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Rotation assisted diffusion of water trimers on Pd{111}

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ABSTRACT

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 a cluster of three water molecules (trimer) based in rotations yields a simple explanation of why the cluster can diffuse faster than a single water molecule by a factor $\approx 10^2$ [1]. This model is based on the differences between the adsorption geometry for the three molecules forming the trimer. 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-like monomer. Translations of the whole trimer imply breaking the strong interaction of the d-like molecule with the surface with a high energy cost. Alternatively, thermal fluctuations can exchange the position of the molecule sitting closer to the surface with a lower energetic cost. Rotations around different axis yield a diffusion mechanism where the strong interaction is maintained along the diffusion path, therefore lowering the effective activation barrier.

1. Introduction

1.1. 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, energy storage, etc (e.g. see pioneering work by Somorjai and others [2–5]). In order to understand these phenomena, it is essential to investigate the interactions established between water molecules and metallic surfaces [6–8].

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 inhomogeneous electronic densities, as shown by detailed quantum chemistry studies of the energy of interaction between water dimers [9]. Finally, water molecules can establish chemical bonds with metal atoms in the surface, as proved by monitoring the redistribution of the electronic clouds in the separated systems [10].

During the diffusion of water molecules on a metal surface, the formation of clusters 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 [1]. 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.

1.2. Experimental

The experiments mentioned above yield an unexpected result. Clusters of two (dimers) and three (trimers) water molecules diffuse on the surface of Pd{111} faster than a single water molecule (monomers) by about 10^4, and 10^2 respectively [1]. 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 activation 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

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by ab-initio techniques and different ways of facilitating the diffusion of clusters of molecules. In this work, we shall focus on the trimer.

1.3. Model

DFT predicts for a single water molecule adsorbed on Pd{111} an adsorption energy of −0.26 eV and a kinetic barrier for diffusion of 0.13 eV. The experimental value obtained from an Arrhenius plot is 0.126 ± 0.007 eV [1].

Regarding the internal structure of clusters of water molecules, theoretical calculations tell us that the molecules forming the cluster adopt different structural positions in order to maximize interactions between water molecules and the metallic surface. 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 [9]. 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 is reduced over 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 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 about 1.8 times the adsorption energy of the single monomer. The added interaction is assigned to the shorter O–Pd bond and the electrostatic contributions of the two extra OH directed towards the metallic surface. Comparison of the calculated activation energies for surface diffusion of the adsorbates via translation shows that monomer diffusion is more likely than trimer diffusion, since a stronger interaction needs to be broken. This mechanism is in disagreement with experimental results mentioned above [1].

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 (phonon) 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'), cf. Fig. 3. The surface phonon supplies the necessary angular momentum for rotations too. This process has a kinetic barrier of 0.06 eV. Rotations continue around the new d' axis and the trimer

