

Interaction of the Hydrogen Molecule with the Palladium Atom. A Force Theoretic Study

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As a model of chemisorption, we studied an interaction of the H_2 molecule with the $^1S(4d^{10})$ and $^3D(4d^95s^1)$ states of the Pd atom. We calculated an accurate Hellmann-Feynman force acting on the H_2 molecule by adding the first derivatives of the hydrogen basis set. The force and density origins of the interaction were clarified. The singlet $Pd(^1S) - H_2$ system, which is the ground state, is attractive but the triplet $Pd(^3D) - H_2$ system is repulsive. The side-on approach is a preferable path. For the $Pd(^1S) - H_2$ system, the Pd-H bonds are gradually formed. The electron density is accumulated in the overlap region of the H_2 molecule and the Pd atom and it pulls the H_2 molecule onto the Pd atom. The bond of the H_2 molecule is gradually weakened. The electrons are transferred from the bonding MO of the H_2 molecule to the empty $5s$ and $5p_z$ AO's of the Pd atom. For the $Pd(^3D) - H_2$ system, the density of the Pd atom tends to keep its spherical symmetry even when the H_2 molecule approaches. The Pd atom in the $4d^95s^1$ configuration is more repulsive than that in the $4d^{10}$ configuration. Therefore, the H_2 molecule is repelled by the Pd atom.

I. INTRODUCTION

Chemisorption of hydrogen molecules on transition metals is an important step for hydrogen storage and activation of molecular hydrogen followed by a variety of catalytic processes.¹⁻⁴ Palladium shows, especially, a unique affinity for hydrogen. The »solubility« of hydrogen in palladium metal markedly exceeds that in the other group 8 metals.¹ Molecular hydrogen can diffuse through metallic palladium at a higher rate than in other platinum-series metals. This process is very selective so that it is used for the purification of hydrogen gas from a mixture. Further, homogeneous palladium complexes also show a variety of catalytic reactions including some industrially important ones (e. g., Hoechst-Wacker reaction).²⁻⁴

The electronic structure and the bonding nature in the diatomics, PdH and PtH have been studied theoretically at various levels of approximation.⁵⁻⁸ For these diatomic hydrides, bonding properties such as bond energy, force constant, etc., are known experimentally for some lower electronic states⁹, so that they offer a good test for various levels of theoretical method. Further, these metal hydrides are thought to be a model product of the dissociative chemisorption of the hydrogen molecule on the metal surface.

Bagus and Björkman⁶ studied the bonding in NiH and PdH by an *ab initio* SCF and CI methods. The bonding between Pd and H is primarily due to the 5s electron in the metal. The *d*-electrons are localized on the metal and participate only slightly in the Pd—H bond. Pacchioni *et al.*⁷ reported a multi-reference CI study on the PdH, PdC, and PdCO molecules based on the effective-core potential SCF MO's. They reported the importance of the choice of the Pd basis set and also of the effects of electron correlation. Their results showed that the effect of electron correlation on PdH is to deepen the potential energy curve. The equilibrium bond length and force constant calculated by the SCF method compare relatively well with experimental results, although for the dissociation energy the SCF result is only half of the experimental value. Wang and Pitzer⁸ also reported a similar effect of electron correlation on PtH. The correlation energy has little effect on the bond length and force constant of the ground state of PtH, but it does contribute significantly to the binding energy. Basch and Topiol⁵ and Wang and Pitzer⁸ further pointed out the importance of the relativistic effect on the electronic structure of PtH.

Bagatur'yants *et al.*¹⁰ studied the approach of the hydrogen molecule to the Pd atom with a fixed H—H length (0.74 Å). They carried out all electron SCF calculations with the minimal and extended basis sets. They showed that formation of the molecular complex is favorable energetically and analyzed the donor-acceptor interactions between H₂ and Pd. They pointed out the important role of the outer 5s and 5p AO's of the Pd atom in the formation of the Pd—H₂ complex.

In this paper we study the interaction of the H₂ molecule with the Pd atom, as a model of the electronic processes in the chemisorption of the hydrogen molecule. We use the effective-core potential (ECP) SCF method¹¹ for the Pd atom.¹² We include the relativistic effects through the ECP potential but neglect, in this paper, the effect of electron correlation. For the ground state of PdH and PtH, the effect of electron correlation was to deepen the potential minima without much affecting the equilibrium length and the force constant.^{7,8}

The force concept based on the Hellmann-Feynman theorem gives a simple and intuitive method of studying chemical phenomena.^{13,14} The force acting on the nucleus A, F_A is determined by the electrostatic interaction of the nucleus A with the electron cloud and the other nuclei surrounding it.

$$F_A = Z_A \int r_{A1}/r_{A1}^3 \rho(r_1) dr_1 - Z_A \sum_{B(\neq A)} Z_B R_{AB}/R_{AB}^3 \quad (1)$$

We used the force concept to obtain a deeper understanding of the nature of the interaction.

Further, an accurate and reliable calculation of the Hellmann-Feynman force has been realized recently.^{15,16} It was shown that the Hellmann-Feynman theorem is essentially satisfied when we add the first derivative bases to the basis set conventionally used. The method has been applied to studies of molecular structure, molecular vibration and chemical reaction.¹⁵⁻¹⁷ In the present model system of chemisorption, Pd—H₂, we are primarily interested in the force acting on the adsorbed molecule H₂, and not in the force acting on the metal, since the metal atom represents here a surface atom of the metal catalyst. Therefore, we have added the first derivatives only to the H₂ basis set which is the [2s] set of Dunning.¹⁸ The added derivative bases describe

well the polarization of the H₂ electron cloud and lead to the satisfaction of the Hellmann-Feynman theorem for the force acting on the protons of the H₂ molecule. Wang *et al.*⁸ found for PtH that the polarization functions centered on the H atom are more important than those centered on the Pt atom.

