CHEM 30100 (Advanced Inorganic Chemistry I) Notes

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Weeks

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Week 1

A Rigorous Definition of Symmetry

1.1 Symmetry: Symmetry Elements and Operations

9/28:
- Dr. Anna Wuttig (AH-nuh WUH-tig).
  - Teaches exclusively on the blackboard.
  - Will record lectures, however; if there is a technical error, she will upload last year's lecture.
- Syllabus.
  - PSets graded on completion, not accuracy.
  - Two exams: One on the first half of the course; one on the second half of the course.
    - Cumulativeness: You'll need to understand the first half to do the second half, but there won't be questions specifically targeted to first-half material.
  - No final.
  - Participation. Showing up to class and working in groups.
- Chris, Dan, Amy, Matt, Jintong, Yibin, Ben, Sara, Ryan, Joe, Owen, Isabella, Pierce are the people.
  - People come from a diversity of chemistry subfields (physical, inorganic, organic, materials, biological).
- Every day will have a handout that we will write on (in pencil).
- Study the learning objectives!
- (Local) symmetry of a molecule helps us predict and describe bonding, spectroscopic properties, and reactivity.
  - We describe symmetry with group theory.
- **Symmetry operation**: An operation which moves a molecule into a new orientation equivalent to its original one (geometrically indistinguishable).
  - Symmetry operations that can be applied to an object always form a **group**.
- **Symmetry element**: A point, line, or plane about which a symmetry operation is applied.
- Symmetry operations.
  1. Identity operation (E): Do nothing; null operation.
  2. Reflection through a plane (σ): Subdivided into...

  - σ_d: dihedral mirror planes, which contain the principle C_n axis and bisect the angles formed between adjacent C_2 axes;
  - σ_h: horizontal mirror planes, in which the mirror plane is perpendicular to the principal C_n axis;
  - σ_v: vertical mirror planes, which contain the C_n axis and are not dihedral mirror planes.

3. Rotation about an axis (C_n): A clockwise[1] rotation about the C_n axis.
4. Improper rotation (S_n): A two-step symmetry operation consisting of a C_n followed by a σ that is perpendicular to C_n (i.e., σ_h).
5. Inversion (i): Take any point with coordinates (x, y, z) to $(-x, -y, -z)$.

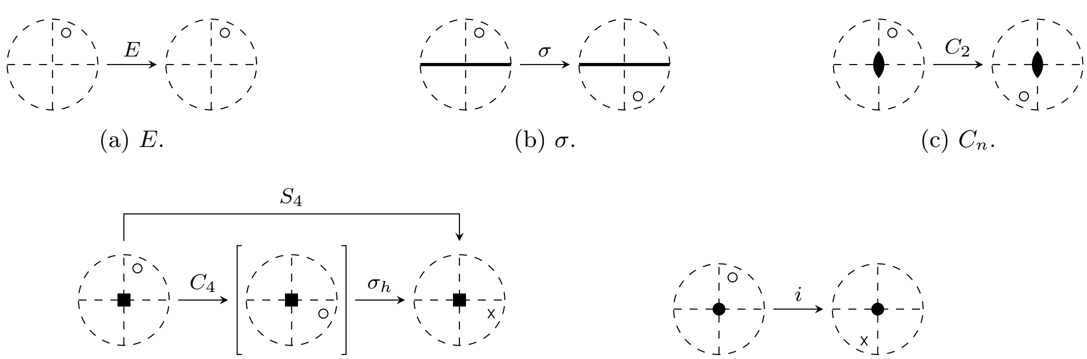
- To describe the operations, we'll introduce **stereographic projections**.

(a) Rotations. (b) Improper rotations.

Table 1.1: Symbols for stereographic projections.

  - We have a working area (the plane of the page is the xy-plane). It is useful to draw quadrants.
  - We describe a general point which experiences our symmetry operation.
    - When the point reflects through the working area, we denote the image with an "X" instead of a circle.
  - We need a gear symbol in the middle for rotations and improper rotations (see Table 1.1).
    - Must stereographic projections be drawn one at a time because it seems that the squares should not be in a reflection?
    - No — the symbols are to help us and should be included somewhere, but there are no hard-and-fast rules.

- Stereographic projections for each of the five elementary symmetry operations.



(a) E. (b) σ. (c) C_n.

