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Neon Matrix Infrared Spectrum of WH_6: A Distorted Trigonal Prism Structure

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Valence shell electron pair repulsion (VSEPR) theory occupies a central position in structural chemistry, and it has enjoyed much predictive success.[1] One exception is for octahedral symmetry, which is predominant in transition-metal chemistry, but CrH_6 and WH_6 hexahydrides are computed to have lower symmetry-distorted trigonal prismatic structures.[2−6] In fact the stabilization for WH_6 is substantial: the C_{3v} prism is well over 100 kcal/mol more stable than the octahedral form, depending on the calculation.[3−6] Although no experimental data are available for WH_6, the closely related $W(CH_3)_6$ molecule has the distorted prismatic structure with three-fold symmetry based on gas-phase electron diffraction and low-temperature single-crystal X-ray diffraction investigations.[7,8] Ab initio and density functional theoretical calculations show that the equilibrium structure of $W(CH_3)_6$ has local C_{3v} symmetry for the WC_6 skeleton,[6] which is the same structure proposed by theory for WH_6.[3−6] The infrared spectrum is sensitive to symmetry, and thus observation of the infrared spectrum of WH_6 could in principle determine the WH_6 structure.

Ongoing investigations of reactions of laser-ablated metal atoms with H_2 in condensing noble gases have found several systems where the initial hydrides formed react with additional H_2 to produce higher hydrides or higher dihydrogen complexes. Examples include TiH_4, HfH_4, $(H_2)AuH$, and $(H_2)RhH_2$.[9−12] We apply this method to the synthesis of WH_6, and we show that the infrared spectrum containing four W−H stretching modes (two a_1 and two e) matches frequencies computed by density functional theory (DFT) for the distorted prismatic C_{3v} structure.

The experiment for reactions of laser-ablated metal atoms with small molecules during condensation in excess neon has been described previously.[11−15] The Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused onto a rotating tungsten target (Johnson-Matthey), and the energy was varied from 5 to 40 mJ/pulse. Laser-ablated tungsten atoms were co-deposited with H_2 in excess neon onto a 3.5 K CsI cryogenic window. FTIR spectra were recorded at 0.5 cm^{-1} resolution on with 0.1 cm^{-1} accuracy using an MCTB detector.

Density functional theoretical calculations of tungsten hydrides and tungsten hydride−hydrogen complexes were done for comparison. The Gaussian 98 program[16] was employed to calculate the structures and frequencies of tungsten hydride molecules using the BPW91 functional,[17] the 6-311++G(d,p) basis set for hydrogen, and SDD pseudopotential and basis for tungsten.[18,19]

Figure 1 illustrates the W−H stretching region from the infrared spectrum of laser-ablated W atom reaction products with 4% H_2 in excess neon during condensation at 3.5 K. Stronger absorptions are observed at 1920.5, 1911.5, 1894.6, 1860.2, and 1831.9 cm^{-1}, and weaker peaks appear at 2004.4, 1953.8, 1927.5, 1080.3, and 840.7 cm^{-1} (latter two not shown). The weaker peaks in concert increase on annealing, decrease on photolysis, increase on further annealing, and acquire another weaker associated peak at 2021.2 cm^{-1} (Figure 1, parts b,c,d).

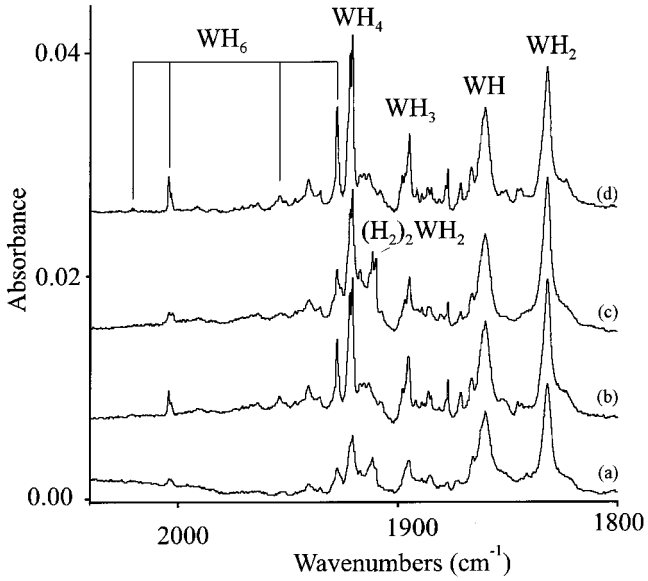

Figure 1. Infrared spectrum in the W−H stretching region for tungsten hydrides prepared by reacting laser-ablated W atoms and H_2 in excess neon during co-deposition at 3.5 K. (a) W and 4% H_2 co-deposited for 1 h in neon, (b) after annealing to 10 K, (c) after broadband photolysis for 15 min, and (d) after annealing to 11 K.

With the help of D_2 and HD substitution on the experimental frequencies and DFT calculations of isotopic frequencies for the minimum energy structures, the stronger above absorptions can be assigned, respectively, to WH_4, $WH_2(H_2)_2$, WH_3, WH and WH_2. The details of these assignments and calculations will be reported in a longer paper.[20] The weaker six band group will be assigned here to WH_6 in the distorted C_{3v} prism structure based on agreement with frequencies computed by DFT.

The strongest four of the six new bands exhibit deuterium counterparts (Table 1) that define H/D isotopic frequency ratios 1.392, 1.393, 1.386, and 1.380, which are appropriate for W−H stretching and bending vibrations. Thus, the four highest frequencies are due to W−H stretching vibrations, and this provides diagnostic information for the new tungsten hydride structure.

