Enhancing dissociative chemisorption of H₂O on Cu(111) via vibrational excitation

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The dissociative chemisorption of water is an important step in many heterogeneous catalytic processes. Here, the mode selectivity of this process was examined quantum mechanically on a realistic potential energy surface determined by fitting planewave density functional calculations spanning a large configuration space. The quantum dynamics of the surface reaction were characterized by a six-dimensional model including all important internal coordinates of H₂O and its distance to the surface. It was found that excitations in all three vibrational modes are capable of enhancing reactivity more effectively than increasing translational energy, consistent with the "late" transition state in the reaction path.

heterogeneous catalysis | mode specific chemistry | reaction dynamics

The dissociative chemisorption of H₂O on transition-metal surfaces, which produces chemisorbed H and OH species, is an important and often obligatory step in many heterogeneous catalytic processes, such as the water-gas shift (WGS) reaction and steam reforming (1). Given our dwindling fossil fuel resources and health-threatening pollution, these reactions have become increasingly important in generating environmentally friendly hydrogen fuels for various high-efficiency applications, such as fuel cells (2). In low-temperature WGS on copper catalysts, for example, the dissociative chemisorption of H₂O has been identified as the rate-limiting step (3). A better understanding of the reaction dynamics and the ultimate control and/or enhancement of the process could potentially benefit many industrial processes that involve H₂O. Despite our increasing understanding of the adsorption and dissociation of water on various metal surfaces, however, few experimental studies have been reported (to the best of our knowledge) on the dynamics of water–metal interaction, and none on dissociative chemisorption (4). In this work, we explore a potentially useful scheme based on mode selectivity to enhance dissociative chemisorption on a copper surface.

Controlling reactivity of a chemical reaction by selecting reactant internal quantum states is a holy grail in chemical dynamics (5). This mode selectivity and related bond selectivity have been experimentally demonstrated for only a few reactive systems in the gas phase (6–13) and on surfaces (14–21). For example, it was shown that both the kinetics and dynamics of the H + H₂O reaction depend sensitively on the vibrational state of the H₂O reactant (6). Similarly, different vibrational excitations of CH₄ have been demonstrated to have varying efficacies in promoting its dissociative chemisorption on transition-metal surfaces, some more effective than translational energy (22). These observations underscore the importance of quantum dynamical effects and inadequacy of statistically based transition state theory for describing mode- and bond-specific chemistry.

A key question in mode- and bond-selective chemistry is whether energy in vibrational coordinates is more effective in promoting reaction than translational energy. The answer lies in details of the underlying potential energy surface (PES) that governs the interaction between reacting partners. Polanyi has pointed out that a "late" barrier on a PES is more easily surmounted by vibrational excitation, while an "earlier" barrier is

more readily overcome by translational energy (23). This is because the "promoting coordinate" coincides with the reaction coordinate near the transition state in each case. However, Polanyi's rule is not always valid; some recent work has revealed significant deviations from this intuitive picture (13), underscoring the complexity of reaction dynamics in polyatomic systems and the need to perform high-dimensional dynamic calculations on accurate PES (24).

The dissociative chemisorption of H₂O shares many similarities with that of CH₄ (25–27), based on existing planewave density functional theory (DFT) studies (28–30). Both molecules have strong local-mode characters and slow intramolecular vibrational energy redistribution. Both reactions are quantum mechanical in nature due to large zero-point energies and high barriers, where tunneling is important. Perhaps most importantly, both have a late barrier, where the bond cleavage occurs after the molecule adsorbs on the surface. It is thus conceivable that vibrational excitation of H₂O might have a large impact on reactivity, as already demonstrated in the case of CH₄.

A full-dimensional quantum dynamical description of polyatomic dissociative chemisorption is still extremely challenging (31). In the case of CH₄, for example, 15 degrees of freedom are needed on a rigid surface, rendering it difficult to develop an accurate, global high-dimensional PES (32–34) and to carry out quantum dynamical calculations. Thus far, most dynamical studies involved low-dimensional models (35–41) and fell short of providing a complete understanding of the complex dynamics. Water dissociative chemisorption, on the other hand, requires nine dimensions, and is thus significantly less demanding. Here, we report the quantum dynamics of this process on Cu(111), using a high-dimensional model that includes most important degrees of freedom. Furthermore, our model has a key feature: A realistic PES based on extensive DFT calculations was used.