(d) S_n. (e) i.

Figure 1.1: Stereographic projections of the elementary symmetry operations.

- Principal C_n axis: The C_n axis for which n is the highest.
  - In a stereographic projection, the C_n axis is the one that is perpendicular to the working area (goes in/out of the page).

[1]Really?

- Example: Give the symmetry elements of NH_3.
  - C_3 axis, 3 σ_v mirror planes (denoted σ_v, σ_v', and σ_v'').
  - The symmetry operations are E, C_3, C_3^2, σ_v, σ_v', and σ_v''. These operations form the C_{3v} point group.
- Direct products of symmetry operations: $YX = Z$ means "operation X is carried out first and then operation Y," giving the same net effect as would the carrying out of the single operation Z.
  - If $YX = XY = Z$, then the two operations Y and X commute.
- What is the direct product of C_2 and σ_h?
  - $\sigma_h C_2 = S_2 = i$. They do commute.
- Do C_4 and $\sigma_{x,z}$ commute? Take the plane of this page as xy.
  - They do not (determine by drawing out both sets of stereographic projections).
- Don't get careless, Steven. This is easy, but it's also easy to make easy mistakes.
- New symmetry operations *of your group* are generated by taking the direct product of two.

1.2 Point Groups

9/30:

- The symmetry operations that apply to a given molecule collectively possess the properties of a mathematical **group**.
- **Group**: A set of symmetry operations that satisfy the following conditions.
  - *Closure*: All binary products must be in the group, i.e., the product of any two operators must also be a member of the group.
  - *Identity*: Must contain an identity, i.e., E must be part of the group.
  - *Inverse*: All elements must have an inverse in the group, and they must commute with their inverse.
  - *Associativity*: The associative law $(A \cdot B) \cdot C = A \cdot (B \cdot C)$ must hold.
- **Abelian** (group): A group in which all direct products commute.
  - Not all groups are Abelian.
- Question: Do C_3 and σ_v form a group?
  - No: No identity (for example).
  - Wuttig draws out a stereographic projection for $C_3 \cdot \sigma_v$ and overlays the first and last picture, showing that $C_3 \cdot \sigma_v$ is a reflection over a new mirror plane σ_v'.
  - C_3 and σ_v do **generate** the set of operations $E, C_3, C_3^2, \sigma_v, \sigma_v', \sigma_v''$, which collectively form the **point group $\boldsymbol{C_{3v}}$**.
- To prove something on a pset or exam, it's probably a good idea to do it in terms of stereographic projections!
- **Point group**: A group such that at least one point in space is invariant to all operations in the group.
- **Group order**: The number of symmetry operations in the group. *Given by* $\boldsymbol{h}$.
- Table activity: Finding E, principal C_n, σ, $C_2 \perp C_n$, C_n position relative to σ (collinear or perpendicular), and i for various point groups.

  - These properties are the ones that distinguish each point group from every other point group.

- Notes on the pedagogy: Animations and/or tangible models should be used to discuss this stuff. PowerPoint slides are definitely the way to go — far more tangible tools; blackboard should be a supplement. It is key to be careful what you say (*element* and *operation* must be consistently used). Dr. Wuttig is skipping a lot of key points (like naming point groups).

- Developing a flow chart that distinguishes between D_{nh}, D_{nd}, D_n, C_{nh}, C_{nv}, C_n, and S_n.

Week 2

Introduction to Representation Theory

2.1 Matrix Representations of Symmetry Operations

10/3:
- Tools for identifying symmetry elements.
  - Chem 3D (visualization).
  - Otterbein University symmetry gallery (examples of molecules that satisfy all of the point groups).
- Gives examples of molecules that satisfy the high-symmetry point groups.
  - $C_{\infty v}$: CO.
  - $D_{\infty h}$: CO_2.
  - T_d: CH_4.
  - T_h: $[Co(NO_2)_6]^{3+}$.
    - T_h is T_d with σ_h symmetry.
  - O_h: $[Co(NH_3)_6]^{3+}$
  - I_h: N/a.
    - 120 symmetry elements in total; we will not be asked to identify all of these!
  - K_h: N/a.
    - Symmetry of the sphere.
  - T, O, I are subgroups of T_h, O_h, I_h, respectively, and only have proper (not improper) rotations. These are very rare point groups. An example of a molecule in the T point group is $[Ca(THF)_6]^{2+}$.
- Learn T, O, I from Otterbein University example and ask questions!
- Low symmetry: C_1, C_i, C_s.
- The mirror plane in a C_s molecule is denoted by σ (no subscript).
- **Vector**: A series of numbers which we write in a row or a column.
- **Matrix**: Any rectangular array of numbers set between two brackets.
- Basics of matrix multiplication: $A \cdot \vec{x} = \vec{y}$ given in terms of matrix multiplication, e.g., if A is $n \times m$ and $\vec{x} \in \mathbb{R}^m$, then

