Density functional study of hydrogen adsorption and dissociation on small Pd$_n$ (n = 1–7) clusters

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ABSTRACT

Density functional theory has been performed to investigate the interaction of H$_2$ and Pd$_n$ clusters (n = 1–7). The local minima configurations for different H$_2$ molecule approach modes towards Pd$_n$ clusters are presented. Our results show that in some cases H$_2$ is physically adsorbed around Pd atom, and in other cases H$_2$ is dissociated to be H atoms. Except for PdH2, Pd$_n$ clusters with H atoms dissociatively adsorbed are most stable. For these most stable PdnH2 clusters ($n \geqslant 2$), the binding energy of hydrogen atom decreases as the number of Pd atom increases until n = 4, and when $n \geqslant 4$, the binding energy almost keeps constant with the H atoms bound sites changing from Pd–Pd bonds to Pd triangle planes. Besides, the adsorption of H$_2$ on other low-lying isomers of Pd$_n$ clusters is also discussed.

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1. Introduction

Palladium is a promising candidate for catalytic applications, particularly for the Pd clusters in the reaction of hydrogenation and dehydrogenation [1,2]. Recently, Pd nanoparticles are used as catalyst to dissociate H$_2$ into H atoms in the process of hydrogen chemisorption on the carbon nanotubes (CNTs) [3–6]. Yoo et al. investigated the hydrogen storage of carbon nanotubes with Pd and La as catalyst [5]. They found that the deposited Pd nanoparticles on the tubes could dissociate H$_2$ with these H atoms stored on the tube surface. Ansón et al. reported that after loading palladium on carbon nanotubes, the hydrogen isotherms presented a steep increase at very low pressure [6]. To improve the catalyst efficiency of Pd nanoparticles, it is important to investigate the hydrogen activation by Pd clusters first.

Experiments showed that the interaction of hydrogen molecules with palladium clusters was strongly dependent on the cluster size [7–10]. Theoretically, there are many studies reported to investigate the law of the interaction between H$_2$ and Pd clusters. Cui et al. studied the electronic structure of Pd$_2$/Pd$_3$ and the reaction mechanism of H$_2$ activation on these clusters with density functional theory on the B3LYP level [11,12]. German et al. analyzed the singlet and triplet potential energy surface cross-sections for many reaction pathways of the interaction between a H$_2$ and a palladium tetramer in detail [13]. Roques et al. studied the properties of the dissociative adsorption of hydrogen molecules on Pd

clusters (n = 5, 7, 10) and compared them with that on infinite Pd (111) surface [14]. Except for the adsorption of single H$_2$, Moc et al. investigated the adsorption of multiple H$_2$ molecules around Pd$_n$ (n = 3, 4, 5) clusters [15,16], and Wang et al. [17] studied that on Pd$_6$ cluster.

Above studies have carefully investigated the H$_2$ activation on each Pd$_n$ cluster. However, the systemical discussion on the size-dependence of the reactivity of Pd clusters with the hydrogen molecules are restricted to n = 1–4 [18]. In this paper, by using the first-principles calculations, we investigated the hydrogen molecules activation by Pd$_n$ clusters (n = 1–7): providing the most stable PdnH2 structures and analyzing the electronic property changes of the structures before and after the adsorption of H atoms.

2. Computational method

The calculations are performed with the density functional theory implemented in Dmol^3 package [19,20]. The spin-unrestricted treatment is carried out with double numerical plus polarization basis set (DNP) and generalized gradient approximation with revised Perdew–Burke–Ernzerhof (RPBE) functional [21]. The core electrons are described with an effective core potential (ECP), which accounts for the relativistic effect expected to be important for heavy element [22,23]. In order to test the accuracy of the methods, we have calculated the bond lengths and binding energies of the Pd$_2$, H$_2$, PdH molecules. The results are presented in Table 1. It shows that the binding energies of these molecules fall within the margin of experimental error, and bond lengths are in agreement with the experimental results.

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Table 1
Bond length (in Å) and binding energy (in eV) of Pd_2, H_2, Pd–H molecules.

