determined for this quasimolecule and its properties interpreted in terms of processes on an extended surface. To model chemisorption one could, in principle, increase the surface cluster by adding substrate atoms until the chemisorption properties become independent of cluster size. One has, however, to keep the cluster reasonably small in order to do, for example, an *ab initio* Hartree-Fock study. The first problem in a cluster study is therefore the number of substrate atoms necessary for the convergence of various chemisorption properties ("size effect"). If, however, the interaction between adsorbate-substrate is sufficiently localized only a few substrate atoms (usually the nearest neighbors to the adatom) have to be included, and a self-consistent-field (SCF) calculation using contracted Gaussian-type-orbital (CGTO) basis sets of modest size becomes possible. This type of calculation, applied to real molecules, gives results of modest accuracy for equilibrium geometries and force constants and gives qualitative guides for relative energies at different points on a potential surface.[1] SCF Hartree-Fock calculations for different adatom-substrate systems such as H/Be (Ref. 2), H/Si (Ref.3), and O/Li (Ref. 4) and, in particular, their comparison with experimental data have also demonstrated the suitability and accuracy of the cluster approach. Using this model we have recently studied the interaction of fluorine and chlorine atoms with the Si(111) surface[5] and we have shown that F atoms can penetrate into the Si lattice by going over a relatively small barrier of ~1 eV whereas the barrier for Cl penetration is ~13 eV. These results provided a model for understanding reactions relevant in plasma etching. The inherent errors of such an SCF calculation will rather likely lead to too high a barrier and too shallow a minimum in the potential curve due to the neglect of correlation effects. Barrier height and binding-energy maxima, however, can become crucial parameters in such a study. The principal subject of this investigation is therefore to determine the main correlation corrections to the self-consistent-field potential curve for H/Si(111). We will investigate the interaction of a hydrogen atom at the open site of the Si(111) surface. This study also complements the recent study for H at the head-on site directly over a surface Si atom[3] and gives more insight and understanding of the different mechanisms in the fluorine and chlorine interaction.[5]

The chemisorption of hydrogen on Si(111) is probably the most studied chemisorption process on semiconductor surfaces. It is well known from experiment[6-8] that atomic hydrogen is easily adsorbed on the Si(111) surface up to monolayer coverage (monohydride phase), whereas molecular hydrogen does not seem to react with the surface, most probably due to the large dissociation energy of H_2 (4.48 eV).[9] On increasing H exposures the formation of a trihydride phase has been suggested[10,11] where SiH_3 radicals are bonded to the surface Si atoms. The trihydride structure can be obtained by removing an entire layer of Si atoms from the clean ideal surface and saturating each of the three dangling bonds of the second-layer Si atoms with hydrogen atoms.

In our study of the interaction of atomic hydrogen with the Si(111) surface, the *ab initio* Hartree-Fock linear-combination-of-atomic-orbitals (LCAO) method is used to calculate the electronic structure of a cluster of ten Si atoms, representing the first four layers of the silicon surface, with a hydrogen atom added at the central symmetry position. The adatom-substrate energy is studied as a function of vertical distance from the surface. The ground state of the cluster does not have a correct dissociation behavior into a bare substrate cluster and a hydrogen atom. We shall show that the same wave-function limitations that lead to incorrect dissociation also lead to too high a barrier for penetration of the surface (cluster) by the H atom. In order to improve the calculated well depth and barrier height, we have gone beyond the one-configuration SCF approximation. The potential curve has also been calculated by using a two-configuration (2*C*) multiconfiguration (MC) SCF wave function which properly allows for both ionic and covalent structures. The results show that the SCF calculation gives qualitatively the correct potential curve with minima and a barrier at about the right distances, but about 1 eV higher than that given by the partially correlated MCSCF treatment.

In Sec. II we discuss the computational details of our calculations: choice of surface clusters, method of calculation, basis sets, and symmetry considerations. In Sec. III we present our results. Section III A gives the discussion of results of the self-consistent-field calculation, Sec. III B the the two-configuration MCSCF treatment. Finally, in Sec. IV, the conclusions for this study are summarized and the possible consequences in the formation of the trihydride phase are discussed.