$$y_i = \sum_{j=1}^{m} a_{ij} x_j$$

  for $i = 1, \dots, n$.

- Matrix representations:
  - E: What matrix A satisfies $A \cdot \vec{x} = \vec{x}$ for all $\vec{x}$? The 3×3 matrix I does.
  - i: What matrix A satisfies $A \cdot \vec{x} = -\vec{x}$ for all $\vec{x}$? The 3×3 matrix $-I$ does.
  - σ_{xy}: What matrix A flips the sign of the z-coordinate of $\vec{x}$? The 3×3 matrix $\text{diag}(1, 1, -1)$ does.
  - C_2: What matrix A flips the sign of the x, y-coordinates of $\vec{x}$? The 3×3 matrix $\text{diag}(-1, -1, 1)$ does.
  - C_3: Consider a C_{3v} molecule.

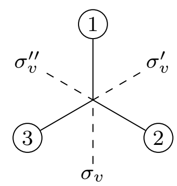


Figure 2.1: C_3 matrix representation setup.

Instead of describing a rotation in $\mathbb{R}^3$ using radians, we can think of a rotation as a permutation of the numbered atoms. So in this example,

$$\underbrace{\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}}_{C_3} \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} = \begin{bmatrix} 2 \\ 3 \\ 1 \end{bmatrix}$$

- We will only be asked for matrix representations of very simple things, e.g., these or 90° or 180° turns.
- The above matrices form a mathematical group, which obeys the same multiplication table as the operations.
  - For example,

$$\underbrace{\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{C_2} \underbrace{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}}_{\sigma_h} = \underbrace{\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}}_{i}$$

- The matrix representations given above are not the "simplest" way of describing these symmetry operations.
  - The simplest way is using the **character**.
  - We find the character using a **similarity transformation** to take our matrix representations to block-diagonalized forms and then compute the characters of the blocks from there.
  - Recall that analogous blocks multiply in a block-diagonal matrix.
- **Character** (of a symmetry operation): The trace (sum of the diagonal elements) of the matrix representation of that operation. *Denoted by* $\boldsymbol{\chi}$.
- **Similarity transformation** (matrix): The matrix which, when conjugated with a matrix representation of a symmetry operation, yields the block-diagonalized form of that matrix. *Denoted by* $\boldsymbol{R}$.
  - We don't need to know how to compute these.

- Similarity transformation example: The C_3 matrix representation given above is not block diagonal, but there exists a matrix R (that we don't have to know how to find) such that

$$RC_3R^{-1} = \left[\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{array}\right]$$

  - The characters of the blocks of the above matrix are 1 and -1, respectively. The character of the overall matrix is still 0.

2.2 Characters and Irreducible Representations

10/5:

- The PSet has been posted — remember that its graded for completion.
  - Answer key will be posted the day it's due.
  - Submit via email or give her a printed copy/write it out on blank paper (preferred).
- Review: NH_3 is in the C_{3v} point group.
- Denote the bond vectors of NH_3 by d_1, d_2, d_3. Let's use them as a basis of the representation Γ. Also label the hydrogen atoms 1-3.

