

# Theoretical Study on the Chemisorption of a Hydrogen Molecule on Palladium

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**Abstract:** Interaction of a hydrogen molecule with palladium in the Pd-H<sub>2</sub> and Pd<sub>2</sub>-H<sub>2</sub> systems is studied theoretically as a model for chemisorption and catalytic action of a metal surface. Sophisticated ab initio theories including electron correlations (CAS-MC-SCF, SAC, and SAC-CI theories) are used for calculations of ground and excited states of the interacting systems. While a single Pd atom in the ground state shows affinity for the hydrogen molecule, it does not catalyze cleavage of the H-H bond, and a triangular adduct form is the stable geometry of the Pd-H<sub>2</sub> system. The lower lying excited states of the Pd atom are all repulsive. On the other hand, the Pd<sub>2</sub> system clearly shows catalytic activity toward hydrogen chemisorption. The H<sub>2</sub> molecule is adsorbed at about 1.5 Å from the metal, and an equilibrium between molecular and dissociated adsorption forms is established, with the latter being more stable than the former by a few kilocalories/mole. The Pd-Pd bond is not weakened in this process, a fact related to the stability of the catalytic surface. The dangling bonds of the Pd surface and electron correlations play very important roles in this catalytic activity. The 4d orbitals of Pd are mainly involved, with the outer 5s orbital playing a secondary role. Without electron correlations, the dissociative adsorption is not explained even qualitatively. There is almost no chance for the excited states to participate in the catalytic process on Pd. This mechanism differs from that proposed for a Ni surface. Lastly, photoelectron spectra are theoretically calculated to explain some interacting features of the observed spectra for the hydrogen-palladium system.

Electronic processes in chemisorption and catalytic action on a metal surface play fundamental roles in chemistry and its applications to industry. Clarification of these electronic processes and construction of predictive models useful for catalyst design are important concerns of theoretical chemists. In the present work, the interaction of a hydrogen molecule with palladium is studied theoretically as a model for chemisorption and catalytic action on a metal surface. Some preliminary results have previously been published.<sup>1</sup>

Chemisorption of a hydrogen molecule on a transition metal is an important step for hydrogen storage as well as a variety of catalytic processes involving activated hydrogen.<sup>2-7</sup> Palladium especially shows a unique affinity toward hydrogen.<sup>2,3</sup> The "solubility" of hydrogen in palladium metal markedly exceeds that of the other group 8 metals.<sup>2</sup> Hydrogen is adsorbed dissociatively on palladium<sup>5b</sup> and the bonding involves d electrons of the metal.<sup>6</sup> Palladium is known to be a good catalyst for many hydrogenation reactions.<sup>3,4,7</sup> A well-known example is that of the hydrogenation reaction of acetylene to form ethylene in which a critical step is the dissociative adsorption of hydrogen on a palladium surface.<sup>7</sup>

Several ab initio theoretical studies have been reported on the electronic structure and the nature of bonding involved in palladium-atomic hydrogen systems, Pd<sub>n</sub>-H (*n* = 1-6),<sup>8-16</sup> and palladium-molecular hydrogen systems, Pd<sub>n</sub>-H<sub>2</sub> (*n* = 1).<sup>17-19</sup> The former system is considered as a model of atomic hydrogen dissociatively adsorbed on a palladium surface.

For the diatomic molecule PdH, experimental bonding properties are known,<sup>20</sup> so that some verification of the theoretical method is possible. Basch and co-workers<sup>8</sup> studied PdH, PtH, and related diatomics by the effective core potential (ECP) MC-SCF method. The importance of the d electrons in the bonding in PdH and PtH was shown. Bagus and Bjorkman<sup>9</sup> examined the bonding in NiH and PdH by ab initio SCF and CI methods. Pacchioni et al.<sup>10</sup> reported a multireference CI study for PdH, PdC, and PdCO based on the ECP SCF MO's and showed the importance of electron correlations.

The interaction of an atomic hydrogen with a small palladium cluster was studied theoretically by several authors.<sup>11-16</sup> Messmer et al.<sup>11</sup> studied Pd<sub>4</sub>H and Pd<sub>6</sub>H systems containing atomic hydrogen at the interstitial site by the SCF X $\alpha$  SW method and compared the results with those for the corresponding Ni and Pt systems. They attributed the high "solubility" of atomic hydrogen

in palladium to a nearly zero net orbital electronegativity difference between the Pd(4d) and H(1s) orbitals in aggregates. This is in contrast to the large electronegativity differences in nickel and platinum aggregates. Louie et al.<sup>12</sup> showed that atomic hydrogen lies in the threefold hollow site of a Pd(111) surface with a Pd-H length of 1.69 Å. The bonding was shown to be predominantly Pd(4d)-H(1s). Fritsche<sup>13</sup> reported SW-X $\alpha$  calculations of Pd<sub>n</sub>-H systems (*n* = 4, 5, 6) as models for chemisorbed and adsorbed hydrogen on palladium. Pacchioni and Koutecky<sup>14</sup> studied Pd<sub>n</sub>-H systems (*n* = 1, 2, 3) by the multireference CI method based on the ECP SCF MO's. They reported the equilibrium geometry of these species and elucidated the nature of the bonding involved.

- (1) (a) Nakatsuji, H.; Hada, M. *Applied Quantum Chemistry, PACH'CHEM, Honolulu, 1984*; Smith, V. H., Jr., Ed.; Reidel: Dordrecht, 1986; p 93. (b) Nakatsuji, H.; Hada, M. *J. Am. Chem. Soc.* **1985**, *107*, 8264.
- (2) Lewis, F. A. *The Palladium-Hydrogen System*; Academic Press: New York, 1967.
- (3) Bond, G. C. *Catalysis by Metals*; Academic Press: New York, 1962.
- (4) (a) Roundhill, D. M. *Adv. Organomet. Chem.* **1975**, *13*, 273. (b) Henry, P. M. *Ibid.* **1975**, *13*, 363. (c) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vols. 1 and 2.
- (5) (a) Conrad, H.; Ertl, G.; Latta, E. E. *Surf. Sci.* **1974**, *41*, 435. (b) Behm, R. J.; Christmann, K.; Ertl, G. *Ibid.* **1980**, *99*, 320. (c) Nyberg, C.; Tengstam, C. G. *Ibid.* **1983**, *126*, 163.
- (6) Demuth, J. E. *Surf. Sci.* **1977**, *65*, 369.
- (7) Wood, B. J.; Wise, H. J. *Catal.* **1966**, *5*, 135.
- (8) (a) Basch, H.; Cohen, D.; Topiol, S. *Isr. J. Chem.* **1980**, *19*, 233. (b) Basch, H.; Topiol, S. *J. Chem. Phys.* **1979**, *71*, 802.
- (9) Bagus, P. S.; Bjorkman, C. *Phys. Rev. A* **1981**, *23*, 461.
- (10) Pacchioni, G.; Koutecky, J.; Fantucci, P. *Chem. Phys. Lett.* **1982**, *92*, 486.
- (11) Messmer, R. P.; Salahub, D. R.; Johnson, K. H.; Yang, C. Y. *Chem. Phys. Lett.* **1977**, *51*, 84.
- (12) (a) Louie, S. G. *Phys. Rev. Lett.* **1979**, *42*, 476. (b) Chan, C. T.; Louie, S. G. *Phys. Rev. B* **1983**, *27*, 3325. (c) Eberhardt, W.; Louie, S. G.; Plummer, E. W. *Ibid.* **1983**, *28*, 465.
- (13) Fritsche, H.-G. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1983**, *38*, 1118.
- (14) Pacchioni, G.; Koutecky, J. *Surf. Sci.* **1985**, *154*, 126.
- (15) Miyoshi, E.; Sakai, Y.; Mori, S. *Surf. Sci.* **1985**, *158*, 667.
- (16) Baykara, N. A.; Andzelm, J.; Baykara, S. Z.; Salahub, D. R. *Int. J. Quantum Chem.*, in press. The authors thank Dr. Salahub for sending this preprint prior to publication.
- (17) Bagatur'yants, A. A.; Anikin, N. A.; Zhidomirov, G. M.; Kazanskii, V. B. *Russ. J. Phys. Chem.* **1981**, *55*, 1157.
- (18) (a) Brandemark, U. B.; Blomberg, M. R. A.; Petterson, L. G. M.; Siegbahn, P. E. M. *J. Phys. Chem.* **1984**, *88*, 4617. (b) Low, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 8321.
- (19) Nakatsuji, H.; Hada, M. *Croat. Chem. Acta* **1984**, *57*, 1371.
- (20) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

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Miyoshi et al.<sup>15</sup> studied the Pd<sub>n</sub>-H system with the model potential SCF MO method.

In marked contrast to the rather well-documented Pd<sub>n</sub>-H systems, very little has appeared in the literature on the interaction of a molecular hydrogen with palladium. Bagatur'yants et al.<sup>17</sup> studied an approach of the hydrogen molecule to the Pd atom with a fixed H-H length (0.74 Å) by the SCF MO method. They showed that formation of a molecular complex was energetically favorable. Brandemark et al.<sup>18a</sup> studied an addition of molecular hydrogen to the Pd atom employing multireference CI calculations. They reported that a stable complex was formed with the binding energy of about 5 kcal/mol. The H-H bond was only slightly longer than that of the free H<sub>2</sub> molecule and the Pd-H distance was as long as 1.93 Å. Low and Goddard<sup>18b</sup> found a transient state at 3.6 kcal/mol above the dissociation limit with a relaxed H-H distance of 1.73 Å and a Pd-H distance of 1.51 Å. We previously studied<sup>19</sup> the interaction of a hydrogen molecule with the <sup>1</sup>S(4d<sup>10</sup>) and <sup>3</sup>D(4d<sup>9</sup>5s<sup>1</sup>) states of the Pd atom by the ECP SCF MO method. The former state was attractive, but the latter was repulsive. We have analyzed the force and density origin of these interactions using the Hellmann-Feynman force concept.<sup>21</sup>

