

THEORETICAL STUDIES OF THE DISSOCIATIVE ADSORPTION OF H₂ ON Ni(001) USING AB INITIO PARAMETERIZED LEPS CALCULATIONS

Vasily I. AVDEEV

Institute of Catalysis, Academy of Sciences of the USSR, Novosibirsk 630090, USSR
and

Thomas H. UPTON *, W. Henry WEINBERG and William A. GODDARD III
*Division of Chemistry and Chemical Engineering **, California Institute of Technology,
Pasadena, California 91125, USA*

Received 18 September 1979; accepted for publication 4 March 1980

Semi-empirical London–Eyring–Polanyi–Sato (LEPS) calculations are reported, comparing the energetics of H₂ dissociation at linear, twofold, and fourfold sites on Ni(001). Parameters for the LEPS method were obtained from the results of first principles calculations of both atomic and molecular hydrogen adsorption on model Ni(001) surfaces. Several pathways are found to require no activation energy for dissociation, of which the most favorable is dissociation across a twofold site with subsequent atomic adsorption at fourfold sites. The experimentally observed β_1 (high coverage) state is found to be consistent with a geometry in which two hydrogen atoms are adsorbed at a single fourfold site.

1. Introduction

The interaction between hydrogen and transition metal surfaces represents an appropriate system with which to begin study of dissociative chemisorption. While the experimental details of hydrogen chemisorption on many metals are complex, it is an attractive problem from a theoretical point of view because of the simplicity of the bond that must be broken.

A number of studies have considered dissociative chemisorption using techniques such as generalized valence bond (GVB) [1], extended Hückel [2,3], CNDO [4], and a variety of more qualitative approaches [5]. Recently, we reported Hartree–Fock (HF) results for the atomic adsorption of hydrogen on large nickel clusters [6] that agreed well with available experimental data for the low index Ni surfaces [7]. As a first step towards examining the dissociative reaction, we report here the results of HF, GVB, and semi-empirical London–Eyring–Polanyi–Sato (LEPS) [8]

* IBM Fellow 1978–79 and AVS Scholar 1978–79.

** Contribution No. 6107.

calculations on possible reaction pathways by which the chemisorption reaction might occur. Of primary importance is the acquisition of a more thorough understanding of the competition between physically adsorbed (molecularly adsorbed) and chemisorbed states, and the degree to which transitions between the two are responsible for the observed lack of an activation energy for dissociative hydrogen adsorption on nickel. While primarily of qualitative interest, the calculations should delineate the dominant interactions and provide a focus for more detailed study.

2. Qualitative considerations

It is well known that hydrogen chemisorbs dissociatively on nickel without an activation energy [7a,c]. A simple qualitative model put forth by Lennard-Jones [9] to explain such phenomena is shown schematically in fig. 1. In this model, the potential surface due to a weakly bound physically adsorbed state is crossed *below* the zero of energy by another surface due to more strongly chemisorbed atoms. Assuming that the energy required to recouple the electrons at the crossing point is small, bond scission will occur without activation.

An adequate theoretical treatment of this problem must be able to consider both types of bonding situations. Since there is limited detailed experimental information concerning the atomic binding limit, and almost none concerning possible physically adsorbed states, it is difficult to parameterize semi-empirical methods accurately. In addition, it is not practical to attempt an investigation of *ab initio* quality capable of considering the vast number of geometries required to construct a potential surface.

Accordingly, we have chosen an intermediate approach. HF calculations have

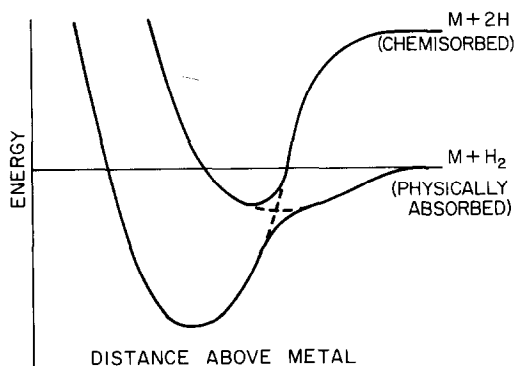


Fig. 1. Qualitative model due to Lennard-Jones, in which unactivated dissociation results from crossing of the physically adsorbed and chemisorbed potential curves.

been carried out previously to characterize the final chemisorbed state [6], and additional HF and GVB calculations are reported here that consider the limit in which the molecular bond is still intact. From these results, we have extracted the information necessary to obtain parameters for the LEPS method, and have generated full potential surfaces for several possible approach geometries on the Ni(001) surface.

