Infrared spectra of the WH₄(H₂)₄ complex in solid hydrogen

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Abstract
The codeposition of laser-ablated tungsten atoms with neat hydrogen at 4 K forms a single major product with a broad 2500 cm⁻¹ and sharp 1860, 1830, 1782, 1008, 551, and 437 cm⁻¹ absorptions, which are assigned to the WH₄(H₂)₄ complex on the basis of isotopic shifts and agreement with isotopic frequencies calculated by density functional theory. This D₂d structured complex was computed earlier to form exothermically from W atoms and hydrogen molecules. Annealing the matrix allows hydrogen to evaporate and the complex to aggregate and ultimately to decompose. Comparison of the H-H stretching mode at 2500 cm⁻¹ and the W-H₂ stretching mode at 1782 cm⁻¹ with 2690 and 1570 cm⁻¹ values for the Kubas complex W(CO)₃(PR₃)₂(H₂) suggests that the present physically stable WH₄(H₂)₄ complex has more strongly bound dihydrogen ligands. Our CASPT2 calculations suggest a 15 kcal/mol average binding energy per dihydrogen molecule in the WH₄(H₂)₄ complex.

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Introduction

The coordination of dihydrogen to metals has attracted considerable attention since the Kubas tungsten complexes were first discovered.¹,² A similar complex was later shown to undergo interconversion between the dihydrogen and dihydride subunits at room temperature in solution.³ The first naked metal complex, Pd(H₂), was prepared by Ozin and Garcia-Prieto in solid krypton and later investigated in solid argon and neon and also using density functional theory by Andrews et al.⁴ The drive to form larger complexes with more dihydrogen has been motivated by the importance of hydrogen storage for potential use as a fuel.⁵ In this regard calculations performed to search for stable larger complexes predicted that the stable WH₄(H₂)₄ complex (Figure 1) would form exothermically from tungsten atoms and six dihydrogen molecules.⁶

The first experimental investigation of naked W atoms reacting with dihydrogen performed in this laboratory found evidence for WH₄ as a major reaction product, and annealing the solid neon matrix increased a group of six sharp new absorptions, which were assigned to WH₆, as formed by the spontaneous reaction of WH₄ and H₂.⁷ These absorptions matched density functional calculated frequencies for the distorted C₃ᵥ prism WH₆ structure, which remains the highest neutral hydride and the only neutral metal hexahydride to be observed experimentally. This distorted structure is more stable than the octahedral form, which has been the subject of extensive theoretical calculations from several groups.⁸–¹¹

Figure 1. Structure of WH₄(H₂)₄ computed at the DFT level of theory.
these absorptions was described as perturbed [WH₄] and shown to be an intermediate for the production of WH₆ in a subsequent full paper.¹² We report here the reaction of laser ablated W atoms with neat normal and para-hydrogen and identify the largest possible physically stable tungsten hydride species, which is the tungsten tetrahydride tetradihydrogen complex calculated earlier.⁶ Further quantum chemical calculations have been performed in order to assign the measured frequencies and to compare the stability of the various WH₄ species possibly formed in the matrix isolation experiments.

**Experimental and Computational Methods**

The experiment for reactions of laser-ablated tungsten atoms with hydrogen molecules during condensation at 4 K has been described in detail previously.¹³ 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, 99.95%). The laser energy was varied from 5 to 20 mJ/pulse. Laser-ablated tungsten atoms were codeposited with 3–4 mmol of normal or para hydrogen molecules onto a 4 K CsI cryogenic window for 30 min using a Sumitomo Heavy Industries Model RDK-205D cryocooler. Hydrogen (Matheson), D₂ and HD (Cambridge Isotopic Laboratories), and H₂ + D₂ mixtures were used in different experiments. FTIR spectra were recorded at 0.5 cm⁻¹ resolution on a Nicolet 750 with 0.1 cm⁻¹ accuracy using a HgCdTe range B detector. Matrix samples were annealed at different temperatures, and selected samples were subjected to broadband photolysis by a medium-pressure mercury arc lamp (Phillips, 175 W) with the outer globe removed.

