H_2 Dissociation at Metal Surfaces

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The dissociation of H_2 at metal surfaces is discussed with particular reference to the role of d electrons. It is shown that the d holes of a transition metal serve initially as sinks for s electrons. This reduces the Pauli repulsion and so the entrance-channel activation barrier. s-d transfer continues into the chemisorption region and allows the formation of metal-H bonds with only a moderate weakening of the metal-metal bonds.

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The basic chemistry of H_2 dissociation on simple metals has been illustrated via model calculations for jellium surfaces.[1,2] Dissociation results from the partial filling of the molecular $1\sigma_u$ antibonding resonance, which broadens and shifts downwards because of interaction with band levels. However, the filling of the $1\sigma_u$ resonance has a strong effect on the energy only for molecule-surface separations $\lesssim 3$ a. u. Prior to this, the interaction displays the Pauli repulsion characteristic of closed shells and the dissociation is therefore entrance-channel activated with activation energies ranging from 0.2 eV for Na to more than 1 eV for Al. Even larger barriers have been predicted for dissociation on noble-metal surfaces.[3,4] On transition metals, H_2 dissociates without apparent activation,[5] and the question arises as to what mechanism suppresses the Pauli repulsion. Recent work has shown that the d electrons are responsible for a marked weakening of the entrance-channel activation barrier.[6] However, no clear picture of their role has yet emerged.

In this Letter we show that an important function of the d electrons in H_2 chemisorption is to serve as sinks for the s electrons. The Pauli repulsion is reduced because the s electrons of a transition metal can revert to the d band and avoid the energy cost of penetrating the H_2 $1\sigma_g$ core. The chemisorption is accompanied by a local filling of d holes which allows metal-H bonds to form with only a moderate weakening of the metal-metal bonds. The mechanism is different from that on simple and noble metals and is illustrated via a comparison of the energy diagrams of Cu_2H_2 and Ni_2H_2. We give first a qualitative argument that illustrates how s-d transfer lowers the entrance-channel activation barrier.

As was first shown by Zaremba and Kohn,[7] the Pauli repulsion when a closed-shell atom or molecule[8] approaches a metal surface is given to lowest order in the overlap between Bloch functions and the H_2 $1\sigma_g$ orbital by

$$E_R = \sum_{\mathbf{k}}^{\epsilon_F} \epsilon'_{\mathbf{k}} - \sum_{\mathbf{k}}^{\epsilon_F} \epsilon_{\mathbf{k}}, \tag{1}$$

where $\epsilon_{\mathbf{k}}$ are the band eigenvalues of the bare-metal potential and $\epsilon'_{\mathbf{k}}$ are the modified eigenvalues that result when the frozen molecule potential is added outside the surface. Because the Bloch tails must become orthogonal to the $1\sigma_g$ orbital, the s-band eigenvalues shift to higher energy so that E_R is positive. The physisorption well results when E_R is combined with the van der Waals attraction. Equation (1) gives a good approximation at large molecule-surface separations. At such separations, it is not obvious that the presence of holes in the d band should influence E_R because the d functions are strongly localized, and their eigenvalues are scarcely affected by the molecular potential (for simplicity, we assume a clean separation of s and d electrons). However, the upward movement of the s eigenvalues causes an imbalance of the s and d Fermi levels so that we must allow for a change in the occupation numbers of the band functions. Equation (1) therefore reads

$$E_R = \sum_{\mathbf{k}}^{\epsilon_F} \delta\epsilon^s_{\mathbf{k}} + \sum_{\mathbf{k}}^{\epsilon_F} \delta n_{\mathbf{k}} \{\delta\epsilon^s_{\mathbf{k}} + \epsilon^s_{\mathbf{k}} - \epsilon_F\}, \tag{2}$$

where $\delta\epsilon^s_{\mathbf{k}}$ are the s-band eigenvalue shifts, $\delta n_{\mathbf{k}}$ ($=0$ or -1) are the changes in the s occupations, and we have assumed that because of the large density of states, transfer to the d shell occurs at the Fermi energy. Equation (2) shows that electrons will tend to flow into the d band whenever $\delta\epsilon^s_{\mathbf{k}} > \epsilon_F - \epsilon^s_{\mathbf{k}}$. Since the $\delta\epsilon^s_{\mathbf{k}}$ are largest for $k_\perp = k_F$, where the Bloch tails penetrate furthest into the vacuum, the most repulsive s electrons will revert to the d band, thereby weakening the Pauli repulsion.[9]

