Model of an H_2-Precursor State on Metal Surfaces

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Dynamical effects of a surface-induced softening of the H−H bond during H_2-surface collisions have been studied by numerical wave-packet simulations. The calculation shows that the zero-point vibrational energy released by the bond softening is fully transferred to the translational motion of the molecule (except for incident energies > 0.2 eV, where vibrational excitation also takes place), and that inelastic processes can trap the molecule in a mobile and long-lived state confined near the surface.

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Precursor states are weakly bound molecular states which are believed to play an essential role as intermediaries in many chemisorption processes.[1] For the H_2 molecule, however, although such states have been demonstrated on Cu surfaces,[2] their role in dissociative chemisorption remains controversial. Rendulic, Winkler, and Karner claimed that two reaction channels, adsorption through a precursor and activated adsorption, coexist on various Ni surfaces,[3] while Robota *et al.* saw no evidence of intermediate trapping of H_2 in a molecular precursor state on Ni(111).[4]

Recent experiments of Comsa and Poelsema seem to demonstrate that on Pt(111), H_2 dissociates only at steps and other surface defects,[5] and led these authors to conclude that a highly mobile molecular bound state carries the molecule from the adsorption place to the dissociation site. According to their model, the precursor state would have the properties of being bound to the surface and at the same time, mobile. Recently, Jackson and Metiu showed that activation barriers to adsorption in the entrance channel can trap H_2 near the surface, but only temporarily.[6] This Letter proposes a possible mechanism for a *long-lived* precursor state, that originates in the quantum-mechanical character of the H-H vibration. *Ab initio* total-energy calculations for H_2 on a Pt cluster show that the interaction with the surface induces a softening of the H−H bond. This softening means a reduction of the zero-point vibrational energy of the molecule, which is transformed into kinetic energy. The dynamical behavior near the surface was studied by explicit solution of the Schrödinger equation for the time evolution of a wave packet in an appropriate model surface potential. The calculation shows that for low incident kinetic energies, $E_{\mathrm{inc}} < 200$ meV, the vibrational motion adjusts adiabatically to the softening of the H−H bond. Therefore, provided the surface does not dissociate the molecule, the energy released from the vibrational degrees of freedom is transferred to the translational motion of the molecule. Moreover, if by an inelastic process the total energy of the molecule becomes smaller than the zero-point energy of the free molecule, it will not be able to escape and will remain confined to a region near the surface, where its zero-point energy is reduced. It may, however, retain a substantial kinetic-energy excess in that state.

The zero-point vibrational energy is related to the strength of the H−H bond by $E^0_{\mathrm{vib}} = \frac{1}{2}(K/\mu)^{1/2}$, where K is the H−H force constant and $\mu = \frac{1}{2}m_{\mathrm{H}}$ the corresponding reduced mass.[7] The interaction of the H_2 molecule with the surface produces necessarily a weakening of the H−H bond. Electron charge accumulates between the protons and the surface in order to minimize the repulsion between them, at the expense of the internal bonding of the molecule. When the molecule dissociates, one has, of course, $E^0_{\mathrm{vib}} \rightarrow 0$. However, even in the absence of dissociation, the weakening of the H−H bond can be quite appreciable when the molecule gets close to the surface. This is illustrated in Fig. 1, which shows the potential energy of an H_2 molecule as a function of the H−H bond length, ρ, for various values of the distance, ζ above the bridge site of a Pt(111) surface, measured from the plane containing the nuclei of the first metal

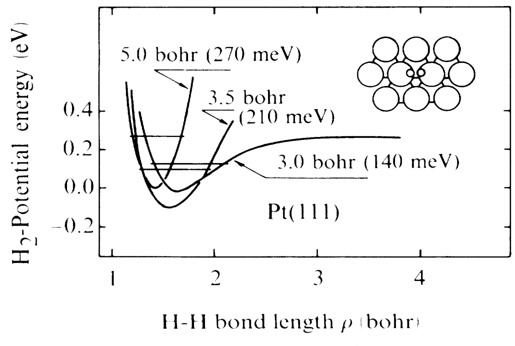

FIG. 1. Potential energy of an H_2 molecule as a function of the H−H bond length, ρ, for three values of the height ζ above a bridge site of Pt(111). The surface was modeled by a Pt_{15} cluster, which is shown schematically. The energies of the vibrational ground states, referred to the minimum values of the potential, $V(\rho_0,\zeta)$, are indicated by the horizontal lines and also given in parentheses.

layer. The molecular axis was kept parallel to the surface, which has been modeled by a Pt_{15} cluster, also shown schematically in Fig. 1. For the total-energy calculation the Kohn-Sham scheme[8] was used, with the local-density approximation for exchange and correlation,[9] and a localized muffin-tin orbital basis[10] including *s*, *p*, and *d* functions in all metal sites. Spin effects were neglected and the core electrons kept frozen, but all valence *d* electrons were incorporated in the calculation.

