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Competition between vibrational excitation and dissociation in collisions of H_2 with Cu(100)

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A four-dimensional dynamics study was performed on vibrational excitation and dissociation of H_2 in collisions with Cu(100). The potential-energy surface was taken from density-functional calculations. Large probabilities for vibrational excitation ($>10\%$) are obtained. Two-dimensional fixed-site calculations show that the vibrational excitation is due to impacts on the top site. Impacts on the bridge and hollow sites are more efficient in causing dissociation.

I. INTRODUCTION

In gas-surface collisions, vibrational excitation may come about in several ways.[1–5] In one mechanism, dissociation over a barrier at which the molecular bond is extended competes with vibrational excitation. This mechanism has been invoked to explain the high vibrational excitation probabilities seen in experiments on scattering of D_2 and H_2 from Cu(111).[4,5] For D_2, probabilities larger than 10% were found. The probabilities for vibrational excitation and dissociation were seen to exhibit a similar dependence on incidence energy E_i, turning on at similar dynamical thresholds lying well above the energetic threshold to vibrational excitation. Rettner, Auerbach, and Michelsen[4] concluded that the coupling responsible for vibrational excitation only reaches sufficient strength close to the barrier to dissociation, and suggested that vibrational excitation is governed by the same region of the potential-energy surface (PES) as dissociative adsorption.

The suggestion that vibrational excitation and dissociation occur at similar collision geometries was next considered in dynamics studies by Darling and Holloway.[6,7] In calculations using a fixed-site model which included molecular rotation, the high vibrational nonadiabaticity seen experimentally[4,5] could not be reconciled with the vibrational efficacy known from dissociation experiments.[8] Here the vibrational efficacy refers to how efficient the initial vibrational energy of the molecule is in promoting dissociation. Their finding led the authors to suggest that vibrational excitation and dissociation occur on different surface sites.[7]

Here we investigate the controversy of whether vibrational excitation and dissociation of H_2 occur on different sites on Cu surfaces, employing a model which explicitly includes the molecule's translational motion parallel to the surface. Of course, including the molecule's motion parallel to the surface in the model allows an investigation of the influence of impacts on different sites, which should enable us to obtain more positive proof concerning the above controversy. In our calculations, we use the Born-Oppenheimer approximation, assuming that nonadiabatic effects can be neglected. This approximation should be reasonable when applied to dissociative chemisorption and vibrational excitation of the molecule: because H_2 has a low electron affinity, electron-hole pair excitations should not play an important role in direct scattering at thermal collision energies.[9] We also neglect the possibility of energy transfer to surface phonons: energy transfer to surface phonons is not an efficient process due to the large mass mismatch between the impacting molecule and the Cu ions.[10] Even if phonon excitation does occur, the amount of energy transferred will usually be small compared to the molecule's vibrational frequency, making it unlikely that the outcome of the scattering event (reflection, vibrational excitation, or dissociation) is greatly affected. The calculations are done for the scattering from the [100] face of copper, but we will show that it is possible to generalize our results to the [111] face, for which experiments are available.

The molecular degrees of freedom which are treated as dynamical variables are the vibrational coordinate r, the molecule-surface distance Z, and the coordinates X and Y for translation parallel to the surface. In our model, the molecule is not allowed to rotate (the angles θ and ϕ defining the orientation of the molecule are kept fixed), but, as will be demonstrated below, this should not affect the principal conclusions arrived at in this work. As detailed below, the potential-energy surface (PES) which defines the interaction of H_2 with the Cu(100) surface was obtained using density-functional theory (DFT) with the generalized gradient approximation (GGA), employing a slab representation for the copper surface. Calculations which used a GGA PES and employed a similar dynamical model but, in addition, also performed averages over the azimuthal angle of orientation ϕ, have already been done for H_2 + Cu(111),[11] but this study focused on the dependence of dissociative chemisorption on incidence angle and did not give results for the vibrational excitation of H_2.

II. METHOD

In the first stage of the calculation, we solve the electronic structure problem to obtain a four-dimensional (4D) PES. The PES was obtained in two stages. First, two-dimensional

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(2D) PES's were calculated for impacts on the high-symmetry top, hollow, and bridge sites. The molecular axis is kept parallel to the surface ($\theta = 90°$). Some arbitrariness is involved in the choice of the orientation angle ϕ determining the projection of the molecular axis on the unit cell; this is resolved by demanding the potential to describe dissociation along the energetically most favorable path. Above the bridge site dissociation occurs into neighboring hollow sites, and, above the top and hollow sites, into bridge sites.