II. INTERACTION OF THE H₂ MOLECULE WITH THE Pd ATOM IN THE ¹S AND ³D STATES

The ground state of the Pd atom is the closed-shell ¹S state with the configuration 4d¹⁰. The first excited state is the ³D state with the configuration 4d⁹5s¹. It lies 19 kcal/mol above the ground state. We have approached the H₂ molecule onto the Pd atom keeping the C_{2v} symmetry (side-on), because, as will be shown below, this is a favorable approach. The H—H length was kept fixed to 0.74144 Å and 1.0 Å. The former is the equilibrium distance of the free hydrogen molecule.

In Figure 1, we have shown the potential energy curves for the side-on approach of the H₂ molecule to the Pd atom. The figure on the left hand side corresponds to the fixed H—H distance of 0.74144 Å and the one on the right hand side corresponds to the H—H distance of 1.0 Å. The lower curve was obtained from the interaction of the singlet 4d¹⁰ state of the Pd atom with the H₂ molecule, and the upper curve was obtained from the interaction of the triplet 4d⁹5s¹ state of the Pd atom with the H₂ molecule. Figure 1 shows that the singlet Pd (¹S)—H₂ system is attractive but the triplet Pd (³D)—H₂ system is repulsive. The energy difference of the ¹S and ³D states of the Pd atom was taken from the experimental value (19 kcal/mol). The calculated value for the atom was -3 kcal/mol, (*i. e.*, the ³D state was calculated to be lower than the ¹S state) because of the lack of electron correlation. The correlation energy is larger for the closed-shell singlet state than for the open-shell triplet state.

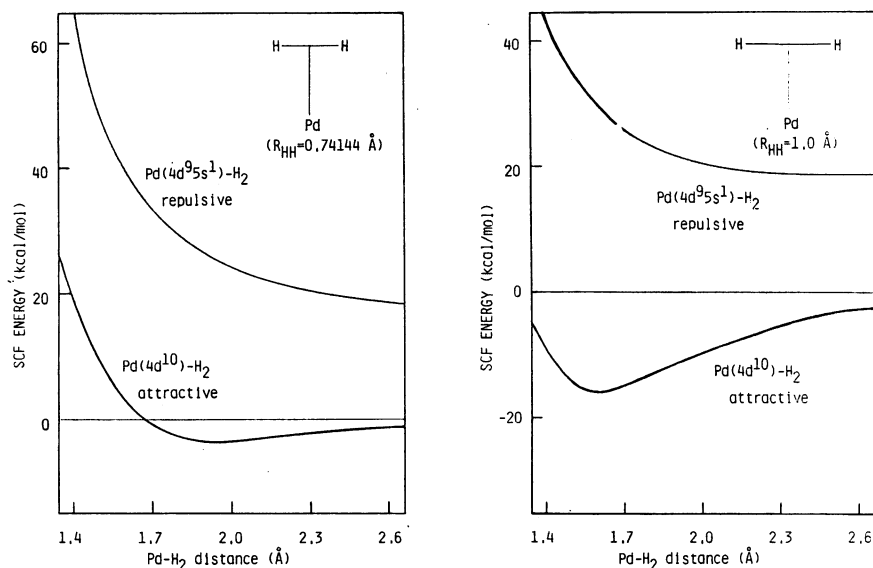


Figure 1. Potential energy curves for the interactions of the H₂ molecule with the ¹S (4d¹⁰) and ³D (4d⁹5s¹) states of the Pd atom. The figures on the left and right hand sides are for the fixed H₂ distances of 0.74144 Å (equilibrium length) and 1.0 Å, respectively.

The existence of the repulsive curve, not far from the attractive curve, is very interesting. It may work in the detachment process of the hydrogen molecule from the Pd metal.

When the H—H length is kept fixed at 0.74144 Å, the stabilization energy for the Pd (1S)—H₂ system was calculated to be 3.6 kcal/mol. It is small in comparison with the experimental value, 9.6 kcal/mol, which is the heat of adsorption of the hydrogen molecule on the bulk palladium metal.¹ The stable Pd—H₂ distance was calculated at 1.90 Å. When the H—H length is elongated to 1.0 Å, the stabilization energy relative to the Pd atom and the elongated H₂ molecule becomes 15.9 kcal/mol and the stable Pd—H₂ distance becomes 1.62 Å, though 20.2 kcal/mol is necessary for this elongation of the free hydrogen molecule.

During the course of the approach, the H₂ molecule fixed at the equilibrium length, 0.74144 Å, receives the force, as shown below, which works to elongate the H—H distance. Therefore, in an actual process, the H₂ molecule approaches the Pd atom while gradually elongating its H—H distance. For this optimal approach the stabilization energy would become larger than the present value. However, in order to obtain a value comparable to the experimental value, inclusion of the electron correlation effect would be necessary. The roles of the second, third, . . . Pd atoms of the metal surface are also of interest.

The triplet interaction of the Pd (3D) atom and the H₂ molecule is repulsive, independent of the H—H distance, though the slope becomes smaller for the interaction with the elongated H₂. We will show later in the force theoretic analysis that the Pd atom in the $4d^95s^1$ configuration is more repulsive than that in the $4d^{10}$ configuration.