The main features of the potential-energy surface, $V(\rho,\zeta)$, can be summarized as follows: (i) the H-H interaction softens as the molecule approaches the surface, such that over a distance of 2–3 bohr, E^0_{vib} drops to $\simeq 50\%$ of its value in the free molecule, $E^0_{\mathrm{vib}}(\infty)=270$ meV. (The energy position of the vibrational ground state is also given in Fig. 1, for each ζ value). (ii) Over the same distance there is an outward shift of $\simeq 0.4$ bohr in the equilibrium H—H bond length ρ_0, with decreasing values of ζ. (iii) The minimum values of the potential, $V(\rho_0,\zeta)$, show a shallow attractive well as a function of ζ, with a minimum of -110 meV at $\zeta=3.5$ bohr, followed by a rather soft repulsive interaction. For other adsorption sites, the adsorption well is weaker or nonexistent, but features (i) and (ii) remain quite similar.[11,12] In order to study how these features influence the dynamical behavior of H_2, the surface potential was simplified to the form

$$V(\rho,\zeta)=\tfrac{1}{2}K(\zeta)[\rho-\rho_0(\zeta)]^2+V_{\mathrm{rep}}(\zeta),$$

where $K(\zeta)=\mu[2E^0_{\mathrm{vib}}(\zeta)]^2$, and all ζ dependences in $V(\rho,\zeta)$ were linearized, to facilitate the interpretation of the numerical results presented below. In the interacting region, $\zeta<\zeta_0=5$ bohr, $E^0_{\mathrm{vib}}(\zeta)$ was chosen proportional to ζ, with $E^0_{\mathrm{vib}}(\zeta_0)=E^0_{\mathrm{vib}}(\infty)$, and the shift $\rho_0(\zeta)$, representing the change in the equilibrium H—H bond length, was assumed to vary at a rate $d\rho_0/d\zeta=0.2$. The term V_{rep} simulates the repulsive effect of the surface and was also taken to be linear in ζ, with a slope -1 eV/bohr for $\zeta<2$ bohr. These values were deduced from the total-energy calculation,[11] and should provide a realistic parametrization of the interaction of H_2 with weakly reactive surfaces. This model potential, however, explicitly excludes the weakly attractive well, as well as the anharmonicity of the potential as a function of ρ, and I shall comment on these points below.

The motion of the molecule as a function of ρ and ζ was studied by numerical integration of the time-dependent Schrödinger equation

$$i\frac{\partial\psi}{\partial t}=-\frac{1}{2\mu}\frac{\partial^2\psi}{\partial\rho^2}-\frac{1}{2M}\frac{\partial^2\psi}{\partial\zeta^2}+V(\rho,\zeta)\psi,$$

with use of the alternating-direction implicit method of Douglas and Rachford on a real-space mesh.[13] Here $M=2m_{\mathrm{H}}$ is the total molecular mass. The H_2 molecule was prepared in an initial state given by

$$\psi(\rho,\zeta,t=0)=(2\alpha/\pi\Delta\zeta)^{1/2}\exp\{ip\zeta-[(\zeta-\zeta_1)/\Delta\zeta]^2-(\alpha\rho)^2\},$$

with $\alpha=(\tfrac{1}{4}\mu K)^{1/4}$, the incident moment of the molecule $p=-(2ME_{\mathrm{inc}})^{1/2}$, pointing towards the surface, and its center of mass, ζ_1 ($>\zeta_0+\Delta\zeta$), chosen such that the initial wave packet was entirely outside of the region of interaction. This wave packet represents an H_2 molecule with the vibrational degree of freedom in its ground state and a Gaussian spatial distribution normal to the surface, with a total width $\Delta\zeta$. In the present calculation a small $\Delta\zeta$ ($=3$ bohr) has been chosen, for it permits a better visualization of the time evolution of the wave packet.

