**Isomer identification, isotopic labeling and reduced mass calculations for IR spectroscopy**

The bond stretch in IR spectroscopy can be modeled using a Hooke’s law model

 = $\frac{1}{2πc}\sqrt{\frac{k}{µ}}$ where k is the force constant of the bond and µ is the reduced mass $\frac{m\_{1}m\_{2}}{m\_{1}+m\_{2}}$. When comparing bond stretches of isotopomers, you can predict the stretch of, for example, a CD stretch from the value of the CH stretch by dividing CH by CD; the force constants can be assumed to be the same and cancelled (or estimated by other methods and used). This process is often used to help identify stretches in the IR spectrum.

**1. Identification of a -agostic interaction**

Agostic interactions are implicated as intermediates along the pathway to interesting organometallic transformations (such as HE, CH activation). In EtTiCl3(dmpe) (dmpe is a bridging diphosphine ligand) the -carbon is involved in an agostic interaction; the C-H bond of the -carbon is donating electron density to the metal, weakening the C-H bond. Note, there is also an -agostic interaction that can sometimes be observed, for example, in CH3TiCl3(dmpe).

In the IR spectrum, CH for a regular alkane is ~2800-3100 cm-1, while the CH for a C-H bond involved in an agostic interaction is ~2300-2600 cm-1. What about the deuterated derivative, CD3CD2TiCl3(dmpe)? Predict CD for a deuterated alkane and one involved in an agostic interaction? Does the band shift into a region readily observable in the IR? Why would you label using 2H instead of 13C (assuming that cost and synthetic considerations are similar).

**2. isomer shifts**

a)

Subtraction of an 18O labeled spectrum from the corresponding 16O spectrum results in a characteristic “derivative-like” feature in the spectrum, and most of the other peaks disappear. An example of this is seen in the S=O stretches of a ligand that reacts with oxygen (*Inorg. Chem.,* **2010**, *49*, 5344-5346). The S=O stretches are observed at 1140 and 1020, while the S=18O stretches are observed at 1095 and 982. Verify that these stretches are due to the 18O label. The observed stretches are for the more polar SO2 (sulfinato) group, not the S=O (sulfenato) group, which was not observed clearly. Use group theory techniques to identify the S=O stretches that are taking place in the SO2 group.

Insert figure 1 from the reference here; also include a figure of complex 2.

b)

Metal oxo stretches in the IR are strong, but buried in the fingerprint region around 800-1000 cm-1, making them difficult to observe. 18O labeling is often used to identify these buried peaks. An oxygen evolving complex model compound was studied, and the observed Mn-O-Mn stretch was observed at 707 cm-1 with a weaker feature at 510 cm-1 (*J. Am. Chem. Soc.*, **2002**, *124*, 11008–11017). Predict the isotopically labeled shifts for the corresponding 18O labeled complex.

**3. (improper?) extension of the model**

The three related compounds O=Mo(NR2)3, S=Mo(NR2)3, and Se=Mo(NR2)3 were all prepared by Professor Johnson as part of his Ph. D. dissertation. The Mo-E stretching vibrations were found in the far-IR using difference methods as explained above. The peaks found are as follows: MoO, 893 cm-1, MoS, 492 cm-1, MoSe, 342 cm-1.

Using this information, you can predict something about the bonding in the three compounds: does one of the three have an anomously strong (or weak) M=E bond such that neglecting the force constant is inappropriate?

a related LO “**IR spectroscopy of metal oxopentahalo complexes”**

another “**IR and Raman Spectroscopy of Cobalt Boronyl Tetracarbonyl, Co(BO)(CO)4”**