III. FORCE AND DENSITY ORIGIN OF THE INTERACTION

As seen from Eq. (1), the Hellmann-Feynman force depends on the three dimensional distribution of the electron density and nuclei. In the present Pd—H₂ system, we have two distinct subsystems which are the Pd atom and the H₂ molecule. We therefore divide the electron density regionally into the one belonging to the Pd atom, the one belonging to the H₂ molecule, and the one belonging to the overlap region of the Pd atom and the H₂ molecule. This regional partitioning of the electron density naturally leads to the analysis of the force acting on the proton of the hydrogen molecule as

$$\begin{aligned}
 F = & \sum_r \sum_s \overset{\text{on Pd}}{P_{rs}} \langle r | f_H | s \rangle - Z_H Z_{Pd} R_{H-Pd} / R_{H-H}^3 ; F(\text{Pd}) \\
 & + \sum_r \sum_s \overset{\text{on H}_2}{P_{rs}} \langle r | f_H | s \rangle - Z_H Z_{H'} R_{H-H'} / R_{H-H}^3 ; F(\text{H}_2) \\
 & + 2 \sum_r \overset{\text{on Pd}}{\sum_s} \overset{\text{on H}_2}{P_{rs}} \langle r | f_H | s \rangle ; F(\text{H}_2\text{—Pd}) \quad (2)
 \end{aligned}$$

where P_{rs} is the bond-order density matrix with respect to the bases r and s . The first term, $F(\text{Pd})$, represents the force acting on the proton due to the electrons and nucleus of the Pd atom, the second term, $F(\text{H}_2)$ represents the force due to the electron density and the other proton of the H₂ molecule

adsorbed on the Pd atom, and the last term, $F(\text{H}_2\text{—Pd})$, represents the force due to the electron density accumulated in the overlap region of the AO's of the H₂ molecule and the Pd atom.

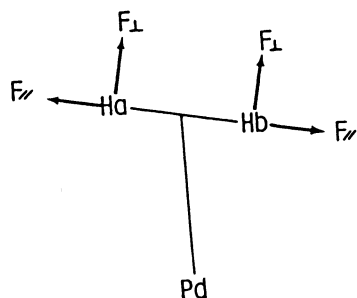
III A. Preference of the Side-on Attack

We first examine a preferable way of attack of the H₂ molecule on the Pd atom. We have put the H₂ molecule 2.0 Å apart from the Pd (¹S) atom and declined it by 10° from the C_{2v} side-on position. Table I shows the force

TABLE I

Force Acting on the H_a and H_b Atoms of the Hydrogen Molecule which is Side-on Slantwise on the Pd Atom. The H—H Distance is 0.74144 Å and the Distance Between Pd and the Center of H₂ is 2.0 Å

Term	H _a		H _b	
	F _⊥	F _∥	F _⊥	F _∥
$F(\text{Pd})$	0.0210	0.0104	0.0301	0.0033
$F(\text{H}_2)$	-0.0046	0.0225	-0.0068	0.0203
$F(\text{H}_2\text{—Pd})$	-0.0188	-0.0230	-0.0220	-0.0130
$F(\text{total})$	-0.0024	0.0099	0.0013	0.0111



analysis and Figure 2 shows the contour map of the density difference defined by

$$\Delta \rho = \rho(\text{Pd—H}_2) - \rho(\text{Pd, } ^1\text{S}) - \rho(\text{H}_2) \quad (3)$$

which shows the reorganization of the electron density due to the interaction between the Pd (¹S) atom and the H₂ molecule.

From the force perpendicular to the H—H axis, F_{\perp} , we see that the hydrogen molecule receive the force which acts to recover the C_{2v} approach. This recovery seems to occur with slipping down the H₂-rod onto the right-hand side, since the force parallel to the bond, F_{\parallel} , is larger for H_b than for H_a. The H₂ molecule tends to elongate the bond as seen from the values of F_{\parallel} .

The origin of the recovering force on the H_a atom, $F_{\text{H}_a\perp}$ is the sum of the forces $F(\text{H}_2\text{—Pd})$ and $F(\text{H}_2)$, which overcomes the repulsion due to the Pd atom, $F(\text{Pd})$. As seen from Figure 2, the force $F(\text{H}_2\text{—Pd})$ reflects an increase in the electron density between the H_a and Pd atoms and $F(\text{H}_2)$ reflects a polarization of the electron density near the H_a atom. The origin of the recovering force acting on H_b, $F_{\text{H}_b\perp}$, is the repulsion due to the Pd atom. Though

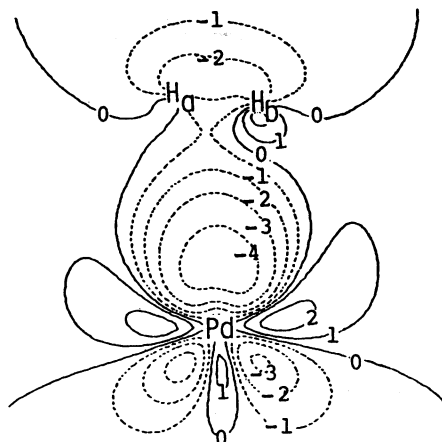


Figure 2. Density difference contour map for the singlet Pd ($1S$)— H_2 system in which the H_2 molecule is side-on slantwise on the Pd atom. The H—H distance is 0.74144 Å and the distance between Pd and the center of H_2 is 2.0 Å. The definition of the density difference is given by Eq. (3). The real lines correspond to an increase in density and broken lines to a decrease, with the contour values of 0, ± 1 , ± 2 , ± 3 , ± 4 , and ± 5 corresponding to 0.0, ± 0.002 , ± 0.005 , ± 0.01 , ± 0.02 , and ± 0.05 a. u., respectively.

a polarization of the electron density near the H_b atom and a bonding interaction between the H_b and Pd atoms are seen from the density difference map, the extent is less than the repulsion due to the Pd atom.

III B. Force and Density Origin of the Interaction for the Pd ($1S$)— H_2 System

We now consider the side-on approach of the H_2 molecule onto the Pd ($1S$) atom. The force acting on the H_2 molecule is divided into the two components, F_z and F_y , shown in Figure 3. The negative of the force F_z is an attractive force of chemisorption, and the force F_y is the force which prolongs the H_2 molecule. Figure 4 shows the contour map of the density difference defined by Eq. (3) for several points of the side-on approach. The H—H distance was kept fixed at 0.74144 Å. In Figure 5, we have shown an analysis of the force of chemisorption, F_z , into the components defined by Eq. (2). The left and right hand sides correspond to the fixed H—H distances of 0.74144 Å and 1.0 Å, respectively. Figure 6 shows a similar analysis of the stretching force, F_y , along the adsorption process.