In order to characterize the dynamical behavior of the H_2 molecule as a function of ζ, the probability density $P(\zeta,t)=\int d\rho\,|\psi(\rho,\zeta,t)|^2$, the vibrational-energy distribution

$$\epsilon_{\mathrm{vib}}(\zeta,t)=P^{-1}(\zeta,t)\int d\rho\,\psi^*(\rho,\zeta,t)[(-1/2\mu)(\partial^2/\partial\rho^2)+V(\rho,\zeta)]\psi(\rho,\zeta,t),$$

and the translational-energy distribution

$$\epsilon_{\mathrm{tr}}(\zeta,t)=-\frac{P^{-1}(\zeta,t)}{2M}\int d\rho\,\psi^*(\rho,\zeta,t)\frac{\partial^2\psi}{\partial\zeta^2}$$

have been calculated, whereby the distribution of the total energy is given by $\epsilon(\zeta,t)=\epsilon_{\mathrm{vib}}(\zeta,t)+\epsilon_{\mathrm{tr}}(\zeta,t)$. These ρ-averaged quantities are shown in Fig. 2 for various cases discussed below. The nonprimed quantities refer to the initial state and the primed ones to the final wave packet, after it has interacted with the surface. The repulsive potential V_{rep} is also shown in the figure.

Figure 2(a) shows the motion of an H_2 molecule with $E_{\mathrm{inc}}=50$ meV. Initially, while the wave packet is in the region $\zeta>\zeta_0$, there is no coupling between the variables ζ and ρ, so that $\epsilon_{\mathrm{tr}}=E_{\mathrm{inc}}$ and $\epsilon_{\mathrm{vib}}=E^0_{\mathrm{vib}}(\infty)$ are separately conserved. In the interacting region, ϵ_{vib} decreases but the motion is fully adiabatic: The vibrational wave function broadens, remaining at all times identical to the local ground-state wave function, and the excess energy is transferred to the translational motion. Observe that the translational energy increases from the initial 50 meV to a maximum of $\simeq 200$ meV at $\zeta=2$ bohr. As a molecule comes out of the interacting region, it slows down again and appears essentially unaffected, displaying only a slightly nonuniform $\epsilon'_{\mathrm{tr}}(\zeta)$ because of the natural broadening of the wave packet P'. The adiabatic character of the motion is demonstrated by the fact that the vibrational-energy distribution is independent of time and, within the accuracy ($\simeq 2$ meV) of the calculation,

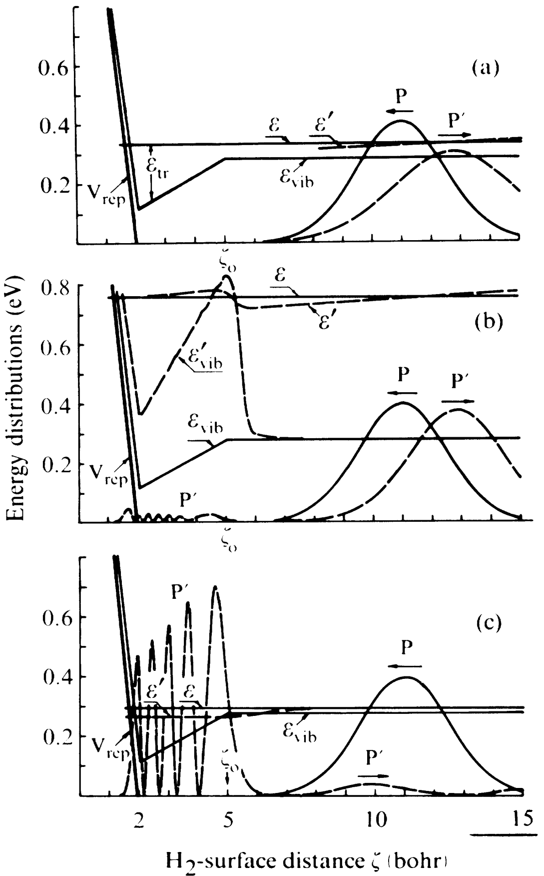

FIG. 2. ρ-averaged probability density $P(\zeta)$ and vibrational- and total-energy distributions $\epsilon_{\text{vib}}(\zeta)$ and $\epsilon(\zeta)$ for the model potential $V(\rho,\zeta)$, showing (a) adiabatic behavior for $E_{\text{inc}}=50$ meV, (b) nonadiabatic behavior for $E_{\text{inc}}=480$ meV, and (c) a wave packet with $E_{\text{inc}}=10$ meV, that gets trapped after losing 7 meV in the collision with the surface. Nonprimed values refer to the initial state and the primed ones to the final state. The translational-energy distribution is given by $\epsilon_{\text{tr}}=\epsilon-\epsilon_{\text{vib}}$.

given by $\epsilon_{\text{vib}}(\zeta)=E^{0}_{\text{vib}}(\zeta)$.[14]

