

Observed and Calculated Infrared Spectrum of Pd(H₂) in Solid Argon: A Ligand-Free Side-Bonded Molecular Hydrogen Complex

Lester Andrews,^{*,†,§} Laurent Manceron,[†]
 Mohammad Esmail Alikhani,[†] and Xuefeng Wang[‡]

LADIR/Spectrochimie Moléculaire, UMR 7075
 Université Pierre et Marie Curie, case courrier 49
 4 Place Jussieu, 75252 Paris Cedex 05, France
 Chemistry Department, University of Virginia
 Charlottesville, Virginia, 22904-4319

Received July 25, 2000

A detailed assessment of the interaction between naked metal atoms and H₂ is of fundamental importance for understanding oxidative addition reactions of metal complexes, clusters and surfaces. Since the discovery¹ of W(CO)₃(PR)₂(η²-H₂), other side-bonded dihydrogen complexes have been characterized by several groups.^{2–7} Furthermore, it has been found experimentally that rate constants for H₂ activation vary with Pd_n cluster size.⁸ This is in accord with recent theoretical studies, which have predicted that the minimum-energy structure is a side-bonded atom–molecule complex,^{11–14} but that Pd₂ can form a stable ring (PdH)₂ species with no H–H bond.^{13,14c} Finally, dihydrogen dissociates completely on a palladium metal surface.^{9,10}

Evidence for naked metal–H₂ complexes in a krypton and xenon matrix study with Pd was interpreted in terms of both end- and side-bonded complexes;^{14b,15} however, our theoretical investigations find a stable minimum only for the side-bonded structure. The contrast with Pt, which is predicted by theory and suggested by matrix-isolation spectroscopy to form a dihydride,^{16,17} prompted us to investigate the reactions of laser-ablated and thermal Pd atoms with H₂ in the more inert argon matrix. We report here

[†] Université Pierre et Marie Curie.

[‡] University of Virginia.

[§] Permanent address for corresponding author. Chemistry Department, University of Virginia, Charlottesville, Virginia, 22904-4319.

(1) (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. (b) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

(2) Sweany, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2374.

(3) (a) Upmacis, R. K.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Whyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.* **1985**, 27. (b) Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3645.

(4) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 794.

(5) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581.

(6) (a) Collman, J. P.; Wagenknecht, P. S.; Hembre, R. T.; Lewis, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 1294. (b) Jackson, S. A.; Hodges, P. M.; Poliakoff, M.; Turner, J. J.; Grevels, F. W. *J. Am. Chem. Soc.* **1990**, *112*, 1221.

(7) Bender, B. R.; Kubas, G. J.; Jones, L.H.; Swanson, B. I.; Eckert, J.; Capps, K. B.; Hoff, C. D. *J. Am. Chem. Soc.* **1997**, *119*, 9179. (b) Heitz, M.; Daniel, C. *J. Am. Chem. Soc.* **1997**, *119*, 8269.

(8) Fayet, P.; Kaldor, A.; Cox, D. M. *J. Chem. Phys.* **1990**, *92*, 254.

(9) Gross, A.; Wielke, S.; Scheffler, M. *Phys. Rev. Lett.* **1995**, *75*, 2718.

(10) Gostern, M.; Sitz, G. O. *J. Chem. Phys.* **1997**, *106*, 7378.

(11) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 8321.

(12) Balasubramanian, K.; Feng, P. Y.; Liao, M. Z. *J. Chem. Phys.* **1988**, *88*, 6955 and references therein.

(13) Chi, Q.; Musaev, D. G.; Morokuma, K. *J. Chem. Phys.* **1998**, *108*, 8418.

(14) (a) Backvall, J. E.; Bjorkman, E. E.; Petterson, L.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1985**, *107*, 7265. (b) Jarque, C.; Novaro, O.; Ruiz, M. E.; Garcia-Prieto, J. *J. Am. Chem. Soc.* **1986**, *108*, 3507. (c) Bloembergen, M. R. A.; Siegbahn, P. E. M.; Svenson, M. *J. Phys. Chem.* **1992**, *96*, 5783. (d) Siegbahn, P. E. M. *Theor. Chim. Acta* **1994**, *81*, 441. (e) See also: Dedieu, A. *Chem. Rev.* **2000**, *100*, 543.

(15) Ozin, G. A.; Garcia-Prieto, J. *J. Am. Chem. Soc.* **1986**, *108*, 3099.