Model		RPBE	Experiment
Pd_2	$d_{Pd–Pd}$	2.615	2.480[a]
	E_b	0.72	0.74 ± 0.26; 1.12 ± 0.24[b]
H_2	$d_{H–H}$	0.747	0.730
	E_b	4.68	4.48
Pd–H	$d_{Pd–H}$	1.555	1.534[c]; 1.529[a]
	E_b	2.25	2.39 ± 0.26[d]

[a] Ref. [24].
[b] Ref. [25].
[c] Ref. [26].
[d] Ref. [27].

3. Results

Pd$_n$ (n = 1–7) clusters are first studied. The cluster structural search scheme used here is to add a new Pd atom on the preceding stable clusters at possible binding sites, and then perform the geometry optimization without symmetry restriction. We obtain many structures of Pd$_n$. To identify whether these structures are in the stable state, frequency calculations have been carried out. The lowest-energy structures and next low-lying isomers with relevant binding energy per Pd atom are shown in Fig. 1. There is no imaginary frequency for all the structures, which proves that all the Pd clusters presented correspond to genuine minima on the respective potential energy surfaces.

For Pd$_2$, the ground state structure is in the triplet state with Pd–Pd length of 2.615 Å. For Pd$_3$, the ground state is an isosceles triangle with two edges slightly shorter due to the Jahn-Teller effect. The magnetic moment is zero, in agreement with the calculation reported by Luo et al. [28], while Moc et al. and Rogan et al. show that the minimum-energy spin configuration of Pd$_3$ is triplet [15,29]. The lowest-energy structure of Pd$_4$ is a slightly distorted tetrahedron in the triplet state. The second low-lying structure (Pd$_4$_1) is a planar square with the energy substantially higher than the ground state (0.8 eV). In the case of Pd$_5$, the ground state is a triangular bipyramid in the D$_{2h}$ symmetry with the magnetic moment of 2μ_B, which is in agreement with previous studies [16,29,28]. The next low-lying configuration (Pd$_5$_1), 0.035 eV

higher in energy, is a tetragonal pyramid. For Pd$_6$, a tetragonal bipyramid is obtained as the ground state, which is 0.18 eV lower in energy than the structure with C$_{2v}$ symmetry as shown in Fig. 1 named as Pd$_6$_1. Both of these two Pd$_6$ configurations are triplets. The ground state of Pd$_7$ is pentagonal bipyramid with the magnetic moment 2μ_B. The second low-lying state of Pd$_7$ (Pd$_7$_1) is got by locating a Pd atom above the triangle surface of tetragonal bipyramid and then optimizing. The energy difference of the two isomeric structures is 0.079 eV. Similar configurations and spin states of Pd$_7$ are reported by Moseler et al. [30].

In the next part, we investigate the hydrogen activation on the ground state and the second low-lying structures of Pd$_n$ clusters (n = 1–7) by making H$_2$ approach the clusters in different ways. The optimized structures are shown in Fig. 2. The binding energy of hydrogen adsorption is evaluated from the calculated energies of cluster with adsorbate, the bare cluster and the H$_2$ molecule using the following equation:

$$E_b = E_{Pd_n} + E_{H_2} - E_{PdnH2} \qquad (1)$$

3.1. PdH2

The ground state of Pd atom has a closed-shell configuration of $4d^{10}$, thus it is less reactive than those open shell atoms such as Pt. So in our calculations, when H$_2$ approaches with the H–H bond towards Pd atom, the H$_2$ could not dissociate but is molecularly adsorbed as shown in Fig. 2 named as PdH2_a. The H–H distance is elongated from 0.747 to 0.867 Å. The Pd–H bond length is 1.712 Å with the H–Pd–H angle of 29.0°. PdH2_a is the ground state of PdH2, having the binding energy of 0.713 eV/H$_2$. Efremenko et al. also found that PdH2_a is most stable with the similar structural parameters ($d_{Pd–Pd}$ = 1.683 Å, ∠HPdH = 30.4°) [18]. Other isomers of PdH2 are shown in Fig. 2. We find that the dissociative adsorption of H$_2$ on the Pd atom is less favorable than the molecularly adsorbed one, and calculations show that it has to overcome an energy barrier of 0.14 eV for the H$_2$ transforming from the molecular one to the dissociative one. Configuration PdH2_c, for which the H and Pd atoms are in the same line, is much more unstable than the ground state with the H–H bond towards the Pd atom, which is in agreement with the previous report [18].
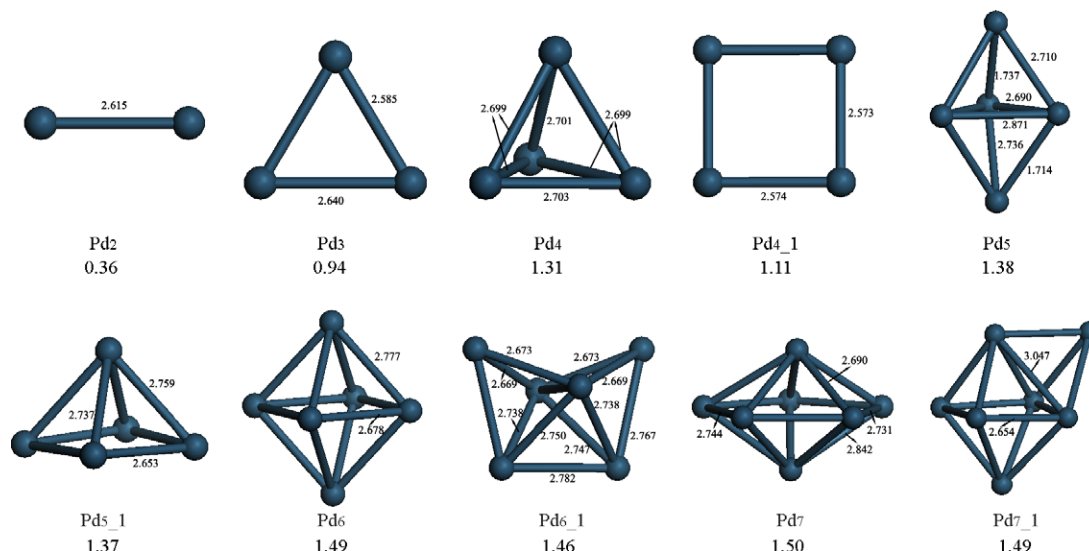
Fig. 1. The ground state and the second low-lying structures of Pd$_n$ (n = 1–7) clusters with the binding energy per Pd atom (E_b) underneath. The bond length is in Å and $E_b = (n E[Pd] - E_t[Pd_n])/n$.
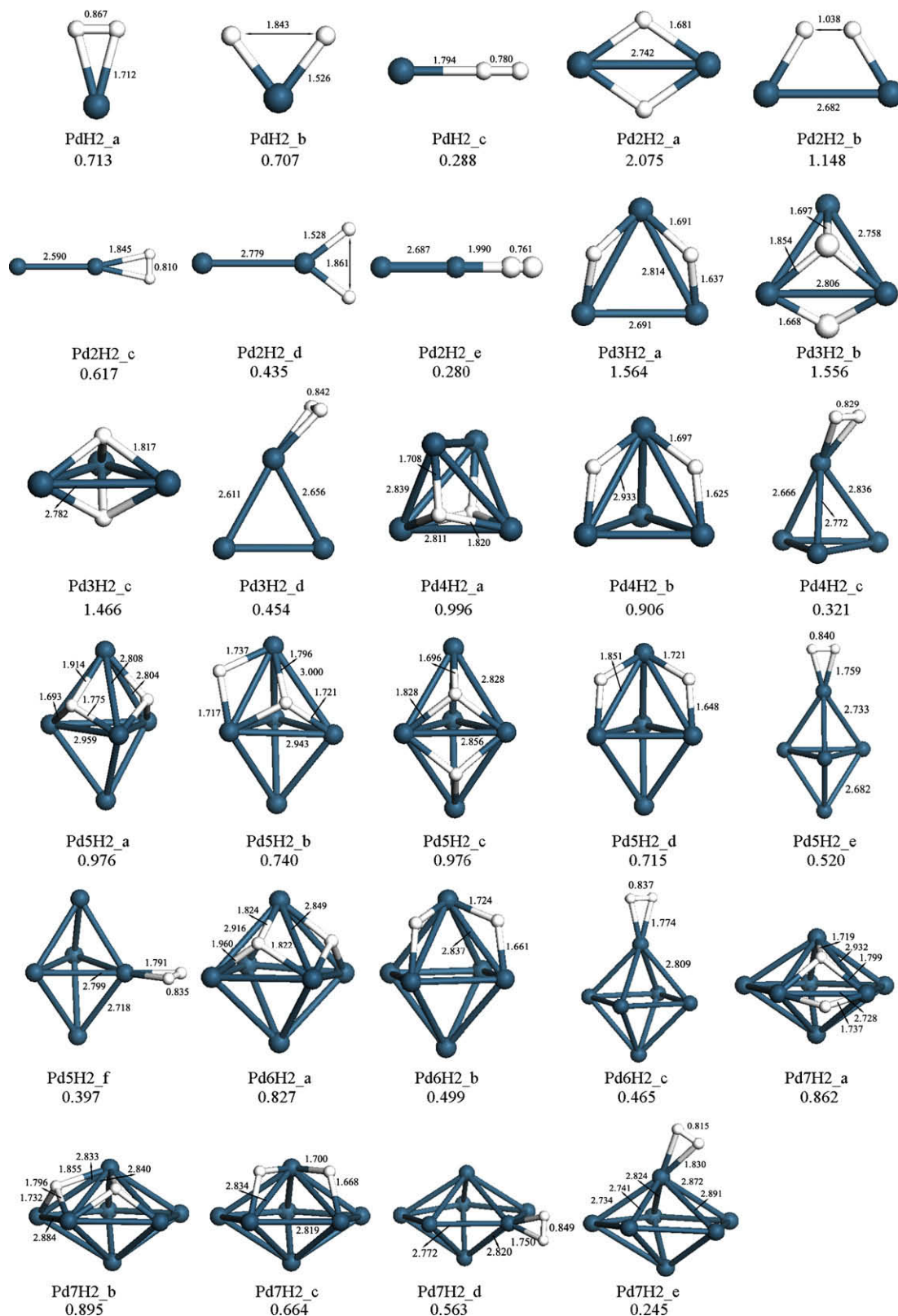
Fig. 2. Optimized geometries of PdnH2 (n = 1–7) clusters. The binding energy per H_2 (eV) is shown underneath and the bond length is in Å.

