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Energetics of hydrogen chemisorbed on Cu(110): A first principles calculations study

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In the current study we present a potential energy surface(PES) for atomic hydrogen chemisorbed on Cu(110) at $\Theta = \frac{1}{8}$ monolayer (ML) obtained from a plane-wave, gradient-corrected, density functional calculation. This PES is markedly different from and significantly more complex than that predicted by empirical embedded atom method (EAM) calculations. Our results, for example, suggest strongly that the hollow (HL) site is not the preferred binding site for this system. In our calculations, both the short bridge (SB) and pseudo-threefold sites are energetically more favorable than the hollow (HL) site. Energetically, we find the SB site to be slightly lower (30 meV) than the pseudo-threefold site. We also find, however, that the calculated vibrational frequencies for the pseudo-threefold site agree more closely with experimental electron energy loss data than for the SB site. In view of the relatively flat region between adjacent pseudo-threefold sites along the cross-channel [001] direction, we speculate that the hydrogen atom motion at low coverages may be two-dimensional rather than quasi-one-dimensional in character. © *2000 American Institute of Physics.* [S0021-9606(00)30640-7]

I. INTRODUCTION

Interfacial metal/hydrogen systems are of appreciable interest. From a practical point of view, the details of the structure and dynamics of such systems are at the core of such processes as the embrittlement of technologically important alloys by hydrogen,[1] hydrogen storage and transport, fuel cell research,[2] and the growth of various thin films. From a theoretical perspective, such systems are challenging in that hydrogen's small mass and uniquely large relative isotopic mass variation often lead to phenomena whose proper description requires a quantum-mechanical as opposed to a purely classical level of theory.

Although still an active area of ongoing research, the necessary quantum-mechanical tools for both equilibrium and time-dependent studies are becoming available.[3] Analogs of classical Monte Carlo and molecular dynamics techniques increasingly make it possible to study physically realistic models of complex, many-body, finite temperature quantum systems without the necessity of introducing untestable approximations. As with their classical counterparts, the level of realism achievable with such techniques is controlled by the quality of the microscopic force laws that are utilized.

The sophistication of the microscopic force laws invoked in a numerical simulation is largely determined by the objectives of the study. If the overall purpose is principally methodological, then empirical models are often sufficient. If, however, the primary focus involves an analysis of system-specific phenomenology, then a more complete description is required.

In the present work, we wish to concentrate on the interfacial dynamics of hydrogen on the Cu(110) surface. Our interest in this system is, in part, an outgrowth of earlier dynamical path integral studies of the vibrational lineshapes for electron energy loss spectra (EELS).[4–6] Those studies have revealed that commonly utilized harmonic models for the analysis of EELS data can be seriously deficient when applied to strongly anharmonic, quantum-mechanical systems. Understanding the details of such limitations is crucial if we wish to utilize such EELS data to probe adsorbate interaction potentials.

The experimental results of Astaldi *et al.*[7] suggest that the H/Cu(110) system may offer an extreme example of the breakdown of the simple normal mode picture of adsorbate vibrational motion. The coverage dependence of the spectral width of electron energy loss features has been offered as evidence of quantum-mechanical delocalization of adsorbed hydrogen. At saturation coverages, the vibrational spectra are sharp and distinctive. As the surface coverage is decreased, however, the spectral width gradually broadens and eventually disappears. The interpretation of this behavior has been in terms of a transition from site-localized vibrational motion at high coverages to tunneling-dominated, delocalized be-

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havior at lower coverages. At high surface adsorbate coverage, the access to adjacent local minima is restricted by repulsive H–H interactions. Under such conditions, H atoms are localized at a particular site and give rise to well-defined vibrational loss features in the high-resolution electron energy-loss spectra (HREELS) spectra. At lower adsorbate coverages, H–H interactions become less important, and, it is argued, H atoms can freely move across the ''flat'' potential energy landscape via a tunneling-dominated mechanism. This interpretation is based on the two-dimensional ''protonic band'' model proposed by Christmann *et al.*,[8] and by Puska and co-workers,[9,10] who have explored its validity for a single H atom on three low-index Ni surfaces. They have proposed that the vibration spectrum should be interpreted not in terms of the conventional localized vibrational mode, but of the interband transition in the band model. In particular, Puska and his co-workers have explained the coverage-dependent effect on the spectrum in terms of the change in the bandwidth and showed that this effect would particularly manifest itself on the (110) surface where delocalization would take place along the trough-like channel in the $[1\bar{1}0]$ direction. Similarly, the effective medium theory (EMT) calculations[11] on H/Cu(110) have indicated that the PES reflects the topology of the actual surface structure in that it is essentially flat along the channel direction, but steep along the [001] or cross-channel direction. Therefore, the motion of an H atom would essentially exhibit the *quasi*-one-dimensional quantum diffusion.