(16) Balasubramanian, K. *J. Chem. Phys.* **1987**, *87*, 2800.

(17) (a) Li, S.; Weiner, H. A.; Van Zee, R. J.; Weltner, W., Jr. *J. Chem. Phys.* **1997**, *106*, 2583. (b) Subsequent work in our laboratories shows that PtH₂ absorbs at 2366 and 2349 cm⁻¹ in solid argon.

(18) Liang, B.; Zhou, M. F.; Andrews, L. *J. Phys. Chem. A* **2000**, *104*, 3905 and references therein.

(19) Tremblay, B.; Manceron, L. *Chem. Phys.* **1999**, *250*, 187 and references therein.

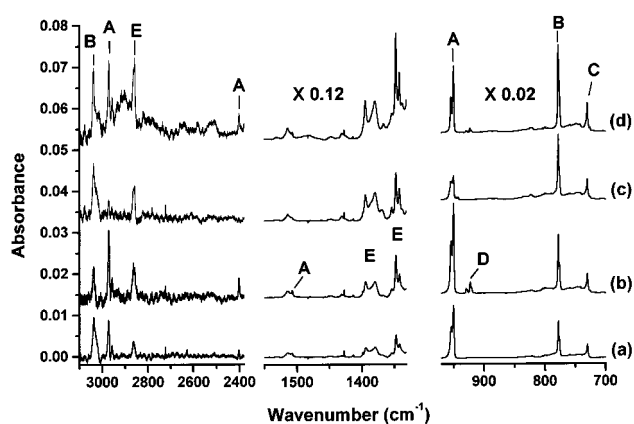


Figure 1. Infrared spectra of products formed by the reaction of thermal Pd atoms with H₂ in excess argon. (a) Pd/H₂/Ar = 0.5/8/100 co-deposited at 9 K for 90 min, (b) after annealing to 19 K, (c) after 365 nm filter photolysis for 80 min, and (d) after annealing to 24 K. Absorbance scale given for 3000–2400 cm⁻¹ region; bands in 1500–1400 cm⁻¹ region have been reduced × 0.12 and in 1000–700 cm⁻¹ region by × 0.02 so the indicated absorbance scale must be × 8 and × 50 for these regions, respectively. A weak, broad background absorption at 3030 cm⁻¹ makes quantitative photometry difficult at this wavenumber.

Table 1. Infrared Absorptions (cm⁻¹) Observed from Thermal-Evaporation and Laser-Ablation Pd Atom Matrix-Isolation Experiments with H₂ in Excess Argon

H ₂	HD	D ₂	identification
3038	2639	2160	B, Pd(H ₂) ₂
2971 ^a	2334	2169, 1916 ^d	A, Pd(H ₂), ν ₁ (a ₁)
2858	2722	2061	E, (PdH) ₂ , a _g + b _{2u}
2402 ^b	1802	1802	A, Pd(H ₂), (3ν ₂)
1953 ^c	1953, 1403	1403	PdH
1507 ^b	1306	1098	A, Pd(H ₂), ν ₃ (b ₂)
	1298		D, Pd–Pd(H ₂)
1395		979	E, (PdH) ₂ site
1348	1330	950	E, (PdH) ₂ , b _{2u}
	951		E, (PdH) ₂ , b _{2u}
954			A, Pd(H ₂) site
950	804	714	A, Pd(H ₂), ν ₂ (a ₁)
929			D, Pd–Pd(H ₂) site
923	796	704	D, Pd–Pd(H ₂)
778	650	586	B, Pd(H ₂) ₂
730	588	549	C, Pd(H ₂) ₃

^a Relative integrated intensities 2971(16), 1507(2), 954, 950(360).

^b Weaker bands observed only in thermal experiments. ^c Strong band observed only in laser ablation experiments. ^d Tentatively assigned to Fermi resonance between ν₁(a₁) and 3ν₂(a₁) of Pd(D₂).

the complete infrared spectrum of Pd(H₂) in solid argon, which is in very good agreement with the density functional theory (DFT) calculated vibrational spectrum. In addition, we identify the novel bis- and tris-H₂ complexes, the related Pd–Pd(H₂) complex, and the stable (PdH)₂ reaction product containing dissociated dihydrogen.

The experimental methods employed for reacting laser-ablated and thermally evaporated Pd atoms with CO and recording infrared spectra of the products in solid argon have been described,^{18,19} and the same methods were used here for H₂. In an argon matrix formed at 7 or 9 K, we expect to trap less than half of the H₂ in the incident argon stream.