Equation (1) is valid asymptotically but cannot describe entry into the chemisorption region. However, the weakening of the Pauli repulsion via *s*-*d* transfer is shown also in cluster calculations where all the relevant energies are treated fully. We consider the systems Cu_2H_2 and Ni_2H_2 with the H_2 constrained to dissociate over the "bridge" position in a planar geometry and the Cu-Cu and Ni-Ni distances taken to correspond with bridge sites of the (100) surfaces (see Figs. 1 and 2). The total energy was calculated with use of the Kohn-Sham scheme[10] with the local-density approximation for exchange and correlation. The calculations are intended to illustrate behavior at the surface and should not be interpreted too literally. We simulate weak coupling to a continuum by allowing the occupation numbers of molecular orbitals whose eigenvalues lie close to the "Fermi" level to be fractional. Each level is regarded as a narrow resonance, and the fractional occupations represent the portions of the resonances that lie below the Fermi level. The energy contours in Figs. 1 and 2 were sketched with use of the results of about forty fully self-consistent calculations for each system.

The energy diagram for Cu_2H_2 (Fig. 1) divides naturally into two regions separated by a "seam." A crucial role is played by a molecular orbital, denoted *a*, that derives primarily from the unoccupied $1\sigma_u$ orbitals of H_2 and Cu_2. For large Z and $D \simeq 1.4$ a. u., the *a* eigenvalue is high lying. Since the *a* level is Cu-H bonding and H-H antibonding, its eigenvalue falls as Z decreases and D increases. The highest-lying σ_g orbital, on the other hand, denoted *b*, is pushed upwards because it must become orthogonal to the $1\sigma_g$ core of H_2. At the seam, a level crossing occurs, and the configuration switches. In region I we have H_2 and Cu_2 molecules repelling, while in region II the configuration is that of two CuH molecules, which also repel. Figure 1 shows a classic case of a "symmetry-forbidden" chemical reaction that is highly activated.

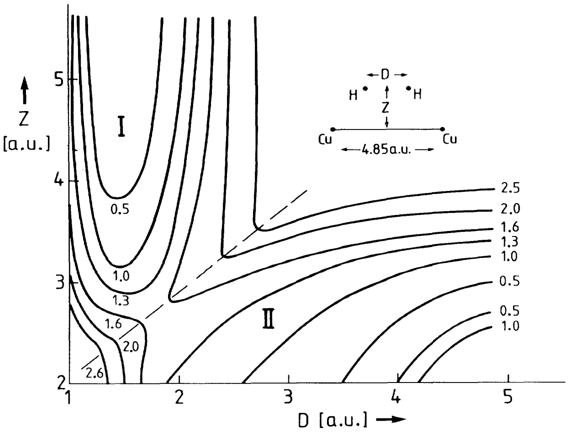

FIG. 1. Energy contours for Cu_2H_2 as a function of D, the H-H separation, and Z, the normal distance between H_2 and Cu_2. The energies are shown in electronvolts relative to the value at $Z = \infty$, $D = 1.4$. The dashed line marks the "seam" where the electronic configuration switches.