As a first step in a more complete study of the complex equilibrium and dynamical phenomenology of the H/Cu(110) system, we examine the energetics of hydrogen adsorption at various coverages using first principles methods. We do so to obtain what is hopefully an accurate description of the microscopic interactions. Such an accurate microscopic force model will then be utilized, either directly or through the construction of an *ab initio* derived model, to probe the structural and dynamical properties of this system.

The organization of the paper is as follows. In Sec. II we briefly describe the electronic structure methods used in the present calculations. In Sec. III we present results from first principles calculations for the simpler H/Cu(111) system at two different coverages [$\Theta=\frac{1}{4}$ and $\Theta=1$ monolayer (ML)]. These preliminary studies permit us to compare results for properties of interest (binding energies, normal mode frequencies) with previous studies and thereby to establish confidence levels for a better characterized system. Finally, we discuss the energetics and vibrational frequencies for a variety of sites on H/Cu(110) at $\Theta=\frac{1}{8}$ ML. In Sec. IV we conclude by presenting a summary of our findings.

II. METHOD OF CALCULATIONS

For all calculations reported here, we utilized the Vienna *ab initio* simulation package (VASP) that is described in detail elsewhere.[12,13] This method is a plane wave density functional theory (DFT) based on the ultrasoft Vanderbilt pseudopotentials.[14,15] All calculations have been performed using the generalized gradient approximation (GGA) of Perdew and Wang (PW91).[16] Other computational details include H and Cu cutoff energies of 350 eV and a Fermi-level smearing scheme with a width of 0.2 eV.[17] Brillouin zone (BZ) integration is performed using the special point sampling technique of Monkhorst and Pack.[18]

To model the interfacial systems reported here, we use a supercell model with six slab layers separated by six vacuum layers to prevent interactions between adjacent slabs. For the clean surface calculations, the top three layers are allowed to relax while the bottom three layers are fixed at their bulk positions. For calculations with adsorbates, hydrogen atoms are put only on one side of the slab. Depending on the study involved, adsorbate calculations are performed using both unrelaxed Cu lattices (all Cu atoms fixed at the final positions obtained from the clean surface calculations) and with relaxed Cu lattices (Cu atoms in the top three layers permitted to move). Ionic relaxation is performed and cross-checked using conjugate gradient and damped molecular dynamics methods (scaling factor of 0.l). An equilibrium Cu lattice distance of 3.64 Å from bulk calculations is used throughout the present study. The binding energy is obtained relative to the clean Cu surface energy and the H-atom spin-polarization energy, 1.11 eV, defined as the difference between the nonspin- and spin-polarized calculations.

III. RESULTS AND DISCUSSION

In this section we present and discuss our major findings for H/Cu(110). To our knowledge, no such systematic, first principles calculations have been done for this system. As a consequence of the relative complexity of the phenomenology of H/Cu(110), we present our discussion in three basic stages. First, we examine a series of properties for the simpler H/Cu(111) system to establish baseline confidence levels in our approach. We then examine H/Cu(110). Finally, we describe results from a number of follow-up studies on H/Pd(110) designed to clarify issues raised by our H/Cu(110) findings.

We first consider the energetics of H/Cu(111) at $\Theta=1$ and $\Theta=\frac{1}{4}$ ML and compare our results with those from other theoretical calculations. The adsorption of H on Cu(111) has attracted interest because of the controversial assignment of the binding site to the bridge (BR) position.[19] More recently, infrared reflectivity adsorption studies have reinterpreted earlier results and have assigned the threefold site as the preferred binding site.[20] Previous first principles calculations on H/Cu(111) have found the face-centered cubic (fcc) site to be marginally more favorable than the hexagonal close-packed (hcp) location.