3. First principles calculations

3.1. Computational details

For the physically adsorbed state, the interaction between the adsorbate and the surface is weak, and hence a relatively simple cluster may suffice to model the surface. Thus, a small eight-atom cluster was selected that emphasizes twofold and

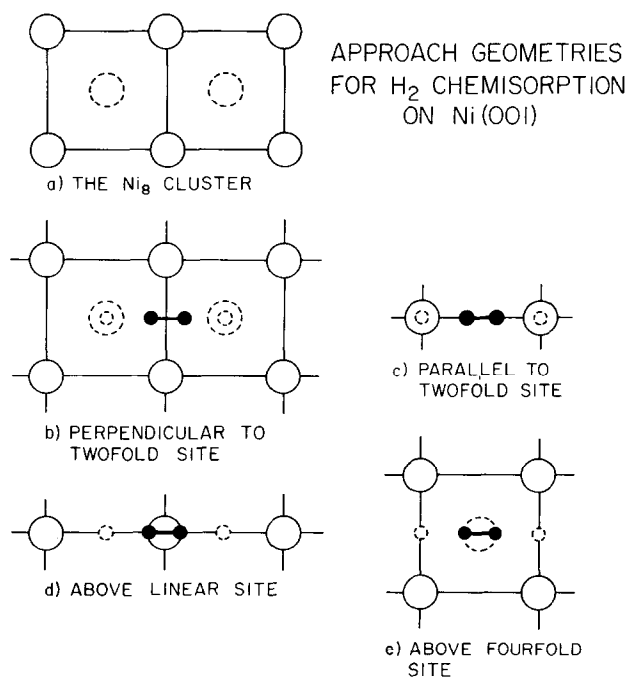


Fig. 2. The Ni_8 cluster and configurations for the $H_2/Ni(001)$ system studied. The small dashed circles are the H atoms for limiting atomic adsorption. The H-H distance is parallel to y , and the middle point of this bond is noted. (a) The Ni_8 cluster. (b) Dissociation across a twofold site ($x = 0, y = a/2$). (c) Dissociation parallel to twofold axis ($x = 0, y = a/2$). (d) Dissociation above Ni atom ($x = 0, y = 0$). (e) Dissociation above fourfold site ($x = a/2, y = a/2$).

fourfold sites (sites calculated previously [6] to be of greatest importance on the Ni(001) surface). This cluster is shown in fig. 2a. An effective potential was used to replace the Ar core and the $3d^9$ shell on each Ni atom, reducing the variational problem to a single valence electron (primarily 4s in character) per metal atom. This procedure has been shown previously to be adequate both for studies of the chemisorption of hydrogen [6] and the electronic states of the cluster [10]. The effective potential was obtained using the method of Melius et al. [11a] and modified [11b] to ensure the correct ordering of the Ni atomic states. In the calculations, the basis set for the Ni atoms consisted of atomic 4s functions [from the $(4s)(3d)^9$ state] [12a], and an unscaled 1s basis was used for the hydrogens [12b]. All calculations on the cluster itself were at the HF level, while calculations on the physically adsorbed state included correlation effects (GVB [12c]) in the H_2 bond.

