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Vibrational and rotational effects in the dissociative adsorption of H₂

S Holloway

Surface Science Research Centre and Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

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Abstract. In this short review, results are presented for theoretical studies concerning the dissociative adsorption of H₂ on metal surfaces. The quantum wavepacket method has been employed for simulating the dynamics and this method is briefly discussed. It is shown that for a potential energy surface that is based upon *ab initio* calculations for the total energy, vibrational excitation of the molecule will increase the dissociation probability. By comparison, the dissociation probability of D₂ is significantly lower. Placing energy in the rotational degree of freedom has the opposite effect. The reasons for this behaviour are discussed in terms of the vibrational-rotational coupling that occurs in the region near to the surface.

1. Introduction

In the field of chemical dynamics, there has long existed the hope that reactivity may be enhanced by placing energy selectively into internal degrees of freedom of the reactants. In terms of application, nowhere is this more important than in the field of surface reactivity since most commercial reactions take place in a heterogeneous environment. To this end, there have been an increasingly large number of papers appearing which discuss how surface reactivity, and in particular dissociative adsorption, can be modified by placing energy into molecular rotations, vibrations and translations. In this short account I will focus on some recent calculations concerning such phenomena.

In the field of gas-surface dynamical simulations, it is possible to broadly divide the field into two; those which employ *classical* methods to simulate scattering and reactivity, and those which use *quantum* mechanics. For reasons of space, I will restrict myself primarily to quantum calculations. This does not mean to imply that classical studies are not of significance, but merely reflect that 'five printed pages' are not enough space to do justice to this work. The interested reader is encouraged to read articles in the book *Dynamics of Gas-Surface Interactions* [1]. It is also possible to divide the quantum work into two, depending upon whether *time-dependent* or *time-independent* methods for solving the dynamics is employed. To some extent the solution methodology is simply a matter of taste: stationary state methods have been used for many years and there are very well established computational procedures that can be obtained from quantum chemistry software houses; time-dependent methods have become fashionable over the past ten to fifteen years and have become feasible

with the advent of fast, cheap computational power. The proliferation of wavepacket methods is, in part, due to pioneering work of Eric Heller [2] who demonstrated in most elegant ways how real space Gaussian wavepackets could be used to understand gas-phase spectroscopies *and* obtain quantitative information. I will restrict myself to such time-dependent methods and leave discussion of stationary state methods to others [3].

In this present work I will focus on the effects of molecular vibrational and rotational energy on dissociative adsorption. The key question that will be addressed is: for a given translational energy is the dissociative adsorption probability enhanced or diminished by initial excitation of (i) vibrational or (ii) rotational energy? The molecule to be studied is hydrogen which is motivated by both experimental and theoretical considerations. Many molecular beam scattering experiments employ hydrogen (see the article by B Hayden in [1]) and there exist potential energy surfaces (PES) for the H_2 /metal interaction [4]. The following section will briefly outline the wavepacket methodology. Following this, results will be presented for the dissociation probability of rotationally and vibrationally excited hydrogen beams. In this section the topology of the potential surface will be related to the surface electronic structure. Finally, conclusions will be presented.

2. Wavepacket dynamics

This can only be a brief introduction to the calculational methods employed in the work presented and for a more detailed account the interested reader is referred to my article in [1]. Let us assume that a PES, $V(\mathbf{R})$ has been obtained from somewhere (there will be more said about this in the following sections). This potential is then placed on a suitably sized grid. The problem is then to solve the time-dependent Schrödinger equation

$$i\frac{\partial\psi(\mathbf{R};t)}{\partial t} = \mathcal{H}\psi(\mathbf{R};t) \quad (1)$$

where \mathcal{H} is the Hamiltonian for the problem,

$$\mathcal{H} = T + V(\mathbf{R}) \quad (2)$$

and T the kinetic energy. In what follows two methods have been employed to solve equation (1), the split operator method and the Chebyshev method.