II. COMPUTATIONAL DETAILS

The cluster models for the high-symmetry sites at the Si(111) surface are described in detail in our study of the interaction of F and Cl with the silicon surface.[5] Thus, we present here only the most important features. In the cluster models used for the present investigation relaxation and reconstruction effects are neglected and the Si atoms are chosen to have their bulk geometry,[12] $d_{\text{Si-Si}} = 4.44$ bohrs. An $Si_{10}H_{13}$ bare surface cluster is considered in the SCF calculation. The Si atoms represent four layers of the surface; three atoms in each of the first, second, and third layers, and one in the fourth layer. The fourth-layer atom is in the center of the triangles formed by the three atoms in each of the three other layers. In order to simulate the remainder of the crystal, the same embedding procedure as in the previous studies[3,5] is applied: Hydrogen atoms are used to embed the cluster. The hydrogen atoms are placed so that each Si atom has the correct number of nearest neighbors (counting both H and Si atoms): four for "bulk," 2nd–4th-layer atoms and three for the first-layer Si atoms. In effect, the H atoms force an sp^3 hybridization of the cluster Si atoms.[3,5] The first-second- and fourth-layer Si atoms each have one embedding H neighbor; the third-layer Si atoms have two hydrogen neighbors ($d_{\text{Si-H}} = 2.80$ bohrs, the experimental distance in silane[13]). Each atom of the first layer has one unpaired electron, the dangling bond, which has essentially sp_z character. This $Si_{10}H_{13}$ cluster is shown in Fig. 1.

For the 2*C*-MCSCF calculation this cluster has been truncated by replacing the Si atoms of the third layer by hydrogen atoms thus modeling only two layers of the Si(111) surface. This will still give reliable results for the interaction above the surface and the potential barrier since the earlier investigations[3,5] indicate that the adsorption process on Si(111) is governed by a strongly localized adsorbate-substrate interaction.

The distance d of the hydrogen atom with respect to the substrate surface is defined as the distance along the surface normal from the center of the plane of the first layer of silicon atoms. The equilibrium value of d, d_e, is determined by minimizing the total energy of the cluster with respect to variations in d.

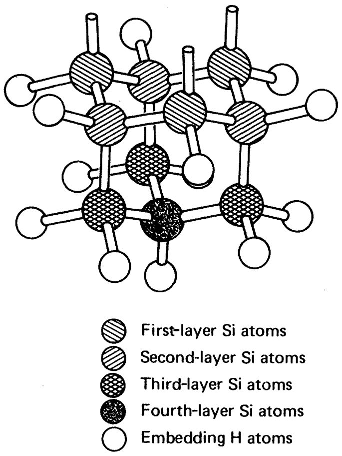

FIG. 1. The four-layer $Si_{10}H_{13}$ cluster used to model the open site of Si(111). The dangling bonds of the first-layer Si atoms are indicated.

For the Hartree-Fock SCF study the LCAO method described by Roothaan for both closed[14]- and open[15]-shell systems and a limited MCSCF program as implemented in the MOLECULE-ALCHEMY SCF (Ref. 16) program system is used. All calculations have been performed for spin-restricted wave functions.

Because the maximum cluster size, $Si_{10}H_{13}$–H, considered in the present study is considerably larger than the Si_4H_9 cluster used to study hydrogen adsorption on the head-on site of Si(111),[3] a smaller Si basis set was used. We choose the same CGTO basis as in the F-Cl study[5] where it was shown that this basis set leads to a tolerable error in the binding energy of about 10% compared with a double-zeta basis augmented by one polarization function.[3] The Si CGTO basis set is minimal for the $1s$, $2s$, and $2p$ core and double zeta for the valence shells ($4s\,3p$) and is essentially an optimized contraction of the Roos-Siegbahn ($10s\,6p$) basis.[17] An unsegmented contraction[18] was used for the innermost basis functions in order to have an optimal representation of the core atomic character. The basis set for hydrogen is taken from the H/Si(111) cluster study[3] ($4s$ contracted to $2s$; in the case of the adsorbing hydrogen this basis is expanded by one p function to allow for more flexibility in forming the chemisorptive bond). Using these basis sets of modest size for the individual atoms the calculation of the SCF potential-energy curve of the $Si_{10}H_{13}$–H cluster, which involves 161 contracted basis functions, and the $2C$-MCSCF calculation of the Si_6H_9–H cluster (101 contracted basis functions) become quite feasible.