Symmetry element	**Matrix**	**Character**
E	$\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}\begin{bmatrix}H_1\\H_2\\H_3\end{bmatrix}=\begin{bmatrix}H_1\\H_2\\H_3\end{bmatrix}$	3
C_3	$\begin{bmatrix}0&1&0\\0&0&1\\1&0&0\end{bmatrix}\begin{bmatrix}H_1\\H_2\\H_3\end{bmatrix}=\begin{bmatrix}H_2\\H_3\\H_1\end{bmatrix}$	0
${C_3}^2$	$\begin{bmatrix}0&0&1\\1&0&0\\0&1&0\end{bmatrix}\begin{bmatrix}H_1\\H_2\\H_3\end{bmatrix}=\begin{bmatrix}H_3\\H_1\\H_2\end{bmatrix}$	0
σ_v (along d_1)	$\begin{bmatrix}1&0&0\\0&0&1\\0&1&0\end{bmatrix}\begin{bmatrix}H_1\\H_2\\H_3\end{bmatrix}=\begin{bmatrix}H_1\\H_3\\H_2\end{bmatrix}$	1
σ_v' (along d_2)	$\begin{bmatrix}0&0&1\\0&1&0\\1&0&0\end{bmatrix}\begin{bmatrix}H_1\\H_2\\H_3\end{bmatrix}=\begin{bmatrix}H_3\\H_2\\H_1\end{bmatrix}$	1
σ_v (along d_1)	$\begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix}\begin{bmatrix}H_1\\H_2\\H_3\end{bmatrix}=\begin{bmatrix}H_2\\H_1\\H_3\end{bmatrix}$	1

Table 2.1: NH_3 symmetry operations, matrices, and characters.

  - Draw out each symmetry operation, its effect on each H atom, and the matrix representation of each. What is the character for each matrix representation? See the above table.
  - The characters for each matrix divide the symmetry operations into three classes (the identity, rotation, and reflection classes).

- If we use the Cartesian axes as our basis, we get the following transformation matrices.

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad C_3 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad {C_3}^2 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_a = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \sigma_b = \begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \sigma_c = \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

  - All of these are block-diagonal, so there must be some similarity transformation that gets us from the matrices in Table 2.1 to these matrices.
  - Notice that the character is preserved under similarity transformation.
- The matrix representations in $\vec{e}$ have blocks, which we can call the 2D block and the 1D block.
- Building a character table with different representations.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_e	3	0	1
Γ_{2D}	2	-1	0
Γ_{1D}	1	1	1

Table 2.2: Some representations of C_{3v}.

  - Γ_e is the representation corresponding to the full 3×3 matrices.
  - Γ_{2D} is the representation corresponding to the 2D blocks.
  - Γ_{1D} is the representation corresponding to the 1D blocks.
  - The latter two are called the irreducible representations; the first one is called a reducible representations. In fact,
$$\Gamma_e = \Gamma_{2D} + \Gamma_{1D}$$
- Every point group has a specific number of irreducible representations (IRRs); are Γ_{2D}, Γ_{1D} it?
  - No — we will use the rules to find the others.
- IRRs have 4 rules.
  1. The number of IRRs: The number of non-equivalent IRRs is equal to the number of classes in the group.
  2. Dimensionality of IRRs: The sum of the squares of the dimensions ℓ of IRRs in a class is equal to the order of the group.
$$\sum_i \ell_i^2 = \sum \chi_i^2(\text{class}) = h$$
  3. Characters of IRRs: The sum of the squares of the characters under any IRR equals the order of the group.
$$\sum_R g(R)\chi_i^2(R) = h$$
  4. Orthogonality rule: The sum of the products of characters under any two irreducible representations is equal to zero.
$$\sum_R g(R)\chi_i(R)\chi_j(R) = 0$$

- Examples of the rules in C_{3v}.
  - Rule 1: C_{3v} has three classes, so it must have there must be one more IRR than listed in Table 2.2.
  - Rule 2: We must have that
$$1^2 + 2^2 + \ell_3^2 = 6$$
  - Rule 3: For Γ_{2D}, for example,
$$(1)(2)^2 + 2(-1)^2 + 3(0)^2 = 6$$
  - Rule 4: With Γ_{1D}, Γ_{2D}, for example,
$$(1)(1)(2) + (2)(1)(-1) + (3)(1)(0) = 0$$
- Finding the last representation of C_{3v}.
  - General procedure: Apply rule 1, then 2, then 4. Check with 3.
  - For example, we can find that the last $\Gamma = (1, 1, -1)$.

2.3 Character Tables and Mulliken Symbols

10/7: • The algebraic rules discussed last lecture are sufficient to derive a character table. They are summarized in the following procedure.
  1. Determine the number of classes in order to find the number of irreducible representations.
  2. All groups have a totally symmetric irreducible representation.
  3. Determine the dimensionality of the irreducible representations.
  4. Apply the orthogonality rule.
  5. Verify using the sum of square of characters rule.
- Example: Deriving the C_{3v} character table using the above strategy.