On the other hand, the electronic structure of a palladium cluster, Pd<sub>n</sub>, seems at present to be in a rather contradictory state. Experimentally, <sup>1</sup>S(d<sup>10</sup>) is known to be the ground state of the Pd atom with the <sup>3</sup>D(d<sup>9</sup>s<sup>1</sup>) state being about 20 kcal/mol higher than the ground state.<sup>22</sup> For Pd<sub>2</sub>, Shim and Gingerich<sup>23</sup> have reported in their ab initio Hartree-Fock CI study that the interaction between the two <sup>1</sup>S(4d<sup>10</sup>) Pd atoms was nonbonding, but that between the <sup>3</sup>D(4d<sup>9</sup>5s<sup>1</sup>) atoms led to several bonding states which were, however, all unstable by 17 to 24 kcal/mol relative to the two Pd atoms in the ground state. This does not explain the existence of the stable Pd<sub>2</sub> molecule with a dissociation energy of 24 kcal/mol.<sup>23</sup> Basch et al.<sup>8a</sup> reported several bound states of Pd<sub>2</sub> which essentially had a d<sup>9</sup>s<sup>1</sup> electronic configuration. However, their results are unreliable since for the Pd atom their ECP method predicted the <sup>3</sup>D state to be below the <sup>1</sup>S state by 4.6 kcal/mol, and the <sup>3</sup>D-<sup>1</sup>S energy separation was in error by 26 kcal/mol in comparison with the experimental value. Miyoshi et al.<sup>24</sup> have studied the Pd<sub>4</sub> cluster by the model potential Hartree-Fock method.<sup>25</sup> They reported that the lowest bonding state of Pd<sub>4</sub> was <sup>3</sup>B<sub>2</sub> arising from three d<sup>10</sup> and one d<sup>9</sup>s<sup>1</sup> atoms. However, this state was unstable by 18 kcal/mol relative to the energy of four d<sup>10</sup> atoms. The AO populations of the valence 5s, 5p, and 4d AO's were 0.26, 0.03, and 9.71, respectively. For the Pd bulk, an energy band calculation gave s and d valence electron populations per atom as 0.37 and 9.63, respectively.<sup>26</sup> Pacchioni and Koutecky studied the Pd<sub>3</sub> clusters which interact with H and CO at the hollow site (most stable geometry).<sup>14,27</sup> They reported that the gross atomic populations of the 5s and 4d AO's of palladium cluster were 0.22 and 9.75, respectively, for the Pd<sub>3</sub>-H system and 0.153 and 9.799, respectively, for the Pd<sub>3</sub>-CO system. In their MR-CI calculations, the systems turned out to be stable with respect to dissociation into Pd atoms and H or CO. Thus, the electronic structure of the Pd cluster seems to be closer to the d<sup>10</sup> configuration, rather than the d<sup>9</sup>s<sup>1</sup> configuration, although this might apparently contradict the customary assumption of the inertness of the closed-shell configuration.<sup>14</sup>

The interaction of a hydrogen molecule with metals other than palladium is also interesting in view of the purpose of the present study. Melius and co-workers<sup>28</sup> have studied chemisorption on

a nickel surface, using Ni<sub>2</sub>-H<sub>2</sub> as a model, by an ECP MC-SCF method. The Ni-H bond was found to be dominated by the 4s orbital, but the 3d electrons on the Ni atoms were also considered important, allowing for a biradical intermediate. Blomberg and Siegbahn<sup>29</sup> studied lower lying states of NiH<sub>2</sub>. Though the ground state was found to be a linear triplet, <sup>3</sup>Δ<sub>g</sub>(<sup>3</sup>B<sub>1</sub>), another lower singlet A<sub>1</sub> state was found to be relatively stable at an HNiH angle as small as 57°. In this <sup>1</sup>A<sub>1</sub> state, the d orbital participated in the Ni-H bond and the two hydrogens were also binding. They concluded that the bonding in this NiH<sub>2</sub> system was essentially the same as that observed for H<sub>2</sub> on a nickel surface. This conclusion was confirmed later by the extensive calculations of the dissociation of H<sub>2</sub> on the Ni<sub>n</sub> (n = 13, 14) clusters.<sup>30</sup> Satoko and Tsukada<sup>31</sup> studied the chemisorption of a hydrogen molecule on Ni, Cu, Ca, and Mg surfaces using an LCAO-Xα method. They suggested that mixing between the H<sub>2</sub> antibonding orbital and the d orbital of the metal atom was important for the dissociative chemisorption of the hydrogen molecule on the Ni and Ca surfaces. Saillard and Hoffmann<sup>32a</sup> studied C-H and H-H activations in Ni and Ti complexes and their surfaces at the extended Hückel level of accuracy. They discussed some similarities and differences between the activation acts in a mononuclear complex and on a surface. Trinquier and Hoffmann<sup>32b</sup> considered similar processes on binuclear complexes.

In this paper, we study the interaction of a hydrogen molecule with palladium in the Pd-H<sub>2</sub> and Pd<sub>2</sub>-H<sub>2</sub> systems as a model for chemisorption and catalytic action on a metal surface, based on a localized model of the interaction, which may be partially supported by earlier investigations.<sup>6,11-15,28,31,33-35</sup> In particular, we focus on the electronic origin of the catalytic activity for the dissociative adsorption of the H<sub>2</sub> molecule on the Pd surface. We also report on calculated ionization spectra of the Pd<sub>2</sub>-H<sub>2</sub> system which are used to explain some interesting features of the experimentally observed spectra. Sophisticated ab initio theories are employed which include electron correlations for both ground, excited (singlet and triplet), and ionized states.

#### Computational Method

The Gaussian basis for the Pd atom is a (3s3p3d)/[3s2p2d] set, and the Kr core is replaced by an effective core potential.<sup>36</sup> Relativistic effects are included through the effective core potential. For hydrogen, we use the (4s)/[2s] set of Huzinaga-Dunning<sup>37</sup> plus their first derivatives which are the p-type functions.<sup>38</sup> Then, we use the Hellmann-Feynman theorem

$$F_H = Z_H \int r_{H1}/r_{H1}^3 \rho(r_1) dr_1 - Z_H \sum_{B(\neq H)} Z_B R_{HB}/R_{HB}^3 \quad (1)$$

to calculate the force  $F_H$  acting on the protons.<sup>38</sup> This force is connected, through eq 1, to the dynamic behavior of the electron density  $\rho(r)$  of the system.<sup>29</sup> In the present model system, we are primarily interested in the force acting on the adsorbed molecule H<sub>2</sub>, and not that on the metal atoms, since here the metal atoms represent surface atoms of the metal catalyst. Therefore, we add

(28) (a) Melius, C. F. *Chem. Phys. Lett.* **1976**, *39*, 287. (b) Melius, C. F.; Moskowitz, J. W.; Mortola, A. P.; Baillie, M. B.; Ratner, M. A. *Surf. Sci.* **1976**, *59*, 279.

(29) Blomberg, M. R. A.; Siegbahn, P. E. M. *J. Chem. Phys.* **1983**, *78*, 986, 5682.

(30) Siegbahn, P. E. M.; Blomberg, M. R. A.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1984**, *81*, 2103.

(31) Satoko, C.; Tsukada, M. *Surf. Sci.* **1983**, *134*, 1.

(32) (a) Saillard, J. Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006. (b) Trinquier, G.; Hoffmann, R. *Organometallics* **1984**, *3*, 370.

(33) (a) Conrad, H.; Ertl, G.; Knozinger, H.; Kuppers, J.; Latta, E. E. *Chem. Phys. Lett.* **1976**, *42*, 115. (b) Demuth, J. E.; Eastman, D. E. *Phys. Rev. B* **1976**, *13*, 1523.

(34) Ozin, G. A.; Power, W. J.; Upton, T. H.; Goddard, W. A. *J. Am. Chem. Soc.* **1978**, *100*, 4750 and the references cited therein.

(35) Muettterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

(36) Hay, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 1390.

(37) (a) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. (b) Dunning, T. H., Jr. *Ibid.* **1970**, *53*, 2823.

(38) (a) Nakatsuji, H.; Kanda, K.; Yonezawa, T. *Chem. Phys. Lett.*, **1980**, *75*, 340. (b) Nakatsuji, H.; Hayakawa, T.; Hada, M. *Ibid.* **1981**, *80*, 94. (c) Nakatsuji, H.; Kanda, K.; Hada, M.; Yonezawa, T. *J. Chem. Phys.* **1982**, *77*, 3109.

(21) (a) Nakatsuji, H. *J. Am. Chem. Soc.* **1974**, *96*, 24, 30. (b) Nakatsuji, H.; Koga, T. In *The Force Concept in Chemistry*; Deb, B. M., Ed.; Van Nostrand Reinhold: New York, 1981; Chapter 3.

(22) Moore, C. E. *Atomic Energy Levels*; National Bureau of Standards: Washington, D.C., 1971; Vol. 3.

(23) Shim, I.; Gingerich, K. A. *J. Chem. Phys.* **1984**, *80*, 5107.

(24) Miyoshi, E.; Sakai, Y.; Mori, S. *Chem. Phys. Lett.* **1985**, *113*, 457.

(25) Bonifacic, V.; Huzinaga, S. *J. Chem. Phys.* **1974**, *60*, 2779. Sakai, Y.; Huzinaga, S. *Ibid.* **1982**, *76*, 2537, 2552.

(26) Andersen, O. K. *Phys. Rev. B* **1970**, *2*, 883.

(27) Pacchioni, G.; Koutecky, J. In *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry*; (NATO ASI Series) Veillard, A., Ed.; Reidel: Dordrecht, 1986; p 465.

Table I. Optimized H-H Distance in the Pd-H<sub>2</sub> System for Several Pd-H<sub>2</sub> Separations, *R* (Å), Calculated by the Hartree-Fock SCF Method

<i>R</i>	optimized <i>R</i> <sub>H-H</sub>	<i>R</i>	optimized <i>R</i> <sub>H-H</sub>
2.6	0.736	1.85 <sup>a</sup>	0.768
2.3	0.742	1.7	0.789
2.0	0.755	1.4	1.017

<sup>a</sup> Optimized geometry.

the first derivative bases only to the hydrogen molecule. The calculated force is used in the optimization process. Wang and Pitzer<sup>39</sup> reported for PtH that the polarization functions centered on the H atom were more important than those centered on the Pt atom.

The optimal path of the hydrogen molecule approach is calculated by the Hartree-Fock method for the Pd-H<sub>2</sub> system and by the CAS-MC-SCF method<sup>40</sup> for the Pd<sub>2</sub>-H<sub>2</sub> system within an 8 (lower) × 2 (upper) active orbital space. The MC-SCF orbitals are optimized within the lower 40 orbital space.<sup>41</sup> For the CAS-MC-SCF computations, a modified version of the program GAMESS<sup>42</sup> is employed. The potential energy curves of the ground and excited states are also calculated by the SAC and SAC-CI theories<sup>43</sup> to get more accurate results. These theories are based on the cluster expansion of the wave function and describe electron correlations more accurately than the MC-SCF method. They have been established as reliable methods for calculating ground, excited, and ionized states.<sup>44,45</sup> The linked operators in the SAC and SAC-CI calculations are selected by the thresholds  $\lambda_g$  and  $\lambda_e$  of  $2 \times 10^{-5}$  and  $1 \times 10^{-4}$  au, respectively.<sup>45</sup> The wave function consists of 500-1100 linked operators which are symmetry adapted in each spin-space symmetry. Details of the algorithms of the SAC and SAC-CI calculations have previously been reported.<sup>43-45</sup>

To confirm the accuracy of the present calculational method, we carried out a CAS-MC-SCF calculation of the PdH molecule. The ground state is <sup>2</sup>T<sup>+</sup> in agreement with the experiment.<sup>20</sup> The calculated values of the equilibrium bond length, vibrational frequency (for the PdD molecule<sup>20</sup>), binding energy, and dipole moment turn out to be 1.570 Å (1.529 Å), 1496 cm<sup>-1</sup> (1446 cm<sup>-1</sup>), 54 kcal/mol (~76 kcal/mol), and 2.81 D (1.977 D), respectively, the parenthesized values being the experimental ones.<sup>20,46</sup> We see that the present method gives reasonable agreement for the equilibrium length and vibrational frequency, though it yields a smaller value for the binding energy.

