

Water Dimer Diffusion on Pd{111} Assisted by an H-Bond Donor-Acceptor Tunneling Exchange

V. A. Ranea,^{1,*} A. Michaelides,² R. Ramírez,¹ P. L. de Andres,¹ J. A. Vergés,¹ and D. A. King²

¹*Instituto de Ciencia de Materiales, Consejo Superior de Investigaciones Científicas, Cantoblanco, E-28049 Madrid, Spain*

²*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom*

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Based on the results of density functional theory calculations, a novel mechanism for the diffusion of water dimers on metal surfaces is proposed, which relies on the ability of H bonds to rearrange through quantum tunneling. The mechanism involves quasifree rotation of the dimer and exchange of H-bond donor and acceptor molecules. At appropriate temperatures, water dimers diffuse more rapidly than water monomers, thus providing a physical explanation for the experimentally measured high diffusivity of water dimers on Pd{111} [Mitsui *et al.*, *Science* **297**, 1850 (2002)].

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A detailed knowledge of the interaction of water with metal surfaces is important to a great number of fields of scientific endeavor, e.g., electrochemistry, heterogeneous catalysis, and energy production. Recently, in an elegant scanning tunneling microscopy (STM) experiment, Mitsui *et al.* directly tracked the motion of individual water monomers and small water clusters on Pd{111} [1]. Diffusion rates for each of the water fragments were determined. A most striking finding was that at 40 K water dimers diffuse $\approx 10^4$ times faster than the other water clusters. This is an important and intriguing experimental observation that needs to be understood. Mitsui *et al.* suggested that the mismatch between the O-O distance in the dimer (2.95 Å in the gas phase) and the Pd-Pd distance (2.75 Å) of the substrate would destabilize the dimer sufficiently to make its diffusion rapid. Density functional theory (DFT) calculations presented here, however, reveal that there is a much more subtle and widely applicable basis for the rapid diffusion of water dimers. It is not directly related to the mismatch between the adsorbate and substrate, rather the origin is in the H-bonding dynamics of the dimer. Because of the H bond, the adsorbed water dimer is asymmetric: the water donating the H bond (**D**) adsorbs 0.5 Å closer to the surface than the water accepting the H bond (**A**) [Fig. 1(a)]. Indeed, **A** is located at 2.90 Å above the surface and is essentially free to rotate around the low lying **D** molecule to which it is tethered [Figs. 1(a) and 1(b)]. This, coupled with the fact that the four hydrogens in the dimer can exchange positions through tunneling, means that the donor and acceptor roles of the water molecules are readily switched [Figs. 1(b)–1(f)]: **A-D** \leftrightarrow **D-A**. Following this exchange, the heights of **A** and **D** above the surface change according to their new roles, and the dimer is thus free to rotate around a new axis centered at the old **A**. The result of this “molecular waltz” is a net translation of the dimer by a surface lattice spacing. Measurements on the gas phase for the splitting associated to the donor-acceptor exchange by tunneling have been performed

with vibration-rotation-tunneling (VRT) spectroscopy [2] and have been accurately reproduced by calculations that solve the Schrödinger equation in the full six-dimensional intermolecular potential surface [3]. Based on our *ab initio* calculation for water on Pd{111}, we show that this interchange allows water dimers to diffuse more rapidly than monomers below 50 K. We conclude that the unexpectedly high diffusion rate of water dimers on Pd{111} demonstrates how H-bonding interactions can assist adsorbate diffusion and is another example of tunneling at low temperatures between nearby minima on a potential energy surface (PES).

The computational approach used here is based on accurate quantum-mechanical calculations within the DFT formalism. The majority of the calculations are performed in periodically repeating supercells [4], which is most appropriate for studying extended systems like the Pd{111} surface. Core electrons are described through ultrasoft pseudopotentials [5] and the kinetic energy cut-off of the plane-waves basis set is 340 eV. The Perdew-Wang 1991 [6] generalized gradient approximation (GGA) is used throughout. The system is described with a 3×3 supercell and a slab of six layers of Pd. A $3 \times 3 \times 1$ *k*-point mesh has been used [7]. A given configuration is considered converged when the total energy change per atom is less than 2×10^{-5} eV, the root-mean-square (rms) displacement of the nuclei is less than 10^{-3} Å, and the rms force on the atomic nuclei is less than 0.05 eV/Å. Owing to the localized nature of the water-substrate interaction [8,9], water monomer and dimer adsorption were also explored on clusters of 10 to 15 Pd atoms. DFT, as implemented in the GAUSSIAN-98 package [10], was used. A correlation consistent polarized triple zeta basis set was employed for H and O and a Stuttgart/Dresden electron core potential basis set for Pd. The Becke-3-Lee-Yang-Parr (GGA) functional was used for the cluster calculations, which were converged to the Gaussian default thresholds. Despite the clear differences between the slab and cluster calculations, adsorption

