

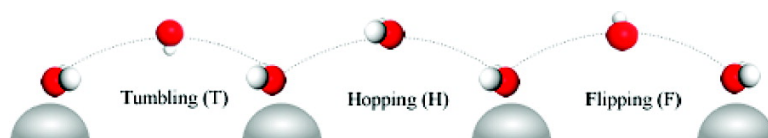
Article

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Molecular Mechanisms of a Single H₂O Diffusion on Palladium Surfaces

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Abstract: Surface diffusion of a water monomer is not as simple as previously imagined. Using state-of-the-art density functional theory, we have obtained important molecular insights relating to the elementary steps of atop-to-atop diffusion of a water monomer. We provide theoretical evidence for an anisotropic effect of rotation-jump coupling on Pd{100}; the preference of H-down tumbling motion along the nearest-neighbor direction of the square lattice was identified. The tumbling motion is attributed to quantum-tunneling-assisted diffusion, while the next-neighbor motion on the square lattice as well as the nearest-neighbor motion on Pd{111} favors molecular-axis-guided classical hopping motion whenever possible. The physical origin of the classical diffusions is discussed in the framework of the electronic structure. Our study gives useful direction for further studies on molecular couplings in the elementary steps.

Introduction

Water reorientations have been found to play important roles in protein folding, cellular transport, and unusual properties of liquid water.¹ Such knowledge is undoubtedly essential in achieving an atomic-scale understanding of the elementary steps in surface processes, which has been fueled by a long-standing desire to manipulate molecular surface motions in single-molecule science.^{2,3} Rotation-jump couplings (RJC) are probably among the key issues in understanding the concerted nature of the elementary steps in surface diffusion. Recently, transient ultrafast infrared (IR) spectroscopy has been successfully used to characterize the RJC of a single CO molecule in its basic step of surface jumps,⁴ showing spectroscopic evidence for the concerted nature of the exited surface molecular motion.⁵ This breakthrough has elevated investigations of RJC into a regime of ultrahigh temporal (femtosecond) resolutions in addition to spatial resolutions of subnanometer scales. In addition to atomic motions,⁶ small molecules like supported water are important candidates in studies of coherent control^{7,8} and quantum effects,⁹ as well as catalysis¹⁰ and proton transfer.¹¹ By means of low-temperature scanning tunneling microscopy (STM), Salmeron and co-workers^{12,13} identified atop-to-atop jumps as elementary

steps for a single H₂O diffusion on Pd{111}. Nonetheless, tremendous experimental challenges hinder the development of a detailed molecular picture regarding the concerted nature of RJC in surface water motions. This is because water molecules are easily damaged upon electronic excitation by an ultrafast laser pulse, and that the monomer exists only at ultralow temperatures and low coverages.^{14,15} Using quantum mechanical calculations, Ranea et al.¹⁶ described a molecular mechanism of cooperative water dimer diffusion on Pd{111}, demonstrating the role of water reorientation in the surface diffusion. In our previous study,¹⁷ we found symmetry-mediated H₂O diffusion on Al{100} and shed new light on the molecular mechanisms of a single H₂O diffusion concerning water orientations. To our knowledge, no detailed information regarding water orientations has been reported for a single H₂O diffusion on different Pd surfaces. RJC in elementary steps of surface water diffusions, therefore, remain mysterious at both temporal and spatial levels. Such fundamental questions as how an H₂O varies its orientation during the single step, whether a single water molecule can perform tunneling-assisted surface motion, and how energy or even molecular orbitals are redistributed within the adsorbate during the elementary steps are still to be resolved either experimentally or theoretically.

Aiming to present an important advance toward identifying the underlying mechanisms, we have, in this study, carried out quantum-mechanical calculations focusing on RJC in the elementary steps of an H₂O motion on two substrate lattices:

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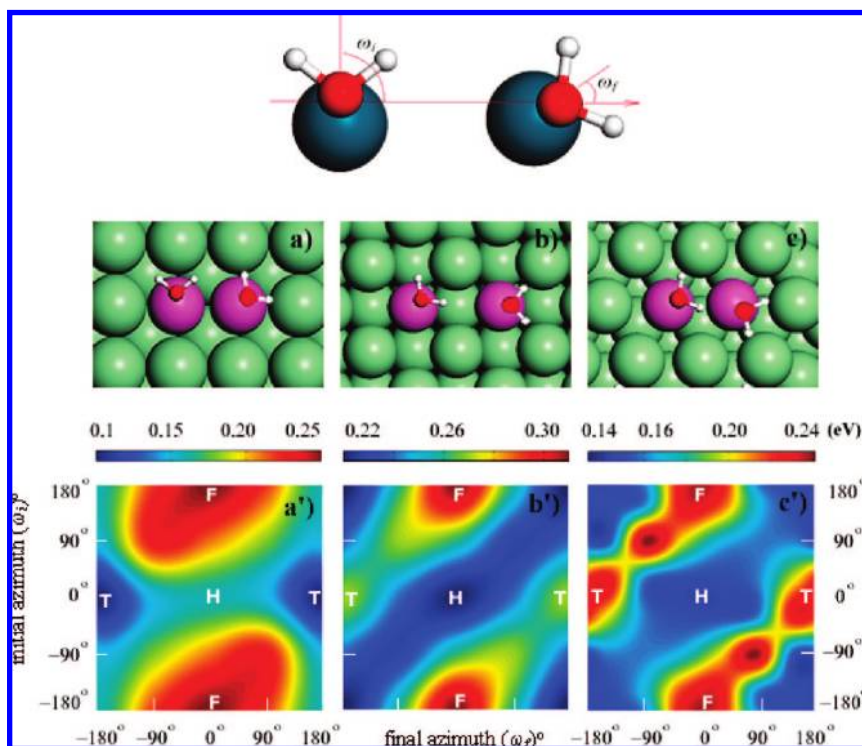


