Six-Dimensional Quantum Dynamics of Dissociative Chemisorption of ($v = 0, j = 0$) H_2 on Cu(100)

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Six-dimensional quantum dynamics calculations are now possible for fully activated dissociative chemisorption of H_2. We present results for the reaction of ($v = 0$, $j = 0$) H_2 on Cu(100). The potential energy surface was taken from density functional theory (DFT), using the generalized gradient approximation. Comparison to experiment suggests that, on average, the DFT method overestimates the barriers to dissociation by 0.18 eV for H_2 + Cu(100). [S0031-9007(97)03092-5]

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The reaction of H_2 on copper is the most studied example of translationally activated molecular dissociation on a metal surface. For the reaction on the (100) face, direct information is available from molecular beam experiments [1]. Indirect information comes from experiments on associative desorption, invoking the principle of detailed balance [2]. The results [1,2] have been used in a fit [3] which describes the reaction probability $R_v(E_i)$ as an S-shaped function of the normal incidence energy E_i,

$$R_v(E_i) = \frac{A}{2}\left(1 + \tanh\frac{E_i - E_0(v)}{W(v)}\right). \quad (1)$$

Here, A is the saturation value of the reaction probability. The dynamical threshold E_0 is a measure of the average barrier height, being the energy E_i at which $R_v = 0.5 \times A$, and W is the width of the curve. The use of the quantum number v as a label signifies a dependence on the initial vibrational state v of H_2 (v is 0 or 1).

While dynamics calculations have explained several experimental trends in the activated dissociation of H_2 on copper, they have so far failed in accurately reproducing the experimental reaction probabilities. Assuming that the Born-Oppenheimer approximation can be used (i.e., neglecting electron-hole pair excitations [4]) and that surface phonons can be neglected [5], accurate calculations can be done if two criteria are met. First, an accurate potential energy surface (PES), describing the electronic molecule-surface interaction as a function of all molecular degrees of freedom, should be available. Second, multidimensional quantum simulations of the reaction [6–9] suggest and classical calculations [10] show that the subsequent dynamics calculation should explicitly treat all six molecular degrees of freedom, if possible, on a quantum footing.

An electronic structure approach with a claim to accuracy is now available. The method uses the generalized gradient approximation (GGA) [11,12] of density functional theory (DFT) [13] in conjunction with a slab representation of the metal surface. It has been used in calculations on both H_2 + Cu(111) [14,15] and H_2 + Cu(100) [15–18]. For the latter system a fully analytical six-dimensional (6D) fit is available [18].

A good way of validating the new electronic structure method is to use a computed PES in 6D quantum dynamics computations to obtain reaction probability curves for comparison to experiment. However, so far 6D quantum calculations have been performed only for one unactivated dissociation problem [H_2 + Pd(100)] [19]. For H_2 on copper, results are needed for higher collision energies, requiring the use of larger basis sets. So far no more than four degrees of freedom were treated with no approximations in quantum dynamical simulations of the reaction of H_2 on copper [6–9], though 6D calculations have been done in a mixed quantum-classical framework [20].

We present results of a 6D quantum dynamical simulation of the fully activated dissociation of ($v = 0$, $j = 0$) H_2 on Cu(100). The PES used is an accurate fit of calculations using the GGA/slab approach. Our calculations test the accuracy of the new electronic structure approach to computing barrier heights for activated dissociation, for a benchmark system. Comparison to experiments shows reasonable agreement with the dynamics results, indicating the DFT method to be reasonably accurate for the present system. The agreement is not precise, suggesting that, on average, the DFT barriers are too high by 0.15–0.2 eV. However, more detailed experiments and dynamics calculations using a more complete PES are required to pass a more definite judgement on the quality of the GGA approximation for the system studied.

The GGA/slab PES we use may be written

$$V = f_c(Z)V_{6D}(r,Z,X,Y,\theta,\phi) + [1 - f_c(Z)]V_{\rm at}(r). \quad (2)$$

In Eq. (2), r is the H_2 bond length, θ and ϕ are the polar and azimuthal angles of orientation of the molecular axis, and Z, X, and Y define the position of the molecule's center of mass, Z being the distance to the surface. Far away from the surface $V_{\rm at}(r)$ describes the gas-phase H_2 potential [Eq. 4(a) of Ref. [18]], the function $f_c(Z)$ [Eq. (2a) of Ref. [18]] switching off the molecule-surface interaction between $Z = 8.14a_0$ and $8.94a_0$. The full expression of the molecule-surface potential V_{6D} is given in Ref. [18] [Eq. (23)], which also gives details concerning the GGA that was used [11], and other aspects of the electronic structure method [21] and fitting procedure. The potential describes the orientational dependence of the interaction up to second order in spherical harmonics, for the molecule being above the high symmetry bridge, top, or hollow sites. The potential depends on both θ and ϕ above the twofold bridge site, for which the lowest barrier (0.48 eV) is found (the atoms moving to the hollow sites). Above the fourfold hollow and top sites, the potential does not depend on ϕ. For impacts of the molecule at low symmetry sites, the potential interpolates between the high symmetry sites.