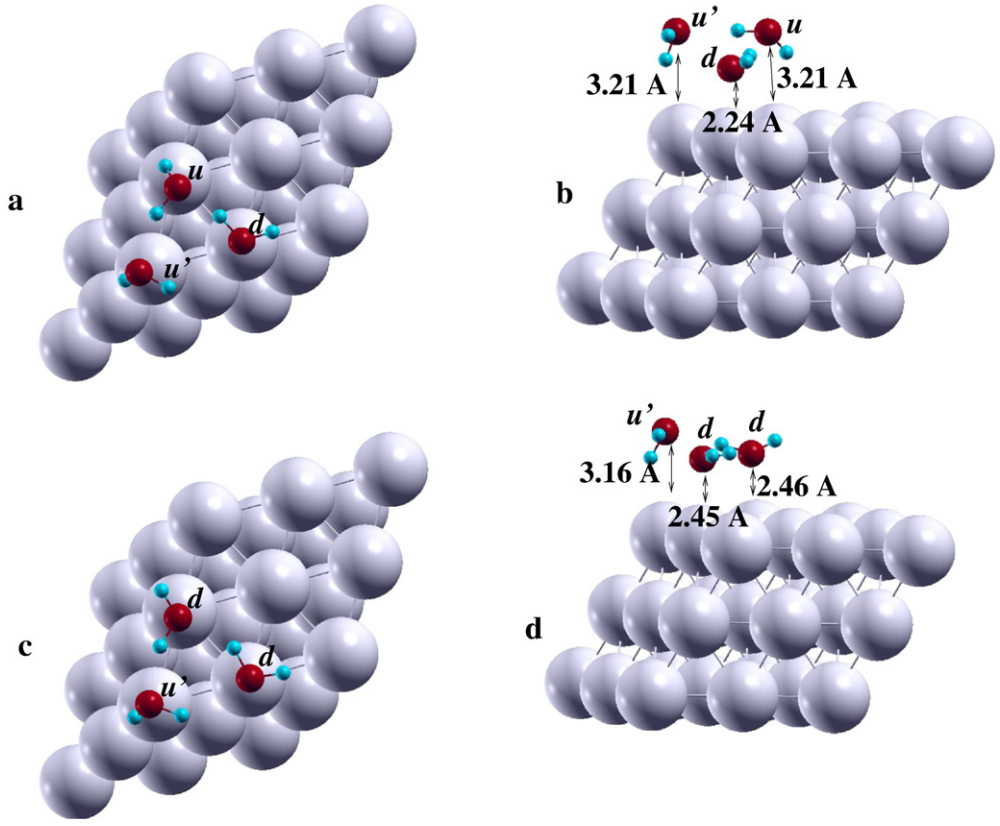

Fig. 1. a and b Top and lateral views of the most stable water trimer adsorption configuration on the Pd{111} surface. Adsorption energy = −0.46 eV. The water monomer labeled d sits at a short distance from the surface (2.24 Å), while the water monomers labeled u(u and u') are far from the metal surface (3.21 Å). c and d Top and lateral views of the transition state (stationary configuration). There are two water monomers labeled d and d' near the surface, and one labeled u farther away. Adsorption energy = −0.40 eV. Distances from the oxygen atoms to the nearest Pd atoms are shown in the lateral views. Big (silver), medium (red) and small (light blue) balls stand for Pd, O and H atoms.

is effectively translated without fully breaking the water–metal interaction along the diffusion path, therefore with a reduced diffusion barrier. We shall come back to this mechanism in more detail later. We remark 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.

A rotational mechanism for the diffusion of a small cluster of molecules is a priori quite reasonable. Compared with a pure translation, it minimizes the number of bonds that need to be broken at a given time along the diffusion path. Such a mechanism is similar in nature to the concerted exchange mechanism suggested first by Bassett and Webber [11], and discussed in the literature by many authors [12–14].

2. Methodology

2.1. Density Functional Theory

Total energies and diffusion barriers have been calculated using first-principles Density Functional Theory (DFT) [15,16]. The Vienna Ab initio Simulation Package (VASP) [17,18] 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) method [19,20], 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 [21]. While total energies are converged to a precision better than 10^{-6} eV, based in different theoretical checks and the comparison with experiments accuracy is estimated as $\approx \pm 0.005$ eV. Atoms are considered in equilibrium when forces are below 0.03 eV/Å. Van der Waals interactions increase adsorption energies by approximately 25%. Within the range of distances relevant for our problem Van der Waals adds a nearly constant offset that cancels out in energy differences, and affects little to the parameters determining diffusion rates and do not affect at all to the main conclusion.

2.2. Structure

The system (adsorbate + substrate + vacuum) is modeled by a rhombohedral supercell with lattice constants: $a = 8.2519$, $c = 20.2130$ Å, $\gamma = 60^{\circ}$ [22]. The atomistic model for the Pd{111} surface consists of a slab formed by a 3×3 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 $3 \times 3 \times 3$ Γ-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 Γ point was used for these clusters.

The adsorption energy has been computed as:

$$E_{ad} = E(adsorbate/srf) - E(adsorbate) - E(srf). \quad (1)$$

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

2.3. Diffusion

Similarly as in reference [9] we compute diffusion rates as the product of a typical frequency, w, giving the number of times the object is approaching the transition state, times the Boltzmann factor giving the probability to pick up a thermal fluctuation with enough energy to overcome the barrier, B:

$$D = we^{-B/k_BT} \quad (2)$$

The value of w can be estimated from typical phonon frequencies. We observe that for relevant values of the barrier, B, or the temperature, T, the exponential function dominates the behavior of the equation. Using a small cluster representative of the interaction between the water molecule and the Pd atoms we have estimated w from the frequencies of the set of normal modes having amplitudes of vibration in the direction of the diffusion path. These values have been computed with a localized basis set of Gaussians [23] (cc-pVTZ [24] for H and O, and sdd for Pd [25]), and are in the range from 5 to 10 THz. These values seem to be acceptable estimates for the experimental value of 1 THz since the experimental error of ± 7 meV in the determination of the barrier affects diffusion rates at $T = 40$ K in factors between 0.1 and 10 via the Boltzmann factor. Therefore, the discrepancy in the prefactor is well inside the error bar for the energy of the transition state, can be absorbed on it, and cancels out in relative comparisons of different temperatures, or between different aggregates.

