Multidimensional Potential Energy Surface for H_2 Dissociation over Cu(111)

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We present *ab initio* density functional calculations within the generalized gradient approximation for H_2 dissociating over Cu(111). The minimum barrier for dissociation is 0.5 eV and shows large corrugation within the unit cell and a strong dependence on the molecular orientation. Dissociation is predicted to depend strongly on translational, vibrational, and rotational degrees of freedom in accordance with experiment. We show that even for a noble metal, the *d* electrons are important for the molecule-surface interaction.

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Hydrogen dissociation on the Cu(111) surface has turned out to become the benchmark for our understanding of the dissociative chemisorption process. A series of molecular beam experiments have measured the detailed dependence of the dissociation probability on the translational, vibrational, and rotational degrees of freedom of the molecule and on the surface temperature [1–6]. Some of the observed effects are understood qualitatively, but the quantitative and overall theoretical description of the process still awaits detailed calculations of the multidimensional potential energy surface (PES) for the dissociation process.

In the present Letter we present the first calculations of the PES for H_2 dissociation outside a laterally infinite Cu(111) surface. We show that density functional calculations are now capable of giving a PES in general agreement with the detailed experimental information available. We present a detailed study of the PES as a function of all six H_2 degrees of freedom and discuss how and why the barrier for dissociation depends critically on both the impact parameter in the surface unit cell and the orientation of the molecule relative to the surface. The calculated potential illustrates unambiguously that simple low-dimensional potentials, while appealing and transparent, cannot describe the full dynamics of the dissociation process on a surface even for a simple diatom like H_2.

Several density functional theory calculations with the local density approximation (LDA) for the exchange-correlation functional have been presented, dealing with various low dimensional aspects of the PES of the H_2 dissociation over Cu "surfaces." The calculated energy barriers differ substantially. They are 1.4 eV when the substrate is approximated by a Cu_2 cluster [7], 0.55 eV for the (111) facet of a Cu_{15} cluster [8], and 0.3 eV for a Cu(100) slab [9].

Here we obtain the multidimensional PES for H_2 outside Cu(111) by means of total energy calculations using *ab initio* pseudopotentials, a plane wave basis, and representing the substrate by a rigid Cu(111) slab of the truncated bulk geometry at the calculated equilibrium lattice constant $a_0 = 3.57$ Å. The use of a rigid substrate is well justified as the Cu atoms (being subject to small forces only) do not have time to move appreciably during a dissociation event due to the large mass ratio between H and Cu.

The PES is calculated by varying all 6 ionic degrees of freedom of the H_2 molecule. The energies are referred to that where the H_2 molecule is right in the middle between two slabs (6.2 Å from either surface). The slab contains four Cu(111) layers. In order to keep the slab thickness small H_2 is adsorbed on one slab surface only [10]. Laterally, the supercells comprise three Cu atoms per layer, which corresponds to a H_2-H_2 distance of 4.4 Å. An accurate description of the metallic properties of the surface is expected with the slab geometry, where all Cu atoms at the surface have the correct coordination of the laterally infinite Cu(111) surface. This is not the case with cluster calculations where in fact most substrate atoms have a wrong coordination.

To describe the Cu we employ the fully separable pseudopotential of Troullier and Martins [11], including the 3*d* states as valence states. The hydrogen is described with the full Coulombic potential. The basis set consists of plane waves with a kinetic energy up to 50 Ry. The surface Brillouin zone is sampled by 18 special **k** points [12] with 3, 6, or 9 **k** points in the irreducible wedge. The Kohn-Sham equations are solved by alternating conjugate gradient minimizations [13] and subspace rotations [14]. Occupation numbers are found according to a Fermi-function distribution at $k_BT = 0.1$ eV and all total energies are extrapolated to zero electronic temperature [14].

The calculations are performed self-consistently within the LDA [15]. The nonlocal exchange-correlation terms within the generalized gradient approximation (GGA) [16] are calculated from the LDA densities. Extensive self-consistent calculations within the GGA have shown this procedure to be an excellent approximation due to the variational property of the total energy functional [16,17].

