Hydrogen chemisorption on palladium surface in a high electric field

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Interaction of hydrogen with palladium surface in the presence of high electric field leads to the formation of complexes, which have been recorded as PdH_x^+ (x = 1, 2, 3, 4). In the present work, quantum chemical calculations with Becke's three parameter hybrid functional using the LYP correlation functional (B3LYP) for hydrogen interaction with both single palladium atom and four- or six-atom clusters (such us tetra- and octahedral voids) have been performed. The binding energies, ionization potentials and free-space dipole moments for PdH_x (x = 1, 2, 3, 4) molecules have been determined and the "critical" field values, characteristic of palladium hydrides field dissociation have been determined. The model of hydrogen adsorption in the threefold hollow site on the surface together with a subsurface interstitial chemisorption has been discussed. It has been found that hydrogen is bound more strongly in the tetrahedral void than in the octahedral one.

Keywords: *ab initio* calculations, metal hydrides, hydrogen chemisorption.

1. Introduction

Due to special activity of palladium as a catalyst for the hydrogenation reaction, the adsorption of hydrogen on its different surfaces has been the subject of a wide variety of both experimental and theoretical investigations. The ability of hydrogen atoms to penetrate the near surface regions of the palladium crystals has been proved on the basis of the thermal desorption studies [1–6]. Thus, the possibility of accommodating a large amount of hydrogen in a small volume enables Pd/H systems to be used as an energy storage.

It is known from the low energy electron diffraction (LEED) studies that hydrogen creates ordered chemisorbed H-phases on the palladium surfaces. In the case of Pd(111) the appearance of two distinct ordered phases with $(\sqrt{3} \times \sqrt{3})R30°$ symmetry at the coverage of 1/3 and 2/3 monolayer has been reported [7]. Under the influence of hydrogen adatoms the changes of Pd(110) surface structure from (1×1) over a (2×1) into a (1×2) have been observed [4]. The final structure is believed to be due to the surface reconstruction.

Duś *et al*. [*eg*. 8] maintain that H_2 interaction with the thin palladium films at a constant temperature of 78 K leads to the formation of PdH_x ($x \approx 0.9$). They have

found two different hydrogen adspecies on Pd surface in the process of hydrogen formation: i) the negatively polarized atomic adspecies, being formed at the beginning of the process, referred to as β^-, and ii) the positively polarized atomic adspecies, arising with the increasing coverage, referred to as β^+. Whereas the β^- seems to be stable on the surface, the β^+ incorporates quickly into the bulk forming hydrides.

The occurrence of hydride ions in the course of the field evaporation process of palladium in hydrogen atmosphere, studied by the magnetic sector atom-probe FIM has been detected [9]. Also, Stępień and Tsong [10] having studied the same process by using the pulsed-laser time-of-flight atom-probe FIM have recorded the occurrence of Pd^+, PdH^+, PdH_2^+, PdH_3^+ and PdH_4^+.

The observed ions seem to be formed after the processes of field desorption and ionization of the respective molecules.

In this paper, we are interested in studying how the presence of an external electric field of the magnitude of several tens of volts per nanometer influences the binding characteristics of PdH_x ($x = 1, 2, 3, 4$) molecules. To solve this problem some quantum chemical calculations based on the density functional theory (DFT) have been performed.

In addition, the process of hydrogen diffusion from the surface into tetra- and octahedral voids in the zero field case has been considered.

2. Methods

For numerical calculations the GAUSSIAN 98 program package [11] was employed. The self-consistent field *ab initio* method with Becke's hybrid functional [12] has been used.

In this functional the exchange functional is a linear combination of the Hartree–Fock exchange and the density-functional theory exchange-correlation having the following form:

$$A^* E_x^{\text{Slater}} + (1 - A)^* E_x^{\text{HF}} + B^* \Delta E_x^{\text{Becke}} + E_c^{\text{VWN}} + C^* \Delta E_c^{\text{non-local}} \tag{1}$$

where the non-local correlation is provided by the LYP expression [13], the VWN correlation functional has been described by Vosko *et al.* [14] and the constants A, B, C have been determined by Becke by fitting to the $G1$ molecule set. The basis set taken for a palladium atom has been CEP-4G [15], since, as for palladium, it is known to give the best accuracy in the all electron calculations.