C_{3v}	E	$2C_3$	$3\sigma_v$	linear	quadratic
A_1	1	1	1	z	z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

Table 2.3: C_{3v} character table.

  - There are three classes; hence, we will have $\Gamma_1, \Gamma_2, \Gamma_3$.
    - See below for an explanation of their labels.
  - Let $\Gamma_1 = (1, 1, 1)$ be the totally symmetric irreducible representation.
  - If we want the sum of the squares of the dimensionalities to be natural numbers which add to $h = 6$, then we must choose $\ell_2 = 1$ and $\ell_3 = 2$.
  - Applying the orthogonality rule, we can find the remaining four values in the table (those in the lower-right block) by inspection.
  - We may, indeed, confirm using the sum of the squares rule.
  - Also see below for an explanation of the Cartesian coordinates on the right-hand side.
- It will be beneficial to have a standard method for naming our irreducible representations.

- **Mulliken symbol**: The designation of an irreducible representation assigned according to the following procedure. *Given by*
  1. All 1D representations are A or B. 2D is E. 3D is T.
  2. Distinguishing A and B.
     (a) $\chi(C_n) = +1 \implies A$.
     (b) $\chi(C_n) = -1 \implies B$.
  3. Numerical subscripts: For groups that contain a secondary C_2 axis (or in its absence, σ_v).
     (a) $\chi(C_2 \text{ or } \sigma_v) = +1 \implies$ Subscript 1.
     (b) $\chi(C_2 \text{ or } \sigma_v) = -1 \implies$ Subscript 2.
  4. Alphabetical subscripts: For groups that contain i.
     (a) $\chi(i) = +1 \implies$ Subscript g.
     (b) $\chi(i) = -1 \implies$ Subscript u.
  5. Prime subscripts: For groups that contain σ_h.
     (a) $\chi(\sigma_h) = +1 \implies$ Superscript $'$.
     (b) $\chi(\sigma_h) = -1 \implies$ Superscript $''$.
- **Symmetric** (IRR wrt. a symmetry operation): An IRR for which the character of the symmetry operation in question is $+1$.
- **Unsymmetric** (IRR wrt. a symmetry operation): An IRR for which the character of the symmetry operation in question is -1. *Also known as* **antisymmetric**.
- Based on the above rules, we can conclude that for C_{3v}, $\Gamma_1 = A_1$, $\Gamma_2 = A_2$, and $\Gamma_3 = E$.
- The last two elements we need to construct the C_{3v} character table are the Cartesian coordinates. These are easy to derive for z-axis elements and groups that contain x- and y-axis rotations (e.g., C_2, C_4). If n is odd, these latter ones will be given to you.
  - There are two types of linear bases to consider: x, y, z and R_x, R_y, R_z. The former corresponds to p orbitals. The latter corresponds to rotations about one of the Cartesian axes.
  - There is one type of quadratic base to consider: $z^2, x^2 - y^2, xy, xz, yz$. These correspond to d orbitals.
  - Wuttig draws out the effect of each symmetry operation in C_{3v} on p_z, d_{z^2}, and R_z. She concludes for the first two that they are totally symmetric with respect to the operations; hence, they are A_1. She also concludes with respect to the last one that it is symmetric to the identity and to rotation, but unsymmetric to reflection about the z-axis; hence, it is A_2.
  - The others are filled in toward us.
- Summary: Anatomy of a character table.
  1. Point group.
  2. Irreducible representations, as denoted by Mulliken symbols.
  3. Classes of symmetry operations.
  4. Characters of irreducible representations.
  5. Linear basis: Axes and rotations (basis functions for the irreducible representations).
     (a) p orbitals: Denoted as z, x, y.
     (b) Rotations around z, x, y: Denoted as R_z, R_x, R_y.
  6. Quadratic basis (basis functions for the irreducible representations).
     (a) d orbitals: Denoted as $z^2, x^2 - y^2, xy, xz, yz$.

- Example: Filling in the C_{2v} character table.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	linear	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Table 2.4: C_{2v} character table.