### Pd-H<sub>2</sub> System

Previously,<sup>19</sup> we studied the interaction of the hydrogen molecule with the ground <sup>1</sup>S(4d<sup>10</sup>) and excited <sup>3</sup>D(4d<sup>9</sup>5s<sup>1</sup>) states of the Pd atom. It was found that the former was attractive, but the latter was repulsive. The force and density origins of these interactions were elucidated. In the present work, we study an optimized approach and the roles of the ground and excited states including the effect of electron correlation.

We consider a side-on approach of the H<sub>2</sub> molecule to the Pd atom.

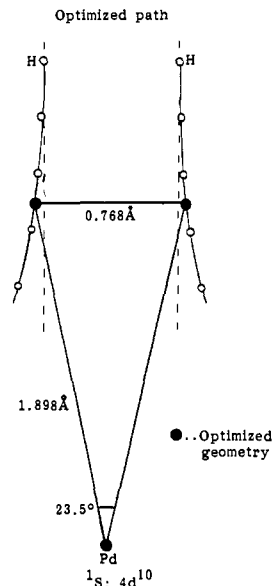
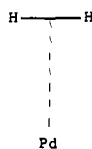


Figure 1. Optimized approach of the hydrogen molecule to the <sup>1</sup>S state of the Pd atom. The triangle shows the optimized geometry of the Pd-H<sub>2</sub> system.

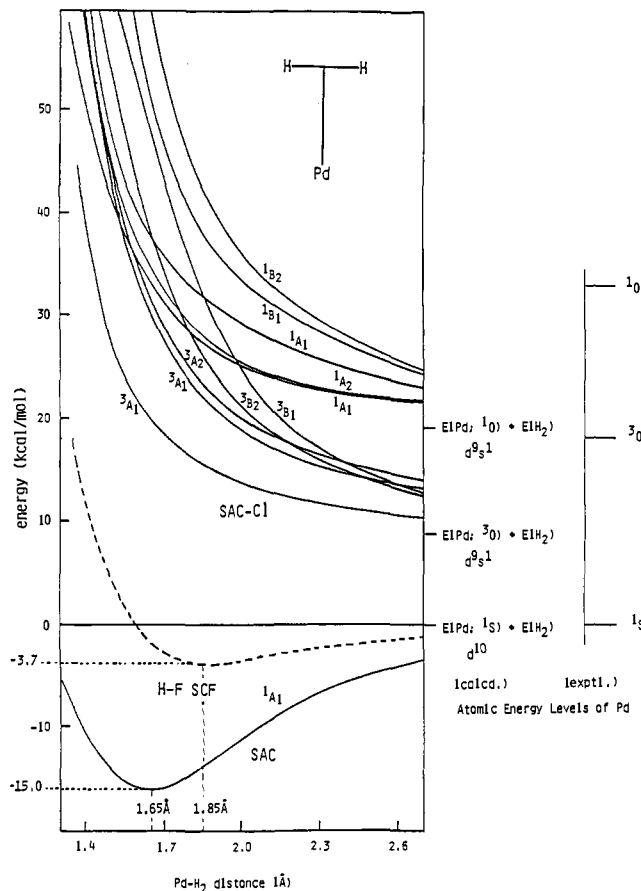


Figure 2. Potential energy curves of the ground and excited states of the Pd<sub>2</sub>-H<sub>2</sub> system calculated by the SAC and SAC-CI methods.

This orientation has previously been shown to be favorable.<sup>19</sup> Figure 1 and Table I show the optimized approach of the hydrogen molecule to the palladium atom in the <sup>1</sup>S state. The most stable geometry of the system is the depicted triangular one. This geometry corresponds to a molecular hydrogen attached to a metal atom. The H-H distance, 0.768 Å, is only slightly longer than the equilibrium length, 0.741 Å, of a free hydrogen molecule. The Pd-H distance is 1.898 Å which is much longer than the bond distance, 1.529 Å, of the free PdH molecule,<sup>20</sup> in agreement with earlier work.<sup>18</sup> The calculated stabilization energy is only 3.7

(39) Wang, S. W.; Pitzer, K. S. *J. Chem. Phys.* **1983**, *79*, 3851.

(40) (a) Roos, B.; Taylor, P.; Siegbahn, P. *Chem. Phys.* **1980**, *48*, 157. (b) Siegbahn, P.; Heiberg, A.; Roos, B.; Levy, B. *Phys. Scr.* **1980**, *21*, 323.

(41) Hada, M.; Nakatsuji, H., to be submitted for publication.

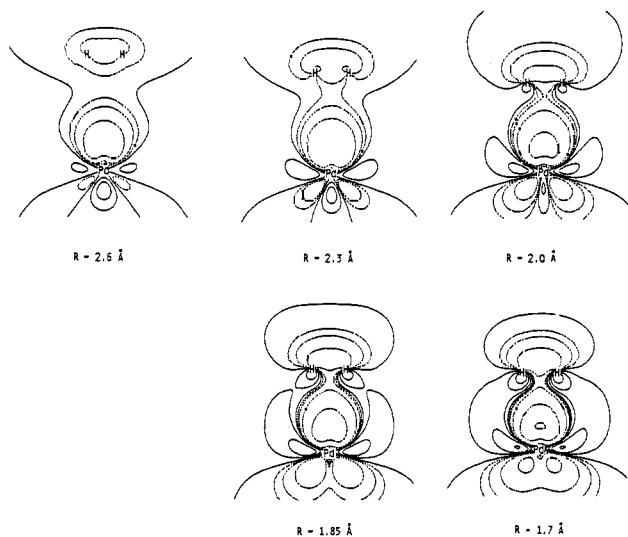
(42) Brooks, B. R.; Saxe, P.; Laidig, W. D.; Dupuis, M. Program System GAMESS; Program Library No. 481, Computer Center of the Institute for Molecular Science, 1981.

(43) (a) Nakatsuji, H.; Hirao, K. *J. Chem. Phys.* **1978**, *68*, 2053. (b) Nakatsuji, H. *Chem. Phys. Lett.* **1978**, *59*, 362; **1979**, *67*, 329.

(44) For example, see: Nakatsuji, H. *J. Chem. Phys.* **1984**, *80*, 3703 and the references cited therein.

(45) Nakatsuji, H. *Chem. Phys.* **1983**, *75*, 425.

(46) Malmberg, C.; Scullman, R.; Nylén, P. *Ark. Fys.* **1969**, *39*, 495.



**Figure 3.** Reorganization of the electron density of the Pd-H<sub>2</sub> system along the optimized path. The geometry at  $R = 1.85 \text{ \AA}$  corresponds to the energy minimum. The difference density is defined by eq 2 of the text.

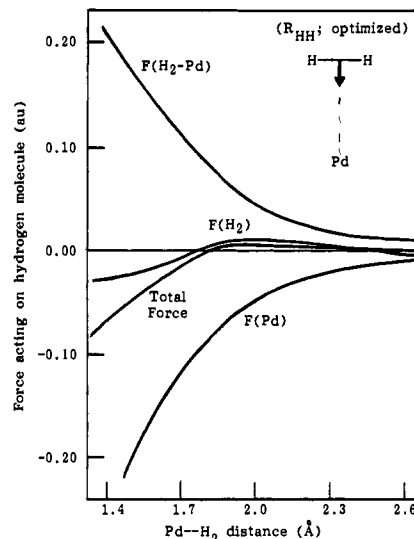
kcal/mol at the Hartree-Fock level. The linear form is more unstable than the triangular form by 37 kcal/mol. The optimized Pd-H distance there is 1.48 Å. It should further be noted that the hydrogen molecule seems to react more easily with the Pd atom (oxidative addition)<sup>18,47</sup> when electronegative ligands are attached to the Pd atom.

Potential energy curves of the Pd-H<sub>2</sub> system are shown in Figure 2. The ground state is calculated by the SAC method, and the singlet and triplet excited states are calculated by the SAC-CI method. The excited triplet states are essentially the <sup>3</sup>D states of the Pd atom interacting with the H<sub>2</sub> molecule, the same being true for the singlets. They are calculated along the optimized path shown in Figure 1. Among the states calculated here, only the ground state is attractive and all the other states are repulsive. These potential curves suggest existence of a detachment or "desorption" process through the excited states of the metal.

In the present approximation, the state separations turn out to be underestimated. The <sup>3</sup>D and <sup>1</sup>D states of the Pd atom are calculated as 9 and 19 kcal/mol above the <sup>1</sup>S ground state, with the corresponding experimental values being 19 and 33 kcal/mol.<sup>22</sup>

We conclude that the single Pd atom shows an affinity to the hydrogen molecule and forms a triangular adduct, but it does not catalyze a cleavage of the H-H bond. A single Pd atom is thus insufficient as a model for chemisorption on a metal surface.

The role of electron correlation is seen to be significant from Figure 2 wherein the broken line corresponds to the Hartree-Fock result. The stabilization energy of the Pd-H<sub>2</sub> system calculated at the SAC level is about 15 kcal/mol relative to the separated systems. The effect of electron correlation on the stabilization energy is about 11 kcal/mol. The Pd-H<sub>2</sub> distance shortens to 1.65 Å in comparison to that at the Hartree-Fock level of 1.85 Å. In the correlated level, the ground state of the Pd-H<sub>2</sub> system turns out to be more stable in our calculations than in those by Brandemark et al.<sup>18a</sup> This stability may be attributed to two reasons: (i) a relativistic effect considered in the present calculations through the effective core potential, and (ii) the existence of the derivative bases at the hydrogen atoms also in the present calculations, though Brandemark et al. added one polarization function on the hydrogen atom. Similar significant effects of the extensive polarization functions on the hydrogen atom were reported by Wang and Pitzer<sup>39</sup> for the PtH system.



**Figure 4.** Force acting on the H<sub>2</sub> molecule in the Pd-H<sub>2</sub> system and its analysis into the components defined in eq 3.

Figure 3 shows the deformation density for the Pd-H<sub>2</sub> system along the optimized path:

$$\Delta\rho = \rho(\text{Pd-H}_2) - \rho(\text{Pd}) - \rho(\text{H}_2) \quad (2)$$

For the free Pd atom, we use the <sup>1</sup>S(4d<sup>10</sup>) ground state. As the hydrogen molecule approaches the Pd atom, the electron is transferred from the H<sub>2</sub> molecule to the Pd atom. The Pd orbitals also rehybridize and the electrons in the 4d<sub>z<sup>2</sup></sub> AO flow into the 5s and 5p AO's.<sup>19</sup> (The z axis points from the Pd atom to the center of the H-H bond.) At  $R = 1.85 \text{ \AA}$ , which corresponds to the equilibrium triangular form, two pincher-like lobes of the Pd atom extend on the right and left toward the H<sub>2</sub> molecule, as if trying to capture it.

