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Nonmonotonic dissociative adsorption of vibrationally excited H_2 on metal surfaces

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Spurred by recent experimental developments in the production of vibrationally excited molecular beams to study reactive scattering on metal surfaces, we have carried out six-dimensional quasiclassical and quantum dynamics simulations for several $H_2(v>0)$-surface systems. We predict a general nonmonotonic behavior of dissociative adsorption of vibrationally excited $H_2(v,J=0)$ molecules as a function of incidence energy whenever this process becomes nonactivated. This prediction is based on results obtained for up to five different activated systems, including pure [Pt(111) and Cu(110)], bimetallic alloy [NiAl(110)], and bimetallic pseudomorphic [Pd/Ru(0001) and Cu/Ru(0001)] surfaces.

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Over the last decade, surface science theorists have made a substantial progress in the description of reactive scattering of diatomic molecules from metal surfaces (see Refs. 1 and 2 and references therein). This has been motivated by the numerous industrial processes that involve heterogeneous catalysis by a metal surface, in which molecular dissociative adsorption is the first and usually the rate-limiting step.[3] Methods of increasing complexity, based on accurate density-functional theory (DFT) descriptions of the molecule/surface interaction,[4,5] have been developed to take into account all molecular degrees of freedom (DOFs) and even phonons[6,7] and electron-hole pair excitations.[8,9] So far, six-dimensional (6D) dynamical calculations, usually within the Born-Oppenheimer and rigid surface approximations, have challenged experimental measurements to an unprecedented degree of accuracy and have provided meaningful interpretations of, sometimes striking, observations such as: the dominant out-of-plane diffraction measured for $H_2/Pt(111)$ (Ref. 10) and $H_2/Pd(111)$ (Refs. 11 and 12); the lack of diffraction peaks in $H_2/Pd(110)$ due to dynamic trapping;[13] the surprisingly low reaction probability observed in $N_2/Ru(0001)$ for incidence energies well above the minimum reaction barrier (MRB) (Ref. 14); the dramatic difference in reactivity between chemically similar systems such as $N_2/W(100)$ and $N_2/W(110)$ (Ref. 15); or the strong nonadiabatic effects that govern the interaction of O_2 with Al(111).[16,17]

Most existing experiments have exclusively considered molecules in their ground vibrational state ($v=0$) since they employ supersonic molecular beams in which vibrationally excited states are barely populated except at relatively high kinetic energy.[18] Vibrational excited molecules can be more efficiently obtained by using stimulated Raman pumping.[19–22] However, only very recently, the advent of experimental setups based on pulsed narrow bandwidth laser Raman excitation have made it possible to perform quantum state resolved reactivity measurements with vibrationally excited polyatomic molecules,[23] e.g., methane,[24–28] on single-crystal surfaces. The latter experiments have provided direct evidence of the central role played by vibrational energy in activating gas-surface reactions (the so-called vibrational efficacy, i.e., the efficiency of vibrational energy in promoting reaction). Similar predictions have been reported from state-of-the-art quantum and classical 6D dynamical methods applied to vibrationally excited molecules.[29–33] But apart from this and in spite of the potentiality of this new generation of experiments, not much new insight on chemisorption or dissociative adsorption of vibrationally excited molecules has been achieved.

In this work, we report a surprising finding that has passed unnoticed in previous work: the general nonmonotomic behavior of the dissociative adsorption probability as a function of incidence energy for $H_2(v,J=0)$ molecules with enough vibrational energy to overcome the lowest dissociation barrier. This is demonstrated by means of 6D quasiclassical and quantum dynamics calculations for five different activated systems: the two single-crystal surfaces Pt(111) and Cu(110), the bimetallic alloy surface NiAl(110), and the two pseudomorphic bimetallic surfaces Pd/Ru(0001) and Cu/Ru(0001). The results of this prediction could be experimentally tested by using the above mentioned stimulated Raman pumping to prepare H_2 molecules in vibrationally excited states.[34]