The split operator method involves dividing the time evolution operator

$$\psi(\mathbf{R};t + \Delta t) = U\psi(\mathbf{R};t) = \exp[-i\Delta t\mathcal{H}]\psi(\mathbf{R};t) \quad (3)$$

in the following way [5]

$$U\psi(\mathbf{R};t) \approx \exp\left[-i\frac{\Delta t}{2}T\right] \exp[-i\Delta tV] \exp\left[-i\frac{\Delta t}{2}T\right] \psi(\mathbf{R};t). \quad (4)$$

An efficient method to evaluate the second-order spatial derivative in the kinetic energy employs the fast Fourier transform (FFT) algorithm [6]. A spatial derivative is mapped into reciprocal space as a multiplication by ik , where k is the wavevector. Similarly, the

second derivative is mapped as a multiplication by $-k^2$. Therefore, by transforming the wavefunction from its real-space to its momentum-space representation with an FFT, the kinetic energy operator simply becomes multiplicative. In this way it is possible to apply each operator in the representation in which it is diagonal. The great efficiency of the FFT algorithm makes the method computationally tractable. In the present context, calculations of vibrational energy transfer have used this method.

It is not possible to use the split operator method for Hamiltonians that mix space and momentum coordinates, an example is the kinetic energy for a rotating diatomic,

$$\mathcal{T} = \frac{1}{2\mu} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} \quad (5)$$

where μ is the reduced mass and r the bond length. It is, however, still possible to use a grid-based FFT method to evaluate the Hamiltonian in such a case using an alternative propagation scheme [7] that involves a polynomial expansion of the evolution operator. The most commonly used method is to use a Chebyshev polynomial expansion of the exponential in equation (3)

$$\exp[-i\mathcal{H}t] \approx \sum_{n=0}^M a_n T_n(-i\mathcal{H}t). \quad (6)$$

The operations of both the translational and rotational energy operators of the Hamiltonian on the wavefunction are again evaluated using the FFT algorithm. Calculations of rotational properties which appear in the next section have used this method.

3. Dynamical simulations

3.1. Vibrational effects

The observation that in H_2 scattering experiments only a certain fraction of the molecules that are incident 'stick' is frequently taken to be evidence that there exists an activation barrier located between the entrance (H_2 + surface) and exit channels ($2H$ + surface) of the PES [8]. An example of this form of topology is shown in figure 1. Assuming the surface to be a static entity, there are six degrees of freedom which are required to describe the interaction of a diatomic with that surface. Since it is only possible to present any two of these sensibly on a piece of paper, the particular slice of the PES shown in figure 1 confines the molecular bond to be parallel to the surface plane. The two selected coordinates are the H-H separation (x) and the distance of the molecular centre-of-gravity from a point in the surface, (Z). This particular cut highlights the translational-to-vibrational (T-V) coupling experienced during a gas-surface encounter. The functional form of the PES is of little importance for present purposes and may be found elsewhere [9]. Suffice to say that it comprises two diabatic states that have been smoothly linked: a physisorption potential describing the interaction of the closed shell H_2 species with the surface and a chemisorption potential which accounts for the interaction of the dissociated fragments (H atoms) with the surface [8]. The location of the activation barrier along the reaction path is crucial for an understanding of the dynamics [10]. The PES shown in figure 1 is an example

