

Dissociative Adsorption of Hydrogen and Oxygen on Palladium Clusters: A Comparison with the (111) Infinite Surface[†]

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Abstract: We report a density-functional study of some properties of the dissociative interaction of hydrogen and oxygen molecules on small palladium clusters ($n = 5, 7$, and 10). The calculated physisorption and chemisorption energies are compared with those of the infinite (111) palladium surface. First, adsorption of atomic hydrogen and oxygen is investigated on the Pd_5 , Pd_7 , and Pd_{10} clusters. Second, the interaction between H_2 (O_2) and the small Pd_5 cluster is examined and compared to the process occurring on an infinite (111) surface. Finally, the simultaneous adsorption of two hydrogen (oxygen) atoms is analyzed in detail. As shown in a previous work, the binding energy of the first hydrogen (oxygen) atom does not depend significantly on the cluster size, and small two-layer clusters ($n \leq 10$) can be used to determine with accuracy the interaction of atomic adsorbates with an infinite (111) palladium surface. In this study, we show that the dissociative chemisorption of H_2 and more especially of O_2 on a small palladium cluster may lead to erroneous binding energy: the cluster's size may prevent an accurate description of the adsorbate–adsorbate interaction as a function of their distance. It is demonstrated that a good choice of both the size and the shape of the cluster is preponderant for a good description of the dissociative adsorption of H_2 and O_2 on an infinite (111) surface.

I. Introduction

Because of their importance in the field of catalysis, the interaction of hydrogen and oxygen species with palladium surfaces is of prime interest. In the past, the adsorption of atomic and molecular hydrogen on the (111) palladium surface was largely investigated by experimental approaches.^{1–7} These studies examined atomic hydrogen chemisorption, and it was found that the most favorable adsorption site on the $\text{Pd}(111)$ surface is the threefold hollow surface site above

the third-layer metal atoms (fcc site).^{1,4,6} Mitsui et al. determined an energetic barrier of 0.09 eV for the diffusion of an individual H atom on the $\text{Pd}(111)$ surface.⁶ The adsorption of H_2 was also investigated.^{1,3,5} Christmann et al. and Conrad et al. concluded to a dissociative adsorption of H_2 on $\text{Pd}(111)$ with an initial adsorption energy of 0.90 eV.^{1,3} Resch et al. also predicted, at low initial beam energies, an indirect dissociation pathway via a molecular precursor state, and the activation energy for the dissociation was estimated to be around 0.05 eV.⁵ At higher beam energies a direct activated dissociative process was observed.⁵ More recently, Mitsui et al. showed by tunneling microscopy observations that aggregates of at least three hydrogen vacancies are required for efficient H_2 dissociation on $\text{Pd}(111)$.⁷

The adsorption of atomic hydrogen on the (111) palladium surface was also theoretically investigated using clusterlike

[†] Dedicated to Professor Dennis R. Salahub on the occasion of his 60th birthday.

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approaches^{3,8–11} and slab approaches^{12–19} in the framework of the density functional theory. All these studies pointed out that the H atoms adsorb preferentially on threefold hollow sites, and the fcc site was determined as the more stable adsorption site.^{10,12–19} The adsorption of the H₂ molecule on small Pd_{*n*} (*n* = 1–6) clusters was also studied by DFT calculations,^{20–22} and several local minima were found. They correspond to H₂ physisorption and other dissociative adsorption modes on the Pd_{*n*} clusters. Periodic calculations showed the H₂ molecule dissociation on the Pd(111) surface.^{23,24} Both activated and nonactivated pathways were found.²³ When the dissociation process is activated, the activation energy remains small (~0.05 eV), in agreement with the experimental evidence.

