Surface Corrugation in the Dissociative Adsorption of H_2 on Cu(100)

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First-principles calculations of the potential energy surface for H_2 dissociation on the Cu(100) surface are presented. The height of the transition state above the surface and energy barrier are mapped over the surface. A very marked surface corrugation is found. Normal mode frequencies at the transition state for two extreme dissociation geometries suggest that zero point energy contributes little to surface corrugation. The local density approximation predicts a zero minimum barrier. Gradient corrections greatly increase the barrier height, but have little effect on the surface corrugation.

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As the simplest example of a gas-surface reaction, a great deal of effort has gone into understanding the dissociative adsorption of hydrogen on metal surfaces. The H_2/Cu system has been particularly widely studied as an example of activated adsorption with a relatively large barrier. The dissociation process has been studied using seeded molecular beam scattering and adsorption experiments and state-resolved time-of-flight measurements of desorption [1,2]. Such experiments have shown that vibrational excitation of the incoming hydrogen molecule always promotes dissociation on the low index surfaces of Cu while the role of molecular rotational energy is more complex. On the Cu(111) surface it has been observed that increasing rotational state J at first decreases, then increases the sticking probability [2]. The dependence of sticking probability on the angle of incidence of the molecular beam has also been measured. For Cu(100) normal energy scaling is found to be a good approximation [3], indicating that only the component of momentum perpendicular to the surface is effective in promoting dissociation. This is usually interpreted as implying that the surface appears very flat to the dissociating molecule.

In order to make progress in understanding the dissociative adsorption of hydrogen on metal surfaces one requires a potential energy surface (PES) for the molecule-surface interaction. The PES can then be used as input in dynamical simulations (quantum or classical) of molecular scattering and adsorption [4]. The role of vibrational excitation in promoting dissociation is now well understood as arising from a dissociation barrier late in the dissociation pathway, i.e., at an extended bond length [4,5]. Simulations including rotational coordinates have been performed [4,6,7] but the role of rotational excitation in dissociation remains unclear. It appears that the experimental results can be reproduced only if there is a strong azimuthal dependence in the PES which implies that the surface is highly corrugated [7]. It then becomes difficult to reconcile the observation of approximate normal energy scaling for the H_2/Cu system with the effects of rotational excitation. The importance of surface corrugation in understanding the sticking probability on different Cu surfaces has been illustrated by six-dimensional simulations [8] using PESs constructed from effective medium theory. In this Letter we aim to investigate the degree of surface corrugation in H_2 dissociation on Cu(100) by using *ab initio* total energy methods to calculate sections of the full PES. In particular, we concentrate on how various properties of the dissociation process (e.g., energy and position of the transition state) vary across the surface unit cell.

The PES is obtained from first-principles total energy calculations using a plane-wave basis set. We use a Car-Parrinello approach, minimizing the total energy by means of a conjugate gradient technique [9]. Exchange and correlation effects are included within both the Ceperley-Alder local density approximation (LDA) [10] and the generalized gradient approximation (GGA) of Perdew and Wang [11]. Gradient corrected energies are obtained by inserting the LDA charge densities into the GGA functional. We find that the error arising from the use of the LDA charge density rather than a self-consistent GGA density is small, as reported in [12]. 16 special k points in the Brillouin zone are used. A Fermi surface (Gaussian) smearing of 1 eV is employed and the energy extrapolated to zero temperature by the method of De Vita and Gillan [13]. The use of a soft Cu pseudopotential constructed by the method of Lin *et al.* [14] allows the use of a 350 eV plane-wave energy cutoff. A similar method has previously been applied to the H_2/Al(110) [15] and the H_2/Mg(0001) [16] systems. A 2D PES for the H_2/Cu(100) system was presented in [17] where further details of the computational method and tests of convergence with respect to k-point density and plane-wave energy cutoff can be found. A supercell of dimension 16 Å × 3.61 Å × 3.61 Å is used with a Cu slab five atomic layers thick and two atoms per layer per cell. We have found a five layer slab to be sufficient for an accurate PES, the PES for a three layer slab being very similar (e.g., the barrier height differs by only

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0.03 eV for the bridge site into hollow sites dissociation path discussed below). The Cu atoms are placed at their bulk equilibrium positions (at the experimental lattice parameter of 3.61 Å) and are not allowed to relax. This is appropriate for a scattering experiment when the Cu atoms have no time to react to the incident hydrogen molecule. Hydrogen molecules are placed at each face of the slab so that inversion symmetry is maintained. This gives monolayer coverage of the Cu surface after adsorption. Tests show that intercell interactions change the energy at the atomic adsorption site by only 0.04 eV per hydrogen atom [17]. Plots of the bonding charge density [18] also show little intercell interaction, indicating that the PES is reasonably well converged with respect to unit cell size.