To obtain the 2D potentials, the Kohn-Sham equations of DFT (Ref. 12) were solved for a number of points (r,Z) using the program BAND.[13] The GGA used consists of adding the Becke correction[14] and the Perdew correction[15] to the energy obtained self-consistently using the local-density approximation.[16] Calculations performed by us show that the GGA employed here yields barrier heights which differ very little (less than 0.1eV) from the barrier heights obtained using the GGA due to Perdew and Wang,[17] which has been shown to yield barrier heights which are in very good agreement with experiment for H_2 + Cu(111).[18] For each site, the DFT results were fitted to an analytical form; for details of the DFT and fitting methods see Refs. 19 and 20. The lowest barrier (0.48 eV) is found for dissociation over the bridge sites.[19(b)] Plots of the 2D PES's for impacts on the hollow and top sites are shown in Fig. 1 [for impact on the bridge site, see Fig. 6 or Ref. 19(b)]. Two-dimensional dynamics calculations on dissociative chemisorption along the energetically most favorable dissociation route and performed using the present PES suggest that the barrier heights in our PES are accurate.[19] The ultimate test of the accuracy of the PES would consist in a fully quantal, six-dimensional dynamics calculation on dissociative chemisorption, but that is not the object of the present work.

The PES is most easily used in the second stage of the calculation (the solution of the Schrödinger equation for nuclear motion) when available in analytical form. To obtain a fully analytical expression for the 4D PES, we write it as an expansion in symmetry-adapted linear combinations of plane-wave functions:

$$V(r,Z,x,y) = V_{00}(r,Z)H_{00}(x,y) + V_{10}(r,Z)H_{10}(x,y) + V_{11}(r,Z)H_{11}(x,y), \tag{1}$$

$$H_{10}(x,y) = \cos Gx + \cos Gy, \tag{2}$$

$$H_{11}(x,y) = 2\{\cos Gx \times \cos Gy\}. \tag{3}$$

In Eq. (1), $H_{00}(x,y) = 1$, and in Eqs. (2) and (3), $G = 2\pi/a_l$, where a_l is the Cu-Cu distance ($4.822a_0$). To obtain the three $V_{nm}(r,Z)$, we demand that the 4D PES interpolate between the three 2D potentials for impacts on the sites discussed above, which amounts to the solution of a simple set of linear equations (see also Ref. 20).

To obtain dynamical information, a wave-packet method is used to solve the Schrödinger equation for nuclear motion. For normal incidence and a potential containing a few plane-wave terms, it is appropriate to expand the wave function on a grid of points in r and Z and in symmetry-adapted functions $H_{nm}(x,y)$:[21]

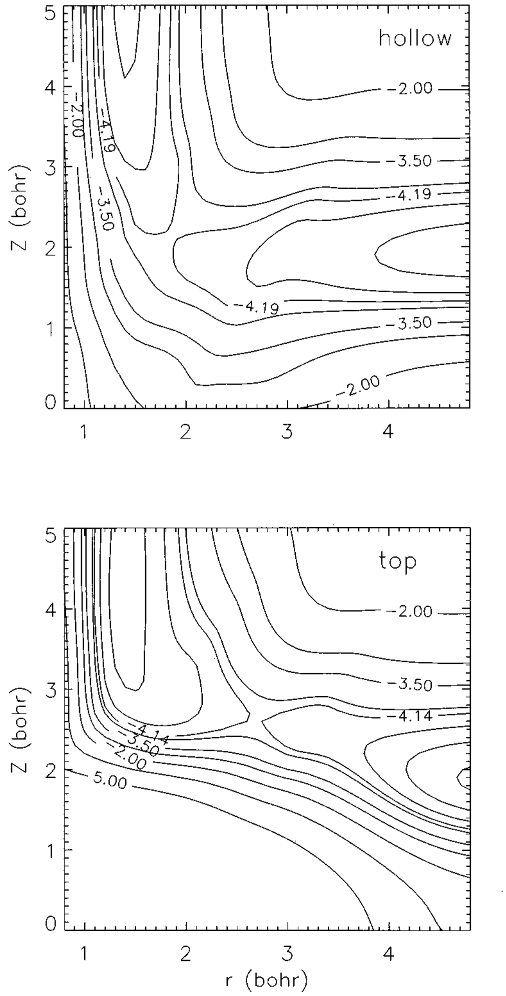

FIG. 1. Contour plots (labels in eV) are shown describing the PES for dissociation above the hollow and top sites.