Concerning oxygen species, experimental studies were first carried out on the adsorption of atomic oxygen on the Pd(111) surface.^{25–28} The threefold adsorption sites are found to be the most stable ones (fcc or hcp sites favored, depending on the authors),^{25,27,28} and the Pd(111) surface relaxation upon O adsorption is found negligible.²⁸ The activation barrier for the diffusion of O atoms on the Pd(111) surface is small.²⁵ Experimental data are also available for O₂ adsorption/desorption and dissociation on Pd(111).^{25,26,29,30} Experiments predict a complex adsorption mechanism consisting of a physisorbed and up to three molecular precursor states. At temperatures below 200 K, several molecular O₂ precursors adsorbed on the surface were characterized. Thus the O₂ adsorption process does not proceed in a single step but through a sequence of several well-defined peroxo molecular precursors followed by the dissociation to atomic oxygen at around 200 K.^{26,29,30} Guo et al. measured the desorption temperature and desorption energy *E*_d of three molecular precursors (*T* = 125 K and *E*_d = 0.33 eV; *T* = 150 K and *E*_d = 0.40 eV; *T* = 200 K and *E*_d = 0.53 eV).²⁶ An activation energy of 2.38 eV was measured for the associative desorption of the O atoms at 800 K.^{25,26} Nolan et al. used EELS and molecular beam techniques to investigate O₂ adsorption on Pd(111) at high energy beam.²⁹ They found a direct molecular chemisorption mechanism at 77 K. Sjövall et al. showed at low coverage that O₂ dissociation is always precursor mediated.³⁰ At low energies, they characterized a physisorbed state prior to the molecular chemisorption. At high beam energies, direct activated adsorption into a chemisorbed molecular precursor state was observed, in agreement with the study of Nolan et al. The adsorption of atomic oxygen was also theoretically investigated on small Pd_{*n*} clusters^{10,31} and on the Pd(111) surface using slab approaches.^{32,33} The fcc adsorption site is predicted to be the most stable site for O adsorption on Pd(111), with an adsorption energy difference between the fcc and hcp sites of 0.2 eV.^{32,33}

In the case of O₂ on Pd(111), several adsorption pathways depending on the initial adsorption position of O₂ on the surface were explored.^{31,32,34–36} Honkala et al. and Eichler et al. found three O₂ molecular states adsorbed on the surface^{32,35} and related them to experimental evidence^{26,29,30} using their vibrational frequencies: the superoxo state was attributed to the top-bridge-top (first O-position of the mass center-second O) adsorption geometry and the peroxo-I to

the top-fcc(or hcp)-bridge adsorption geometries that presented degenerated O₂ adsorption energies. None of the calculated O₂/Pd(111) configuration could be related to the third precursor state (peroxo-II) which was experimentally identified.

In the present paper, we first consider the adsorption and diffusion of atomic hydrogen and atomic oxygen on Pd_{*n*} (*n* = 5, 7, 10) clusters (section III). The interaction of H₂ and O₂ molecules with the small Pd₅ clusters is therefore investigated (section IV). It is followed by the study of successive adsorption of two hydrogen or oxygen atoms to examine the chemisorbed H–H and O–O interactions on the (111) surface (section V). We compare our results with results from periodic calculations or experimental investigations for the infinite (111) surface.

II. Method of Calculation

Our calculations are based on the density-functional theory and performed in the framework of the LCGTO-MCP-LSD method incorporated in the deMon program package release 3.3.^{37–38} The Vosko-Wilk-Nusair local potential³⁹ is used, and the nonlocal gradient-based corrections of Perdew^{40–42} are added for the exchange and correlation terms. We use a 16-electron relativistic model core potential⁴³ for the palladium atoms. The valence 4p, 4d, and 5s electrons are treated explicitly with a (2211/2111/121) orbital basis set. A corresponding (3,4;3,4) auxiliary basis set is used for the fits of the charge density and the exchange-correlation potential. The H and O atoms are described by the (41/1*) and (5211/411/1) orbital basis sets and the corresponding (4,2;4,2) and (5,2;5,2) auxiliary basis sets, respectively.

Small Pd_{*n*} clusters (*n* = 5, 7, 10) are used in this study to investigate the adsorption of H₂ and O₂ as well as the chemisorbed H–H and O–O interactions on the (111) surface. In order to compare our results with those of an infinite (111) surface, the Pd–Pd interatomic distances are frozen at the experimental bulk value, *d*(Pd–Pd) = 2.75 Å. The calculations are done with spin polarized wave functions. It is shown that the most stable spin states for each system have a multiplicity of *m* = 1 for Pd_{*n*}, H₂, and Pd_{*n*}H₂; *m* = 2 for Pd_{*n*}H; and *m* = 3 for O, O₂, Pd_{*n*}O, and Pd_{*n*}O₂. In order to describe the electron transfer during the adsorption process, a Mulliken population analysis is done for each system.

III. Atomic Adsorption on Small Two-Layer Pd_{*n*} Clusters

In a first step, we study the chemisorption process of atomic hydrogen and oxygen on the surface of the clusters. The effects of the size of the cluster and of the nature of the adsorption site are reported together with the equilibrium Pd–O bond lengths and the activation energies for the diffusion on the surface.