Some of the dissociation geometries considered are shown in Fig. 1. The unit cell and high symmetry sites of the (100) surface (top, bridge, and hollow) are marked as are the four coordinates corresponding to rotation and to translation in the plane of the surface. Two-dimensional sections of the PES, calculated using the GGA, are shown in Figs. 2(a) and 2(b) for dissociation about the bridge site into hollow sites and about the hollow site into bridge sites. We refer to these as "*h-b-h*" and "*b-h-b*" geometries, respectively. These figures show the total energy of the H_2/Cu system as a function of height z above the surface and bond length d for a molecule which is incident with its axis parallel to the surface. Each PES is interpolated from about 35 data points. As expected, the barrier is in the exit channel so that vibrational energy is effective in promoting dissociation. The energy barriers are found to be 0.99 and 1.06 eV for the *h-b-h* and *b-h-b* geometries, respectively. The two potential energy surfaces are quite different and in particular the curvature of the reaction path, which is an important feature affecting the dissociation probability [19], is clearly greater for the *b-h-b* case. For comparison, the same PESs calculated within the LDA are shown in Figs. 3(a) and 3(b). The LDA energy barriers are found to be 0.06 and 0.13 eV for the *h-b-h* and *b-h-b* geometries, respectively. The main reason for the difference between the GGA and LDA results is due to the poor description of the free H_2 molecule within the LDA, and particularly its severe overestimate of the total energy of H_2 [20]. From the results of Ref. [20] the total energy of the H_2 molecule is −30.89 and −31.81 eV for LDA and GGA, respectively (cf. the experimental value of −31.97 eV). The GGA therefore significantly decreases the total energy of the H_2 molecule when it is far from the surface (i.e., in the entrance channel), but the difference between the LDA and GGA decreases as the hydrogen atoms become embedded in the electron density of the Cu slab [18]. The GGA therefore results in a greatly increased barrier height.

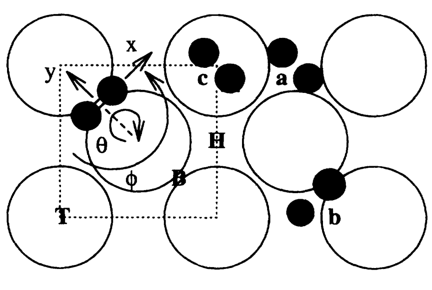

FIG. 1. Plan view of the Cu(100) surface showing Cu atoms (large open circles), the $\sqrt{2} \times \sqrt{2}$ supercell (dashed lines) and the high symmetry sites in the surface: top (T), bridge (B), and hollow (H). An H_2 molecule is shown dissociating about a bridge site into hollow sites (referred to in the text as the *h-b-h* geometry). The four coordinates perpendicular to height z and bond length d are indicated. Some other geometries considered are also shown, which we denote (a) *b-h-b*, (b) *b-h*, and (c) *b-t-b* (see text).

