

DISSOCIATIVE ADSORPTION OF HYDROGEN ON COPPER: STEPPED VERSUS UNSTEPPED SURFACES*

A.R. GREGORY and R. SILBEY**

*Department of Chemistry and Center for Materials Science and Engineering,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*

Received 23 May 1977

A simple quantum chemical theory of dissociative adsorption is introduced and applied to the chemisorption of hydrogen on copper. Hydrogen is predicted to chemisorb more readily on the stepped (311) surface than on either of its component low index faces.

The results of experiments utilizing a variety of techniques indicate that the structure of the surface plays an important role in the chemisorption of hydrogen on metals. For example, surface potential studies involving evaporated metal films and single crystal faces provide ample evidence for this conclusion [1]. LEED studies indicate that hydrogen chemisorbs readily on platinum (111) surfaces with (100) and (11 $\bar{1}$) steps, but not on the individual (100) and (111) platinum crystal faces [2]. Molecular beam and permeation studies indicate that the activation energy for dissociative adsorption of hydrogen on copper depends on the crystallographic characteristics of the surface [3].

The increased activity of the Pt (111) surfaces with (11 $\bar{1}$) steps was highlighted recently when the results of a molecular beam investigation of hydrogen-deuterium exchange on such surfaces were interpreted to mean that they are three or four orders of magnitude more efficient in promoting exchange than the parent (111) face [4]. However, this interpretation has proven controversial [5] and there is a clear need to elucidate the role that steps play in the chemisorption process.

It is the purpose of this note to introduce a simple theoretical model which predicts significant differ-

ences between adsorption on certain stepped surfaces and their unstepped counterparts. In this model the diatom-solid interaction potential, \mathcal{U} , is expressed as a sum of interactions between the diatom AB and the individual solid atoms, i.e., as a sum of three-body potentials. It is further assumed that the ad-molecule atoms and the solid atoms can all be treated as one-electron atoms. Then the *three-body* potential U_i between the diatom and the i th solid atom can be equated to the difference between a three-atom London-Eyring-Polyani-Sato (LEPS) potential [6] and the diatom singlet potential, ${}^1u_{AB}$. We thus write

$$\mathcal{U} = \sum_i U_i + {}^1u_{AB},$$

$$U_i = Q_{Ai} + Q_{Bi} + Q_{AB} - 2^{-1/2} [(\alpha_{Ai} - \alpha_{Bi})^2 + (\alpha_{Ai} - \alpha_{AB})^2 + (\alpha_{Bi} - \alpha_{AB})^2]^{1/2} - {}^1u_{AB},$$

$$Q_{kl} = \frac{1}{2}({}^1u_{kl} + {}^3u_{kl}), \quad \alpha_{kl} = \frac{1}{2}({}^1u_{kl} - {}^3u_{kl}),$$

where ${}^1u_{kl}$ and ${}^3u_{kl}$ denote the lowest singlet and triplet potential curves, respectively, of the diatom kl .

The model is an extension of the simple LEPS valence bond approach for constructing potential surfaces for bimolecular reactions. In the limit where the distance between the atoms of the ad-molecule is infinite, it reduces to the pairwise additive model for atom-solid interactions. McCreery and Wolken [7] have also extended the LEPS approach to diatom-solid interactions, formulating the interaction as a

* Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

** Supported partially by the NSF.

single, simplified, four atom, LEPS potential and representing the surface by a static, periodic, background potential.

We have used our model to investigate the dissociative adsorption of hydrogen on copper. The lowest singlet and triplet pairwise potentials are represented by Morse

$${}^1u(r) = {}^1u_0 \{ \exp[-2 {}^1\beta(r-r_0)] - 2 \exp[-{}^1\beta(r-r_0)] \}$$

and anti-Morse

$${}^3u(r) = \frac{1}{2} {}^3u_0 \{ \exp[-2 {}^3\beta(r-r_0)] + 2 \exp[-{}^3\beta(r-r_0)] \}$$

functions, respectively. Accurate functions of this type have been reported for the hydrogen molecule [8]. The parameters of the singlet pairwise H-Cu potential function were adjusted so that the adatom-solid potential conforms with the experimental heat of adsorption data [1] which pertain to the (100), (110) and (111) faces and to the stepped (311) face. The latter consists of (100) terraces, two atomic rows wide, separated by (111) steps, one atomic layer high[†].

Bond strengths on the low-index faces are found to increase with the adatom's local coordination number. The maximum bond energy sites on these faces are thus found to be those with the maximum number of nearest neighbors. As expected, binding is more uniform on the close-packed (111) surface than on any of the other surfaces. The presence of the steps on the (311) surface makes a significant difference to the binding energies of the sites on the component (100) and (111) facets. Their effect is to increase the strength of the bonds formed with many of these sites. Roughly speaking, the nearer the site to the bottom of the step, the stronger is the bond formed with the adatom and the more sensitive is the bond to the direction of approach of the adatom. The maximum bond energy calculated for the (311) surface exceeds that calculated for the (110) surface by less than 2 kcal/mole, but exceeds those calculated for the (100) and (111) surfaces by substantial amounts. The calculated maximum bond energies are in the order (311) > (110) > (100) > (111)[#].