Figure 1 contrasts infrared spectra for Pd and H₂ co-deposited with excess argon: the spectra reveal new absorptions, which shift with HD and D₂ substitution, as listed in Table 1. All of these bands increase in different proportions on annealing the matrix, Figure 1b. With lower H₂ and higher Pd concentration the D and E bands are more prominent. Significantly, the C band is favored more than B, which is enhanced over the A bands with

Table 2. Frequencies (cm^{-1}), Infrared Intensities (km/mol , in parentheses) and Structures Calculated for $\text{Pd}(\text{H}_2)$ and PdH_2 at the B3LYP/6-311++G(2d, 2p)/SDD Level^a

		a_1	b_2	a_1
$\text{Pd}(\text{H}_2)^b$	Pd–H: 1.698 Å	996	1444	2935
1A_1	H–H: 0.854 Å	(170)	(8)	(83)
	H–Pd–H: 29.7°			
PdH_2^c	Pd–H: 1.577 Å	529	2094	2199
1A_1	H–Pd–H: 72.3°	(0)	(97)	(2)

^a These calculations predict H_2 bond length (0.743 Å) and harmonic frequency (4417 cm^{-1}) and Pd–H bond length (1.541 Å) and harmonic frequency (2014 cm^{-1}). ^b $\text{Pd}-\eta^2\text{-H}_2$ complex, 17.5 kcal/mol more stable than $\text{Pd} + \text{H}_2$. ^c PdH_2 molecule, 5.0 kcal/mol higher energy than $\text{Pd}(\text{H}_2)$.

increasing H_2 at constant Pd concentration. The A, B, and C bands maintain constant relative intensities at constant H_2 with increasing Pd concentration, so that a common Pd content is apparent. Finally, the stronger bands in Table 1 and the PdH absorption were observed in laser-ablation experiments, which gave 10–20% of the 950 cm^{-1} band absorbance using 2% H_2 .

The A bands at 2971, 1507, and 950 cm^{-1} maintain approximately constant relative intensities over 10-fold changes in both Pd and H_2 reagent concentrations. Furthermore, irradiation at 365 nm selectively reduces the A band, destroys D, leaves C unchanged, and slightly increases the B and E bands (Figure 1c). Final annealing restores the A bands (Figure 1d). In separate experiments 540, 580, and 632 nm photolyses destroy D and increase E bands with little effect on the A, B, and C absorptions.

The structure and frequencies of $\text{Pd}(\text{H}_2)$ were calculated using DFT in Gaussian 98 with several functionals and basis sets, and the B3LYP, largest H basis, SDD pseudopotential results^{20–23} are reported in Table 2. Similar calculations work well for the H_2 and PdH molecules.

The A bands arise from the first product formed at low reagent concentrations. A single intermediate component with HD and one D_2 counterpart show that a single dihydrogen molecule is involved in the reaction to form species A. The stronger 2971 and 950 cm^{-1} absorptions are observed in the laser-ablation experiments, which generate much lower Pd atom fluxes. Hence, we conclude that the A absorptions are due to the side-bonded $\text{Pd}(\text{H}_2)$ complex, an assignment which is strongly supported by the DFT/B3LYP calculated frequencies in Table 2. Finally, the strong 950 cm^{-1} band for $\text{Pd}-\eta^2\text{-H}_2$ in solid argon is in accord with the krypton and xenon matrix spectra,¹⁵ but the bands assigned in that work to $\text{Pd}-\eta^1\text{-H}_2$ are in fact due to the higher $\text{Pd}(\text{H}_2)_{2,3}$ complexes, which result from the addition of more H_2

molecules to $\text{Pd}(\text{H}_2)$ and will be described in a later full paper.²⁴ No evidence is found in this work for an end-bonded complex. The Pd–HH complex is an inversion transition state with an imaginary bending frequency in our DFT calculations.