The molecular orbitals of Ni_2H_2 have been described,[11] and we restrict ourselves here to bare essentials. Low-lying Kohn-Sham states of Ni_2 have two *d* holes in molecular orbitals of π or Δ symmetry that are nominally antibonding.[12] If the energy of Ni_2H_2 is calculated with these *d* holes intact, the system displays a Pauli repulsion that is even stronger than for Cu_2H_2. For example, with $Z = 4.0$ a.u. and $D = 1.5$ a.u., the repulsion is 0.5–0.9 eV depending on which *d* holes we choose to leave unoccupied. However, the eigenvalue corresponding to the empty *d*-like orbital, denoted δ, was far below the Fermi level, while the *b* level, with a strong Ni (4*s*) component, is high lying, as in Cu_2H_2, because it must become orthogonal to the $1\sigma_g$ H_2 core. A change of configuration involving transfer of electrons from the *b* to the δ level equilibrates the eigenvalues and lowers the total energy quite appreciably, as can be seen in Fig. 2. The energy minimum was found to correspond to *b*-level occupancies of 1.6, 0.8, and 0.4[13] for Z=4.5, 4.0, and 3.5 a.u., respectively, and for the optimum values of D. The effect is analogous to that discussed in more qualitative terms above, and the result is an entrance-channel activation barrier of only 0.1 eV, somewhat smaller than that found previously for on-top dissociation.[6]

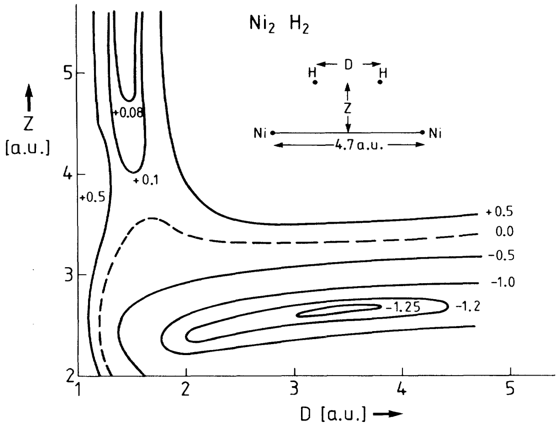

FIG. 2. Energy contours for Ni_2H_2. The dashed line shows the zero-energy contour. The electronic configuration changes continuously for $Z \gtrsim 3.5$, with fractional occupations (see text), but is constant, with integral occupations, throughout the chemisorption region. Note that the H-H separation can vary by as much as 2.5 a.u. with essentially no change in the energy. We caution that this diagram refers to surface dissociation and not to gas-phase Ni_2H_2 (see text).

In the chemisorption region Cu_2H_2 and Ni_2H_2 show strongly different behaviors. Because of the number of electrons and level structure, Cu_2H_2 must choose between two configurations. Either the a level or the b level is fully occupied. (Fractional occupations lower the energy only close to the seam.) In the former case we have H_2 and Cu_2, while in the latter we have two repelling CuH units, i.e., the dissociation of H_2 proceeds only at the cost of breaking the Cu-Cu bond. For Ni_2H_2, however, neither the a nor the b orbital need be occupied. The transfer of electrons to the δ level, which is only marginally Ni-Ni antibonding, competes, and the Ni-H bonds form with only a moderate weakening of the Ni-Ni bond. This is the reason for the large binding energy and the different character of the dissociated state for Ni_2H_2 as compared with Cu_2H_2.

While we might expect a blurring of the two extreme situations for adsorption on the surface, the basic picture should be similar. The gradual local transfer of s electrons to the d shell that weakens the Pauli repulsion for transition metals continues into the chemisorption region, and dissociative adsorption can occur without a strong involvement of antibonding s-like metal orbitals. Figure 2 shows that the chemisorbed H atoms in Ni_2H_2 are confined to a narrow, but long, trough whose shape suggests a remnant of H-H bonding. We may call this a partial dissociation, as compared with a complete dissociation for Cu_2H_2. Such a state may occur at surface sites of low coordination but could be strictly a feature of the small cluster. The electrons of a cluster are better able to respond to the H_2 than metal electrons, which are involved in bonding between many sites. Kohn-Sham calculations for H monolayers on Ni(100) show center-site H to be stable with a binding energy of 3.2–3.4 eV.[14] This is a slightly larger binding energy per H atom than we find for Ni_2H_2 (2.9 eV), which suggests that H_2 dissociation on Ni(100) ends with H atoms at center sites. Figures 1 and 2 predict desorption energies of about 1.1 and 1.3 eV for Cu and Ni, respectively. These are somewhat larger than, but in reasonable correspondence with, values suggested by the measured desorption temperatures of 320[15] and 370 K,[5] respectively.