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The PES for the H_2 molecule dissociating perpendicular to the Cu-Cu bridge is given in Fig. 1(a). The molecule is kept parallel to the surface and centered over the bridge as shown in the inset. This is the favored configuration for H_2 dissociation over Cu(111). The PES is displayed as a function of the molecular bond length b and the molecular center of mass distance Z from the Cu surface. The PES shows a dissociation barrier of 0.73 eV positioned where the bond length has been extended by more than 33%, i.e., in the *exit channel.* Numerous experimental investigations [1–3] have established that the dissociation of H_2 (and D_2) on Cu(111) is an activated process. A strong coupling between the sticking probability and the vibrational state of the impinging molecule has been singled out from molecular beam experiments [2,3]. Together with intense theoretical work on model potentials [18] this coupling is taken as an indication that the barrier for dissociation for the H_2/Cu(111) system lies in the *exit channel.* The considerable barrier for dissociation and the position of the transition state in the exit channel revealed by Fig. 1(a) is therefore in qualitative agreement with experiment.

In Fig. 1(b) is shown the PES that comes out of a theoretical description within the LDA, i.e., without gradient corrections. The barrier for dissociation is almost absent in this description and further it is shifted to the entrance channel with the molecular bond length extended only moderately (less than 10%). This renders the LDA in both quantitative and qualitative disagreement with experiment and represents a serious failure of the LDA. The LDA was first shown to be inappropriate for molecule-surface interaction potentials in a study of H_2 dissociation on Al(110) [17]. The too low barrier within the LDA was analyzed in Ref. [17] and understood as arising from the underestimation of the Pauli repulsion between a spatially too extended $1\sigma_g$ of the H_2 and the electronic states of the metal. This conforms well with the present findings and with the general findings of nonlocal exchange-correlation functionals being substantially better than the LDA in describing the atomization energies of small molecules [16,19,20]. In fact, nonlocal exchange correlation has shown to be required already for a proper qualitative description of molecule-molecule reaction energetics [21]. Also we note that the chemisorption energies for the H_2/Cu(111) system at coverage 2/3 change substantially from the endothermic 0.13 eV/molecule in the GGA description to an exothermic -0.75 eV/molecule in the LDA. The former is a more reasonable value [22] and the GGA thus also provides better *chemisorption* energies.

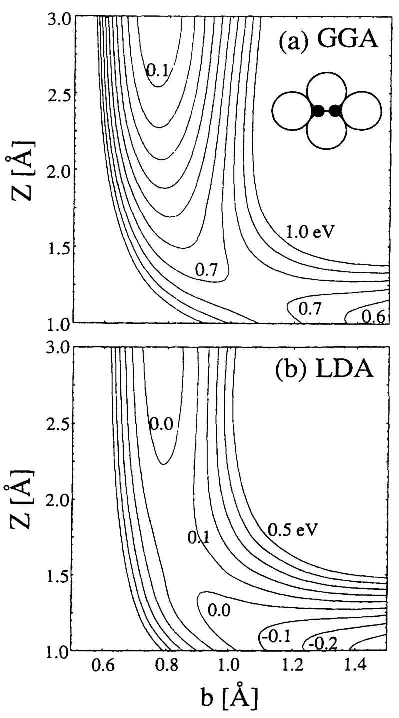

FIG. 1, (a) The PES for H_2 dissociation over Cu(111) calculated within the GGA. The inset shows the dissociation geometry. (b) Same as (a) but calculated with the LDA only.