The symmetry behavior of the clusters is described by the point group C_{3v} with irreducible representations a_1, e (doubly degenerate), and a_2. Symmetry-adapted basis functions are used in all calculations.

III. RESULTS AND DISCUSSION

A. The self-consistent-field calculation

As described in more detail elsewhere,[5] the ground state of the $Si_{10}H_{13}$ substrate cluster is found to have the open-shell configuration $a_1^1e^2$, where the a_1 and e orbitals are different combinations of the essentially sp_z dangling bonds of the three surface Si atoms. In order to simplify the treatment of the cluster, the energies and wave functions have been obtained for the average of configurations[19] of the $a_1^1e^2$ open shells rather than for a specific spin and spatial coupling. Several configurations, again using the average of configuration formalism, were investigated for $Si_{10}H_{13}$–H in order to determine the one with the lowest energy. As can be seen from the binding curves in Fig. 2 there are two configurations which lead, depending on the distance from the surface, to the state with lowest energy.

The configurations of the two states may be written schematically as follows:

$$\Psi_{\rm I} = \cdots e^2(\text{Si surface } sp_z)a^2(\text{Si–H } s \text{ bonding}) \, , \quad \text{(1a)}$$

$$\Psi_{\rm II} = \cdots e^2(\text{Si surface } sp_z)a^1(\text{Si surface } sp_z)\, a^1(\text{H } s). \quad \text{(1b)}$$

For both states e^2(Si surface sp_z) is a dangling-bond orbital only slightly perturbed from that found for the bare $Si_{10}H_{13}$ cluster. For $\Psi_{\rm I}$, a^2(Si–H s bonding) denotes a doubly occupied bonding orbital formed from the $Si_{10}H_{13}$ dangling-bond state of a symmetry with the H s orbital. For $\Psi_{\rm II}$, the a^1(Si surface sp_z) represents essentially the $Si_{10}H_{13}$ bare-cluster dangling bond and a^1(H s) essentially the H s orbital. Rigorously this characterization for $\Psi_{\rm II}$ is correct at larger H–$Si_{10}H_{13}$ separation, at smaller distances the two open-shell a orbitals acquire bonding and antibonding character.

The binding curves of the hydrogen atom approaching the $Si_{10}H_{13}$ cluster as function of surface distance are shown for both states. In the region 1.0 bohr $\leqslant d \leqslant$ 3.5 bohrs the lowest-energy configuration, $\Psi_{\rm I}$, has the e^2 dangling-bond open shell. This state shows a minimum at about 2.5 bohrs (1.33 Å) from the surface and leads to a barrier height of about 2.7 eV at the surface. We can see that $\Psi_{\rm I}$ goes to quite the wrong energy at infinite separation of H from $Si_{10}H_{13}$. This behavior has a striking similarity to the Hartree-Fock (HF) potential curve of the hydrogen molecule as function of internuclear distance.[20] The HF ground-state energy shows a minimum at about the right internuclear distance, but not as low as that given by the Heitler-London method, and goes to the wrong energy at infinite internuclear separation. The reason for this error is that the Hartree-Fock molecular wave function is an equal mixture of the nonionic Heitler-London (HL) function and an ionic function. At infinite internuclear separation the energy is too high, on account of the contribution from the ionic-type terms. This, as we discuss further below, explains reasonably the relative behavior of the potential curves for $\Psi_{\rm I}$ and $\Psi_{\rm II}$ for $d > \sim 2$ bohrs. The behavior for smaller d, in particular the fact that $\Psi_{\rm II}$ leads to a lower energy for $d \sim 0$ where $\Psi_{\rm I}$ has its barrier maximum appears somewhat surprising. Our analysis below shows, however, why the same limitation in the SCF wave function of $\Psi_{\rm I}$ which leads to the large-d problems also leads to (or