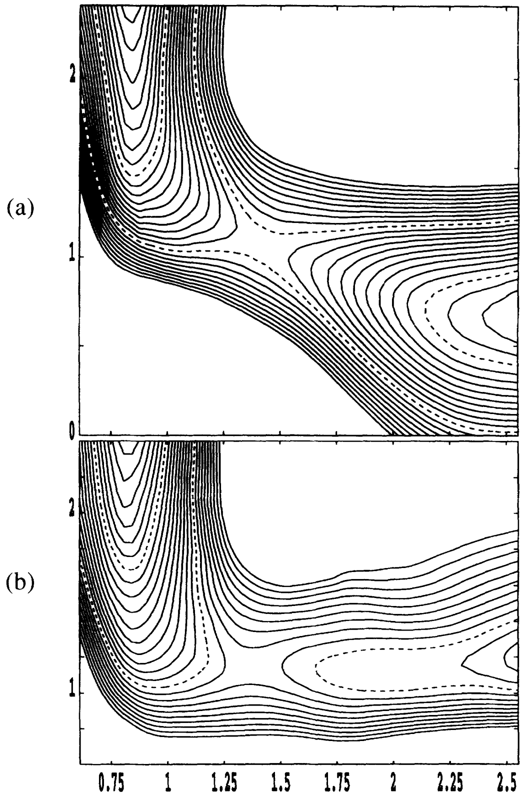

FIG. 2. (a) GGA potential energy surface for H_2 dissociation about the bridge into hollow sites. The vertical axis is the height z of the molecule above the surface and the horizontal axis is the H-H bond length d, both in angstroms. Contour spacing is 0.05 eV with highlighted contours at 0.5 and 1.0 eV above energy of free molecule (dashed lines). (b) As above but for dissociation about the hollow into bridge sites.

In order to investigate the corrugation of the surface experienced by an incoming molecule we have calculated the dissociation barrier for the center of mass of the molecule incident over eight points in the irreducible wedge of the surface cell (with the optimum orientation of the molecule at each point). In each case the transition state is located from forces (in the z-d plane) and energies at about six points in the vicinity [21,22]. The results for the GGA barrier energy and height above the surface are shown in Figs. 4(a) and 4(b) (LDA results show a similar amount of corrugation, although the absolute

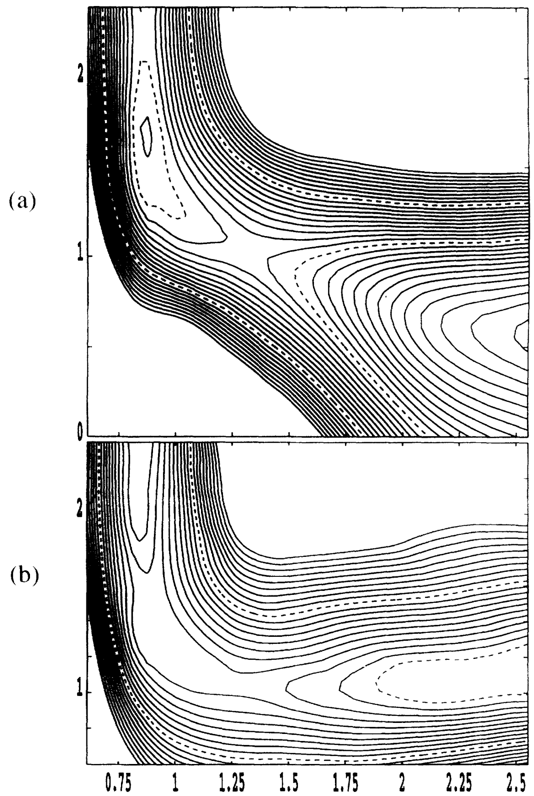

FIG. 3. LDA potential energy surfaces (cf. GGA result in Fig. 2). Dissociation (a) about bridge into hollow sites and (b) about hollow into bridge sites. Contours at 0.0 and 0.5 eV highlighted.