In spite of the failure of the LDA to provide accurate total energies, the LDA densities and densities of states are still utilized in the GGA calculations and provide a good basis for a conceptual understanding of the processes studied. As an example we consider in Fig. 2 the development of the LDA projected densities of states along the reaction path. Shown are the bonding ρ_+ and antibonding ρ_- projected densities of states, $\rho_\pm(\epsilon) = \sum_i |\langle\psi_i|\delta(\mathbf{R}_1) \pm \delta(\mathbf{R}_2)|\psi_i\rangle|\delta(\{\varepsilon - \varepsilon_i)\}$, where $\delta(\mathbf{R}_1)$ and $\delta(\mathbf{R}_2)$ represent delta functions at the positions of the hydrogen atoms. It is clearly seen how the dissociation is accompanied by the gradual filling of the antibonding molecular state as also seen in earlier jellium-based calculations [23]. The barrier for dissociation is governed by the cost in energy of orthogonalizing the metal states sticking out into vacuum to the bonding H_2 state. By moving into the molecular antibonding state the metal electrons orthogonalize to the

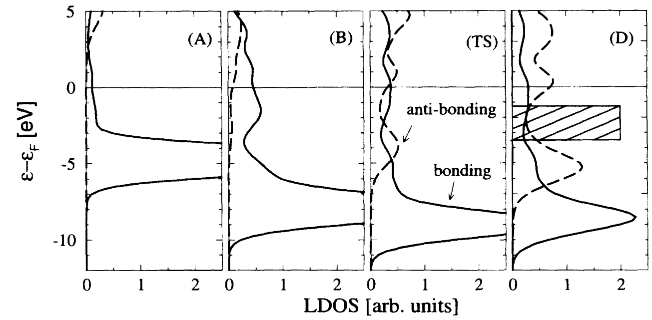

FIG. 2. The molecular bonding (full line) and antibonding (dashed line) density of states along the optimum reaction path. All contributions are broadened by a Gaussian of width 1 eV. The hatched region in (D) gives the position of the Cu d band.

bonding state. Once the antibonding state begins to fill the H-H bond becomes weaker and the dissociation is facilitated. Figures 2 (TS) and (D) further show how the antibonding molecular state is present as several resonances avoiding the position of the *d* band, shown as a hatched region, a few eV below the Fermi level. This reflects a rather strong hybridization of the antibonding state with the Cu *d* states and evidences that the metal *d* states play an important role in surface chemistry—even on a noble metal surface.

Table I summarizes some results of convergence tests for the barrier height. Increasing the basis set is seen to cause a negligible change in the barrier height. However, the barrier is lowered somewhat when the number of electronic states in the calculation, N_i, is increased either by increasing the number of Cu atoms per supercell or by increasing the number of **k** points. To quantify the degree of convergence of the barrier that is reached for a certain N_i we inspect the work function change ΔW on the clean surface of the slab as the H_2 dissociation takes place on the other surface. If the slab is thick enough for surface-surface interactions to be small and if the screening properties of the Cu are well enough described then ΔW is zero. A necessary condition for the barrier on the slab system to reflect the barrier on a semi-infinite crystal surface is therefore that $|\Delta W|$ is small. This is best obtained by the last three entries of Table I and the barrier height for these is seen to vary from 0.48 to 0.54 eV. Our calculations therefore suggest that the barrier on the semi-infinite crystal surface is about 0.5 eV, which is a theoretical result in good agreement with the barrier heights that have been deduced to explain experiment [18]. This gives confidence that parameter-free calculations can now predict also quantitatively the details of PES.

The barrier for dissociation depends strongly on the point of impact in the unit cell and the orientation of the incoming molecule. This can be illustrated by looking at the normal mode frequencies of the molecule in the transition state. We find frequencies of 50, 60, 100, and 130 meV. These are essentially associated with the translations, X and Y, along $[11\bar{2}]$ and $[\bar{1}10]$, the azimuthal angle ϕ, and the polar angle θ.

TABLE I. Convergence tests for the GGA barrier height E_a (in eV) found in Fig. 1(a). E_{cut} (in Ry) is the basis set cutoff. $N_\perp$ and $N_\parallel$ are the number of Cu layers and the number of Cu atoms per layer per supercell, respectively. N_k is the number of **k** points. $Ni = \frac{11}{2} N_\perp N_\parallel N_k$ is the number of electronic states. ΔW is the change (in eV) of the work function of the clean slab surface.

