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Prediction of Redox Potentials, Electronic Properties, and Spectroscopic Characteristics of Hydrogen Atoms Covalently Bonded to Palladium

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Article Information

Article Type
Research Article

Article History
Received: *30 Nov 2024*
Revised: *13 Jan 2025*
Accepted: *02 Mar 2025*
Published Online: *04 Mar 2025*

Keywords
Palladium hydride
QTAIM
Spectrum
Bonding
Reaction energy

Abstract

Various properties of hydrogen atoms covalently bonded to palladium are predicted for four states of molecular palladium hydride including singlet neutral, triplet neutral, cation, and anion PdH_2. These properties are calculated using the hybrid density functional method with a triple-zeta basis set, incorporating diffuse and polarized elements. In this respect, electronic and spectroscopic properties of molecular palladium hydride are investigated to get insight into palladium-hydrogen bond and its properties. To assess and compare stability of PdH_2, reaction energies for its formation, oxidation and reduction were calculated. The results showed triplet state of PdH_2 is more stable than singlet, while the opposite is true for atomic palladium. IR and UV-Vis spectra of the four states of PdH_2 were calculated and compared, revealing significant differences in both the frequencies and intensities of the peaks. The Quantum Theory of Atoms in Molecules (QTAIM) was applied to examine the Pd-H bonding properties from an electronic structure perspective. All bonds were identified as closed-shell in nature, except for one Pd-H bond in the PdH_2 cation, which exhibited a different character.

Cite this article: Khademi, A., Kheirmand, M., Azami, S. A. (2025). Prediction of Redox Potentials, Electronic Properties, and Spectroscopic Characteristics of Hydrogen Atoms Covalently Bonded to Palladium. DOI: 10.22104/hfe.2025.7079.1313

Publisher: Iranian Research Organization for Science and Technology (IROST)
DOI: 10.22104/hfe.2025.7079.1313

1 Introduction

Palladium hydride (PdH_2) stands out as a compound with immense significance across multiple disciplines. Its distinctive properties facilitate advancements in hydrogen storage, catalysis, electronics, and other advanced applications [1–3]. As a metal hydride, (PdH_2) represents a crucial intersection of materials science, chemistry, and engineering. Palladium, a rare transition metal in the platinum group, is renowned for its exceptional catalytic properties and high resistance to corrosion, making it a valuable component in advanced scientific and industrial applications. When palladium interacts with hydrogen, it absorbs hydrogen gas to form palladium hydride (PdH_2). This formation is a reversible process, allowing palladium to release the absorbed hydrogen under specific conditions. This reversibility makes palladium hydride an excellent candidate for applications requiring efficient hydrogen storage and controlled release [4–6].

Palladium's ability to absorb hydrogen is extraordinary, as it can take in many times its own volume of hydrogen at room temperature, resulting in the formation of palladium hydride. This compound exhibits metallic-like conductivity and undergoes notable changes in volume, making it unique and highly versatile for various applications. Therefore, PdH_2 can store large amounts of hydrogen, making it an attractive option for energy storage solutions [2, 3]. As a catalyst, palladium hydride facilitates various chemical reactions, including hydrogenation processes, where hydrogen is added to unsaturated compounds. Additionally, palladium hydride exhibits good electrical conductivity, which is essential for electronic applications. Its stability across a wide range of temperatures further makes it suitable for various industrial processes [4–6].

One of the most significant applications of palladium hydride is in hydrogen storage systems [1–3]. The phase transition between palladium and palladium hydride is marked by a significant change in volume and density, which can be utilized in mechanical applications. As the world moves toward cleaner energy alternatives, hydrogen fuel cells have gained increasing importance. Palladium hydride provides a compact and efficient way to store hydrogen gas safely, and its high absorption capacity enables the development of smaller storage tanks compared to conventional methods [2, 4, 5].

Palladium is already recognized for its catalytic properties, but palladium hydride takes this a step further [1–3]. The PdH_2 can be employed as a catalyst in hydrogenation reactions, where it facilitates the addition of hydrogen to double bonds in organic compounds. This application is particularly valuable in the pharmaceutical industry for synthesizing various drugs and in the food industry for converting unsaturated fats into saturated ones. Moreover, palladium hydride can promote dehydrogenation reactions, where hydrogen is removed from compounds, making it valuable in the production of olefins and other chemical intermediates [7–9].