The vibrational frequencies of $\text{Pd}(\text{H}_2)$ are of interest particularly as a model compound for side-bound hydrogen in transition metal complexes. The strong 950 cm^{-1} band is due to the symmetric Pd– H_2 stretching mode, which is in the range 950–850 cm^{-1} reported for this mode in transition metal complexes,^{1,25} and the much weaker 1507 cm^{-1} band is assigned to the antisymmetric Pd– H_2 stretching mode. The 2971 cm^{-1} band is the important H–H stretching fundamental, which is 1188 cm^{-1} lower than the 4159 cm^{-1} frequency for the H_2 diatomic molecule²⁶ and in the range 3080–2650 cm^{-1} for $\eta^2\text{-H}_2$ transition metal complexes.^{1,3} These bands show the large H/D ratios expected for hydrogen motions; the low 950/714 = 1.331 ratio indicates significant anharmonicity in the metal– H_2 potential function. Finally, the DFT calculations predict the H–H frequency within 1.2% and the Pd– H_2 modes within 4.3 and 4.8%. The calculated infrared intensities are qualitatively in agreement with observed values although the H–H stretching intensity is overestimated by an order of magnitude.

The bonding between Pd and H_2 subunits was investigated using the natural bond orbital (NBO) method.²⁷ Occupancy of the σ bonding orbital of the H_2 molecule decreased slightly on going from free H_2 to the Pd– H_2 complex (2e versus 1.9e). This is in line with weakening of H–H bonding upon complexation. In addition, no bonding orbital between the palladium atom and dihydrogen molecule was found. The effective charge transfer from metal to ligand was calculated to be only 0.06e. From the NBO analysis, the σ donation (from σ orbital of H_2 to the vacant 5s orbital of Pd) and π back-donation (from the filled 4d orbital of Pd to the dihydrogen σ^* orbital) were found to be 0.17 and 0.23e, respectively. Therefore, the interaction between Pd and H_2 arises from two cooperatively coupled intermolecular donor–acceptor delocalizations that lead to overall charge reorganization with little net transfer.

The higher-energy open PdH_2 dihydride predicted by earlier calculations^{11,12,14d} was not observed based on the lack of any appropriate product bands predicted in the 2000 \pm 100 cm^{-1} region (Table 2). The more stable side-bonded $\text{Pd}(\text{H}_2)$ complex is the only primary reaction product observed here. Any PdH_2 dihydride formed by laser-ablated Pd, which is capable of the endothermic (52 kcal/mol calculated) reaction to give PdH, relaxes to the more stable $\text{Pd}(\text{H}_2)$ complex. The $^2\Sigma^+$ PdH radical has been characterized by ESR spectroscopy in similar matrix-isolation experiments using laser-ablated Pd atoms and H_2 .²⁸

The weak D band at 923 cm^{-1} exhibits H_2 , HD, and D_2 counterparts 27, 10, and 10 cm^{-1} below the strong A bands, and the weaker Pd(HD) band at 1306 cm^{-1} shows a weaker D component at 1298 cm^{-1} . From the Pd concentration studies, species D clearly contains more Pd than $\text{Pd}(\text{H}_2)$. The visible photochemical conversion of species D into E suggests that D is a Pd– $\text{Pd}(\text{H}_2)$ complex since the E bands are appropriate for assignment to the singlet $(\text{PdH})_2$ ring, which is the most stable Pd_2H_2 structure.^{13,14c} In addition the spectra reveal two strong bands for Pd(HD)Pd and a combination band of symmetric and antisymmetric fundamentals. The E frequency observed at about 70% of the diatomic PdH value and the HD and D_2 shifts are appropriate for this $(\text{PdH})_2$ assignment,²⁹ which is in agreement with our DFT frequency calculations.²⁴ Finally the $\text{Pd}(\text{H}_2)$ and $(\text{PdH})_2$ products are significant as they show that two Pd atoms are capable of H_2 dissociation, but one cold Pd atom is not, in agreement with earlier calculations.¹³

Acknowledgment. This work was supported by C.N.R.S. Grant UMR 7075 and N.S.F. Grant CHE97-00116, and the Université Pierre et Marie Curie for an invited Professorship and the University of Virginia for a Sesquicentennial Associateship for L.A. JA002737U

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S. and Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(21) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(22) (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (b) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(23) Andrae, D.; Haussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.

(24) Andrews, L.; Wang, X.; Alikhani, M. E.; Manceron, L., to be published.

(25) Eckert, J. *Spectrochim. Acta* **1992**, *48A*, 363.

(26) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*, Van Nostrand Reinhold: New York, 1979.

(27) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(28) Knight, L. B., Jr.; Cobranchi, S. T.; Herlong, J.; Kirk, T.; Balasubramanian, K.; Das, K. K. *J. Chem. Phys.* **1990**, *92*, 2721.

(29) Souter, P. F.; Kushto, G. P.; Andrews, L.; Neurock, M. *J. Am. Chem. Soc.* **1997**, *119*, 1682.