E_{cut}	$N_\perp$	$N_\parallel$	N_k	N_i	ΔW	E_a
50	4	3	18	1188	−0.22	0.73
70	4	3	18	1188	−0.22	0.76
50	4	4	18	1584	−0.14	0.64
50	6	3	18	1782	−0.21	0.64
50	6	4	18	2376	−0.07	0.48
50	8	3	18	2376	0.00	0.48
50	4	3	54	3564	0.04	0.54

Figure 3 visualizes the barrier dependence in the (X,Y) plane for two values of ϕ. The figure has been constructed by fitting a cosine expansion of the barrier variation with calculated values of the barrier at high symmetry points in the unit cell. It is clear that there is a strong variation of the barrier height with X, Y, and ϕ. This variation is strongly coupled to the variation in the atomic chemisorption energy over the unit cell, which is quite reasonable since the barrier for dissociation is in the exit channel and thus expected to be governed by final state effects. We find the atomic chemisorption energy to be 0.16 eV higher for the bridge than for the threefold hollow site and as much as 0.65 eV higher for the on-top site. This immediately explains why dissociation over the bridge site into the on-top sites has a barrier which is 0.7 eV higher than the minimum one, whereas the barrier for on-top dissociation into the hollow sites is only 0.25 eV higher than the lowest value.

Figure 4 shows how the potential energy rises as the molecule-surface separation decreases for an upright molecule with fixed bond length $b = 0.8$ Å over the bridge site compared with the molecule parallel to the surface, perpendicular to the bridge. The faster increase for the upright molecule is consistent with expectations

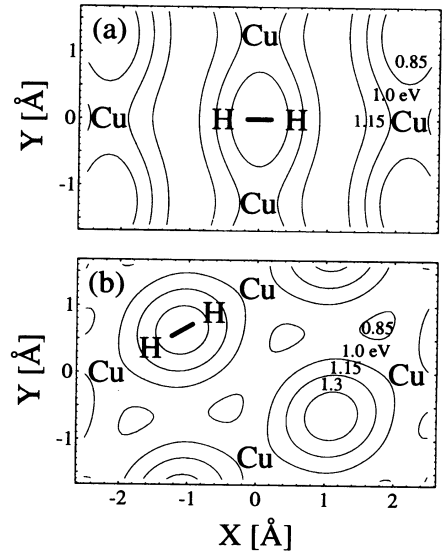

FIG. 3. The barrier height as a function of X, Y. The "Cu" marks the atomic positions in the Cu(111) surface. (a) $\phi = 0$. A molecule is depicted in the optimum reaction geometry, perpendicular to the Cu-Cu bridge, having (b,Z)=(1.1 Å,1.2 Å). (b) $\phi = \pi/6$. A molecule is shown in the worst case transition state, dissociation parallel with the bridge, having (b,Z)=(1.7 Å,1.5 Å).

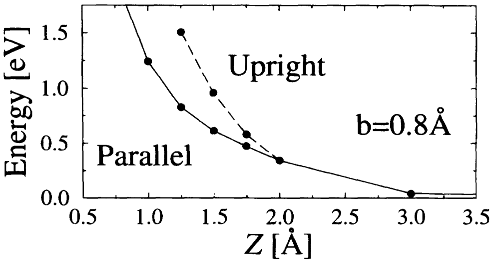

FIG. 4. The potential energy of a molecule parallel to surface, perpendicular to the bridge (solid), and of an upright standing molecule (dashed). The bond length is fixed at b=0.8 Å.

of a larger orthogonalization energy due to the larger overlap of the metallic and molecular states for the upright standing molecule compared to a molecule parallel to the surface.

The strong dependence of the barrier on X, Y, ϕ, and θ clearly shows that a full description of the dynamics of the dissociation process requires a treatment of all degrees of freedom [24], and the strong dependence on the latter two coordinates shows that the dissociation probability must couple to the rotational degrees of freedom, too, in accordance with experimental [4] and theoretical work [25].