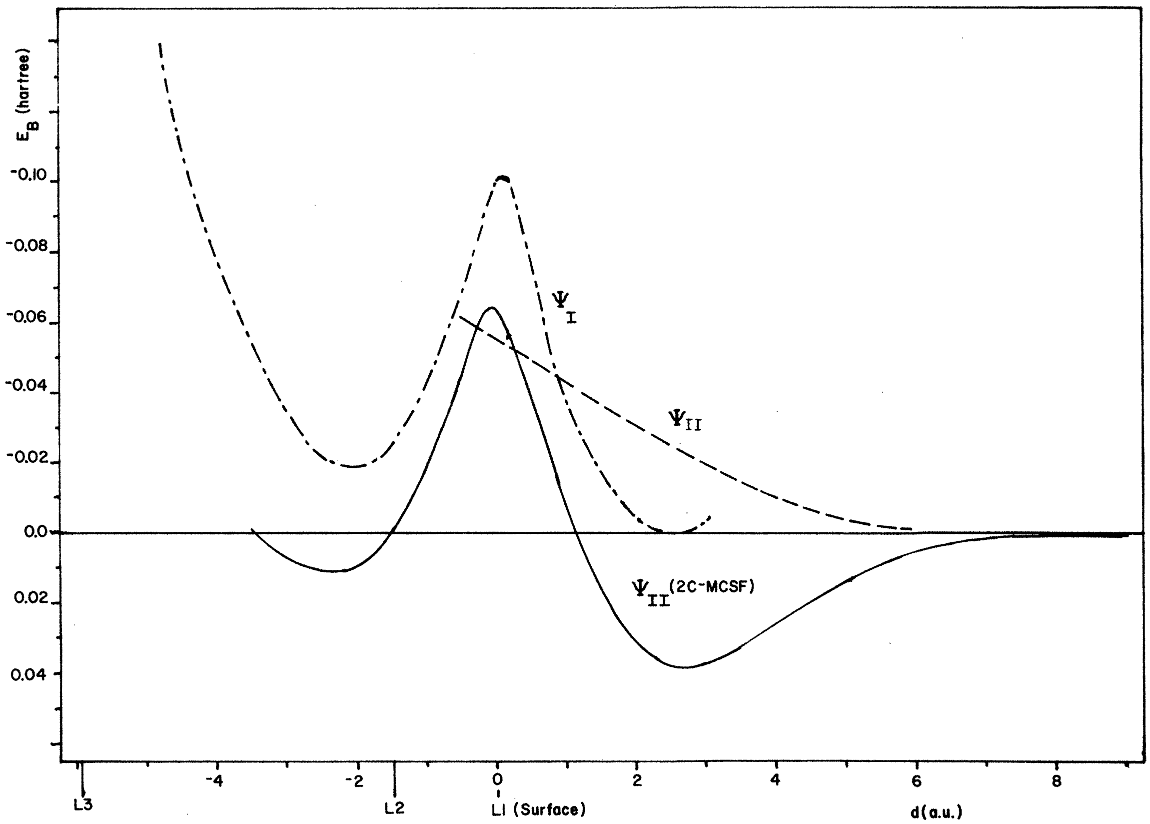

FIG. 2. SCF interaction potential curves for the configurations Ψ_I and Ψ_{II} and 2C-MCSCF interaction potential curve for Ψ_{II} (2C-MCSCF) as a function of distance d of the hydrogen atom from the surface cluster. The position of the layers of the Si surface are marked. The zero of the binding energy E_B is the sum of the energies of the substrate cluster and the hydrogen atom.

explains) those at small d.