3.2. Results and discussion

The ground state of the Ni_8 cluster was found to be closed-shell, 1A_1 , with an electronic configuration of $1a_1^2 2a_1^2 1b_1^2 1b_2^2$. The orbital energy spectrum of this cluster is shown in fig. 3a. If an H_2 molecule approaches the cluster in the geometry shown in fig. 2b with the H–H distance constrained to be that of free H_2 , we find that there is a local minimum at a distance of 2.2 au above the surface (the smallest Ni–H distance is 3.29 au). The orbitals of the system retain their separated “molecular” character and thus this state represents a physically adsorbed hydrogen molecule. This is reflected in the Ni_8H_2 orbital energy spectrum, shown in fig. 3b, in which only the H_2 orbital changes position significantly. While the bond energy of

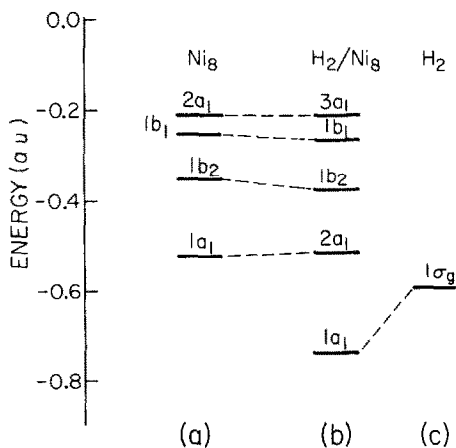


Fig. 3. Correlation diagram for the Ni_8-H_2 interaction. (a) Separate Ni_8 orbital energies. (b) The Ni_8H_2 orbital energies. (c) Separate H_2 orbital energy.

14 kcal identifies this as a physically adsorbed state, it is not clear that it would be stable with respect to H–H bond elongation. Our aim in this calculation was to obtain parameters for describing physically adsorbed states, and calculations involving H–H stretching were not undertaken.

4. Semi-empirical calculations

4.1. Computational details

The LEPS approximation has been used extensively to model gas phase dynamics [13] and more recently has been applied to the study of hydrogen chemisorption on tungsten [14] and copper [15]. Results have shown that the method provides a reasonable description of adsorption phenomena, and it is attractive in its simplicity. Following McCreery and Wolken [14], one assumes that for the interaction between the metal and hydrogen molecule, a simple four-electron valence bond treatment is applicable. The individual pairwise interactions included in such a treatment are indicated by the lines in fig. 4a. This is simplified further to include only the dominant interactions (H₁–H₂, H₁–M₁, H₂–M₂) as in fig. 4b. The corresponding energy expression is [14]

$$E(R) = J_{H_1H_2} + J_{H_1M_1} + J_{H_2M_2} - [K_{H_1H_2}^2 + (K_{H_1M_1} + K_{H_2M_2}) \times (K_{H_1M_1} + K_{H_2M_2} - K_{H_1H_2})]^{1/2}, \quad (1)$$

where J_{ij} is a coulomb interaction and K_{ij} is an exchange interaction between centers i and j . These quantities are assumed to be related to bonding (Morse) and antibonding (anti-Morse) functions through the formulae,

$$E_{ij}^b \approx (J_{ij} - K_{ij}) / (1 + \Delta_{ij}) \approx D_{ij} \exp[-\alpha_{ij}(r - r_e)] \{ \exp[-\alpha_{ij}(r - r_e)] - 2 \}, \quad (2)$$

$$E_{ij}^a \approx (J_{ij} + K_{ij}) / (1 - \Delta_{ij}) \approx D_{ij} \exp[-\alpha_{ij}(r - r_e)] \{ \exp[-\alpha_{ij}(r - r_e)] + 2 \}, \quad (3)$$

where Δ_{ij} is an adjustable parameter [8], and the remaining parameters are those of the Morse function: D_{ij} is the dissociation energy, r_e the equilibrium separation, $\alpha_{ij} = k(\mu/D_{ij})^{1/2}\omega$, μ is the reduced mass, and ω the vibrational frequency. Thus, it

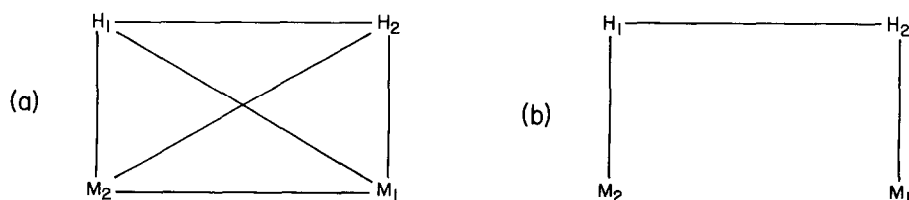


Fig. 4. Valence bond diagram for H₂-M interaction. (a) Full four-electron diagram. (b) Modified to include only dominant interactions.