3. Results

3.1. Adsorption geometry

The water monomer adsorbs near a top position at a height of 2.41 Å. 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. The plane determined by the three atoms in the water molecule is nearly parallel to the surface plane. This has been interpreted as mainly due to the interaction of the occupied $1b_1$ molecular orbitals with the metal electronic states [10]. To perform a translation of the molecule this equilibrium configuration needs to be broken, hence giving rise to a diffusion barrier. 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 neighboring sites shown in Fig. 1a. The most stable adsorption configuration yields an adsorption energy of −0.26 eV. The other 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 comes as nearly parallel to the metal surface. Therefore, we estimate a diffusion barrier of 0.13 eV along the bridges, and 0.15 eV along the hollows.

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 centered 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, therefore, these two paths are considered equivalent for the purpose of diffusion.

Interactions between the water molecules in the trimer dictate that one of them stays closer to the surface, at about 2.24 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 ≈ 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 with palladium, and interact with the surface mostly electrostatically. Such a dipole image–dipole interaction is quite independent from the atomic position and explains the quasi-barrierless rotation of the trimer around *d*. 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 notice 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 interactions since some parametrization, even if minimal, would be needed (e.g., one of the best options may imply to derive polarizability, dispersions coefficients and atomic radii for the water molecule and the Pd surface from free atomic values[26,27]). Since the addition of Van der Waals is not expected to alter our conclusions, especially in view of the nice agreement with experimental values, we feel it is not worth to break the full first-principles approach adopted. Furthermore, Van der Waals interactions tend to favor maximum coordination configurations. Therefore, these would be more important near the hollows/bridges/tops, in that order, and should tend to make the barrier softer, if any.

3.2. 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, cf. Fig. 2a[28]. This process corresponds entirely to a translation of the object, and results in an activation energy for the monomer of 0.13 eV. The same mechanism for the trimer results in a barrier of 0.26 eV; adsorption energies for sites B, E, F, J, and K were locally in equilibrium with adsorption energy of −0.20 eV, while positions A, C, D, G, H, and I were unstable and moved spontaneously to the other sites, cf. Fig. 2b. Therefore, a mechanism for diffusion based on translations predicts that the monomer should be faster than the trimer. This result is in disagreement with the experiments [1] and calls for an alternative mechanism.

Our alternative model for the surface diffusion of a water trimer is based on a stationary configuration where the trimer adopts a configuration *d d′u* instead of the most stable *d u′u*. This configuration has an energetic cost of 0.06 eV. It is interesting to notice that since both down-like monomers sit at the same height with respect to the surface it permits an exchange of the axis of rotation that results in a net translation of the trimer. Therefore, the mechanism relies on two key points. (i) The optimum configuration, *d u′u*, can rotate quasi-barrierless around the axis through *d*, Fig. 3. (ii) A transition state with configuration *d d′u*, where *d* and *d′* sit at about the same distance from the Pd{111} surface. The lifetime of this metastable configuration is determined by the normal modes that tend to restore the optimum configuration. Frequencies for these normal modes have not been computed due to the complexity of the trimer, but we hypothesize that are in the same order of magnitude as the ones obtained for the monomer, since its adsorption resembles so much the one of *d*-like low-lying monomers.

Fig. 3 shows top views of several optimized configurations for the clockwise rotation of the water trimer around the *d* monomer. The pictures are for rotations of 0°, 15°, 30°, 45° and 60°. This last configuration is equivalent to the 0° configuration. Clockwise or anticlockwise rotations around the *d* monomer of *n* times 60°, where *n* is an integer number, produce equivalent final configurations. In these calculations, all the atoms in the trimer and the atoms in the external layer of palladium are free to move accordingly to the calculated forces applied on them. Only atoms in the two deepest layers of the Pd substrate have been constrained to their semi-infinite positions. All these configurations are stationary configurations.