3. Results and discussion

The first step of our work was to determine the binding characteristics of PdH_x ($x = 1, 2, 3, 4$).

In Table 1, the theoretical values of binding energy (per H atom), ionization potential and free-space dipole moment of palladium hydride species are compiled.

T a b l e 1. Binding characteristics of palladium hydrides in the equilibrium states.

Hydrides	Binding energy [eV]	Ionization potential [eV]	Dipole moment [Debye unit]
PdH	3.20	8.82	2.079
PdH_2	3.38	8.76	2.191
PdH_3	3.27	8.74	2.742
PdH_4	2.98	9.35	0.288

T a b l e 2. Geometry of palladium hydride molecules in the equilibrium states.

Molecule	Pd–H distance [nm]	H–Pd–H angle [deg]
PdH	0.167	—
PdH_2	0.154	72.0
	0.154	
PdH_3	0.162	20.5
	0.216	
	0.216	
PdH_4	0.165	86.8
	0.165	86.8
	0.151	76.4
	0.151	

In addition, the values of bond lengths and valence angles of the molecules in the equilibrium states are summarized in Tab. 2. The geometry of the molecules has been optimized relative to the total energy minimum with respect to all independent internal coordinates (bond length, valence and dihedral angles). The binding energy has been calculated according to the following equation:

$$E_b = \frac{E_{total}(PdH_x) - \left[E_{total}(Pd) + x\,E_{total}(H)\right]}{x}, \quad x = 1, 2, 3, 4 \tag{2}$$

where $E_{total}(PdH_x)$ is the total energy of the system considered, $E_{total}(Pd)$ and $E_{total}(H)$ are the total energies of palladium atom and interacting hydrogen atom/atoms.

All the molecules considered seem to be stable in free space in the absence of an electric field. The field desorption process in which palladium hydride ions were recorded took place in the field of 26.7 V/nm [10]. In the present study, we are interested whether in such electric fields the palladium-hydrogen systems are still stable.

In order to answer the above question, the total energy scan for PdH and PdH^+, as a function of the separation distance between Pd and H atoms, both in the absence and in the presence of an external electric field was done. The results are shown in Figs. 1 and 2. The electric vector in our computations is parallel to the molecular z axis.

The following conclusions can be drawn from the diagrams presented:
 – the external electric field hardly changes the geometry of PdH,
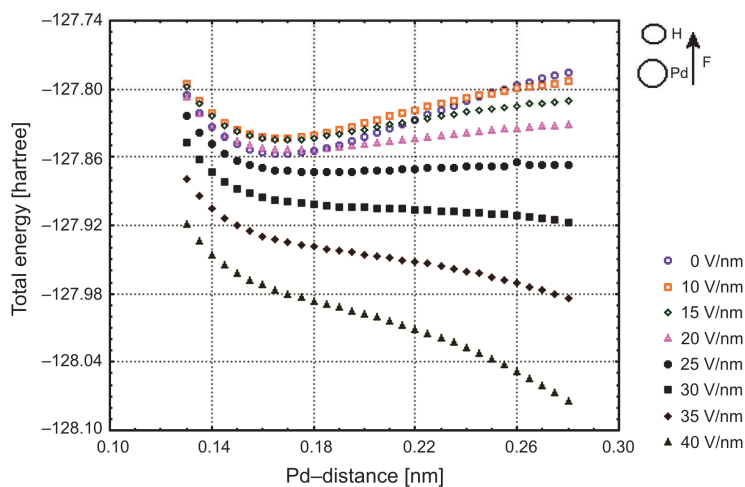 – in the case of PdH^+, a small increase of the bond length is observed,

Fig. 1. Total energy changes depending on the hydrogen–palladium distance.
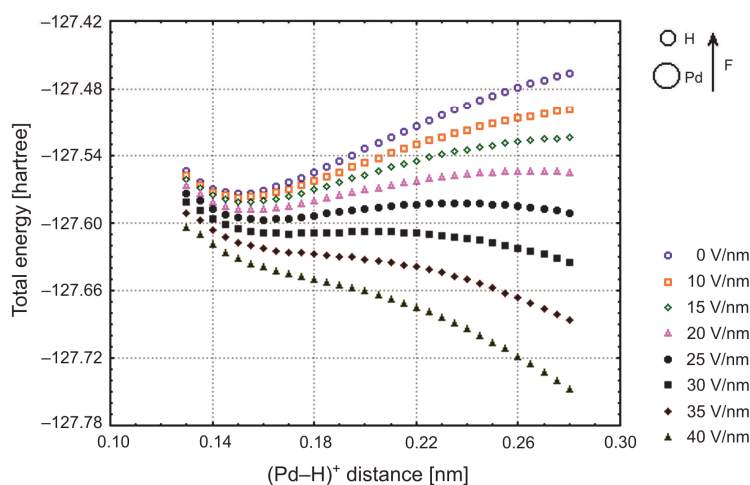