Table 1
Bond values and Morse parameters for H–H and H–Ni interactions
Bond values calculated for atomic adsorption ^{a)}

Site	z_e (au)	D (eV)	ω (cm ⁻¹)
Linear	2.83	1.56	2286
Twofold	1.87	2.73	1428
Fourfold	0.57	3.04	592

Calculated H–Ni Morse parameters

i	z_i (au)	d_i (eV)	ω_i (cm ⁻¹)
0	1.87	2.73	1428
1	0.30303	-0.13553	0.29657
2	-0.04545	-0.07875	0.00385

Morse parameter for H–H ^{b)}

r_0	D_0 (eV)	ω (cm ⁻¹)
0.7416	4.476	4395

^{a)} Upton and Goddard [6].

^{b)} Herzberg [16].

remains only to determine empirical forms for E_{ij}^b and E_{ij}^a and to substitute them into eq. (1) to obtain the potential energy surface.

The Morse parameters of the H–H bond are well known [16], and are shown in table 1. For the H_{*i*}–M_{*i*} Morse function, the parameters are assumed to be dependent on surface site, as [14]

$$E_{HM}^b = D \exp[-\alpha_{HM}(z - z_e)] \{ \exp[-\alpha_{HM}(z - z_e) - 2] \}, \quad (4)$$

where the dissociation energy D , the equilibrium distance z_e , and the vibrational frequency ω are functions of x and y (in the surface plane),

$$D = D_0 [1 + d_1 S(x, y) + d_2 P(x, y)], \quad (5)$$

$$z_e = z_0 [1 + z_1 S(x, y) + z_2 P(x, y)], \quad (6)$$

$$\omega = \omega_0 [1 + v_1 S(x, y) + v_2 P(x, y)]. \quad (7)$$

The functions S and P are determined by the structure of the surface,

$$S(x, y) = \cos(2\pi x/l_1) + \cos(2\pi y/l_2), \quad (8)$$

$$P(x, y) = 1 + \cos(2\pi x/l_1) \cos(2\pi y/l_2), \quad (9)$$

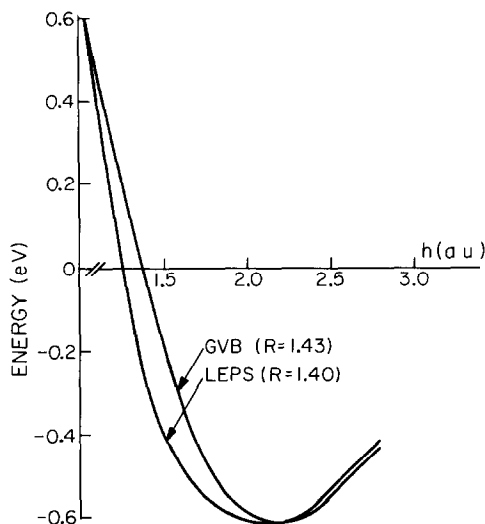


Fig. 5. Comparison of calculated GVB results for Ni_8H_2 and LEPS potential curve [eq. (1)]. Sato parameter is 0.2.

where for Ni(001), $l_1 = l_2 = 4.7$ au.

With values obtained earlier [6] from ab initio studies of bonding a hydrogen atom at onefold, twofold, and fourfold sites on Ni(001), sufficient information is available to fit each of the three parameters for D , z_e , and ω . The bond values used in the fitting, and the resulting parameters are collected in table 1.