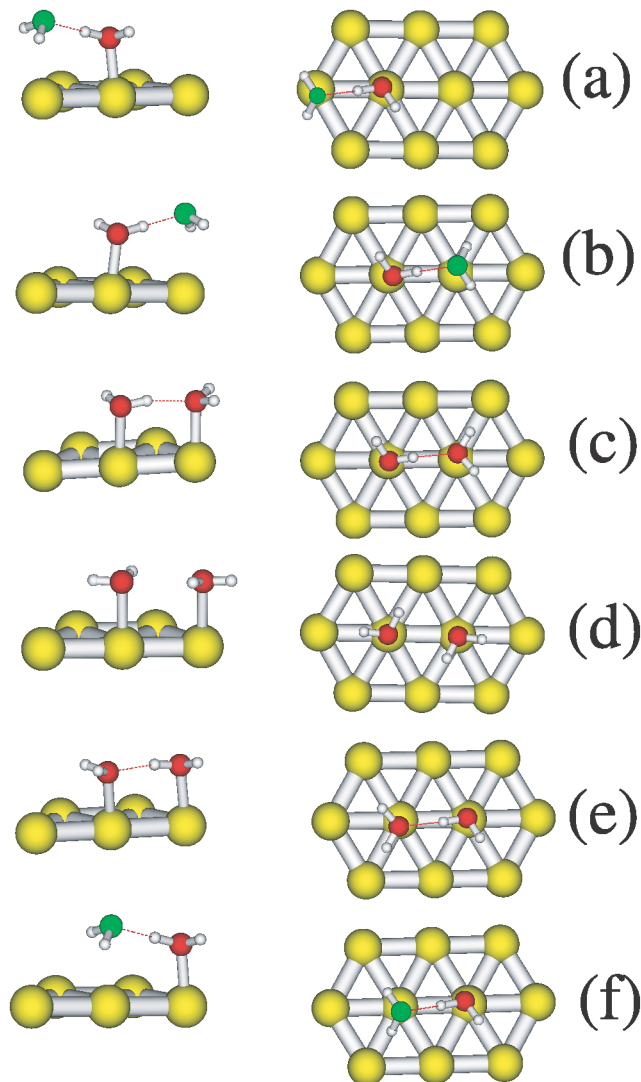


FIG. 1 (color online). Mechanism for water dimer diffusion on Pd{111} (top and side view). Step (a) to (b) involves a nearly free rotation of the dimer; step (b) to (c) is the wagging motion of the dimer, which brings both water molecules to a similar height above the surface from where they can undergo donor-acceptor tunneling interchange (c)-(e). From step (e) to (f), the dimer restores its equilibrium geometry having translated one lattice spacing [compare (a) and (f)].

energies and equilibrium geometries agree reasonably well, which is taken as an indication of the robustness of the results presented here.

STM experiments and DFT slab calculations agree that water monomers adsorb at, or very close to (within 0.2 \AA), the atop sites on Pd{111} [1,8]. The orientation of the water molecule could not be determined experimentally; however, DFT predicts that the molecular plane lies nearly parallel to the surface. With the current slab model, at $\theta = \frac{1}{9} \text{ ML}$, we obtain an adsorption energy of 0.33 eV . The Pd-O distance is 2.50 \AA and the Pd atom beneath O is raised 0.05 \AA above the plane of the other Pd surface atoms. For comparison, the cluster calculations predict an adsorption energy of 0.29 eV and a Pd-O

distance of 2.51 \AA , with an outward relaxation of the underlying Pd atom by 0.04 \AA .