From the total force curve shown in Figure 5, we can estimate an equilibrium Pd— H_2 distance. It is 1.92 Å and 1.64 Å for the systems with the fixed H—H distances of 0.74144 Å and 1.0 Å, respectively. These results are in close agreement with those obtained from the potential energy curves shown in Figure 1 (1.90 Å and 1.62 Å, respectively). This is a matter of course since the present wavefunctions essentially satisfy the Hellmann-Feynman theorem.

From Figure 4, we can see a density origin of the 'chemisorption' of the H_2 molecule on the Pd ($1S$) atom. As the H_2 molecule approaches, the Pd atom

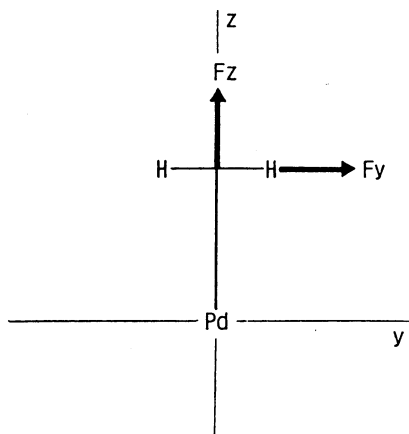


Figure 3. Definition of the force acting on the H₂ molecule which approaches side-on to the Pd atom.

extends its right and left lobes of the density from the outside of the H₂ molecule. These lobes grow up to form a bond between Pd and each hydrogen. It becomes conspicuous at 1.7 Å. From Figure 5, we confirm that the origin of the attractive force is the $F(\text{H}_2\text{—Pd})$ term. The electron density accumulated in the overlap region between H₂ and Pd attracts H₂ to chemisorb on the Pd atom. The Pd—H bonds are formed as the H₂ molecule approaches.

Further, as seen from Figure 4, the electron density decreases in the internuclear region of the H₂ molecule, so that the bond between the hydrogen atoms is weakened as the H₂ molecule approaches the Pd atom. As seen from Figure 6, the proton of the H₂ molecule always receive the force which prolongs the H₂ distance. The origin of this force is $F(\text{H}_2)$. Namely, the decrease in the electron density in the H₂ molecule causes a deshielding of the inter-proton repulsion. The repulsion from the Pd atom, $F(\text{Pd})$, also works to elongate the H—H distance.

We will see later that the increase in the electron density in the overlap region of Pd and H₂ and the decrease in the density in the H₂ region are mainly due to an electron-transfer interaction from the bonding MO of the H₂ molecule to the vacant 5s and 5p_z AO's of the Pd atom.

When the H—H length is elongated, in response to the force shown in Figure 6, the electron density reorganizes itself as shown in Figure 7. It is for the H—H distance of 1.0 Å. The distance between Pd and H₂ is 2.0 Å. Comparing Figure 7 with the corresponding contour map shown in Figure 4, we see that an elongation of the H₂ distance very much facilitates the formation of the Pd—H bond. The left and right lobes of the Pd atom extend up to the two protons to form the Pd—H bond. In Figure 5, the effect of elongating the H—H distance on the force of interaction F_z is shown. The left and right figures correspond to the H—H distances of 0.74144 Å and 1.0 Å, respectively. By an increase in the H—H distance, the H₂ system receives more attractive force from the Pd atom. The origin is an increase in the $F(\text{H}_2\text{—Pd})$ force. Namely, the electron density more accumulated in the bond region of Pd and H as