The time-dependent wave packet (TDWP) method was used to compute reaction probabilities. The method uses a symmetry-adapted basis set in the scattering wave function, allowing considerable computational savings when modeling scattering at normal incidence [22]. This feature is advantageous for systems obeying normal energy scaling, like H_2 + Cu(100) [3]. The basis set describes rotational motion and translational motion parallel to the surface. A grid representation is used for describing motion in r and Z [8]. To propagate the wave function in time a new expression of the evolution operator [23] is used which incorporates the absorbing boundary conditions that are required to keep the grid small and allows the use of real algebra in the expensive part of the calculation. The algorithm is made more efficient by using a projection operator formalism [24]. State-to-state probabilities for (in)elastic scattering of H_2 are obtained from S-matrix elements which are computed using a scattering amplitude formalism [25]. Summing the state-to-state probabilities yields probabilities for vibrationally (in)elastic scattering $P(v \rightarrow v')$ as well as initial state selective reaction probabilities R_v.

The calculation employs 100 points in Z over the range $[-1a_0,\ 13a_0]$, and 40 points in r over the range $[0.522a_0, 6.522a_0]$. In the basis set, we use all rotational channels with $j \leq 24$, and all diffraction functions with $|n| + |m| \leq 11$. The propagation time was 1.94 ps. These parameters were selected to yield converged reaction probabilities and vibrational excitation probabilities for $E_i \leq 0.78$ eV. Convergence at higher incidence energies required a larger rotational basis set (we used channels with $j \leq 28$) but less propagation time (0.73 ps). With the parameters used, reaction probabilities are accurate to within better than 0.01, and vibrational excitation probabilities to within better than 0.003.

Computed reaction probabilities are compared to experiment [3] in Fig. 1. The computed R_0 is seen to saturate at $A = 0.28$, compared to an experimental value of 0.388. Experimentally, A should not be well established [the value computed for H_2 + Cu(111) in Ref. [3] is 0.622; from more detailed experiments a value of 0.24 was obtained [26]], so we are not so concerned with this difference. More important to our comparison is the dynamical threshold for which we obtain 0.76 eV, compared to an experimental value of 0.582. This suggests that the barriers which were computed to construct the H_2 + Cu(100) PES are too high, by 0.18 eV on average. Before drawing further conclusions, we first discuss two factors to consider in comparing theory and experiment, and then make a comparison with the related H_2 + Cu(111) system.

First, the fit [3] to which we compare is based on limited experimental information [1,2], requiring assumptions to be made concerning, for instance, the role of rotations and the kinetic energy spread in the molecular beams [1]. Concerning the latter, Michelsen and Auerbach [3] note that the energy spread in the beams may well be larger than indicated [1] and used in the fit by a factor of 2. It is also not clear how accurate the molecular beam results [1] are: Rettner *et al.* [26] report adsorption probabilities for H_2 + Cu(111) which are lower than the results of Anger *et al.* [1] for the same system by an order of magnitude, without being able to account for the difference. If the results of Anger *et al.* [1] for H_2 + Cu(100) are also too large the true value of $E_0(0)$ should be larger than the estimate from the fit, yielding increased agreement with our calculations.

Second, the computed 6D potential necessarily contains only a limited number of expansion functions describing the dependence on X, Y, θ, and ϕ. Improvements can be made by computing terms which describe the interaction for impacts on low symmetry sites and by expanding up to fourth order in spherical harmonics above the high symmetry sites to also describe the azimuthal dependence

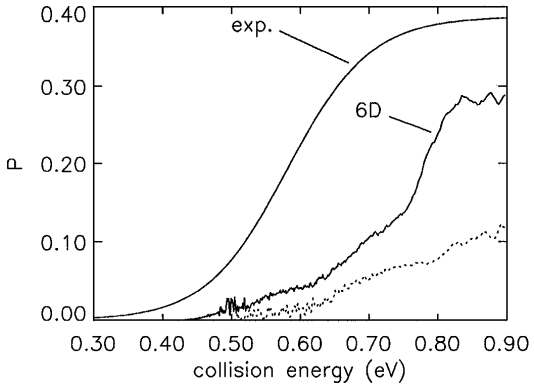

FIG. 1. The 6D probability for dissociation is compared to the experimental reaction probability curve [3]. Also shown is the calculated probability for vibrational excitation $P(v = 0 \rightarrow 1)$ (dotted curve).

of the interaction above the fourfold sites. Improving the potential for impacts at low symmetry sites may favor reaction at *low* energies: other DFT calculations on H_2 + Cu(100) [15] have revealed the existence of a barrier on a low symmetry site which was found to be *lower* (though only by about 0.03 eV) than the lowest barrier for dissociation above the higher symmetry sites (for the bridge-to-hollow configuration). Improving the description of the fourfold sites may diminish the reaction at *high* energies, as dissociation paths will be sampled that are less favorable than the top-to-bridge and hollow-to-bridge paths on which the potential is now based. The net effect of these improvements may well be that the theoretical value of $E_0(0)$ shifts down by some unknown, though probably small, amount, increasing somewhat the agreement between experiment and theory for H_2 + Cu(100).