For both surface adsorbate coverages, we use (1×1) and (2×2) unit cells along with the respective $(10\times10\times1)$ and $(5\times5\times1)$ grids for the BZ integrations (cf. Fig. 1). Other computational details are as described in Sec. II. Table I summarizes our findings.

In agreement with previous theoretical calculations, we find the fcc site to be the preferred binding site. It is lower by a few meV than the hcp site, while the BR site is substantially higher in energy. Our absolute binding energy of 2.51 eV differs from the $\Theta=\frac{1}{4}$ ML value of 3.24 eV reported previously,[21] although it is in relatively good agreement with the value of 2.37 eV reported for $\Theta=\frac{1}{3}$ ML.[22] It should be

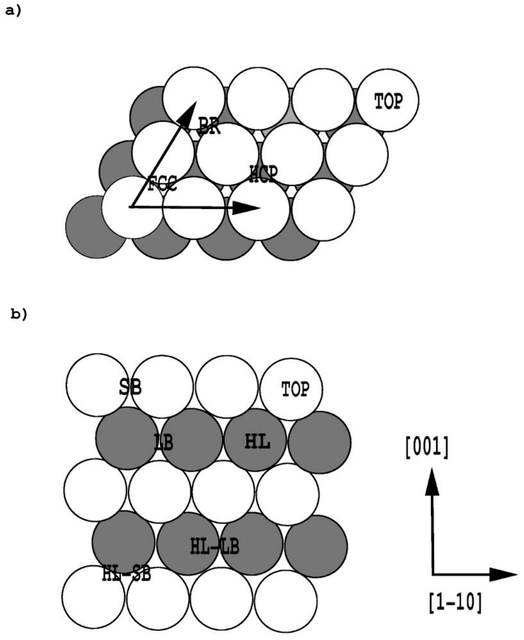

FIG. 1. Top views of (a) Cu (111) and (b) Cu (110) surface with highly symmetric sites. The shaded atoms are in the second layer. Arrows indicate the unit vectors used for the (2×2) unit cell in the H/Cu(111) calculations.

noted that the present calculations utilize appreciably more slab layers than did Ref. 21 (six vs two) and also implement a gradient as opposed to local density approximation. Although the absolute energetics differ, we note that $\Theta=\frac{1}{4}$ ML results from Ref. 21 for the energy difference between the threefold and BR sites agree well (0.12 vs 0.15 eV) with results from the present study. Other data such as the binding height and bond length at $\Theta=1$ ML and $\Theta=\frac{1}{4}$ ML show similar good agreement. It is interesting to note that the energy barrier located at the BR site shows a very strong coverage dependency, as can be seen by the change in the relative difference in the binding energy between the hollow threefold and the bridge sites, from 0.24 eV at $\Theta=1$ ML to 0.15 eV at $\Theta=\frac{1}{4}$ ML coverage. From this, we infer that strong repulsive H–H interactions would play a significant role in dynamics of H atoms on Cu(111) surface.

We also present in Table I our calculated vibrational frequencies at $\Theta=1$ ML for the highly symmetric H/Cu(111) sites. These values are in good agreement with the results of previous calculations.[23] Furthermore, the perpendicular, symmetric stretch frequencies show good agreement with experimental data.[20] It should be noted that these perpendicular frequencies are higher than the parallel mode frequencies, in agreement with results for other fcc systems such as H/Pt(111) (Ref. 24) and H/Ag(111).[25] The calculated parallel mode frequency of 124 meV for the fcc site in H/Cu(111), on the other hand, is higher than the reported experimental value of 96 meV.[20] Previous studies for the H/Pd(111) (Ref. 5) and H/Ni(111) (Ref. 6) system have found that relatively strong anharmonic effects can significantly lower the excitation energies for the laterally polarized vibrational motion, but tend to play only a minor role in the perpendicular direction. Further studies will be required to determine if such effects are also significant for H/Cu(111).