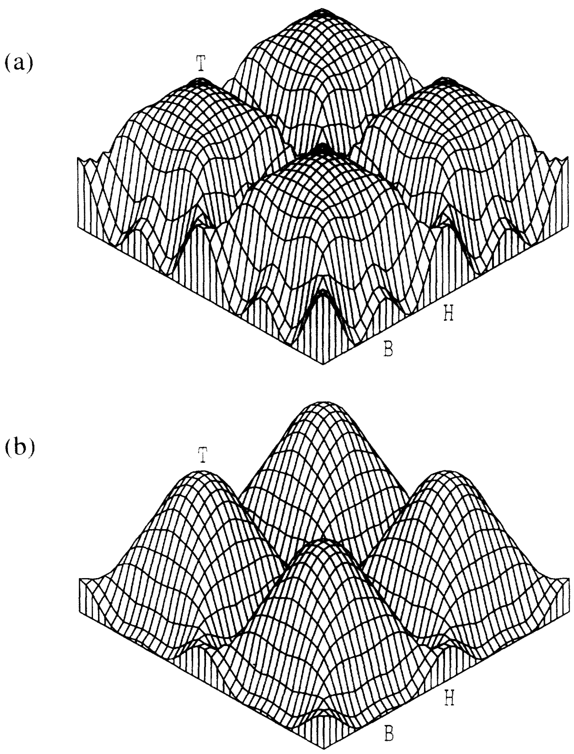

FIG. 4. Corrugation of Cu surface experienced by dissociating H_2 molecule. (a) Variation of energy barrier with position of molecular center of mass on the surface: maximum barrier 1.21 eV (at T), minimum barrier 0.93 eV (between B and H). (b) Variation of height z above the surface in the transition state: maximum height 1.40 Å (at T), minimum height 1.08 Å (between B and H).

values of barrier energies are much lower). The lowest barrier energy occurs for dissociation into neighboring bridge and hollow sites, which we denote as the "*b-h*" geometry (see Fig. 1), for which the dissociation barrier is 0.93 eV (the LDA gives essentially zero barrier). In this case the molecule is *not* parallel to the surface but tilted by about 20° so that the hydrogen atoms point towards the atomic adsorption sites at the bridge and hollow. The highest barrier occurs at the top site, the most favorable path here being into bridge sites, with the molecular axis parallel to the surface. We denote this "*b-t-b*" and find that the barrier is 0.28 eV higher than that for the most favorable (*b-h*) geometry. Thus, there is significant corrugation of the surface with high barriers above the atomic sites on the surface and channels along the lines joining bridge and hollow sites where the dissociation barrier is lower. The results for the height of the transition state above the surface show a similar picture, i.e., the height above the top site is much greater than that above the bridge and hollow sites and the points between them. The height varies by 0.32 Å over the surface. At first sight, the degree of surface corrugation indicated by Fig. 4 is inconsistent with the experimental observation of normal energy scaling. However, very recent dynamical simulations [23] have shown that the energy corrugation of Fig. 4(a) leads to momentum parallel to the surface tending to *inhibit* dissociation, whereas the height corrugation of Fig. 4(b) leads to parallel momentum *enhancing* dissociation. If the positions with a high energy barrier are correlated with the transition state being a large distance from the surface (as in Fig. 4) then the two effects tend to cancel out [23], giving a combined effect which approximates to normal energy scaling.

Finally, we wish to explore the PES further in the coordinates perpendicular to the z-d plane, with particular regard to the importance of zero point energy in the dissociation process. We have therefore calculated the normal modes at the transition states in the *h-b-h* and *b-t-b* geometries as representing extremes of barrier height. The normal mode frequencies are shown in Table I. Here x refers to displacement of the molecular center of mass along the molecular axis, i.e., towards hollow (bridge) for the *h-b-h* (*b-t-b*) case. y refers to displacement perpendicular to the molecular axis in the plane of the surface. ϕ and θ refer to molecular rotation in the plane of the surface (i.e., helicopter rotations) and out of the plane of the surface (i.e., cartwheel rotations), respectively (see Fig. 1). For the *b-t-b* geometry it is found, as one might expect, that cartwheel rotations are strongly hindered while

TABLE I. Calculated normal mode frequencies at the transition state for bridge to hollow (*h-b-h*) and top to bridge (*b-t-b*) dissociation. The dissociation geometries are shown in Fig. 1.

	Frequency (meV)	
Coordinate	(*h-b-h*)	(*b-t-b*)
z-d	140	210
z-d	$100i$	$115i$
x-θ	100	195
x-θ	$35i$	$10i$
y	85	20
ϕ	125	45

helicopter rotations and motion in the x-y plane are relatively free. However, this is not true for the *h-b-h* geometry for which the variation of energy with respect to ϕ is as large as the variation with respect to θ. This demonstrates another aspect of surface corrugation, where the degree of rotational and translational hindering at the transition state is also a rapidly varying function of position across the surface. One important feature of the results for dissociation about the bridge site is the instability of the transition state with respect to the x-θ normal mode corresponding to the molecule "sliding down" into a neighboring hollow site. This is in agreement with the lower dissociation barrier found for the *b-h* geometry. Although the vibrational frequency in the z-d plane perpendicular to the reaction path is greatly reduced from the value for the free molecule (490 meV at 350 eV cutoff), the frequencies in the other dimensions almost completely compensate for this reduction. The sum of the (real) normal mode frequencies at the saddle point is 450 meV (470 meV) for the *h-b-h* (*b-t-b*) case so that in both cases only a small fraction of the zero point energy of the incoming molecule may aid dissociation. This also suggests that zero point energy has a small effect on the energy corrugation seen by molecule, although for a complete picture further calculations are required for other dissociation geometries.

