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Dissociation Path for H₂ on Al(110)

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The minimum energy path is calculated for an H₂ molecule dissociating on an Al(110) surface within local density functional theory. The properties of the potential energy surface along the five H₂ ionic coordinates perpendicular to the reaction path are also determined and shown to be essential for an understanding of the dissociation dynamics.

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A complete description of the dynamics of the dissociation of a molecule impinging on a solid surface still stands as one of the major goals in surface science. Such a description is a test of our understanding of the interaction of gas molecules with surfaces, and it will provide the microscopic basis for an understanding of surface reactions, including heterogeneous catalysis.

Much progress has been made lately by combining results of molecular beam scattering experiments with dynamical simulations of the adsorption process [1]. The weakest point in this approach is the construction of the interaction potentials used in the simulations. Even for the most studied subclass of systems, hydrogen dissociating on a metal surface, there is still no example where the full reaction path has been determined *ab initio*. Most potentials used in dynamics simulations are model potentials [2] or based on approximate total energy methods [3]. Since the first self-consistent calculations of the electronic structure and energetics of H₂ dissociation on jellium [4], a number of calculations for H₂ interaction with metal clusters have given important information on the interaction potential typically along certain high symmetry directions in the problem [5, 6]. Most recently Feibelman has performed a set of calculations of the stability of H₂ at three different distances above a Rh(001) surface [7]. From this he suggests that high symmetry reaction paths may not be the ones with the lowest energy and that the transition state for the dissociation process is not necessarily related geometrically to the final state, that is, the molecule does not dissociate directly into the sites where the chemisorbed atoms are most stable.

In the present Letter we present the results of a calculation of the full minimum energy path for an H₂ molecule adsorbing and dissociating on an Al(110) surface. The calculation is performed within the local density approximation using a method derived from the one suggested by Car and Parrinello [8]. The method has the important feature that it allows the simultaneous minimization of the energy with respect to the electronic and ionic degrees of freedom in the system. We show that the minimum energy path is a straightforward dissociation into the most stable final state. We investigate the transition state in detail by calculating the vibrational frequencies

for all the degrees of freedom perpendicular to the reaction coordinate, and this forms the basis for a detailed discussion and modeling of the molecular beam experiments for H₂ on Al(110) by Berger and Rendulic [9].

The geometry of the system we treat is illustrated in Fig. 1. We consider a periodic array of Al(110) slabs 5 layers thick and with 5 layers of vacuum in between and with a hydrogen molecule approaching each of the two slab surfaces in each cell. The calculations were done for both a (1 × 2) and a (2 × 1) surface unit cell in order to make sure that the symmetry of the unit cell does not affect the results. With this geometry the system will end up having a monolayer of atomic hydrogen chemisorbed on the surface. Since the H-H distance in the H₂ molecule is small compared to the unit cell dimensions we find it unlikely that interactions between molecules in adjacent unit cells during the adsorption process should have a major effect on the results.

The calculational framework is the total energy pseudopotential method using the Ceperley-Alder local exchange-correlation potential [10]. Aluminum is represented by an *ab initio* nonlocal pseudopotential of the Kerker type on the Kleinman-Bylander form [11]. This gives an excellent representation of the bulk properties of aluminum including energies of defects like stacking faults [12]. For hydrogen the bare Coulomb potential is

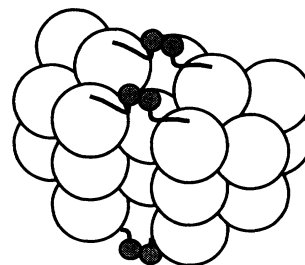


FIG. 1. The geometry of an H₂ molecule along the minimum energy path approaching an Al(110) surface. A molecule approaches the surface in each of the (1 × 2) unit cells and on each side of the five-layer slab used in the calculation, but the interaction between the molecules is small and does not affect the results.

used. 64 (outfolded) \mathbf{k} points for integrating over the first Brillouin zone are used. Looping over these, the solutions in a plane-wave basis of the Kohn-Sham equations are found by means of an all-bands minimization technique closely related to the band-by-band minimization of Teter, Payne, and Allan [13].