TABLE I. Energetics at highly symmetric sites on H/Cu(111) at $\Theta=1$ and $\Theta=\frac{1}{4}$ ML. ΔE denotes the binding energy obtained from the difference between the total energy of H/Cu(111) and the sum of clean Cu surface energy and H atom spin-polarization energy. h is the binding height above the surface. d_1 is the distance to the closest Cu atom. ω Sym. and Asym. correspond to the symmetric and asymmetric stretch mode frequency, respectively. Figures inside parentheses are from the relaxed configuration.

Site	ΔE (eV)	h (Å)	d_1 (Å)	ω (eV)	
				Sym.	Asym.
$\theta=1$					
FCC	2.382(2.395)	0.853	1.714	137	124
a			1.69	139	115
HCP	2.376(2.397)	0.857	1.716	138	125
BR	2.15(2.16)	1.02	1.64	156	157
a			1.62	160	152
TOP	1.47(1.47)	1.51	1.51	216	
$\theta=\frac{1}{4}$					
FCC	2.509(2.530)	0.907	1.741(1.796)		
b	3.24	0.852		134	
c	2.37	0.953		142	
HCP	2.494(2.511)	0.911	1.744(1.748)		
c	2.36	0.957		143	
BR	2.36(2.38)	1.05	1.66(1.68)		
b	3.12	1.01		153	
c	2.22	1.08		136	
TOP	1.88(1.88)	1.52	1.52(1.53)		
b	2.25	1.53		219	
c	1.83	1.52		212	

[a] Reference 23.

[b] Reference 21.

[c] Reference 22. $\theta=\frac{1}{3}$ ML.

We now turn our attention to the principal focus of the present study, H/Cu(110). There have been two different assignments of the binding site on H/Cu(110). On the basis of the low vibrational frequency characteristic from the HREELS measurements, two different experimental groups have assigned 68 and 81 meV features to the symmetric stretch mode at the LB and HL sites, respectively.[26,28] Likewise, the semiempirically constructed PES for H_2 on Cu(110) finds the HL site as the binding site and the LB site as a transition state.[27] On the other hand, 78 and 118 meV energy losses[7] have been attributed to the parallel and perpendicular vibrational modes at the pseudo-threefold site on the basis of the selection rules and the similarity to the results from H/Ni(110).[29] [See also the recent theoretical calculations on H/Ni(110) for comparison.[30]] The pseudo-threefold site assignment, with which a (1×3) super structure or its variant is usually associated, is consistent with the general trend found on H/fcc(110); H atoms form a ''zigzag'' pattern along the rows of substrate atoms in the $[1\overline{1}0]$ direction separated by three or several more rows in the [001] direction.[31,32] The origins of the disagreements in the vibrational frequency measurements and the corresponding assignments are not clear. However, the definite coverage has not been specified in the studies, except for Ref. 7.

It is interesting to note that despite its ''simple'' electronic structure, atomic H on Cu(110) exhibits a variety of complex phenomena including the structural phase transition depending upon the coverage and temperature. At a tempera-

TABLE II. Energetics at highly symmetric sites of H/Cu(110) at $\Theta=\frac{1}{8}$ ML from the first principles calculations and the EAM calculations at infinite dilution limit. ΔE denotes the binding energy. d_1 is the distance to the closest Cu atom. ω sym. and asym. correspond to the symmetric and asymmetric stretch mode frequency, respectively. Figures inside parentheses are from the relaxed configuration.

				ω (eV)		
Site	ΔE (eV)	h (Å)	d_1 (Å)	Sym.	Asym.	Asym.
$\theta=\frac{1}{8}$						
SB	2.37(2.40)	1.04	1.66	154	147	35
HL-SB	2.34(2.37)	0.59	1.68	56	134	128
LB	2.28(2.29)	0.16	1.83	105	90	67
HL-LB	2.16(2.21)	0.38	1.69			
HL	2.07(2.10)	0.47	1.63	162		
TOP	1.82(1.84)	1.52	1.52	217		
SUB	1.70(1.77)	−1.26	1.82			
EAM calculations $\theta=$infinite dilution limit						
SB	1.73	1.47	2.29	159	110	
HL-SB	1.93	1.19	1.95			
LB	2.15	0.88	1.97	107	158	49
HL-LB	2.25	0.78	2.02			
HL	2.33	0.78	2.06	127	67	41
TOP	1.35	1.83	1.83	193		