A simple example of how this mechanism produces the translation of the trimer within this model is shown in Fig. 4 and it is described as follows:

1. We start with a trimer in an optimum configuration with water molecules labeled *d*, *u′* and *u* as shown in Fig. 4a.
2. We consider a clockwise rotation of 120° around the monomer *d* (i. e., two consecutive quasi-free rotations of 60°). This step is quasi-barrierless, cf. Fig.4b.
3. Picking up a thermal fluctuation (phonon), monomer *u′* goes down to *d′*. This configuration corresponds to the transition state with *d*, *d′*, *u*, cf. Fig. 4c. This process is endothermic by 0.06 eV.
4. Thermal fluctuations tend to transform one of the two 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* where the axis of rotation has been moved. This process is exothermic by 0.06 eV.

A comparison between Fig. 4a and d shows that the new configuration corresponds to a net translation of the trimer.

4. Conclusions

Using ab-initio Density Functional Theory we have rationalized the role of rotations lowering the effective diffusion barrier of a water trimer

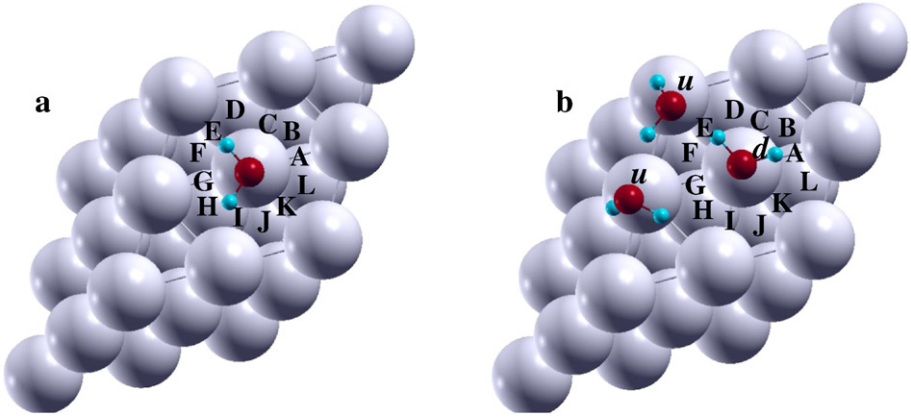

Fig. 2. a Top view of the most stable water monomer adsorption on the Pd{111} surface. Adsorption energy = −0.26 eV. The letters show the neighbor adsorption configurations also tested for the water monomer adsorption. Adsorption energy is −0.13 eV for configurations A, E, G and K, and −0.11 eV for configurations B, C, D, F, H, I, J and L. b Top view of a stable water trimer adsorption on the Pd{111} surface (idem Fig. 1a). In order to calculate the activation energy for the trimer, the whole trimer was translated to the neighboring sites. The letters around the water monomer labeled *d* indicate where this monomer was initially located. Adsorption energy is −0.20 eV for configurations B, E, F, J and K. Big (silver), medium (red) and small (light blue) balls stand for Pd, O and H atoms.