3.2. Pd2H2

When H_2 approaches Pd dimer with the H–H bond perpendicular to the Pd–Pd bond, it dissociates with both H atoms adsorbed on bridge positions (Pd2H2_a). No activation transition state exits in this process as reported in previous literatures. The ground state Pd2H2_a is a planar structure with the binding energy of 2.075 eV. Cui et al. reported a similar Pd2H2 structure with an H–Pd–Pd–H dihedral angle of 168.5° as the most stable one, which is also included in our calculation [11]. We find that comparing with the

planar configuration, the nonplanar one is 3 meV higher energetically with one imaginary frequency. Parallel approach of H_2 towards Pd_2 makes the H–H bond slightly elongate to 1.038 Å, shown as Pd2H2_b. This structure is metastable with two imaginary frequencies. By analyzing the vibrational modes corresponding to the imaginary frequencies, we speculate that the metastable structure can translate to the ground state (Pd2H2_a). The configurations of Pd2H2_c, Pd2H2_d, Pd2H2_e are obtained by making the H_2 approach Pd atom along the axis of Pd dimmer. Their stability is much less than that of Pd2H2_a and Pd2H2_b with the binding energies no more than 1 eV. Frequency analysis shows that these three configurations are all metastable, which can translate to the structures with both H atoms adsorbed on the bridge site of Pd_2.

3.3. Pd3H2

Configurations of Pd3H2_a, Pd3H2_b and Pd3H2_c can be obtained by direct interaction of H_2 with the Pd_3 cluster. Our results show that the configuration with two H atoms bound on the bridge site (Pd3H2_a) is more stable than the one with H atoms adsorbed on the triangular face (Pd3H2_c). And the stability of the configuration with one H on the bridge site and another on the triangular face (Pd3H2_b) lies between that of Pd3H2_a and Pd3H2_c. These three structures have also been reported by Moc et al. and Cui et al. [15,12]. They found that the total energy difference of the structures Pd3H2_a and Pd3H2_b is very small, which is same as our results. The difference is that in their results the Pd3H2_b is little more stable than Pd3H2_a. In the case of the molecular adsorption of H_2 around Pd atom (Pd3H2_d), the H–H bond is elongated with the binding energy of 0.454 eV. And the Pd–Pd bonds only have a slight change compared with pure Pd_3.