Plane waves with a kinetic energy up to 500 eV are used. A test of the dependence of the binding energy $\Delta E = E(\text{Al and H}_2) - E(\text{Al}) - E(\text{H}_2)$ on the cutoff for various points along the reaction path shows this to be enough for convergence to within 0.02 eV. With this cutoff the energy of the free H_2 molecule is found to be -4.75 eV relative to the free atoms, the bond length is 0.79 \AA , and the vibrational frequency is 515 meV , in excellent agreement with other local density calculations and experiment [14]. For a (1×1) overlayer of atomic hydrogen chemisorbed on the Al(110) surface, we find the most stable position of the hydrogen atom to be the on-top site with a vibrational frequency perpendicular to the surface of 220 meV , in excellent agreement with experiments on Al(100) [15]. Previous calculations for H chemisorption on jellium including the Al pseudopotential in first-order perturbation theory also give results in rather good agreement with those of the present calculation [16].

In the present Letter we shall concentrate on the reaction path, which we define as the path connecting the initial and final states with the property that all (5 in the case of H_2) degrees of freedom perpendicular to it have a minimum at the path. This is the natural adiabatic starting point for descriptions of the dynamics. We have determined this path by first "driving" the reaction by varying one coordinate and simultaneously minimizing the energy with respect to the other five coordinates of the H_2 molecule. The coordinate we have chosen to drive the system with is $Z - b$ where Z is the height of the molecular center of mass above the first surface layer, and b is the H-H bond length. Having determined the position of the saddle point in this way we then use steepest descent to find the reaction path. We have not varied the Al ionic coordinates both because the forces on them are small and, more importantly, because during the time it takes for the H_2 molecule to dissociate the much heavier metal atoms will not have time to move appreciably.

Figure 2 shows the minimum total energy and the variation of Z and b along the reaction coordinate. The dissociation is activated and from the transition state the molecule dissociates directly into the most stable atomic chemisorption site on the surface.

We have made a complete normal mode analysis of the vibrations of the molecule at the top of the barrier. The results are shown in Fig. 3. The five modes orthogonal to the reaction path all have relatively high energy. This implies that the barrier for dissociation varies significantly with impact parameter and with the orientation of the molecule relative to the surface. Such a picture has also been suggested for H_2 dissociation on Cu sur-

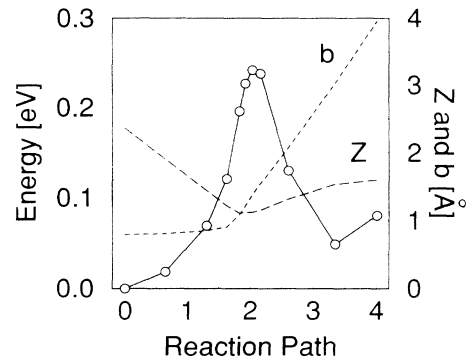


FIG. 2. The total energy per H_2 molecule along the minimum energy path. The energy is measured relative to the energy of the free H_2 molecule. The reaction coordinate is defined as the sum of $|\Delta \mathbf{R}|$ in \AA , where \mathbf{R} is the six-dimensional vector specifying the Cartesian coordinates of the two hydrogen atoms. Note that the chemisorption minimum is located before the on-top site is reached completely. This effect is peculiar to the (1×2) unit cell geometry [it is not found for a (1×1) or (2×1) unit cell], and indicates some residual attraction between the two H atoms. Also shown is the variation of the center of mass Z and the H_2 bond length b (in \AA) along the minimum energy path.

faces based on effective medium calculations [3]. From the norm $\omega_q = 113 \text{ meV}$ of the imaginary frequency along the reaction coordinate we can make a WKB estimate of the tunneling probability $P = \exp[-2\pi(E_0 - E)/\hbar\omega_q]$ for incoming molecules with translational energies E below the minimum barrier E_0 . It is clear that tunneling is only important at energies very close to E_0 .