Figure 2(b) shows the motion of an H_2 molecule with $E_{\text{inc}}=480$ meV and illustrates a case of nonadiabatic behavior. In addition to the continuous vibrational- to translational-energy transfer in the interacting region, as displayed in Fig. 2(a), there is here some excitation of the first vibrational excited state, of energy $E^{1}_{\text{vib}}(\zeta)$. In the present example, E_{inc} is not large enough to excite the vibrational motion of the free H_2 molecule $[E^{1}_{\text{vib}}(\infty)-E^{0}_{\text{vib}}(\infty)=540$ meV in our model], so that the excited fraction of the wave packet cannot escape from the surface. This fraction ($\simeq 3\%$) can be clearly seen in the part of the final state P' confined in the interacting region and characterized by a vibrational energy $\epsilon'_{\text{vib}}(\zeta)=E^{1}_{\text{vib}}(\zeta)$, which is 3 times as large as for the ground state. The trapped excited state, however, is short lived and eventually returns to the ground state and escapes too. Energy conservation requires that for the range of ζ values where vibrational excitation takes place, $\epsilon>E^{1}_{\text{vib}}(\zeta)$, which implies that $E_{\text{inc}}\gtrsim 54$ meV. Nevertheless, the nonadiabatic character of the motion, as revealed by the fact that $\epsilon_{\text{vib}}(\zeta)\neq E^{0}_{\text{vib}}(\zeta)$, begins to be appreciable only for $E_{\text{inc}}>200$ meV. For smaller energies the rate of excitation of vibrational modes, which is proportional to ϵ_{tr}, is too small to be observable.[15]

Figure 2(c) illustrates the trapping of an H_2 molecule with $E_{\text{inc}}=10$ meV. An inelastic process has been modeled by displacing the repulsive wall backwards with constant velocity, v_{rep}, while the wave packet interacted with it. To simulate a collision with a Pt atom, a value of v_{rep} equal to 0.02 of the maximum velocity of the wave packet and a total displacement of 0.2 bohr was chosen, which yielded a molecule energy loss of $\Delta E=7$ meV, in agreement with the classical value $4(M/m_{\text{Pt}})\epsilon_{\text{tr}}$ evaluated at the surface. In this case, the final-state wave packet P' splits into two parts. The part which was not acted upon by the time-dependent forces escapes with almost no loss in velocity, while the part that was in contact with V_{rep} when the displacement occurred has its total energy reduced below the zero-point energy of the free molecule and becomes trapped in the interacting region. (The oscillations in P' result from the boundary condition that imposes a node in the wave function at the surface.) The actual weights of the two parts of the wave packet, which give the probabilities of escape ($\simeq 25\%$) and trapping ($\simeq 75\%$), are specific of the rather simple way the inelastic process has been modeled and should not be overemphasized. For a quantitative estimate of these probabilities a realistic treatment of the interaction of H_2 with surface phonons is necessary.[16] However, the present calculation shows that trapping in a long-lived state is possible, and that the translational energy of the trapped molecule is quite large ($\simeq 160$ meV).

The main result of the calculation is that for H_2 molecules with thermal energies, the translational kinetic energy at the surface is strongly enhanced, that is, $\epsilon_{\text{tr}}\gg E_{\text{inc}}$. This fact has two important consequences: (i) The energy ΔE lost in the collision with the surface is also enhanced, such that it becomes sufficiently large to trap the molecule. (ii) The trapped molecule has a kinetic energy which is large compared with typical activation energies for motion along the surface and it should be very mobile. It should also be long lived on the surface, provided it does not receive energy from surface phonons.

Finally I discuss two aspects of the potential-energy surface, which have been left out in the dynamical simulation. The weakly attractive well as a function of ζ was neglected, in order to be able to extract dynamical information by simple inspection of the calculated energy distributions and to demonstrate that the above results are not a feature of a specific potential. Use of a more realistic potential as a function of ζ may add some structure in the dynamical behavior of H_2, but would not alter any of the arguments presented above. Less trivial was the neglect of the anharmonicity of the potential as a function of ρ, since this is a feature that may lead to dissociation of the molecule. Notice in Fig. 1 that the initial energy of the molecule (including zero-point energy) is larger than the activation energy for dissociation at $\zeta = 3$ bohr. Nevertheless, in the adiabatic regime the molecule cannot dissociate as long as the H-H interaction has a bound state: The excess energy is taken out of the vibrational degree of freedom, which remains always in the ground state, while the time evolution of the center of mass of H_2 is determined by the effective potential $V(\rho_0,\zeta) + E^0_{\text{vib}}(\zeta)$. The latter is, therefore, the appropriate potential to be used in classical simulations.

In summary, it has been shown that the zero-point energy released by the softening of the intramolecular H—H bond acts as a virtual attractive potential well, which in the presence of inelastic processes can trap the H_2 molecule in a long-lived precursor state. In the trapped state, the molecule is not locally bound to the surface in the chemical sense, but dynamically confined to the region where the softening takes place and free to move along the surface.

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