To perform this study we have used the Born-Oppenheimer approximation and the static surface model. The 6D potential-energy surfaces (PESs) for $H_2/Pt(111)$,[35] $H_2/Cu(110)$,[36] $H_2/NiAl(110)$,[37] $H_2/Pd/Ru(0001)$,[38] and $H_2/Cu/Ru(0001)$ (Ref. 38) have been taken from previous works in which they were successfully used to describe diffraction and dissociative adsorption of $H_2(v=0)$. In all cases, the PESs were obtained by interpolation of DFT data set using the corrugation reducing procedure (CRP) method.[39] To carry out the dynamical study we have performed both quasiclassical (QC),[40] in which the zero-point energy (ZPE) of the molecule is included, and quantum (Q) (Ref. 30) methods. In the case of QC simulations, each trajectory is computed by integrating the Hamilton equations of motion, and the QC dissociation probabilities are obtained as an average over the molecular initial conditions, which are sampled using a standard Monte Carlo method. The quantum dynamics calculations have been carried out by using a time-dependent wave packet (TDWP) method. The method uses a discrete variable/finite representation for all DOFs, the initial wave packet is propagated in time using the split-operator method and the reflected wave packet is analyzed using a scattering amplitude formalism.

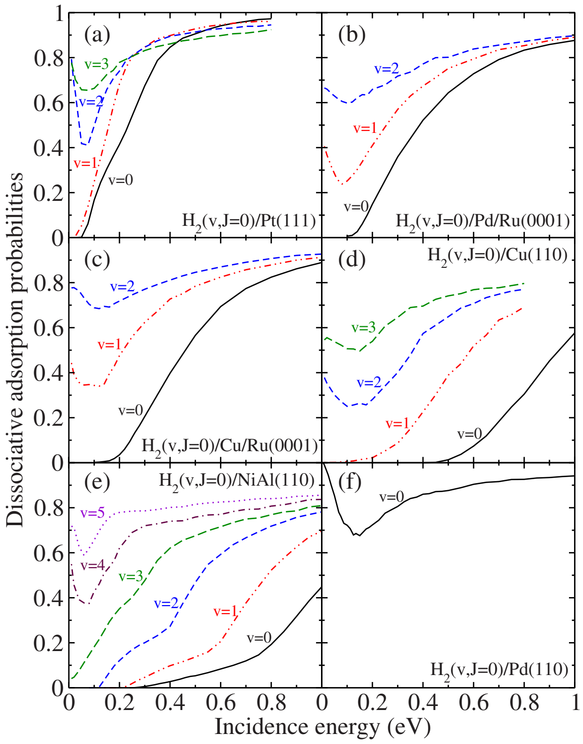

FIG. 1. (Color online) Quasiclassical dissociative adsorption probabilities as a function of the incidence energy for $H_2(v,J=0)$ on: (a) Pt(111), (b) Pd/Ru(0001), (c) Cu/Ru(0001), (d) Cu(110), (e) NiAl(110), and (f) Pd(110).

Quasiclassical dissociative adsorption probabilities for $H_2(v,J=0)$ impinging on the surfaces mentioned above are shown in Figs. 1(a)–1(e). From these figures one can see, on the one hand, that $H_2(v=0,\ J=0)$ dissociative adsorption probabilities increase monotonically with incidence energy (for energies above the MRB), as expected for activated systems. On the other hand, there is always a minimum v value beyond which the dissociative adsorption probability becomes nonmonotonic, i.e., it decreases with incidence energy until it reaches a minimum and then increases again. The minimum vibrational energy required for such a nonmonotonic behavior is not the same in all cases, but it is always higher than the MRB of the system (i.e., the nonmonotonic behavior appears when the systems are *de facto* nonactivated). It is also worth noticing that this behavior does not depend on the specific location of the MRB since it is observed in early-barrier, $H_2/Pt(111)$ [Fig. 1(a)], and late-barrier systems (all the others).

To discard possible artifacts due to the use of quasiclassical dynamics, we have also performed quantum dynamics calculations for dissociative adsorption of $H_2(v>0,\ J=0)$ on Pd/Ru(0001) and Cu/Ru(0001) surfaces. Quantum and quasiclassical probabilities are compared in Fig. 2. As can be seen, the agreement between them is excellent over the entire energy range. In particular, the Q results reproduce the nonmonotonic behavior obtained quasiclassically. The only difference is the presence in the quantum dynamics reaction probabilities of typical oscillations caused by resonances (see Ref. 41 and reference therein).

