[10]For the two fluoranil salts (compounds G and J) $h\nu_{CT}$ could not be measured, and so the values in Fig. 3 were obtained by shifting the $h\nu_{CT}$ of compounds F and E.

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Adsorption and Dissociation of H_2 on Mg Surfaces

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A self-consistent calculation of the potential-energy surface for a molecule (H_2) on a metal surface [Mg(0001)] is presented. The following experimentally observable adsorption features are identified and interpreted: (i) an activation barrier for molecular adsorption, (ii) a mobile molecularly chemisorbed state ("precursor state"), (iii) an activation barrier for dissociation (E_a^d), and (iv) a strong dependence of E_a^d on the adsorption-site geometry.

For surface physics the understanding of the role of surfaces in chemical reactions, in particular the adsorption of a gas molecule, is imperative. Kinetic experiments have revealed various forms of adsorption: associative, dissociative, activated, nonactivated, or proceeding via precursor states, e.g., molecularly adsorbed states, in which the molecule is trapped on approaching the surface and is then free to move along the surface in order to seek out the preferred site of adsorption or dissociation.[1]

So far, theoretical descriptions of molecular adsorption processes on an atomic scale are scarce. Aspects of relative stabilities[2] and activation energies[3] have been deduced from calculations of one-electron energy distributions. Total energies, giving adiabatic potential-energy curves, have only crudely been obtained in semiempirical schemes.[4] The nature of the precursor state has been even less investigated, most authors describing it as a molecule weakly bound to the surface by van der Waals forces, as suggested by Lennard-Jones.[1]

This Letter presents results from detailed calculations of the potential-energy surface for H_2 on the Mg(0001) surface. These lead to a picture of the adsorption process for H_2 on Mg(0001) (Fig. 1) that can be summarized as follows: (i) As the molecule approaches the surface, it meets a bar-rier. It is directed towards the atop position (Fig. 1), where the barrier is lowest [the point denoted X in Fig. 1(a)]. Behind this barrier there is a molecularly chemisorbed state [denoted M in Fig. 1(b)], with a bond length only slightly larger than that of free H_2. (ii) A molecule accomodated into this state is almost free to move along the surface, i.e., it has a negligible activation energy for migration [well M of Fig. 1(a)]. (iii) The dissociation of the molecule above the atop site into two separate H atoms in the energetically more favorable bridge [B in Fig. 1(b)] or center sites is hindered by a second activation barrier [at D in Fig. 1(b)]. (iv) For the dissociation over the bridge site into the adjacent center sites we find that the activation energy is much lower (0.1 eV as compared to 0.5 eV in Fig. 1). Therefore, when the molecule has reached the molecularly adsorbed state M, it migrates around until it finds a bridge site, where it can easily dissociate. The chemisorption state M is consequently a good candidate for a *precursor state*.[1]

These results have been obtained with a method earlier applied to *atomic* potential-energy curves for H adsorbed on Al, Mg, and Na (Ref. 5) and Si, O, Cl, and Na on Al.[6] The calculations are self-consistent solutions of the Kohn-Sham equations with exchange and correlation effects described in the local-density approximation with

the embedding scheme of Gunnarsson and Hjelm-berg.[7] First, the energy of, e.g., a hydrogen atom $E_H{}^{Je}$ has been calculated in the jellium model for the metal, where ion cores are smeared out as a semi-infinite uniform positive back-ground. Lattice effects, $\Delta E_H{}^1$, are then account-ed for by treating the difference ΔV between the pseudopotentials from the ion cores and the po-tential from the positive background in first-order perturbation theory.[5,6] The energy of a hydrogen atom at a position $\vec{r}$ outside the surface is thus calculated as $E_H(\vec{r}) = E_H{}^{Je}(z) + \Delta E_H{}^1(\vec{r})$,[5] where z is the distance from the surface. The weakness of the pseudopotentials makes this a reasonable procedure.[5,6]

The energy $E_{H_2}(\vec{r}, \vec{R})$ of an H_2 molecule cen-tered at the position $\vec{r}$ outside the surface and with the nuclei at $\vec{r} + \frac{1}{2}\vec{R}$ naturally splits into two parts,[8,9]

$$E_{H_2}(\vec{r}, \vec{R}) = E_{extra}(\vec{r}, \vec{R}) + E_{intra}(z, \vec{R}), \qquad (1)$$

where $E_{extra}(\vec{r}, \vec{R})$ is the energy that two hydrogen atoms would have at these positions, if there were no H-H interaction, and $E_{extra}(\vec{r}, \vec{R}) = E_H(\vec{r} + \frac{1}{2}\vec{R}) + E_H(\vec{r} - \frac{1}{2}\vec{R})$. The weakness of ΔV allows the relatively small intramolecular interaction energy E_{intra} to be approximated by its value in the jellium model at each distance z from the sur-face and at each internuclear separation R. In the jellium model, E_{intra} has been calculated self-consistently for H_2 perpendicular[8] and paral-lel[9] to the surface. The accuracy obtained with these approximations, amounting to some tenths of an electron volt in total energies and to small-er values for energy differences, is sufficient to identify some of the concepts of adsorption kinet-ics and to give them an interpretation in terms of the electron structure of the adsorbate-sub-strate system. "Chemical accuracy" ($\sim kT \sim 0.025$ eV at room temperature) is not obtained, how-ever.