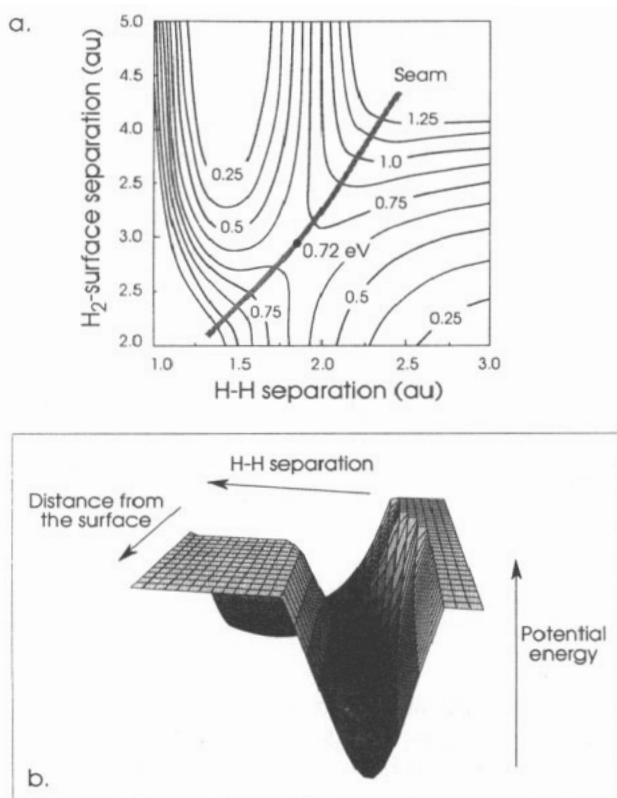


Figure 1. The H₂/Cu interaction potential used in the calculation of Holloway and Hand [14]. (a) A contour plot showing the main topological features: a structureless entrance channel representing the intact molecule, an activation barrier which is located at a molecular separation in excess of the neutral molecule, and an exit channel corresponding to atomic adsorption. Energies are in eV and are measured with respect to a molecule infinitely far from the surface. (b) A perspective view which looks down the entrance channel.

of a barrier located toward the exit channel and is based upon a calculation for H₂ interacting with a small Cu cluster [11].

The asymptotic initial state wavefunction was taken to be a product of a Morse oscillator in vibrational state n and a minimum uncertainty Gaussian function centred at Z_i with a mean initial momentum p_Z ,

$$\psi(x, Z; t = 0) = \chi_n(x)g(Z - Z_i, p_Z). \quad (7)$$

This state is propagated in time using equation (4) until an asymptotic final state is attained. The two possible fates for the molecule are reflection from the surface in the vibrational state n' (not necessarily = n) or dissociative adsorption. Computational details have been presented elsewhere [9, 12, 13]. Figure 2 shows the results for the dissociation probabilities as a function of translational energy for H₂ and D₂. The following features are immediately obvious:

(i) increasing the translational energy always enables molecules to dissociate, ultimately with unit probability;

- (ii) placing energy in vibrational degrees of freedom enhances dissociation; and
- (iii) for a given translational energy and vibrational state, more H_2 dissociates than D_2 .

These results can be understood quite simply by considering the change in the zero point energy as the reaction path is traversed (see figure 1). At each point along the reaction path, the motion will evolve vibrationally adiabatically. Since the frequency of vibration of the H_2 'entity' will be reduced along this path, there will be significant V-T exchange [10]. For a barrier located in the entrance channel of the reaction, this will result in a negligible effect; for a barrier located further around the reaction path this will have a considerable effect, as evidenced by the data shown in figure 2. These data may be comprehensively understood working within this framework: translational energy will always be effective simply because of the basic topology of the surface; vibrational energy will act to reduce the height of the effective barrier because of the increased V-T occurring for the states with higher n ; the vibrational states of the heavier isotopes are lower and, as a consequence, the perceived activation barrier will appear higher [14].

