Week 4

Spectroscopy

4.1 IR Selection Rules and Stretching Mode Analysis

10/17:
- Fill out the Google Form to indicate topics we want Wuttig to cover during the review session.

- The most common experiments we do to determine normal modes are IR and Raman experiments.
    - Vibration modes can be IR and/or Raman active.
    - IR spectroscopy probes direct absorption of IR light to excite vibrational modes.
    - We will first determine the IR selection rules.

- IR selection rules:
    - We want $\Delta v = \pm 1$.
    - The transition moment integral is for transitions $v \to v'$; it is written as

    $$M_{vv'} = \int_{-\infty}^{\infty} \Psi^*(v')\mu\Psi(v)\,\mathrm{d}x$$

    where μ is the electric dipole moment and $[M_{vv'}]^2$ is the probability of the transition.

- If μ were a constant, then
    $$M_{vv'} = \mu \int_{-\infty}^{\infty} \Psi^*(v')\Psi(v)\,\mathrm{d}x = 0$$
    since $\Psi^*(v')$ and $\Psi^*(v)$ are orthogonal functions.
    - Therefore, μ cannot be a constant; it needs to be a function of x and needs to change during the vibration for the transition to be allowed.

- A more general form of $[M_{vv'}]^2$ is

    $$[M_{vv'}]^2 = \int_{\text{all space}} \Psi^*(v')\hat{\mu}\Psi(v)\mathrm{d}\tau$$

    - In order for the above integral to not evaluate to zero, the direct product of the excited state wave function, transition dipole moment, and ground state wave function must contain the totally symmetric IRR. Symbolically,

    $$\Gamma_{\text{IRR}}(\Psi(v')) \times \Gamma_{\text{IRR}}(\hat{\mu}) \times \Gamma_{\text{IRR}}(\Psi(v))$$

    decomposes into a sum of IRRs including A_1.

- Bottom line: A vibration will be IR active if it causes a change in the electric dipole moment of a molecule. A fundamental mode will be IR active if the normal mode which is excited belongs to the same representation as any one or several of the Cartesian coordinates.

- What modes are IR active for water?

  - Recall that the vibrational modes for H_2O are a_1 corresponding to ν_a, b_2 corresponding to ν_{as}, and a_1 corresponding to δ.

    ■ Looking at the character table, we notice that both a_1, b_2 transform as a linear function (z, y, respectively), so all modes are IR active.

    ■ More specifically, let's look at b_2. If b_2 transforms as a linear function, it *is* true that it is IR active. Here's why: If b_2 transforms as a linear function, then it will be a component of $\hat{\mu}$. In this case, when we take the direct product $\Gamma_{v'} \times \hat{\mu}$, one term we will evaluate is $b_2 \times b_2$. But by the second of the three important theorems, the direct product of any representation times itself will contain the totally symmetric irreducible representation, which is required for IR visibility as per the third of the three important theorems.

  - Show by direct product analysis that these IR modes are allowed.

    ■ The first transition (ν_a) goes from $a_1 \to a_1$ (the ground state is relaxed, hence a_1, and the excited state is Γ_{vibs} for ν_a, which is a_1). It follows that

    $$\Psi^*(v')\hat{\mu}\Psi(v) \sim {}^{[1]}a_1 \begin{pmatrix} a_1 \\ b_1 \\ b_2 \end{pmatrix} a_1 = \begin{pmatrix} a_1 \\ b_1 \\ b_2 \end{pmatrix}$$

    Since the result of our calculation contains the totally symmetric representation (in its first entry), we know that v_a is allowed.

    ■ The asymmetric stretch has ground a_1 and excited state b_2. $\hat{\mu}$ is the same as before.

    $$\Psi^*(v')\hat{\mu}\Psi(v) \sim b_2 \begin{pmatrix} a_1 \\ b_1 \\ b_2 \end{pmatrix} a_1 = \begin{pmatrix} b_2 \\ a_2 \\ a_1 \end{pmatrix}$$

    Since it still contains the all-symmetric wavefunction, it's allowed.
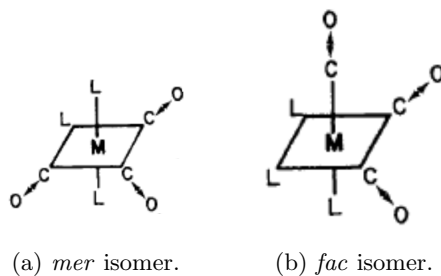
- Example:

(a) *mer* isomer. (b) *fac* isomer.

Figure 4.1: Isomers of an octahedral $ML_3(CO)_3$ complex.

1. Determine the number, symmetries, and IR activities of the carbonyl stretching modes for the two isomers of an octahedral $ML_3(CO)_3$ complex.

   - Since we are asked to determine the *carbonyl stretching* modes, we choose as our basis set the three vectors which run parallel to the CO bonds in both cases.

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[1] $\sim$ denotes "transforms as."

- The point group of the *mer* isomer is C_{2v}; the point group of the *fac* isomer is C_{3v}.
- With this information, the rest of the question is fairly straightforward.

2. The IR spectrum of the compound $Mo(CO)_3[P(OCH_3)_3]_3$ exhibits bands at 1993, 1919 and 1890 cm^{-1}. The IR spectrum of compound $Cr(CO)_3(CHCH_3)_3$ exhibits bands at 1942 and 1860 cm^{-1}. Based on your answer from part (1), how would you assign the *fac* vs. *mer* structure of these two complexes?

- From part (1), determine which structure gave rise to three nondegenerate stretching modes, and which gave rise to two.

- This example shows that we can determine the stretching modes for just some functional groups.

- Be careful with what the basis set is!

- Example: Structures for OsO_4N.

