

A DFT Study of the Mechanism of the Spontaneous Activation of H₂ by Ni, Pd, Pt, and Pd₂

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The bending energy profiles of ¹A₁ and ³B₂ electronic states have been calculated for the M:H₂ (M = Ni, Pd, and Pt) compounds using three parameters functional (B3LYP). It has been shown that the σ_{H–H}-bond activation leading to the dihydride species in a singlet state is possible for the nickel and platinum atoms, while for Pd, the complex Pd–H₂, weakly bound with respect to Pd(¹S₀) + H₂, is formed spontaneously. In the first case, Ni and Pt, the interaction beginning from the triplet state of the metal center correlates with the hydride species (³B₂ state) after passing a high barrier height (46.5 and 11.5 kcal/mol, for Ni and Pt, respectively). An inter-system crossing favors the activation of the σ_{H–H}-bond in the singlet state (¹A₁). For Pd, another mechanism occurs. The dihydride species may be formed starting from the molecular complex (¹A₁) by a slightly endothermic process through low activation energy (6 kcal/mol). For the Pd₂ dimer, whose ground state is a triplet state, the dissociation of H₂ is similar to that of the Ni and Pt atoms. The mechanism implies an inter-system crossing between the singlet and triplet states. After the crossing point, a nonplanar mechanism implying a folding of the Pd–Pd–H₂ planes is proposed.

1. Introduction

Hydrogen activation by metal centers is an important reaction in commercial processes and basic chemistry. Recent experimental works found that platinum and nickel insertions are spontaneous giving the metal–dihydrides,^{1,2} but η²-coordination of the Pd–H₂ complex is the most favorable compound.^{3–5} The experimental findings are supported by theoretical calculations at the correlated level of theory.^{5–13} All the theoretical works found that the ground electronic state of the M:H₂ (M = Ni, Pd, or Pt) is a singlet state, while the triplet state is a metastable isomer (for Ni and Pt) or an unbound compound (for Pd). They pointed out also that the ground-state structure corresponds to a metal–dihydride (for Ni and Pt) or to a side bonding (η²-coordination) of dihydrogen (for Pd). The latter point was clearly evinced by Balasubramanian et al.^{8,9} in scanning the singlet and triplet potential energy profiles of Pd– and Pt–H₂ at a high level of calculations (CASSCF/CI).

Furthermore, Andrews et al. in a recent combined experimental–theoretical work⁵ showed that two Pd atoms dissociate molecular hydrogen with no activation energy, in agreement with the other theoretical predictions.^{11,12}

Since the electronic properties of a metal center play an important role in such interaction, we present in this paper a comparative study of the potential energy profiles of Ni–, Pd–, and Pt–H₂ in the singlet and triplet electronic states in order to provide some insight into the comprehension of the difference between these compounds. In addition, we report a complete theoretical description of the mechanism of the spontaneous dissociation of H₂ by Pd₂, studying the potential energy profiles of the singlet and triplet states considering four H₂ approaches to the Pd₂ dimer.

2. Results and Discussion

All calculations have been performed with the Gaussian 98 quantum chemical package¹⁴ using a density functional (DFT) method. The DFT calculations have been carried out with Becke's three parameters hybrid method¹⁵ using the Lee–Yang–Parr gradient-corrected correlation functional¹⁶ (denoted as B3LYP). We have used the Stuttgart (MWB) quasi-relativistic pseudo potentials (MWB)^{17,18} for Pd and Pt, which is a semi-core potential (*c*28/*v*18 for Pd and *c*60/*v*18 for Pt, denoted as SDD in the Gaussian code). In SDD, the 18 valence electrons are represented explicitly using the (8*s*7*p*6*d*)/[6*s*5*p*3*d*]-GTO contraction scheme. For the Ni and H atoms, we have used the 6-311++G(2*d*,2*p*) extended basis set of Pople et al.^{19–21}

We have to keep in mind that calculations of total atomic energies as well as of the ordering of the low-lying electronic states are to be checked in terms of the basis set and the functional used. Results obtained with B3LYP (¹S – ³D = 42.2, 18.8, and 8.1 kcal/mol, respectively for Ni, Pd, and Pt) are in good agreement with the experimental²² and previous theoretical data.^{11,23,24} The size-consistency property was also checked when calculating the binding energies.