All that remains is to obtain values for the Δ_{ij} . This parameter is highly sensitive to the form of the potential surface being considered. Following McCreery and Wolken, we have used the same Δ parameter for each Morse curve. This was obtained by adjusting Δ in such a way as to cause the total energy function $E(R)$ in eq. (1) to reproduce as closely as possible the potential curve for the molecule–solid interaction described in the previous section. The resulting fit is shown in fig. 5, where the $E(R)$ function is compared with GVB results for physically adsorbed H_2 on the Ni_8 cluster.

By parameterizing the LEPS equations in this manner, information is included that allows discrimination between different possible bonding schemes on the Ni(001) surface. Given the large differences in calculated binding energies for different sites (see table 1), it is unlikely that experimental studies could provide sufficient information to define such a parameterization.

4.2. Results and discussion

For simplicity, only approach geometries with the H_2 axis parallel to the surface were considered. They are shown schematically in figs. 2b–2e, where initial posi-

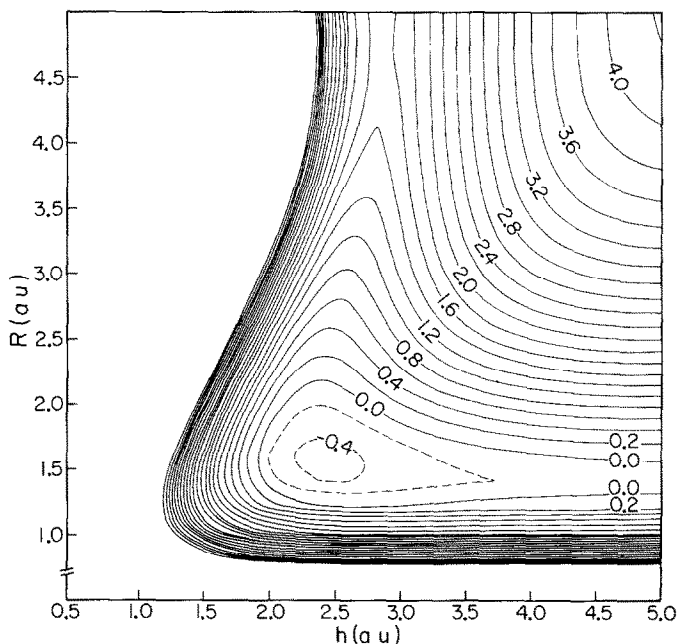


Fig. 6. Potential energy contours in R, h coordinates for interaction of H_2 with Ni(001). The starting energy point is taken as zero at $h \rightarrow \infty$, and the interval between contours is 0.2 eV. For all potential surfaces, the Sato parameter was $\Delta = 0.2$. The dashed lines represent negative values of energy. The H_2 is adsorbed above and parallel to a twofold site (see fig. 2c).

tions of the hydrogen molecule are indicated by small dark circles, and final atomic positions by small dashed circles.

For an approach with the H–H axis above and parallel to a twofold site, as in fig. 2c, the potential surface shown in fig. 6 is obtained. In this figure, the H–H separation plotted along the ordinate (R) and the height of the molecule above the surface is indicated along the abscissa (h). As may be seen, dissociation to linearly adsorbed atoms will not occur, as there is a minimum in the surface that retains the H–H bond.

It is unlikely, however, that the minimum indicated here represents a stable, molecularly adsorbed state. A similar approach geometry, shown in fig. 2b, allows the hydrogen molecule to approach the surface above the twofold site. In this case the H–H axis is above and perpendicular to the site axis, and the final state is one in which both atoms are adsorbed at fourfold sites. The potential surface for this configuration in fig. 7 indicates that there is no barrier to dissociative adsorption at fourfold sites.