$$\Psi(t) = \sum_{nm} f_{nm}(r,Z,t,)H_{nm}(x,y). \tag{4}$$

The initial wave function is a product of $\Psi_v(r)$ describing initial vibration and a Gaussian wave packet in Z. The Chebyshev method[22] is used to propagate the wave function in time, using appropriate methods[21,23] to evaluate the action of the Hamiltonian on Ψ. The Hamiltonian contains kinetic terms describing the motion in r and in X,Y, and Z, and the potential [Eq. (1)]. Probabilities $P(v_i \rightarrow v_f nm)$ for transitions from an initial vibrational state v_i to a final state with quantum numbers v_f for vibration and n and m for diffraction are obtained using an asymptotic analysis method allowing a high-energy resolution.[24] Vibrational probabilities $P_{v_i v_f}$ are obtained by summing the $P(v_i \rightarrow v_f nm)$ over n and m, and dissociation probabilities R_{v_i} by summing the $P_{v_i v_f}$ over v_f and subtracting from 1. Additional details are given elsewhere.[25]

III. RESULTS

Probabilities for vibrational transitions and for dissociation are shown in Fig. 2 as functions of E_i, for scattering of

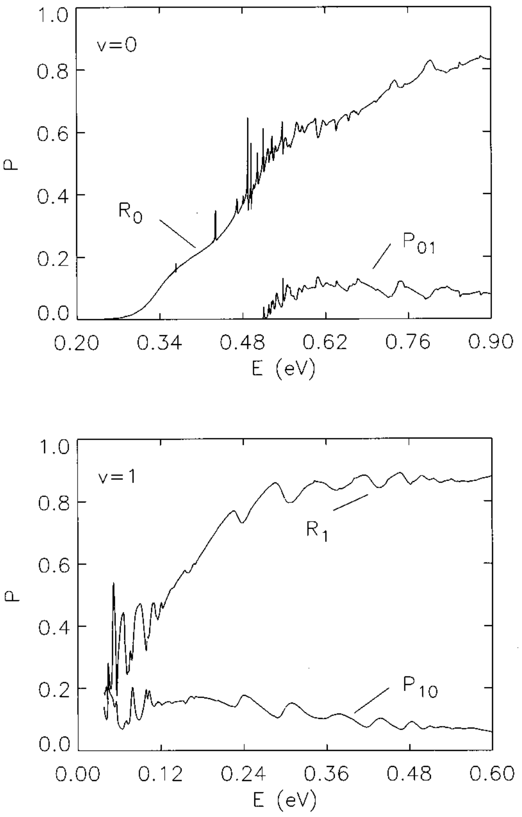

FIG. 2. The 4D probabilities for dissociation and for vibrationally inelastic scattering are shown as a function of E_i for two initial vibrational states of H_2.

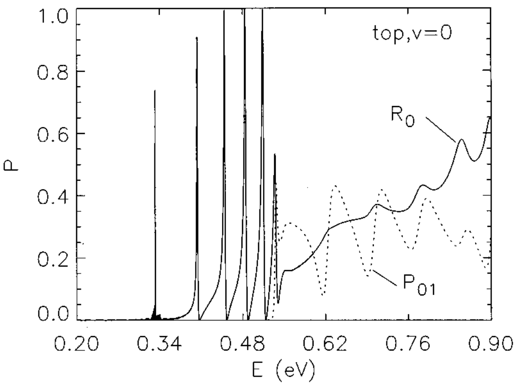

FIG. 3. The 2D probabilities for dissociation and for vibrational excitation are shown as a function of E_i for impact on the top site.