ture below 140 K and the estimated coverage less than $\Theta=0.3$ ML, all the above-mentioned studies observe the distinctive (1×3) phase from the low-energy electron diffraction (LEED) measurements. Also, below $T=120$ K, several $(1\times n)$ phases, n ranging from 1 to 4, have been reported from He scattering experiments.[33] As either the temperature or coverage increases, it is believed that the (1×3) phase changes to the (1×2) ''missing row'' type reconstruction phase[34] [For interesting comparison, see also works on hydrogen induced reconstruction for H/Pd(110).[35,36]] Hence, owing to the existence of several phases sensitive to the coverage and temperature, it is rather difficult to state decisively what the binding site is from those contradicting results.

Our calculated results for the energetics and vibrational frequencies of H/Cu(110) are summarized in Table II. These calculations utilize a (4×2) unit cell, where 4 and 2 Cu atoms are placed along the $[1\bar{1}0]$ and $[001]$ directions, respectively, on each slab. A $(3\times3\times1)$ grid is utilized for the BZ integrations. A single hydrogen atom is placed on several symmetric surface sites, including the hollow (HL), long-bridge (LB), short-bridge (SB), top (TOP), and two pseudo-threefold sites (HL-SB and HL-LB), midpoints between the HL and two bridge sites along the $[1\bar{1}0]$ and $[001]$ directions, respectively.

We see from Table II that the SB site is predicted to be the minimum energy location (see Fig. 2). The HL and HL-LB sites are 300 and 100 meV higher in energy, respectively, than the SB position. The HL-SB site, located at about the midpoint between the HL and SB sites, 0.92 Å from the SB site, appears to be a shallow minimum at the foot of a sharply rising potential energy hill leading to the HL site. The present calculations predict that the HL-SB site is only slightly higher in energy (30 meV) than the SB position. This difference is within the likely margins of error of the present method, precluding a definitive assignment of the ordering of these two sites. Perhaps the most significant result of Table II is the prediction that the region bounded by the two neighboring HL-SB sites is relatively flat, particularly if zero-point effects are considered. (We note here that a similar finding that the energy barrier along the cross-channel direction is flatter than along the channel direction has been recently reported on H/Ni(110) by Kresse and Hafner.[30]) Finally we see that the energy of the LB site is 110 meV (70 meV) higher

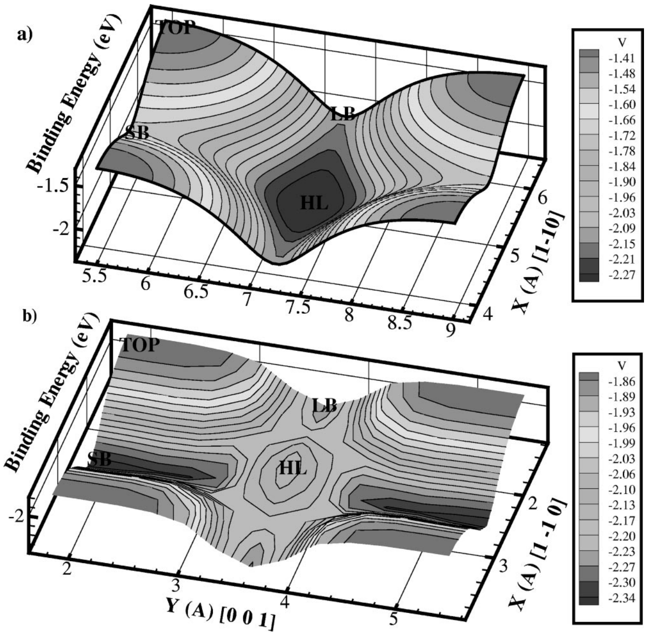

FIG. 2. The PES from (a) the EAM and (b) first principles calculations. Both calculations were done in the unrelaxed configuration where Cu atoms were frozen at the final positions obtained from the clean Cu surface calculation. For the EAM calculations, binding energy at a site was obtained with respect to the infinite separation between the Cu(110) surface and a single H atom. For the first principles calculations, it was obtained as the difference between the total energy from H/Cu(110) and the sum of the clean Cu(110) surface energy and spin-polarization energy of H atom.

