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Quantum dynamics of water dissociative chemisorption on rigid Ni(111): An approximate nine-dimensional treatment

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The quantum dynamics of water dissociative chemisorption on the rigid Ni(111) surface is investigated using a recently developed nine-dimensional potential energy surface. The quantum dynamical model includes explicitly seven degrees of freedom of D2O at fixed surface sites, and the final results were obtained with a site-averaging model. The mode specificity in the site-specific results is reported and analyzed. Finally, the approximate sticking probabilities for various vibrationally excited states of D2O are obtained considering surface lattice effects and formally all nine degrees of freedom. The comparison with experiment reveals the inaccuracy of the density functional theory and suggests the need to improve the potential energy surface. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4947492]

I. INTRODUCTION

Dissociative chemisorption (DC) of a gaseous molecule on a metal surface, which produces two adsorbed species at the expense of an intramolecular bond, is the necessary first and often rate-limiting step in many heterogeneous processes.1 Hence, it is of great importance to understand the underlying dynamics of the DC reaction. Using advanced laser and high vacuum techniques, recent quantum state resolved molecular beam experiments have explored the fascinating mode-specific and/or bond-selective features in the DC of methane, providing convincing evidence that not all forms of energy are equal in promoting this reaction.2–4 The vibrational efficacy, which is the ability of a particular excitation of a vibrational mode to promote the reaction relative to the same amount of translational energy, was found to be mostly non-uniform. Inconsistent with statistical models, these experiment results have thus stimulated many dynamical models based on wave packet and classical trajectory calculations on multidimensional potential energy surfaces (PESs).5–8 Interestingly, it has been shown that the mode specificity and associated bond selectivity can be rationalized by a simple transition-state based model.7–9

More recently, mode specificity was found to be quite general for DC of polyatomic molecules, such as water and carbon dioxide.10,11 In particular, the mode specificity and bond selectivity in water DC, which is of fundamental importance in steam reforming and the water gas shift reaction, were first predicted on Cu(111) by some of us using a quantum dynamical (QD) model based on a six-dimensional (6D) global PES fitted to a large number of density functional theory (DFT) points.12–14 In this 6D model, the two lateral (X and Y) coordinates and azimuthal angle were ignored, assuming the surface to be flat. Subsequently, Beck and co-workers reported the first quantum-state resolved experiment on the DC dynamics of D2O on Ni(111),10 demonstrating a strong enhancement of reactivity by exciting the anti-symmetric stretching (v3) mode of D2O with one and two quanta. These experimental findings were reproduced semi-quantitatively using a similar 6D QD model on an empirically scaled global DFT PES.10 Perhaps, more interestingly, our QD results demonstrated that excitations of all three vibrational modes of water enhance the dissociation more effective than the same amount of translation energy, thus very different from earlier observations in methane dissociation. Later, we reported the first nine-dimensional (9D), globally accurate PES for water DC on the rigid Ni(111) surface based on a large number of DFT points and studied the effects of impact sites and incident angles of the impinging water on the dissociation process using a quasi-classical trajectory (QCT) method.15 The 9D QCT calculations gave slightly smaller vibrational efficacies than previous 6D QD calculations but revealed that the PES topography at different surface sites has a more significant impact on the reactivity than the barrier height alone. In addition, translational energy parallel to the surface was found to have a non-negligible role in promoting the reaction. More recently, Farjamnia and Jackson16 studied the mode-specific and bond-selective water DC dynamics on Ni(111) by means of their reaction path Hamiltonian (RPH) method.17 Their results qualitatively reproduced many of our findings, but the vibrational efficacies were all found to be much smaller and closer to unity. It is worth noting that an accurate 9D PES for H2O/Cu(111) has recently been developed by Liu et al.,18 who have also performed the seven-dimensional (7D) QD calculations at fixed surface sites and proposed

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an azimuthal-averaging model, which approximates the 7D reaction probabilities by averaging over the azimuthal-fixed 6D counterparts. Finally, the influence of surface electron-hole pairs on the DC dynamics was recently examined using a friction model on the 9D PES and found to be relatively weak.