Figure 4 shows the force acting on the hydrogen molecule along the optimized path depicted in Figure 1. The force components are defined by<sup>19</sup>

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

$$F = F_{\text{H}} + F_{\text{H}'} \quad (3b)$$

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 protons 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 in the H<sub>2</sub> region and the other proton of the H<sub>2</sub> molecule. The force  $F(\text{H}_2)$  in the direction toward the Pd atom is entirely due to the polarization of the electron cloud of the hydrogen atom in that direction. It arises as a result of adding the derivative bases (polarization functions) to the hydrogen [2s] basis. The last term,  $F(\text{H}_2\text{-Pd})$ , represents the force due to the electron density accumulated in the overlap region of H<sub>2</sub> and Pd. As seen from Figure 4, the attractive force stems mostly from this force. This is in conformity with the behavior of the electron density shown in Figure 3. The force  $F(\text{Pd})$  is repulsive throughout the process and the force  $F(\text{H}_2)$  is relatively small in this system. A more detailed force analysis has been presented elsewhere.<sup>19</sup>

### Pd<sub>2</sub>-H<sub>2</sub> System

(i) **Energetics of the Interaction.** We first study a favorable orientation of an H<sub>2</sub> molecule toward a Pd<sub>2</sub> fragment. The Pd-Pd distance is fixed as 2.7511 Å throughout the present calculations. This value corresponds to the observed distance for the fcc crystal

(47) (a) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857. (b) Kitaura, K.; Obara, S.; Morokuma, K. *J. Am. Chem. Soc.* **1981**, *103*, 2891. (c) Noell, J. O.; Hay, P. J. *Ibid.* **1982**, *104*, 4578; *Inorg. Chem.* **1982**, *21*, 14.

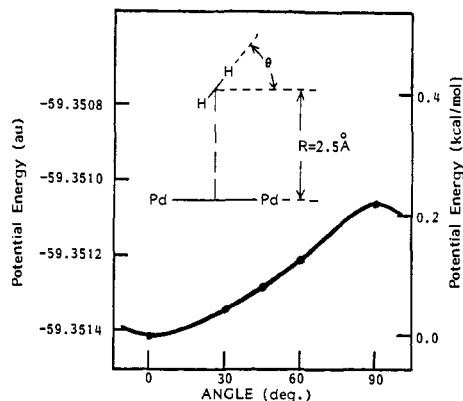


Figure 5. Potential curve for the orientation of the H<sub>2</sub> molecule on the Pd<sub>2</sub> fragment.

Table II. Optimized H–H Distance in the Pd<sub>2</sub>–H<sub>2</sub> System for Several Pd<sub>2</sub>–H<sub>2</sub> Separations, *R* (Å), Calculated by the CAS–MC–SCF Method

point	<i>R</i>	optimized <i>R</i> <sub>H–H</sub>
A	3.0	0.735
B	2.5	0.739
C	2.0	0.787
D	1.5	0.847
E	1.5	1.2000
F	1.5	1.4000
G <sup>a</sup>	1.5	1.94 (2.1 <sup>a</sup> )
H	1.5	2.7511

<sup>a</sup>Second minimum calculated by the SAC method appears near here (cf. Figure 10).

structure.<sup>48</sup> In Figure 5, the potential curve for the orientation of the H<sub>2</sub> molecule relative to the Pd<sub>2</sub> fragment is shown. The distance between the centers of H<sub>2</sub> and Pd<sub>2</sub> is 2.5 Å. The side-on orientation ( $\theta = 0^\circ$ ) is seen to be most favorable. Therefore, we consider only the side-on approach of the H<sub>2</sub> molecule.

In Figure 6A, we display the force acting on the H<sub>2</sub> molecule when it approaches the Pd<sub>2</sub> fragment with the H–H distance fixed to that of the free molecule. At points a and b, the H<sub>2</sub> molecule feels an attractive force, but it is too small to be indicated in the figure. At point c, the H<sub>2</sub> molecule experiences a force which is attractive and tends to elongate the H–H distance. At point d, the force is repulsive and works to elongate the H<sub>2</sub> distance. When the H–H distance is elongated to point e, the force again becomes attractive.

In Figure 6B and Table II, we give the optimized H–H distance up to the Pd<sub>2</sub>–H<sub>2</sub> distance of 1.5 Å. The change in the H–H distance is small. The distance is slightly longer than the corresponding distance in the Pd–H<sub>2</sub> system shown in Table I. When *R* is 1.5–1.6 Å, a second minimum appears at the elongated H–H distance, which is discussed in detail below.

Potential curves of the H<sub>2</sub> molecule interacting with the Pd<sub>2</sub> fragment are plotted in Figure 7 for several distances, *R*. They are calculated by the CAS–MC–SCF method.<sup>40</sup> When *R* is larger than 2.5 Å, the potential of the H<sub>2</sub> molecule is very similar to that of the free hydrogen molecule. When H<sub>2</sub> approaches Pd<sub>2</sub> at *R* = 2.0 Å, the H–H distance becomes longer, but the potential curve is still very steep. However, at *R* = 1.4–1.6 Å, the potential curve suddenly (catastrophically) flattens out for elongation of the H–H distance. At *R* = 1.6 Å, a double-well potential curve appears, and at *R* = 1.5 Å, the system becomes considerably more stable than at *R* = 1.6 Å. Here, the second minimum seems to appear near *R*<sub>H–H</sub> = 1.75 Å besides the first minimum at *R*<sub>H–H</sub> = 0.847 Å. At *R* = 1.4 Å, the first minimum is more stabilized than that at *R* = 1.5 Å but the second minimum disappears. When H<sub>2</sub> approaches Pd<sub>2</sub> even closer at *R* = 1.0 Å, the system becomes very unstable. Thus, stable adsorption of the H<sub>2</sub> molecule seems to

Table III. Characteristic Internuclear Separations (Å) at the Two Minima Corresponding to the Molecular and Dissociative Adsorption States of the Pd<sub>2</sub>–H<sub>2</sub> System Calculated by the SAC Method

distance	molecular adsorption	dissociative adsorption	free molecule (exptl)
H–H	0.90	2.10	0.74144
Pd–H	1.78	1.53	1.5285

occur at about 1.5 Å from the Pd surface.

Figure 8 shows the potential curve for the approach of the H<sub>2</sub> molecule to the Pd<sub>2</sub> fragment. It is a plot of the minimum energies of the potential curves shown in Figure 7. At *R* = 1.5–1.6 Å, the minimum corresponding to the shorter H–H distance is shown. At *R* infinity, the Pd<sub>2</sub> fragment is in the <sup>1</sup>Σ<sub>g</sub> state in which the Pd atom essentially has the d<sup>10</sup> electronic configuration. This is the ground state of the Pd<sub>2</sub> fragment within the CI<sup>23</sup> and the SAC calculations. From this curve we see that the Pd<sub>2</sub> fragment adsorbs the H<sub>2</sub> molecule without a barrier up to a distance about 1.5 Å from the Pd<sub>2</sub> “surface”. The calculated heat of adsorption is about 15 kcal/mol which is smaller than the experimental value, 24.4–28.8 kcal/mol, for the bulk Pd surface.<sup>5</sup>

The energy level diagrams of the ground and excited states are calculated by the SAC and SAC–CI method at Pd<sub>2</sub>–H<sub>2</sub> separations of 2.0 and 1.5 Å and shown in Figure 9. The ground state is the <sup>1</sup>A<sub>1</sub> state which is the same as the state we studied above by the CAS–MC–SCF method. At *R* = 2.0 Å, the energy splitting between the ground and excited states is about 32 kcal/mol. The lowest excited state here is the <sup>3</sup>A<sub>1</sub> state with many singlet and triplet excited states above it in a rather narrow energy region. Among others, the second <sup>1</sup>A<sub>1</sub> state lies about 45 kcal/mol above the ground state. When the H<sub>2</sub> molecule approaches the Pd<sub>2</sub> fragment closer, the energy level splitting between the ground and excited states increases. The smallest separation at *R* = 1.5 Å is about 51 kcal/mol, and the second <sup>1</sup>A<sub>1</sub> excited state lies about 67 kcal/mol above the ground state. Thus, we see that it is difficult for the excited states to participate in the chemisorption process.

The behavior of the H<sub>2</sub> molecule on the Pd<sub>2</sub> “surface” is very interesting. In order to obtain a reliable potential curve of the H<sub>2</sub> molecule adsorbed at 1.5 Å from the Pd<sub>2</sub> surface, we have employed the SAC method. The potential curves of the excited states are also computed by the SAC–CI method. Figure 10 shows the results. The ground-state curve clearly shows two potential minima. The minimum at *R*<sub>H–H</sub> = ~0.89 Å corresponds to *molecular* adsorption and the one at *R*<sub>H–H</sub> = ~2.1 Å to *dissociative* adsorption. This calculation suggests an equilibrium exists between the molecular and dissociative forms on a metal surface, i.e.,

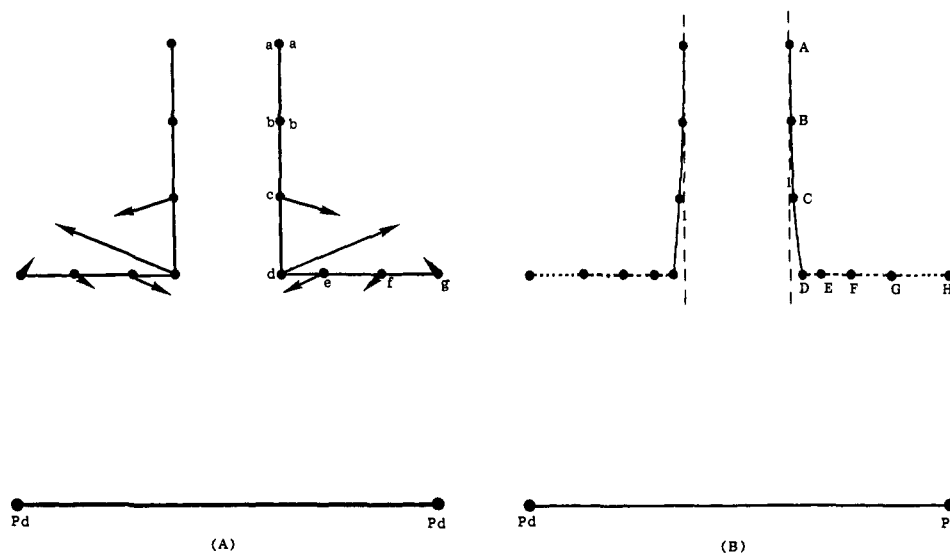


The dissociative form is more stable than the molecular form by 2.2 kcal/mol and the barrier height is 5.6 kcal/mol. However, since the motion along the metal surface is not energetically optimized at this level of the calculation, the actual barrier could be smaller. This result is in agreement with recent experimental work by Nyberg and Tengstal<sup>5c</sup> who have shown hydrogen is adsorbed dissociatively on palladium at all temperatures (*T* > 10 K). Table III lists the characteristic internuclear separations of the Pd<sub>2</sub>–H<sub>2</sub> system corresponding to these two energy minima. In the dissociative adsorption form, the Pd–H distance is about 1.53 Å which is close to the experimental internuclear distance of the free PdH molecule, 1.529 Å.<sup>20</sup>