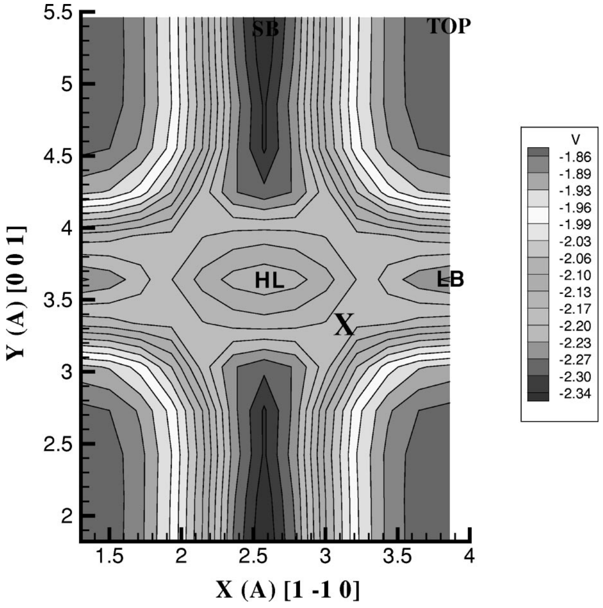

FIG. 3. The transition state, marked by X, is located at about the midpoint between the two sites with the energy barrier of 170 meV with respect to the SB-HL site. The calculation was done in the unrelaxed configuration.

than the SB (HL-SB) position. The binding height with respect to the surface plane at the LB site is small, 0.16 Å, with the H atom forming an almost linear Cu–H–Cu structure along the [001] direction as opposed to the triangular bridge structure found at the SB site. The nearest-neighbor bond lengths at both the SB and HL-LB sites are comparable, 1.66 and 1.68 Å, respectively. Moreover, the total charge transfer from neighboring Cu atoms is also approximately the same at both sites.

As indicated in Table II, our finding that there is a steep potential energy hill at the HL site is in sharp contrast with the predictions of EAM calculations. Because it ignores anisotropy in the chemical bonding and basically tries to maximize adsorbate coordination number, EAM theory predicts that the HL site is the preferred binding location. At the EAM level, the HL site places the H atom 0.74 Å above the surface plane. This makes the nearest-neighbor distance, the one to the underlayer Cu atom, 2.07 Å. This is very close to the next-nearest-neighbor distance, the one to the 4 Cu atoms at the corners of the unit cell, 2.29 Å. In contrast, the HL binding site height in the VASP calculations is 0.47 Å, which makes the nearest- and next-nearest Cu distances 1.65 and 2.24 Å, respectively.

The present calculations suggest that the minimum energy pathway for H/Cu(110) has a nontrivial, multidimensional character. Figure 3 shows the transition state for the SB to LB motion obtained from the nudged elastic band method.[37] The transition state along this pathway is located near the midpoint between the HL-SB and LB locations. The barrier height predicted by unrelaxed (relaxed) calculations is about 170 (200) meV relative to the HL-SB (SB) sites. A similar barrier position has been found for the H/Pd(110) system.[38] In contrast with previous Pd results, however, in which the energy barrier at the SB site changes from 0.11 to 0.18 eV when lattice relaxation is included, we find essentially no change in the barrier energy for the Cu(110) system since the substrate relaxation lowers the binding energy for all the sites accordingly. (We refer the reader to Papoian *et al.*[39] for a detailed analysis of the chemical bonding structure combining the DFT calculations and the chemical bonding analysis scheme called crystal orbital Hamilton population (COHP) for the change in the bonding structure depending upon the binding site.) In addition to the two-dimensional nature of the minimum energy pathway, as the H atom moves through the (SB, HL-SB, LB) sequence there is appreciable perpendicular motion of the adsorbate. The minimum energy H-atom heights for these three positions along the pathway are (1.04, 0.59, 0.15) Å, respectively. Thus, although energetically flat, perpendicular adsorbate motion along the minimum energy pathway is significant.