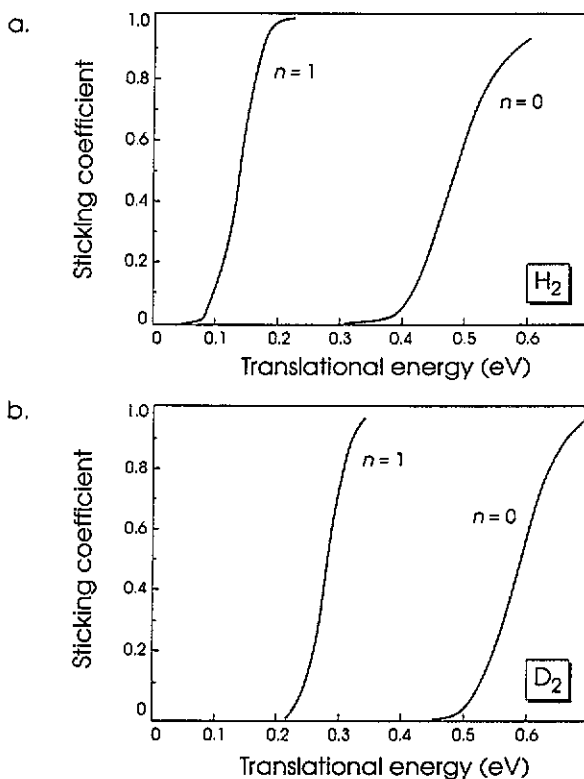


Figure 2. Sticking coefficient as a function of initial translational energy for (a) H_2 and (b) D_2 scattering from a Cu surface. The curves refer to incidence with the molecule in either its vibrational ground state or the first excited state. It is quite clearly seen that for the PES shown in figure 1, vibrational energy significantly enhances dissociative adsorption.

Using this basic model it is possible to interpret a wide range of recent molecular beam data for the dissociative adsorption of H_2 on Cu surfaces [15, 16]. It has been

experimentally verified that by putting excess energy in the vibrational coordinate, it is possible to increase the probability of dissociative adsorption and, as a consequence, decrease the survival probability for $n = 1$ molecules [17].

3.2. Rotational effects

If we pursue the arguments in the previous sub-section and consider the effects of translational-to-rotational (T-R) coupling, then it is important to have an *a priori* knowledge of the form of the PES. *Ab initio* calculations for H_2 on jellium surfaces [18] and small clusters [19] have shown that the activation barrier for dissociation is lower when the molecule is oriented with its bond axis parallel to the surface rather than perpendicular to it. If we extend this thinking and attempt to include surface morphological effects, then it follows that the local point group of dissociative transition state will determine the structure of the activation barrier [20]. As an example of this form of PES, figure 3 shows the variation in the activation barrier where motion in the vibrational degree of freedom has been treated adiabatically. The physical surface is an FCC (110), and the PES is applicable to a simple metal substrate such as aluminium. The θ direction is the polar angle and the ϕ direction is the azimuthal angle that the molecular bond makes with a high-symmetry direction in the surface. The barrier is independent of ϕ for $\theta = 0$ and has a value of approximately 1.5 eV. As θ is increased to $\pi/2$, the barrier drops, ultimately to a minimum value of approximately 0.25 eV for $\phi = \pi/2$. The difference in barrier height obtained by restricting the molecule to lie flat and rotating about the ϕ direction by $\pi/2$ is approximately 0.3 eV.

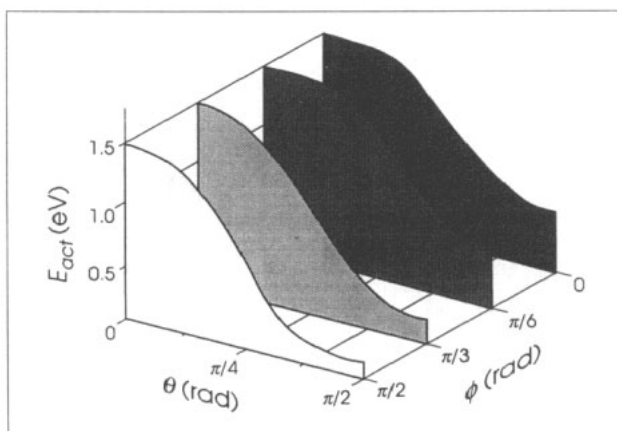


Figure 3. The value of the activation barrier as a function of θ and ϕ for the potential energy surface employed in the rotational study. The symmetry of the FCC (110) surface is C_{2v} and this is reflected in the PES. The barrier is high if the molecule approaches with its bond axis normal to the surface and drops as the molecule tips over being a minimum at $\theta = \pi/2$ and $\phi = \pi/2$.