As shown in Fig. 1, the six-dimensional model consists of all three vibrational coordinates of H₂O expressed in Jacobi coordinates (r_1, r_2, and θ_1): the distance between the center of mass (COM) of H₂O and the surface (z), and two rotational angles (θ_2 and φ) for the H₂O moiety. The translational coordinates of the H₂O moiety in the xy plane are fixed at the transition state geometry, and the surface corrugation is ignored. While reduced-dimensional in nature, we believe that this model should capture most important features of the reactive process. However, we need to keep in mind that the full-dimensional model will probably lead to a higher effective barrier because of the distribution of trajectories reaching the surface with nonoptimal transition state geometries.

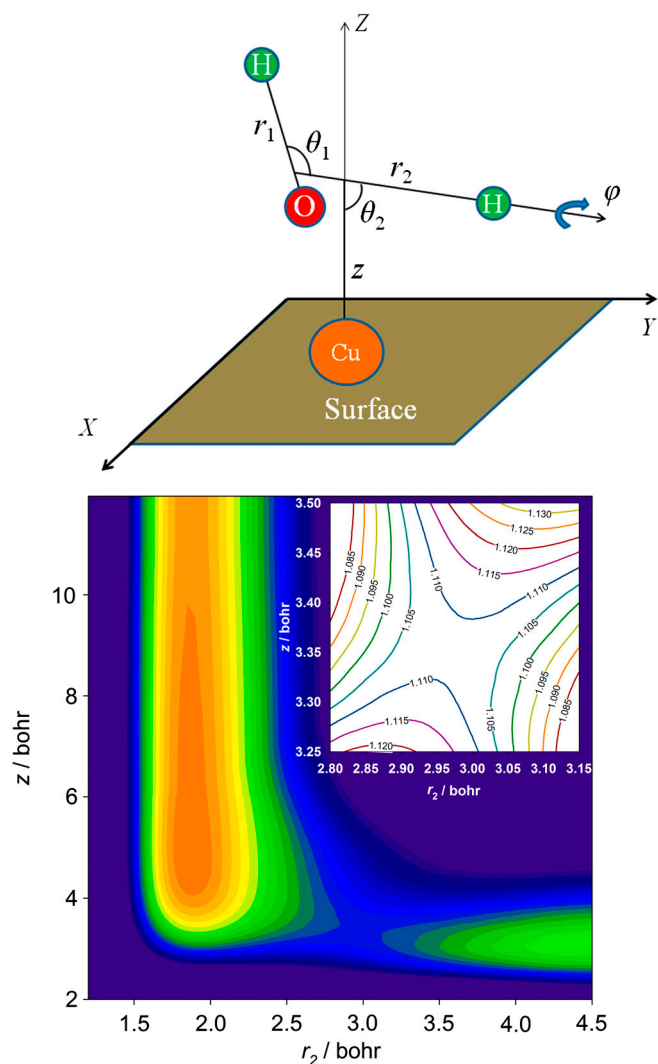## Six dimensional model for H₂O on Cu(111) surface

Fig. 1. Coordinates used in the reduced-dimensional model for the H₂O-dissociative chemisorption on Cu(111) (*Upper*) and contour plot of the PES as a function of *z* and r_2 with other coordinates optimized (*Lower*). (*Inset*) A close-up map of the transition state region where the contours are relative to the H₂O + Cu(111) asymptote with an interval of 0.005 eV.

Fig. 2. Dissociation probabilities as a function of the total energy for several initial vibrational states of H₂O on Cu(111) in linear (*Upper*) and log (*Lower*) scales. The total energy is relative to the energy of the H₂O + Cu(111) asymptote.