Despite these successes, a complete description of the mode-specificity in water DC on metal surfaces has not yet been achieved. Specifically, it is unclear whether the high efficacies for the three vibrational modes of water found in 6D models persist when all molecular degrees of freedom (DOFs) are included quantum mechanically. Moreover, in previous 6D and RPH calculations, the PES was scaled in order to achieve better agreement with the experimental data. However, the scaling depends on the comparison between theory and experiment and can be settled only with fully coupled 9D QD calculations with corrections of lattice effects, which remain formidable at current stage.

One promising approximate approach proposed in the DC of diatomic molecules is the site-averaging scheme of Dai and Light, improved recently by Zhang, Fu, and co-workers, in which the 6D reaction probability is approximated by a weighted sum of site-specific results obtained with the two DOFs of lateral motion frozen. This site-averaging model has been tested in several DC processes of diatomic molecules with notable barriers and found to be reasonably accurate. We have further extended this scheme to the D$_2$O/Ni(111) case, averaging over 6D reaction probabilities at specific sites but fixing the azimuthal angle at the values of site-specific transition states. Later, 7D QD studies on H$_2$O/Cu(111) have shown that the 6D model with this azimuthal sudden approximation significantly overestimates the reactivity, due apparently to strong azimuthal anisotropy at some sites.

In this work, we present explicitly 7D QD results for the DC of water at fixed surface sites. In addition, 9D dissociation probabilities are obtained by averaging the site-specific 7D results. After correcting the lattice effects using Jackson’s sudden models, the approximate 9D QD model specific initial sticking probabilities are obtained for the first time. Comparison to the experimental data provides valuable information on the accuracy of the PES. This article is organized as follows. Section II describes the 7D quantum model, site-averaging model, and computational details. Site-specific and site-averaged results are then presented and discussed in Sec. III. The conclusions are given in Sec. IV.

II. THEORY

Since the DC of water involves the transfer of hydrogen, the dynamics is best treated with quantum mechanics, particularly at low collision energies where tunneling becomes important. A full-dimensional model for the DC of water on a rigid surface includes nine DOFs, as defined in Fig. 1(a). In this work, all calculations are for D$_2$O because it was studied in the recent experiment. The reduced-dimensional QD model used here fixes the two lateral coordinates (X, Y) of the center of mass (COM) of D$_2$O at a specific site within the surface unit cell. The resulting fixed-site Hamiltonian can be expressed in the seven remaining coordinates as ($\hbar = 1$ hereafter)

$$\hat{H} = \frac{1}{2\mu_1} \frac{\partial^2}{\partial r_{12}^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial r_{22}^2} - \frac{1}{2M} \frac{\partial^2}{\partial Z^2} + \frac{j^2}{2\mu_1 r_1^2} + \frac{j^2}{2\mu_2 r_2^2} + V(r_1, r_2, Z, \theta_1, \theta_2, \varphi, \phi; X, Y).$$

(1)

Here, $r_1$ is the bond length of the non-dissociative OD bond, $r_2$ the distance between COM of OD and D, the corresponding reduced masses are $\mu_1 = m_D m_O/(m_D + m_O)$, $\mu_2 = m_O m_D/(m_{OD} + m_D)$, $M$ is the total mass of D$_2$O, and $(X, Y, Z)$ are Cartesian coordinates of D$_2$O COM with the origin placed at the top site. $j$ and $J$ are the OD and D$_2$O angular momentum operators, respectively. $V$ is the 7D PES with the $(X, Y)$ components frozen at specific values.

