Role of Rotations on Surface Diffusion of Water Trimers on Pd{111}

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Diffusion barriers for a cluster of three water molecules on Pd(111) have been estimated from ab-initio Density Functional Theory. A model for the diffusion of the trimer based in rotations yields a simple explanation of why the cluster can diffuse faster than a single water molecule by a factor $\approx 10^2$. This model is based on the differences between the adsorption geometry for the three monomers forming the cluster. One member interacts strongly with the surface and sits closer to the surface (d) while the other two interact weakly and stay at a larger separation from the surface (u). The trimer rotates nearly freely around the axis determined by the d monomer. Translations of the whole trimer imply breaking the strong interaction of the d monomer with the surface. Alternatively, thermal fluctuations exchange the actual monomer sitting closer to the surface with a lower energetic cost. Rotations around different axis introduce a diffusion mechanism where a strong interaction is kept along the diffusion path between the water molecule defining the axis of rotation and the Pd underneath.

Keywords: water ; monomer ; trimer ; water clusters ; diffusion ; rotation assisted ; Pd{111} ; ab-initio ; density functional theory

I. INTRODUCTION

a. General Adsorption and diffusion of water molecules on metal surfaces play an important role in a series of phenomena such as catalysis, corrosion, energy production, storage, etc (e.g. see pioneering work by Somorjai and others [2]). In order to understand these phenomena, it is essential to investigate the interactions established between water molecules and metallic surfaces.

The water molecule has a permanent dipole that facilitates long-range dipole-dipole electrostatic interactions between molecules and with the image dipoles induced in the metal. In addition, hydrogen bonds between molecules play an important role in clustering processes. At the distances that are of concern here, these are made of electrostatic interaction between electronic densities, as shown by detailed quantum chemistry studies of the energy of interaction between water dimers. Finally, oxygen atoms can establish chemical bonds with metal atoms in the surface, as seen by monitoring the redistribution of the electronic clouds in the separated systems.

During the diffusion of water molecules on a metal surface, the formation of clusters of molecules by processes of growth and nucleation has been observed. In a series of elegant experiments Salmeron et al. have used scanning tunneling microscopy for the study of the diffusion of those aggregates of water molecules. Atomic resolution observations of diffusion of several clusters formed with one to six water molecules have been reported, and the number of water molecules in these clusters could be counted. The experimental resolution was not enough to elucidate their internal structure, but such information can be obtained by applying theoretical techniques based on ab-initio Density Functional Theory (DFT). Accuracy and credibility of these methods rest on their ability to provide a simple and reasonable physical explanation of experiments and in the agreement that can be achieved between theoretical predictions and experimental data.

b. Experimental The experiments mentioned above yield an unexpected result. Clusters of two and three water molecules diffuse on the surface of Pd {111} faster than the water monomer by about $10^4$, and $10^2$ respectively. These factors have been measured at 40 K, and a typical frequency related to diffusion has been established from an Arrhenius plot as $10^{12}$ MHz. Therefore, we deduce from the experiment a reduction of at least a 10% in the diffusion barrier for the water trimer with respect to the water monomer, in spite of the fact that the trimer displays extra interactions with the surface and has an adsorption energy that approximately doubles the one for the monomer. We seek an explanation based on physical interactions computed by ab-initio techniques and different ways of facilitating the diffusion of these clusters. In this work we shall focus in the trimer.

c. Theoretical Model A single water molecule adsorbs near a top position at a height of 2.41 Å, and with an adsorption energy of $-0.26$ eV. Interactions between the H atoms and the metal surface make the adsorption position to be slightly off the symmetric atop by about 0.12 Å in agreement with previous results. This has been interpreted as mostly due to the interaction of the occupied $1b_1$ molecular orbitals with the metal electronic states. To perform a translation of the molecule this equilibrium configuration needs to be broken, hence giving rise to a diffusion barrier. We estimate this barrier as 0.13 eV from the difference with the adsorption energy over symmetric neighbouring sites located near the bridges. The experimental value obtained from an Arrhenius plot is $0.126 \pm 0.007$ eV.

Regarding the internal structure of clusters of water molecules, theoretical calculations tell us that different components (monomers) adopt different structural positions in order to maximize external interactions between water molecules and the metallic surface, and the internal interactions among them (hydrogen bonds). For example, in the case of the water dimer a molecule adsorbs closer to the substrate...
while the other one sits in a higher position. For simplicity of notation, we shall call them down (d) and up (u). Using this information Ranea et al. have physically explained the faster diffusion of dimers over monomers. According to their model clusters made of two molecules are nearly free rotors around the axis defined by the monomer located closer to the surface. Diffusion takes place by the combined action of a thermal fluctuation bringing the two molecules in the dimer to a similar height and the concerted tunneling of the four protons to produce an exchange between the characters d and u of the two water molecules. The total probability for such an event is computed as the product of the individual probabilities, i.e., the addition of individual contributions to the barrier, and the effective diffusion barrier for the dimer results lower than the one for the monomer in an amount compatible with the experimental observation.