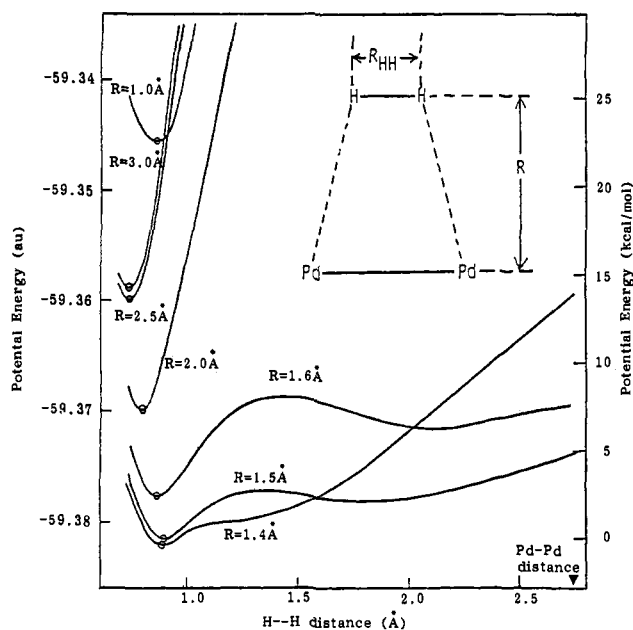
Thus, we conclude that the Pd<sub>2</sub> fragment shows catalytic activity for the dissociative adsorption of the H<sub>2</sub> molecule. The H<sub>2</sub> molecule with the binding energy as large as 104 kcal/mol<sup>20</sup> is dissociated, with almost no barrier, into two atomic hydrogens on the Pd<sub>2</sub> “surface”, as it is on an extended surface.

(ii) **Electronic Mechanism of Chemisorption.** Next a mechanism by which the Pd<sub>2</sub> shows catalytic activity for the dissociative adsorption of the H<sub>2</sub> molecule must be considered. From Figure 10, we see that the excited states of the Pd<sub>2</sub>–H<sub>2</sub> system are well separated from the ground state throughout the dissociative process

(48) *Handbook of Chemistry and Physics*; CRC Press: Cleveland, Ohio, 1984–1985; F-167.



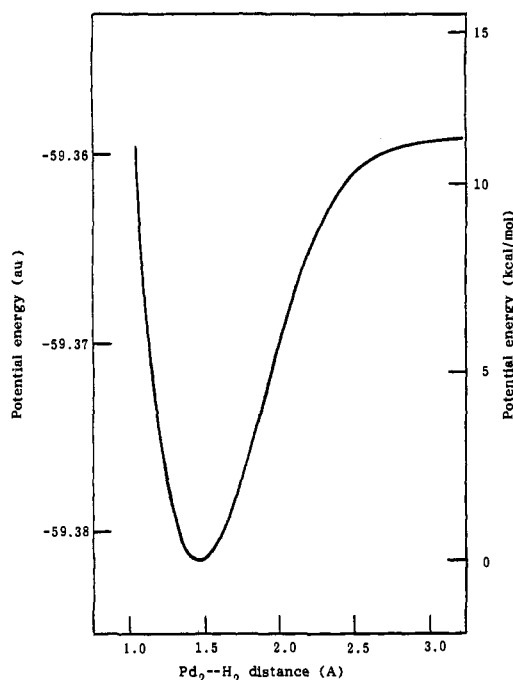
**Figure 6.** (A) The force acting on the H<sub>2</sub> molecule when it approaches the Pd<sub>2</sub> fragment with the H-H distance fixed to that of the free molecule. The coordinates of the points a to g are defined in the notation ( $R, R_{\text{H-H}}$ ) as a (3.0, 0.741 44), b (2.5, 0.741 44), c (2.0, 0.741 44), d (1.5, 0.741 44), e (1.5, 1.2), f (1.5, 2.0), g (1.5, 2.7511) in Å units. (B) The optimized H-H length calculated by the CAS-MC-SCF method from  $R = 3.0$  Å to  $R = 1.5$  Å. The points A to G are defined in the notation ( $R, R_{\text{H-H}}$ ) as A (3.0, 0.735), B (2.5, 0.739), C (2.0, 0.787), D (1.5, 0.847), E (1.5, 1.0), F (1.5, 1.4), G (1.5, 2.1), H (1.5, 2.7511) in Å units.



**Figure 7.** Potential curves for the H-H stretching of the Pd<sub>2</sub>-H<sub>2</sub> system at different Pd<sub>2</sub>-H<sub>2</sub> separations (CAS-MC-SCF method).

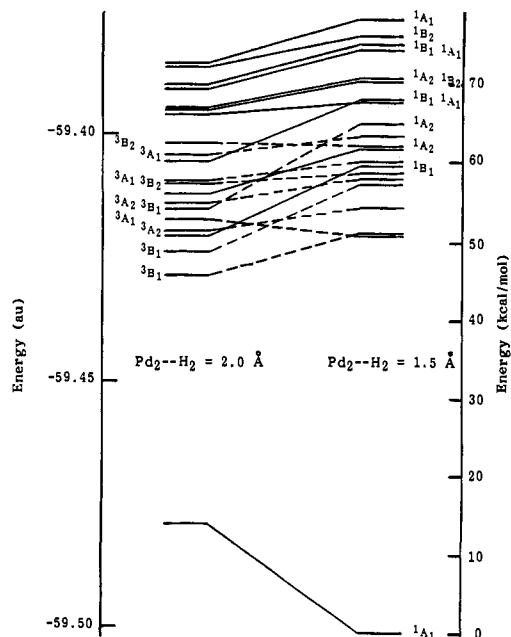
of the H<sub>2</sub> molecule on the surface. No excited states seem to experience an avoided crossing with the ground state. Thus, we conclude that there is almost no chance for the excited states to participate in the chemisorption process on a palladium surface. The mechanism of the chemisorption of the H<sub>2</sub> molecule on a Pd surface differs from that proposed for a Ni surface by Melius et al.<sup>28</sup>

The mechanism of chemisorption on a palladium surface is explained from the orbital correlation diagram shown in Figure 11. This is based on an analysis of the natural orbitals of the MC-SCF calculations. The left-hand side shows the bonding and antibonding MO's of the hydrogen molecule. The MO's of the ground state of the Pd<sub>2</sub> fragment are shown on the right-hand side. The occupied orbitals are mainly composed of d orbitals and the unoccupied orbitals are the bonding and antibonding pair of the 5s AO's. The MO's of the Pd<sub>2</sub>-H<sub>2</sub> system are shown at the center. Here, the following two interactions are important. One is the electron-transfer interaction from the  $\delta_u$  ( $d_z-d_z$  antibonding) MO of the Pd<sub>2</sub> to the  $\sigma_u$  (s-s antibonding) MO of H<sub>2</sub>.

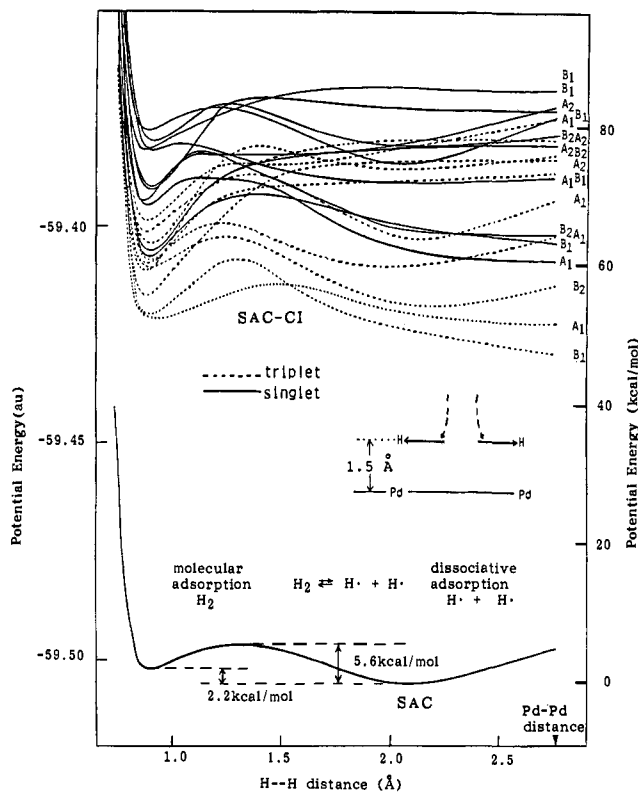


**Figure 8.** Potential energy curve of the Pd<sub>2</sub>-H<sub>2</sub> system during the molecular adsorption step of the H<sub>2</sub> molecule to the Pd<sub>2</sub> fragment (CAS-MC-SCF method).

This interaction is designated as a  $b_2$  interaction since the MO's involved have  $b_2$  symmetry. The other is the electron-transfer interaction from the  $\sigma_g$  (s-s bonding) MO of H<sub>2</sub> to the  $\sigma_g$  (5s-5s bonding) MO of the Pd<sub>2</sub>. This interaction is similarly termed an  $a_1$  interaction. These interactions are shown by the bold lines in Figure 11. In the  $b_2$  interaction, the  $\delta_u$  MO of the Pd<sub>2</sub>, which is initially a lone-pair d orbital, mixes with the antibonding  $\sigma_u$  MO of H<sub>2</sub>, leading to a weakening of the H-H bond and a formation of the Pd-H bond. The  $a_1$  interaction also works to relax the H-H bond, since an electron is removed from the bonding  $\sigma_g$  MO. These 4d<sub>z</sub> and 5s AO's of the Pd<sub>2</sub> fragment correspond to the so-called "dangling" bond of the metal surface. During the initial molecular adsorption step, the  $b_2$  and  $a_1$  interactions are gradually enhanced, so that when  $R$  becomes 1.5-1.6 Å, the H-H bond is weakened and can be elongated with almost no barrier. As the H-H bond is elongated, two Pd-H bonds are

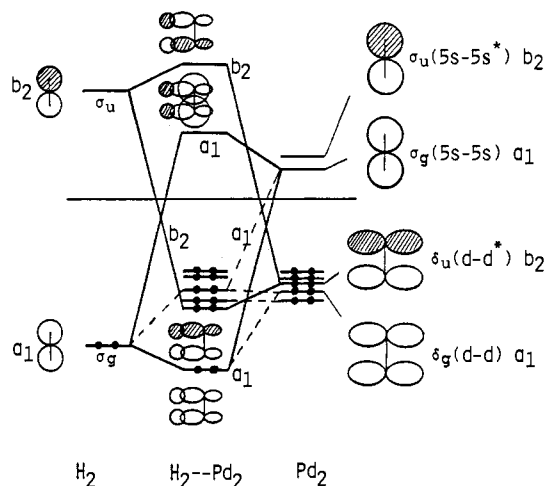


**Figure 9.** Energy level diagram of the ground and excited states of the  $\text{Pd}_2\text{-H}_2$  system at  $\text{Pd}_2\text{-H}_2$  separations of 2.0 and 1.5 Å along the molecular adsorption step shown in Figure 6B (SAC and SAC-CI methods).