Interaction potentials were calculated for various

approaches of a hydrogen molecule, held fixed at its ground state equilibrium distance, toward each of the copper surfaces. The atom-solid and diatom-solid potential curves were then used in conjunction with a model formulated by Lennard-Jones [9] to estimate activation energies for dissociative adsorption. We adjusted two of the parameters of the triplet pairwise H-Cu potential function until the calculated minimum activation energy on the (110) surface agreed with the observed value, after subtracting the zero-point energy of the hydrogen molecule[‡]. Using these parameters, we calculated attractive H₂-Cu(s) potential curves for the four surfaces under investigation and the correct order [3] for the activation energies on the low index faces^{##}.

The calculated minimum activation energies are in the reverse order to the calculated maximum H-Cu(s) bond energies. This is consistent with the suggestion [3] that the H₂-Cu(s) potential is not as sensitive to the details of the surface as the H-Cu(s) potential in their crossing region. The order of the activation energies can then be understood simply in terms of small shifts of the atomic potential relative to the molecular potential. It is therefore no surprise that the effect of the steps on the (311) surface is to substantially lower the activation energies for approaches towards most of the sites on the two facets of the (311) surface as compared with the approaches towards the component faces. However, it should be noted that the lowest activation energies for the (311) surface are obtained when the hydrogen molecule approaches sites above the (100) facet not very far from the projection of the bottom of the step on the uppermost (311) plane, along paths normal to the (311) face. Dissociative adsorption is predicted to proceed without activation on this surface.

The present results for hydrogen-copper interactions differ from those of a recent extended Hückel calculation of hydrogen-nickel interactions [10] in that the latter predict that the bond energy on the (100) face decreases as the coordination number increases and that edge sites on stepped surfaces are the most active. These differences may be due in part to

[†] The final parameter values are ${}^1u_0 = 0.316$ eV, $r_0 = 2.34$ Å and ${}^1\beta = 1.43$ Å⁻¹.

[#] Their values (in eV) are, (100):2.17; (110):2.49; (111):1.91; (311):2.56.

[‡] The final parameter values are given by ${}^3u_0 = 0.6 {}^1u_0$, ${}^3\beta = 1.5 {}^1\beta$.

^{##} The calculated minimum values (in eV) are, (100):0.48; (110):0.09; (111):0.70.

the greater participation of metal d-orbitals in hydrogen-nickel chemisorption; however, recent experiments [11] indicate that hydrogen is highly coordinated on Raney nickel. Full details of our calculations and results will be reported at a later time.

We would like to thank Dr. Alan Gelb for his contribution to the initial phase of this work.

References

- [1] J. Pritchard and F.C. Tompkins, *Trans. Faraday Soc.* 56 (1960) 540;
J. Pritchard, *Trans. Faraday Soc.* 59 (1963) 436;
W.A. Crossland and J. Pritchard, *Surface Sci.* 2 (1964) 217;
C.S. Alexander and J. Pritchard, *J. Chem. Soc. Faraday Trans. 1* 68 (1972) 202;
J. Pritchard, *J. Vacuum Sci. Technol.* 9 (1972) 895;
J. Pritchard, T. Catterick and R.K. Gupta, *Surface Sci.* 53 (1975) 1.
- [2] B. Lang, R.W. Joyner and G.A. Somorjai, *Surface Sci.* 30 (1972) 454.
- [3] M. Balooch and R.E. Stickney, *Surface Sci.* 44 (1974) 310;
M. Balooch, M.J. Cardillo, D.R. Miller and R.E. Stickney, *Surface Sci.* 46 (1974) 358.
- [4] S.L. Bernasek, W.J. Siekhaus and G.A. Somorjai, *Phys. Rev. Letters* 30 (1973) 1202;
S.L. Bernasek and G.A. Somorjai, *J. Chem. Phys.* 62 (1975) 3149.
- [5] K.E. Lu and R.R. Rye, *Surface Sci.* 45 (1974) 677;
I.E. Wachs and R.J. Madix, *Surface Sci.* 58 (1976) 590.
- [6] F. London, *Z. Electrochem.* 35 (1929) 552;
H. Eyring and J.C. Polanyi, *Z. Physik. Chem. (Leipzig)* B12 (1931) 279;
S. Sato, *J. Chem. Phys.* 23 (1955) 592, 2465.
- [7] J.H. McCreery and G. Wolken, *J. Chem. Phys.* 63 (1975) 2340.
- [8] R.N. Porter and M. Karplus, *J. Chem. Phys.* 40 (1964) 1105.
- [9] J.E. Lennard-Jones, *Trans. Faraday Soc.* 28 (1932) 333.
- [10] D.J.M. Fassaert and A. van der Avoird, *Surface Sci.* 55 (1976) 313.
- [11] A.J. Renouprez, P. Fouilloux, G. Coudurier, D. Tocchio and R. Stockmeyer, *J. Chem. Soc. Faraday Trans. 1* 73 (1977) 1.