The following questions are designed to be a deep dive into the first molecular dihydrogen complex, reported in the article “Characterization of the First Examples of Isolable Molecular Hydrogen Complexes, M(CO)3(PR3)2(H2) (M = Mo, W; R = Cy, *i*-Pr). Evidence for a Side-on Bonded H2 Ligand” by Kubas and co-workers, *J. Am. Chem. Soc.*, **1984**, *106*, 451-452 (DOI: 10.1021/ja00314a049).

This article shows that molecular hydrogen can be a neutral L-type ligand bound in a side-on fashion. The complexes were structurally characterized, which had not been performed before. These H2 complexes are relevant to catalytic hydrogenation reactions (among others).

**Structure and bonding**

**Question 1.** Look at the complex shown here (Figure 1 from the Kubas paper). Describe it using CBC notation (geometry, VN, LBN, dn and VEC).

**Question 2:** Given the answer to question 1 above, predict the geometry and electron count of the starting material, W(CO)3(PCy3)2, before the addition of H2?

The authors saw a reversible color change when H2 was added or removed from M(CO)3(PR3)2, indicating that the species reacted with H2 but that the H2 could by removed to regenerate the starting materials. The authors could have studied the reaction using UV-Vis spectroscopy, 31P NMR spectroscopy, 13C NMR spectroscopy, Raman Spectroscopy, or other techniques. However, 1H NMR and IR spectroscopy were ideal to study the H2 ligand itself.

**Question 3.** The H2 ligand was structurally characterized on the W(CO)3(P-*i*-Pr3)(η2-H2) complex. Both X-ray diffraction and neutron diffraction were used. Why is it hard to locate the structures of hydrogen atoms with X-ray diffraction? *Hint: X-rays diffract due to electron density while neutron diffraction relies on nuclear cross-section which varies strongly with different isotopes but is strong for both H and D.*

**Question 4.** Sketch the frontier orbitals involved in the interaction of the metal and the H2 fragment. *Hint: you can use a Dewar-Chatt-Duncanson model to describe the bonding*. What would you predict the H2 bond length in the bound H2 be as compared to free H2? The authors describe this dihydrogen complex as being an “arrested form of oxidative addition.” While we haven’t discussed OA yet, what do you think this means?

**IR and NMR spectroscopy**

In Newtonian mechanics and in the analysis of molecular vibrations in IR/Raman spectroscopy, the reduced mass, , allows the 2-body problem to be solved as a 1-body problem. Reduced mass, , is defined as: .

**Question 5:** Calculate the reduced mass for H2, HD, and D2. Use 1.008 g/mol for the atomic weight of H and 2.014 for the atomic weight of D.

The vibrational frequency of a molecule, , can be derived using simple harmonic motion considerations: , where *k* is the force constant of the “spring.” Using this information, one can calculate the vibrational frequency of H2 and D2 given that *k*HH = 574.9 N/m and *k*DD = 577.0 N/m (normally one would calculate the force constant from experimental data). The  in Hz can be converted to cm-1 (wavenumber) using c = . This is a fussy calculation that requires m to be in kg so the results are provided:

H2: 





D2: 





**Question 6a**. Table 1 of the Kubas paper presents IR data for three isotopomers: W(η2-H2) (2690 cm-1), W(η2-HD) (2360 cm-1), W(η2-D2) (1900 cm-1). Use the harmonic motion model presented above to predict the expected shift in frequency for the peaks seen for W(η2-HD)(CO)3(PCy3)2 and W(η2-D2)(CO)3(PCy3)2 relative to that of W(η2-H2)(CO)3(PCy3)2. Make the assumption that the H-H, H-D and D-D springs will have essentially the same force constant (the small difference shown above can be considered “the same”). *Hint: use ratios!*

**Question 6b.** How does this data support the proposal that these molecules have h2-H2 ligands rather than two adjacent hydride ligands?

**Question 7**. Explain why the signal of the H-D complex is a 1:1:1 triplet in the 1H NMR spectrum.

**Question 8:** How is it possible to differentiate spectroscopically or chemically between a complex with a η2 bound H2 molecule like W(CO)3(P-*i*-P3)2(η2-H2) and a dihydride complex like W(CO)3(P-*i*-P3)2H2?