Quantum chemical calculations were performed using density functional theory (DFT), Moeller–Plesset perturbation theory (MP2), and multiconfigurational methods followed by second-order perturbation theory (CASSCF/CASPT2). The TURBOMOLE package was employed for the DFT and MP2 calculations. Scalar relativistic effects were incorporated by employing on the tungsten atom the (8s7p6d2f1g)/[3s2p1d] effective core potential (ECP) basis set with 60 core electrons.¹⁶ A valence triple-ζ basis set plus polarization functions, (5s2p1d)/[3s2p1d], was used on the hydrogen atoms. We will refer to this series of basis sets as TZVPP. The gradient-corrected BP86 (5s2p1d)/[3s2p1d], was used on the hydrogen atoms. We will refer to this series of basis sets as TZVPP.

The MOLCAS 7.0 package was employed for the CASSCF/CASPT2 calculations.²⁰ For CASSCF calculations on the WH₄ molecule, the orbitals formed by linear combinations of 6s as well as 5d orbitals on tungsten with 1s orbitals on the hydrogens were included in the active space, resulting in an active space formed of 10 electrons in 10 orbitals. The same active space was also employed in the calculations on WH₂⁺, WH₃⁻. For this species, calculations with 12 electrons in 12 orbitals and 14 electrons in 14 orbitals were also performed, in which these extra orbitals are delocalized on the H₂ moieties. In the subsequent CASPT2 calculations, no orbitals were frozen. This method has proven to be successful in the study of metal compounds.²¹

Coupled cluster calculations, with single and double excitations and perturbative triple excitations, CCSD(T), were also performed using the MOLCAS 7.0 package.²⁰ The same active space as that in the CASSCF calculations was employed. In total, 20 electrons were correlated for WH₄ and 38 electrons, for WH₂⁺. For both the CASSCF/CASPT2 and CCSD/CCSD(T) calculations the Douglas–Kroll–Hess approximation was employed to account for scalar relativistic effects.²² All-electron basis sets of atomic natural orbital type, developed for relativistic calculations (ANO-RCC) with the Douglas–Kroll–Hess Hamiltonian, were used for all the atoms.²¹ The contraction was 9s8p6d4f1g3 for W and 3s2p1d for H.

**Results**

Matrix-isolation infrared spectra are presented for laser ablated tungsten atom reactions with pure hydrogen samples. Density functional theoretical calculations of the structures and vibrational frequencies of tungsten hydrides and hydrogen complexes are given for comparison.

**Infrared Spectra.** Figure 2 illustrates infrared spectra in selected regions for tungsten ablation and reaction with pure normal hydrogen during condensation at 4 K. The most prominent new absorptions are observed at 1859.1, 1830.3, and 1732.8 cm⁻¹ with weaker bands at 2500, 1781.6, 1007.6, and 551.5 cm⁻¹ (marked with arrows). The weak 1911.5 cm⁻¹ feature is most likely due to WH₄ molecules on the surface as it falls below the strong 1920.5 cm⁻¹ neon matrix counterpart for this molecule, which is the expected matrix shift relationship.¹²,¹³ Annealing this sample to 6 K had little effect on the spectrum, while full arc irradiation (>220 nm) reduced the absorptions and a subsequent annealing to 6.3 K only sharpened them. The seven absorptions marked with arrows track together on annealing and UV irradiation, and they are thus associated with a common new product species. A final annealing to 7 K allowed the hydrogen matrix to evaporate and the new product to aggregate leaving behind no infrared absorptions (Figure 2b–e).

Two investigations with 99.9% para-hydrogen samples gave almost the same stronger absorptions, but since we can collect less para-hydrogen sample, the weaker bands were not observed.

In solid deuterium the weak WD₄ band was observed at 1378.2 cm⁻¹ along with a broad 1790 cm⁻¹ band and new sharp absorptions at 1332.6, 1321.2, 1282.5, and 719.9 cm⁻¹. Irradiation (240–380 nm) increased these bands by 50%, but a full arc (>220 nm) reduced them slightly, as is illustrated in Figure 21.
3. The ortho-deuterium $J = 0$ rotational state host produced slightly sharper bands shifted a few cm$^{-1}$ (Table 1).

Mixed isotopic solid molecular hydrogen spectra are compared in Figure 4, and the absorptions are collected in Table 1. Absorptions in pure HD and HD/D$_2$ are slightly shifted as these are different solid environments. No bands were observed in the 2200 or 1500 cm$^{-1}$ regions with HD. A fringe structure prevented the observation of weak broad higher frequency bands with H$_2$/D$_2$.

