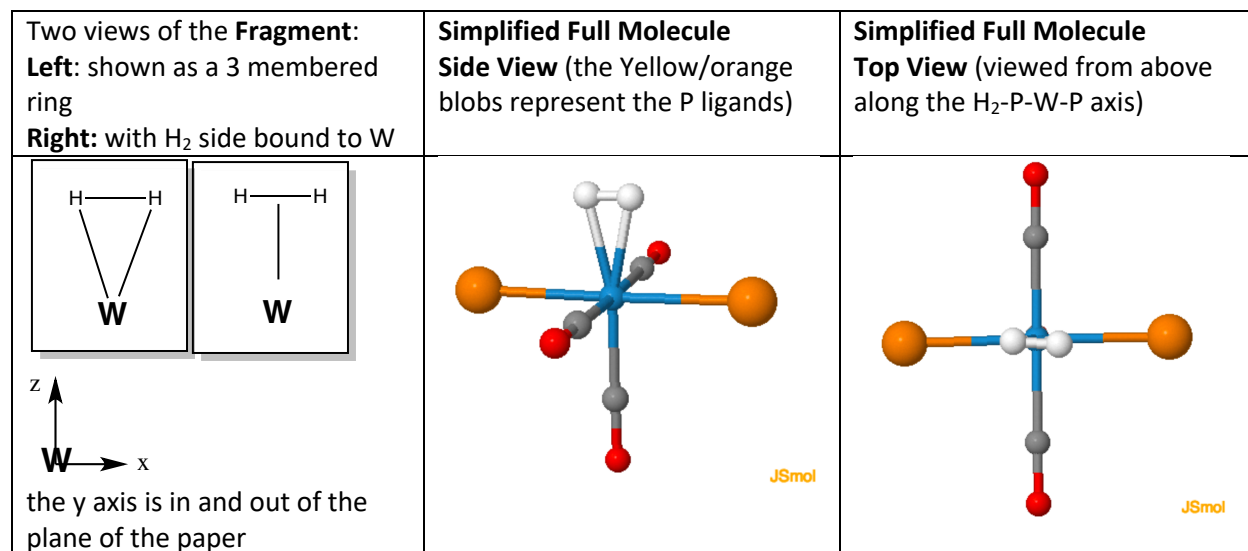


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### Supplemental, In-Class Exercise: Identification of the Six Fundamental Vibrations associated with the $\eta^2$ -H<sub>2</sub> fragment in the *mer-trans*-W(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>( $\eta^2$ -H<sub>2</sub>) molecule

In the text of Kubas' 1984 paper ("Characterization of the First Examples of Isolable Molecular Hydrogen Complexes; M(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>) (M = Mo, W; R = Cy, *i*-Pr). Evidence for a Side-on Bonded H<sub>2</sub> Ligand" G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, H. J. Wasserman; *J. Am. Chem. Soc.*, **106**, **1984** p. 451-452) when addressing the vibrational spectroscopy the authors state: "Of the six fundamentals expected from  $\eta^2$ -M-H<sub>2</sub> binding, four are observed (Table 1)". Before arriving in class, you have all independently determined the number of vibrational, rotational, and translational modes for the  $\eta^2$ -M-H<sub>2</sub> fragment treating it as if it were a stand-alone 3-atom molecule. You should have assigned a symmetry label to each type of motion and have added a description of each type of vibrational motion. Share the results of your analysis with your team and make sure that you all came up with the same answer. Check to make sure your answer is correct before proceeding with the remainder of the analysis.

As a review the molecule can be assigned C<sub>1</sub> symmetry if viewed as in Figure 1 of the paper, or as (close to) C<sub>2</sub> if one views the molecule as observed with "spherical blobs" for the P(*i*-Pr)<sub>3</sub> ligands, or as C<sub>2v</sub> if one views the H-H bond as parallel with P-W-P bond axis (the solution found when the molecule is geometry and energy minimized computationally (using a DFT calculation and a LANL2DZ basis set). The authors also suggest that this is the approximate orientation of the H<sub>2</sub> ligand (and Molecular Orbital Theory arguments should suggest that as well).

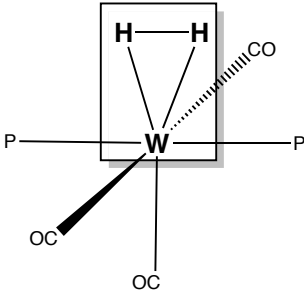
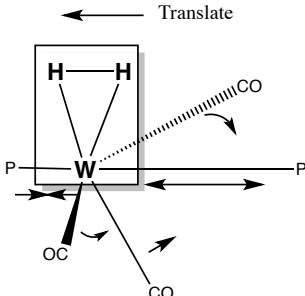


**Figure 1:** Geometry and defined axis system for the *mer-trans*-W(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>( $\eta^2$ -H<sub>2</sub>) molecule.

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In your group, you will now try to find the “3 missing” fundamental vibrations associated with the  $\eta^2$ -M-H<sub>2</sub> fragment when the fragment is placed within the full molecule.

**Method 1:** Imagine the fragment placed back into the molecule. Now examine all the modes of motion (vibrations, rotations, and translations) **of the fragment within the full molecule** to see if you can find a total of six modes that are uniquely described as vibrations associated with movement within or associated with the fragment. A test is that these motions should be “formally isotope sensitive” (Kubas, “Metal Dihydrogen and  $\sigma$ -Bond Complexes” 2001, Springer). Therefore replacing H with D in the H<sub>2</sub> ligand should shift the frequency of the observed vibration. Here is one example of the analysis testing a translation of the fragment along the x axis.