The 7D wave function is expanded by the radial and rotational basis functions. The overall rotational basis is described by $Y_{jM}^{JM}(\theta_1, \theta_2, \varphi, \phi)$, which is defined as

$$Y_{jM}^{JM}(\theta_1, \theta_2, \varphi, \phi) = \sum_K D_{MK}^{JM}(\theta, \phi) e^{-iK\varphi} \times \sqrt{\frac{2l+1}{4\pi}} \langle jK|0JK \rangle y_{JK}(\theta_1, 0),$$

(2)

where $D_{MK}^{JM}(\phi, \theta_2, \varphi)$ is the Wigner rotation matrix, which can be expressed as $e^{-iM\phi} D_{MK}^{JM}(\theta_2) e^{-iK\varphi}$, $y_{JK}(\theta_1, 0)$ is the spherical harmonics, $j$ and $J$ are the angular momentum quantum numbers associated with OD and D$_2$O, respectively. $K$ and $M$ are the projections of $J$ on $r_2$ and the surface normal, respectively.

FIG. 1. (a) Nine coordinates defined in the our dynamical model for H$_2$O/Ni(111). (b) Schematic diagram indicating the site positions and numberings in the symmetry unique region of the unit cell in the site-averaging model.
The vibrational basis along \( r_i \) (\( i = 1 \) or \( 2 \)) consists of the reference vibrational eigenfunctions \( \chi_{n_i}(r_i) \), which satisfy the equation

\[
\left[ -\frac{1}{2\mu_i} \frac{\partial^2}{\partial r_i^2} + V_{r_i}(Z_{\text{ref}},r_i,\ldots) \right] \chi_{n_i}(r_i) = \epsilon_{n_i} \chi_{n_i}(r_i),
\]

where \( V_{r_i}(Z_{\text{ref}},r_i) \) is the one-dimensional reference potential depending on \( r_i \) only for which the molecule is far above the surface and \( \theta_i \) and the other vibrational coordinate are fixed in the equilibrium values of free water. Sine basis functions are used for the translational coordinate \( Z \). Taking advantage of an \( L \)-grid saving scheme, the whole wave function is split into two regions, namely, the asymptotic and interaction regions, for which the number of basis functions and the grid ranges are different, as given in Ref. 24.

The initial wave packet was placed in the reactant asymptote \( (Z = Z_r) \) as a product of a Gaussian wave packet and internal state wave function of the reactant

\[
|\Psi_i(t = 0)\rangle = Ne^{-(Z-Z_r)^2/2\delta^2} |\Psi_{v_1,v_2,v_3}J_{K_a,K_c}\rangle,
\]

where the internal state of the \( \text{D}_2\text{O} \) is specified by the rotational and vibrational quantum numbers \( (J_{K_a,K_c} \text{ and } (v_1,v_2,v_3)) \) and the initial momentum in the \( Z \) direction is given by \( k_i = \sqrt{2\mu_i E_i} \), where \( E_i \) is the initial mean incident energy. Since we only consider the rotationless molecule in this work, the indices for rotational quantum numbers are dropped hereafter. Only normal incidence is simulated here.

The time-dependent Schrödinger equation was solved using the split-operator method and the initial state-specific dissociation probability \( (P_0) \) was computed with the flux approach in the product channel at \( r_2 = r_{2f} \)

\[
P_0^{v_1,v_2,v_3,J_0,M_0}(E_n) = \frac{1}{\mu_2} \text{Im} \langle \Psi_{v_1,v_2,v_3}^{+} | \delta(r_2 - r_{2f}) \frac{\partial}{\partial r_2} | \Psi_{v_1,v_2,v_3}^{+}\rangle_{r_2=r_{2f}},
\]

where \( E_n \) is the normal incident energy and \( |\Psi_{v_1,v_2,v_3}^{+}\rangle \) is the time-independent scattering wavefunction, which is related to time-dependent wave packet by a half-range Fourier transformation.