The size effects are studied by using small two-layer Pd_{*n*} clusters (*n* = 5, 7, 10). These clusters are shown in Figure 1. Three different adsorption sites are studied labeled “h” and “f” for the adsorption on threefold hollow hcp and fcc sites, respectively, and “b” for the adsorption on bridge sites (see Figure 1). In each case, the adsorbate-cluster surface

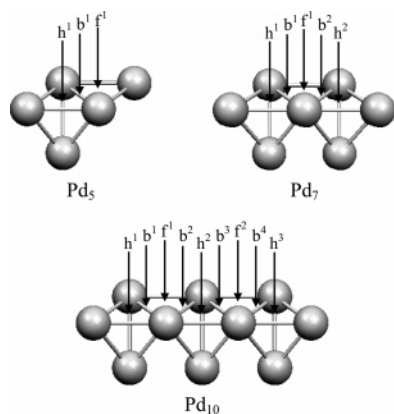


Figure 1. Small palladium clusters used for the study of adsorption of atomic and molecular species on threefold hcp (h), threefold fcc (f), and bridge (b) sites.

Table 1. H Adsorption on hcp, fcc, and Bridge Sites of the Pd₅, Pd₇, and Pd₁₀ Clustersⁱ

	site	E_{ads}	$d(\text{Pd}-\text{H})$	$q(\text{H})$
Pd ₅ H	h ¹	-2.96	1.79	-0.12
Pd ₅ H	b ¹	-2.73	1.71	-0.07
Pd ₅ H	f ¹	-2.94	1.79	-0.13
Pd ₇ H	h ¹ or h ²	-2.91	1.80	-0.13
Pd ₇ H	b ¹ or b ²	-2.68	1.72	-0.09
Pd ₇ H	f ¹	-2.83	1.79	-0.13
Pd ₁₀ H	h ¹ or h ³	-2.87	1.80	-0.12
Pd ₁₀ H	h ²	-2.86	1.79	-0.15
Pd ₁₀ H	b ¹ or b ⁴	-2.70	1.71	-0.07
Pd ₁₀ H	b ² or b ³	-2.73	1.71	-0.08
Pd ₁₀ H	f ¹ or f ²	-2.84	1.79	-0.14
experimental		-2.68 ^a		
other computa-	hcp	-3.8 to -3.4 ^b		
tions	hcp	-2.82 ^c		
	fcc/hcp/bridge	-2.65/-2.59/-2.45 ^d		
	fcc/hcp/bridge	-2.69/-2.60/-2.60 ^e		
	fcc/hcp/bridge	-2.73/-2.67/-2.55 ^f		
	fcc/hcp/bridge	-2.79/-2.74/-2.61 ^g		
	fcc/hcp/bridge	-2.73/-2.69/-2.58 ^h		
	fcc/hcp/bridge	-2.57/-2.49/-2.35 ⁱ		

^a Reference 2. ^b Reference 9 (cluster approach). ^c Reference 11 (cluster approach). ^d Reference 12 (periodic computations). ^e Reference 13 (periodic computations). ^f Reference 14 (periodic computations). ^g Reference 15 (periodic computations). ^h Reference 18 (periodic computations). ⁱ Reference 19 (periodic computations). ^j E_{ads} is the adsorption energy (in eV), $d(\text{Pd}-\text{H})$ is the distance between the hydrogen atom and the nearest Pd neighbor (in Å), and $q(\text{H})$ is the hydrogen Mulliken net charge.

distance is optimized. Adsorption energies E_{ads} are calculated by using the equation

$$E_{\text{ads}} = E(\text{Pd}_n\text{X}) - [E(\text{X}) + E(\text{Pd}_n)] \quad (1)$$

where X = H or O, and $E(\text{X})$, $E(\text{Pd}_n)$, and $E(\text{Pd}_n\text{X})$ are the DFT total energies of X, Pd_n, and Pd_nX systems. Adsorption energies of atomic hydrogen on Pd_n are given in Table 1; the most favorable structures correspond to the H adsorption on fcc or hcp sites without any significant energy gap between both sites ($\Delta E_{\text{ads}} = 0.02$ – 0.08 eV). The adsorption on a bridge site is less favorable and corresponds to a diffusion barrier between two adjacent threefold sites. The