The initial wavepacket is again taken to be a product state

$$\psi(x, Z; t = 0) = \mathcal{Y}_{J, m_J}(\theta, \phi) g(Z - Z_i, p_Z) \quad (8)$$

where $g(Z, p_Z)$ is again a translating Gaussian but $\mathcal{Y}_{J, m_J}(\theta, \phi)$ is a spherical harmonic [21]. Central to what follows is the contention that in an experiment where some fraction S_0 of the incident molecules dissociatively adsorb on a surface, the rotational state

distribution of the reflected fraction ($1 - S_0$), contains valuable information regarding the transition state. The initial wavepacket is propagated using equation (6) but now the final possibilities are reflection into the J', m'_J rotational state (not necessarily $= J, m_J$) or dissociative adsorption.

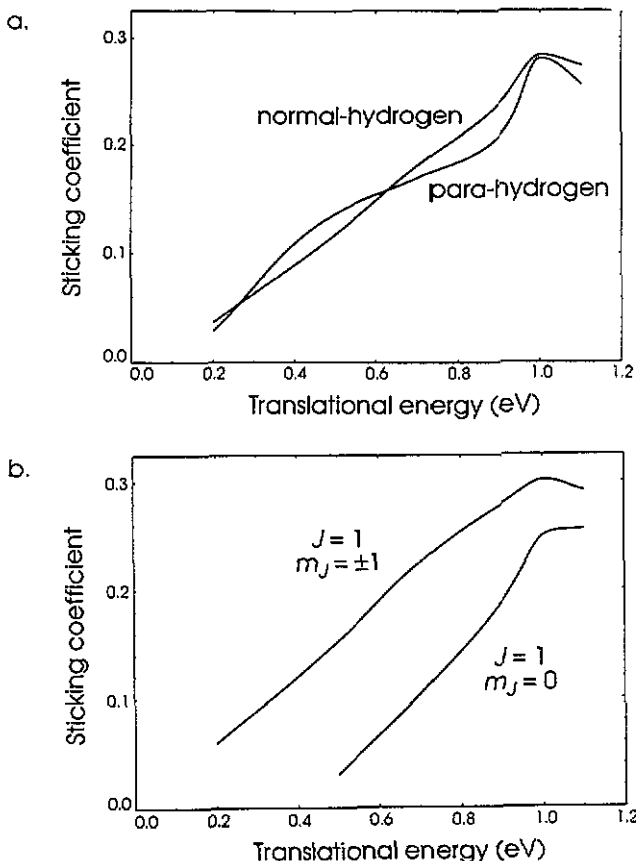


Figure 4. Results for the sticking coefficient as a function of translational energy for (a) normal- and *para*-hydrogen, and (b) the two m_J states for $J = 1$ H_2 . The upper curve (a) demonstrates that the small energetic difference between the two forms gives rise to essentially no difference in dissociation probability. The lower data (b) show that there is a significant angular momentum constraint mirrored in the dissociation probabilities that can be traced to the expectation value of the molecular orientation in the specific quantum states.