To achieve numerical convergence, a total of 300 sine basis functions ranging from 2.0 to 17.0 bohrs were used for \( Z \) with 130 basis functions in the interaction region; and 6 vibrational basis functions for both \( r_1 \) and \( r_2 \) were used in the asymptotic region, while 30 for \( r_2 \) in interaction region ranging from 1.0 to 5.5 bohrs to allow the dissociation. The size of the rotational basis set is given by, \( J_{\text{max}} = 37, I_{\text{max}} = 35, K_{\text{max}} = 27, \) and \( M_{\text{max}} = 12 \). The flux was analyzed at \( r_{2f} = 3.6 \) bohrs and the damping function that absorbs the wave packet at the edges of the grid starts from \( Z = 15.0 \) bohrs and \( r_2 = 3.7 \) bohrs. The time step for the propagation was 0.1 a.u. and the wave packets were propagated up to 22,000 a.u. in order to converge the reaction probability down to \( 10^{-7} \) or so at very low energies. We note that the final reaction probabilities obtained in the wave packet calculations are multiplied by a factor of \( 2 \) to account for the two equivalent O–D bonds. Some 6D calculations were also performed in which \( M_{\text{max}} = 0 \) and the azimuthal angle is fixed at specific values with other parameters the same as the 7D ones. It should be noted that the 6D treatment here is more realistic than reported in our previous publication, where the PES was collapsed to have the inversion symmetry with respect to \( \phi \) within the flat surface model. The results are thus somewhat different.

Following Liu et al. who have recently demonstrated for the DC of HCl(DCl) on Au(111) and H2 on Cu(111) that the 6D exact dissociation probabilities can be well represented by averaging 4D fixed-site ones with a sufficiently larger number of sites, we approximate the 9D dissociation probabilities by averaging 7D results over many sites. The validity of the site-averaged model is based on the assumption that dynamical steering is minimum. In our PES, the C\text{C\text{C\text{C}}}_\text{v\text{v}} symmetry is enforced, which assumes that two hollow sites, i.e., the fcc and hcp sites, are indistinguishable. This approximation, which is justified because of the negligibly small energy differences between the two sites, allows us to focus on an irreducible triangular region of the unit cell, shown in Fig. 1b. In order to test the convergence of the site averaging with respect to the number of sites, we started from three sites with high symmetry, namely, the top, bridge, and hollow sites, then added new sites progressively to cover the irreducible triangle up to 15 sites, as displayed in Fig. 1b. Each site-specific probability is multiplied by a weight determined by the population of each site in a unit cell when averaging.

### III. RESULTS AND DISCUSSION

#### A. Site-specific dynamics

All dynamical calculations reported here used the 9D PES recently developed for the DC of water on the rigid Ni(111) surface. This PES accurately represents over 25,000 points computed by plane wave DFT with the PW91 functional using the high-fidelity permutation invariant polynomial-neural network (PIP-NN) method. It is worth noting that the DFT points span the entire dynamically relevant configuration space, without a bias to high symmetry sites, thus guaranteeing the faithful description for the PES at any selected site.

It has been noted in Ref. 26 that the site-specific barrier height on this PES ranges from 0.67 to 0.87 eV. Interestingly, our previous QCT calculations have indicated that the site-specific reactivity is not entirely controlled by the barrier height. Rather, the topography of the PES, particularly the looseness/tightness of the transition state and the angle characterizing the “elbow” PES, greatly influences the reactivity. Thus, it is difficult to predict site-specific reactivity solely based on the corresponding barrier height.

Here, we first examine the impact of the azimuthal anisotropy of the barrier height in site-specific DC dynamics. In Fig. 2, the dependence of the barrier height with respect to the azimuthal angle \( \phi \) is shown for several surface sites, with other coordinates fixed at corresponding saddle point values. It is interesting to note that the azimuthal angle dependence of barrier height is very different from site to site. For example, the top site is nearly isotropic due apparently to the fact that there is little hindrance for the molecule atop. This azimuthal isotropy implies that the flat-surface approximation should perform well. At other sites, however, the barrier height varies drastically with the azimuthal angle, and the difference
between maxima and minima can be more than 1.0 eV. For these sites, the flat-surface approximation is thus not expected to work well, and the azimuthal angle should be included in a higher-dimensional dynamical model.