In this paper, we extend these ideas to the water trimer. In the potential energy surface (PES) of the water trimer adsorbed on the Pd{111} surface a minimum was found for a configuration with an energy of −0.46 eV. In this configuration one water molecule is strongly bound to the Pd atom underneath it while the other two molecules forming the trimer stay over Pd atoms but at a larger distance from the surface than the first molecule. By similarity with the dimer, we label the three water molecules as d, u and u', cf. Fig. 1. The O-Pd distances are 2.24 Å for d and 3.21 Å for both u and u'. The molecular plane of the water molecule labeled d is nearly parallel to the surface plane with the hydrogen atoms only slightly higher from the surface. The adsorption configuration of this monomer is similar to the adsorption configuration of the isolated water molecule, but it is 0.17 Å closer to the surface. There is one H-bond between each of the pairs of molecules, while the other hydrogen atoms are almost pointing to the surface in the molecules with the labels u. The calculated adsorption energy for the trimer is −0.46 eV, i.e. about 1.8 times the adsorption energy of the single monomer. This comparison shows the importance of the H-bonds inside the water trimer compared against the water-metal bonding. Comparison of the calculated activation energies for surface diffusion of the adsorbates via translation (in any direction) shows that monomer diffusion is more likely than trimer diffusion, since a stronger interaction needs to be broken. This result is in disagreement with experimental results mentioned above.12

As an alternative to translations we introduce a model where the water trimer diffuses by rotation of the whole cluster around the d molecule. At some point during that rotation the trimer picks up a thermal fluctuation to transform one of the two u molecules into a d one (labeled d'), and later on the d molecule is transformed into a u-like one (labeled u'). This process has a kinetic barrier of 0.06 eV. Rotations continue around the new d' axis and the trimer is effectively translated without fully breaking the water-metal interaction, therefore with a reduced diffusion barrier. We shall come back to this mechanism in more detail later. Notice that unlike the water dimer, the trimer is purely classical and the mechanism is based on thermal fluctuations only. Tunneling processes for the trimer involve too many protons, and their total mass reduces the likelihood of these processes below the values estimated for thermal processes.

II. METHODOLOGY

d. Density Functional Theory Total energies and diffusion barriers have been calculated using first-principles density functional theory (DFT).13,14 The Vienna Ab initio Simulation Package (VASP)13,14 code was used to investigate the water trimer diffusion on the Pd{111} surface. The Kohn-Sham equations were solved using the projector augmented wave (PAW) method15,16 and a plane-wave basis set including plane waves up to 400 eV. Electron exchange and correlation energies were calculated within the generalized gradient approximation (GGA) in the PBE form.17 While total energies are converged to a precision better than 10−6 eV, the comparison of key values with an LDA functional, and the error bars in the experiments, allow us to estimate accuracy as ±0.01 eV. Atoms are considered in equilibrium when forces are below 0.03 eV/Å. El criterio de convergencia que utilicé es el normalmente usado, cada componente de la fuerza aplicada a cada átomo que puede moverse es menor que 0.03 eV/Å. Valores below those thresholds are considered indistinguishable in this paper. Van der Waals interactions increase adsorption energies by approximately 25%. Within the range of distances relevant for our problem we find that Van der Waals adds a nearly constant offset that cancels out in energy differences and affects very little to the parameters determining diffusion.
rates.

e. Structure The system (adsorbate + substrate + vacuum) is modelled by a rombohedral supercell with lattice constants: \( a = 8.2519 \text{ Å}, c = 20.2130 \text{ Å}, \gamma = 60^\circ \). The atomistic model for the Pd\{111\} surface consists of a slab formed by a \( 3 \times 3 \) two-dimensional cell parallel to the surface with a set of three layers in the perpendicular direction. The vacuum separator is larger than 10 Å defining the surface and preventing spurious interactions between images in the periodic system. Water molecules have been adsorbed on only one side of the slab. The two atomic planes located on the other side remain fixed in the corresponding positions to a semi-infinite system, while atoms on the last layer in contact with the adsorbates, and the adsorbates themselves, can freely relax in all directions. The first Brillouin zone was sampled with a \( 3 \times 3 \times 1 \) \( \Gamma \) centered mesh. A cubic cell with lattice constant 15 Å was used to calculate the optimized structures and energies of the water monomer and trimer isolated species. Only the \( \Gamma \) point was used for these clusters.