Calculations

Since WH$_4$(H$_2$)$_4$ is the cluster most likely to be present in the matrix, we have focused our analysis on the aggregation of WH$_4$ with 4H$_2$ molecules. The structures of the WH$_4$ and WH$_4$-(H$_2$)$_4$ species have been optimized at the DFT and MP2 levels of theory. The relevant bond distances are reported in Table 2, and the harmonic vibrational frequencies are reported in Table 3. Other WH$_4$ species and isotopic modifications have also been investigated, and their optimized structures and vibrational frequencies are reported in Supporting Information.

The agreement between seven measured and calculated frequencies identifies the WH$_4$(H$_2$)$_4$ species prepared in the matrix. In Table 3 we do not report BPE frequencies because they are very similar to the BP86 ones (they differ at most by a few wavenumbers). The DFT frequencies are closer to the measured frequencies than the MP2 values. It is well-known that wave function based methods, like MP2, suffer from basis-set incompleteness more than the DFT method. An estimate of the basis-set superposition error, using as dissociating fragments WH$_4$ and 4H$_2$, shows an energy correction of 12 kcal/mol for the MP2 method, while it is less than 1 kcal/mol for DFT. As a consequence MP2 overestimates the bond strength between W and the H$_2$ moieties and predicts frequencies about 10–15% larger than DFT, in particular for the W–H(H$_2$) stretching modes. Despite this discrepancy, the seven fundamental peaks needed to describe the WH$_4$(H$_2$)$_4$ complex are also identified at the MP2 level.

CASSCF/CASPT2 single-point energy calculations were performed on WH$_4$ and the WH$_4$(H$_2$)$_4$ complex in order to examine the electronic structure of these two species. Electron density plots are shown below.

Discussion

The new infrared spectrum in solid hydrogen will be assigned to the highest tungsten hydride based on isotopic shifts and comparison with frequencies computed by density functional theory (DFT). The important mechanism for the W and hydrogen reaction will be considered.

Identification of WH$_4$(H$_2$)$_4$. The infrared spectra shown in Figure 2 reveal diagnostic absorptions due to molecular subunits that identify this new tungsten hydride complex. Since WH$_4$ has tetrahedral symmetry, it has been characterized by the triply degenerate antisymmetric W–H stretching and bending modes at 1920.5 and 525.2 cm$^{-1}$ in solid neon, and the weak new band at 1911.5 cm$^{-1}$ in the solid hydrogen experiment can be assigned to WH$_4$ trapped on the surface where limited coordination can occur. The strong new absorptions at 1859.1 and 1830.3 cm$^{-1}$ are slightly lower but still appropriate for W–H stretching modes as the 1.3951 and 1.3853 isotopic H/D frequency ratios indicate, and the new 551.5 cm$^{-1}$ band is likewise due to an analogous H–W–H bending mode. Hence, the new product contains two or more W–H...
Infrared spectra of WH₄(H₂)₄ Complex in Solid Hydrogen

**Table 1.** Infrared Absorptions (cm⁻¹) Observed from W Atom Reactions with Hydrogen in Solid Neon and Hydrogen Isotopic Samples

<table>
<thead>
<tr>
<th>H₂/Ne</th>
<th>para-H₂</th>
<th>H₂</th>
<th>HD</th>
<th>H₂ + D₂</th>
<th>D₂</th>
<th>ortho-D₂</th>
<th>Identification</th>
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<tr>
<td>1920.5</td>
<td>1912.6</td>
<td>1911.5</td>
<td>1859.7</td>
<td>1859.1</td>
<td>1859.7/1338.7</td>
<td>1857.2/1325.1</td>
<td>1378.2</td>
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<tr>
<td>1860.5</td>
<td>1859.7</td>
<td>1859.1</td>
<td>1838.5/1318.8</td>
<td>1838.5/1318.8</td>
<td>1839.1</td>
<td>1333.7</td>
<td>WH₄(WD₄)</td>
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<tr>
<td>1832.2</td>
<td>1830.9</td>
<td>1830.3</td>
<td>1728.2</td>
<td>1718, 1263</td>
<td>1728.2</td>
<td>1263.5</td>
<td>WH₄(H₂)₁₃</td>
</tr>
<tr>
<td>1785.1</td>
<td>1782.0</td>
<td>1781.6</td>
<td>1728.2</td>
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<td>1728.2</td>
<td>1263.5</td>
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<tr>
<td>999.6</td>
<td>1000.8</td>
<td>1007.6</td>
<td>549.6</td>
<td>551.5</td>
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<td>551.5</td>
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<tr>
<td>434.8</td>
<td>436.5</td>
<td>437.2</td>
<td>436.5</td>
<td>437.2</td>
<td>437.2</td>
<td>437.2</td>
<td>WH₄(H₂)₁₃</td>
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</table>