Fig. 2. Calculated total energy changes of $(Pd–H)^+$ depending on the distance.

– in the field of 30 V/nm the disintegration of PdH is observed; the "critical" field value for PdH^+ seems to be 35 V/nm,

– the minimum of the total energy decreases with the increasing electric field strength.

Next, the potential energy surfaces (PES) for PdH_2 have been reconstructed. In Fig. 3, the PES in the case of zero field and with an electric field of the magnitude of 40 V/nm are presented. It is interesting to note, that PdH_2 species do not dissociate in the field of the order of 40 V/nm, which was the highest studied.

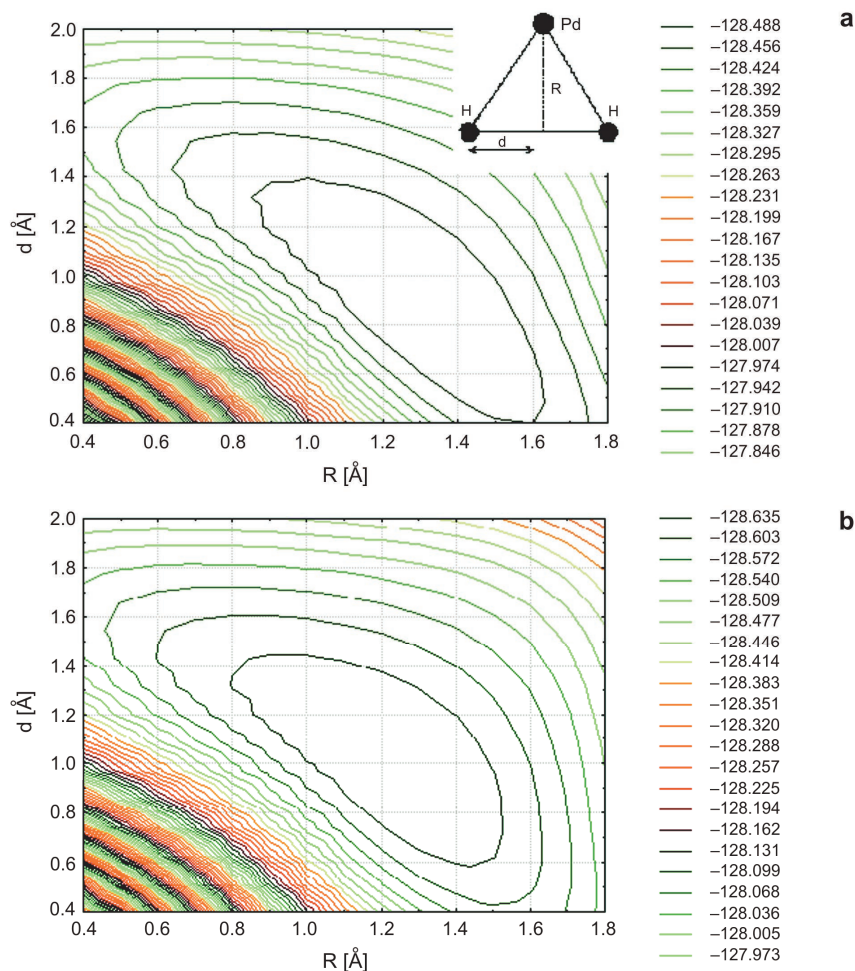Fig. 3. Contour plots of the potential energy surface for PdH$_2$: 0 V/nm (**a**), 40 V/nm (**b**).

For the zero field case a minimum is seen for the following values: $R = 0.125$ nm and $d = 0.09$ nm (the meaning of these parameters is shown in Fig. 3). Due to the applied electric field, the hydrogen–hydrogen distance increases and the distance between the palladium atom and the mass center of H–H system decreases. The values of parameters R and d depending on the electric field strength are listed in Tab. 3.