We shall now analyze our SCF results in a very similar way to the hydrogen-molecule problem as treated by Slater.[20] The two orbitals which dominate exclusively the interaction of the hydrogen atom and the substrate cluster are the H 1s orbital and the Si dangling-bond (sp_z) orbital of a_1 symmetry. In a simple analysis we can therefore discuss the states in terms of these two functions. In the LCAO method we can form two molecular orbitals from the hydrogen 1s (denoted by $a_{1\text{H}}$ or a) and the silicon dangling-bond orbital ($a_{1\text{Si}}$ or b), namely the symmetric bonding function g,

$$g=[2(1+S)]^{-1/2}(a+b)\,, \tag{2a}$$

and the corresponding antisymmetric function u, given by

$$u=[2(1-S)]^{-1/2}(a-b)\,. \tag{2b}$$

S is the overlap integral $\langle a|b\rangle$. For simplicity, we set the coefficients of a and b in g and u equal to one although properly these should be treated as variational parameters.

If we have each electron in one of these orbitals the two determinantal wave-functions representing a singlet will be (using Slater's notation)

$$\begin{aligned} g^+g^- &= [2(1+S)]^{-1} \\ &\quad\times[a(1)a(2)+b(1)b(2)+a(1)b(2)+b(1)a(2)] \\ &\quad\times\frac{\alpha(1)\beta(2)-\beta(1)\alpha(2)}{\sqrt{2}}\,, \end{aligned} \tag{3a}$$

$$\begin{aligned} u^+u^- &= [2(1+S)]^{-1} \\ &\quad\times[a(1)a(2)+b(1)b(2)-a(1)b(2)-b(1)a(2)] \\ &\quad\times\frac{\alpha(1)\beta(2)-\beta(1)\alpha(2)}{\sqrt{2}}\,. \end{aligned} \tag{3b}$$

The three triplet components are g^+u^+, g^-u^-, and $(g^+u^-+g^-u^+)/\sqrt{2}$, g^+u^+, for example, given by

$$g^+u^+=[2(1-S^2)]^{1/2}[b(1)a(2)-a(1)b(2)]\,\alpha(1)\alpha(2)\,. \tag{3c}$$

In the e^2a^2 configuration the bonding function g is doubly occupied as in g^+g^- of Eq. (3a). We see that the resulting state g^+g^- is made up of equal parts of the Heitler-London-type covalent function $a(1)b(2)+b(1)a(2)$, and the ionic function $a(1)a(2)+b(1)b(2)$. Hence, there is a chance of one-fourth that both electrons will be found on the hydrogen atom and a chance of one-fourth that both will be in the dangling-bond orbital. This clearly leads to the wrong dissociation behavior at infinite separation. However, this state also has too high an energy if the hydrogen atom is in the surface region, -1.0 bohr $\leqslant d \leqslant +1.0$ bohr, as can be seen from the calculated potential curve (Fig. 2). The reason for this error can now become understood. In the surface region there is no appreciable overlap between the hydrogen 1*s* orbital and the Si (sp_z) orbital. [If the H atom is at the surface ($d=0$) its distance to the first-layer Si atom is 2.2 Å. The sp_z dangling bonds are perpendicular to the surface.] Hence, the Si–H bonding is quite weak in this region and a HL-type wave function is appropriate here *as well as* in the large separation regime. The molecular orbital chosen to be occupied by both electrons leads to an overestimation of the ionic contributions. No amount of variation will cause the wave function g^+g^-, given by the HF SCF method, to approach the correct value at infinite separation or for distances in the surface region.

In the $e^2a^1_{1\mathrm{Si}}\,a^1_{1\mathrm{H}}$ configuration we have one electron each in the hydrogen 1*s* orbital and in the Si (sp_z) dangling bond. This corresponds either to a triplet state, e.g., g^+u^+ [Eq. (3c)], or to the Heitler-London-type function $[a(1)b(2)+b(1)a(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)]$, representing the singlet. It does not contain any ionic contributions. The energy of this nonionic state approaches the correct value at infinite separation and leads to a lower energy if the hydrogen atom is in the surface region, but does not yield a well in the potential curve. This is, of course, because Ψ_{II} or gu does not account for bonding but can be regarded either as having an equal occupation of a bonding and an antibonding level (g and u) or, equivalently, as occupation of two nonbonding levels [a and b; see Eq. (3c)]. The curve is always repulsive because of the overlap of the Si(a) and H(b) charge distribution.[20]