We also present in Table II normal mode estimates of the corresponding vibrational frequencies. In discussing these frequencies, it is useful to keep in mind that normal mode models commonly utilized in the analysis of EELS data have limitations when considering strongly quantum-mechanical systems. Prior work has shown, for example, that zero-point effects can produce large anharmonic corrections in predicted excitation energies.[4–6]

We now focus on three results of Table II, the vibrational frequencies calculated for the SB, LB, and HL-SB locations. The SB and LB sites have C_{2v} symmetry and thus have three nondegenerate vibrational modes. Our calculated vibrational frequencies for this site are (154,147,35) meV while the corresponding values for the SB site are (105,90,67) meV. These values correspond to the symmetric stretch perpendicular to the surface plane and to the two parallel modes corresponding to the asymmetric stretch and wagging mode in and out of the bridge plane, Cu–H–Cu, respectively. In line with expected trends,[40,41] the symmetric stretch frequency of the low-coordinate SB site is relatively high. With the proposed zigzag pattern along the $[1\bar{1}0]$ direction,[29] the symmetry of the HL-SB site is lowered from the C_{3v} to C_s point group which has reflection symmetry about the mirror plane along the [001] direction. The degeneracy of the parallel modes is thus lifted. From dipole selection rules, with the scattering plane aligned along the [001] direction, only two-dipole active modes should be observed. They are the ones that are perpendicular to the tilted trigonal plane whose normal is in the [111] direction $(A', \omega_\perp)$, and parallel to the [001] direction, $(A', \omega_\parallel)$. If the scattering take place along the $[1\bar{1}0]$ direction an additional, nondipole active mode $(A'', \omega_\parallel)$ is observable in the off-specular direction.[29] Our calculated vibrational frequencies for the HL-SB site are 128, 134, and 56 meV. These correspond to motion along the $[1\bar{1}0]$ direction, and in the plane formed by the [110] and [001] directions, respectively.

The first point to be made concerning the calculated vibrational frequencies for the three sites is that the results vary appreciably from position to position. This observation, and the relative flatness of the potential energy surface between the HL-SB and SB sites, suggest that the vibrational spectrum at low coverages could be relatively complicated. With the scattering along the $[1\bar{1}0]$ direction and the measurements taken only in the specular direction, Astaldi *et al.*[7] observed EELS losses at 79 and 118 meV for H/Cu(110) at $\Theta=\frac{1}{3}$ ML. The loss features at 79 and 118 meV have been assigned by Astaldi *et al.* to the parallel and perpendicular modes, respectively. For the second lowest energy HL-SB site, we find the ''perpendicular'' frequency to be the lowest (56 meV) and the ''parallel'' mode the highest (134 meV). The reason for the quotation marks on the mode labels is that the plane formed by those eigenvectors is actually rotated by about 47° with respect to that formed by the [110] and [001] directions. Hence, the perpendicular mode is 12° off from the normal of the tilted trigonal plane. Similarly, the ''parallel'' mode is no longer completely parallel to the surface, but has a small perpendicular component as well.

For comparison, we consider the vibrational frequencies for the H/Pd(110) system. Recent VASP studies of that system have found the pseudo-threefold HL-SB site to be the preferred binding site,[38] lower in energy than the LB and SB site by 70 and 110 meV, respectively. The HL-SB minimum is thus appreciably deeper for Pd(110) than that found in Cu(110). Using the same parameters that have been used in the above-mentioned Pd study, we have calculated the normal modes for the HL-SB site on H/Pd(110) at $\Theta=1$ ML. We have obtained results qualitatively similar to those for the Cu(110) system. In particular, the parallel and perpendicular modes are 119 and 93 meV, respectively, while the $(A'',\ \omega_{\parallel})$ mode frequency along the $[1\bar{1}0]$ direction is 102 meV. These results agree well numerically with the EELS loss features of 100 and 120 meV at $\Theta=1$ ML and at 87–89, 96–100, and 121–122 meV below $\Theta=\frac{1}{3}$ ML.[42] It should be noted, however, that the polarization assignments of the theoretical and experimental features disagree.