Figure 3 displays the 7D dissociation probabilities ($P_0$) at several surface sites as a function of the normal incident energy. The 7D results are compared with the 6D model in which the azimuthal angle is fixed at 5° (top) or 125° (bridge) (denoted as azimuthal-fixed 6D), and an approximate 7D model in which the fixed azimuthal results obtained in the 6D model are averaged (denoted as averaged 6D). As expected, all three models yield almost identical $P_0$ at the top site because the barrier height is ~0.75 eV at all azimuthal angles. At the bridge site, on the other hand, the averaged 6D probability reproduces the 7D result reasonably well, while the 6D model with fixed azimuthal angle at $\phi = 125^\circ$ overestimates the reactivity by roughly an order of magnitude at lowest energies and ~50% at highest energies. In this latter case, it is clear that the flat-surface assumption is not valid and the azimuthal anisotropy of the PES needs to be included in the dynamical model. To this end, the 7D model gives a more quantitative description of the site-specific dynamics for water DC than the previous 6D model that ignores the azimuthal angle dependence. The situation here is quite similar to the DC of water on Cu(111), discussed in detail by Zhang and co-workers.\textsuperscript{18} We will thus focus on 7D results hereafter.

Figure 4 presents selected site-specific 7D reaction probabilities for the vibrationally ground state of D$_2$O. Interestingly, the general pattern of the site-specific reactivity found in our previous azimuthal-fixed 6D calculations\textsuperscript{26} remains unchanged, although the absolute dissociation probability for each site (except the top site) is typically much lower. Specifically, Site 1 represents the minimum energy barrier, which dominates the reactivity at super low collision energies. For higher collision energies above 0.7–0.8 eV, the bridge and hollow sites become increasingly more reactive. As discussed in our previous work,\textsuperscript{26} this is because the corresponding transition states are much looser in spite of higher barrier heights and the topography of the PES renders it easier for energy flow from the translational DOF to the reaction coordinate. On the contrary, the top site is the least reactive because its transition state is very tight and the PES topography does not favor energy flow from the translational DOF to the reaction coordinate.

Figure 5 compares the 7D mode specific reaction probabilities at the top, bridge, as well as hollow sites, where $(v_O, v_\phi, v_s)$ represent the vibrational quanta for the symmetric stretching, bending, and anti-symmetric stretching modes of D$_2$O, respectively. Again, the site-specific mode specificity observed in previous azimuthal-fixed 6D calculations\textsuperscript{26} does not change qualitatively. Although the top site is much less reactive than the other two sites for the ground state reaction, excitations of the stretching modes promote the reactivity much more strongly than other sites, particularly at low energies. The mode specificity at all sites is consistent with our Sudden Vector Projection (SVP) model, which attributes the ability of a reactant mode in promoting the reaction to the projection of the corresponding normal mode vector onto the reaction coordinate at the transition state.\textsuperscript{7,8}

Quantitatively, the vibrational efficacy is conveniently defined as $\eta = [E_r(0, P_0) - E_r(v, P_0)] / \Delta E_v$, where $\Delta E_v$ is the vibrational excitation energy and $E_r(0, P_0) - E_r(v, P_0)$ is...
FIG. 5. Site-specific 7D dissociation probabilities for D$_2$O in the (000), (010), (100), and (001) states, at the top, bridge, and hollow sites.

the translational energy difference at a given dissociation probability for the ground and excited vibrational states.$^2$ It is found that $\eta$ depends heavily on the incident energy. It is in the range of 1.57–2.06, 1.58–2.13, 1.64–2.66 at the top site, 1.07–1.34, 1.03–1.56, 1.05–1.69 at the bridge site, while 0.98–1.34, 1.06–1.64, 1.00–1.40 at the hollow site, for the (010), (100), and (001) states of D$_2$O, respectively. The overall larger vibrational efficacies at the top site are understandable from the topography of the PES. As discussed in Ref. 26, the top site features a near right-angled “elbow” reaction pathway, which is very ineffective for transferring translational energy in the Z direction into the cleaving O-D bond. However, it is perfect for transferring vibrational energy to the reaction coordinate, leading to much larger efficacies for vibrationally excited states. Additionally, it is interesting to note that the (001) state is more reactive at the top and bridge sites, while less reactive at the hollow site than the (100) state, consistent with the findings in the similar H$_2$O/Cu(111) system.$^{19}$