Table 2. O Adsorption on hcp, fcc, and Bridge Sites of the Pd₅, Pd₇, and Pd₁₀ Clusters^c

	site	E_{ads}	$d(\text{Pd}-\text{O})$	$q(\text{O})$
Pd ₅ O	h ¹	-3.67	2.11	-0.53
Pd ₅ O	b ¹	-3.50	2.03	-0.50
Pd ₅ O	f ¹	-3.96	2.11	-0.55
Pd ₇ O	h ¹ or h ²	-3.77	2.11	-0.54
Pd ₇ O	b ¹ or b ²	-3.38	2.04	-0.52
Pd ₇ O	f ¹	-3.79	2.11	-0.50
Pd ₁₀ O	h ¹ or h ³	-3.79	2.11	-0.58
Pd ₁₀ O	h ²	-3.74	2.12	-0.48
Pd ₁₀ O	b ¹ or b ⁴	-3.36	2.03	-0.50
Pd ₁₀ O	b ² or b ³	-3.29	2.05	-0.48
Pd ₁₀ O	f ¹ or f ²	-3.66	2.10	-0.50
other computa-	hollow/bridge	-3.51/-3.34 ^a		
tions	hcp/fcc/bridge	-3.41/-3.60/-3.05 ^b		

^a Reference 31 (periodic computations). ^b Reference 32 (periodic computations). ^c E_{ads} is the adsorption energy (in eV), $d(\text{Pd}-\text{O})$ is the distance between the oxygen atom and the nearest Pd neighbor (in Å), and $q(\text{O})$ is the oxygen Mulliken net charge.

activation energy is of the order of 0.25 eV showing that one hydrogen atom can easily diffuse over an (111) palladium surface. All calculated adsorption energies depend weakly on the size of the cluster showing that the H-surface interaction is localized. Furthermore the cluster-H distances remain almost constant for the same types of adsorption sites, ~ 0.82 Å (fcc and hcp) and ~ 1.02 Å (bridge) as well as the hydrogen net charge which is of 0.12 – 0.15 e⁻ for adsorption on fcc or hcp sites and 0.08 e⁻ on bridge sites. In the case of atomic oxygen adsorption (Table 2) the most favorable structures correspond also to the adsorption on fcc and hcp sites. The adsorption on a bridge site is about 0.2–0.5 eV higher in energy. The cluster-O distances are almost unchanged for the same types of adsorption sites, ~ 1.39 Å (fcc and hcp) and ~ 1.50 Å (bridge). The electronic transfer from the cluster to the adsorbate is significant. The oxygen net charge is around 0.50 – 0.55 e⁻ for adsorption on fcc or hcp sites and 0.50 e⁻ on bridge ones. The diffusion barrier between two adjacent hollow sites is of the order 0.20–0.50 eV. As for hydrogen, various properties of O adsorption are nearly size independent, showing that the O–Pd surface interaction is localized.

IV. Molecular Adsorption on Small Two-Layer Pd_n Clusters

Here we turn our attention to the study of the molecular interaction of H₂ and O₂ with a small two-layer Pd₅ cluster, and we discuss the meaning of differences between a cluster-like approach and periodic calculations or experimental investigations on the infinite Pd(111) surface. To do this, we chose to investigate the adsorption process of H₂ and O₂ following the pathway corresponding to an initial fcc-hcp orientation of the diatomic molecule over the cluster's surface (Figure 2). We restrain our study to a two-dimensional potential where both variables are the X–X bond length r and the Pd surface–X₂ distance z . Thus the adsorption energies are given by

$$E_{\text{ads}}(r,z) = E(\text{Pd}_n\text{X}_2)(r,z) - [E(\text{Pd}_n) + E(\text{X}_2)] \quad (3)$$

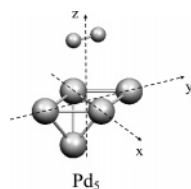


Figure 2. Initial adsorption position of H₂ and O₂ on the Pd₅ cluster.

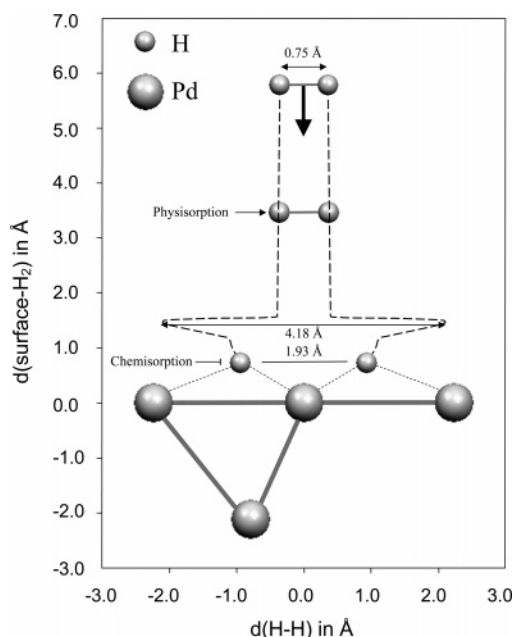


Figure 3. H–H equilibrium distances (Å) as a function of the surface-H₂ distances (Å) for the adsorption pathway displayed in Figure 2. Large circles are Pd atoms and small ones, H atoms.