A related geometry is the one shown in fig. 2d. Here the H_2 molecule dissociates

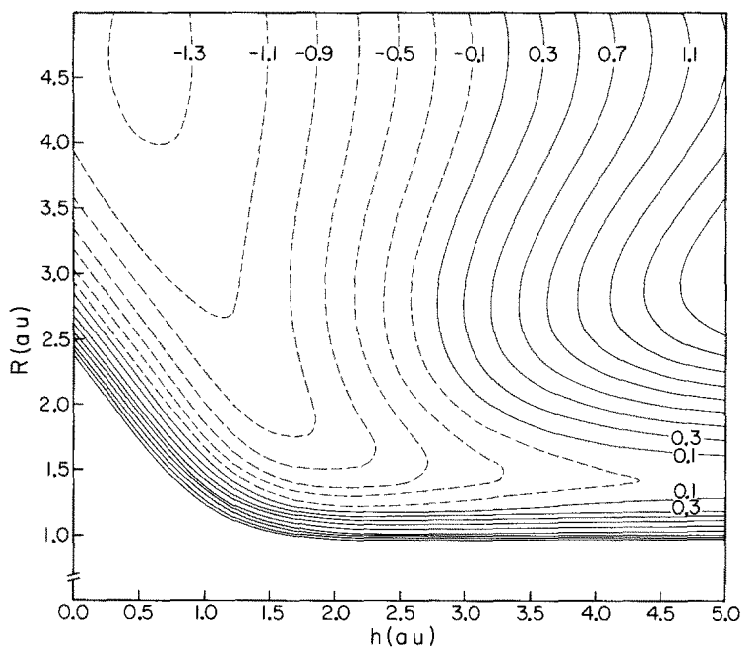


Fig. 7. As in fig. 6 except the approach of the H_2 is to a short-bridged site to form atomic adsorption on a fourfold site (see fig. 2b).

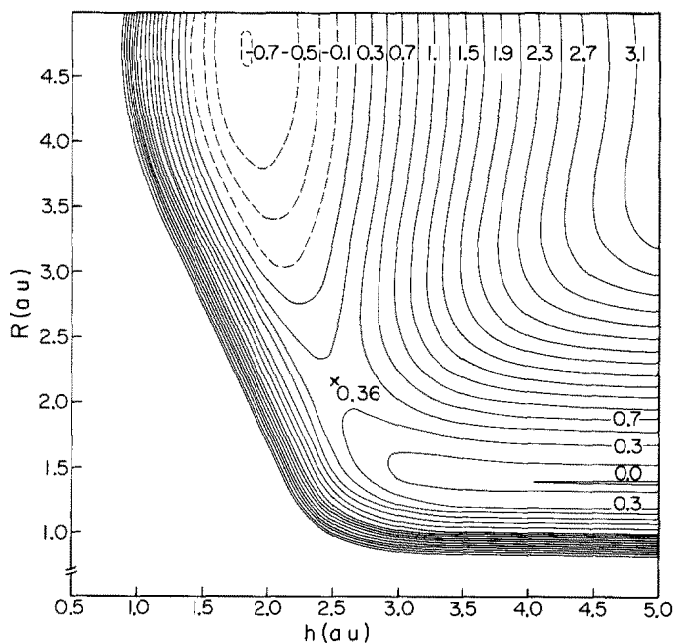


Fig. 8. As in fig. 6 except the H_2 is adsorbed on a linear site (see fig. 2d).

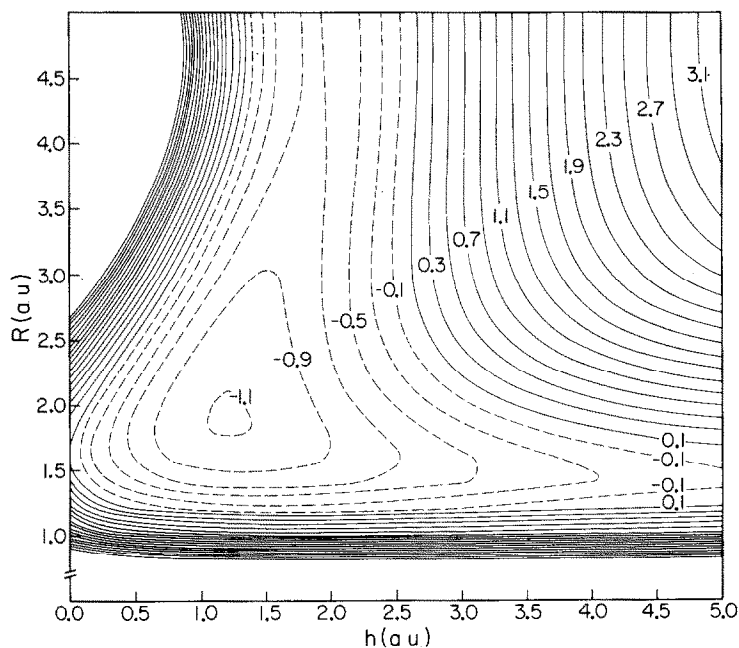


Fig. 9. As in fig. 6 except the H_2 is adsorbed at a fourfold site (see fig. 2e).