Water monomer diffusion was examined by careful exploration of the PES between the various high symmetry sites on Pd{111} (with the water monomer in different orientations). Although the saddle points for adsorbate diffusion do not always correspond to high symmetry sites on the substrate [11,12], here we find that the lowest energy diffusion pathway goes from near-atop to near-atop sites via the bridge site. The barrier for this process is 0.19 eV (0.20 eV if the substrate is allowed to relax). The PES for water diffusion on this substrate is reasonably flat; the barrier over both the hcp and fcc hollow sites (allowing the surface to relax) is 0.22 eV . The barrier for monomer diffusion determined in the STM experiments of Mitsui *et al.* [1] is 0.13 eV , which is $\approx 0.06 \text{ eV}$ lower than our calculated barrier. This is in reasonable agreement, at the level of what can be expected from current state-of-the-art DFT calculations of surface processes. This error is on the same level as the difference in adsorption energy between the slab and the cluster calculations ($\approx 0.05 \text{ eV}$) and provides an estimate of the absolute systematic error due to the intrinsic limitations of the theoretical approach employed (e.g., GGA approximation, pseudopotential theory). However, in the following, our conclusions are based solely on differences on diffusion barriers. In light of the high level of convergence achieved with the current computational setup, relative errors between the different barriers are considerably less than the above values.

Several possible structures for the adsorbed water dimer at different surface sites were considered. The most stable dimer identified is displayed in Fig. 1(a). The chemisorption energy of the dimer on the surface (relative to an intact dimer in vacuum) is 0.65 eV . The dimer exhibits several interesting characteristics. First, the heights of the water molecules above the surface differ substantially: the low lying water molecule (H-bond donor **D**) is 0.50 \AA closer to the substrate than the high lying one (H-bond acceptor water **A**). Compared to the water monomer, the **D** water is 0.10 \AA closer to the surface and interacts strongly with it, whereas the **A** water interacts weakly with the substrate at 2.90 \AA from it. In fact, the **A** water can easily rotate around the low lying **D** water to which it is bonded [Figs. 1(a) and 1(b)], with a barrier of only 0.02 eV . Facile rotation of the high lying **A** water is a key observation and strongly influences the preferred dimer diffusion mechanism. Second, similar to the monomer, the water molecules in the dimer are not located above the precise atop sites. The **D** and **A** monomers are displaced by 0.19 and 0.35 \AA , respectively. This indicates that the water molecules in the dimer are not constrained to remain exactly above the atop sites. Third, the O-O distance in the adsorbed dimer is 2.74 \AA . This is $\approx 0.2 \text{ \AA}$ shorter than the equilibrium O-O distance in the gas phase dimer. This, coupled with the shorter O-Pd distance between the **D** water in the dimer, (compared

to the monomer) strongly suggests that the H bond and the **D**-metal bond in the dimer are reinforced in a cooperative manner. Finally, we note that the top layer Pd atoms directly beneath the dimer become buckled. The Pd underneath the oxygen in **D** is raised above the Pd top layer by 0.05 Å, whereas the Pd underneath the oxygen in **A** is pushed down by the same amount.

Mechanisms for the diffusion of the dimer across the Pd{111} surface were investigated. These involved simultaneously translating both water molecules in the dimer across bridge and threefold hollow sites in a number of different orientations. In addition, diffusional processes with each molecule in the dimer adsorbed at different surface sites were considered. However, the lowest diffusion barrier identified for the dimer was 0.26 eV. In fact, any time the **D** water in the dimer moved over a bridge site, the barrier was close to 0.26 eV; the energy was typically insensitive to the location of the **A** water. Therefore the lowest calculated diffusion barrier for the dimer is about 30% higher than the corresponding barrier for a single water monomer, the opposite of what is seen experimentally. In search of an alternative mechanism that might explain the rapid diffusion of the water dimer, we recall Feibelman's recent studies which showed that an adsorbed H₂O-OH overlayer on Ru{0001} is more stable than a pure H₂O bilayer [13,14]. Thus we considered the possibility that the fast moving dimer species observed experimentally are H₂O-OH clusters, rather than pure H₂O-H₂O dimers. We find that on Pd{111} a H₂O-OH cluster and an isolated chemisorbed H atom are ≈ 0.1 eV less stable than an intact adsorbed H₂O-H₂O dimer. These two species become roughly degenerate when zero point corrections are taken into account. This is mainly because of the replacement of a stiff O-H stretch mode (≈ 3500 cm⁻¹) with softer H-Pd modes (the H-Pd vertical stretch, e.g., is at ≈ 1000 cm⁻¹). It is interesting that such a half-dissociated dimer would diffuse very quickly on the surface (the diffusion barrier is ≈ 0.1 eV). However, our calculations reveal that there is an important barrier to form this species through the cleavage of an O-H bond in the adsorbed dimer (≈ 0.9 eV). The high dissociation barrier and the lack of experimental evidence for dissociation make the H₂O-OH clusters not an attractive alternative for the fast moving dimer species.