**Figure 4.** Infrared spectra for the laser-ablated W atom and mixed isotopic hydrogen reaction product trapped in the solid molecular hydrogen reagent at 4 K. (a) W + HD, (b) after 240–380 nm irradiation, (c) after annealing to 7 K, (d) after >220 nm irradiation, (e) after annealing to 7.5 K, (f) W + 50/50 H₂ + D₂ mixture, (g) after annealing to 6 K, (h) after annealing to 6.7 K, (i) after >220 nm irradiation, and (j) after annealing to 7.4 K.

**Table 2.** Bond Distances (Å) in WH₄(H₂)₄ at Various Levels of Theory

<table>
<thead>
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<th>DFT/PBE</th>
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<td>1.74 (1.71)</td>
<td>1.72 (1.69)</td>
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<td>W−H(H₂)</td>
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<td>1.84</td>
<td>1.81</td>
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<td>H−H(H₂)</td>
<td>0.88</td>
<td>0.89</td>
<td>0.87</td>
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</table>

**Table 3.** Frequencies (cm⁻¹) Calculated at the DFT/BP86/TZVPP Level of Theory for WH₄(H₂)₄ (Singlet State, D₂d Symmetry)

<table>
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<tr>
<th>obs freq</th>
<th>calc freq</th>
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<th>symm</th>
<th>mode description</th>
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<td></td>
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<td>e</td>
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<td>b₁</td>
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<td></td>
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<tr>
<td>1160</td>
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<td>1471</td>
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<td>1903</td>
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<td>totally sym stretch W−H</td>
</tr>
<tr>
<td>2500</td>
<td>2657</td>
<td>e</td>
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<td>2683</td>
<td>11</td>
<td>b₂</td>
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<tr>
<td>2740</td>
<td>0</td>
<td>a₁</td>
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<td>totally sym stretch H−H</td>
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</table>

*Observed here in solid hydrogen. Calculated infrared intensity (km/mol). Mode irreducible representation in D₂d symmetry.

Hydride bonds. Second, the new absorptions at 2500, 1781.6, 1007.6, and 437.2 cm⁻¹ arise from the presence of side-bound dihydrogen molecules in this new product. The broad 2500 cm⁻¹ band is characteristic of the H−H stretching mode for strongly complexed dihydrogen molecules as this mode was first observed at 2690 cm⁻¹ in the Kubas complex. The 2500 cm⁻¹ band is consistent with the H−H stretching mode, which is in very good agreement with the neon matrix 1920.5 and 525.2 cm⁻¹ values that serve to calibrate the present calculations. The reaction product complex has symmetry reduced to D₂d and the DFT prediction of e and b₂ W−H stretching modes at 1868 and 1844 cm⁻¹ is in very good agreement with the strongest observed W−H stretching bands at 1859.1 and 1830.3 cm⁻¹. The antisymmetric degenerate (e) and antisymmetric combination of symmetric (b₂) H−W−H stretching modes is further confirmed by comparing harmonic calculated H/D ratios (1.4109, 1.4012) with the observed ratios (1.3951, 1.3853, respectively). The slightly lower H/D ratio is due to more W participation in the symmetric normal mode, which follows for the lower calculated and observed H/D ratios.

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The observed H/D ratios are both lower than the harmonic calculated values owing to anharmonicity in the observed frequencies. Note from the experimental spectrum that the 1830.3 cm\(^{-1}\) band is 1.5 times stronger than the 1859.1 cm\(^{-1}\) absorption. Our calculation predicts the relative infrared intensities as 212/106, which is as accurate as can be expected for these calculations. Finally, the doubly degenerate H–W–H bending mode predicted at 565 cm\(^{-1}\) for WH\(_4\)(H\(_2\))\(_4\) is observed at 551.5 cm\(^{-1}\); such an agreement is as good as can be expected for this model and molecule.

The four modes involving the W–(H\(_2\)) linkage predicted at 2657, 1790, 1065, and 414 cm\(^{-1}\) are observed slightly lower except for the lowest frequency bending mode, which is observed slightly higher. The important diagnostic H–H stretching mode is observed as a broad band at 2500 cm\(^{-1}\). This is of course dominated by the strong calculated e mode, but the weaker b\(_2\) mode is too close to be resolved for such a broad absorption (Table 3).