where X₂ is H₂ or O₂, and then $E(X_2)$ is the total energy of the X₂ molecule in the gas phase. The diatomic molecule center of mass is positioned over a bridge site, while both adsorbate atoms are respectively over an fcc and hcp adsorption site (Figure 2). Such an approach is chosen because for example previous theoretical studies concerning the dissociative adsorption of H₂ on Pd(100) surfaces showed that a rotation of the hydrogen molecule out of a plane parallel to the surface increases the energy.⁴⁵ Thus the diatomic molecule axis is kept parallel to the cluster surface and perpendicular to the Pd–Pd bond (Figure 2). The molecule is moved toward the cluster's surface following the *z*-axis, and the H–H bond length is optimized for each surface–adsorbate distance. The corresponding adsorption pathways are displayed in Figures 3 and 4.

IV.1. H₂ Adsorption on Pd₅. Figure 3 shows the variation of the H–H bond length *r* when H₂ is moved toward the cluster surface. All the properties associated with the precursor state, transition state, and chemisorbed state are summarized in Table 3. When *z* = 3.42 Å, the H₂ molecule stabilizes in a precursor state. In this state, no electron transfer between the cluster and the adsorbate is observed, and *r* remains equal to 0.75 Å (Figure 3, Table 3). The H–H Mayer bond order is equal to 1, and no chemical bond is formed between the adsorbate and the substrate. Therefore, this

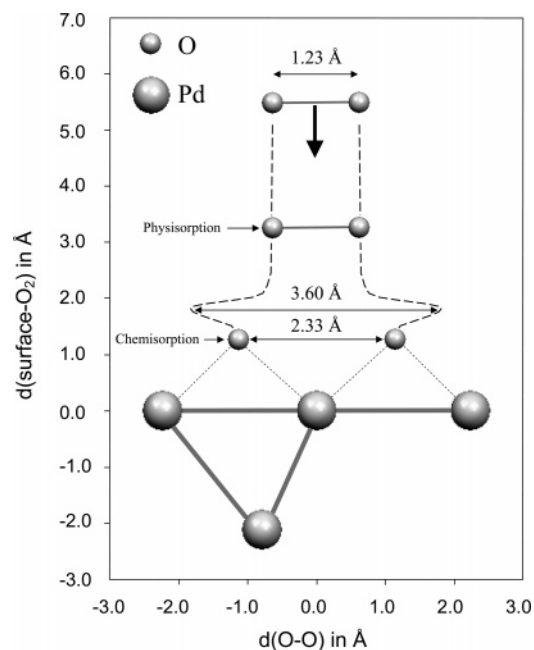


Figure 4. O–O equilibrium distances (Å) in function of the surface-O₂ distances (Å) for the adsorption pathway displayed in Figure 2. Large circles are Pd atoms and small ones, O atoms.

Table 3. Various Parameters of the Adsorption Process of H₂ and O₂ on the Pd₅ Cluster

	H ₂			O ₂		
	phys.	TS	chem.	phys.	TS	chem.
<i>r</i> (Å)	0.75	0.90	1.93	1.23	1.25	2.33
<i>z</i> (Å)	3.42	1.45	0.84	3.20	1.95	1.39
BO(X–X)	1.0	1.0	0.10	2.0	2.0	1.20
<i>q</i> (X) (au)	0.0	0.0	–0.13	0.0	0.0	–0.72
energy (eV)	–0.06	0.15	–0.91	–0.42	0.31	–0.29

precursor state can be identified as the physisorption of H₂ on the cluster surface. The physisorption energy E_{phys} is small and equal to –0.06 eV on Pd₅ (see Table 3). When H₂ continues to move toward the cluster surface, a transition state is observed whose energy is equal to +0.15 eV on Pd₅ (Table 3). It corresponds to an activation energy of 0.21 eV. The (H–H) bond length *r* increases slightly to 0.90 Å, and the bond order remains equal to 1. No charge transfer is observed between the molecule and the cluster. At *z*_J = 1.59 Å a sharp transition is observed. *z*_J corresponds to the edge of the jellium which would represent the metal in a simple metal-like description; it is equal to the distance between two (111) planes. Thus H₂ is dissociated when placed in a region of high electronic density. Each H atom is screened by the electron density of the cluster. The electrostatic repulsion leads to a H–H distance of 4.18 Å. Finally, when *z* continues to decrease, the H–Pd_{*n*} interaction increases, and the H atoms locate on the hcp and fcc sites leading to a decreasing of *r*. At the chemisorption sites, the H atoms are slightly bound (BO = 0.10), but the electrerepulsion is also significant so that the H–H distance reaches 1.93 Å while the hcp-fcc distance is only 1.59 Å.