2.1. Singlet and Triplet States of Ni–, Pd–, and Pt–H₂.

Figure 1 shows the bending potential energy profiles, PEF, of the singlet and triplet states of NiH₂ in the perpendicular approach of Ni to H₂ where the H–H distance was optimized for each value of *R*. As one can readily see, both singlet and triplet states of Ni can dissociate H₂, forming a very weak bend HNiH compound. In line with previous theoretical studies,^{6,7} the ¹A₁ state was found to be slightly more stable than the ³B₂ state. Contrary to the ¹A₁ profiles, the ³B₂ profiles which correlate with the ground state has a large barrier (≈ 46.5 kcal/mol) to insertion. Starting from the Ni(³D) configuration, the dihydride of Ni (in a singlet state) is formed from a switch between two profiles after the first crossing point. This inter-system crossing occurs at *R* = 1.85 Å, with an activation energy

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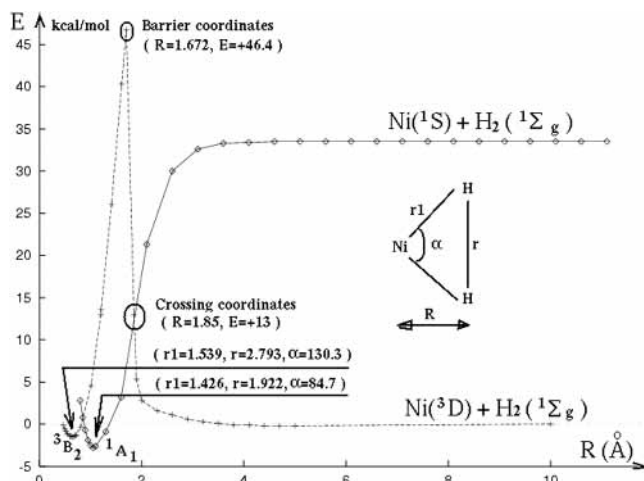


Figure 1. Singlet and triplet potential energy profile (PEF) of NiH₂. Distance (Å) and angle (deg).

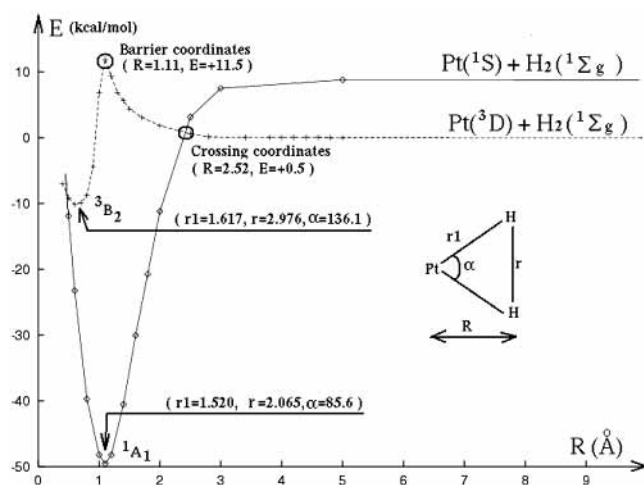


Figure 2. Singlet and triplet PEF of PtH₂. Distance (Å) and angle (deg).

about of 13 kcal/mol. One can consider that the experimental observation of HNiH is only possible when this energy is provided. We note that the detection of the HNiH molecule in argon matrix¹ corroborates this hypothesis, because the nickel metal atoms were prepared using Nd:YAG laser vaporization. As shown in Figure 1, the ¹A₁ and ³B₂ states cross again at $R = 0.82$ Å that has a very low barrier (≈ 0.5 kcal/mol) smaller than the zero-point vibrational energy (ZPVE) of the ³B₂ structure. The latter property allows any way the HNiH molecule to be stabilized, in the ¹A₁ surface, even if the ³B₂ structure were made at first.