  - Special case where the two σ have different characters: With respect to determining which of the bottom two representations is B_1 and which is B_2, we must pick a σ_v to use as a reference and stick with it.

Week 3

Applications of Representation Theory

3.1 Reducible Representations and Direct Products

10/10:

- PSet is due at the beginning of next class. Email or submit in paper. Show your work!
- Since molecules have more than one point, we need to work with the characters of reducible representations. In particular, when applying group theory to chemical problems, we need to find the IRRs whose sum is the reducible representation.
- **Reduction formula**: The formula which takes a Γ_{red} and decomposes it into a sum of Γ_{IRR}s. *Given by*

$$n(\Gamma_A) = \frac{1}{h}\sum_i g(R)\chi_{\text{IRR}}(R)\chi_{\text{RR}}(R)$$

  - $n(\Gamma_A)$ is the number of times the IRR A occurs in Γ_{red}.
  - h is the order of the group.
  - $g(R)$ is the order of the class under the symmetry operation R.
  - $\chi_{\text{IRR}}(R)$ is the character of the IRR under the symmetry operation R.
  - $\chi_{\text{RR}}(R)$ is the character of the reducible representation under the symmetry operation R.
- Recall $\Gamma_{\text{red}} = (3, 0, 1)$ in C_{3v} from Lecture 2.2.
  - The number of times each IRR appears is, according to the reduction formula:

$$\begin{aligned}
n(A_1) &= \frac{1}{6}(1\cdot 1\cdot 3 + 2\cdot 1\cdot 0 + 3\cdot 1\cdot 1) = 1\\
n(A_2) &= \frac{1}{6}(1\cdot 1\cdot 3 + 2\cdot 1\cdot 0 + 3\cdot -1\cdot 1) = 0\\
n(E) &= \frac{1}{6}(1\cdot 2\cdot 3 + 2\cdot -1\cdot 0 + 3\cdot 0\cdot 1) = 1
\end{aligned}$$

- Simple cases (like this and the next one) we can often do by inspection.
- Example: $\Gamma_{\text{RR}} = (6, 0, 0)$.
  - Decompose it into $A_1 + A_2 + 2E$.
- **Direct product** (of two representations): The (reducible or irreducible) representation obtained by multiplying the characters of the two representations which correspond under each operation. *Denoted by* $\boldsymbol{M} \times \boldsymbol{N}$, where M, N are Mulliken symbols.

- Examples:
  - $A_1 \times E = E$.
  - $A_2 \times E = E$.
  - $E \times E = A_1 + A_2 + E$.
  - $A_2 \times A_2 = A_1$.
- We now dive into how to use the symmetry properties of a collection of orbitals to determine the states that arise by populating them with electrons. To do this for a given basis set of valence atomic orbitals, we need to ask what set of IRRs they fall into.
- Procedure.
  1. Generate the characters of this representation by examining the trace of the relevant transform matricies.
     - $+1$ on the diagonal if a particular basis function is left unchanged during the symmetry operation.
     - 0 on the diagonal if the basis function is transformed to another function.
     - -1 on the diagonal if the function is converted into minus itself.
     - Indeed, only basis set elements that do not move contribute to the trace (i.e., character) of the representation.
  2. Check that the dimension is greater than the largest dimension permissible in the point group. If so, we need to reduce to IRRs. This is an important step to construct SALCs.
- Example: Consider the set of H_{1s} orbitals of NH_3 as the representation.
  - $\Gamma_{3H_{1s}} = (3, 0, 1)$ since all 3 orbitals stay under E, all orbitals move under $2C_3$, and 1 orbital stays under $3\sigma_v$.
  - Decompose into $A_1 + E$.
  - Therefore, the $1s$ orbital of H within C_{3v} of NH_3 transforms in $a_1 + e$ symmetry.
  - Note that we use lowercase Mulliken symbols for atomic/molecular orbitals and vibrational modes and uppercase Mulliken symbols for electronic states.
  - This $a_1 + e$ symmetry for the H_{1s} group orbitals implies that there are 3 SALC orbitals: 1 of a_1 symmetry and 2 of e symmetry.
- Example: H_2O.
  - $\Gamma = (2, 0, 0, 2) = A_1 + B_2$.