The initial increase in energy seen in Fig. 1,
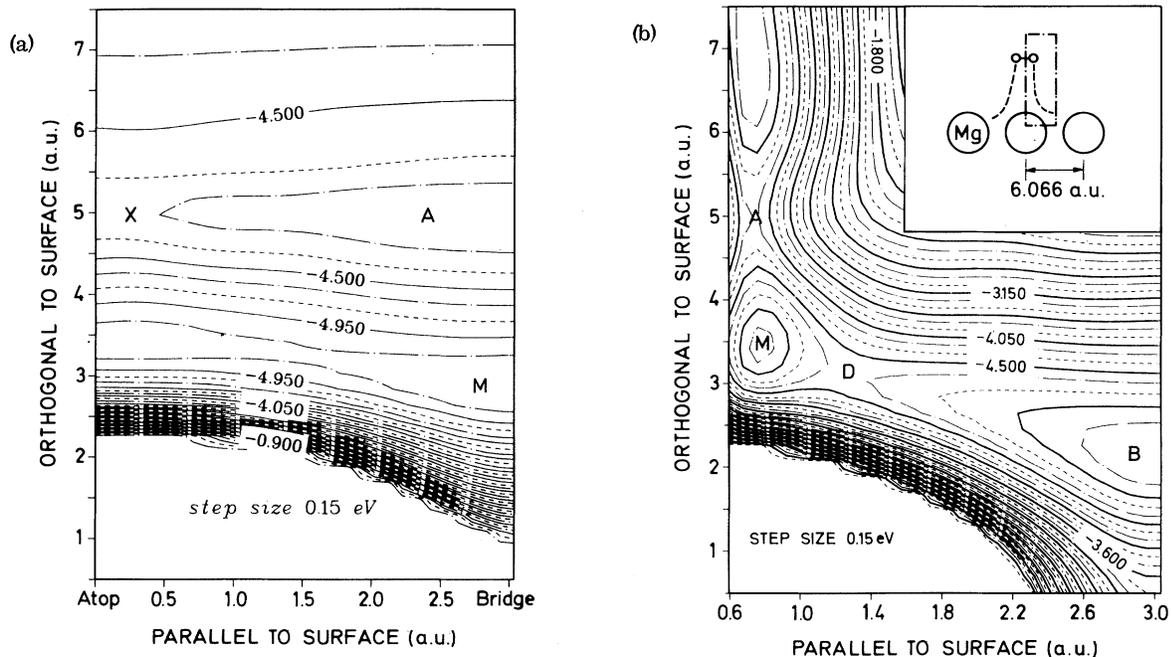
FIG. 1. Equipotential-energy curves for H_2 on a Mg(0001) surface, (a) with H_2 parallel to the surface and a bond length of $R = 1.5$ a.u., and (b) dissociating over the atop site into the bridge sites (see geometry in inset). The en-ergies in electron volts are relative to those of the free atoms. The molecular adsorption energy in M is thus only 0.4 eV relative to a free molecule. The distance from the surface is measured from the first atomic layer, and the distance parallel to the surface, which in (b) equals one-half the H-H separation R, is measured from the atop site towards the bridge site. The coordinate of (a) gives the midpoint between the two protons. Note that a mole-cule that has surmounted the activation barrier A cannot automatically transfer its kinetic energy perpendicular to the surface into the H-H vibrations parallel to the surface. Therefore, the molecule will not dissociate immedi-ately, even though the dissociation barrier D is of the same size as A.

