

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 $v \rightarrow v'$; it is written as

$$M_{vv'} = \int_{-\infty}^{\infty} \Psi^*(v') \mu \Psi(v) dx$$

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

- If μ were a constant, then

$$M_{vv'} = \mu \int_{-\infty}^{\infty} \Psi^*(v') \Psi(v) dx = 0$$

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

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

- 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 H₂O 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 $a_1 \rightarrow a_1$ (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 ν_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:

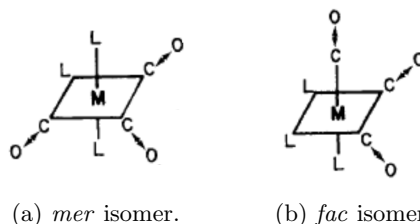


Figure 4.1: Isomers of an octahedral $\text{ML}_3(\text{CO})_3$ complex.

1. Determine the number, symmetries, and IR activities of the carbonyl stretching modes for the two isomers of an octahedral $\text{ML}_3(\text{CO})_3$ 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.
 - 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.

¹ \sim denotes “transforms as.”

2. The IR spectrum of the compound $\text{Mo}(\text{CO})_3[\text{P}(\text{OCH}_3)_3]_3$ exhibits bands at 1993, 1919 and 1890 cm^{-1} . The IR spectrum of compound $\text{Cr}(\text{CO})_3(\text{CHCH}_3)_3$ 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 then 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:

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

- 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

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

- 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 from 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 Cartesian 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:

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

- 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.

4.3 Special Spectroscopic Bands

10/21:

- Calculators that aren't connected to the internet are permitted. Arrive by 9:25. Think of it as a quiz more than an exam — there's only so much you can do in 50 minutes.
- **Polarization:** When electric fields are restricted to a specific direction by filtration.
- Recall H_2O and its vibrational modes ν_1, ν_2, ν_3 , which are symmetric stretch, bending, and asymmetric stretch, respectively. Consider the *hypothetical* case where we can “hold” water molecules such that they are oriented on the Cartesian plane.

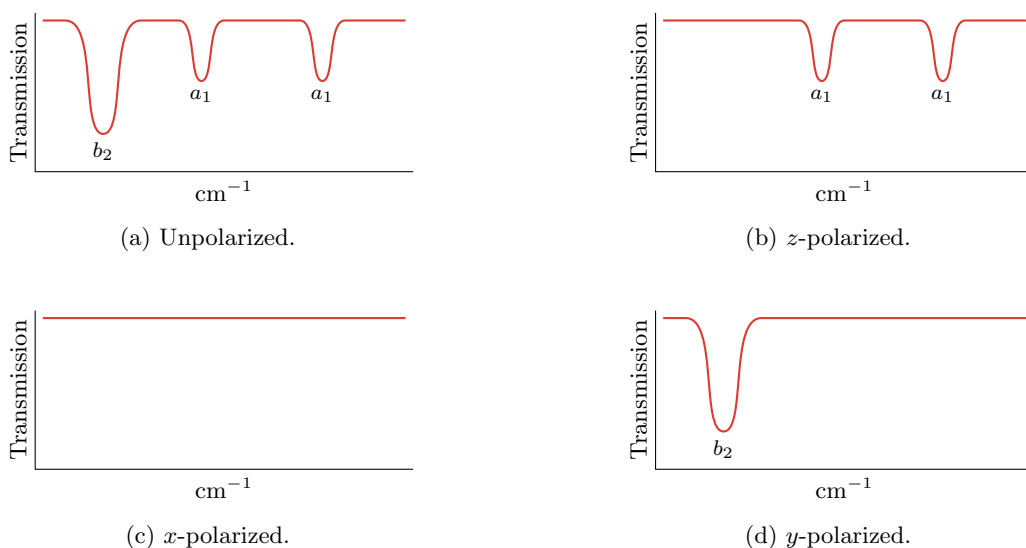


Figure 4.2: Polarized IR spectra of H_2O .

- The unpolarized IR spectrum would be the result of what we predicted last time.
- The z -polarized spectrum: ν_1, ν_2 are a_1 and hence transform with the same symmetry as z . You filter out the b_2 for a z -polarized spectrum.

- y -polarized gives you just b_2 .
- x -polarized gives you nothing.
- Linear functions give you the right answer, but you can also rationalize from the vectors.
 - For example, drawing out the vectors for ν_1 in H_2O , you see that the major dipole moment is in the z -direction. Same for ν_2 . However, for ν_3 , the major dipole moment is in the y -direction.
 - What we're polarizing here is the incoming IR radiation. If all molecules were held with the correct orientation and then we shot z -polarized light at them, only vibrations in the z direction would get excited (x, y are equally and oppositely cancelled).
- Polarization is most commonly used in Raman spectroscopy.
- Experimental setup.