In conclusion, we have performed first-principles calculations of the potential energy surface for H_2 dissociative adsorption on the Cu(100) surface. The minimum dissociation barrier is found to be essentially zero in the local density approximation, while gradient corrections increase the barrier to 0.9 eV. Significant corrugation of the surface is found, with both the barrier energy and the height above the surface of the saddle point varying over the surface (by 0.28 eV and 0.32 Å, respectively). The approximate normal energy scaling which has been observed experimentally is likely to arise as a result of a cancellation of the effects of these two types of corrugation. Normal mode frequencies indicate that molecular rotations in the plane of the surface may be strongly hindered in the transition state at some points on the surface. Results for two dissociation geometries indicate that only a small fraction of the molecular zero point energy can aid dissociation and that zero point energy has a minimal effect on surface corrugation.

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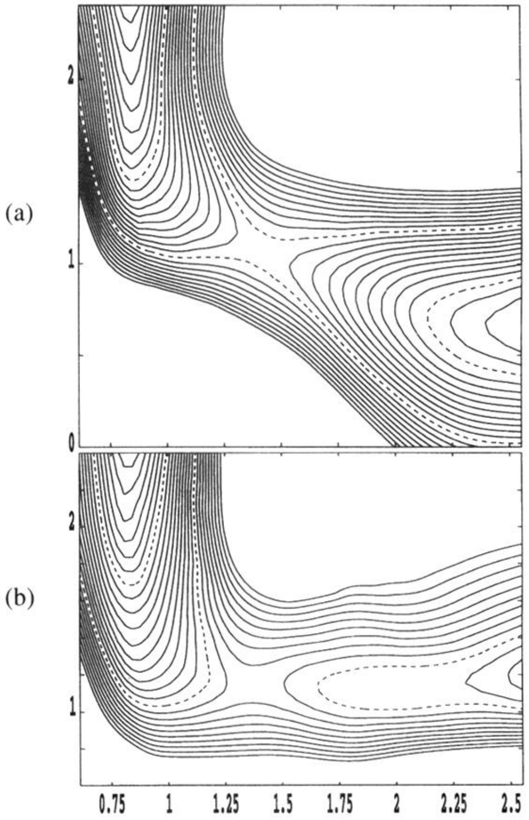

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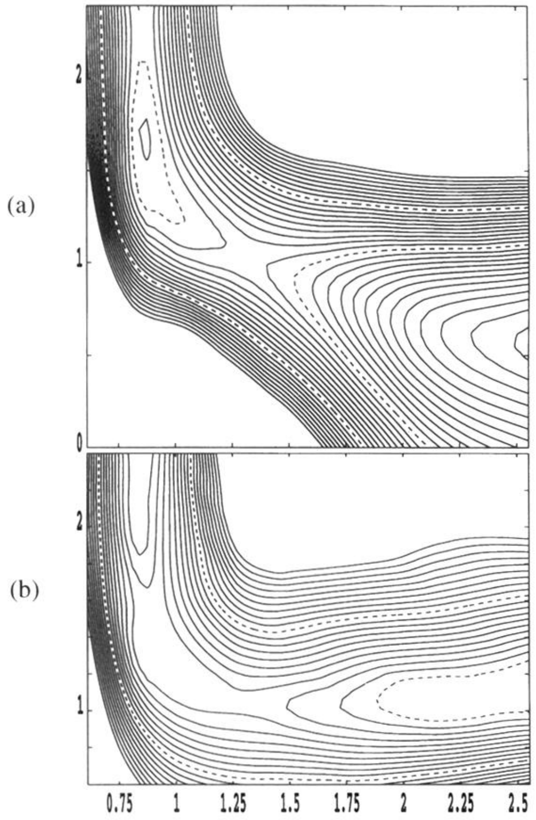

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