3.4. Pd4H2

For the approach of H_2 towards the lowest-energy state of Pd_4 cluster, we obtain two stable dissociative structures (Pd4H2_a and Pd4H2_b) by overcoming energy barriers. Both of the dissociated H atoms are adsorbed on the adjacent triangular faces or bridge sites, respectively. The binding energy of H atoms on the triangular faces is 0.09 eV higher than that on the bridge sites. These structures are also reported by German et al. and Moc et al. [13,15] in which H atoms on the triangular faces are more favorite with the binding energy about 0.2 eV larger than that on the bridge sites. These two configurations are not the most stable in both our results and previous studies [13,15]. Our calculation also finds that when H_2 approaches the Pd_4 cluster, it is apt to be adsorbed around the Pd atoms, with the binding energy of 0.321 eV (Pd4H2_c).

We also investigate the adsorption of H_2 on the second low-lying structure of Pd_4 cluster (Pd4_1). After the optimization, we find that Pd4_1 is unstable upon the approach of H_2 and the structure changes to be the ground state of Pd_4 (Pd_4) with H_2 adsorbed on it.

3.5. Pd5H2

For the ground state of Pd_5 cluster, we find that when H_2 approaches the Pd–Pd bonds perpendicularly, it dissociates with H atoms adsorbed on the adjacent triangular faces (Pd5H2_a and Pd5H2_c) or with one H atom on the bridge site and another on the triangular face (Pd5H2_b). The binding energy of Pd5H2_a and Pd5H2_c is 0.976 eV, which is larger than the one reported by Moc et al. (0.76 eV) [16]. And for Pd5H2_b, the adsorption energy is less, about 0.740 eV. When H_2 approaches Pd_5 with H–H bond parallel to the Pd triangular face, H–H bond can also break and the H atoms bind on the adjacent bridge sites with the binding energy of 0.715 eV, named as Pd5H2_d. This structure is also found

by Moc et al. which is less stable than Pd5H2 with H atoms adsorbed on the adjacent triangular faces just like the results in our study [16]. For the approach of H_2 towards Pd_5 in other ways, the H_2 can easily move to be absorbed around Pd atoms. There are two kinds of Pd atoms with different coordination number for Pd_5 cluster. Our results show that H_2 molecule adsorbed around threefold coordinated vertex atoms (Pd5H2_e) is more stable than that on fourfold one (Pd5H2_f) with the binding energy 0.123 eV larger.

Calculations of the adsorption of H_2 around Pd5_1 show that upon the approach of H_2 towards Pd atoms, two different results are obtained. For the first one, H_2 can be bound around Pd atoms of Pd5_1 with a much lower binding energy of 0.19 eV, comparing with that of H_2 adsorbed around Pd atom of the ground state structure Pd_5, and for the second one, the adsorption of H_2 makes the configuration Pd5_1 transform to be the ground state of Pd_5 (Pd_5).

3.6. Pd6H2

The Pd_6 cluster is a octahedron structure. We have tried many ways for the H_2 approaching it. The results show that when H_2 approaches the bridge site of Pd_6 cluster with the H–H bond perpendicular to the Pd–Pd bond, H_2 could dissociate with both H atoms adsorbed on the adjacent triangular faces (Pd6H2_a). The binding energy is calculated to be 0.827 eV/H_2 with magnetic moment zero. If H_2 approaches the center of the triangular face with the H–H bond parallel to the face and Pd–Pd bond, the dissociated H atoms would be adsorbed on the adjacent Pd–Pd bonds (Pd6H2_b) with the total energy 0.328 eV higher than that with the H atoms adsorbed on the triangular faces (Pd6H2_a). In other cases when H_2 approaches from other directions, it always moves to be physically adsorbed around the Pd atoms. The binding energy is 0.465 eV and the H–H distance is elongated to be 0.837 Å, as shown in Pd6H2_c.