Figure 2 displays both singlet and triplet potential energy profiles of PtH₂. The geometrical parameters of the ¹A₁ structure calculated here are very close to those obtained by Balasubramanian using a high level of calculations (CASSCF/CI).⁸ PtH₂ curves qualitatively resemble those of NiH₂. One should note that the barrier on the PtH₂ triplet surface is smaller than that of NiH₂. On the other hand, the inter-system crossing has very low barrier (0.5 kcal/mol) with respect to Pt(³D) + H₂ reference. It explains that the formation of the HPtH molecule should be actually easier than that of the HNiH compound. In addition, the presence of a second crossing point, close to the bottom of the ³B₂ minimum, allows the ³B₂ metastable structure to be passed into the ¹A₁ structure without activation energy.

Figures 3 shows both the singlet and triplet curves of PdH₂ along the reaction path ($R: 10 \rightarrow 0.5$ Å) in a perpendicular

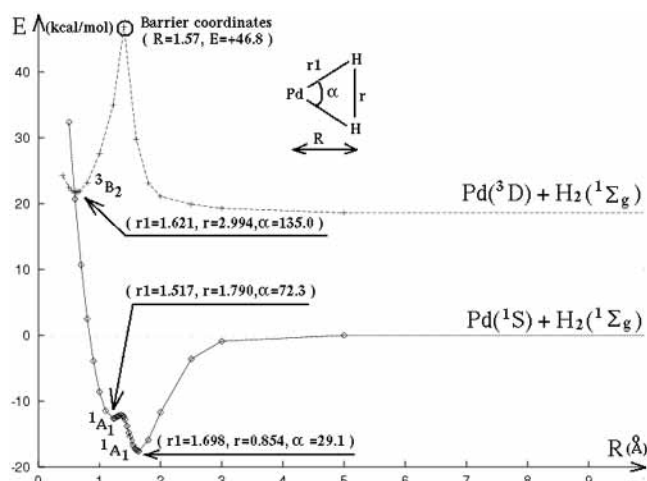


Figure 3. Singlet and triplet PEF of PdH₂. Distance (Å) and angle (deg).

approach. The potential energy curves of PdH₂ significantly differ from both the NiH₂ and PtH₂ ones. The Pd(¹S) electronic state does not favor the presence of a first inter-system crossing point between triplet and singlet states. In agreement with Balasubramanian,⁹ three minima were found for the PdH₂ compound. The most stable of structures corresponds to a weak complex ($D_e = 17.9$ kcal/mol with respect to the fragments in the ground state) in which H₂ is slightly perturbed by Pd(¹S). A second minimum corresponding to a dihydride of Pd was calculated in the singlet surface. The latter dihydride cannot be stabilized because of the very low barrier height (≈ 0.8 kcal/mol smaller than ZPVE) for the isomerization on the ¹A₁ surface. The last minimum was found in the triplet state (³B₂) which corresponds to a dihydride of Pd. This structure was calculated to be unbound with respect to Pd(¹S) + H₂ by about 22 kcal/mol. Its experimental observation should be very difficult because of the inter-system crossing that occurs at the minimum of the ³B₂ state.