Results

Single-point planewave DFT calculations have been carried out in the coordinate space defined by the aforementioned model. A total of 25,741 points were fit to an analytical PES form using the permutation-invariant polynomial approach of Bowman et al. (42). Fig. 1 displays the PES as a function of *z* and r_2 with other coordinates optimized. It is clear that the PES, dominated by a shallow physisorption well and a late transition state for the cleavage of the O—H bond, is smooth in the relevant configuration space. As discussed in *SI Materials and Methods*, the fit accurately reproduces all important stationary points as well as the minimum energy path. The quantum dynamics of the dissociative chemisorption was investigated on the PES using a Chebyshev wave packet–based flux method (43). The five lowest rotationless vibrational levels were studied: (0,0,0), (0,1,0), (0,2,0), (1,0,0), and (0,0,1), where the three quantum numbers are symmetric stretching, bending, and antisymmetric stretching modes, respectively.

Fig. 2 shows the calculated reaction probabilities in both linear and log scales. To facilitate a fair comparison, these results are plotted in total energy referenced to the H₂O + Cu(111) asymptote. It is clea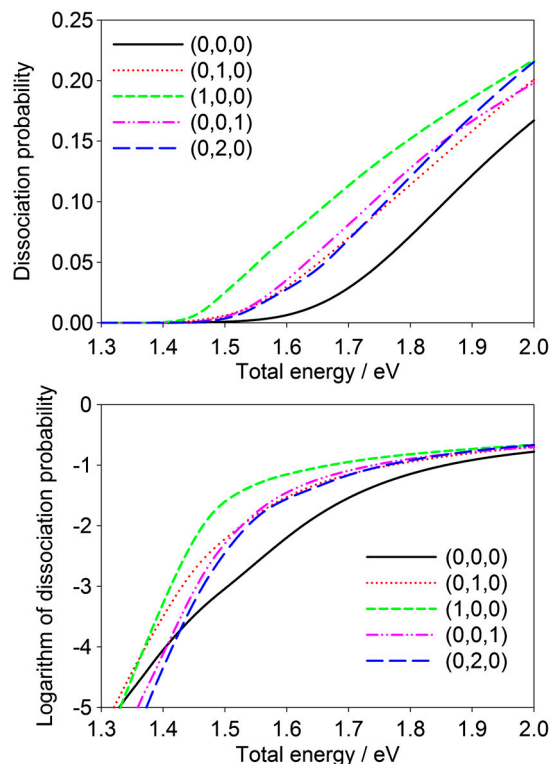r that vibrational excitations in H₂O enhance the reaction probability for the dissociative chemisorption. The excitation in the symmetric stretching mode has the largest effect, while excitations in the bending and antisymmetric stretching modes also enhance reactivity, but generally with smaller magnitudes. The enhancement due to stretch excitations is understandable based on Polanyi's rule: The energy flows directly into the reaction coordinate at the late barrier. Similarly, the involvement of the bending mode in the reaction coordinate is evidenced by the fact that the transition state H—O—H angle (117.4°) is significantly larger than that in isolated H₂O (104.4°).

From the log plot in Fig. 2, it is clear that tunneling is the dominant mechanism for the reaction at low energies. Indeed, there is already substantial reaction probability below the activation barrier (approximately 1.49 eV) for the vibrationless reactant. The enhancement by vibrational excitation is also apparent from this plot. For example, at the total energy of 1.5 eV, the reaction probabilities (P_{n_1,n_2,n_3}) of the (0,0,0), (0,1,0), (0,2,0), (1,0,0), and (0,0,1) states of H₂O are 0.000915, 0.00608, 0.00360, 0.0255, and 0.00483, respectively. The reaction is enhanced relative to the (0,0,0) state by 6.64, 3.93, 27.9, and 5.28 times for the four excited vibrational states, respectively.

The enhancement can be quantified by the so-called vibrational efficacy, which is often expressed as $\eta = [E_i(0, P) - E_i(v, P)]/(E_v - E_0)$, where $E_i(0, P)$ and $E_i(v, P)$ are the translational energy yielding a specific reaction probability P for the ground (0) and vibrationally excited (*v*) states, with E_0 and E_v as the corresponding energies (22, 41). A value larger than unity thus indicates that the vibrational mode is more effective in promoting the reaction than translational energy. As shown in Table 1, excitations in all vibrational modes are capable of promoting the reaction more efficiently than translational energy. The vibrational efficacy is typically better at high energies and large reaction probabilities.