H_2 dissociation on Al(110) has been studied experimentally using a molecular beam technique by Berger and Rendulic [9]. The sticking probability is found to increase from zero at a beam kinetic energy of about 0.3 eV . The behavior is qualitatively similar to the much more studied case of H_2 dissociation on various Cu surfaces [17], except that the onset of sticking on Al(110) is at a somewhat larger energy than on Cu. There is, however, an important qualitative difference between the two systems. For the $\text{H}_2/\text{Al}(110)$ system increased vibrational excitation of the incoming molecule does not seem to increase the sticking probability measurably [9], whereas for the H_2/Cu system it is believed to be very important for the sticking at low kinetic energies [2, 17].

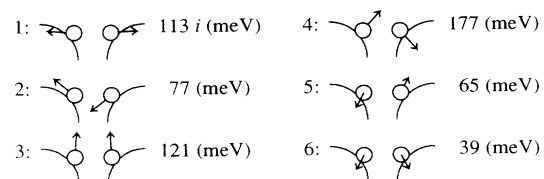


FIG. 3. The normal modes of the molecule at the transition state and their frequencies.

A coupling between vibrational excitations in the incoming molecule and sticking is possible when some or all of the vibrational energy is transferred to kinetic energy along the reaction coordinate during the process and this transfer is *before* the barrier for dissociation [2]. The potential we calculate for Al(110) appears quite similar to the potentials proposed for various Cu surfaces in this respect [2, 3]. The main difference from the Cu potentials is that the curvature of the reaction path is considerably larger for the Al(110) potential. Indeed, the reaction coordinate makes a more than 90 deg turn at the transition state because the molecule dissociates from a fairly open long bridge site into the on-top sites. The hydrogen atoms have to move *out* of the surface to reach the final state. This is very peculiar to Al because this is the only known system where the atomic hydrogen chemisorption site is (close to) on top. The sharp turn of the reaction path must result in a larger "centrifugal barrier," and the lack of vibrational coupling for the H₂/Al(110) system might be related to this. Only a detailed dynamics simulation can answer this problem.

We now turn to consider the other 4 H₂ degrees of freedom, the two translations of the molecule parallel to the surface and the two molecular rotations. Far from the surface the molecule can translate and rotate freely, but as can be seen in Fig. 3, all modes become fairly high frequency vibrations in the transition state. This means that if we include *all* the modes orthogonal to the reaction coordinate in the transition state, the sum of the frequencies is 478 meV, which is very close to the vibrational frequency of 515 meV in the free molecule. The zero point energies in the initial and the transition states are therefore essentially the same, and in the lowest-energy path there will be no possibility of energy transfer between zero point energy and translational energy [6].

We will make a very simple model for the effect of the 2 translational and the 2 rotational degrees of freedom on the sticking probability, which is a slight generalization of the "hole" model proposed by Karikorpi *et al.* [18]. Accepting that the coupling between the H-H vibration and the translational energy along the reaction coordinate is not important for the sticking probability the model should give the kinetic energy variation of the sticking probability. The model is classical and is valid in the limit where the time it takes for the molecule to reach the surface is so short that the molecule does not have time to react on the corrugation of the potential closer to the surface. At the beam energies of interest here this is not unreasonable.

Under these assumptions an approaching molecule feels the dissociation barrier $E_a(\mathbf{u})$ at the position in the unit cell and angle that it had in the gas phase. A molecule approaching the surface with a kinetic energy E will either be reflected from the surface when E is smaller than $E_a(\mathbf{u})$ or dissociate otherwise. Given E there will be a hole where the barrier $E_a(\mathbf{u})$ is smaller than E [18].

The sticking probability is simply given by the volume of the hole Ω_s relative to the total volume Ω_0 available to the incoming beam.