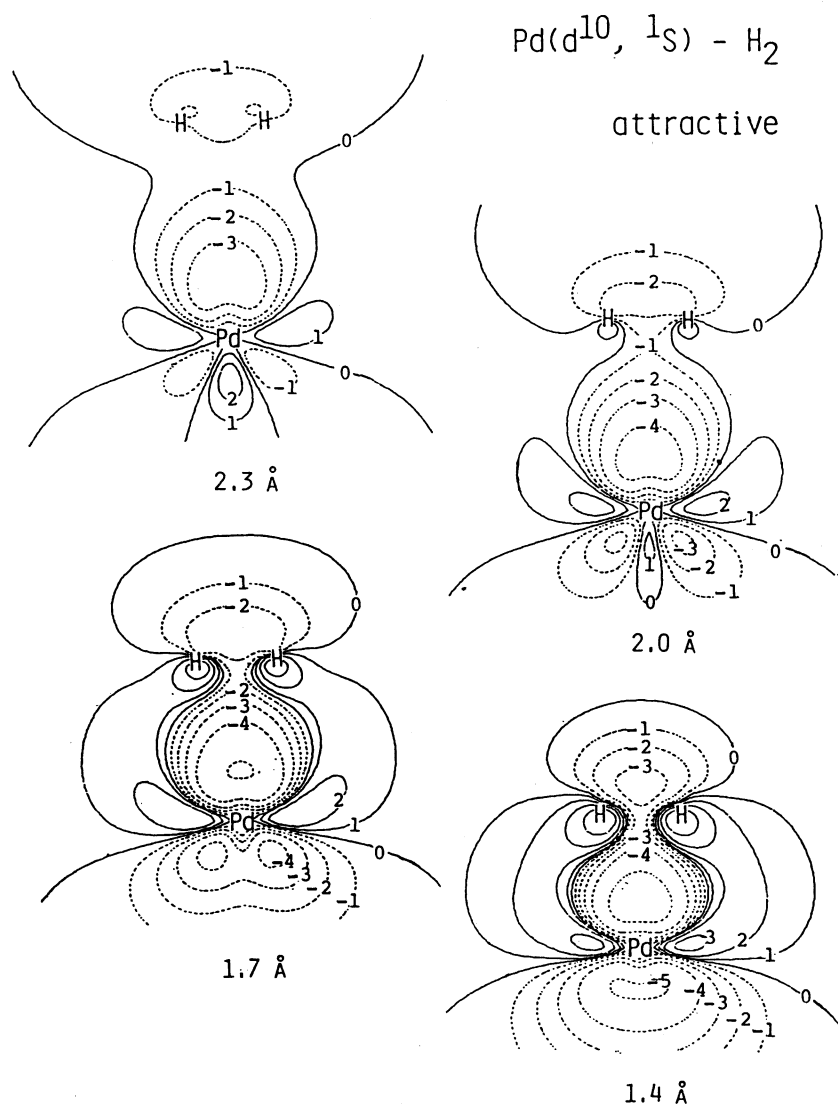


Figure 4. Density difference contour maps for the singlet $\text{Pd}(d^{10}, 1s) - \text{H}_2$ system. The H—H distance is kept at 0.74144 Å and the distance between Pd and H_2 is given below each map. The definition of the density difference is given by Eq. (3). The real lines correspond to an increase in density and broken lines to a decrease, with the contour values of 0, ± 1 , ± 2 , ± 3 , ± 4 , and ± 5 corresponding to 0.0, ± 0.002 , ± 0.005 , ± 0.01 , ± 0.02 , and ± 0.05 a. u., respectively.

shown in Figure 7 attracts more the protons to the Pd atom. The other components of the force, $F(\text{H}_2)$ and $F(\text{Pd})$, do not change much between the two systems.

The H_2 molecule receives the force F_y , which prolongs the H—H distance when it is kept at 0.74144 Å. However, when it is elongated to 1.0 Å, the

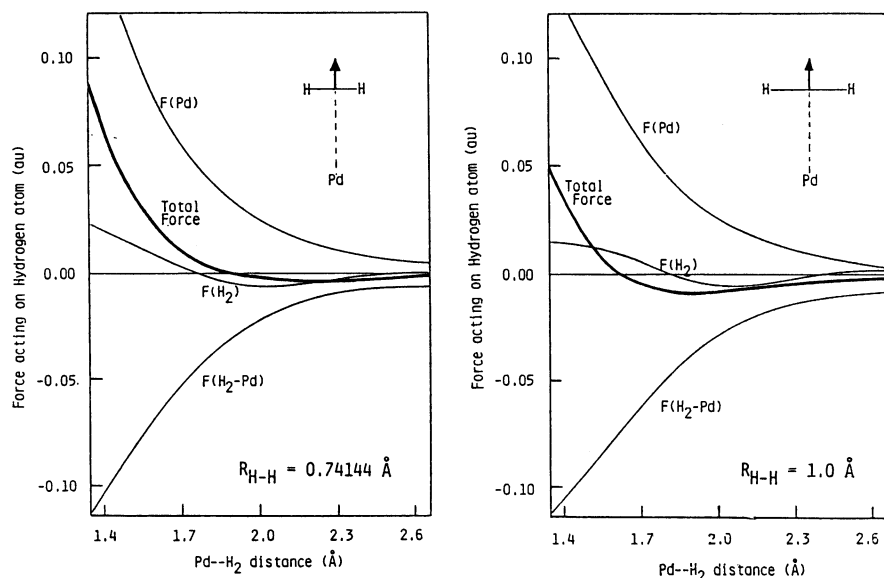


Figure 5. The analysis of the force F_z acting on the H₂ molecule of the singlet, Pd(¹S)—H₂ system. The definition of the forces is given by Eq. (2). The left and right hand sides correspond to the fixed H—H distances of 0.74144 Å and 1.0 Å, respectively.

protons receive the reverse force. At the Pd—H₂ separation of the 2.0 Å, the force F_y is 0.0037 a. u. for H₂ with $R_{HH} = 0.74144$ Å and -0.0828 a. u. for H₂ with $R_{HH} = 1.0$ Å. The equilibrium length of H₂ at this Pd—H₂ separation is estimated to be 0.772 Å.

The interaction between the H₂ molecule and the Pd atom may further be understood in terms of the electron transfer and back-transfer interactions as in the Dewar-Chatt-Duncanson model²⁰ of the interaction between platinum and the olefine double bond. In Figure 8, we have shown the population analysis of the Pd(¹S)—H₂ system along the Pd—H₂ distance. The upper side shows the changes in the gross atomic charges of the Pd and H atoms and the lower side shows the atomic orbital populations.

As the hydrogen molecule approaches the Pd atom, the electron is transferred from the H₂ molecule to the Pd atom. Qualitatively speaking, the orbital interactions between the H₂ molecule and the Pd atom are that the bonding MO of H₂, σ_{H_2} donates an electron to the metal AO's and that the antibonding MO of H₂, $\sigma_{H_2}^*$ receives the back-donated electron from the Pd atom. The $4d_{z^2}$, $5s$, and $5p_z$ AO's of the Pd atom can interact with the bonding σ_{H_2} MO, and only the $4d_{yz}$ AO interacts with the antibonding $\sigma_{H_2}^*$ MO. In Figure 9, we have given an MO interaction diagram. As the H₂ molecule approaches, the $5s$, $5p_z$, and $4d_{z^2}$ AO's hybridize very rapidly and form $4d_{z^2} - (5s + 5p_z)$ hybrid and $(5s + 5p_z) + 4d_{z^2}$ hybrid with appropriate mixing coefficients (prehybridization step on the left hand side of Figure 9). The two electrons originally in the d_{z^2} AO occupy the former hybrid and the latter one is left unoccupied. The electron of the σ_{H_2} MO is transferred to the unoccupied hybrid and forms a bond