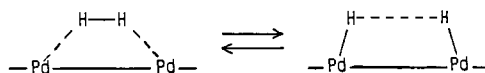


**Figure 10.** Potential energy curves of the ground and excited states of the  $\text{Pd}_2\text{-H}_2$  system as a function of the H-H distance of the  $\text{H}_2$  molecule 1.5 Å from the  $\text{Pd}_2$  fragment (SAC and SAC-CI methods).

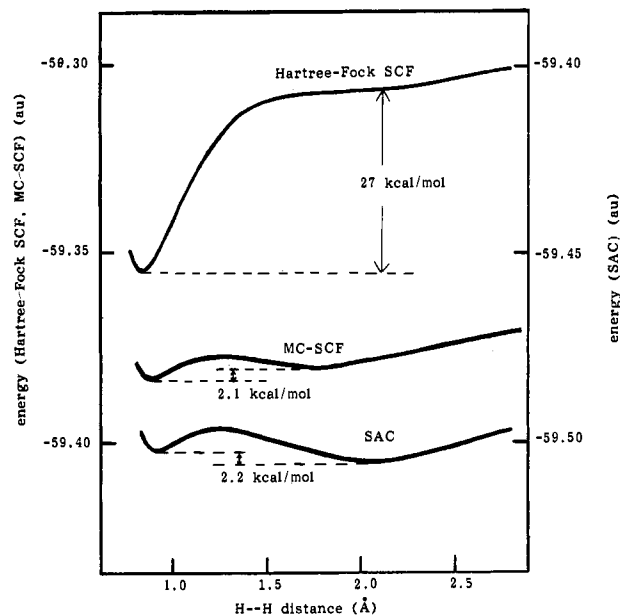
formed and this stabilizes the system. At the minimum corresponding to the dissociative adsorption, the Pd-H distance is about 1.53 Å which is close to the Pd-H distance of the free PdH molecule. Thus, this process may be written as the bond alternation process shown in Figure 12. It is a symmetry-allowed process in which the d electrons of the  $\text{Pd}_2$  fragment play an important role. The 5s AO's are of secondary importance. This agrees with results of UPS (UV photoemission spectroscopy) experiments.<sup>6</sup> The existence of the  $4d_3$  MO of the  $\text{Pd}_2$  fragment in a matching energy region is a prerequisite for this catalytic action.



**Figure 11.** Schematic orbital correlation diagram for the interaction of  $\text{H}_2$  and  $\text{Pd}_2$ .



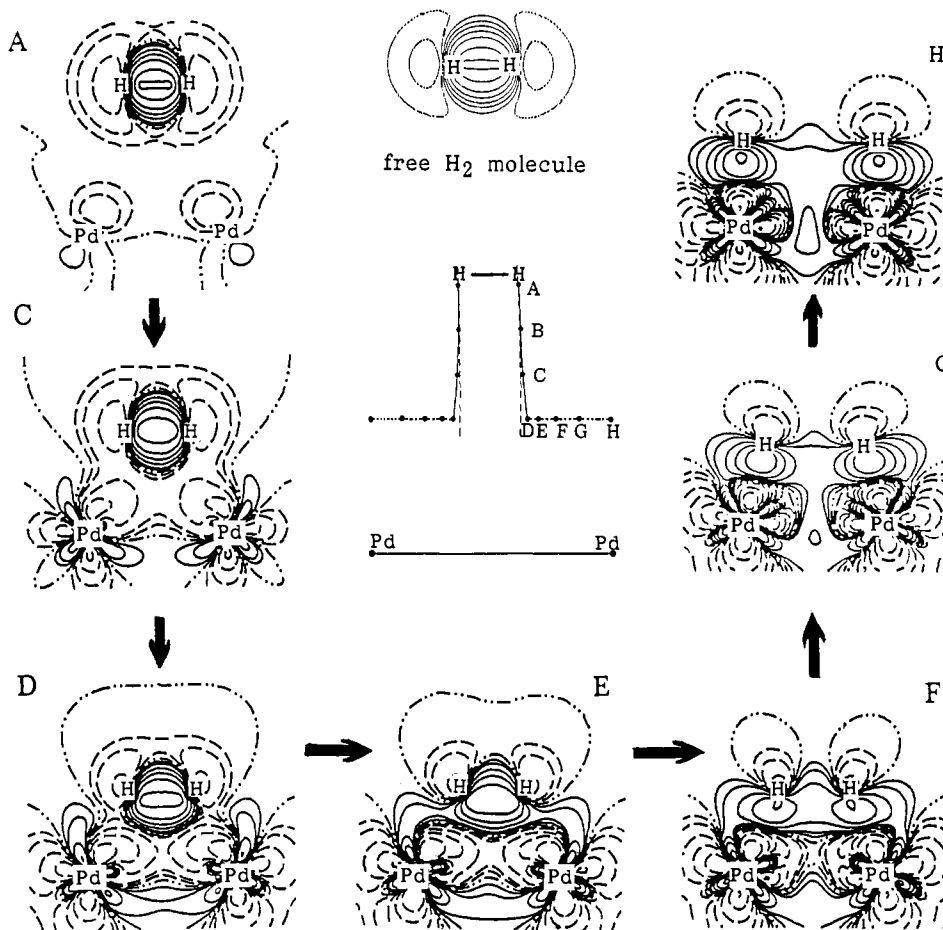
**Figure 12.** Bond alternation mechanism in the dissociative process of the  $\text{H}_2$  molecule on the palladium "surface".



**Figure 13.** Potential energy curves for the H-H separation of the  $\text{Pd}_2\text{-H}_2$  system with the  $\text{Pd}_2\text{-H}_2$  distance at 1.5 Å calculated by the Hartree-Fock, CAS-MC-SCF, and SAC methods.

Another interesting implication of the correlation diagram shown in Figure 11 is that the Pd-Pd bond is not weakened in this process, as indicated in the bond alternation mechanism of Figure 12. In the  $b_2$  interaction, the Pd-Pd interaction is strengthened since an electron is removed from the antibonding  $d_3$  MO. In the  $a_1$  interaction, bonding between the two Pd atoms should increase because an electron is transferred to the 5s-5s bonding MO. Since the bonding nature of these  $4d_3$  and 5s MO's is rather weak, the change in the Pd-Pd distance will be small. However, this fact is important, implying the stability of a catalytic surface; namely, the Pd atom is not lost from a metal surface as a PdH molecule.

Though the qualitative features of the mechanism can thus be well-explained from the MO diagram shown in Figure 11, dissociative adsorption is not described quantitatively (or even qualitatively) without considering the effect of the electron correlation. Figure 13 shows potential energy curves for the H-H separation of the  $\text{Pd}_2\text{-H}_2$  system with the  $\text{Pd}_2\text{-H}_2$  distance fixed

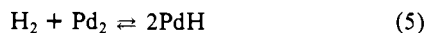


**Figure 14.** Reorganization of the electron density of the Pd<sub>2</sub>-H<sub>2</sub> system along the path shown in the figure center. The density difference is defined by eq 6 of the text.

at 1.5 Å. The Hartree-Fock theory can explain only the molecular adsorption and not the dissociative adsorption. At  $R_{\text{H-H}} = 2.1$  Å, the energy is higher than the molecular adsorption form by about 27 kcal/mol. At the MC-SCF level, the second minimum corresponding to the dissociative adsorption appears. However, it is higher than the first minimum by 2.5 kcal/mol. At the SAC level, which incorporates much more correlation effects than the MC-SCF level (a different scale is employed for the SAC energy on the right-hand side of Figure 13), the dissociative adsorption form is more stable than the molecular adsorption form by 2.2 kcal/mol. This is in agreement with the experimental observation.<sup>5b</sup> We thus see that the correlation effect is much larger for the dissociative adsorption form than for the molecular adsorption form. In Table IV, a summary of the effects of the electron correlation on the H-H and Pd-H distances is presented. It may be seen that the correlation effect is important, not only for the energy level of the dissociative form, but also for its geometry. The H-H distance is seen to be elongated on incorporation of the electron correlation.

In conclusion, the electronic origin of the dissociative adsorption of the H<sub>2</sub> molecule on palladium is the existence of the dangling bond on the surface and the electron correlation. In particular, the d orbital of palladium plays an essential role. The electronic process may be viewed as the bond alternation mechanism shown in Figure 12. In the dissociative process of the H<sub>2</sub> molecule, the system is stabilized by forming new Pd-H bonds, but the Pd-Pd bond is not weakened. The stability of the Pd-Pd bond during this process implies a stability of the catalytic surface. The electron correlation is necessary to describe dissociative adsorption even qualitatively.

Lastly, we should note that writing the bond alternation mechanism shown in Figure 12 as



**Table IV.** H-H and Pd-H Distances (Å) at the Molecular and Dissociative Adsorption States Calculated by the Hartree-Fock, MC-SCF, and SAC Methods

method	molecular adsorption H-H	dissociative adsorption	
		H-H	Pd-H <sup>a</sup>
Hartree-Fock	0.83		
CAS-MC-SCF	0.85	1.83	1.55
SAC	0.90	2.10	1.53

<sup>a</sup> The Pd-H distance of the free PdH molecule is 1.5285 Å (ref 20).

represents an oversimplification of the actual phenomena. From a simple energetic balance, this reaction seems to be exothermic since the bond energy of the two PdH molecules is larger than the sum of the bond energies of H<sub>2</sub> and Pd<sub>2</sub>.<sup>20,23,46</sup> However, catalytic activity does not correspond to the exothermic character, but rather to a lowering of the reaction energy barrier. Furthermore, reaction 5 does not explain the stability of the catalytic surface.

**(iii) Density and Force in the Chemisorption Process.** The above mechanism for catalytic activity is supported by the behavior of the electron density during the process. The change in the electron density along the optimized path of the approach of the H<sub>2</sub> molecule to the Pd<sub>2</sub> fragment is displayed in Figure 14 (at points A-H in Figure 6B). The map is defined by the electron density difference,

$$\Delta\rho = \rho(\text{Pd}_2\text{-H}_2) - \rho(\text{Pd}_2) - \rho(\text{H}) - \rho(\text{H}) \quad (6)$$

For the Pd<sub>2</sub> fragment, the density is for the  $^1\Sigma_g$  ground state. The density of the free H<sub>2</sub> molecule is given for a comparison in Figure 14.