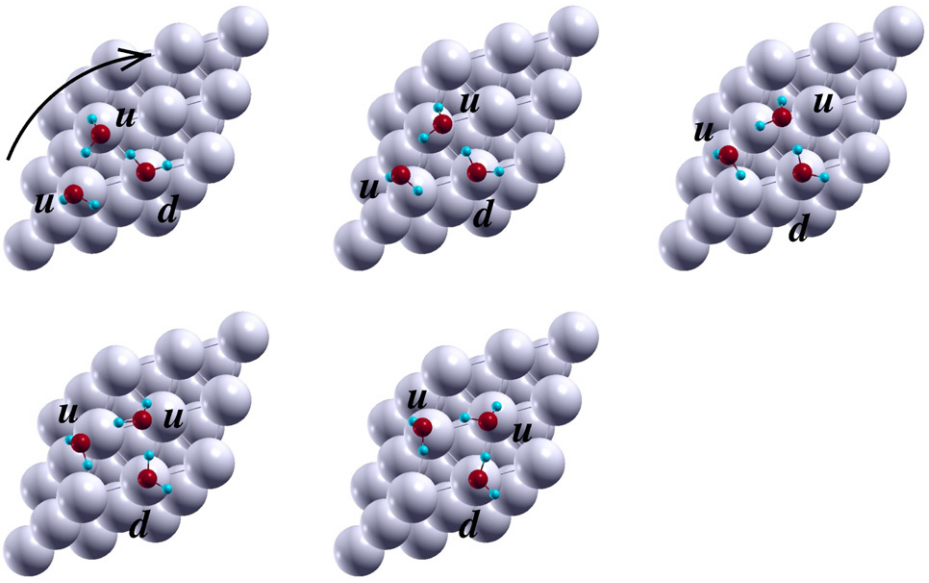

Fig. 3. Clockwise rotation of the water trimer around the axis defined by the monomer *d*. Top view of the most stable water trimer adsorption configurations on the Pd{111} surface for rotations of 0° (Fig. 1a), 15°, 30°, 45° and 60°. Adsorption energy = −0.46 eV. Every optimization was performed without constrains, except for the atoms of the two deepest layers of the Pd{111} surface. Big (silver), medium (red) and small (light blue) balls stand for Pd, O and H atoms.

on Pd{111}. This model can explain in a simple way why trimers diffuse faster than monomers; monomers cannot use the extra degree of freedom afforded by rotations in a larger cluster like the trimer. These rotations allow the trimer to minimize the bonds to the surface to be broken while moving from one cell to the next one. This is a classical diffusion mechanism where the trimer picks up thermal fluctuations from surface phonons to overcome the barriers.

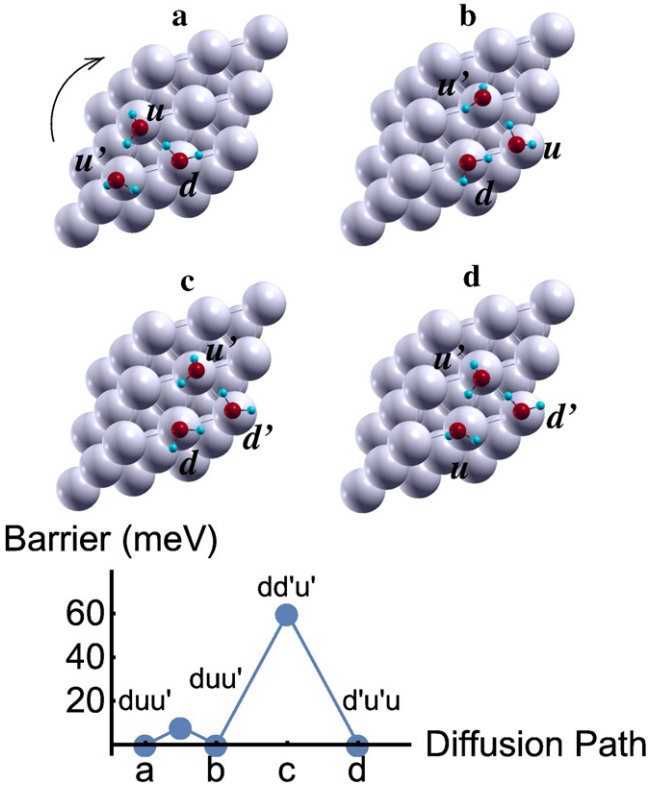

Fig. 4. Upper panel: Model of the water trimer diffusion via rotations with an activation energy of 0.06 eV. (a) Water trimer adsorbs in its most stable configuration *d u u′*. (b) Trimer rotates clockwise by 120° around monomer *d*. (c) Monomer *u′* changes configuration to *d′* (endothermic process by 0.06 eV, transition state). (d) Initial monomer *d* changes to *u′* (exothermic process by 0.06 eV). The trimer is again in an optimum configuration but the *d*-like member has been translated by a unit cell vector. Big (gray), medium (red) and small (light blue) balls stand for Pd, O and H atoms. Lower panel: schematic representation of the energy along the diffusion path.

The comparison of diffusion rates for the monomer against a larger cluster of molecules like the trimer seems to us the best chance to prove the model against experiments. We exclude the dimer because the extra channel due to tunneling, and larger objects like the tetramer or more because as the number of bonds to the surface grows rotations become less efficient for diffusion. While rotations cannot help the monomer to diffuse faster, the added degree of freedom can facilitate it for the trimer. An isotopic substitution [29] is not likely to be helpful in this case, as far as we can see it. It would affect phonon frequencies, i.e. the prefactor in Eq. (2), but not the chemical bonds responsible for the barriers in the exponential function. This is in contrast to the two diffusion mechanisms compared here, that change the height of the effective barriers. In contrast, the change in frequencies would affect similarly to diffusion rates computed for direct translation and concerted rotations.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.susc.2015.10.052.

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