The adsorption energy has been computed as:

\[
E_{\text{ad}} = E(\text{adsorbate}/\text{srf}) - E(\text{adsorbate}) - E(\text{srf})
\]  

(1)

The first term of equation (1) is the energy of the optimized configuration of the adsorbate on the clean relaxed surface. The second term of equation (1) is the gas phase energy of the isolated adsorbate. The third term of equation (1) is the energy of the clean optimized Pd\{111\} surface. With this definition stable configurations come as negative values of \( E_{\text{ad}} \).

g. Adsorption geometry The cluster of three water molecules (trimer) interacting with the Pd\{111\} surface displays an equilibrium configuration with an adsorption energy of –0.46 eV. The trimer is centred on a hollow site, with the oxygen atoms located near Pd top positions. The difference in the calculated adsorption energies for the trimer centered in the fcc and in the hcp hollow configurations is less than 0.01 eV.

Interactions between the water molecules in the trimer dictate that one of them stay closer to the surface, at about 2.2 Å (water monomer labeled \( d \) in Fig. 1a and b), while the other two sit at a larger distance of 3.21 Å (water monomers labeled \( u \) and \( u' \) in Fig. 1a and b). There is an attractive electrostatic interaction between each of the two water molecules labeled \( u \) or \( u' \), and the surface. The absolute value of the adsorption energy, 0.46 eV, is higher than the corresponding to the monomer, 0.26 eV, by a factor \( \approx 1.8 \). Therefore, we interpret that the two \( u \)-like monomers account for about the same interaction energy as an isolated monomer. Two H-bonds keep the water trimer internally bound and are located near the plane defined by the three oxygen atoms. Two OH directions point away from that plane, towards the metallic surface. If these two are constrained to point away from the surface the interaction is weakened by 0.28 eV. We conclude that the two \( u \)-like members of the trimer do not form strong direct bonds between the oxygen atoms and the palladium, and interact with the surface mostly electrostatically. Therefore, the water trimer is bound to the Pd\{111\} surface via the lone pair of the oxygen atom of the water molecule labeled \( d \) in Fig. 1. It is interesting to note that adsorption of a single water molecule (monomer) takes a geometrical configuration similar to the position of the member \( d \) in the trimer. We are not taking into account Van der Waals like interactions since some parametrization would be needed that it would imply breaking the first-principles approach we have adopted. Van der Waals is expected not to alter our conclusions based on chemical and H-bonds interactions. Van der Waals interactions tend to favour maximum coordination configurations. Therefore, these would be more important near the hollows/bridges/peaks, in that order.

Using the same conditions as for the trimer (i.e. the same set of pseudopotentials, exchange and correlation potential, and other parameters like the energy cutoff and the k-mesh) the adsorption of a water monomer on the Pd\{111\} surface is calculated on the top site and on the twelve neighbour sites shown in Fig. 2a. The most stable adsorption configuration locates the oxygen atom of the water monomer near the top of a Pd atom, at a distance of 2.41 Å, with an adsorption energy of –0.26 eV. The other adsorption configurations resulted in adsorption energies of –0.13 (A, E, G and K), and –0.11 (B, C, D, F, H, I, J and L) eV. In all the configurations, the plane of the water monomer is nearly parallel to the metal surface.

h. Diffusion barriers The activation energy for diffusion of the water molecule from one top to the next one is obtained by calculating the energy difference between the high-symmetry sites in the pathway. This process corresponds en-
We propose an alternative model for the surface diffusion of water based on a stationary configuration where the monomer is described here:

- (a) We start with a trimer in an optimum configuration which water molecules labeled $d, u'$ and $u$ as shown in Fig. 4a.

- (b) We consider a clockwise rotation of $120^\circ$ around the monomer $d$ (i.e., two consecutive free rotations of $60^\circ$). This step is quasi-barrierless. See Fig 4b.
• (c) Monomer $u'$ goes down to $d'$. This configuration corresponds to the transition state with $d,d',u$. This process is endothermic by 0.06 eV. Thermal fluctuations (phonons) tend to transform any of the down-like monomers into an upper-one with equal probability. Let’s assume the initial monomer $d$ goes up to $u$. The trimer has reached again an optimum configuration with $u',d',u$. This process is exothermic by 0.06 eV.

IV. CONCLUSIONS

Using ab-initio Density Functional Theory we have explained why the mere translation of a water trimer cannot explain its experimental diffusion rates on Pd\{111\}. We have introduced a model for diffusion where rotations of the trimer, combined with picking up thermal fluctuations from surface phonons, rationalize the low value determined for the effective diffusion barrier.

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