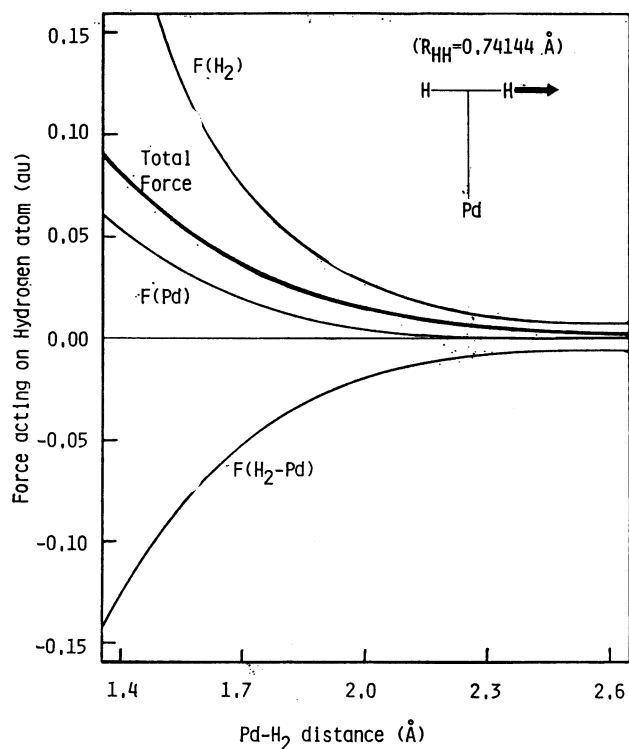


Figure 6. The analysis of the force F , acting on the H_2 molecule of the singlet $Pd(^1S)-H_2$ system with the fixed $H-H$ length of 1.0 Å. The definition of the forces is given by Eq. (2).

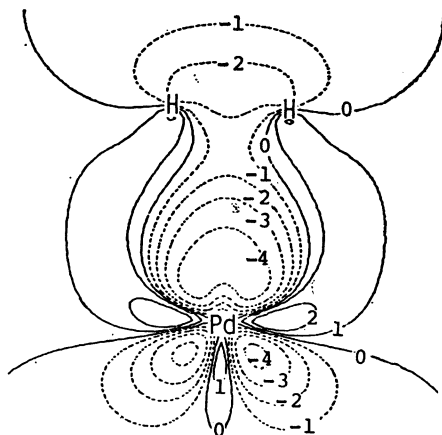


Figure 7. Density difference contour map for the singlet $Pd(d^{10}, ^1S)-H_2$ system with the $H-H$ length of 1.0 Å and the $Pd-H_2$ distance of 2.0 Å. The density difference is defined by Eq. (3). The real lines correspond to an increase in density and broken lines to a decrease, with the contour values of 0, ± 1 , ± 2 , ± 3 , ± 4 , and ± 5 corresponding to 0.0, ± 0.002 , ± 0.005 , ± 0.01 , ± 0.02 , and ± 0.05 a. u., respectively.

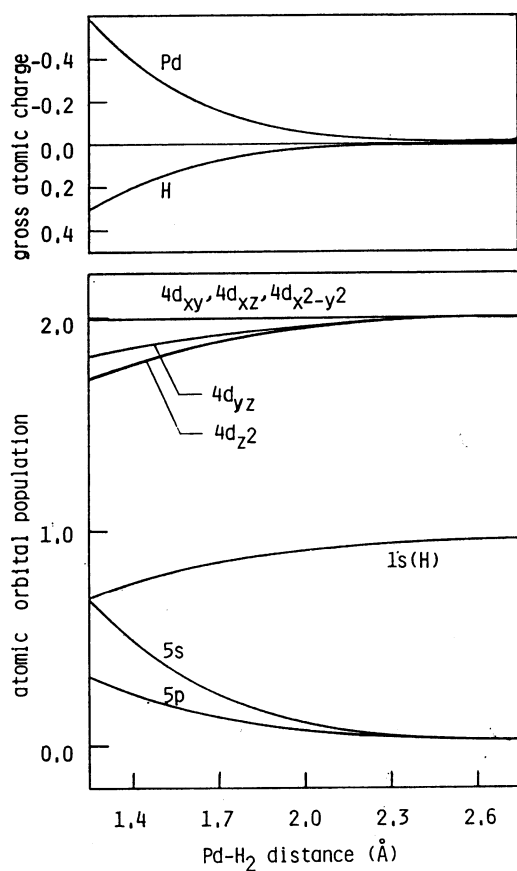


Figure 8. Gross atomic charge (upper side) and atomic orbital population (lower side) of the singlet Pd ($1S, 4d^{10}$)—H₂ system against the Pd—H₂ distance. The H—H distance was kept at 0.74144 Å throughout the approach.

between Pd and H₂. The increase in the 5s and 5p_z AO population and the decrease in the 4d_{z²} AO population shown in Figure 8 are due to this MO interaction. The back-transfer interaction from the Pd 4d_{yz} AO to the $\sigma_{H_2}^*$ MO seems to be smaller than the transfer interaction.¹⁰ The slope of the 4d_{yz} AO population is smaller than that of the 5s and 5p_z AO populations and the gross charge of the hydrogen atom is positive.

From the above discussion, we conclude that the bonding between the Pd atom and the H₂ molecule is primarily due to the overlap between the 5s—5p hybrid of the Pd atom and the 1s AO's of the H₂ molecule. The participations of the 4d AO's are secondary.

We note that the decrease in the electron density in the 4d_{z²} AO is also understood as being due to the induced inner excitation of the electrons from the 4d_{z²} AO to the 5s and 5p_z AO's caused by an interaction between Pd and H₂. Such an interaction is usually called the 'polarization' term.²¹