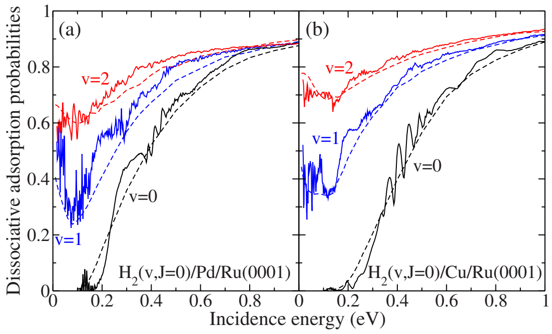

FIG. 2. (Color online) Dissociative adsorption probabilities as a function of incidence energy for $H_2(v,J=0)$ on (a) Pd/Ru(0001) and (b) Cu/Ru(0001). Full line: quantum calculations. Dashed line: quasiclassical dynamics.

A similar nonmonotonic behavior has already been found for nonactivated dissociative adsorption of H_2 in its vibrational ground state on, e.g., Ni(110),[42] Pd(100),[43] Pd(111),[39] or Pd(110) (Ref. 44) [see Fig. 1(f)] by performing both classical (ZPE not included in the calculation) and quantum simulations. In those cases, the nonmonotonic behavior was shown to arise from the so-called dynamic trapping:[45] as a result of the PES anisotropy and corrugation, the molecule looses translational normal energy in favor of other molecular DOFs thus preventing the molecule from going back into the vacuum, producing its temporal trapping near the surface, and thus favoring dissociation. This mechanism is more efficient at low incidence energies, in contrast with direct dissociation that dominates at high energies. The combination of these two mechanisms leads to a nonmonotonic behavior of the dissociative adsorption probabilities as a function of incidence energy. To detect the possible presence of dynamic trapping in our systems, we have evaluated the fraction of trajectories leading to dissociation after two or less rebounds and after more than two rebounds. These probabilities can be related to the direct and dynamical trapping mechanisms, respectively. Figure 3(a) shows these results for $H_2(v=2,\ J=0)$ on Pd/Ru(0001). It can be seen that the trapping contribution is very low and, that, in fact, the nonmonotonic behavior is already present in the direct dissociation probability curve. The same conclusion is obtained for the other systems investigated here.

Once discarded dynamic trapping as the source of the observed nonmonotonic behavior, we turn our attention toward the role played by the molecular rotational DOFs. The fundamental role played by these DOFs in the dissociation of $H_2(v=0)$ has been investigated in previous work (see Refs. 46 and 47 and references therein): in order to dissociate, the molecule must change its orientation in the course of the collision until it lies nearly parallel to the surface in its vicinity. For the activated systems investigated here, this is only possible if the molecule has enough vibrational energy to overcome the MRB. In this case, the actual dissociation probability depends on (i) the number of available reaction paths and (ii) the ability of the molecule to reach the appropriate orientation. Figure 3(b) shows, for the case of $H_2(v=1,\ J=0)/Pd/Ru(0001)$, the initial angular distribution of H_2 molecules whose trajectories end up in dissociation. At very low incidence energy, 10 meV, this distribution is broad