The experimental assignment of a higher frequency to the perpendicular motion on fcc(110) systems is generally made by analogy with H/fcc(111) systems. The vibrational frequency of a symmetric stretch mode at the threefold sites, fcc and hcp, has been found to be higher than that of the doubly degenerate parallel mode and also has been confirmed from the present calculations on H/Cu(111). When the scattering of electrons off the adsorbate is due to the dipole interactions, the parallel mode results in a smaller loss intensity in the spectrum because of the dipole moment cancellation from the image dipole. On the other hand, the perpendicular mode results in much stronger intensity since the perpendicular dipole moment strongly interacts with the incoming electrons. In the HREELS studies done on H/fcc(110), including Cu(110), it has been found that the lower frequency has stronger loss intensity. Despite this fact, all the studies on H/fcc(110) have assigned the lower frequency to the parallel mode in analogy to H/Cu(111) with the exception of Dinardo *et al.*[43] In particular, the recent study on Ag(110), which has similar atomic electronic structure to the Cu atom, has reported observing the two dipole-active losses, 60 and 105 meV with the scattering along the [001] direction.[44] The loss intensity is stronger at 60 meV than at 105 meV. The lower frequency has been assigned to the parallel mode in accordance with the precedence. However, the $(A'',\ \omega_{\parallel})$ mode is not observed in the off-specular measurement with the scattering plane along the $[1\bar{1}0]$ direction. Instead, Sprunger and Plummer[44] report an increase in intensity around 105 meV when the scattering plane is along the $[1\bar{1}0]$ direction. With this, they speculate that the $(A'',\omega_{\parallel})$ mode might be almost degenerate with the $(A',\ \omega_{\perp})$ mode, 105 meV, whose intensity is much smaller than that at 60 meV. The results from that study would strongly support the results from the present calculations. When the scattering is along the [001] direction on Cu(110), only the ''parallel'' and ''perpendicular'' modes with the respective 56 and 134 meV losses will show up. When the scattering plane changes to the $[1\bar{1}0]$ direction, the $(A'',\omega_{\parallel})$ mode, which would have been silent, will show up in the off-specular measurement. Since the $(A'',\omega_{\parallel})$ and the parallel modes correspond to the lateral motion, the loss intensity will be much smaller than that of the perpendicular mode. Moreover, since the $(A'',\omega_{\parallel})$ mode is almost degenerate with the parallel mode, which also has some perpendicular component due to the tilted angle, the difference in frequency between the two is below the experimental resolution limit. Thus, when the off-specular measurement is taken with the scattering along the $[1\bar{1}0]$ direction, increased intensity will result as it might have on H/Ag(110). This effect could have been observed on H/Cu(110). Unfortunately, only the specular measurements in the $[1\bar{1}0]$ direction have been done on H/Cu(110).[7]

IV. CONCLUSION

We have investigated the energetics of the H/Cu(110) system at $\Theta=\frac{1}{8}$ ML by first principles density functional calculations. Our purpose has been to obtain a more accurate description of the PES in order to begin to understand the dynamics of adsorbed hydrogen atoms at low temperature and low surface coverages.

Several results have emerged from our study. We have found, in contrast to the predictions of EAM theory, that the surface hollow site is not the preferred surface binding site in this system. Both the short-bridged and pseudo-threefold sites are energetically more favorable. The energy differences between the short-bridged and pseudo-threefold sites are sufficiently small that present results are not likely to be able to resolve them reliably. Indeed, we have found that the overall potential energy landscape is very different from previous models. The landscape is marked by a relatively flat region between adjacent pseudo-threefold sites along the [001] direction and a relatively large potential energy maximum at the hollow site. If true, such a potential energy surface geometry suggests that the picture of the dynamics in this system as being essentially quasi-one-dimensional in nature is qualitatively incorrect. Instead, transchannel adsorbate motion would be appreciable, an issue that could presumably be probed by measuring the anisotropy of relevant surface diffusion coefficients.[45] We have found that the calculated vibrational frequencies as discussed in Sec. III vary appreciably for the different, energetically similar surface positions. We have also found the frequency of the perpendicular, symmetric stretch mode at the pseudo-threefold site to be lower than that of the parallel mode.

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