Overall this agreement is excellent, and it confirms the present preparation of the WH\(_4\)(H\(_2\))\(_4\) tungsten hydride dihydrogen complex. Typically density functional theory overestimates observed frequencies owing in part to the lack of anharmonic correction, and the overestimates are consistent for the strong W–H stretching modes calculated and observed here.

Finally, based on the ligand H–H stretching and W–H stretching frequencies for the important Kubas complex W(CO)\(_3\)-(PR\(_3\))\(_3\)(H\(_2\)), namely 2690 and 1570 cm\(^{-1}\), and our most stable tungsten hydride dihydrogen complex, WH\(_2\)(H\(_2\))\(_2\), 2500 and 1782 cm\(^{-1}\), the dihydrogen ligands are bound more strongly in WH\(_4\)(H\(_2\))\(_4\) than in the Kubas complex. This is consistent with the measured 7 kcal/mol H\(_2\) binding enthalpy for the W(CO)\(_3\)-(PCy\(_3\))\(_2\)(H\(_2\)) complex and our CASPT2 calculated average 15 kcal/mol binding energy for the WH\(_4\)(H\(_2\))\(_4\) complex (see below). Although WH\(_4\)(H\(_2\))\(_4\) cannot yet be prepared in synthetic quantities, it does represent the most stable hydride species that can be formed from W atoms and dihydrogen molecules, both computationally and experimentally.

**Neon Matrix Reactions.** The W and H\(_2\) reaction was first investigated in solid neon where the unique WH\(_6\) molecule and the WH\(_4\) precursor were identified from W–H stretching modes at 2021, 2004, 1954, and 1927 cm\(^{-1}\) and at 1920 cm\(^{-1}\), respectively. Other features at 1925.7 and 1911.5 cm\(^{-1}\) were recognized as an intermediate related through annealing and UV irradiation interconversion to WH\(_6\). Since the WH\(_4\)(H\(_2\))\(_2\) complex is unstable in favor of WH\(_6\) (the former converges to the latter on calculation), this intermediate was first suggested as WH\(_2\)(H\(_2\))\(_2\) and later as (WH\(_4\))(Ne)(H\(_2\)). In addition strong absorptions at 1860.2 and 1831.9 cm\(^{-1}\) in the initial solid neon deposite were assigned to WH and WH\(_2\) on the basis of deuterium shifts, HD stretching modes in the 2200 and 1500 cm\(^{-1}\) regions along with the presence of W–H and W–D and W–H\(_2\)–H\(_2\)–W stretching. HD shifts, and clear-cut trends in the calculated W–H stretching frequencies. Notice the 30% growth in the latter two bands (Figure 1, ref 7) on annealing to 10 K. At the time of this earlier work, we did not have a sample window cold enough to deposit solid hydrogen, namely 4 K, so the spectrum in Figure 2 was not available to contribute to our interpretation of W and H\(_2\) reaction products. The neon matrix experiment was repeated with 6% H\(_2\), and the product absorptions were stronger at 1860.5, 1832.2, and 1785.1 cm\(^{-1}\) along with weaker bands at 999.6 and 434.8 cm\(^{-1}\). A fringe structure prevented the measurement of a band in the 2500 cm\(^{-1}\) region. Notice now the agreement between the former two neon matrix bands at 1860.2 and 1831.9 cm\(^{-1}\) and the present hydrogen matrix bands at 1859.1 and 1830.3 cm\(^{-1}\) both in profile and band position and recognize the small red shift expected from solid neon to solid hydrogen. In addition the lower three bands measured in solid neon involving the W–(H\(_2\)) linkage are in good agreement with the solid hydrogen values. It is clear that the H\(_2\) reagent is mobile enough upon condensation in excess neon at 4 K to effect sufficient aggregation to attain the most stable product that is also formed in pure solid hydrogen. Under these conditions WH and WH\(_2\) are probably too reactive to survive and be trapped. Hence, the latter neon matrix bands must be reassigned to the WH\(_6\)(H\(_2\))\(_4\) tungsten hydride dihydrogen complex in solid neon.