When H_2 approaches the second low-lying structure of Pd_6, we find similar phenomena as found in Pd4_1 and Pd5_1: upon the approach of H_2, Pd6_1 may change to be the ground state of Pd_6 (Pd_6), or H_2 is adsorbed around the Pd atoms of Pd6_1 with a similar binding energy of 0.48 eV as that around the ground state structure of Pd_6.

3.7. Pd7H2

The ground state of Pd_7 is a pentagonal bipyramid. Many approaching ways of H_2 towards the cluster are tried. Our results show that H_2 could be dissociated in three ways. When H_2 approaches perpendicularly to the Pd–Pd bond which is in the base-pentagonal plane, it is dissociated with one H atom adsorbed on the bridge site and another adsorbed on the triangular face (Pd7H2_a). The magnetic moment is zero with the hydrogen binding energy of 0.862 eV/H_2. If H_2 approaches perpendicular to the Pd–Pd bond which connects the vertex atoms and basal plane atoms, H_2 is dissociated with both H atoms adsorbed on the adjacent triangular faces (Pd7H2_b). The binding energy is 0.895 eV/H_2. If H_2 approaches the triangular face with the H–H bond parallel to the basal plane bonds, it could dissociate with the dissociated hydrogen atoms adsorbed on the adjacent Pd–Pd bonds as shown in Pd7H2_c. The total energy is 0.231 eV higher than that with both H atoms adsorbed on the adjacent triangular faces. For other approach modes of H_2 towards the Pd_7 cluster, H_2 always moves to be physisorbed around Pd atoms (Pd7H2_d and Pd7H2_e). Like the structure of Pd_5, there are two different kinds of Pd atoms in the ground state structure of Pd_7. The results show that H_2 prefers being adsorbed around the fourfold coordinated Pd atoms than on fivefold coordinated Pd with the binding energies of 0.563 and 0.245 eV, respectively.
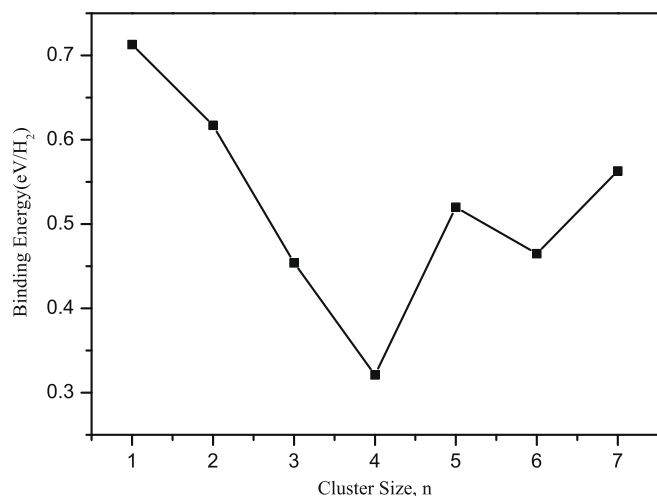
Fig. 3. Size dependence of the hydrogen binding energy for the PdnH2 structures with the H_2 molecularly adsorbed around the Pd atoms.

Interestingly, we find the binding energies of H_2 adsorbed around the Pd atoms of the second low-lying state configuration of Pd_7 (Pd_7_1) are between 0.588 and 0.666 eV, which are larger than that on the lowest-energy structure of Pd_7 (Pd_7). And similar to the above studies, the Pd_7_1 structure can change to be the ground state structure (Pd_7) upon the adsorption of H_2.