IV.2. O₂ Adsorption on Pd₅. As in the case of H₂ adsorption, from the unlike O₂ adsorption pathways studied by Honkala et al.,³² we chose to investigate the adsorption pathway corresponding to an fcc-hcp O₂ initial adsorption position (results in Table 3). For the same reasons as H₂ adsorption on Pd₅, we have constrained the O₂ dynamic adsorption process to 2D cuts of the 6D PES. The molecular axis is kept parallel to the cluster surface and perpendicular to the Pd–Pd bond (Figure 2). The adsorbate is moved toward the Pd₅ surface following the *z*-axis, and the O–O bond length is optimized for each value of *z*. The adsorption pathway is displayed in Figure 4. As it was the case for H₂, we first observed a physisorbed state located at *z* = 3.2 Å, with an energy of –0.42 eV. In this state, no electron transfer is observed between the cluster and the molecule. The O₂ molecule still has the same conformation as that in the gas phase, *d*(O–O) = 1.23 Å (Figure 4), the O–O bond order is still equal to 2, and no chemical bond is observed between the adsorbate and the substrate. On the other side, the physisorption energy of O₂ is much larger than that of H₂ showing that the electronic cloud of O₂ is strongly polarized by the presence of the palladium surface. At *z* = 1.95 Å, a transition state is determined with an energy of 0.31 eV leading to an activation energy for the dissociated chemisorption of 0.73 eV. At this point, the O₂ species is still molecular, the O–O length increasing very slightly to 1.25 Å. At *z*_f = 1.59 Å a sharp transition is observed. Thus O₂ is dissociated, and the electrostatic repulsion leads to a O–O distance of 3.6 Å. Finally, when *z* continues to decrease, the O–Pd_{*n*} interaction increases, and the O atoms locate on the hcp and fcc sites leading to a decreasing of *r*. At the chemisorption site, the O atoms are always relatively bounded (BO = 1.20), but the electrorepulsion is large (*q*(O) = –0.72 au) so that the O–O distance reaches 2.33 Å (in place of 1.59 Å for the hcp-fcc distance). Finally, we can notice that, for this pathway, no molecular chemisorbed precursor is observed on the surface and that this reactional pathway is activated. It is in good agreement with the periodic calculations of Honkala et al.³² Furthermore, comparison of physisorption and chemisorption energies show that the O₂ molecule may dissociate on Pd₅. Honkala et al.³² found that the adsorption of two oxygen atoms constrained on two adjacent adsorption sites (fcc-hcp) is endothermic. Our results show that the O₂ adsorption process on the small Pd₅ cluster is different relatively to an infinite (111) surface for low coverage.

V. Interaction between Chemisorbed Atoms on Small Two-Layer Pd_{*n*} Clusters

In this part, we study the interaction between two adsorbed atoms (hydrogen or oxygen) on the Pd₅, Pd₇, and Pd₁₀ clusters (Figure 1). The first atom being adsorbed in the most stable position, i.e., the hcp site, the second one is allowed to migrate on other threefold sites (hcp or fcc). The range of the atom–atom interaction is then discussed and compared to the reference state where the two atoms are not in interaction. The pathway of the hcp-fcc dissociative adsorption was analyzed more particularly. In fact, it is known that the most stable end configuration of the dissociation is the