Figure 1. Contour maps of energy barrier $E(\omega_i, \omega_f)$ for surface diffusion of a single H₂O on Pd surfaces. The top panel shows the schematic diagram of the atop-to-atop diffusions $P(\omega_i, \omega_f)$. (a) The nearest-neighbor diffusions and (b) the next-neighbor diffusions on Pd{100}, where ω_i and $\omega_f = \{135^\circ, -90^\circ, -45^\circ, 0^\circ, 45^\circ, 90^\circ, 135^\circ, 180^\circ\}$. (c) The nearest-neighbor diffusions on Pd{111}, where ω_i and $\omega_f = \{-150^\circ, -90^\circ, -30^\circ, 30^\circ, 90^\circ, 150^\circ\}$. The horizontal color bar on the top of each plot marks the spectrum of energy barrier. The letters (T, H, and F) on each contour map represent the diffusion pathways highlighted in the scheme.

Pd{111} and Pd{100}. We have identified a strong anisotropic effect of the RJC's in the basic steps of water motion on the square lattice; a preference for classical hopping over other RJC's was found for an H₂O motion along the next-neighbor direction, while in the nearest-neighbor case the favored mechanism of the H-down out-plane coupling, namely tumbling diffusion, was theoretically identified as a detailed atop-to-atop diffusion. We have shown that lattice symmetry has a significant effect on tuning the preferred couplings; the classical hopping mode turns out to be the energetically favored nearest-neighbor motion on Pd{111}. The physical origin of the classical diffusions are discussed from the perspective of the electronic structure.

Results and Discussions

As a first step toward elucidating a molecular mechanism for surface water diffusions, the stationary properties, including binding and orientation, should be investigated. Our results of geometry optimizations confirm the stable on-top adsorption geometries, showing good agreement with previous *ab initio* calculations^{18,19} as well as experimental results.^{20,21} In-plane and out-of-plane rotations originating from the molecular symmetry (C_{2v}) represent the basic actions of H₂O reorientations in bulk water. For a supported H₂O, however, there exist H-up and H-down configurations due to the onset of substrate lattices. To model the elementary step of the surface diffusions, the optimized on-top configurations with various water orientations

Scheme 1. Surface Motions of an H₂O on Pd: Tumbling, Hopping, Flipping, or Others?



(Figures S1, S2, Supporting Information) were used as the initial and final images to generate the atop-to-atop diffusion paths. We noticed that the generated initial diffusion pathways include all those diffusion modes to be tested. The linear synchronous transit (LST) method²² was used to find energy barriers of the pathways.

Our common finding is that a water monomer exhibited preferential couplings and orientation preferences in the elementary steps, which is clearly evidenced by the existence of energy barrier minima for the elementary steps of the surface motions. Although having distinct substrate lattice symmetries, the energy barrier pattern for the next-neighbor motion on Pd{100} (Figure 1b') was found to be similar to that of the nearest-neighbor motion on Pd{111} (Figure 1c'), signifying that both systems have the most favored diffusion mechanism: the simple hopping mode (Scheme 1). The calculated energy barrier for water/Pd(111), 0.14 eV, was found to be very close to that of a previous STM measurement (0.13 eV).¹² This similarity suggests that thermally activated monomeric H₂O molecules do exert the hopping mechanism, which further validates the results. However, the observed nearest-neighbor motions on Pd{100} contradict the classical picture. The strongest coupling was found to be the tumbling (T) mode

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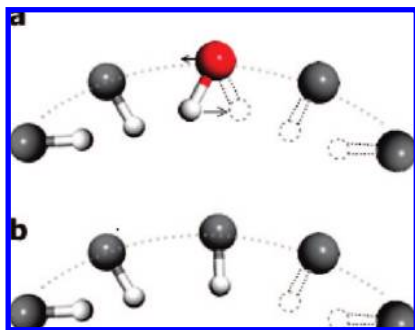


Figure 2. Schematic diagrams of (a) the calculated tumbling diffusion of H₂O monomer along the nearest-neighbor direction on Pd{100} and (b) the case of D₂O diffusion.

Table 1. Isotope Effects of Water Motion along the Nearest-Neighbor Direction of the Pd Surfaces^a

system	hopping	flipping	tumbling
H ₂ O/Pd{100}	0.16 (0.17)	0.24 (0.25)	0.09 (0.15)
H ₂ O/Pd{111}	0.14 (0.15)	0.23 (0.23)	0.22 (0.22)

^a Energy barriers in parentheses are related to D₂O motions.