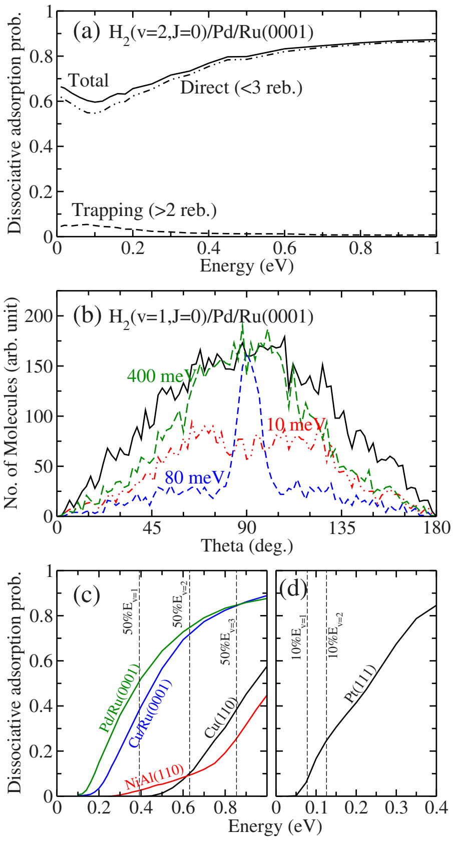

FIG. 3. (Color online) (a) Dissociative adsorption probability as a function of incidence energy for $H_2(v=2, J=0)$ on Pd/Ru(0001) (full line). Dot-dashed line: direct contribution (≤ 2 rebounds). Dashed line: trapping contribution (>2 rebounds). (b) Molecular angular distribution for $H_2(v=1, J=0)$. Back solid line: initial distribution; dot-dashed red line: initial distribution of the dissociated molecules for $E_i=10$ meV; dashed blue line: initial distribution of the dissociated molecules for $E_i=80$ meV; long-dashed line: initial distribution of the dissociated molecules for $E_i=400$ meV. (c,d) Dissociative adsorption probability as a function of incidence energy for $H_2(v=0, J=0)$ on all surfaces investigated in this work. Vertical dashed lines represent vibrational energies effectively transferred to the translational motion (see text).

and very similar to the initial one. So, although the number of accessible reaction paths is very limited, reorientation of the molecule along the trajectory is very efficient and, consequently, the dissociation adsorption probability is high. As the incidence energy increases up to 80 meV [where the probability reaches its minimum value—see Figs. 1(b) and 2(a)], the number of available reaction paths increases monotonically (as predicted, e.g., by the so-called hole model), but, as shown in Fig. 3(b), molecular reorientation becomes substantially less efficient and, consequently, the dissociative adsorption probability decreases. At high enough incidence energy, the number of accessible reaction paths is so large that almost any initial molecular orientation leads to dissociation [see Fig. 3(b) for 400 meV] and the dissociative adsorption probability must increase. The same arguments apply to the other systems investigated here. Reorientation is less effective when the molecule has significant rotational energy ($J>0$). Therefore, experiments seeking for this phenomenon should preferentially consider molecules with $J=0$. This can be done by using pulsed narrow bandwidth laser Raman excitation as described in the introduction.[34]

We discuss now the effects that determine the minimum vibrational energy needed to induce a nonmonotonic behavior of the dissociative adsorption probability. The necessary condition is of course that the vibrational energy E_v is larger than the MRB. But this is not sufficient since what really matters is the fraction of the initial vibrational energy transferred to the reaction coordinate. For all the systems investigated here (as well as for nonactivated adsorption[48]), it is the dynamics in the entrance channel (well before the position of the MRB) what determines if a molecule will dissociate or not. In this region, vibrational energy is almost exclusively transferred to the normal translational motion. The efficacy of this energy transfer is of the order of 50% for all systems investigated here (in agreement with previous work, see Ref. 33 and references therein), except for the early-barrier system H_2/Pt(111) for which it is around 10%. In Fig. 3(c) we have plotted the energy values $0.5\times E_v$ and $0.1\times E_v$ corresponding to these energy transfers together with the $v=0$ dissociative adsorption probability curves given in Fig. 1. To obtain a nonzero dissociative adsorption probability of $H_2(v>0)$ at zero (or nearly zero) incidence energy, the corresponding $H_2(v=0)$ probability must take a significant value (e.g., >0.15) at the incidence energy $0.5\times E_v$ [or $0.1\times E_v$ for H_2/Pt(111)]. As can be seen, this occurs for $v=1$ in H_2/Pd/Ru(0001) and H_2/Cu/Ru(0001), for $v=2$ in H_2/Pt(111), and for $v=3$ in H_2/Cu(110) and H_2/NiAl(110). These are close to the lowest v values for which the dissociative adsorption probability curves exhibit a pronounced nonmonotonic behavior in Fig. 1 (the precise v values depend on the actual vibrational efficacy).

In conclusion, we have found a general nonmonotonic behavior of the dissociative adsorption probability as a function of incidence energy for vibrational excited $H_2(v,J=0)$ molecules on metal surfaces. We have shown that such a behavior is a consequence of a direct dissociation mechanism. By analyzing the calculated trajectories of the adsorbed molecules, we have found that the initial decrease in the adsorption probability curve is the result of a less efficient reorientation of the molecule as the incidence energy increases. This prediction could be experimentally tested by using pulsed narrow bandwidth laser Raman excitation to prepare $H_2(v,J=0)$ molecules in vibrationally excited states.[34]

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