across the linear site, with the atoms assuming positions at adjacent twofold sites. The potential surface for this approach in fig. 8 shows a local minimum at small H–H separation and a barrier with respect to dissociation.

Finally, we consider an approach of the H_2 molecule directly over a single fourfold site (fig. 2e). A local minimum appears in the potential surface, shown in fig. 9, for an elongated bond distance of about $R = 1.9$ au and a height above the surface of $h = 1.2$ au. Since the LEPS method does not adequately assess the effects of spin recoupling [17] in bond formation, it is difficult to determine whether such a state represents an elongated molecularly adsorbed state, or atoms adsorbed at the same fourfold site. More exact calculations would be required to resolve this question. In any case, such a state is not stable with respect to migration of one atom to an adjacent fourfold site, as comparison with fig. 7 will show.

5. Conclusions

From the potential surfaces described above, it is possible to extract qualitative information about the competition between physically adsorbed and dissociatively adsorbed hydrogen. Comparing figs. 6, 7, and 9 (in each case fixing the H–H bond

distance at 1.43 au), we find that each leads to binding, as was suggested by the GVB calculations in section 3. These states are only transitional; in each case there is a subsequent pathway to fourfold atomic binding states without an additional barrier. Thus, at low coverage, we would expect the model discussed in section 2 to be qualitatively correct: activation-free dissociation results from a crossing between physically adsorbed and chemisorbed state potential surfaces. However, at higher coverages we might expect the situation to be altered. Local minima exhibited in figs. 6 and 9 will become absolute minima in situations where adjacent fourfold sites are filled.

This interpretation appears to be consistent with the experimental details. A number of investigators have observed two binding states on single crystal [Ni(001) and Ni(111)] [7c] and polycrystalline samples [7e]. The so-called β_2 -state is more strongly bound and obeys second-order desorption kinetics, indicating atomic adsorption. The β_1 -state is slightly less strongly bound and appears only after complete filling of β_2 . Experiments with polycrystalline surfaces indicate that this state may also follow second-order desorption kinetics, and an analysis of flash desorption lineshapes suggests the presence of repulsive interactions between adsorbed atoms. We would identify this state with the minimum shown in fig. 9, and note that the experimental details lend support to the interpretation of this state as involving adjacent atom adsorption.

Finally, we note that the results obtained here predict behavior different from that based on extended Hückel calculations [3]. However, extended Hückel calculations predict that the bonding of an H atom is strongest to single Ni atoms and weakest to highly coordinated sites, whereas our previous HF results [6] and recent experimental evidence [7f–h] find the opposite. Thus the EH prediction that an approach geometry, such as that shown in fig. 6 is very favorable, may be associated with the EH finding that the linear site is most favorable for atomic hydrogen binding on Ni(001) [2].

6. Summary

We have presented a qualitative examination of the dissociative adsorption of hydrogen on Ni(001), in which unactivated dissociation is possible from several interaction geometries. Configurations are indicated in the calculations that may identify the β_1 form of hydrogen on Ni(001) as a pair of H atoms adsorbed at a single fourfold site. Limitations in the LEPS method preclude a detailed analysis of the nature of this state, and more exact calculations will be required.

Acknowledgments

This work represents one phase of the Joint US–USSR Exchange Program in Chemical Catalysis and was supported by the National Science Foundation under

Grant Number CHE77-10629. In addition, one of us (W.H.W.) is grateful for support from the Camille and Henry Dreyfus Foundation in the form of a Teacher-Scholar Award.