These considerations allow us to explain from the ordering of the two lowest-lying states (¹S and ³D) of Ni, Pd, and Pt the particular case of Pd, inactive in dissociating H₂, versus Ni and Pt, active to dissociate H₂. In contrast to Ni and Pt, Pd(¹S) cannot activate H₂, because its triplet state is not easily available. The mechanism of the Ni– and Pt–H₂ interaction is substantially different from the Pd–H₂ interaction. In the case of Ni– and Pt–H₂, two inter-system crossings play a substantial role. The first crossing point, located before the product on the PEF curves, leads to the formation of a dihydride–metal in the singlet state (¹A₁ symmetry). A second one allows the triplet dihydride product (³B₂) to be derived with no activation energy to the singlet dihydride product (¹A₁). On the contrary, for Pd–H₂, the first inter-system crossing does not exist, due to the ordering of two low-lying electronic configurations of Pd. Consequently, the direct product of the interaction is a molecular complex, in which perturbed H₂ is bound to a metal center. The second crossing point present for Pd–H₂ is actually inefficient, because the triplet HPdH dihydride (³B₂) remains unbound with respect to Pd(¹S) + H₂. In addition, even though the endothermic isomeric reaction from the molecular complex (¹A₁) to the singlet HPdH dihydride (¹A₁) could take place through a low activation energy (6 kcal/mol), the reverse reaction occurs immediately, because of very low activation energy (0.8 kcal/mol).

2.2. Singlet and Triplet States of Pd₂–H₂. As stated above, the existence of a crossing point between triplet and singlet states in the entrance channel is an indispensable key leading to the

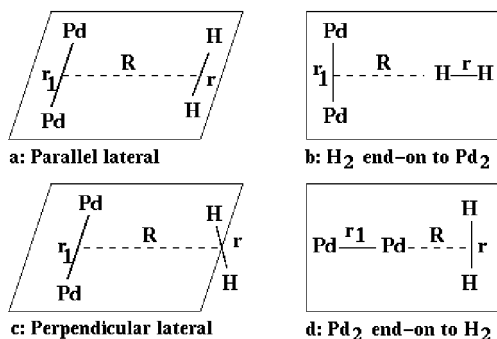


Figure 4. Four C_{2v} approaches of H₂ to Pd₂.

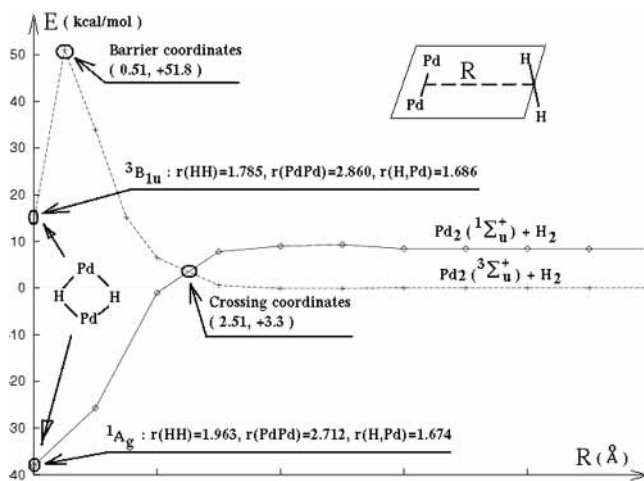


Figure 5. Singlet and triplet PEF of Pd₂-H₂ in the perpendicular lateral approach (Figure 4c). Distance (Å) and angle (deg).

dissociation of H₂ by an atomic center. In this part, we study the H₂ activation by two Pd atoms applying the crossover rule.

As displayed in Figure 4, four H₂ approaches to Pd₂ within the C_{2v} symmetry have been considered.

We should note that, in a previous theoretical work, Castillo et al. studied these four H₂ interaction modes with the Pd dimer using a high correlation method (MC-SCF).¹⁰ They used a fixed value for the Pd-Pd bond distance taken from the bulk structure to calculate only the singlet PEF curve.

In the present work, for both the singlet and triplet PEF calculations, the H-H and Pd-Pd bond distances have been optimized when varying the R value (Figure 4).

In line with the previous theoretical works,^{10,11,12} the ground state of Pd₂H₂ was calculated to be of 1A_g symmetry (D_{2h}), stable with respect to the ground electronic states of the Pd₂ and H₂ by about 38.1 kcal/mol.

Let us comment on the dissociation mechanism of H₂ by Pd₂ for the different approaches. For the first one (Figure 4a), there is no dihydrogen capture in the triplet state, while in the singlet state only a molecular complex is formed. For the latter, the optimized geometry was found to be a trapezium structure ($R = 1.384$, $r = 1.001$, and $r_1 = 2.636$ Å) and to be stable by about 19.2 kcal/mol, with respect to Pd₂($^3\Sigma_u^+$) + H₂.