If dimers cannot diffuse faster than monomers through simple translation mechanisms and if dissociation of the dimer is unlikely, one must look to mechanisms involving internal rearrangement of the dimer that may explain the STM findings. In particular, we recall that the H bonds in small water clusters rapidly rearrange through quantum tunneling, as shown by VRT spectroscopy [2]. The donor-acceptor interchange tunneling in the free water dimer, for example, has a tunneling rate of 10^9 s⁻¹ [2] through an ≈ 0.025 eV barrier. This is several orders of magnitude faster than the highest diffusion rates measured by the STM experiments (about 10^2 s⁻¹) [1]. Indeed, we now

show how this facile H exchange and quasifree rotation of the dimer, which has been identified above, can yield an unexpected mechanism for dimer diffusion. An example is shown in Fig. 1, which can be summarized by the following sequence of events: (i) Rotation of the dimer around an axis perpendicular to the surface going through the oxygen in **D** and the Pd underneath. The low barrier translates into a basically unhindered rotation. The result of this step is that the **A** water is now located above a different Pd atom. (ii) A "wagging" vibrational mode of the adsorbed dimer, with a frequency of ≈ 100 cm⁻¹, brings the **A** molecule closer to the surface while the height of the **D** molecule remains essentially unchanged. The energy required to bring both oxygens to the same height above the surface, V_0 , is 0.11 eV (Pd substrate atoms are kept in their ideal positions). (iii) The water molecules then exchange their roles as H-bond donor and acceptor molecules [Figs. 1(c)-1(e)]. The transition state for this process has a twofold rotation axis perpendicular to the surface, passing through the center of mass of the water dimer [Fig. 1(d)] and the barrier, V_1 , is 0.11 eV. As discussed below, this step can proceed through tunneling of the H atoms. (iv) Once the two molecules have interchanged their respective roles as donor and acceptor of the H bond, the dimer restores its asymmetric equilibrium structure. The overall result is a net displacement of the dimer by a single lattice spacing.

Depending on the temperature and the barrier, diffusion via the donor-acceptor interchange tunneling mechanism can be much faster than mere thermal diffusion. The correlation of the Euler-related angles for the concerted rotation associated to the donor-acceptor interchange tunneling implies that this process can be approximately described by a one-dimensional potential [e.g., Fig. 4(b) in [3]]. Therefore, here we solve numerically a 1D Schrödinger equation with a barrier of 0.025 eV (gas phase), and a separation between wells of 2.2 Å, to obtain for the donor-acceptor interchange a tunneling rate of 10^9 s⁻¹, in good agreement with the full solution of the Schrödinger equation. The barrier has been modeled by a quartic, which is a realistic shape. However, we have considered other approximations (e.g., square wells or WKB approximation on a triangular barrier) that result in slightly different rates but do not modify our overall conclusions. For the same problem on the surface, we solve again numerically the 1D Schrödinger equation where the barrier in the quartic has been increased up to our *ab initio* value, 0.11 eV. The tunneling rate decreases by 4 orders of magnitude, which is still fast enough for the process to occur on the timescale of STM experiments. We remark that our model is not strictly one-dimensional; simply the total rate has been computed as the product of individual rates along different 1D reaction coordinates that have been previously optimised in a multidimensional parameter configuration space (i.e., different optimal directions have been followed). Transmission coefficients, T_b , are derived from this numerical