We expand the total energy at the transition state in terms of the four normal modes perpendicular to Z and b :

$$E_a(\mathbf{u}) = E_0 + \sum_{i=1}^4 \frac{1}{2} k_i u_i^2, \quad (1)$$

where E_0 is the minimum barrier, $\mathbf{u} = (u_1, u_2, u_3, u_4)$ is the displacement vector, and k_i denotes the force constant for the i th mode. The latter are given directly by the frequencies of the second, fourth, fifth, and sixth modes in Fig. 3. The hole will be a four-dimensional ellipsoid with radii s_i given by $s_i = \sqrt{2(E - E_0)/k_i}$, and the volume is $\Omega_s = \frac{\pi^2}{2} s_1 s_2 s_3 s_4$. The total volume of possible configurations is $\Omega_0 = A_s 4\pi (\frac{b_0}{2})^2$, where A_s is the area of the (1×2) unit cell and b_0 is the equilibrium free H₂ bond length.

The sticking probability in this simple model is $s(E) = \Omega_s/\Omega_0$, and the result is shown in Fig. 4 together with the experimental results of Berger and Rendulic [9]. In the figure we also include a semiclassical result where $s(E)$ has been folded with a Fermi function having the correct WKB tunneling and transmission form discussed above far above and below the barrier. The agreement is quite good, considering the crudeness of the model and serves to illustrate that if there is no coupling between the H-H vibration and the translational energy, the absolute

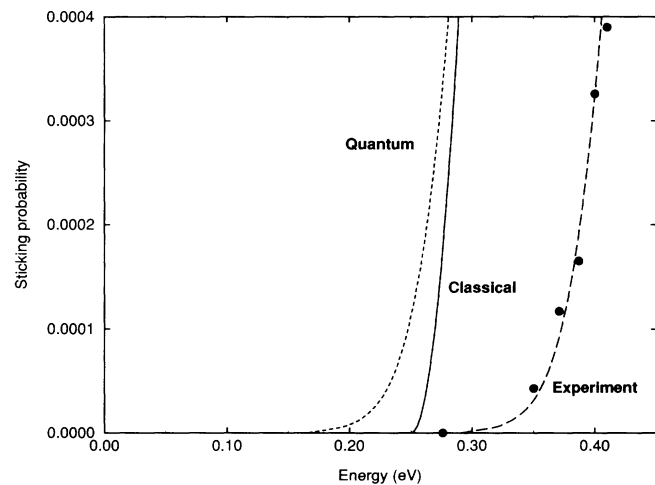


FIG. 4. The calculated sticking probability using the classical "hole" model (full curve). The dotted curve gives a quantum estimate where the classical barrier distribution is folded with a Fermi function having the correct WKB tunneling and transmission form far above and below the barrier. The experimental results of Berger and Rendulic [9] are shown as circles. The dashed curve through the experimental results is the quantum result displaced by 0.12 eV to higher energies.

magnitude of the minimum barrier is described to within about 0.1 eV by the calculated potential. Even though one must be careful with absolute interaction energies in the local density approximation, the level of agreement in Fig. 4 supports the underlying no-coupling assumption.

In conclusion, we have presented the first *ab initio* local density functional determination of the minimum energy path for a surface dissociation reaction. The path shows no indication of a molecular precursor and a straightforward dissociation into the most stable final state. The latter finding is different from that of Ref. [7] for H₂ on Rh(100). This could be due to differences in the possible dissociation configurations on the two surfaces. By studying the transition state in detail we have arrived at a simple "hole" model which is able to give a reasonable description of the experimental molecular beam data. A complete description of the H₂ dissociation on Al(110) must, however, await a detailed simulation of the motion of the hydrogen atoms on the potential energy surface. In particular, the lack of a coupling between vibrational excitations of the incoming molecule and the sticking probability suggested by the molecular beam experiments remains a puzzle.

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