For the second approach (Figure 4b), as for the first approach, there is no capture in the triplet surface. We cannot therefore obtain the H₂ activation by Pd₂ through these two channels.

Figure 5 displays the perpendicular lateral Pd₂ toward H₂. As one can readily see, two minima have been found at $R = 0$ Å (planar structures) in the singlet and triplet states, namely 1A_g and $^3B_{1u}$, corresponding to the ground and excited electronic states of Pd₂-H₂. The $^3B_{1u}$ structure was calculated to be

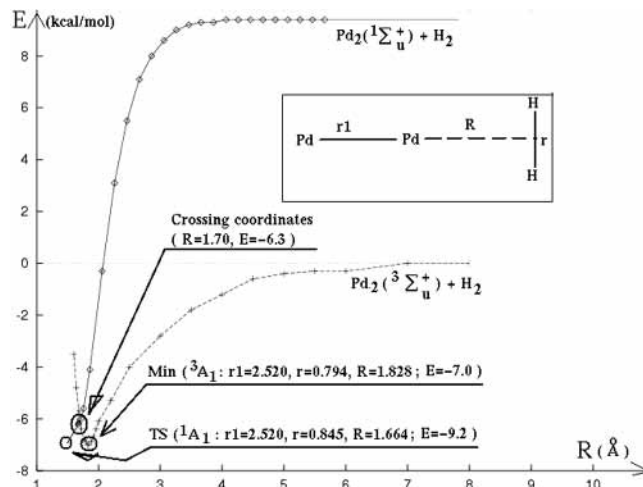


Figure 6. Singlet and triplet PEF of Pd₂-H₂ in the Pd₂ end-on to H₂ approach (Figure 4d). Distance (Å) and angle (deg).

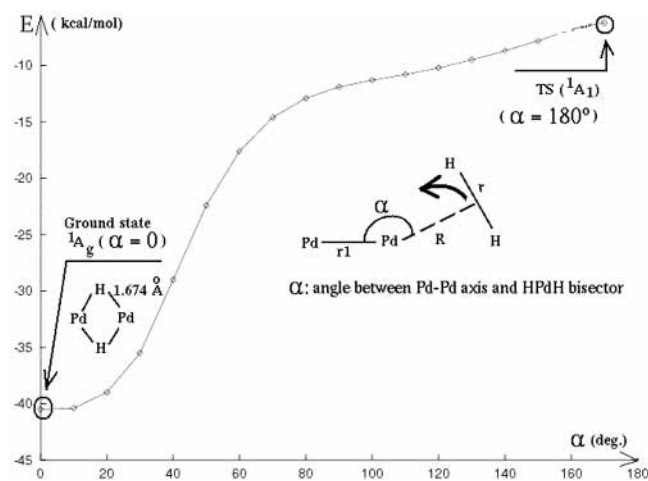


Figure 7. Folding mode in the singlet PEF of Pd₂-H₂. Distance (Å) and angle (deg).

unbound with respect to the ground-free fragments. Inspection of the PEF curves shows that a crossover point occurs in the entrance of this channel favoring thus the activation of H₂ in the 1A_g structure. It should be noted that this reactive channel is possible via a low barrier height (≈ 3.3 kcal/mol) for a center-of-mass distance $R \approx 2.5$ Å. This barrier could be kinetically overcome. This mechanism for the dissociation of H₂ has been previously proposed,¹⁰⁻¹² but without activation energy because the PEF of the two surfaces were not explored.