The electronics science and technology also benefits from the unique properties of palladium hydride [1, 2, 10]. Its metallic conductivity makes it suitable for use in thin-film technologies and as an electrode material in sensors. For instance, PdH_2 can be used in hydrogen sensors to detect the presence of hydrogen gas in various environments, including industrial settings and fuel cell technologies [5–7, 10, 11]. Palladium and its alloys are also used in membrane technology for separating hydrogen from other gases. Palladium hydride membranes enable selective permeation of hydrogen while effectively blocking other gases [4–6, 10, 11]. This property is particularly useful for purifying hydrogen for fuel cells and other applications that require high-purity hydrogen [7, 11].

Although palladium is a precious metal compared to other hydrogen storage materials, it possesses critical properties that make it a strong candidate for hydrogen storage. These include lightweight properties, availability, rapid hydrogen adsorption/desorption kinetics, the ability to adsorb/desorb hydrogen at low temperatures and pressures, and long-term recyclability. Additionally, the primary source of hydrogen production is based on synthesis (SYN) gas. From all these perspectives, palladium stands out as the most feasible candidate for both storing and purifying hydrogen [5].

In contrast to many studies on palladium-hydrogen interactions, there is a lack of detailed and clear analysis regarding hydrogen atoms covalently bonded to single atom palladium. Most of the existing research focuses on the periodic structure of palladium or the adsorption of molecular hydrogen onto the palladium surface [12]. In this regard, this study characterizes PdH_2 from various perspectives, including redox potentials and spectroscopic properties.

2 Computational Details

The molecular structure of PdH_2 is optimized using M062X/DGDZVP and M062X/6-311++G** for palladium and hydrogen, respectively [13, 14]. vibrational frequency calculations are performed to obtain the IR spectrum and to verify the molecular stability with respect to vibrational normal modes. Time-dependent density functional theory (TDDFT) is also employed to predict the UV-Vis spectrum [8, 9]. Quantum theory of atoms in molecules (QTAIM) [15] is also applied to identifybond critical points (BCPs) and interatomic bond paths (BPs) [16]. Gaussian16 suite of programs is used to perform all calculations including geometry optimizations and spectra [17].

3 Results and Discussion

In this section, various electronic and spectroscopic properties of PdH_2 will be examined, including its molecular structure, electron density analysis, and IR and UV-Vis spectra, all calculated at the theoretical level mentioned in the previous section. To provide a comprehensive overview of PdH_2 properties, different states of the molecule are studied, including singlet neutral, triplet neutral, and the cation and anion states as the oxidized and reduced forms of PdH_2.

Figure 1 displays molecular structures of the singlet and triplet neutral, cation, and anion forms of PdH_2. According to Figure 1, the singlet neutral and cation structures exhibit linear geometries, while the triplet neutral and anion structures are bent. The singlet neutral structure is symmetric, with both Pd-H bond lengths equal to 1.64 Å. Although PdH_2^+ is also linear, the two Pd-H bonds are not equivalent. One of the bonds elongates to 2.22 Å, while the other remains within the range of 1.46-1.68 Å, as shown in Figure 1. Both the anion and neutral triplet are bent with C_{2v} point group; however, anion is more bent by ~ 14 degrees.

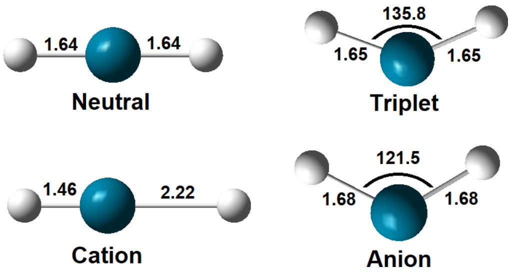

Fig. 1. Molecular structures of singlet and triplet neutral, cation, and anion of PdH_2, where bond length and angles are in Angstroms and degrees.