We next consider the related system H_2 + Cu(111), for which much more detailed information is available from experiments [26]. Molecular beam experiments put the dynamical threshold for this system at 0.59 eV [26]. An estimate for a theoretical 6D value based on the DFT/GGA/slab method [14] may be obtained by extrapolating results of a 5D, approximate dynamical ("hole") model [15]. The reaction probabilities computed using this model were in good agreement with results of quasi-5D dynamical calculations [7]. From the hole model, a dynamical threshold value of 0.9 eV can be obtained (see Fig. 4 of Ref. [15]). From this number should be subtracted a value of $\approx$0.23 eV to account for the convergence of the PES used (see caption of Fig. 4 of ref. [15]). To account for the motion in the degree of freedom which was neglected (θ), half the frequency of the cartwheel rotation (0.13 eV, see Table III of Ref. [14]) should be added. In this way we obtain a theoretical threshold value of $0.9 - 0.23 + 0.06 = 0.73$ eV, which is larger than the experimental value [26] by 0.14 eV.

Taken together, the comparisons for H_2 + Cu(100) and H_2 + Cu(111) suggest that the DFT/GGA/slab method overestimates reaction barriers for H_2 + Cu systems by about 0.1–0.2 eV. The *size* of the deviation is in broad agreement with calculations on barrier heights in molecular systems [27]. However, the *direction* of the differences is not the same: the DFT/GGA method tends to compute barriers for molecular systems which are too low. At present, we cannot account for this difference. We note that our findings for surfaces is presently based on limited evidence [mostly concerning experiments for H_2 + Cu(100), while 6D calculations have not yet been done for H_2 + Cu(111)].

The reaction probability shows some structure due to narrow resonances, especially near $E_i = 0.5$ eV. These resonances were also seen in 4D calculations on scattering at fixed orientation [8]. The structure is due to trapping of the molecule at the surface near a top site [8], due to excitation of the molecular bond which is weakened near the surface.

TABLE I. Reaction probabilities R_0 and probabilities for vibrational excitation $P(v = 0 \rightarrow 1)$ are given for a few collision energies E_i.

E_i (eV)	R_0	$P(v = 0 \rightarrow 1)$
0.45	0.003	0.0
0.55	0.042	0.005
0.65	0.066	0.036
0.75	0.137	0.071
0.85	0.280	0.104

In Fig. 1, we also show the computed vibrational excitation probability $P(v = 0 \rightarrow 1)$. In broad agreement with experiments investigating vibrational excitation of H_2 on Cu(111) [28], vibrational excitation is found to be efficient at higher energies, with $P(v = 0 \rightarrow 1) \approx 0.1$ at $E = 0.9$ eV. Calculations which investigated the influence of impact site [8] show that the vibrational excitation is mostly due to collisions with top sites.

The dynamics method employed here is "exact" (within limits imposed on the convergence of the results which are due to restrictions on the size of the scattering basis set). Consequently, our results can also be used to validate more approximate dynamical treatments, such as mixed quantum-classical trajectory methods. Calculated values of R_0 and of $P(v = 0 \rightarrow 1)$ are therefore given for a few energies in Table I.

The 6D results are compared with results of lower dimensionality quantum dynamical calculations in Fig. 2. The 2D results are for fixed impact and orientation, the molecule following the most favorable dissociation route found for the high symmetry sites [17]. Four-dimensional results are given for a model which includes parallel translational motion but excludes rotations [8], and for a so-called fixed-site (bridge) model, which includes rotations [9]. The results confirm [10] that motion in

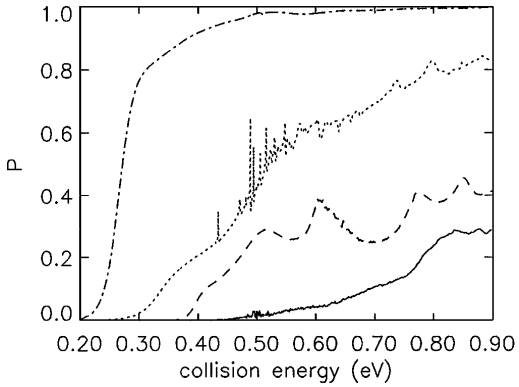

FIG. 2. The 6D probability for dissociation (solid line) is compared to results of 2D calculations (·—·), 4D calculations including parallel translational motion (···), and 4D calculations including rotational motion (---).

all six degrees of freedom affects the reaction, and that all six degrees of freedom should be taken into account in the calculation of reaction probability. The lower dimensionality model which most closely approximates the 6D results is the 4D fixed-site model.

In conclusion, we have presented results of 6D quantum dynamics calculations on the activated dissociation of ($v = 0,\ j = 0$) H_2 on Cu(100), employing a PES which was taken from DFT calculations using a GGA/slab approach. Comparison of the results to experiments suggests that he DFT method is reasonably accurate for the present system. The agreement is not precise, suggesting that the DFT/GGA/slab method overestimates reaction barriers by 0.15–0.2 eV on average, for H_2 + Cu(100). More detailed experiments, and dynamics calculations employing a more complete PES are required to establish more confidently the quality of the GGA result for the system investigated.

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