At last, the Pd₂ end-on to H₂ approach provides an effective channel to the formation of the 1A_g product. This mechanism could be treated in two steps. The formation of two planar intermediates: 3A_1 and 1A_1 structures are sketched in Figure 6. The first structure corresponds to a local minimum displaying a molecular complex, while the second one corresponds to a transition state with one imaginary out-of-plane frequency. The crossover point presents a very low barrier (0.7 kcal/mol), less than the zero-point energy of the 3A_1 molecular complex. In a second step, the molecular complex evolves in the singlet surface from the TS (1A_1) state toward the ground state (1A_g) of the HPd₂H structure. Figure 7 depicts the singlet PEF along the α angle (the angle between Pd-Pd axis and HPdH bisector), where all the other geometrical parameters have been optimized for each value of α . According to the imaginary out-of-plane frequency of TS, the H₂ molecule folds up the complex plane leading to the rhombic structure (HPd₂H) without activation

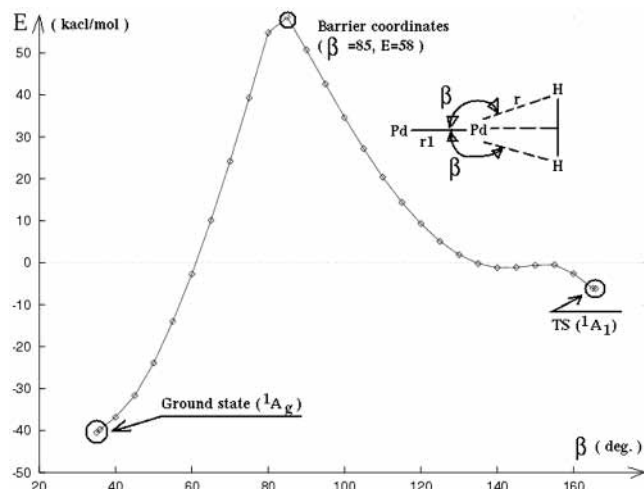


Figure 8. Opening mode in the singlet PEF of Pd₂-H₂.

energy (Figure 7). Moreover, in the later case, the evolution of the molecular TS complex through the planar opening of the two hydrogen atoms around Pd₂ is displayed in Figure 8. We note that this mechanism presents a high barrier going from the molecular complex (TS ¹A₁) to the final product (¹A_g). The energetic barrier is located for $R \approx 0$ Å or for $\beta \approx 90^\circ$. This barrier is expected if one remembers that the linear HPdH was found to be an unbound structure by 21.8 kcal/mol with respect to free Pd(¹S) + H₂.

3. Conclusions

In the present paper, the dissociation of H₂ by Ni, Pd, Pt, and Pd₂ has been studied. Our main findings can be summarized as follows.

(1) The stationary points in the singlet and triplet surfaces, calculated here, are in good agreement with previous theoretical investigations as well as with available experimental data.

(2) It has been demonstrated that the dissociation of the $\sigma_{\text{H-H}}$ bond in dihydrogen is effective only for the metal center for which the triplet state is the ground electronic state. In this case, the triplet state of the product is always less stable than the singlet one.

(3) Two inter-system crossings have been calculated for the Ni- and Pt-H₂. The first crossover point, located in the entrance channel, allows the intermediate compound to evolve in the singlet surface, leading thus without activation energy into the final product, namely a dihydride-metal. The second crossover point, located near of the minimum of the triplet stationary point, would make going from the triplet compound to the singlet one, if the triplet compound was formed in any case. In the case of the Pd-H₂ interaction, the formation of a dihydride of Pd is not possible, because of the lack of the first crossing point in the entrance channel. In the singlet surface of Pd-H₂, a dihydride of Pd was calculated to be less stable than

the molecular complex. In addition, the activation energy when going from the dihydride to the molecular complex of Pd has been found to be very low, less than the ZPVE value of the dihydride of Pd.

(4) For Pd₂-H₂, the same feature as in the Ni- and Pt-H₂ systems has been found and two dissociative mechanisms have been suggested. It has been shown that two of the four approaches enable the dihydrogen molecule to be dissociated by Pd₂. In the case of a perpendicular lateral approach, the dissociation of H₂ requires low activation energy, while there is no activation in the Pd₂ end-on approach toward H₂.

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