Table 1 includes the energetic properties of PdH_2 via a reaction perspective, presented as relative energies. The first two rows of the table focus on the singlet-triplet energy gap for atomic palladium and PdH_2. The first row shows that singlet palladium atom is more stable than the triplet palladium by $\sim 36\,\text{kcal/mol}$. In contrast, singlet PdH_2 is less stable, and triplet PdH_2 is more stable than by $\Delta E = 6.29$ and $\Delta G = 11.72\,\text{kcal/mol}$. The third and fourth row of Table 1 include the formation of singlet and triplet PdH_2 from a hydrogen molecule and singlet and triplet palladium, respectively. According totheir reaction energies, both reactions are exothermic, indicating favorable hydrogen adsorption onto atomic palladium. The fifth and sixth rows of Table 1 include the oxidation and reduction of the most stable structure of PdH_2, i.e., $^3PdH_2$. These rows show that the oxidation of this molecule is significantly endothermic, while its reduction is exothermic.

Table 1. Energetic properties of PdH_2 as ΔE and ΔG for different reactions in kcal/mol.

Reaction	ΔE	ΔG
$^1Pd \longrightarrow {}^3Pd$	36.73	36.08
$^3PdH_2 \longrightarrow {}^1PdH_2$	6.29	11.72
$^1Pd + H_2 \longrightarrow {}^1PdH_2$	−50.19	−32.01
$^3Pd + H_2 \longrightarrow {}^3PdH_2$	−93.20	−79.81
$^3PdH_2 \longrightarrow {}^2PdH_2^+ + e^-$	205.83	208.87
$^3PdH_2 + e^- \longrightarrow {}^2PdH_2^-$	−45.92	−46.85

Table 2. IR active normal modes for singlet and triplet neutral, cation, and anion PdH_2. Frequencies and intensities are in cm^{-1} and atomic units, respectively.

Molecule	Frequency	Intensity	Type
$^1PdH_2$	992.15	6.87	Bending
	1444.35	3665.75	Asymmetric stretching
$^3PdH_2$	689.19	60.94	Bending
	1496.95	141.84	Asymmetric stretching
	1655.42	9.84	Symmetric stretching
$^2PdH_2^+$	319.61	20.06	Bending
	582.30	0.28	Stretching
	2321.23	11.41	Stretching
$^2PdH_2^-$	545.75	230.31	Bending
	1134.75	1727.87	Asymmetric stretching
	1466.53	324.00	Symmetric stretching

Figure 2 shows IR spectra, and Table 2 includes the frequencies and IR intensities of the active normal modes of singlet and triplet neutral, cation, and anion PdH_2. Although, for symmetric linear triatomic atomic molecules, two bending and asymmetric stretching vibrational normal modes are active in IR, only a single peak appears in the IR absorption spectrum of singlet neutral PdH_2 at $1444.35\,cm^{-1}$. The reason for this is that the bending vibrational peak is quite small and appears at $992.15\,cm^{-1}$, as shown infirst row of Table 2. Similarly, just a single peak is observable for PdH_2 cation, for the same reason. IR spectra of the other two bent structures, is composed of three peaks, with their intensities being noticeably comparable. However, the strongest absorption corresponds to the asymmetric stretching mode. A comparison of the present results with literature spectra shows a fair agreement with experimental data [18].