In figure 4(a) are shown the results for the translational energy dependence of the dissociation probability for normal- and *para*-hydrogen. There is little discernible difference between the two curves, reflecting that the small energetic difference between the $J = 0$ and 1 states is practically immaterial in the dissociation process. The dissociation probability peaks at a translational energy of approximately 1.0 eV and then begins to drop. This arises because at lower energies, the molecules have more time during the round-trip to reorient and attain more favourable dissociation geometries; at higher energies this is not the case and as a result the dissociation probability falls [21]. The rotational state distributions, P_{J, m_J} , for *para*- and *ortho*-hydrogen are shown in figure 5. As has been observed previously [22], the distributions show that as the

activation barrier is exceeded, the higher J -states begin to grow in. Since H_2 shows almost no rotational excitation in the absence of dissociation [23], the appearance of high J -states in the scattered P_{J,m_J} distributions is indicative that the dissociated fractions have not been selected uniformly from θ - ϕ space [21, 22, 24]. Additionally, the scattering serves to align the reflected flux as evidenced by the equivalence $P_{J,+m_J} = P_{J,-m_J}$ and $P_{J,+m_J} \neq P_{J,m'_J}$ for $|m_J| \neq |m'_J|$. Unlike the results for the dissociation probability, there is a significant difference between the *para* and normal P_{J,m_J} distributions.

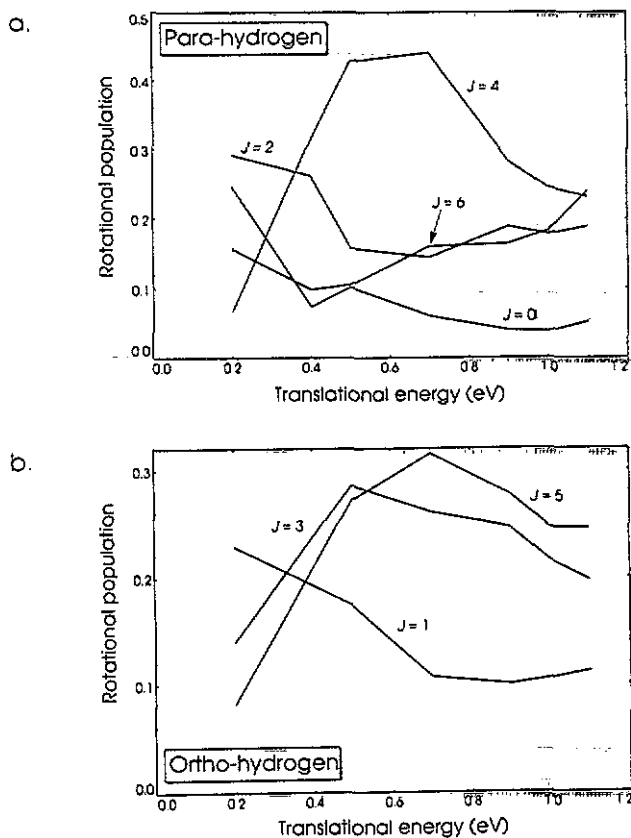


Figure 5. The rotational state distributions, P_{J,m_J} , as a function of translational energy for (a) *para*- and (b) *ortho*-hydrogen. As was observed previously, as the minimum activation barrier is exceeded, the higher J -states become populated as a consequence of the dissociation.

While the exact numerical results will, of course, depend upon the precise form of the PES, it is instructive to investigate the individual behaviour of the various $J = 1$ angular momentum contributions. In figure 4(b) the dissociation probabilities for $J = 1$ molecules in the $m_J = 0$ and ± 1 states are shown. Now there is a considerable difference between the results, with the $m_J = 0$ fraction being consistently lower than that for the $m_J = \pm 1$ component. This, in turn, implies that for a given translational energy the odd- J components in the P_{J,m_J} distributions for the normal hydrogen will be dominated by the contribution from the $m_J = 0$ state. The reason for this may be understood with reference to figure 6 where a schematic figure of the molecular scat-

tering geometries are depicted [20]. Molecules having $m_J = 0$ have J predominantly parallel to the surface (cartwheeling), while those with $m_J = \pm 1$ have J inclined at an angle with respect to the surface and are undergoing rotations that are a mixture of cartwheels and helicopters (J parallel to the surface normal). Since helicopter motion favours dissociation, the $m_J = \pm 1$ states will exhibit a higher probability for dissociative adsorption than those with $m_J = 0$. The results shown in figure 4(b) then follow directly. This is a particularly interesting result since it implies that for the present class of PES the angular momentum constraints regarding the dissociation appear far more important than the energetic ones.