B. Site-averaged dynamics and comparison to experimental data

The approximated 9D reaction probabilities are obtained by averaging the site-specific 7D reaction probabilities. Figure 6 shows the convergence of the averaging procedure with respect to the number of sites for D$_2$O in its vibrationally ground and excited states. As pointed out previously,$^{22–24,26}$ including only three or four sites in the averaging does not represent the converged $P_0$ well. The reaction probabilities start to converge with six sites and become almost indistinguishable with nine and fifteen sites included in the averaging.

To make the theory-experiment comparison more quantitative, lattice effects are approximately taken into account using Jackson’s well tested lattice relaxed sudden (LRS) models,$^{32}$ which rely on the changes of barrier location and height with the motion of the surface atom interacting with the molecule at the transition state. To this end, two corrections are adapted to the static QD reaction probabilities. On one hand, the so called “electronic coupling” can be reasonably described by a potential term $-\beta Q$ that changes the barrier height at $Q$, where $Q$ is the displacement of the Ni atom under the water molecule from the surface plane and $\beta$ is the force of each Ni atom at the transition state on the rigid surface. The reaction probability curve for a different $Q$ value is assumed to be shifted in the translational energy by this amount from that of $Q = 0$ (rigid). On the other hand, the vibration of the surface atom also influences the location of the transition state alone the Z axis. This so-called “mechanical coupling” can be described by a displacement $\alpha Q$ and treated using a surface mass model, where $\alpha = \Delta Z_{TS}/Q_{TS}$ representing the ratio of the Z shift of the molecular center and the $Q$ shift of the Ni atom at transition state.$^{32,33}$ Here, parameters $\alpha$ and $\beta$ were extracted from the DFT calculations of the transition state with and without surface relaxation. Specifically, $\alpha = 0.69$ and multiple Ni atoms were found have nonzero forces, including $\beta_{max} = 0.64$ eV/Å and some others bigger than 0.10 eV/Å. These values were kept the same for each initial state of D$_2$O. Since $\beta$ values are much smaller here than that in the CH$_4$ dissociation on Ni surfaces,$^5$ no significant thermal broadening of the reactivity at low energies was found. However, the lattice recoil due to the “mechanical coupling,” which removes the energy from the reaction coordinate, lowers the reactivity to some extent, especially at high energies.

The resultant initial sticking probabilities ($S_0$) are compared to the experimental data of Hundt et al. in Fig. 7.$^{10}$ Not surprisingly, all initial vibrational excitations of D$_2$O are found theoretically to greatly enhance the DC reactivity, and the vibrational efficacies gradually increase with the translational energy, especially for the (100) and (001) states. Specifically, the vibrational efficacies estimated
from $S_0 = 10^{-6}$–$10^{-2}$ range from 1.44 to 1.57 for (010), 1.40–1.97 for (100), and 1.43–2.02 for (001), respectively. These values are in qualitative agreement with our previous 6D QD single-site results on a scaled PES,\textsuperscript{10} 9D QCT results on the 9D PES,\textsuperscript{15} and especially the azimuthal-fixed 6D site-averaged results.\textsuperscript{26} The near-equivalent high efficacies for two stretching modes have been well predicted by the SVP model,\textsuperscript{8} which can be attributed to the local-mode character of the stretching vibrations. However, the SVP model underestimates the efficacy for the bending vibration.

Quantitatively, the 9D QCT calculations reported in our earlier work\textsuperscript{15} underestimate the vibrational efficacies by 0.1–0.2 for bending and anti-symmetric stretching excitations, while the scaled 6D single-site calculations overestimate the efficacies at low energies.\textsuperscript{10} These results, as well as similar observations in recent work of Liu et al. for $\text{H}_2\text{O}/\text{Cu}(111)$,\textsuperscript{19} have provide convincing evidence that the mode specificity in water DC on metal surfaces is quite different from that in methane dissociation, where the vibrational efficacies are closer to or even less than unity, especially for bending modes.