To overcome the incorrect mixing of the covalent and ionic structures at infinite separation and in the surface region for the g^+g^- state and still take account of the H–Si bonding we must go beyond the Hartree-Fock SCF approximation. The obvious thing to do is, as in the case of the hydrogen molecule, to make linear combinations or configuration interactions of the g^+g^- and u^+u^- states.[20,21] In the limit where S goes to zero the function $(g^+g^- - u^+u^-)/\sqrt{2}$ becomes precisely the Heitler-London-type covalent function, $a(1)b(2)+b(1)a(2)$, whereas in the intermediate region we may expect to decrease the energy and to obtain binding by varying the amount of the ionic contribution. We therefore recalculated the potential curve for H on the open site of the Si surface using a two-configuration MCSCF wave function of exactly the type described above which properly allows for both ionic and covalent structures.

B. 2*C*-MCSCF calculation

The two-configuration MCSCF calculation is carried out for the smaller, two-layer, substrate cluster plus the adsorbing hydrogen atom. As described in Sec. II this should have no effect on the potential curve for hydrogen far enough away from the third and fourth layer, i.e., on the barrier for penetration and the adsorption minimum above the surface. The composition of this cluster is $\mathrm{Si_6H_9}$–H. The MCSCF calculations for g and u (and the other orbitals as well), of course are fully variational. In particular this means that the restricted LCAO form of g and u in Eqs. (2a) and (2b) is replaced effectively by

$$g=N_g(\alpha a+\beta b)\ , \tag{4a}$$

$$u=N_u(\beta a-\alpha b)\ , \tag{4b}$$

and, schematically

$$\Psi_{\mathrm{II}}(2C-\mathrm{MCSCF})=e^2(\text{surface } sp_z)(C_1g^2+C_2u^2). \tag{5}$$

We stress that the average of configuration formalism for the open-shell e^2 coupling is used in Ψ_{II} (2*C*-MCSCF).

The interaction potential curve as a function of distance of the hydrogen atom from the surface is shown in Fig. 2. It is very similar to the SCF binding curve for the e^2 configuration, but shifted down everywhere below the SCF ground-state energy by about 1 eV. We also see that the energy now goes to its proper value at infinite separation. It is easy to verify that in the average of configuration formalism, the energy of Ψ_{II} (2*C*-MCSCF) at large H–$\mathrm{Si_{10}H_{13}}$ distance does go indeed exactly to the SCF energy of H plus the average of configuration SCF energy of $\mathrm{Si_{10}H_{13}}$. (This follows because the interaction of H and Si at large separation is zero and hence obviously independent of whether the H spin is parallel or antiparallel to the Si open-shell spins. This will not be true, as we see below for distances near the surface. There the way the averaging of H and Si spins is made will affect the energy.) For the hydrogen atom there is a well with a minimum of 1 eV at 1.4 Å above the surface. In addition there is a second well with a depth of 0.3 eV at 1.2 Å below the surface. The height of the barrier for penetration of the surface is reduced to 1.8 eV. The reason that the 2C-MCSCF barrier is still slightly higher than that found for the SCF configuration for Ψ_{II} is the following. Using the average-of-configurations method in the SCF calculation triplet coupling of the $a_{1\mathrm{Si}}^1$ and $a_{1\mathrm{H}}^1$ orbitals is implicitly included. This leads to a lower total energy than the resulting singlet coupling of the linear combination $(g^+g^- - u^+u^-)/\sqrt{2}$ in case of the two-configuration MCSCF calculation.