Table 4. Chemisorption Energy of Two Hydrogen Atoms Coadsorbed on Various (111) Sites^c

	sites	<i>E</i>		<i>q</i> (H)		BO(H–H)
		<i>E</i> _{ads}	Δ <i>E</i> _{ads}	H ¹	H ²	
Pd ₅ H ₂	h ¹ /f ¹	–0.91	+0.09	–0.12	–0.13	0.10
	Inf	–1.02				
Pd ₇ H ₂	h ¹ /f ¹	–0.72	+0.12	–0.14	–0.12	0.10
Pd ₇ H ₂	h ¹ /h ²	–0.69	+0.23	–0.13	–0.13	0.00
	Inf	–0.92				
Pd ₁₀ H ₂	h ¹ /f ¹	–0.59	+0.22	–0.12	–0.13	0.10
Pd ₁₀ H ₂	h ¹ /h ²	–0.54	+0.29	–0.13	–0.14	0.00
Pd ₁₀ H ₂	h ¹ /f ²	–0.56	+0.25	–0.12	–0.13	0.00
Pd ₁₀ H ₂	h ¹ /h ³	–0.65	+0.19	–0.13	–0.13	0.00
	Inf	–0.82				
other work ^a	hcp/hcp	–0.73				
other work ^b	hcp/fcc	–0.69				
	hcp/hcp	–0.89				
	fcc/fcc	–0.99				

^a Reference 12 (periodic computations – coverage = 1). ^b Reference 23 (periodic computations). ^c *E*_{ads}(eV) is the H¹ plus H² adsorption energy, *q*(H) is the Mulliken net charge located on each H atom, and BO is the H–H bond order. The different adsorption sites are illustrated in Figure 1.

fcc–fcc one's (see ref 23), but only the hcp-fcc configuration is available on the three studied clusters.

V.1. Hydrogen–Hydrogen Interactions. Hydrogen–hydrogen interactions when chemisorbed on Pd₅, Pd₇, and Pd₁₀ are summarized in Table 4. The first atom is chemisorbed on the h¹ site, while the second one is chemisorbed on other three-hollow sites f¹ (5, 7, 10), h² (7, 10), and f² and h³ (10). Chemisorption energies as well as charge transfer and bond orders between the two atoms are reported. In each case the adsorption energy is compared to that of two atoms occupying the same sites without interaction (Δ*E*_{ads} in Table 4) and to the more stable chemisorption configuration where both atoms are chemisorbed on hcp sites, without interaction (labeled Inf in Table 4). Concerning the nearest neighbor adsorption sites, i.e., h¹/f¹ the adsorption energy decreases smoothly with the size of the cluster showing that the size effects are not negligible. Nevertheless, in each case, the chemisorption is dissociative which is not the case for the infinite surface.³² Chemisorption on these sites shows that a significant electrostatic repulsion arises between both atoms due to the electron transfer from the cluster to the H atoms (*q*(H) = –0.13 e). On the other hand, electrostatic repulsion is partially compensated by a small chemical binding energy, the bond order of the H–H bond being equal to 0.10. The h¹/h² interaction (Pd₇, Pd₁₀) is not more stable than the h¹/f¹ configuration. In that case the net charges of the H atoms are the same, but the electrostatic repulsion is smaller due to a larger H–H distance. On the other hand, there is no more attractive chemical binding between both atoms. Finally, the h¹/h³ configuration is the more stable on the Pd₁₀ cluster, but there is always a repulsive energy of the order of 0.17 eV.

V.2. Oxygen–Oxygen Interactions. Oxygen–oxygen interactions when chemisorbed on Pd₅, Pd₇, and Pd₁₀ are summarized in Table 5. As for hydrogen adsorption, the first atom is chemisorbed on the h¹ site, while the second one is

Table 5. Chemisorption Energy of Two Oxygen Atoms Coadsorbed on Various (111) Sites^b

	sites	<i>E</i>		<i>q</i> (O)		BO(O–O)
		<i>E</i> _{ads}	Δ <i>E</i> _{ads}	O ¹	O ²	
Pd ₅ O ₂	h ¹ /f ¹	–0.25	+1.64	–0.74	–0.70	1.20
	Inf	–2.18				
Pd ₇ O ₂	h ¹ /f ¹	–0.34	+1.58	–0.73	–0.62	1.13
Pd ₇ O ₂	h ¹ /h ²	–1.30	+0.70	–0.61	–0.61	0.03
	Inf	–2.0				
Pd ₁₀ O ₂	h ¹ /f ¹	–0.29	+1.42	–0.72	–0.66	1.17
Pd ₁₀ O ₂	h ¹ /h ²	–1.42	+0.37	–0.65	–0.52	0.04
Pd ₁₀ O ₂	h ¹ /f ²	–1.48	+0.22	–0.61	–0.50	0.00
Pd ₁₀ O ₂	h ¹ /h ³	–1.75	+0.09	–0.61	–0.61	0.00
	Inf	–1.84				
other work		–2.39 ^a				

^a Reference 2 (experimental). ^b *E*_{ads}(eV) is the O¹ plus O² adsorption energy, *q*(O) is the Mulliken net charge located on each O atom, and BO is the O–O bond order. The different adsorption sites are illustrated in Figure 1.