References

- [1] C.F. Melius, J.W. Moskowitz, A.P. Mortola, M.B. Baillie and M.A. Ratner, *Surface Sci.* 59 (1976) 279.
- [2] (a) A. van der Avoird, S.P. Liebman and D.J.M. Fassaert, *Phys. Rev. B* 10 (1974) 1230.
(b) H. Deuss and A. van der Avoird, *Phys. Rev. B* 8 (1973) 2441.
- [3] D.J.M. Fassaert and A. van der Avoird, *Surface Sci.* 55 (1976) 291, 313.
- [4] G. Blyholder, *J. Chem. Phys.* 62 (1975) 3193.
- [5] (a) S.C. Ying, J.R. Smith and W. Kohn, *Phys. Rev. B* 11 (1975) 1483.
(b) S.W. Wang and W.H. Weinberg, *Surface Sci.* 77 (1978) 14.
(c) B.I. Lundqvist, J.K. Norskov and H. Hjelmberg, *Surface Sci.* 80 (1979) 441.
- [6] (a) T.H. Upton and W.A. Goddard III, *Phys. Rev. Letters* 42 (1979) 427.
(b) T.H. Upton, W.A. Goddard III and C.F. Melius, *J. Vacuum Sci. Technol.* 16 (1979) 531.
- [7] (a) K. Christmann, O. Schober, G. Ertl and M. Neumann, *J. Chem. Phys.* 60 (1974) 4528; *Surface Sci.* 40 (1973) 61, and references cited therein.
(b) T.N. Taylor and P.J. Estrup, *J. Vacuum Sci. Technol.* 11 (1974) 244.
(c) J. Lapujoulade and K.S. Neil, *Surface Sci.* 35 (1973) 288; *J. Chim. Phys.* 70 (1973) 797.
(d) J. Küppers, *Surface Sci.* 36 (1973) 53.
(e) K.Y. Yu, D.T. Ling and W.E. Spicer, *J. Catalysis* 44 (1976) 373.
(f) M.A. Van Hove, G. Ertl, K. Christmann, R.J. Behm and W.H. Weinberg, *Solid State Commun.* 28 (1978) 373.
(g) K. Christmann, R.J. Behm, G. Ertl, M.A. Van Hove and W.H. Weinberg, *J. Chem. Phys.* 70 (1979) 4168.
(h) S. Andersson, *Chem. Phys. Letters* 55 (1978) 185.
- [8] S. Sato, *J. Chem. Phys.* 23 (1955) 592, 2465.
- [9] See, for example, A.J.B. Robertson, *Catalysis of Gas Reactions by Metals* (Springer, New York, 1970).
- [10] C.F. Melius, T.H. Upton and W.A. Goddard III, *Solid State Commun.* 28 (1978) 501.
- [11] (a) C.F. Melius, B.D. Olafson and W.A. Goddard III, *Chem. Phys. Letters* 28 (1974) 457.
(b) M.J. Sollenberger, M.S. thesis, *California Institute of Technology* (1975).
- [12] (a) S.P. Walch and W.A. Goddard III, *J. Am. Chem. Soc.* 100 (1978) 1338.
(b) S. Huzinaga, *J. Chem. Phys.* 42 (1965) 1293.
(c) W.A. Goddard III, T.H. Dunning, Jr., W.J. Hunt and P.J. Hay, *Acc. Chem. Res.* 6 (1973) 368.
- [13] J.T. Muckerman, *J. Chem. Phys.* 54 (1971) 1155; 56 (1972) 2997.
- [14] J.H. McCreery and G. Wolken, *J. Chem. Phys.* 63 (1975) 2340.
- [15] A. Gelb and M.J. Cardillo, *Surface Sci.* 59 (1976) 128; 64 (1977) 197; 75 (1978) 199.
- [16] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand-Reinhold, New York, 1950).
- [17] While the LEPS method does include the mixing of the two linearly independent four-electron singlet spin functions, the mixing is determined by the four-center geometry via eq. (4). While such a treatment is qualitatively acceptable, it is inadequate to address detailed questions of spin coupling.