On the basis of the above results, changes of the bond length r and the angle between the hydrogen–hydrogen bonds α in the PdH$_2$ equilibrium state have been studied. Although the presence of an external electric field leads to the increase of the angle between palladium–hydrogen bonds, the hydrogen–palladium distance remains practically constant.

T a b l e 3. Geometry of the PdH$_2$ in the equilibrium state depending on the applied field value.

Field [V/nm]	R [nm]	d [nm]	α [deg]	r [nm]
0	0.125	0.090	71.5	0.154
10	0.123	0.092	73.6	0.154
20	0.121	0.095	76.3	0.154
30	0.120	0.098	78.5	0.155
40	0.118	0.100	81.0	0.155

Similar investigations have been made for PdH$_2^+$ ion and the results are given in Fig. 4 and Tab. 4. They show that the presence of the external electric field elongates palladium–hydrogen bonds and increases the angle between the bonds.

Since it is known that metal hydrides are defined as interstitial compounds in which hydrogen atoms occupy the position inside the tetra- or octahedral voids, the next goal
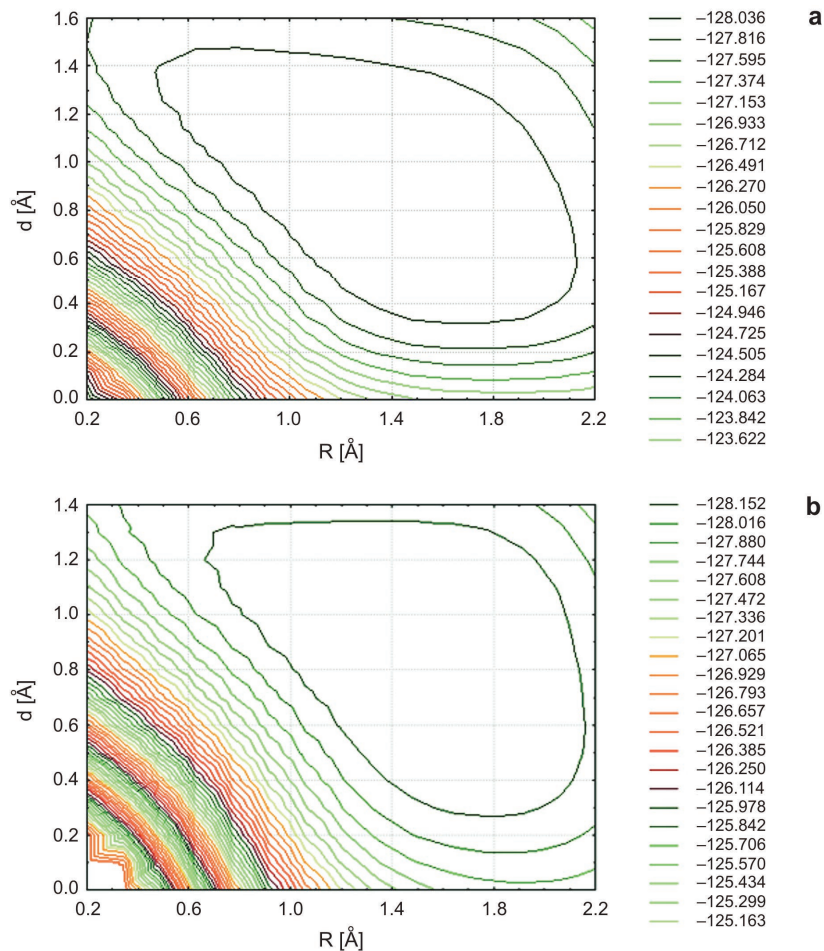

Fig. 4. Contour plots of the potential energy surface for PdH$_2^+$: 0 V/nm (**a**), 40 V/nm (**b**).

T a b l e 4. Geometry of the PdH_2^+ in the equilibrium state depending on the applied field value.

Field [V/nm]	R [nm]	d [nm]	α [deg]	r [nm]
0	0.195	0.040	46.36	0.199
10	0.195	0.040	46.36	0.199
20	0.195	0.040	46.36	0.199
30	0.200	0.045	50.72	0.205
40	0.200	0.050	56.14	0.206

of this paper is to shed some light on the interaction of hydrogen atom with the clusters consisting of four or six palladium atoms that imitate the model of the tetra- and octahedral voids. In both cases 3-fold hollow sites together with a subsurface interstitial position have been considered.