Table 1. Vibrational efficacies for four lowest-lying excited vibrational states in dissociative chemisorption of H_2O on Cu(111)

Vibrational state	Vibrational energy/eV	Vibrational efficacy, η				
		$P = 10^{-5}$	$P = 10^{-4}$	$P = 10^{-3}$	$P = 10^{-2}$	$P = 10^{-1}$
(0,1,0)	0.191	1.05	1.17	1.39	1.52	1.46
(0,2,0)	0.377	0.884	0.971	1.11	1.24	1.26
(1,0,0)	0.427	0.999	1.08	1.22	1.38	1.45
(0,0,1)	0.438	0.932	0.995	1.11	1.22	1.25

In Fig. 3, the same reaction probabilities are plotted in translational energy, which is the common way to plot the sticking probability (S_0) in experimental studies. It is clear that vibrationally excited H_2O dominates the reaction at low translational energies. However, the population of a vibrationally excited reactant is typically small at a given temperature, weighted by Boltzmann's factor. Nonetheless, the tunneling nature of the reaction still leads to substantial reactivity from these states. Assuming a temperature of 700 K for the incident water, which can, for example, be realized by controlling the nozzle temperature of a molecular beam (22), the populations of the three H_2O overtones are 0.0422 (bending), 0.000840 (symmetric stretching), and 0.000702 (antisymmetric stretching). Boltzmann-weighted reaction probabilities in Fig. 3 still show the dominance of excited H_2O molecules in the reaction at low translational energies.

Discussion

The enhancement of reactivity observed here appears to be qualitatively similar to that found in the gas phase $H + H_2O$ reaction, which also has a late barrier. Indeed, it has been shown by full-dimensional wave packet studies that excitations in the three vibrational modes of H_2O enhance reactivity, with the bend

Fig. 3. Dissociation probabilities as a function of the translational energy for several initial vibrational states of H_2O on Cu(111) without (*Upper*) and with (*Lower*) Boltzmann weighting.

showing the smallest effect (43, 44). Both gas phase and surface reactions especially indicate that the excitation in the symmetric stretching mode of H_2O has a greater enhancement. However, the surface reaction has no H-exchange channel, which dominates the gas phase reaction (44).

The effect of vibrational excitation on dissociative chemisorption has been examined in several other systems. In the "trivial" case of diatom (H_2), vibrational excitation significantly enhances reactivity because the internuclear distance is intimately associated with the reaction coordinate (31). The dissociative chemisorption of CH_4 is more complicated because of its many vibrational modes (22). On Ni, for example, the excitation of the symmetric stretching (v_1) mode of CH_4 led to significant enhancement relative to the same amount of translational energy (18), while the antisymmetric stretching (v_3) mode offered similar efficacy as translational motion (14, 15, 17). Similar observations have been reported for the gas phase reaction between CH_3D and Cl (11). These results are consistent with the water dissociative chemisorption case discussed above. Reaction path analyses of the CH_4/metal systems suggest that as CH_4 approaches the surface, its symmetry is perturbed and localization emerges. Indeed, the v_1 mode of CH_4 is shown to be adiabatically correlated with the reaction coordinate near the transition state (33, 34), which explains the vibrational mode selectivity. We expect a similar scenario for the H_2O/metal case.

The experimental observation of mode selectivity in water-dissociative chemisorption is expected to be possible, but unique molecular properties of the dipolar H_2O molecule could lead to complications that are absent in methane-dissociative chemisorption. For example, it is known that H_2O has a larger adsorption energy and forms adlayers networked by hydrogen bonds (4). How the existence of an adsorbed water layer would affect the reaction is still unknown.

To summarize, we have developed a high-dimensional model for the dissociative chemisorption of water on a copper surface that includes all important internal modes, as well as the distance between water and the surface. A global PES that accurately captures all important features of the H_2O–Cu interaction, including a late transition state, was constructed for the reactive process. The quantum dynamics on the PES showed that H_2O vibration plays a central role in its dissociative chemisorption on Cu(111). Excitation in the symmetric stretching mode greatly enhances the reaction probability, while such enhancement from exciting bending and antisymmetric modes is less pronounced. The enhancement can be understood in terms of Polanyi's rule, which attributes the effect of mode selectivity to the involvement of stretching vibration in the reaction coordinate. These theoretical predictions should motivate future quantum state–resolved experimental explorations of this important process, which is involved in many industrial heterogeneous catalytic processes.