The coefficients in the two-configuration ansatz $C_1\, g^+g^- + C_2 u^+u^-$ reflect what we have discussed before. Their variation along the surface normal is shown in Table I. For $d\rightarrow\infty$ they approach the limit $1/\sqrt{2} = 0.707$ ($C_1 = 0.73$, $C_2 = -0.68$ for $r = 8$ bohrs); that is, the ionic contributions in Eqs. (3a) and (3b) cancel. C_1 reaches its maximum around the minimum of the outer well ($C_1 = 0.96$, $C_2 = -0.28$). This corresponds to the region where the bonding of the H s with the Si (sp_z) dangling bond is strongest. Hence, the importance of the g^2 (bonding) term in Eq. (5) is greatest. For $d = 0$ (surface) the coefficients approach again the limit $1/\sqrt{2}$: $C_1 = 0.71$, $C_2 = -0.70$. This equal weighting represents the fact that the H and Si are essentially nonbonding when H is in (or near) the plane of the surface. These results confirm the qualitative analysis in Sec. III A. At the bottom of the inner well a second maximum for C_1 is found ($C_1 = 0.97$, $C_2 = -0.22$).

TABLE I. The coefficients in the 2C-MCSCF ansatz $C_1 g^+g^- + C_2 u^+u^-$ as a function of distance from the surface and gross charge on H as obtained from a Mulliken population analysis.

d (a.u.)	C_1	C_2	Q
8	0.73	−0.68	1.00
7	0.77	−0.64	1.00
6	0.81	−0.58	1.01
5	0.87	−0.49	1.03
4	0.92	−0.39	1.05
3	0.95	−0.30	1.06
2.5	0.96	−0.28	1.05
2	0.96	−0.26	1.04
1.5	0.96	−0.26	1.03
1	0.96	−0.28	1.03
0.5	0.93	−0.36	1.02
0	0.71	−0.70	1.03
−0.5	0.95	−0.30	1.10
−1	0.97	−0.24	1.13
−1.5	0.98	−0.22	1.12
−2	0.97	−0.23	1.09
−2.5	0.96	−0.26	1.04
−3	0.95	−0.31	1.00
−3.5	0.92	−0.38	0.98

We may examine charge-transfer effects in the bonding, that is to say departures of α and β in Eq. (4) from 1. These should be distinguished from the contributions of ionic- and covalent-like terms in Eqs. (3a)–(3c). The charge-transfer effects are indicated qualitatively by the Mulliken gross-population analysis[22] given in column III of Table I. We note from Table I that in the 2C-MCSCF calculation hydrogen stays mostly neutral. Some charge is transferred (0.06e) towards hydrogen at the bottom of the outer well. When the barrier reaches its maximum height this amount is reduced to 0.02e.

Since the well with a minimum of 1 eV at 1.4 Å above the surface suggests that atomic hydrogen can stabilize above the open threefold site we calculated the parameters for hydrogen vibrations perpendicular to the surface from the binding curve shown in Fig. 2. Assuming that the silicon part is rigidly connected to the rest of the substrate with infinite mass the vibrational energy $\hbar\omega$ is given, in the harmonic approximation, by

$$\hbar\omega = \hbar(\kappa/m_{\mathrm{H}})^{1/2} ,$$

where κ is the curvature of the respective binding curve at equilibrium distance and m_{H} is the mass of the hydrogen. The results are given in Table II. For comparison the vibrational parameters are also calculated from the SCF binding curve. We note from Table II that they agree within 10% with the values obtained from the 2C-MCSCF calculation ($\omega_{\mathrm{SCF}} = 112$ meV, $\omega_{2C\text{-MCSCF}} = 102$ meV). We give in Table II also the vibrational energy for H at the inner well ($\omega_{\mathrm{SCF}} = 129$ meV). (The value of the 2C-MCSCF calculation is not given since it is likely to be less appropriate for comparison since the third and fourth silicon layers are not taken into account in the substrate cluster.) For head-on chemisorption a vibrational energy of 280 meV was calculated.[3,23] Electron-energy-loss (EEL) spectroscopy gives 257 meV.[24] Our results predict that H in a three-fold site, either above or below the surface, will have a considerably different and smaller, ~100 meV, energy than that found for H

TABLE II. Parameters for hydrogen vibrations perpendicular to the surface. Here, κ is the curvature of the binding curve at equilibrium distance (see Fig. 2).