3.2 Projection Operations and SALCs

10/12:

- PSet 2 is posted and due 10/21.
  - Go over questions on the HW in the review classes prior to exams.
- **Symmetry-Adapted Linear Combination**: An orthonormal linear combination of one or more sets of orthonormal functions (which are either atomic orbitals or internal coordinates of a molecule) taken in such a way that the combinations form bases for irreducible representations of the symmetry group of the molecule. *Also known as* **SALC**.
- Last time, we investigated the SALCs of NH_3. We found them by decomposing a reducible representation of the H_{1s} basis set to its irreducible representations and naming them via the character table.

- Goal: What do the SALCs of NH_3 look like?
  - We know that we need 3 SALCs, 1 of a_1 symmetry and 2 of e symmetry.
  - To achieve the goal, we apply the **projection operator** to each irreducible representation.
- **Projection operator** (on an IRR): The operator defined as follows, which acts on IRRs. *Denoted by* $\hat{\boldsymbol{P}}$. *Given by*

$$\hat{P}(\Gamma_i) = \frac{\ell_i}{h} \sum_R \chi_i(R)\hat{R}$$

  - ℓ_i is the dimension(ality) of the IRR.
  - Γ_i is the IRR.
  - $\hat{R}$ is the symmetry operation to be applied to the basis.
  - $\chi_i(R)$ is the character of the given symmetry operation for Γ_i.
  - In other words, we need to evaluate what happens to the H_{1s} orbitals under each symmetry operation.
- It follows that we need the character table to evaluate what happens to the H_{1s} orbitals for each symmetry operation.
  - Note that for the projection operator, we do *not* do this by class (i.e., we do need to apply *every single* symmetry operation)[1].
  - Focus on one orbital in particular, and see to which orbital each symmetry operation takes it.
- NH_3 example.
  - We have

$$E : x_1 \mapsto x_1 \quad C_3 : x_1 \mapsto x_2 \quad {C_3}^2 : x_1 \mapsto x_3 \quad \sigma_v : x_1 \mapsto x_1 \quad \sigma_v' : x_1 \mapsto x_3 \quad \sigma_v'' : x_1 \mapsto x_2$$

  - We can do the same for where x_2, x_3 go.
  - It follows that

$$\hat{P}(A_1)_{x_1} = 1x_1 + 1x_2 + 1x_3 + 1x_1 + 1x_3 + 1x_2 = 2(x_1 + x_2 + x_3) \approx x_1 + x_2 + x_3$$

    - This implies that under the totally symmetric representation, all orbitals are the same, as we might expect. Note that the constant factor of 2 does not affect the functional form and therefore does not affect the symmetry properties.
    - We don't carry through ℓ_i/h because it's a constant??
    - Note that

$$\hat{P}(A_1)_{x_2} = \hat{P}(A_1)_{x_3} = \hat{P}(A_1)_{x_1}$$

  - As another example,

$$\hat{P}(E)_{x_1} = 2x_1 - x_2 - x_3 + 0x_1 + 0x_3 + 0x_2 = 2x_1 - x_2 - x_3$$

  - Similarly,

$$\hat{P}(E)_{x_2} = 2x_2 - x_3 - x_1$$
$$\hat{P}(E)_{x_3} = 2x_3 - x_1 - x_2$$

  - Note that all of these functions must be orthonormal.
    - We have three functions, but we only need 2 in e! Thus, we employ the orthonormal rule to figure it out.

[1]Notice that the order of the class is not present in the projection operator!

- We have that the first and second, and first and third are not orthogonal:

$$(\Psi_{E,x_1},\Psi_{E,x_2}) = (2)(-1)+(2)(-1)+(-1)(-1) = 3 \neq 0$$
$$(\Psi_{E,x_1},\Psi_{E,x_3}) = (2)(-1)+(-1)(-1)+(-1)(2) = 3 \neq 0$$

- What we can do is take a linear combination of 2 and 3 so that it's orthogonal to 1.
- Let's try

$$\Psi_{E,\text{new}} = \Psi_{E,x_2} - \Psi_{E,x_3} = 3x_2 - 3x_3 \approx x_2 - x_3$$

- Indeed,

$$(\Psi_{E,x_1},\Psi_{E,\text{new}}) = (2)(0)+(-1)(1)+(-1)(-1) = 0$$

as desired.
- Note that adding does not get us something orthogonal.