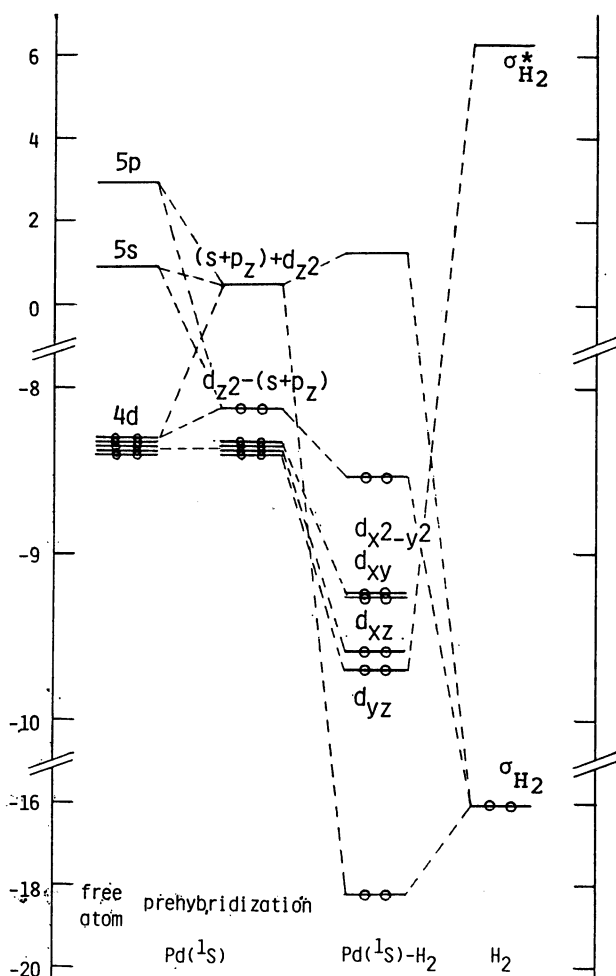


Figure 9. An MO interaction diagram for the singlet Pd ($1S, 4d^{10}$)-H₂ system.

III C. Force and Density Origin of the Repulsive Interaction Between Pd (3D) and H₂

Though the singlet ground state of the palladium is attractive for H₂, the lowest triplet state is repulsive. Figure 10 shows the density difference map for the interaction between the H₂ molecule and the Pd atom in the 3D (d^9s^1) state. It is defined by

$$\Delta \rho = \rho(\text{Pd-H}_2) - \rho(\text{Pd}, ^3D) - \rho(\text{H}_2) \quad (4)$$

where $\rho(\text{Pd}, ^3D)$ is calculated for the averaged electronic configuration, $d_{xy}^2 d_{zx}^2 d_{yz}^{5/3} d_{z^2}^{5/3} d_{x^2-y^2}^{5/3} 4s^1$, which has circular symmetry on the yz plane. Figure 11 shows the force F_z and its analysis.

Even when the H₂ molecule approaches the Pd (3D) atom up to 2.3–2.0 Å, the electron density does not accumulate well in the overlap region. At 2.0 Å,

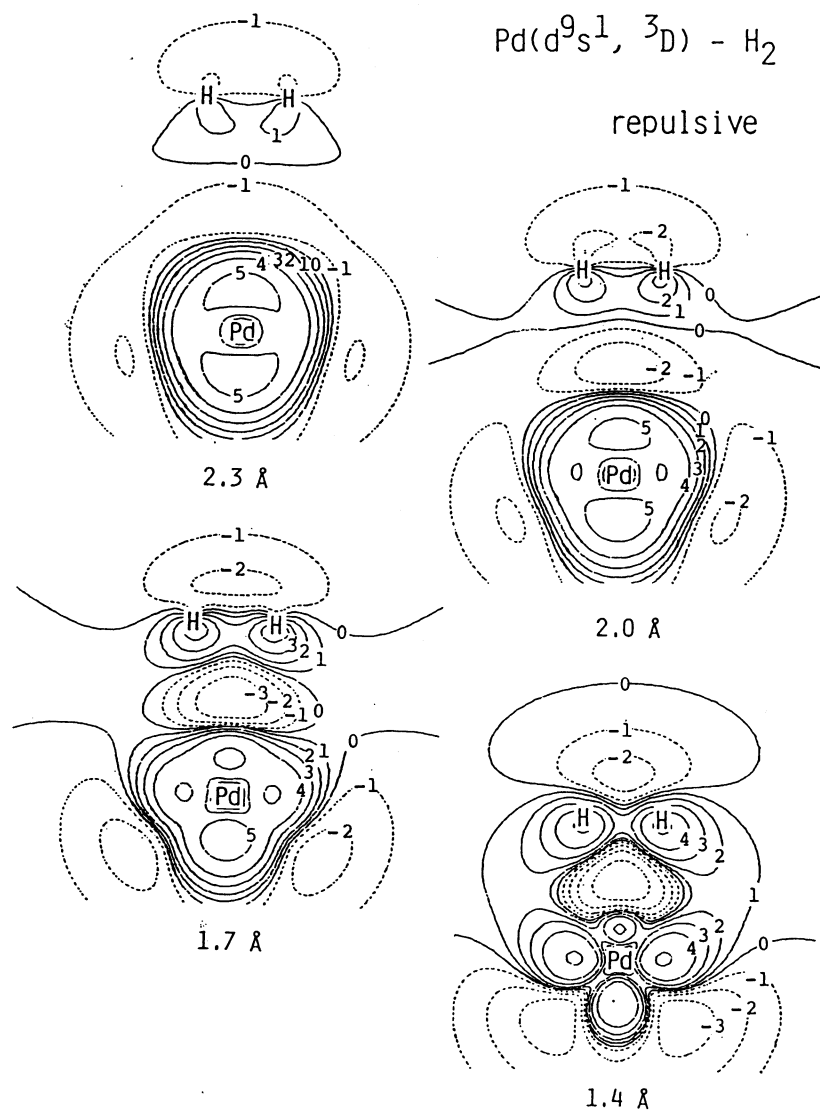


Figure 10. Density difference contour maps for the triplet $\text{Pd}(4d^9 5s^1, ^3D) - \text{H}_2$ system. The H—H distance is kept at 0.74144 Å and the distance between Pd and H₂ is given below each map. The density difference is defined by Eq. (4). The real lines correspond to an increase in density and broken lines to a decrease, with the contour values of 0, ± 1 , ± 2 , ± 3 , ± 4 , and ± 5 corresponding to 0.0, ± 0.002 , ± 0.005 , ± 0.01 , ± 0.02 , and ± 0.05 a. u., respectively.