At point A ( $R = 3$  Å) the electron density of the system is essentially that of the free molecules. The density of Pd<sub>2</sub> changes



only slightly. At point C ( $R = 2.0 \text{ \AA}$ ), the density of the system undergoes considerable change. At point D, which corresponds to the molecular adsorption state, the density of  $\text{Pd}_2$  extends on the right and left toward  $\text{H}_2$ . The overlap density between the two Pd atoms increases. The density of  $\text{H}_2$  is polarized considerably toward  $\text{Pd}_2$ . However, in this state, the density in the  $\text{H}_2$  region still remains similar to that of the free  $\text{H}_2$  molecule. This reflects the fact that point D corresponds to the molecular adsorption state. From points D to H the  $\text{H}_2$  molecule is elongated on the  $\text{Pd}_2$  surface ( $R = 1.5 \text{ \AA}$ ). When  $R_{\text{H-H}}$  becomes  $1.0 \text{ \AA}$  (point E), a bond between Pd and H is formed. The positive region of the increased density makes a bridge between  $\text{Pd}_2$  and  $\text{H}_2$ . When  $R_{\text{H-H}}$  is  $1.4 \text{ \AA}$  (point F), the H-H bond almost disappears and the Pd-H bond is strengthened. At point G ( $R_{\text{H-H}} = 2.1 \text{ \AA}$ ), the density of the  $\text{H}_2$  bond region essentially disappears. That density remains strongly polarized toward  $\text{Pd}_2$ . The density originally in the  $\text{H}_2$  region is transferred to the two Pd-H regions, resulting into the formation of the Pd-H bond. This reflects the fact that point G corresponds to the dissociative adsorption state. There is also an enhancement of the electron density in the interatomic region of  $\text{Pd}_2$ , implying that the Pd-Pd bond is not weakened in the catalytic process. (This is shown on the right-hand side of Figure 12 by the solid line connecting the two Pd atoms.) At point H ( $R_{\text{H-H}} = R_{\text{Pd-Pd}}$ ), the density is essentially an extrapolation of those for the points F and G. The energy corresponding to this geometry is about  $5 \text{ kcal/mol}$  higher than that for point G. Thus, the behavior of the electron density supports the bond alternation mechanism shown in Figure 12. It also indicates that the formula given by eq 5 is an oversimplification of the actual phenomena.

The behavior of the electron density shown in Figure 12 is reflected in the force acting on the hydrogen molecule calculated by the Hellmann-Feynman formula given by eq 1. An analysis of the force acting on the hydrogen molecule is made as:

$$F_{\text{H}} = \sum_r \sum_s^{\text{on Pd}_2} P_{rs} \langle r | f_{\text{H}} | s \rangle - Z_{\text{H}} Z_{\text{Pd}} \mathbf{R}_{\text{H-Pd}} / R_{\text{H-Pd}}^3 - Z_{\text{H}} Z_{\text{Pd}'} \mathbf{R}_{\text{H-Pd}'} / R_{\text{H-Pd}'}^3; F(\text{Pd}_2)$$

$$+ \sum_r \sum_s^{\text{on H}_2} P_{rs} \langle r | f_{\text{H}} | s \rangle - Z_{\text{H}} Z_{\text{H}'} \mathbf{R}_{\text{H-H}'} / R_{\text{H-H}'}^3; F(\text{H}_2)$$

$$+ 2 \sum_r \sum_s^{\text{on Pd}_2 \text{ on H}_2} P_{rs} \langle r | f_{\text{H}} | s \rangle; F(\text{H}_2\text{-Pd}_2)$$

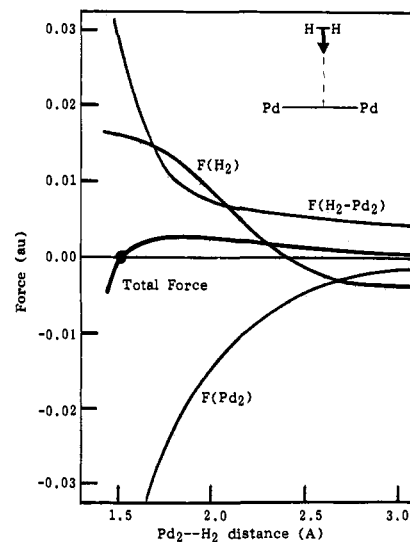
$$(7a)$$

$$F = (F_{\text{H}} + F_{\text{H}'})/2 \quad (7b)$$

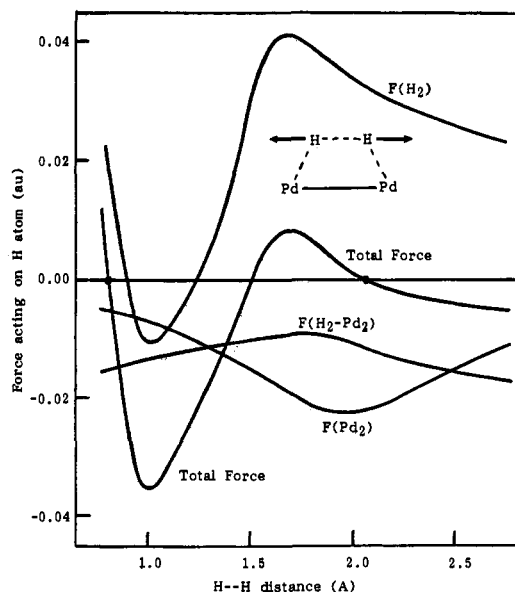
This analysis is similar to the one defined by eq 3 for the Pd-H<sub>2</sub> system. The physical meanings of the force components  $F(\text{Pd}_2)$ ,  $F(\text{H}_2)$ , and  $F(\text{H}_2\text{-Pd}_2)$  are also very similar to those defined there. We note here that  $F(\text{Pd}_2)$  includes the force acting on H due to the electrons in both atomic and overlap regions of  $\text{Pd}_2$ . The component  $F(\text{H}_2\text{-Pd}_2)$  represents the force due to the electron cloud in the overlap region between  $\text{H}_2$  and  $\text{Pd}_2$ , including nearest-neighbor and next-nearest-neighbor interactions. The component  $F(\text{H}_2)$  has exactly the same meaning as that in eq 3.

Figure 15 shows a plot of the force acting on the  $\text{H}_2$  molecule directed toward the  $\text{Pd}_2$  fragment along the optimized path from points A to D shown in Figure 6B. The crossing of the total force across the zero line near  $R = 1.5 \text{ \AA}$  corresponds to the molecular adsorption state. The primary origin of the attractive force is  $F(\text{H}_2\text{-Pd}_2)$  in the beginning and final stages, and  $F(\text{H}_2)$  in the intermediate stage ( $1.5 \text{ \AA} < R < 2.0 \text{ \AA}$ ). This means that during the initial and final stages, the accumulation of the electron density in the overlap region of  $\text{H}_2$  and  $\text{Pd}_2$  is important, but in the intermediate stages, polarization of the electron cloud of  $\text{H}_2$  toward  $\text{Pd}_2$  is more important. We note that this polarization component  $F(\text{H}_2)$  arises since we have added the derivative bases (polarization functions) to the hydrogen [2s].<sup>38</sup> This confirms the importance of the derivative bases on  $\text{H}_2$  as in the case of  $\text{PtH}$ .<sup>39</sup> The component  $F(\text{Pd}_2)$  is repulsive throughout the process.

Figure 16 shows the force which works to elongate the H-H distance of the  $\text{H}_2$  molecule adsorbed on the  $\text{Pd}_2$  surface. The  $\text{Pd}_2\text{-H}_2$  distance is fixed at  $1.6 \text{ \AA}$ . The crossings of the total force



**Figure 15.** Force acting on the  $\text{H}_2$  molecule toward the  $\text{Pd}_2$  fragment in the  $\text{Pd}_2\text{-H}_2$  system along the molecular adsorption step from points A to D shown in Figure 6B. The force analysis is defined by eq 7 of the text.

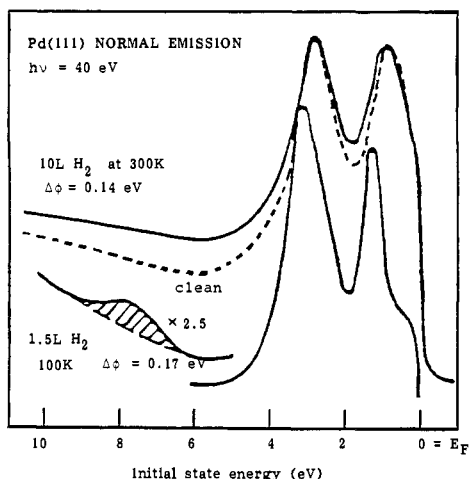


**Figure 16.** Force acting on the  $\text{H}_2$  molecule to prolong the H-H distance of the  $\text{Pd}_2\text{-H}_2$  system with the  $\text{Pd}_2\text{-H}_2$  distance of  $1.6 \text{ \AA}$ . The force analysis is defined by eq 7 of the text.

across the zero line at  $R_{\text{H-H}} = 0.85 \text{ \AA}$  and at  $R_{\text{H-H}} = 1.94 \text{ \AA}$  correspond to the molecular and dissociative adsorption forms, respectively. The crossing at  $R_{\text{H-H}} = 1.5 \text{ \AA}$  corresponds to the maximum (i.e., the top of the barrier) dividing these two minima. From Figure 16 it may be seen that the total force is essentially parallel to the component  $F(\text{H}_2)$ ; viz., the stretching force of  $\text{H}_2$  is determined primarily by the amount of the electron density in the internuclear region of  $\text{H}_2$ . The positive (repulsive) contribution of  $F(\text{H}_2)$  in the longer region including the dissociative adsorption state is due to transfer of the electron density from the  $\text{H}_2$  region to the surface region, which is intermediate between  $\text{H}_2$  and  $\text{Pd}_2$ . This is evident from the density difference map (e.g., see points D and G) shown in Figure 14. The negative (attractive) contribution of  $F(\text{H}_2)$  is seen only near the molecular adsorption state. The components of  $F(\text{H}_2\text{-Pd}_2)$  and  $F(\text{Pd}_2)$  both work to shorten the H-H distance. The former is due to the overlap density between  $\text{H}_2$  and  $\text{Pd}_2$ , and the latter is due mainly to the nuclear repulsion.

#### Ionization Spectra of $\text{Pd}_2\text{-H}_2$ System

Photoelectron spectra of the hydrogen adsorbed on a palladium surface show some interesting features. Figure 17 reproduces the

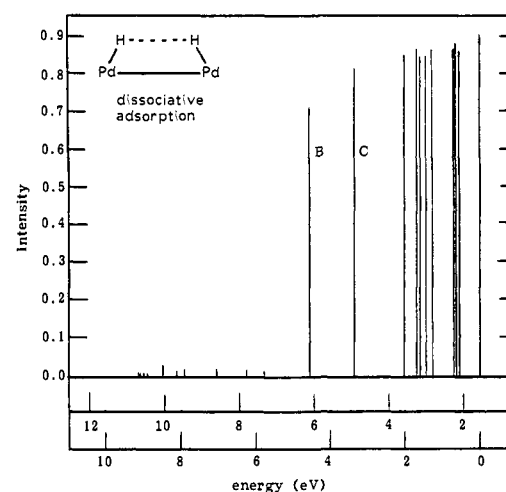
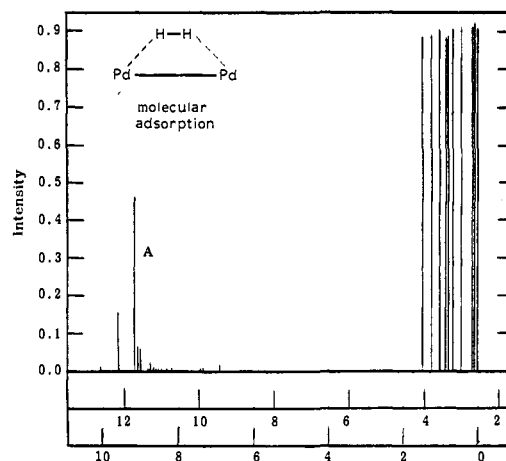


**Figure 17.** Normal-emission photoemission spectra of clean and H-exposed surfaces at 100 and 300 K. This is taken from Figure 12 of ref 49.

experimental spectra reported by Eberhardt et al.<sup>49</sup> Low-temperature ( $T \sim 100$  K) chemisorption produces a new photoemission band at 7–9 eV from the bottom of the palladium d band. However, on increasing the temperature ( $T \sim 300$  K), this band becomes almost invisible. The spectrum at higher temperature differs from that of the clean surface only slightly in the higher energy (4–10 eV) region. Further, this phenomenon is irreversible; viz., the H-induced band does not appear again even if the system is cooled down again to the lower temperature region. These results seem to suggest an existence of at least two different kinds of adsorption species for hydrogen on a palladium surface.