Materials and Methods

The global PES used in our dynamical calculations was obtained by fitting 25,741 planewave DFT points using the permutation-invariant polynomial approach of Bowman et al. (42): $V = \sum_{l_1 l_2 l_3 l_4 l_5 l_6} c_{l_1 l_2 l_3 l_4 l_5 l_6} S[y_{12}^{l_1} y_{13}^{l_2} y_{14}^{l_3} y_{23}^{l_4} y_{24}^{l_5} y_{34}^{l_6}]$, where S is the symmetrization operator. The H, H, O, and "surface" atoms are labeled as 1, 2, 3, and 4, respectively, and $y_{ij} = \exp(-r_{ij}/a)$, where r_{ij} is the distance between atoms i and j, $a = 1.5$ bohr. Here, the surface atom is
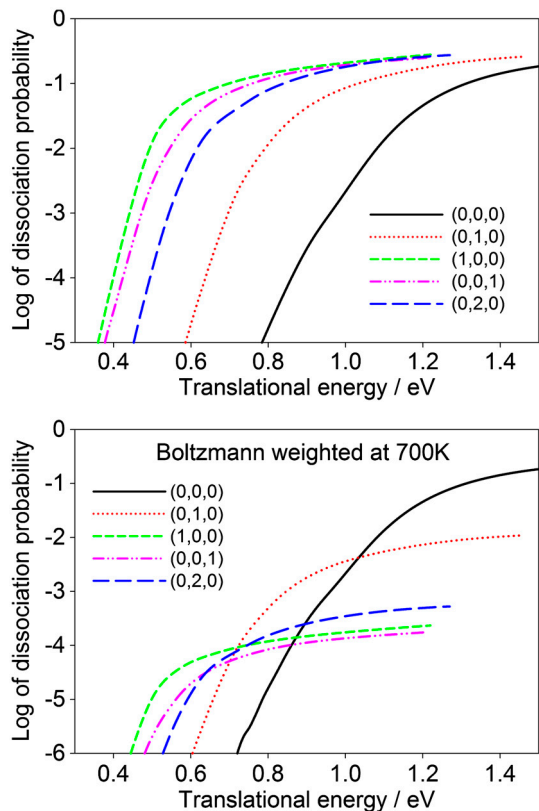
placed at the projection of the H_2O COM in the xy plane. We included all terms up to total degree ($l = l_1 + l_2 + l_3 + l_4 + l_5 + l_6$) of six, resulting in 918 terms. The expansion coefficients were determined by a weighted least-squares method.

The standard DFT single-point calculations were carried out using the Vienna ab initio simulation package (VASP) (45, 46) with a model including a H_2O molecule on a three-layer Cu(111) slab with a 2 x 2–unit cell. The details of the planewave DFT calculations can be found in *SI Materials and Methods*. Points with energies above 6 eV from the global minimum energies and points for which the surface H atom is on nonrelevant Cu atoms were excluded. In order to give a better description of the stationary points, weights of points near the H_2O molecule asymptote (approximately 1,000 points), the physisorbed H_2O(approximately 2,500 points), and the transition state (approximately 1800 points) were increased by a factor of 10. The overall rmsd for the fit is 110 meV, but significantly smaller (84 meV) for points below 2.0 eV.

To obtain quantum mechanical reaction probabilities, we have modified a wave packet method described in our recent work (43). Briefly, initial wave packets corresponding to various H_2O ro-vibrational states were launched towards the Cu surface, propagated with the Chebyshev propagator. The six-dimensional wave packet and Hamiltonian were discretized in the Jacobi coordinate system with a mixed grid/basis representation. Reaction probabilities were obtained using a flux method at a dividing surface placed behind the transition state. More details of the quantum dynamic method can be found in *SI Materials and Methods*.

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