The description of the chemisorption behavior of H_2 on Ni given above is different from that suggested by the early work of Melius *et al.*[11] On the basis of multiconfiguration self-consistent-field calculations for Ni_2H_2 for the three geometries corresponding in our notation to $Z = 2.8$ a.u., $D = 1.4$, 2.1, and 4.7 a.u. (Fig. 2), these authors concluded that similar dissociation mechanisms and chemisorbed states obtain for both H_2-Cu and H_2-Ni. They proposed that the presence of d holes in the latter case lowers an activation barrier within the chemisorption region by allowing concomitant changes of symmetry of the s and d systems that preserve the overall symmetry of the state during the dissociation. Hybridization of s and d electrons played no essential role, and the chemisorption completed with the d holes more or less intact.

This picture poses two major problems. Firstly, as pointed out above, intact d holes lead to an entrance-channel energy barrier that attains a large value even when the H_2 molecule is far (~ 4 a.u.) from the surface. This barrier was not found by Melius *et al.* because no calculations were performed for $Z > 2.8$ a.u., and no attempt was made to refer the energy of the reference configuration, $D = 1.4$ a.u., $Z = 2.8$ a.u., to that of the isolated fragments. Secondly, the state of Ni_2H_2 proposed by Melius *et al.* as representative of dissociative chemisorption corresponds to two more or less independent NiH units, i.e., is similar to that which we find for Cu_2H_2. However, this would seem to imply that the chemisorbed state of H on Ni is thermodynamically unstable in that the gas-phase reaction $H_2 + Ni_2 \rightarrow 2\ NiH$ is endothermic by 1.6 eV. The picture of Melius *et al.*, therefore, does not explain the experimental facts that H_2 dissociates on Ni apparently spontaneously and that chemisorbed H is stable up to room temperature. Our picture, on the other hand, is consistent with these observations. A continuous switch of configuration involving a net transfer of electrons to the d band suppresses the entrance-channel barrier and leads to a state representative of chemisorption that has a negative energy with respect to desorbed H_2. The Ni d holes play an important role in stabilizing this state, though as found by Melius *et al.*, the major part of the binding energy is nevertheless due to the s electrons. A partial filling of the d holes on H chemisorption is consistent with the conclusion of Weinert and Davenport[14] that the magnetic moment of the surface layer of ferromagnetic Ni is strongly reduced.

Whereas Melius *et al.* considered isolated Ni_2H_2 with all the concomitant symmetry and spin constraints, we have suppressed these constraints because we seek to model the behavior at a surface where the d electrons are itinerant. The energy diagram in Fig. 2 was drawn up within a model explicitly tailored to the surface and, because of the relaxation of symmetry constraints and the absence of Hund's rule effects, does not give the correct energy diagram for *isolated* Ni_2H_2. We believe that its major features are relevant for dissociation at the surface, however.

We conclude with some brief remarks. (i) The measured dissociation probability for a room-temperature H_2 gas on Ni surfaces is $\simeq 0.1$.[5] That this is not larger could suggest a small barrier or be due to other causes. Since calculations, albeit with obvious limitations, have shown a small barrier, it may be worthwhile to try to trap physisorbed H_2 on a low-temperature surface. (ii) Because the lowering of the entrance-channel activation barrier on transition metals involves excitation of *d* electrons with a large effective mass, the possibility of strong electronic nonadiabaticity must be considered. For example, it may be possible to observe coherent scattering of H_2 molecules even when the incident energy exceeds the activation-barrier height of the adiabatic energy surface. (iii) The theoretical prediction of a high barrier for H_2 dissociation on Cu surfaces is compatible with the early value of 0.9 eV quoted by Kwan[16] and with the permeation data of Comsa and David.[17] However, other workers[18,19] have reported substantially smaller values that are difficult to reconcile with theory.

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