$v=0$ and $v=1$ H_2. The probabilities show sharp features, which are due to resonances as discussed below. Importantly, we calculate large probabilities ($P_{01}>10\%$) for vibrational excitation of H_2 scattering off Cu(100), in agreement with the experiments on scattering of D_2 and H_2 from Cu(111).[4,5] We also calculate high probabilities (P_{10}=10–20 %) for vibrational deexcitation. Note that to obtain fully energy-resolved results, large propagation times were required. The results for scattering of $v=0$ H_2 and for collision energies in the range 0.2–0.6 eV were obtained from a single wave-packet calculation employing a total propagation time of 648 000 atomic units of time (15.7 ps), resulting in a spectral resolution of 0.13 meV.

To find the cause of the efficient vibrational excitation, additional calculations were done using a 2D fixed-site model. Figure 3 presents results for impacts on the top site, showing large values (10–40 %) of P_{01} for E_i larger than the ($v=0\rightarrow1$) threshold (0.504 eV). In contrast, the calculated P_{01} were less than 1% for scattering off the hollow and bridge sites over the entire range of E_i studied (0.2–0.9 eV). Dissociation over these sites is more efficient, R_0 rising above 90% for $E_i>0.39$ and 0.50 eV for impacts on the bridge and hollow site, respectively (see Fig.4). The 2D results show that in our 4D model of scattering of H_2 from Cu(100), vibrational excitation occurs through impacts near the top sites, while dissociation dominates in impacts on the hollow and bridge sites. Extrapolating to H_2 + Cu(111), our results agree with the suggestion of Darling and Holloway[7] that dissociation and vibrational excitation take place on different sites.

The top-site PES (Fig. 1) has special features explaining its efficiency for vibrational excitation. Compared to other sites, at the top site the Pauli repulsion increases much more rapidly close to the surface, because the molecule impacts on an atom. Then the only way for the molecule to climb the reaction path is to extend its bond length in a region of high curvature. The H_2 molecule is small relative to the Cu atom with which it collides, and the deeper bridge sites into which dissociation occurs exert a strong pull on the atoms only once they have started to roll off the Cu atom. This implies an especially late barrier coming after a region of high curvature (see also Ref. 25). It is precisely on such a PES that vibrational excitation is efficient.[6,7] In Cu(100) and Cu(111), the top sites are obviously of a similar nature, and the vibrational excitation seen in the experiments on H_2 + Cu(111) (Refs. 4 and 5) should also be due to impacts near the top site. As is the case for dissociation of H_2 over Cu(100), for H_2 + Cu(111) the lowest barrier for dissociation occurs for impacts on the bridge sites, with the atoms dissociating to hollow sites.[18] Thus while our conclusion that reaction and

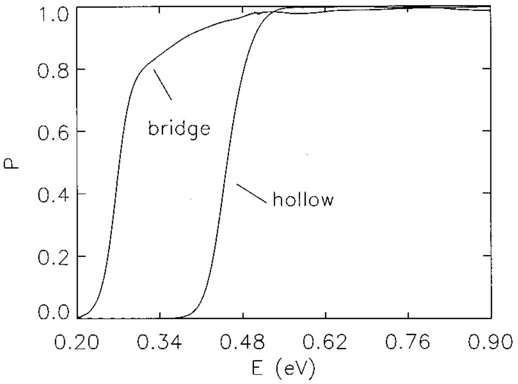

FIG. 4. The 2D dissociation probability is shown as a function of E_i for H_2 approaching the surface in its $v=0$ vibrational state, for impacts on the bridge and hollow sites.

vibrational excitation occur on different sites is based here on calculations for scattering from the [100] face, it can be generalized to the scattering from the [111] face, for which more detailed experiments are available.