4. Discussion

The direct interaction of H_2 with Pd_n clusters (n = 1–7) in different approaching ways has been investigated. Our results show that the H_2 could easily move to be molecularly adsorbed around Pd atoms, and also can be dissociated by overcoming certain barriers with the dissociated H atoms adsorbed on the surface of the clusters. As for the molecular adsorption of H_2 around Pd atoms, the frequency analysis shows that these structures are not the stable state with imaginary frequency for every one. It indicates that the molecular adsorption of H_2 around Pd atom is precursor state, which will change to be dissociative one with H atoms adsorbed on the surface. Fig. 3 shows the size dependence of the binding energy of H_2 physisorbed around the Pd atom with the H–H bond towards the Pd atoms. For n = 5 and 7, we choose the larger binding energy. It is shown that as the number of Pd atoms in the clusters in-

creases, the binding energy decreases first and then increases with n = 4 lowest. Compared with the physisorption of H_2 on the Pd (111) surface [31], where the binding energy is 0.21 eV/H_2, the binding energy of H_2 on the cluster is higher. The Hirshfeld population calculation shows that the electron transfer between the H atoms and Pd atoms is almost zero and the molecular adsorption of H_2 does not affect the magnetic moment of the clusters.

Using the method of the direct interaction of H_2 and Pd_n clusters, we cannot find all the possible configurations of PdnH2 and so can not identify the most stable configurations of PdnH2. Therefore, next we try to find all the possible PdnH2 structures by locating two H atoms at different sites of the Pd_n clusters and performing the optimization.

Our results find that the PdnH2 structures are less stable when the H atoms bond to the Pd atom than around Pd–Pd bonds or Pd triangular faces. Fig. 4 presents the most stable configurations of the PdnH2 clusters. All the structures are stable with no imaginary frequency. The most stable configurations of PdnH2 (n = 1–3) have been included in the above discussion. In the following, we will discuss the structures of PdnH2 (n = 4–7). For Pd4H2, the structure with two H atoms adsorbed on the two Pd–Pd bonds, which is not adjacent, is most stable. This is consistent with all the previous studies [13,15,18]. And the hydrogen binding energy of 1.311 eV/ H_2 is also in the range of other theoretical results. For Pd5H2, the most stable structure is the configuration with two H atoms adsorbed on the triangular faces, which have one common Pd atom. Moc et al. also reported the similar structure as the most stable one, and there is only some difference in the binding energy and geometrical parameters from ours, which may be caused by the different calculation methods used [16]. As for Pd6H2, the structure is most stable when the two H atoms are adsorbed on the triangular faces which are not adjacent at all. The most stable dihydride Pd6H2 reported by Wang et al. is on the triplet potential energy surface, and our results show that the energy of the dihydride Pd6H2 in singlet state is much lower [17]. Similar to Pd6H2, Pd7H2 with the two H atoms adsorbed on the triangular faces which are not adjacent at all is most stable.

Compared these most stable configurations, we find that for n = 2–4, the H atoms prefer to be bound on the bridge sites of the Pd–Pd bonds, and for n = 5–7, the binding energies of PdnH2 cluster with H atoms adsorbed on the Pd triangle planes are larger. The change of hydrogen locating sites in the most stable PdnH2 clusters indicates that hydrogen adsorption on the clusters gradually likes to be on the Pd bulk surface when $n \geqslant 4$, because as reported in the previous studies, the adsorption of H atom on the
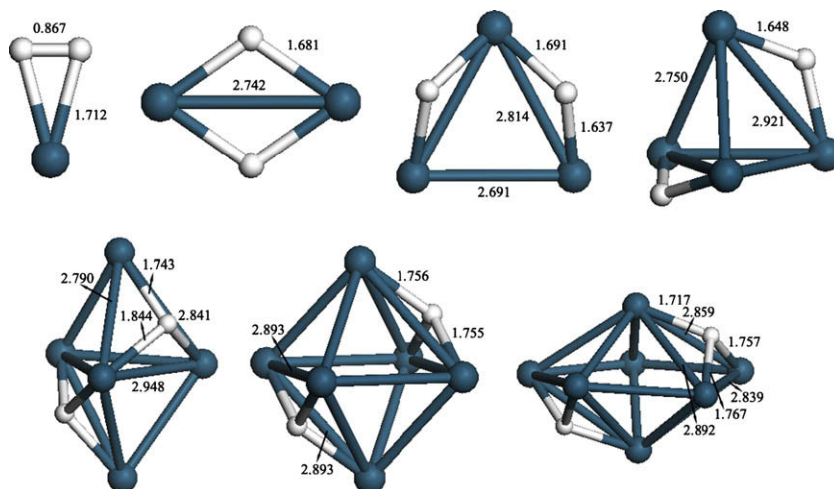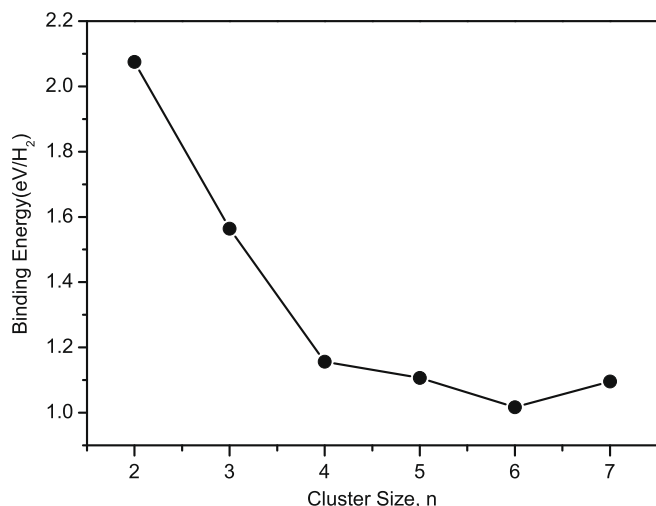