Let us now turn to the quantitative comparison between experiment and theory. Although the calculated ground state sticking probability ($S_0$) appears to match the measured laser-off data in Figure 7, this agreement is fictitious, because the experimental nozzle temperature ($T_N$) allows the population of roughly a dozen of vibrationally excited states of $\text{D}_2\text{O}$, which contribute significantly to the reactivity.\textsuperscript{10} The seemingly good agreement of the (000) probability with the laser-off data in fact suggests that the theoretical results overestimate the reactivity. Unfortunately, the calculations of the dissociation probabilities for all the relevant low-lying $\text{D}_2\text{O}$ vibrational states involved in the laser-off measurements are too demanding. Instead, we provide a crude estimate of the laser-off reactivity by assuming that these vibrationally excited states all have a constant vibrational efficacy relative to $v = 0$, e.g., $\eta = 1.3$. The theoretically estimated laser-off data are then obtained by the Boltzmann weighted sum of the state specific reaction probabilities at a given $T_N$, shown as open circles in Fig. 7. It is clear that the contributions from vibrationally excited states increase the laser-off $S_0$ by roughly an order of magnitude, which cannot be neglected. This overestimation of reactivity is also confirmed by the much larger calculated $S_0$ of the (001) state, where the corresponding experimental data are shown in the figure.

Now, the difference between experimental and theoretical data suggests that the barrier height for the DC reaction is probably too low, confirming our earlier argument using a 6D
Indeed, it has been found in the DC of H₂ and CH₄ that the PW91 functional typically underestimates the barrier height, while the RPBE functional sometime overestimates it. Using the same slab model, we have obtained that the RPBE barrier height (1.03 eV) for water DC is ~0.36 eV higher than the PW91 one (0.67 eV). In addition, the adsorption energy of RPBE is only about one fifth of that of PW91. However, one is reminded that the reaction probability in this system is largely controlled by the topography of the PES, rather than the barrier height alone. Hence, it is not clear that the use of different functionals will necessarily reach a better agreement with experiment. One possible solution is to develop specific reaction parameter (SRP) DFT as a linear combination of results from two different functionals, as has been done for the DC of H₂ on copper surfaces. To that end, it will be necessary to perform explicit QD calculations based on the PES constructed from the RPBE energies.

IV. CONCLUDING REMARKS

In the present work, we have investigated the mode specificity for water dissociative chemisorption on Ni(111) by performing site-specific 7D QD calculations using a recently developed 9D PES. The two lateral DOFs have been considered approximately based on a site-averaging scheme and the lattice effects have been corrected using Jackson’s lattice relaxed sudden models, resulting in the formally 9D initial sticking probabilities that can be compared directly with the experimental data. It is found that previous 6D QD site-averaged results with azimuthal angle fixed at the most favorable positions overestimated the absolute dissociation probability substantially due to the strong azimuthal anisotropy of the PES at most sites. More importantly, the 7D QD results reported here have confirmed some important observations from previous 6D QD and 9D QCT calculations. For example, vibrational excitations in all three modes of water are much more effective than the same energy of translation activation in promoting this reaction. In addition, the site-specific reactivity depends sensitively on the topography of the PES.

The calculated results here present the best theoretical estimates so far with the fewest approximations for the DC of D₂O on Ni(111). Unfortunately though, the calculated reactivities still overestimate the experimental data. The disagreement between experiment and theory suggests that the barrier height on our PES based on the PW91 functional is underestimated by 0.2–0.5 eV. Since the RPBE functional yields a barrier height that is ~0.36 eV higher than the PW91 value, it may be possible to design a better PES for water dissociative chemisorption on Ni(111) by optimizing the specific reaction parameter that balances the PW91 and RPBE functionals. The RPBE based PES will be reported in a follow-up publication and the related work toward the determination of the chemically accurate PES for this prototypical gas-surface reaction is underway in our labs.

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