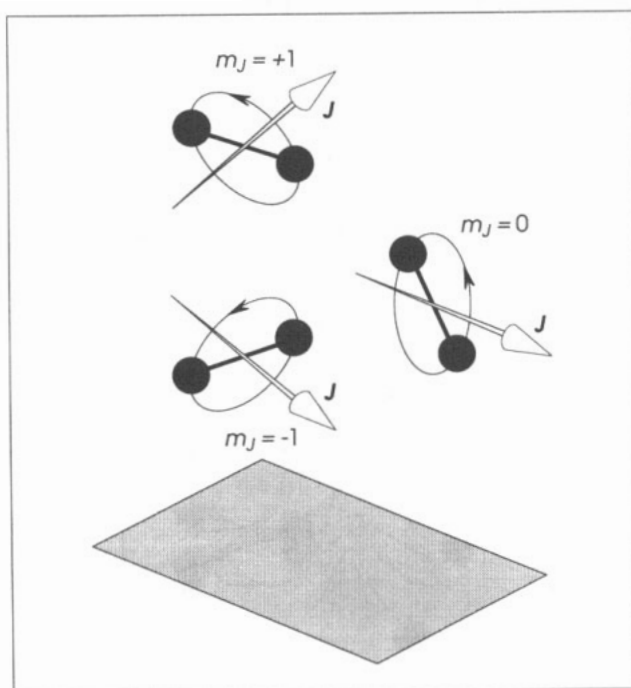


Figure 6. Schematic figure showing the average orientation of the H_2 molecule in the three $J = 1$ quantum states. From this figure it may be appreciated that molecules in the $m_J = \pm 1$ states have their molecular axis parallel to the surface for a greater fraction of time during a rotational period than those having $m_J = 0$. This, in turn, goes some way to explain the differences in dissociation probabilities shown in figure 4(b).

3.3. Rotational-vibrational coupling

To complete this discussion it is instructive to consider the role of the coupling that exists between rotations and vibrations (v-R) near the surface. Figures 7(a) and (b) show a schematic PES for the vibrational and rotational coordinates in free space and at a position near the surface for a late barrier PES (it is important to bear in mind that there is always coupling between these two degrees of freedom via the kinetic energy, equation (5)). The figure, based loosely on a calculation for free hydrogen and H_2 outside a jellium surface [18] shows the modification to the ground state $^1\Sigma_g$ potential, as the surface electrons interact strongly with those on the molecule. For distances corresponding to a compression of the molecular bond ($x < 0$) there

is very little change expected to the PES since this region of space is dominated by the local molecular properties that are not strongly affected by the presence of the surface. When the molecular bond is extended, the PES is changed significantly and differentially in θ . For $\theta = 0$, extending the molecular bond has the effect of pushing one atom into the metal, while the other goes into the gas phase. In each case the process costs energy and so the potential contours bunch up in the x -direction. For $\theta = \pi/2$, the molecule is lying flat on the surface with a weakened vibrational stretching frequency. If the bond is further extended, an activation barrier is encountered before the chemisorbed state is reached. This dissociation channel will show some structure related to the surface periodicity as diffusion barriers are traversed [25].