Eberhardt et al.<sup>49</sup> suggested that a transition of the hydrogen atom from a chemisorbed surface state to a *subsurface* state caused the observed change in the spectrum. The invisible state at higher temperature was considered to be due to the subsurface state. Muscat,<sup>50</sup> on the other hand, suggested that at higher temperature, hydrogen gained higher mobility on the surface, which resulted in vanishing of the spectral peak. However, this does not seem to explain the irreversibility. Baykara et al.<sup>16</sup> theoretically calculated the ionization spectra of the hydrogen atom lying on a surface and at several interstitial (subsurface) sites of a palladium cluster. The spectra calculated for the chemisorbed surface state explained well the observed new band, but essentially the same peaks were also calculated for the subsurface state, though the peaks appeared at higher positions.

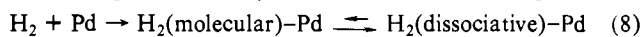
The temperature dependence of the H-induced features of the spectra on the Pd surface thus remains unknown to some extent. In particular, a difficulty seems to lie in the explanation of the irreversibility, namely, the nonappearance of the H-induced features on cooling down again to the lower temperature region. We calculate the ionization spectra of the Pd<sub>2</sub>-H<sub>2</sub> system by the SAC-CI method.<sup>43,45</sup> Since the H<sub>2</sub> molecule on the Pd<sub>2</sub> fragment has two potential minima corresponding to molecular adsorption and dissociative adsorption, we calculate spectra for these two states. Figure 18 shows the resultant theoretical spectra. The upper and lower ones are calculated for points D and G of Figure 6B, respectively, which correspond to the molecular and dissociative adsorption forms, respectively. The lower horizontal scale, showing relative values, should be used in comparisons with Figure 17. For the molecular adsorption, the weakened H–H bonding peak is calculated at 9.2 eV. It is denoted as peak A in Figure 18. The ionization energy of the free H<sub>2</sub> molecule is 14.5 eV.<sup>20</sup> For the dissociative adsorption, the peak due to the H–H bonding disappears and the peaks due to the Pd–H bonding appear at 4.5 and 3.3 eV. They are denoted as B and C in Figure 18. For the free PdH molecule, the ionization energy is calculated as 7.3 eV,



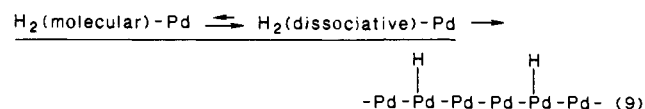
**Figure 18.** Ionization energy spectra of Pd<sub>2</sub>-H<sub>2</sub> system. Upper and lower figures are for molecular and dissociative adsorption forms, respectively. Two horizontal energy scales are given. The upper one is an absolute scale and the lower one is relative to the first peak of the d band.

which is 5.9 eV from the first peak of the metal d band of the dissociative adsorption state of Pd<sub>2</sub>-H<sub>2</sub>.

Now, we relate the theoretical spectra to the experimental observations. The H-induced feature observed at low-temperature chemisorption is attributed to a rapid equilibrium between molecular and dissociative adsorption states. When H<sub>2</sub> is adsorbed at low temperature, the system is in the underlined equilibrium.



The dissociative form is more stable than the molecular form by about 2.2 kcal/mol. In the dissociative form, peaks B and C are at 3.5–4.5 eV. They are almost on the shoulder of the d band. Peak A of the molecular form lies at about 9 eV. At equilibrium, these peaks would shift to the central region through a rapid exchange. This corresponds to the H-induced feature shown in Figure 18 by the shaded lines. When the system is warmed up, essentially all the hydrogens are dissociated and the atoms migrate quite freely on the surface,<sup>51</sup> namely



This results in a smearing out of the peak as Muscat pointed out.<sup>50</sup> In the dissociative form, the H-induced peaks are almost on the shoulder (left-hand side) of the d band. Even when the system is cooled again, there is little chance for the two hydrogen atoms to approach as closely as they were initially during equilibrium

(49) Eberhardt, W.; Greuter, F.; Plummer, E. W. *Phys. Rev. Lett.* **1981**, *46*, 1085. Eberhardt, W.; Louie, S. G.; Plummer, E. W. *Phys. Rev. B* **1983**, *28*, 465.

(50) Muscat, J. P. *Surf. Sci.* **1984**, *148*, 237.

(51) Pusker, M. J.; Nieminen, R. M.; Manninen, M.; Chakraborty, B.; Holloway, S.; Nørskov, J. K. *Phys. Rev. Lett.* **1983**, *51*, 1081.

with the molecular adsorption state, since the molecular form is more unstable than the dissociative form. Therefore, the H-featured peak does not appear again. Thus, in the present interpretation, the underlined equilibrium between the molecular and dissociative forms in eq 9 is considered important to explain the spectra observed during low-temperature chemisorption. When heated up, the hydrogen atom migrates rather freely on the surface. We note that the above interpretation offers only one possibility, since the present study provides only a crude model for chemisorption on an extended surface. More extensive study is necessary for a definite conclusion.

### Summary and Concluding Remarks

In the present work, we have theoretically studied the interaction and reaction of a hydrogen molecule with the Pd atom and the Pd<sub>2</sub> fragment. It provides a model for chemisorption on the assumption of the cluster model for a metal surface.

A single Pd atom has a definite affinity toward the hydrogen molecule, resulting in a triangular adduct form, but it does not catalyze cleavage of the H-H bond. The origin of the attractive force is the electron density accumulated in the overlap region between H<sub>2</sub> and Pd. The lower lying excited states of Pd are all repulsive for H<sub>2</sub>. Since the excitation energies are rather small, this suggests a detachment process through the excited states of the system.

Pd<sub>2</sub> fragment clearly shows catalytic activity for the hydrogen chemisorption. The H<sub>2</sub> molecule is adsorbed and dissociated very smoothly on the Pd<sub>2</sub> "surface" at about 1.5 Å from the metal. There is a smooth equilibrium between the molecular and dissociative forms with a barrier of few kilocalories/mole. The dissociative form is more stable by about 2 kcal/mol. This catalytic ability of Pd<sub>2</sub> is interesting and rather surprising, considering the fact that the bonding energy of the H<sub>2</sub> molecule is as large as 104 kcal/mol. The calculated heat of adsorption is about 15 kcal/mol in comparison with the experimental value of 21–24 kcal/mol. Based on this equilibrium, we considered an explanation for some features of the photoelectron spectra of the hydrogen-adsorbed palladium surface.

The mechanism for catalytic cleavage in the present system differs from the one proposed for a nickel surface by Melius et al.,<sup>28</sup> as there is almost no chance for the excited states to participate in the chemisorptive process on a palladium surface. This mechanism also differs from the one proposed for Ni and Ca surfaces.<sup>29–31</sup> The catalytic ability here originates from the participation of the dangling bond on a surface and from the electron correlation. A qualitative feature of the mechanism is understood from the orbital correlation diagram. The electron correlation is important even qualitatively to explain the dissociative adsorption. The existence of the nonbonding 4d electrons in the Pd<sub>2</sub> fragment and the gradual lowering of the H-H antibonding MO in the molecular adsorption step is important to catalytic cleavage of the H-H bond. Further, the Pd-Pd bond

is not weakened in this catalytic process, a fact important from the viewpoint of the stability of the palladium catalyst. The importance of the 4d orbitals of the palladium would seem to be a common feature of palladium chemistry.

A question may be raised that if the stabilization energy of the Pd<sub>2</sub>-H<sub>2</sub> system is overestimated relative to that of the free system, Pd<sub>2</sub> and H<sub>2</sub>, the same results may be obtained. In other words, if the hydrogens are bound to the Pd<sub>2</sub> system too strongly, the hydrogens of the Pd<sub>2</sub>-H<sub>2</sub> system will not be reactive enough to show further catalytic reactions such as hydrogenation reactions. This question can be answered unambiguously by studying the reactivity of the present system Pd<sub>2</sub>-H<sub>2</sub> for the hydrogenation reaction. In separate papers,<sup>52</sup> we have examined the hydrogenation reaction of acetylene on a palladium surface to form ethylene.

Recently, Harris and Andersson<sup>53</sup> have looked at the dissociation of H<sub>2</sub> on Ni and Cu metals using M<sub>2</sub>-H<sub>2</sub> as a model. They used the Kohn-Sham local density method,<sup>54</sup> suppressing the spin-space symmetry constraint to the system. They concluded that the gradual local transfer of s electrons to the d shell on Ni is important for reducing the entrance-channel activation barrier and to allow formation of the M-H bonds with only a moderate weakening of the metal-metal bond. This view differs from the present one for the Pd<sub>2</sub>-H<sub>2</sub> system and also from the one reported by Siegbahn et al.<sup>29,30</sup>

Lastly, we note that the present results seem to give indirect support for the local model for chemisorption on a metal surface. Actually, an H<sub>2</sub> molecule with the H-H length of 0.74 Å can "see" only a few palladium atoms within its interaction radius (e.g., van der Waals radius), since the Pd-Pd length in solid is as large as 2.75 Å. Though an addition of more Pd atoms to the cluster would improve, for example, the heat of adsorption, the kinetic nature of the dissociated hydrogen, etc., the essential features of chemisorption seem to be adequately described by the present system. Further, based on the present study, we propose an experiment on the reaction between a small Pd cluster and a hydrogen molecule. We expect that molecular beam experiments should provide an interesting view of catalytic activity.

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**Registry No.** H<sub>2</sub>, 1333-74-0; Pd, 7440-05-3; Pd<sub>2</sub>, 12596-93-9.

(52) (a) Nakatsuji, H.; Hada, M. In ref 27, p 477. (b) Nakatsuji, H.; Hada, M.; Yonezawa, T. *Surf. Sci.*, in press.

(53) Harris, J.; Andersson, S. *Phys. Rev. Lett.* **1985**, *55*, 1583.

(54) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.