(Figure 1a'), which is a combination of H-down out-of-plane rotation with the lateral jump, but the precise H-down configuration is excluded from the diffusion path (Figure 2a). The obtained energy barrier (0.09 eV) of the tumbling diffusion is 30% lower than that of a classical diffusion path (Figure 2b) that includes precise D-down water over the bridge site as a transient image. This observation might suggest a nonclassical water motion along the nearest-neighbor direction on Pd{100}. This assertion is further supported by our observation of an exclusive isotopic effect of water motion along the nearest-neighbor direction on the square lattice (Table 1). These results indicate that molecular tunneling of a single H₂O over the bridge site occurs (Figure 2a), and the precise H-down configuration over the bridge site was excluded from the basic step of surface H₂O diffusions. The second feature is that the symmetry of the energy pattern is a direct reflection of the symmetry match between the H₂O and the substrate lattice. In all the favored couplings of the water motion, the molecular axis was found to be along the atop-to-atop direction, suggesting that the symmetry match controls the molecular mechanisms of the surface motions.

To supply physical origins of the classical couplings, we proposed an orbital evolution model for various surface motions (Figure 3). It has been shown that $d_{z^2}-1b_1$ mixing is responsible for on-top water adsorption.¹⁶ In a previous publication,²³ we found that Pd $4d_{z^2}$ is also responsible for the upright water adsorption on the bridge site of Pd{100}, and that Pd $4d$ orbitals (e.g., d_{yz} and d_{xy}) and the Pd $5s$ state play a vital role in flat-lying water adsorption over the bridge site. Thus, the binding orbitals involved in the course of the hopping diffusion follow the order of $(d_{z^2}, 5s) \rightarrow (d_{yz}, d_{xy}) \rightarrow (d_{z^2}, 5s)$, and $p_z \rightarrow p_z \rightarrow p_z$ for the Pd and O atoms, respectively. This observation clearly suggests that the transient electronic nature of the hopping mode involves $d-d$ transitions. Because of the small energy changes, it is very efficient for transitions between different d -orbitals. This makes the classical hopping motion energetically practical. For the flipping mode, evolution of the O $2p$ orbitals showed the sequence $p_z \rightarrow p_y \rightarrow p_z$, in addition to the order of $(d_{z^2}, 5s) \rightarrow (d_{z^2}, 5s) \rightarrow (d_{z^2}, 5s)$ for Pd $4d$

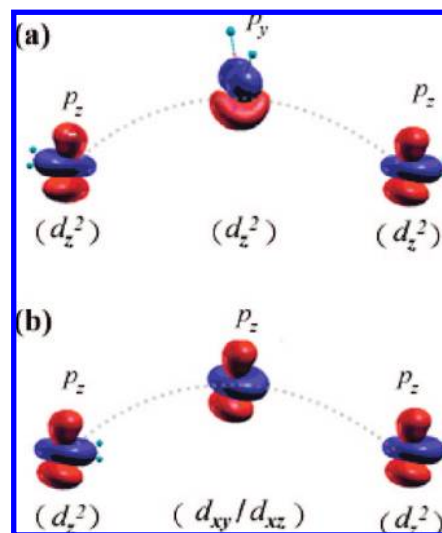


Figure 3. Schematic diagram of orbital evolution in (a) flipping and (b) hopping motions. The involved d -orbitals of substrate Pd atoms are shown in parentheses.

orbitals. Compared with the $d-d$ transitions, $p-p$ transitions experience substantial energy changes, giving insights on how and why the unfavored flipping mode exhibits the highest energy barriers (Figure 1). This observation indicates that the hopping mode is more efficient than the flipping mode for a thermally excited H₂O at low temperatures. Furthermore, this model provides a clue for controlling the surface motion by exciting a specific d -orbital, thus leading to a desired molecular coupling. Thus, electron density dynamics during the elementary steps can be an important issue for attosecond science. For example, taking inspiration from quantum control,²⁴ the d -wave symmetry of the substrate atoms can be selectively distorted by using ultrafast electronic excitations (such as Raman scattering and ultrafast X-ray²⁵), causing repulsive O-Pd interaction and leading to couplings of out-of-plane or in-plane rotations.

Conclusions

In summary, in elucidating the detailed mechanism of rotation-jump couplings, we have presented a molecular picture of the elementary steps of monomeric water motion on perfect Pd surfaces. For the surface motion on the square lattice, we found an anisotropic effect on the preferential mechanisms of rotation-jump couplings in the elementary steps: the nearest-neighbor motion favors coupling of the H-down out-of-plane rotation with the lateral jump, while in-plane rotation plays a vital role in the lateral jump in both the next-neighbor direction on Pd{100} and the nearest-neighbor motion on Pd{111}. Our investigation shows the importance of recognizing lattice symmetry and symmetry matches in order to reach a molecular understanding of molecular couplings.

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Supporting Information Available: Computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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