The reaction probabilities for impacts on the bridge and hollow sites (Fig. 4) show the smooth dependence on E_i seen usually in 2D calculations (see for instance Fig. 3 of Ref. 26). In contrast, the 2D reaction probability for impact on the top site shows sharp peaks (see Fig. 3). An analysis presented elsewhere[25] shows the peaks to be due to resonances, involving trapping at the surface. In the mechanism[27] causing trapping, the H_2 bond is weakened at the surface (see Fig. 1). This lowers the frequency of the molecular vibration, allowing the population of a $v=1$ like state at E_i below the threshold for the $v=0 \rightarrow 1$ transition in the gas phase. At such E_i, the excited molecule does not have enough translational energy to escape to the gas phase until it gives back its vibrational quantum. While trapped, time is available to tunnel through the barrier, the peaks showing that the trapping efficiently promotes dissociation. This mechanism was noted before in dynamics calculations on scattering of H_2 from Cu(111) using a PES based on the local-density approximation of DFT and a cluster representation of the copper surface.[27] Note that the mechanism which is operative here differs somewhat from the mechanism causing trapping in a model calculation which employed an elbow potential with a very late barrier.[26] In that calculation, the lowering of the frequency which enables the trapping is due to a reduced mass effect, and the vibrational mode which is excited in the molecule-surface metastable complex is in fact the molecule-surface vibration.

The 4D reaction probabilities (Fig.2) also show peaks which are due to resonances. An analysis of these resonances in terms of widths and the motions to which incident translational motion is transferred to cause the trapping will be presented elsewhere.[25] It should be noted here that the resonances could be sensitive to the neglect of rotational motion. The widths of the resonances should also be sensitive to the neglect of electronic nonadiabacity. While electron-hole pair couplings should not be very important for the direct scattering of initially vibrationless H_2, such couplings may be effective in quenching the molecular vibration if the molecule remains trapped at the surface for some time.[2] The presence of this extra decay channel should lead to an increase of the width of the resonance.

Coming back to our 4D results for H_2 + Cu(100), we note that vibrational deexcitation is also an efficient process. This is relevant to a recent experiment[28] on scattering of H_2 from Cu(110) at $E_i=78$ meV. A survival probability of the initial ($v=1$, $j=1$) H_2 state of 75% was found, and, since only minimal dissociation is expected to take place at 78 meV,[29] the vibrational deexcitation probability is near 25%. To explain the efficiency of this process, a nonadiabatic mechanism was invoked,[28] involving coupling to electron-hole pairs.[2] It is not fully clear whether such a mechanism could also be efficient enough in the case that the vibrational deexcitation occurs in a direct collision, and our results suggest that the direct adiabatic mechanism involving impacts on top sites could also contribute significantly to the vibrational deactivation seen experimentally.[28]

We now return to the approximations made in the 4D model of fixing θ and ϕ. In a six-dimensional (6D) calculation considering all molecular degrees of freedom, collision geometries with $\theta \approx 90°$ but ϕ different from considered here also contribute. However, we expect that averaging over ϕ will not change our results, in that all collisions with the top site and $\theta \approx 90°$ will be efficient in causing vibrational excitation. For impact on the top site, consider the longer dissociation route to the hollow sites. The reaction path will still exhibit a large curvature and a barrier which is probably even later than for dissociation into the bridge sites, if anything implying more efficient vibrational excitation. A reaction path of such form is unlikely for collisions with the deeper-lying, softer sites.

In a 6D calculation, tilted orientations also contribute to the scattering. Collisions in which the molecular axis is oriented more perpendicular to the surface do not contribute to dissociation; we expect the same to be true for vibrational excitation. Assuming that inclusion of the polar rotation in our model would lead to similar decreases in vibrational excitation and reaction, we find that our vibrational excitation probabilities may decrease by a factor 2–2.5: A saturation value of 0.39 was obtained for the dissociation probability of H_2 on Cu(100) (for normal energy scaling),[8] whereas our 4D calculations yield a value of approximately 0.9. This implies that the probability for vibrational excitation of H_2 on Cu(100) should not be much higher than 4–5%, though larger values are possible for D_2. We do not expect our main conclusion, that vibrational excitation and dissociation occur most efficiently on different sites, to be affected.

IV. SUMMARY

We have performed 4D and 2D dymanics calculations on the scattering of H_2 from Cu(100). The calculations yield positive proof that efficient vibrational excitation occurs mostly in impacts near the top site, while impacts near the hollow and bridge sites are more effective in causing dissociation. Top-site collisions are effective in promoting vibrational energy transfer because the reaction path is already highly curved in front of the barrier which is especially late. Reaction occurs more efficiently above the hollow and bridge sites because the reaction barriers are lower for impacts on these sites. These conclusions should also apply to the scattering of D_2 and H_2 from the [111] face of copper, for which experimental results concerning vibrational excitation are available.

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