This means that intervening bands must be considered for intermediate species such as WH\(_6\)(H\(_2\))\(_2\). In this regard new calculations (Table S1) predict that the strongest WH\(_6\)(H\(_2\))\(_2\) complex absorption will red shift 10–15 cm\(^{-1}\) from isolated WH\(_6\) and the above 1925.7, 1911.5 and associated 515.6 cm\(^{-1}\) bands are best reassigned to WH\(_2\)(H\(_2\)). At this point it is speculative, but the 1895.3 cm\(^{-1}\) band increases and decreases along with WH\(_4\) on annealing and irradiation, and it could be due to a higher complex such as WH\(_6\)(H\(_2\))\(_2\) on the way to the final WH\(_6\)(H\(_2\))\(_4\) product.

**Reaction Mechanism.** The co-deposition of W with pure HD contributes to our understanding of the reaction mechanism. The absence of bands for H–D and W–HD stretching modes in the 2200 and 1500 cm\(^{-1}\) regions along with the presence of major bands in the W–(H\(_2\)) and W–(D\(_2\)) stretching regions demonstrates that WH\(_2\)(HD)\(_2\) complexes are not formed. Furthermore, the intensities of bands in the W–H stretching region are substantially stronger than those in the W–D stretching region, in excess of the 2:1 relative intensity expected for H and D vibrational infrared intensities. Clear shifts occur in the strong W–H stretch to 1838.5 cm\(^{-1}\) and the W–D stretch to 1338.7 cm\(^{-1}\) relative to the all-H and all-D species, which shows that the WH\(_3\)D\(_2\) primary hydride is formed (see calculated frequencies in Tables S2–S5). Thus, the spectrum in pure HD is dominated by the WH\(_3\)D\(_2\)(H\(_2\))D\(_2\) molecule. This suggests the participation of WH\(_6\) in the mechanism of formation for WH\(_6\)(H\(_2\))\(_4\), which requires the dissociation of the reagent molecules and allows scrambling of the H and D in the products initially formed. The preference for WH\(_3\)D\(_2\)(short D) over WH\(_3\)D\(_2\)(long D) isotopic modifications and the fluxional nature of WH\(_6\) owing to low barrier heights among the several structures have been noted. Analogous isotopic scrambling has been observed in the Rh and Cr deuterium hydride systems.

When the activated complexes produced in the exothermic reactions do finally relax, thermodynamic control leads to the formation of WH\(_3\)D\(_2\)(H\(_2\))D\(_2\) as opposed to WH\(_3\)D\(_2\)(HD)\(_2\). The stability of one complex over the other cannot be assessed with regular computational methods, because we are in regime with the Born–Oppenheimer approximation. However, just looking at the computed zero-point energies, the WH\(_3\)D\(_2\)(H\(_2\))D\(_2\) isotopic molecule is the most stable species by 0.1 kcal/mol.


which is consistent with the above spectroscopic identification
of this more stable isotopomer. This represents an isotopic
exchange as the HD reagent allows the formation of WH\textsubscript{3}D\textsubscript{3} in
the structural form where the three D occupy the short bond
positions owing to lower zero-point energy, which demonstrates
the fluxional nature of WH\textsubscript{6}.\textsuperscript{12} Now the present pure HD
experiment shows the formation of WH\textsubscript{2}D\textsubscript{2}(H\textsubscript{2})\textsubscript{2}(D\textsubscript{2})\textsubscript{2} and not
WH\textsubscript{2}D\textsubscript{2}(HD)\textsubscript{4} again owing to lower zero-point energy for the
former complex. This also requires that the WH\textsubscript{3}D\textsubscript{3} and WH\textsubscript{2}D\textsubscript{2}
complexes initially formed are sufficiently energized by reaction
exothermicity to again equilibrate all of the H and D present.
Then when the final WH\textsubscript{6}D\textsubscript{6} species is formed, reaction energy
activates randomization of H and D, and relaxation gives the
most stable, based on zero-point energy, final WH\textsubscript{2}D\textsubscript{2}(H\textsubscript{2})\textsubscript{2}(D\textsubscript{2})\textsubscript{2}
complex, as observed in Figure 4a.