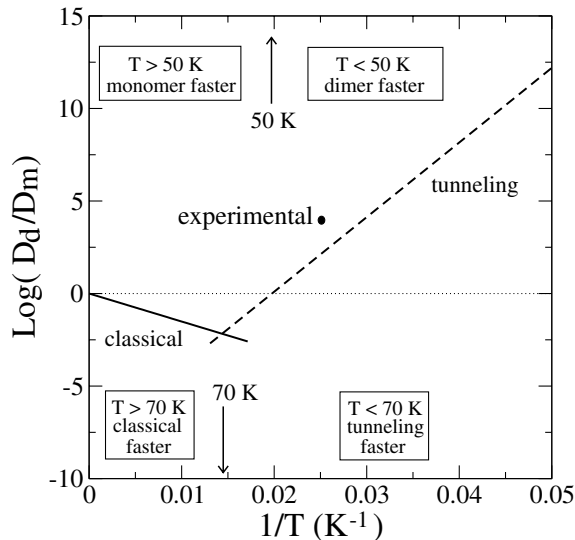


FIG. 2. Diffusion rates, as a function of temperature, for a water dimer relative to a water monomer on Pd{111}. Classical versus quantum regimes are observed above and below 70 K, respectively. Below 50 K dimers diffuse faster than monomers.

procedure, and to facilitate its manipulation they are fitted to a functional form derived from the WKB approximation:

$$T_b = e^{-2 \int p(x) dx} = e^{-\alpha \sqrt{V_1}}, \quad (1)$$

where α takes a value of $55 \text{ eV}^{-1/2}$ for a particle mass corresponding to four H atoms. The dimer diffusion rate, D_{d-t} , where the wagging oscillation of the dimer is accounted for thermally and H-bond rearrangement is accomplished through tunneling, is computed from

$$D_{d-t} = W e^{-V_0/k_B T} e^{-\alpha \sqrt{V_1}}, \quad (2)$$

where W is a typical attempt frequency (taken here as 10^{12} s^{-1} [1]), V_0 is the barrier for the wagging oscillation, and V_1 is the barrier for the donor-acceptor interchange. The corresponding diffusion rate for a classically activated process, D_{d-c} , is given by

$$D_{d-c} = W e^{-(V_0+V_1)/k_B T}. \quad (3)$$

In Fig. 2 the ratios of the rates D_{d-t}/D_m and D_{d-c}/D_m are plotted as a function of temperature, where D_m is the (classical) rate for monomer diffusion using our calculated barrier of 0.19 eV. Two important findings can be gleaned from this figure. First, dimer diffusion, through the tunneling mechanism, D_{d-t} , is faster than thermally activated dimer diffusion, D_{d-c} , at temperatures below 70 K. Second, below 50 K, tunneling becomes sufficiently rapid so that dimer diffusion is faster than monomer diffusion. Therefore, the model presented here predicts that, at the temperature of the experiments (40 K), dimers diffuse faster than monomers. However, the agreement with the experiment can only be considered as qualitative. At the experimental temperature, the model predicts that dimer diffusion is 2 orders of magnitude more rapid than monomer diffusion, whereas, experimentally, this has

been estimated to be at least 4 orders of magnitude. The point at 40 K on Fig. 2 corresponds to this experimental lower bound. It is only at 33 K that the model predicts dimer diffusion rates more than 4 orders of magnitude greater than the monomer rate. This difference, however, should not be overstated. Bearing in mind the intrinsic exponential dependence of the diffusion rates on the magnitude of the calculated barriers, small uncertainties in the barriers lead to large variations in rates.

In conclusion, a novel mechanism for water dimer diffusion on metal surfaces has been proposed. The mechanism, which relies on the ability of H bonds to rapidly rearrange through quantum tunneling, demonstrates how H-bonding interactions can assist diffusion on metal surfaces. Further, it leads to three important general predictions: (i) at low temperatures there will be a crossover for dimers from a quantum to a classical diffusion regime; (ii) dimer diffusion should exhibit an isotope effect: $\text{D}_2\text{O}-\text{D}_2\text{O}$ should diffuse 10 times more slowly than $\text{H}_2\text{O}-\text{H}_2\text{O}$ in the tunneling regime; and (iii) dimers will diffuse faster than monomers below a given temperature.

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