In conclusion, we have presented a parameter-free calculation of the PES for H_2 dissociation over Cu(111). The corrugation of the barrier height over the unit cell we understand to a large degree as caused by the corrugation of the chemisorption energy over the unit cell. The metal d states were seen to play an important role in the dissociation process—even for the noble metal surface. The very detailed experimental investigations of this system allowed for an assessment of the quality of present calculated PES and the calculated barrier of 0.5 eV was concluded to be in excellent agreement with experiment. A full theoretical description of the sticking behavior of H_2 dissociation on Cu(111) will still have to await simulations of the dynamics based on the presented PES. However, it is clear already that the high degree of corrugation of the barrier height will cause a wealth of details in the sticking behavior as a function of the translational, vibrational, and rotational degrees of freedom of a H_2 molecule impinging on the Cu(111) surface.

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[1] G. Anger, A. Winkler, and K.D. Rendulic, Surf. Sci. **220**, 1 (1989).

[2] H.F. Berger, M. Leisch, A. Winkler, and K.D. Rendulic, Chem. Phys. Lett. **175**, 425 (1990); see also B.E. Hayden and C.L.A. Lamont, Phys. Rev. Lett. **63**, 1823 (1989).

[3] C.T. Rettner, D.J. Auerbach, and H.A. Michelsen, Phys. Rev. Lett. **68**, 1164 (1992); **68**, 2547 (1992).

[4] H.A. Michelsen, C.T. Rettner, and D.J. Auerbach, Phys. Rev. Lett. **69**, 2678 (1992).

[5] H.A. Michelsen, C.T. Rettner, D.J. Auerbach, and R.N. Zare, J. Chem. Phys. **98**, 8294 (1993).

[6] A. Hodgson, J. Moryl, and H. Zhao, Chem. Phys. Lett. **182**, 152 (1991).

[7] J. Harris and S. Andersson, Phys. Rev. Lett. **55**, 1583 (1985).

[8] J.E. Müller, Surf. Sci. **272**, 45 (1992).

[9] J.A. White and D.M. Bird, Chem. Phys. Lett. **213**, 422 (1993).

[10] J. Neugebauer and M. Scheffler, Phys. Rev. B **46**, 16067 (1992).

[11] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).

[12] S.L. Cunningham, Phys. Rev. B **10**, 4988 (1973).

[13] M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias, and J.D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).

[14] M.J. Gillan, J. Phys. Condens. Matter **1**, 689 (1989).

[15] D.M. Ceperly and B.J. Alder, Phys. Rev. Lett **45**, 566 (1980); J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[16] J.P. Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992).

[17] B. Hammer, K.W. Jacobsen, and J.K. Nørskov, Phys. Rev. Lett. **70**, 3971 (1993).

[18] D. Halstead and S. Holloway, J. Chem. Phys. **93**, 2859 (1990); S. Küchenhoff, W. Brenig, and Y. Chiba, Surf. Sci. **245**, 389 (1991).

[19] A.D. Becke, J. Chem. Phys. **96**, 2155 (1992).

[20] B.G. Johnson, P.M.W. Gill, and J.A. Pople, J. Chem. Phys. **98**, 5612 (1993).

[21] L. Fan and T. Ziegler, J. Am. Chem. Soc. **114**, 10890 (1992).

[22] C.S. Alexander and J. Pritchard, J. Chem. Soc. Faraday Trans. I **68**, 202 (1972).

[23] J.K. Nørskov, A. Houmøller, P. Johansson, and B.I. Lundqvist, Phys. Rev. Lett. **46**, 257 (1981).

[24] C. Engdahl, B.I. Lundqvist, U. Nielsen, and J.K. Nørskov, Phys. Rev. B **45**, 11362 (1992); K. Gundersen, K.W. Jacobsen, J.K. Nørskov, and B. Hammer, Surf. Sci. **304**, 131 (1994).

[25] S. Holloway, J. Phys. Condens. Matter **3**, S43 (1991); C. Engdahl and B.I. Lundqvist, Chem. Phys. Lett. **215**, 103 (1993).