we find a line of 0.0 a. u. intersecting the Pd atom and the H₂ molecule. In comparison with the case of the attractive system, $\text{Pd}(^1S) - \text{H}_2$ shown in Figure 4, the electron density of the Pd atom shown in Figure 10 is less af-

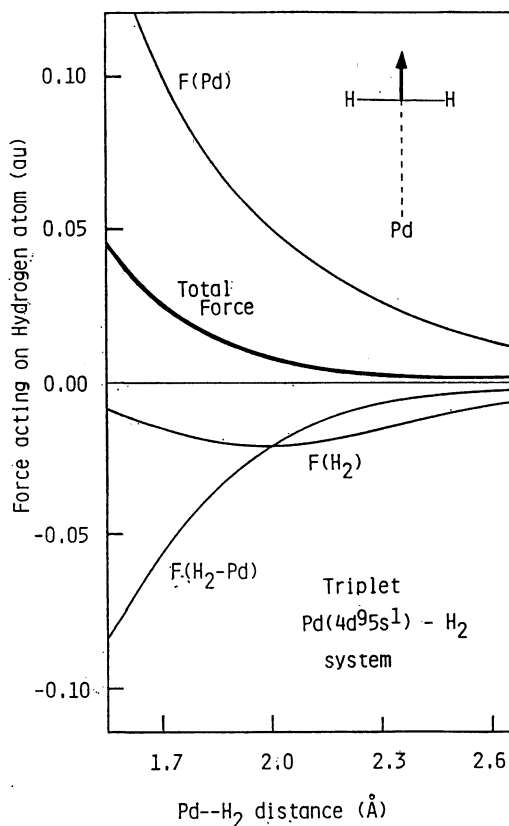


Figure 11. The analysis of the force F_z acting on the H_2 molecule of the triplet $Pd(^3D)-H_2$ system. The definition of the forces is given by Eq. (2).

ected by an approach of the H_2 molecule and tends to keep its spherical symmetry. Comparing the force analysis shown in Figure 11 with that of Figure 5, we see that the repulsion due to the Pd atom, $F(Pd)$, increases more rapidly in the present case than in the previous case. The attractive part of the force, $F(H_2-Pd)$ and $F(H_2)$, can not overcome this repulsive force. The reason that the Pd atom in the $4d^9 5s^1$ configuration is more repulsive than that in the $4d^{10}$ configuration is as follows. We first note that the $5s$ orbital of Pd is more diffuse than the $4d$ orbital. The atomic radii $\langle r \rangle$ of the Hartree-Fock AO's of the $^3D(d^9 s^1)$ state of Pd are⁶

$$\langle r \rangle_{4d} = 0.765 \text{ \AA}, \quad \langle r \rangle_{5s} = 1.945 \text{ \AA}$$

Since the $5s$ orbital is more diffuse than the $4d$ orbital, the electron in the $5s$ orbital is less able to shield its central nucleus than the electron in the $4d$ orbital, when the attacking H_2 molecule is not far away. Therefore, the Pd atom in the $4d^9 5s^1$ configuration is more repulsive than the Pd atom in the $4d^{10}$ configuration.

IV. CONCLUSION

We studied the interaction of the hydrogen molecule with the palladium atom in the singlet ground state ($4d^{10}, ^1S$) and in the lowest triplet state ($4d^95s^1, ^3D$), as a model of the chemisorption of the H₂ molecule on the Pd metal. We used the effective core potential method and calculated the accurate Hellmann-Feynman force of the H₂ system adding the first derivatives of the hydrogen basis set. We used an intuitive force concept for studying the origin of the interaction.

We found that the singlet Pd (1S)—H₂ system is attractive but the triplet Pd (3D)—H₂ system is repulsive. The side-on approach is found to be the preferable path. For the Pd (1S)—H₂ system, the Pd—H bonds are gradually formed as the H₂ molecule approaches. The electron density is accumulated in the overlap region between H₂ and Pd and it causes the F (H₂—Pd) force which pulls the H₂ molecule onto the metal atom. As the hydrogen molecule approaches, the protons receive the force which prolongs the H—H distance. This is due to the decrease in the electron density in the bonding region of the two hydrogens. In an MO interaction picture, this reorganization of the electron density is due to an electron transfer from the bonding MO of the hydrogen molecule to the empty hybrid orbital of the 5s, 5p_z, and 4d_{z²} AO's of the Pd atom. The back-transfer of electrons from the 4d_{yz} AO to the antibonding orbital of the H₂ molecule is small.

For the triplet Pd (3D)—H₂ system, the electron density of the Pd atom is less affected by the approach of the H₂ molecule and tends to keep its spherical symmetry. Further, the Pd atom in the $4d^95s^1$ configuration is more repulsive than that in the $4d^{10}$ configuration. This is because the electron density in the $4d^95s^1$ configuration is less able to shield its Pd nucleus than the electron density in the $4d^{10}$ configuration, since the 5s orbital is more diffuse than the 4d orbital. Therefore, the H₂ molecule is repelled by the Pd atom.

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SAŽETAK

Interakcija molekule H₂ sa atomom paladija primjenom koncepta Hellmann-Feynmanove sile

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Kao model za kemisorpciju razmotrena je interakcija molekule H₂ i atoma Pd u singuletnom ¹S (4d¹⁰) i tripletnom ³D (4d⁹5s¹) stanju. Sila kojom atom Pd djeluje na H₂ izračunana je vrlo točno. Ustanovljeno je da je sila privlačna za singulet, a odbojna za triplet. Pri veznoj interakciji dolazi do gomilanja elektronske gustoće u regiji prekrivanja atoma Pd i molekule H₂, što se događa na račun smanjenja gustoće duž veze H—H. Pri tome se tvori nova veza Pd—H, a slabi veza između atoma vodika. Dolazi i do migracije naboja iz vezne MO H₂ u prazne 5s5p_z orbitale atoma Pd.