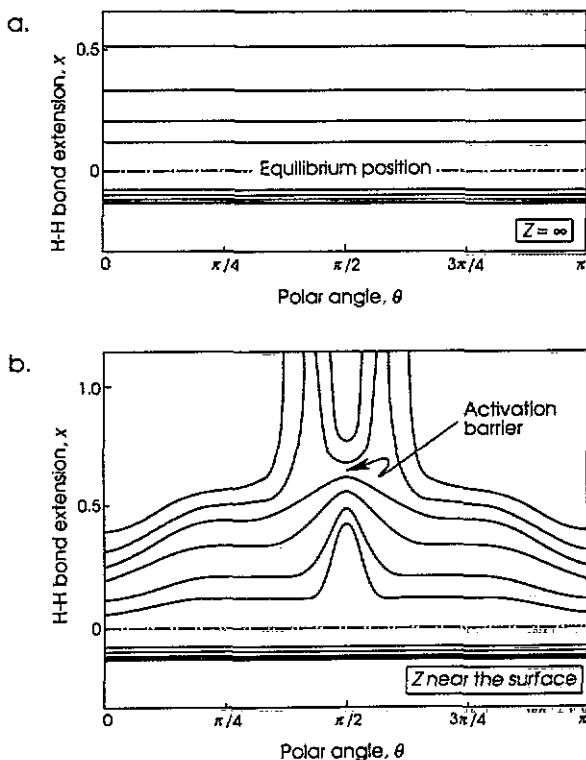


Figure 7. A slice through a late barrier PES showing the effects of rotational-vibrational coupling. At distances far from the surface, (a) $V(\theta, x)$ is decoupled and the only mixing arises through the kinetic energy (equation (5)). Close to the surface, (b) a dissociation channel opens up for a geometry corresponding to the molecule lying flat on the surface. In order to reach this channel, the molecule must pass over an activation barrier in the x -coordinate. Consideration of motion on this surface immediately explains why vibrational energy will promote dissociation whereas rotational energy will hinder it.

As the molecule nears the surface in a scattering simulation, the PES in x - θ will gradually change from figure 7(a) to 7(b). For illustrative purposes consider the motion of a classical trajectory over this PES. Vibrational energy corresponds to oscillations in the x -direction while rotational energy is represented by motion in θ . Vibrational excitation in the molecule will invariably lead to an enhancement in dissociation simply because in the exit channel, the reaction coordinate and the vibrational coordinate

are one and the same. R-V coupling is extremely weak. This is apparent from looking at the planar-like contours for bond compression in figure 7. In order that motion in θ becomes transformed to motion in x , there needs to be pronounced structure in this repulsive back wall; there is none. Putting excess energy in rotations actually diminishes dissociation as has been shown theoretically [21] and this follows naturally from the PES in figure 7. If the velocity in θ is increased, the dissociation channel will appear narrower to the rotating molecule and hence the dissociation probability will fall. As usual, these arguments will be modified with the inclusion of other PES features such as surface corrugation or attractive forces. However, the basic principles will still obtain and the general fact will remain that in dissociative adsorption of H_2 , R-V will be a weak effect.

4. Conclusions

In this short review, attention has been paid to the changes occurring in the dissociative adsorption probability for H_2 on metal surfaces as the molecular internal energy is modified. The general conclusions are:

(i) For systems having an activation barrier towards the exit channel, vibrational energy is particularly effective for promoting molecular dissociation. There is a significant isotope effect in favour of the lighter species which arises from the difference in zero-point energy and the tunnelling probability.

(ii) Rotational energy makes little difference to the dissociation probability. The rotational quantum of energy is too small to give a large effect. During dissociation, the rotational state distribution in the scattered flux will show significant occupation of high J -states for an initially cold beam. This T-R coupling may be easily understood by examination of the transition state geometry for the dissociating molecule. In general the polar and azimuthal angles will not be sampled uniformly during the dissociation process and this leads directly to rotational excitation.

(iii) Rotational-vibrational coupling will be generally quite weak. Since placing energy in the vibrational coordinate will increase dissociation, this implies that rotational energy will not be particularly efficient in promoting dissociation.

It is hoped that work of this nature will continue to provoke experimentalists into making surface dynamical measurements. Although it is appreciated that these are often difficult and time-consuming, if an understanding of the gas-surface interaction potential is to be obtained, they will be a necessary partner to theoretical dynamical simulations.

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