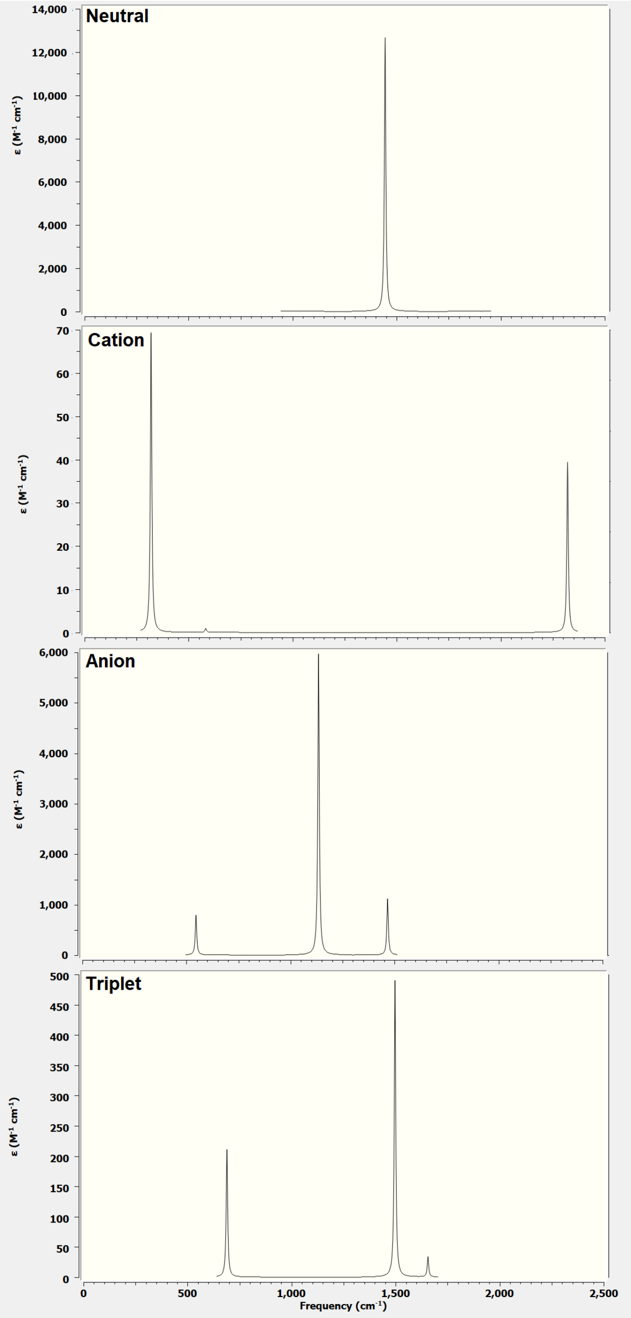

Fig. 2. IR spectra of singlet and triplet neutral, cation, and anion PdH_2**.**

Figure 3 depicts UV-Vis spectra of singlet and triplet neutral, cation, and anion PdH_2. The vertical axis scales indicate exhibits that singlet neutral PdH_2 possesses strong absorption with amolar absorptivity (ε) of up to ≈ 50000. The UV-Vis spectrum of singlet neutral PdH_2 is composed of multiple peaks between 100-200 nm, as well as a broad peak around ≈ 1000 nm. The UV-Vis spectrum of the anion PdH_2 consists primarily of two peaks, located around 200 nm and 300 nm, with comparable intensity. In contrast, the UV-Vis spectrum of triplet PdH_2 is more complex, featuring a combination of both sharp and broad peaks that contribute to its overall spectrum.