First, the new tungsten hydride formed here with four W−H stretching frequencies cannot be octahedral WH_6, which has one allowed triply degenerate W−H stretching mode. Second, the observed frequencies are not compatible with DFT predictions for the slightly higher energy C_{5v} parachute and umbrella structures and the C_{3v} hemisphere structure in terms of the number of observable (by calculated intensity) and relative positions of the W−H stretching modes.[20] However, the agreement between the four observed neon matrix W−H stretching frequencies and their relative intensities with those predicted by DFT for the distorted

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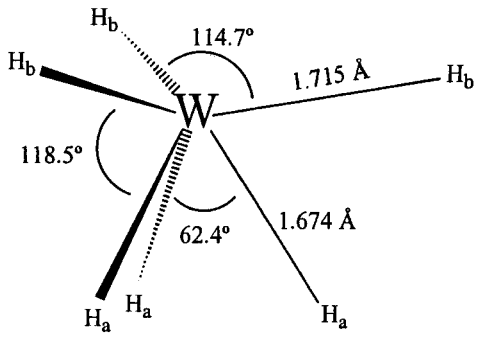
Table 1. Neon Matrix Observed and DFT Calculated Frequencies (cm^{-1}) for WH_6 in the Distorted Trigonal Prism Structure[a]

observed			calculated
H_2	D_2	HD	H_2 (mode, intensity, km/mol)
2021.2 (3)[b]			2059.3 (a_1, 45)
2004.4 (40)	1439.9	1432.5	2039.9 (e, 72 × 2)
1953.8 (12)		1952.6	1963.7 (a_1, 92)
1927.5 (100)	1384.1	1927.5	1949.8 (e, 141 × 2)
1080.3 (30)	779.2	797.9	1155.1 (a_1, 101)
			946.1 (e, 14 × 2)
840.7 (14)	609.1		894.0 (e, 60 × 2)
			805.8 (a_2, 0)
			758.6 (a_1, 10)
			709.5 (e, 9 × 2)

[a] C_{3v} structure calculated at BPW91/6-311G(d,p)/SDD level: top three W−H bonds are 1.715 Å, H−W−H angles are 114.7°; bottom three W−H bonds are 1.674 Å, H−W−H angles are 62.4°. $^1A_1$ ground-state WH_6 molecule. [b] Relative integrated band absorbances.

C_{3v} prism WH_6 structure (Table 1) is remarkable. Although frequencies calculated with the B3LYP functional[20] and at the all-electron SCF level are higher,[3] the band profile and relative intensities are similar to those reported here for the BPW91 functional.

The distorted C_{3v} prism structure computed here and shown below for the $^1A_1$ ground-state WH_6 molecule is almost the same as that calculated earlier.[3−6] In addition, displacement coordinates show that the two highest W−H stretching frequencies are due mostly to the trigonal WH_3 subgroup with the shorter $W-H_a$ bonds and acute H_a-W-H_a angles, and the next two frequencies are due to the WH_3 subgroup with the longer $W-H_b$ bonds and obtuse H_b-W-H_b angles. Thus, each WH_3 subunit exhibits symmetric (a_1) and antisymmetric doubly degenerate (e) stretching modes, and vibrational coupling between these WH_3 subunits is minimal. The four W−H stretching modes are calculated 38, 35, 10, and 22 cm^{-1} (or 1.9, 1.7, 0.5, and 1.1%) too high by the BPW91 density functional, which is excellent agreement. However, the relative intensities do not fit quite as well, as the calculation overestimates the a_1 W−H stretching intensities. Bending and deformation modes are predicted 65 and 53 cm^{-1} (or 6.0 and 6.3%) too high with reasonable relative intensities. It is clearly more difficult to compute accurately lower-frequency bending vibrational motions.



Reaction with HD gives WH_3D_3 in four isotopic modifications, but the WD_3(short)H_3(long) isotopomer with the lowest zero-point energy appears to be favored although weak bands are found for other isotopomers. The lowest-energy isotopomer exhibits the four HD frequencies listed in Table 1, which are near values for the WH_3(long) and WD_3(short) subunits of the WH_6 and WD_6 isotopic molecules, respectively. The WH_3D_3 spectrum also supports the present assignments and substantiates this first experimental evidence for tungsten hexahydride.

It is interesting to note that broadband (240−700 nm) photolysis decreases WH_6 and produces the 26.0 kcal/mol higher energy high-spin $WH_2(H_2)_2$ complex, but further annealing allows the exothermic reformation of WH_6. It appears that WH_6 is stable but facile and that H_2 molecules must be in a favored orientation for reaction with WH_2 to form WH_6.

$$WH_6(^1A_1, C_{3v}) \underset{8-11\ K}{\overset{240-700\ nm}{\rightleftharpoons}} WH_2(H_2)_2(^3A'', C_s)$$

The present neon matrix experiments provide the proper dynamic conditions for reaction of laser-ablated W atoms and H_2 to form WH_2 during condensation in excess neon at 3.5 K. Some WH_2 reacts with more H_2 to form WH_4 and WH_6. The latter reactions also occur on annealing the solid neon host to 8−11 K, which allows diffusion and spontaneous reaction of H_2 with WH_2 and WH_4. The WH_6 formed here is identified by D_2 and HD isotopic substitution and by excellent agreement with frequencies computed by DFT for the distorted C_{3v} prism structure. Thus, structure determination is made by matching observed frequencies with frequencies calculated for a unique structure. Although there is evidence for higher hydride anion species in the solid state,[21] WH_6 is the highest neutral hydride and the only neutral metal hexahydride to be observed experimentally.

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