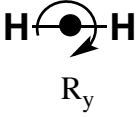
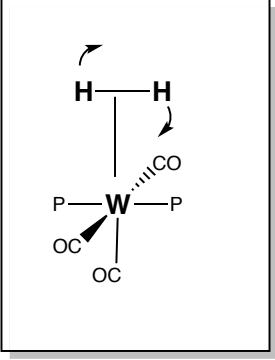
	
<p><b>Place the fragment within the molecule.</b></p>	<p><b>Test the translation along the P-W-P axis (the x axis in our axes system):</b>  When you translate the fragment along the P-W-P axes, you will see that the specific translation results in an asymmetric P-W-P stretch coupled to a bend of the three CO ligands bound to W. This translation is better described as a W-P-W asymmetric stretch/W-(CO)<sub>3</sub> bend. This motion is not substantially H/D isotope sensitive.</p>

Examine all the remaining motions with this type of test and designate those that you believe result in motions primarily associated with motions of the fragment (where “no” other atoms/bonds in the molecule are moving) and which should show substantial frequency sensitivity to H/D isotope substitution in the H<sub>2</sub> ligand.

**Method 2:** In his book “Metal Dihydrogen and  $\sigma$ -Bond Complexes” (2001, Springer) Kubas takes a slightly different approach to deciding that there should be 6 fundamental vibrations associated with the  $\eta^2$ -MH<sub>2</sub> fragments. In contrast to examining the full fragment moving, Kubas looks **only at motions of the H-H fragment** first outside of, and then when placed back into the full molecule. The H<sub>2</sub> diatomic should have 3N modes of motion and 3N-5 vibrations (so only 1 vibration: the H-H stretch). The free H<sub>2</sub> molecule has 3 translations: x, y and z translations, and two rotations; a unique R<sub>z</sub> rotation (along the H-H bond) and a R<sub>y</sub> and R<sub>x</sub> rotation that are degenerate in the free H<sub>2</sub> molecule (but not degenerate when the H<sub>2</sub> is placed back in the full molecule see below). Note that we are using the previously assigned axis system (See Figure 1). If you now place the H-H in the molecule and allow the H<sub>2</sub> fragment to vibrate, rotate and translate within the molecule, determine if each type of motion gives rise to a molecular motion within the full molecule that could be depicted as a vibration. Note that the The H-H stretch is a

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given. It is one of the 6 fundamental vibrations. Now look for the other 5 vibrations. An example follows:

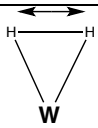
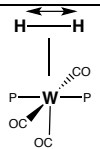
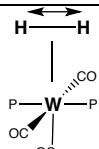
Motion for the H <sub>2</sub> diatomic	Same motion within the full molecule
 <p style="text-align: center;"><math>R_y</math></p>	
<p>Rotation about the y axis (as defined in our axes System in Figure 1. <math>R_y</math> has <math>B_1</math> symmetry in <math>C_{2v}</math></p>	<p><math>B_1</math> (asymmetric) of <math>B_1</math> Symmetry</p>

As a group, carry out Kubas' method to test **every motion** of free H<sub>2</sub> when it is placed back into the full molecule to determine if you can find 4 more motions that could be described as vibrations within the full molecule (and note: all of these motions should be characteristically sensitive to D labeling!).

In the worksheet on the following page, contrast your results in Method 1 and Method 2 to a that provided in "A Brief Summary of Relevant Data Presented in Chapter 8 (Vibrational Studies of Coordinated Dihydrogen) of Kubas' book ("Metal Dihydrogen and  $\sigma$ -Bond Complexes" (2001, Springer).) Match each vibrational mode from Method 1 to Method 2 to Kubas's depiction, and then using your own choice of words describe each motion and give each mode a label using Kubas' nomenclature. Finally go to the animations of the vibrational modes for *mer-trans*-W(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>( $\eta^2$ -H<sub>2</sub>) where R = *i*-Pr<sub>3</sub> and (<https://molecularviz.org/Index-Kubas.html>) match your modes with each animation. The entry for the H-H stretch (the easy one of course!) is provided in the first row of your worksheet.

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### Worksheet Answer

Method 1	Method 2	Kubas' depictions	Description Label Symmetry Label Animation
 <p>Fragment A<sub>1</sub> mode</p>			<p>H-H Stretch <math>\nu_{\text{H-H}}</math> A<sub>1</sub> symmetry in C<sub>2v</sub> Vibration of the H-H Stretch in MH<sub>2</sub>.</p>

And in summary, to quote from Kubas: **“Thus 6 fundamental vibrations are expected to be isotope sensitive: “three stretches:  $\nu_{\text{H-H}}$ ,  $\nu_{\text{as(M-H}_2\text{)}}$ ,  $\nu_{\text{s(M-H}_2\text{)}}$ ; two deformations,  $\delta_{\text{(M-H}_2\text{) in-plane}}$  and  $\delta_{\text{(M-H}_2\text{) out-of-plane}}$ ; and a torsion (H<sub>2</sub> rotation)  $\tau_{\text{(H}_2\text{)}}$ .”**