**Bonding.** Note that annealing in the neon matrix (Figure 1b,
ref 7) increased WH\textsubscript{4}, WH\textsubscript{6}, and the bands we have reassigned
here to the final WH\textsubscript{4}(H\textsubscript{2})\textsubscript{4} product. This underscores the
spontaneous reaction of tungsten atoms with hydrogen molecules
to form this highest tetrahydride, tetradihydrogen complex.
Figure 5 compares the reaction exothermicities for W atom
reactions with \( n \) molecules of hydrogen to form the most stable
hydrides and hydride complexes calculated at the BP86/TZVPP
level of theory with zero-point energy correction. These energies
are slightly higher using CCSD(T), CASPT2, and MP2, which
in part accounts for dispersion interactions. The most significant
point here is that four H\textsubscript{2} molecules are bound to WH\textsubscript{4} to form
the physically stable WH\textsubscript{4}(H\textsubscript{2})\textsubscript{4} tungsten hydride dihydrogen
complex. Correction for BSSE further reduces these total binding
ergies to 50, 59, and 65 kcal/mol at the BP86, CASPT2, and
MP2 levels of theory, respectively, for the four dihydrogen
molecules. Since the MP2 approach is known to overestimate
the interactions between closed shell fragments, more accurate
calculations of the binding energy were performed at the
CASPT2 and CCSD(T) levels of theory, using the DFT
optimized structures. At the CCSD(T) level of theory, including
the ZPE and BSSE corrections, the binding energy is predicted
to be 56 kcal/mol. These highly correlated methods, CASPT2
and CCSD(T), thus predict a larger binding energy than DFT.

It is very interesting to consider the bonding of the H\textsubscript{2}
molecules in the supercomplex species. There is definitely an
electronic effect: in the triplet ground state of the WH\textsubscript{4} molecule
the two unpaired electrons reside in two W 5d orbitals, while
in the singlet ground state of the supercomplex the two electrons
are paired and they reside in bonding orbitals between W and
the H\textsubscript{2} moieties. It thus seems that the presence of the extra H\textsubscript{2}
moieties has an electronic effect on WH\textsubscript{4}, in the sense that it
implies a bond formation between W and the H\textsubscript{2} moieties and
a change in the ground state. The partial charges, according to
a Mulliken analysis, are also different in the two cases. In WH\textsubscript{4},
the W has a partial charge of +1.57, and the H\textsubscript{2} of −0.39, while,
in WH\textsubscript{4}(H\textsubscript{2})\textsubscript{4}, the W has a partial charge of +0.46 and H(WH\textsubscript{4})
has a partial charge of −0.18. The absolute values are probably

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**Figure 5.** Energy level diagram for tungsten hydrides and dihydrogen complexes calculated at the BP86/TZVPP level of theory including zero-point energy correction but not basis set superposition error.

**Figure 6.** Electron density plots (0.04 iso density level) for WH\textsubscript{4} and the WH\textsubscript{4}(H\textsubscript{2})\textsubscript{4} complex calculated at the CASSCF level of theory.
not relevant, but the relative values are interesting and they show that WH₄ becomes less ionic in the presence of the 4H₂ moieties. Inspection of the total electron density calculated with a contour value of 0.03 for the two species indicates that a real bond occurs between the H₂ moieties and W (Figure 6). This is also confirmed by the values of the relevant bond distances computed at the DFT level of theory (Table 2): in WH₄ the W–H bond distance is 1.71 Å; in WH₄(H₂)₄ the W–H(hydride) bond distance is 1.74 Å, the W–H(H₂) bond distance is 1.85 Å and the H–H(H₂) bond distance is 0.88 Å. A similar calculation on an isolated H₂ molecule predicts a bond distance of 0.75 Å. As mentioned before, the MP2 results show a shorter W–H(H₂) bond length.

Conclusions

Laser-ablated W atoms codeposited with pure hydrogen at 4 K form a major product, which is identified as the WH₄(H₂)₄ complex on the basis of seven diagnostic infrared absorptions, their isotopic shifts, and agreement with isotopic frequencies calculated by density functional theory. This $D_{2d}$ structured complex is calculated to form spontaneously from W atoms and hydrogen molecules. Warming the sample above 7 K allows the hydrogen matrix to evaporate and the complex to aggregate and ultimately to react with itself and decompose. Comparison of the H–H stretching mode at 2500 cm⁻¹ and the W–H₂ stretching mode at 1782 cm⁻¹ with 2690 and 1570 cm⁻¹ values reported for the W(CO)₃(PR₃)₂(H₂) complex¹ suggests that the present physically stable WH₄(H₂)₄ complex has more strongly bound dihydrogen ligands. The average binding energy per dihydrogen ligand in our supercomplex is 15 kcal/mol computed at the CASPT2 level of theory. Hence, the four H₂ ligands interact strongly with WH₄ and alter the electronic state from triplet to singlet.

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Supporting Information Available: Tables of calculated frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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