Fig. 4. The most stable configurations of PdnH2 clusters with the H_2 dissociatively adsorbed.

Fig. 5. Size dependence of the hydrogen binding energy for the most stable PdnH2 clusters.

Table 2
Binding energy per H_2, HOMO–LUMO gap, Hirshfeld charge on per H atom for PdnH2 clusters in their most stable dissociative configurations. The data in the parentheses mean the HOMO–LUMO gaps of the Pd_n clusters.

n	E_b (eV)	Gap (eV)	Charge (e)
2	2.075	2.014 (0.352)	−0.1257
3	1.564	1.179 (0.303)	−0.1235
4	1.156	0.759 (0.629)	−0.1358
5	1.107	0.547 (0.133)	−0.1340
6	1.017	0.396 (0.239)	−0.1374
7	1.096	0.249 (0.348)	−0.1390

threefold hollow site of the bulk Pd surface is also the most stable [32,31].

Fig. 5 shows the size dependence of the binding energy for the hydrogen dissociative adsorption on the Pd_n cluster. The binding energy of H atoms decreases as the number of Pd atom increases. For $n \geqslant 4$ the binding energy is around 1.00 eV, which is similar to the binding energy of H atoms adsorbed on the bulk Pd surface [31].

The dissociative adsorption of H_2 on the Pd_n cluster is dictated by a charge transfer process, in which the hydrogen atom gets the electron from the nearby Pd atoms. Table 2 shows the calculated Hirshfeld charges of H atoms in the most stable state. The data show that the electron got by H atom which is adsorbed on the bridge sites of Pd–Pd bond is obviously less than that on the triangular faces and as the number of Pd atoms increases, the charges on H atoms increase slightly. Calculation of magnetic moments of PdnH2 shows that dissociative adsorption of H atoms makes all the Pd_n clusters nonmagnetic. We also calculate the gaps of Pd_n and PdnH2 clusters, as shown in Table 2. We find that the gaps of PdnH2 decrease as the number of Pd atoms increases, and for the Pd_n, there is no such rule. Compared with the gaps of Pd_n clusters with or without hydrogen atoms adsorbed, it shows that for $n = 2$–6, the gaps of the PdnH2 are larger than that of Pd_n clusters, especially for Pd2H2 and Pd3H2.

5. Conclusion

In this paper, we calculate the stable configurations for the molecular and dissociative adsorption of H_2 on Pd_n clusters. For the molecular adsorption, H_2 is easily adsorbed around the Pd atoms. The binding energy is larger than that of H_2 adsorbed on the bulk Pd surface. For the dissociative adsorption of H_2 on the Pd_n, the hydrogen atoms are most stable to be adsorbed on the bridge site of Pd–Pd bonds for $n = 2$–4, while for $n = 5$–7, the PdnH2 configurations with H atoms adsorbed on the triangle are most stable. Hirshfeld population analysis shows that H atoms dissociatively adsorbed on the Pd_n clusters get electron from the nearby Pd atoms, and the amount of electron obtained slightly increases as the number of Pd atoms increases.

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