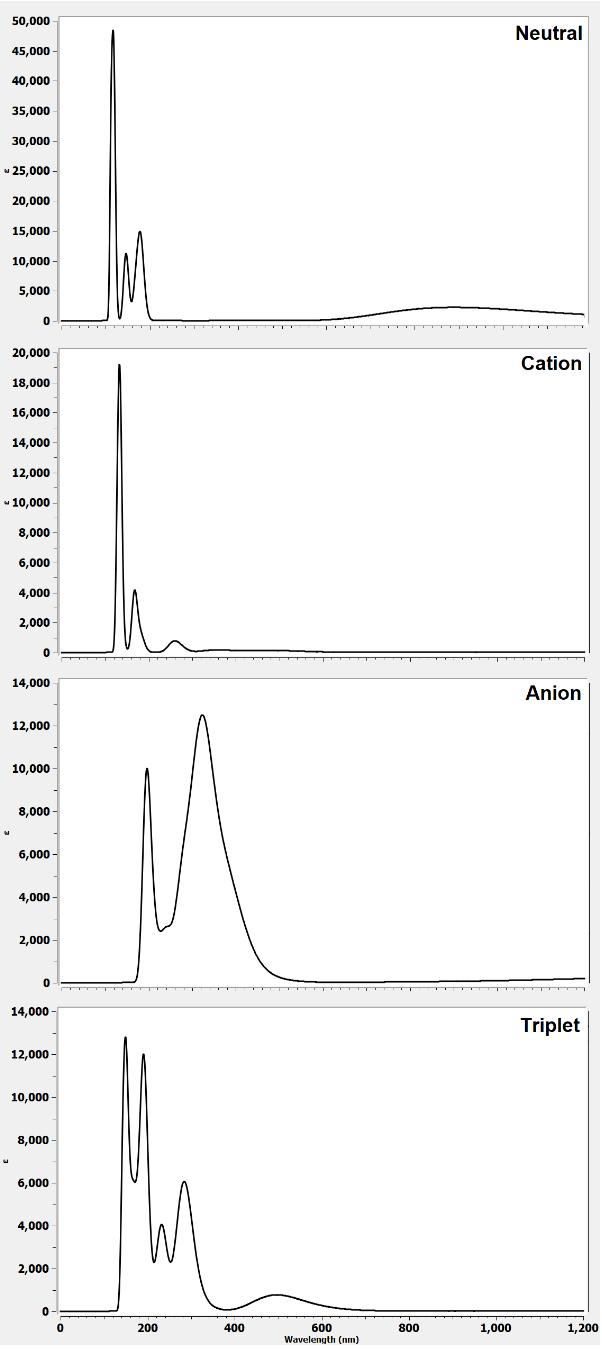

Fig. 3. UV-Vis spectra of singlet and triplet neutral, cation, and anion PdH_2**.**

To gain insight into the electronic structure of different states of PdH_2, QTAIM analysis is conducted on these species. Figure 4 displays QTAIM molecular graphs, BCPs, and atomic charges for singlet and triplet neutral, cation, and anion PdH_2. Electron densities and their Laplacian at the BCPs are also shown in this figure to examine Pd-H bonding properties. As the electron density values at the BCPs in Figure 4 show, all values are greater than 0.1 a.u., except for the BCP at the longer Pd-H bond in the cation PdH_2, which is significantly small (0.025 a.u.) and suggests a pre-dissociation bond. The Laplacian values are all positive, indicating a closed-shell interaction between palladium and hydrogen atoms, except for the shorter Pd-H bond in cation PdH_2, which exhibits a covalent bond character.

The atomic charges of singlet and triplet neutral PdH_2 in Figure 4 show that the palladium atom carries a positive charge, with the singlet state showing a greater positive charge on palladium compared to the triplet state. In the cationic state, the palladium atom is also more positively charged than the hydrogen atoms, contributing to approximately 70% of the total positive molecular charge. This tendency for palladium to carry a positive charge is also observed in the anion PdH_2, where the palladium charge is less negative than that of the two hydrogens. In this case, the hydrogen atoms are responsible for about 80% of the total negative molecular charge.

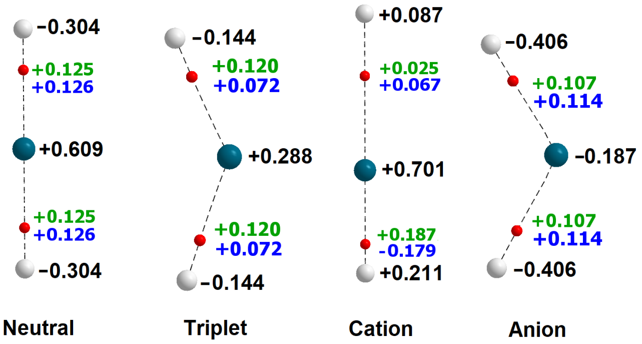

Fig. 4. QTAIM molecular graphs (dotted lines), BCPs (small red spheres), and atomic charges (black numbers) of singlet and triplet neutral, cation, and anion PdH_2, where electron densities (green numbers) and their Laplacian (blue numbers) values at the BCP are shown in atomic units.

4 Summary and Concluding Remarks

The interaction between palladium and hydrogen atoms can result in the formation of singlet and triplet PdH_2. While singlet palladium is more stable than the triplet palladium atom, it has been found that triplet PdH_2 is more stable than the singlet form. In terms of molecular geometry, singlet neutral and cation PdH_2 adopt linear structures, while the triplet neutral and anion PdH_2 exhibit bent structures. Oxidized and reduced PdH_2 are also analyzed from energetic, electronic, and spectroscopic perspectives, and the results reveal distinct differences in their properties. The IR spectra of singlet and triplet neutral, cation, and anion PdH_2 are clearly distinguishable, as their peaks correspond to different wave numbers. The UV-Vis spectrum of singlet neutral PdH_2 shows significant differences in the intensities of its peaks, while the spectra of the other three states differ in terms of the locations of their peaks. Finally, the electronic structures of the species were analyzed using QTAIM, revealing that the Pd-H bonds are of the closed-shell type, except for one Pd-H bond in the cation. The distribution of atomic charges in all four species also indicates a stronger tendency for the palladium atom to carry a positive charge compared to the hydrogen atoms.

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