when the molecule approaches the surface, is analogous to the kinetic-energy repulsion found when other closed-shell adsorbates such as the isoelectronic He approach a surface.[10] For H_2, the repulsion levels off to an activation barrier because the antibonding H_2 orbital is shifted down and gradually filled as the molecule approaches the surface (Fig. 2). This filling of the antibonding H_2 orbital, on the other hand, weakens the H-H interaction E_{intra} as indicated in Fig. 2. The activation barrier for molecular adsorption can therefore also be thought of as being due to the fact that the H-H interaction (E_{intra}) starts weakening before the H-surface bonds (E_{extra}) have started building up. In this E_{intra}/E_{extra} picture the activation energy E_a^d for dissociation is due to the existence of the residual H-H interaction even close to the surface. Since the filling of the antibonding resonance and thereby the size of the H-H interaction depend on the H_2-surface distance, there is a distribution of E_a^d's that depends on where in the molecular well M the dissociation takes place. E_a^d is smallest when the molecule dissociates from the twofold bridge site, where the minimum in M is close to the surface, into
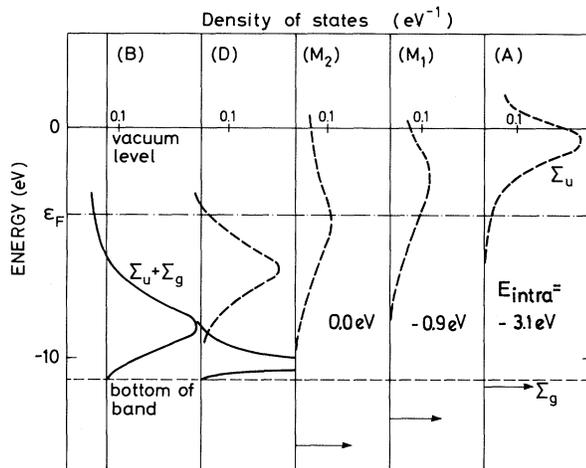
FIG. 2. Development in the one-electron density of states along the reaction path in Fig. 1(b). First the antibonding (Σ_u) and bonding (Σ_g) H_2 states are shifted down as the distance d to the first Mg layer decreases for an almost constant H-H distance R. Two spectra are shown corresponding to $d = 3.5$ a.u. (M_1) and $d = 2.5$ a.u. (M_2) in the molecular minimum (M) in Fig. 1(a). As the antibonding resonance is filled the H-H interaction E_{intra} goes to zero. As the molecule dissociates $M \rightarrow D \rightarrow B$ the bonding-antibonding splitting decreases and finally two noninteracting H resonances result.

the threefold center sites, which are the most stable sites for atomic adsorption.[5] This site specificity of E_a^d is very important in an interpretation of experimental kinetic data.

Finally, the repulsion from E_{intra} prevents the H atoms from getting close enough to the substrate atoms to really feel the differences between the different sites. This makes the activation energy for molecular diffusion all over the surface very small. Similarly, it is the kinetic repulsion that makes atomic adsorbates migrate easily, however, only along certain diffusion paths.[5]

Surface specificity is a characteristic of the chemisorption process.[1,11] To illustrate this, we have also made calculations for the more open, fictitious Mg fcc (100) surface. The primary difference from the (0001) surface is that the activation energy for molecular adsorption is found to be zero. This can be understood in terms of a changing relation between E_{extra} and E_{intra} from one surface to another, E_{intra} being primarily influenced by the overlap between adsorbate and substrate electron orbitals, while E_{extra} is also affected by the local interaction with the metal-ion cores.[8,12] For an open surface the conduction electrons reach less far out from the first atomic layer, thus reducing the overlap. This means that E_{intra} will not start increasing before E_{extra} starts decreasing, and the outer activation barrier is lowered. The absence of an outer activation barrier outside the open surface is a strong indication of the possibility that adsorption into the precursor state is more efficient at steps on the (0001) surface. The molecule can then move to the terraces and dissociate.[13]

The bond of the precursor state M is chemical, although weak, resulting from cancellations between the simultaneous buildup of the H-surface bond (E_{extra}) and weakening of the H-H bond (E_{intra}). The large electronic rearrangements behind it are shown in Fig. 2. A physisorbed state should exist outside the outer activation barrier as it does for the rare gases. This state would be less suited as a precursor than the state M, because the weak interaction with the substrate at the large distances will make the trapping into the precursor state less efficient.

We therefore suggest that, rather than being physisorbed, one kind of molecular precursor states may be chemisorbed states like state M above.[14] These very special states, where, e.g., a single H atom can bind chemically both to another H atom and to the surface, are character-

ized by the partial filling of molecular-orbital resonances close to the Fermi level.[15] The qualitative E_{extra}/E_{intra} picture should be generalizable to other adsorbates and substrates. For transition-metal substrates, the primary new effect is expected to be an additional interaction between the d-band and the antibonding H_2 resonance around the Fermi level. This will tend to decrease the activation energy for molecular adsorption. As for the quantitative predictions of the calculations, we restrict ourselves to noting that the finding of an activation energy around 0.5 eV for H_2 adsorption on Mg(0001) is in agreement with the measured very low initial sticking probability $s \simeq 10^{-6}$ for H_2 outside polycrystalline Mg (at room temperature).[16] With a trapping efficiency of unity, this corresponds to an experimental activation energy of 0.35 eV.

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