Table 6. Cluster Size Effects on the Dissociative Chemisorption Energy, Transition State Energy, and Physisorption Energy of H₂ and O₂^b

	<i>E</i> _{chem}		<i>E</i> _{TS}		<i>E</i> _{phys}	
	H	O	H	O	H	O
Pd ₅	–0.91	–0.29	+0.15	+0.31	–0.06	–0.42
Pd ₇	–0.72	–0.34	+0.30	+0.33	–0.08	–0.39
Pd ₁₀	–0.59	–0.29	+0.31	+0.35	–0.08	–0.66
other work ^a	–0.694		+0.019			

^a Reference 23 (periodic computations). ^b All values are in eV.

chemisorbed on the other threefold sites: f¹ (5, 7, 10), h² (7, 10), f², and h³ (10). Chemisorption energies as well as charge transfer and bond orders between the two atoms are also reported. Concerning the nearest neighbor adsorption sites, i.e., h¹/f¹ the adsorption energy decreases significantly with the size of the cluster showing that the size effects are not negligible. In each case, the chemisorption is not dissociative, the physisorption energy being lower in energy (see Table 6). Chemisorption on these sites show that a strong electrostatic repulsion arises between both atoms due to the electron transfer from the cluster to the O atoms (*q*(O) = –0.72 e). On the other hand, electrostatic repulsion is significantly compensated by a non-negligible chemical binding energy, the O–O bond order being equal to 1.20. Nevertheless the chemisorption energy becomes six times smaller compared to the case where the two O atoms chemisorb without interaction. Contrarily to the case of hydrogen adsorption, the h¹/h² configuration for oxygen adsorption on Pd₇ and Pd₁₀ is much more stable than the h¹/f¹. In that case the net charges of the O atoms are slightly lower, and the electrostatic repulsion is smaller due to a larger O–O distance. The chemical binding between both atoms becomes very small. Finally, the h¹/h³ configuration is the more stable on the Pd₁₀ cluster, with a repulsive energy decreasing to 0.09 eV.

VI. Conclusion

We present first-principle calculations of some properties of the dissociative interaction of hydrogen and oxygen molecules on Pd₅, Pd₇, and Pd₁₀ palladium clusters.

In the first part of our work, we studied the adsorption of a single hydrogen and oxygen atom. In both cases, we find that there is no cluster size effect on the H (O) adsorption energies which are equal on the three clusters when we compare the same types of adsorption sites. The hcp and fcc threefold hollow sites are found to be the most stable without a significant energy gap. The calculation of the energy barriers shows that both atoms can diffuse over a (111) palladium surface.

In the second part, we investigated the adsorption of H₂ and O₂ on the small two-layer Pd₅ cluster. Our results show that H₂ adsorbs dissociatively on the Pd₅ cluster with an electron transfer from the surface toward each hydrogen atom of about 0.13 e[–]. Due to this small negative charge carried by each hydrogen atom there is a weak electrostatic repulsive effect between both hydrogen atoms. It induces a weak destabilization of the adsorption energies relatively to a single adsorption. For oxygen adsorption, our calculations show that O₂ cannot adsorb dissociatively on the Pd₅ cluster because the only two available threefold sites are too close. When O₂ adsorbs on the cluster's surface, there is an electron transfer toward each oxygen atom of about 0.75 e[–] which induces a strong O–O repulsive effect due to the short distance between them. Due to this electrostatic effect, the physisorbed state on Pd₅ is found to be more stable than the chemisorbed one.

In the last part of this work we investigated the coadsorption H–H or O–O on various three-hollow sites. Due to the adsorbate–adsorbate electrostatic repulsive interactions, there is a size effect which depends on the number of threefold hollow sites available on the cluster surface. This effect is stronger for oxygen than for hydrogen because the electron transfer toward oxygen atoms is greater than on hydrogen atoms.

This study clearly shows that the dissociative chemisorption of H₂ and more especially of O₂ on a small palladium cluster may lead to erroneous binding energies due to the cluster shape: the close threefold hollow sites on the cluster's surface may prevent an accurate description of the adsorbate–adsorbate interactions as a function of their distance. However, a good choice of both the size and the shape of the cluster can lead to a good description of the dissociative adsorption process of H₂ and O₂ on an infinite (111) palladium surface.

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