Cluster	Method	κ (Hartree/a_0^2)	(cm^{-1} ; meV)	
$Si_{10}H_{13}$–H (outer well)	SCF	0.030 68	900.6	112
Si_6H_4–H (outer well)	2C-MCSCF	0.025 60	822.6	102
$Si_{10}H_{13}$–H (inner well)	SCF	0.041 20	1043.6	129

adsorbed in the head-on site.[24] Hartree-Fock methods applied to real molecules give values for vibrational frequencies that are characteristically 10% too large. Accordingly, we would expect that observed frequencies for H in one of these threefold sites should be somewhat smaller than the calculated SCF cluster values in Table II. Our calculations suggest that the energy for H below the surface should be somewhat larger than for adsorption above. However, they should be regarded with caution because of the limitations in the accuracy of the calculation and other factors including the role of surface relaxation and reconstruction.

The EELS measurement for H/Si(111) was performed on a cleaved silicon surface. Subsequent exposure did not increase the magnitude of the peak nor was any other peak observed. This is consistent with the observed ultraviolet photoemission spectra[11] (UPS) which show that the spectra of the cleaved and annealed surfaces do not change on further H exposure. If one starts, however, from a 1×1 surface the UPS spectrum does change.[10,11] The sequential appearance of the photo-emission spectra of Si(111):H and Si(111):SiH_3 (suggested by Pandey *et al.*[10]) on adsorption is observed. If adsorption at the threefold chemisorption site plays a role in the formation of SiH_3 radicals then the corresponding surface vibrations, calculated in this study, should be observable by high-resolution EEL spectroscopy. The calculated difference of about 15 meV between vibrations of hydrogen sitting above and below the surface could lead to a high-energy shoulder in the peak around 100 meV if penetration of the surface is possible. (A typical resolution of the EEL spectrometer is 10 meV.[24]

IV. CONCLUSION

In this study we have examined the interaction of a hydrogen atom at the open site of an Si(111) surface. It complements the adsorption study of fluorine and chlorine at this surface. The analysis shows that the nature of bonding changes very substantially when the hydrogen atom is in the potential minimum, either above or below the surface, or at the surface itself. In such a case a single-configuration HF wave function has extra limitations. We analyzed the wave function in terms of covalent and ionic structures and performed a two-configuration–MCSCF calculation which substantially improved the energetics. This simple MCSCF treatment, though not of high quantitative accuracy, corrects the most severe deficiencies of the SCF approach. Both well depth for hydrogen adsorption and barrier for surface penetration are lowered by ~1 eV. An important result of this study is the prediction of a low-frequency vibration for H on Si(111) at ~100 meV, considerably smaller than the vibrational energy for head-on adsorption at ~257 meV. An EELS measurement of hydrogen chemisorption on a Si(111) 1×1 surface could verify this prediction.

The sequential appearance of a peak at 257 meV (head-on chemisorption) and at ~100 meV (open-site chemisorption) would also support the role of hydrogen interaction at the threefold open site in the formation of an SiH_3 surface species. Namely, a plausible mechanism for the formation of Si(111):SiH_3 emerges if we assume the following reaction path (alternatively or in addition to the disordered vacancy model of Pandey *et al.*[10] which assumes that already 27% of the surface atoms are missing): The release of energy in the adsorption of hydrogen atoms to the surface dangling bonds (head-on chemisorption) can contribute to the penetration of H atoms at three adjacent open sites. If another H atom adsorbs (or has already been adsorbed) directly over the central silicon an SiH_4 complex is formed which can be easily desorbed as SiH_4. This mechanism leads to the eventual removal of the entire surface monolayer of Si(111). Adsorption to the three dangling orbitals of the Si atoms in the second layer can then occur thus leading to the formation of Si(111):SiH_3, the trihydride phase, which is energetically more favorable than the monohydride phase.[10] The formation of the stable trihydride phase most likely also explains why further etching (more than one monolayer) of the Si substrate does not occur. Crucial tests of our proposed mechanism would be provided by observation of volatile SiH_4 and a peak around 100 meV (with a possible high-energy shoulder) in an EEL spectrum of an Si(111) 1×1 surface exposed long enough ($t > 2$ min) to atomic hydrogen.

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