It is shown in Figs. 5 and 6 that the binding energy of hydrogen in the 3-fold hollow site is equal to 4.79 eV in case of tetrahedral void and 2.25 eV in the second void case. In view of the experimental value of 2.77 eV [2], our results do not seem to be reliable. This can be due to a small number of palladium atoms taken into account. Hence, our results should be interpreted only qualitatively.

The diffusion from the surface into the void seems to be an activated process and requires energy of 1.32 eV and 0.92 eV, respectively. On the other hand, the inverse process needs activation energy of 0.16 eV and 0.07 eV.

The binding energy of palladium hydride on the surface between the first and second metal planes amounts to 3.63 eV and 1.40 eV, respectively. Comparing these amounts we can state that hydrogen is bound more strongly in the tetrahedral void.

It is interesting to note that hydrogen atom is located above the center of the void. In the case of the tetrahedral void it is shifted 0.02 nm towards the surface, in the second case the shift is equal to 0.03 nm. This fact can be explained by creating stronger
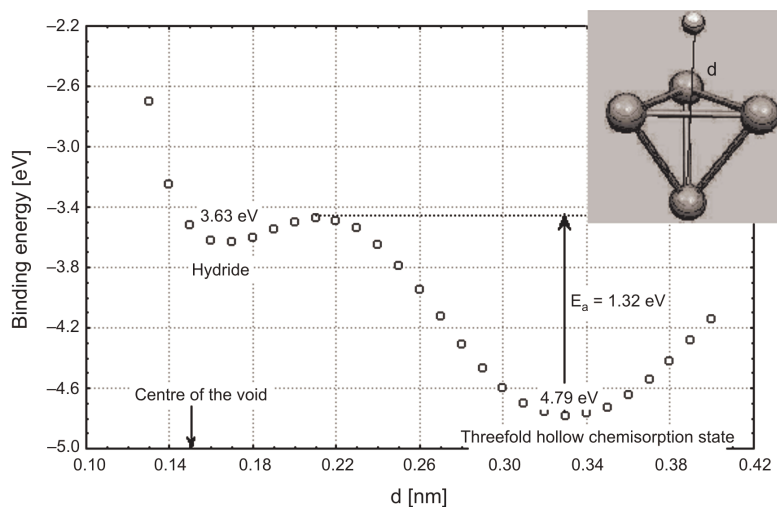

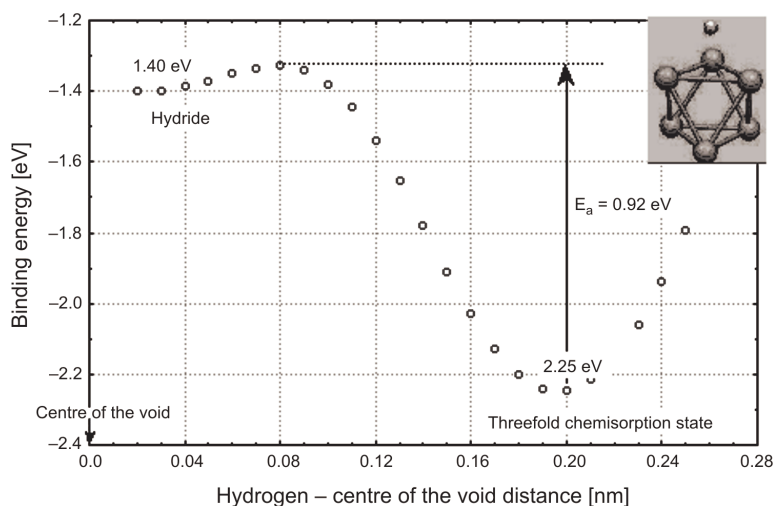Fig. 5. Hydrogen inside the tetrahedral void.

Fig. 6. Hydrogen inside the octahedral void.

palladium hydrogen bonds due to the existence of unsaturated bonds of the surface layer [16].

In view of the results presented, we can state that palladium hydrides are formed near the surface in the interstitial positions of crystal structure, however PdH_x molecules and their ions can exist free in space.

Next, we would like to complement our study of the interaction of a hydrogen atom and palladium clusters with the computation including the influence of external electric fields.

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