- This molecule has four reasonable structures, having symmetry C_{2v}, C_{3v}, C_{4v}, and C_s. It is a great example! Especially when paired with preceding molecules using some subset of these character tables.

4.2 Raman Selection Rules and Normal Mode Analysis

10/19:
- PSet 2 is due at the beginning of class on Friday.

- Raman and IR are complementary, and together they can distinguish geometric possibilities of an unknown molecule.

- **Raman spectroscopy**: A type of spectroscopy which probes inelastic scattering of light where the loss in energy corresponds to a vibrational frequency (**Stokes shift**).

- In Raman, you go to **virtual energy states**.

- **Virtual energy state**: The coupling of a photon with a high energy state.

- **Rayleigh scattering**: The amount of energy put in is the amount of energy you get out. *Also known as* **elastic scattering**.

- Doesn't give us a change, so we filter this out.

- **Stokes Raman scattering**: The photon out has less energy than the photon in; some energy was scattered.

- We excite from the ground state to a virtual energy state, and then fall back down but not all the way to the ground state, i.e., the electron remains in an excited state even after emitting its photon.

- **Anti-Stokes Raman scattering**: The photon out has more energy than the photon in; we start at a higher energy state and then fall back to ground.

- We excite from an excited state to a virtual energy state, and the fall back down all the way to the ground state.

- A vibrational mode will be Raman active if the polarizability of the molecule changes during the vibration. A fundamental transition will be Raman active (i.e., will give rise to a Raman shift) if the normal mode involved belongs to the same representation as one or more of the components of the polarizability tensor of the molecule.

- Transition probability in Raman:

$$M_w^2 = \left[\int_{-\infty}^{\infty} \Psi_{v'}^* \hat{\alpha} \Phi_v \mathrm{d}\tau \right]^2$$

- Polarizability describes the shape of the electron cloud and can be described by a tensor.

$$\begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

- The matrix above is the polarizability tensor, and the right vector above describes the electric field.
- Three α values are redundant: The matrix above is symmetric, so

$$\alpha_{xz} = \alpha_{zx} \qquad\qquad \alpha_{yz} = \alpha_{zy} \qquad\qquad \alpha_{yx} = \alpha_{xy}$$

- Thus, $\hat{\alpha}$ has six different components.
- If you do the math, you learn that the transition is allowed if the symmetric IRR is in the direct product and the normal mode is a quadratic function.

- Recall: Linear for IR, quadratic for Raman.

- Example: The nine modes of vibration, two pairs of which are degenerate, are derived below for XeF_4. Show that the b_{1g} fundamental transition is allowed for Raman but forbidden for infrared.

$$\Gamma_{\text{vibs}} = a_{1g} + b_{1g} + b_{2g} + a_{2g} + a_{2u} + b_{2u} + 2e_u$$

  - Checking the D_{4h} character table, we see that the two linear representations are a_{2u} and e_u. Thus,

$$\Psi_{v'}^* \hat{\mu} \Psi_v \sim b_{1g} \begin{pmatrix} a_{2u} \\ e_u \end{pmatrix} a_{1g} = \begin{pmatrix} b_{2u} \\ e_u \end{pmatrix}$$

  Thus, since a_{1g} doesn't appear, the IR transition is not allowed.

  - Checking the D_{4h} character table, we see that the four quadratic representations are a_{1g}, b_{1g}, b_{2g}, and e_g. Thus,

$$\Psi_{v'}^* \hat{\mu} \Psi_v \sim b_{1g} \begin{pmatrix} a_{1g} \\ b_{1g} \\ b_{2g} \\ e_g \end{pmatrix} a_{1g} = \begin{pmatrix} b_{1g} \\ a_{1g} \\ a_{2g} \\ e_g \end{pmatrix}$$

  Thus, since a_{1g} appears, the Raman transition is allowed.

- **Fundamental transition**: A transition starting from the ground state.

  - Ψ_v is always the totally symmetric IRR for a fundamental transition.
  - The wording "b_{1g} fundamental transition" in the previous example means "the transition form a_{1g} to b_{1g}."
  - Essentially, we're not dealing with overtones, not starting from an excited state, no coupling, nothing fancy.
  - We will briefly talk about overtones later.

- Example: Determine the symmetries and activities of the normal modes of vibration for the cyclopropenyl cation. Use all atoms ($N = 6$), i.e., use the Cartesion displacement method.

  - Point group: D_{3h}.
  - $\Gamma_{xyz} = (3, 0, -1, 1, -2, 1)$.
  - $\Gamma_{\text{unmoved}} = (6, 0, 2, 6, 0, 2)$.
  - $\Gamma_{3N} = (18, 0, -2, 6, 0, 2) = 2A_1' + 2A_2' + 4E' + 2A_2'' + 2E'$.
  - $\Gamma_{\text{vibs}} = 2A_1' + A_2' + 3E' + A_2'' + E''$.

- Operators:

$$\hat{\mu} = \begin{pmatrix} e' \\ a_2'' \end{pmatrix} \qquad\qquad \hat{\alpha} = \begin{pmatrix} a_1' \\ e' \\ e'' \end{pmatrix}$$

- a_1' is Raman active, e' is both, a_2'' is IR active, and e'' is both.

• You only need uppercase Mulliken symbols for character tables and Tanabe-Sugano diagrams.

• **Rule of mutual exclusion**: No normal modes can be both infrared and Raman active in a molecule that possesses a center of symmetry.

• Question: Spectrum analysis. What symmetry element must be present?

- Observation: Lack of coincidental IR and Raman peaks in the spectra of benzene.
- Thus, no linear bases or quadratic bases overlap. The linear must all be -1 and the quadratic must all be 1.
- Thus, an inversion i is present.