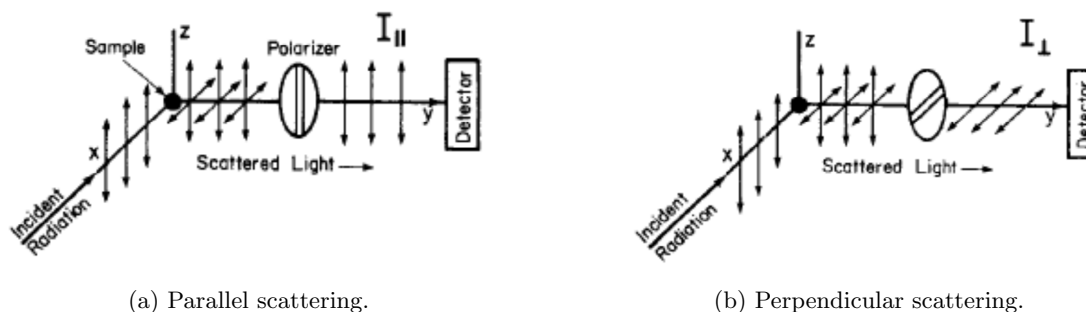


Figure 4.3: Raman polarization setup.

- We place the sample solution at the origin of our coordinate system, shoot xz -polarized light down one axis, and measure the polarization of the emitted radiation down a perpendicular axis.
- From this setup, we can determine the extent to which the molecules that absorb plane-polarized light emit light in the same plane or in a perpendicular plane.
- **Depolarization ratio:** The following quantity, where I_{\perp} is the intensity of the scattered light polarized in the plane perpendicular to the incident light and I_{\parallel} is the intensity of the scattered light in the same plane as the incident light. Denoted by ρ . Given by

$$\rho = \frac{I_{\perp}}{I_{\parallel}}$$
- Depolarized (unpolarized) bands will exhibit $\rho \approx 3/4$. In contrast, polarized bands will exhibit ρ values between 0 and $3/4$.
 - Polarized bands appear from vibrations that are totally symmetric.
 - The more highly symmetric the molecule, the closer ρ is to zero (polarization is high).
- Example: For each IR transition of the cyclopropenyl cation, determine the direction of the adsorption. Determine which Raman active fundamentals of the compound are polarized or depolarized.
 - IR: The polarization of the e' adsorption is (x, y) and the direction of polarization of a_2'' is z .
 - What does the degenerate polarization of e' mean?? Does it mean that either x - or y -polarized light will excite this transition?
 - Raman: a_1' is your most polarized Raman active mode. e' and e'' are polarized but not as much.
- Most IR spectra show more bands than we predict for fundamentals. These are **overtones**, **combination bands**, and **hot bands**.

- **Overtone:** A band that occurs when a mode is excited beyond $v = 1$ by a single photon. *picture*
 - Example: If our three normal modes are $\Psi_1(0)\Psi_2(0)\Psi_3(0)$ and we excite one of them such that it goes to a third state $\Psi_1(0)\Psi_2(3)\Psi_3(0)$. This is the **second overtone** of the normal mode ν_2 . We are taking $v = 0$ to $v = 3$ here.
 - The energy of this transition would be approximately 3 times the fundamental $v_0 \rightarrow v_1$.
- **Combination band:** A band that occurs when more than one vibration is excited by one photon. *Also known as combo band.*
 - Example:

$$\Psi_1(0)\Psi_2(0)\Psi_3(0) \rightarrow \Psi_1(1)\Psi_2(1)\Psi_3(0)$$
 - Example:

$$\Psi_1(0)\Psi_2(0)\Psi_3(0) \rightarrow \Psi_1(2)\Psi_2(0)\Psi_3(1)$$
 - I.e., you can throw in overtones, too.
 - What this means for the energy: Energy of the combination band transition is the sum of the energies of the individual transitions.
 - Energy for example 1: $v_1 + v_2$.
 - Energy for example 2: $2v_1 + v_3$.
- **Hot band:** A band that occurs when an already excited vibration is further excited.
 - Example:

$$\Psi_1(0)\Psi_2(1)\Psi_3(0) \rightarrow \Psi_1(0)\Psi_2(2)\Psi_3(0)$$
 - The probability of this event depends on the temperature because it relies on the thermal population of an already excited state.
 - The population increases as a function of temperature.
 - Thermal population of the initial state is low, but it increases with temperature and hence is called a *hot* band.
- The selection rules for predicting whether an overtone, combo band, or hot band is possible use the same direct product math.
 - We won't cover this in depth, though.
- **Fermi resonance:** The mixing of two states, which can have two effects:
 1. The overtone can gain intensity from the nearby fundamental of the same symmetry.
 2. Both energy levels are shifted away from each other.
- Predicting when Fermi resonance occurs is hard; it is done only after ruling out the possibility of an overtone, combo band, or hot band as accounting for your data.
- Example: CO_2 .
 - Since there are four normal modes, you might predict four IR bands.
 - The δ_d bending modes have $E = 667\text{ cm}^{-1}$. You'd predict their first overtone to have $E = 1334\text{ cm}^{-1}$. However, this mode has a similar symmetry to the symmetric stretch ν_s at $E = 1337\text{ cm}^{-1}$. Thus, they will mix via Fermi resonance, producing two really strong bands at 1388 cm^{-1} and 1286 cm^{-1} .
 - According to Wuttig, it is purely a coincidence that energies in this example are similar; states don't only mix when their energies are similar.