– Normalize the SALCs.
- At this point, we have that

$$\Psi_{A_1\text{ SALC}} = x_1+x_2+x_3 \qquad \Psi_{E\text{ SALC}} = 2x_1-x_2-x_3 \qquad \Psi_{E\text{ SALC}} = x_2-x_3$$

- Normalization means adjusting the normalization constant N such that

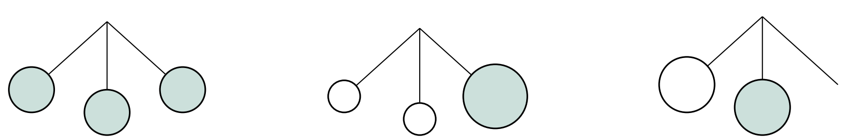
$$\int [N(x_1+x_2+x_3)]^2 = 1$$

- More simply, we multiply each of the above by 1 over the square root of the sum of the squares of the extant coefficients. So

$$\Psi_{A_1\text{ SALC}} = \frac{1}{\sqrt{1^2+1^2+1^2}}(x_1+x_2+x_3) = \frac{1}{\sqrt{3}}(x_1+x_2+x_3) \qquad \Psi_{E\text{ SALC}} = \frac{1}{\sqrt{2^2+(-1)^2+(-1)^2}}(2x_1-x_2-x_3) = \frac{1}{\sqrt{6}}(2x_1-x_2-x_3)$$

$$\Psi_{E\text{ SALC}} = \frac{1}{\sqrt{0^2+1^2+(-1)^2}}(x_2-x_3) = \frac{1}{\sqrt{2}}(x_2-x_3)$$

– Lastly, we can draw the orbitals.



(a) Ψ_{a_1}. (b) Ψ_{e_a}. (c) Ψ_{e_b}.

Figure 3.1: NH_3 SALCs.

3.3 Vibrational Modes and Symmetry

10/14: • Purposes of the basis set → RRs → IRRs → SALCs workflow.

1. Helps us understand the symmetry properties of molecular vibrations (we are going to look at this first).
2. Helps us understand MO diagrams (we will look at this after Exam 1).

- Symmetry properties of molecular vibrations: Any vibrational motion of a molecule can be decomposed in a combination of normal modes, and all normal modes form the basis of an irreducible representation of the point group of the molecule.
- How many normal modes do we have for a given molecule?
  - N atoms.
  - $3N$ degrees of freedom.
  - 3 translations.
  - 3 rotations (2 for linear molecules).
  - $3N-6$ (resp. $3N-5$) vibrations (i.e., normal modes).
- How to determine normal modes.
  1. Determine the point group.
  2. Consider the motion of atoms independently.
  3. Use the Cartesian displacement method, reduce $\Gamma_{\text{Cartesian}}$ to IRRs, and compare with the character table to determine which can be accounted for by translation (x,y,z) and rotation (R_x,R_y,R_z).
  4. Use the stretching and/or bending vectors as basis sets and use $\hat{P}$ to determine what the normal modes look like.
- Example: H_2O.
  1. C_{2v}.
  2. 3 degrees of freedom for each atom (atom i can move in the x_i,y_i,z_i direction for $i=1,2,3$).
  3. Multiple steps:
     (a) Find $\Gamma_{\text{unmoved}}=(3,1,1,3)$.
     (b) Find Γ_{xyz}: From the relevant character table, $\Gamma_{xyz}=A_1+B_1+B_2=(3,-1,1,1)$.
     (c) Find $\Gamma_{\text{Cartesian}}=\Gamma_{\text{unmoved}}\times\Gamma_{xyz}=(9,-1,1,3)$.
     (d) Apply the reduction formula: $\Gamma_{\text{Cartesian}}=3A_1+A_2+2B_1+3B_2$.
     (e) Notice that A_1 corresponds to the z-translation, A_2 corresponds to the z-rotation, B_1 corresponds to the x-translation and y-rotation, and B_2 corresponds to the y-translation and x-rotation. If we want to determine the vibrational modes of symmetry, we need to subtract out the modes corresponding to translations and rotations of the full molecule. Thus,

$$\Gamma_{\text{vibs}}=3A_1+A_2+2B_1+3B_2-(A_1+A_2+2B_1+2B_2)=2A_1+B_2$$

  4. Multiple steps:
     (a) Stretching IRR(s): Label the bond vectors r_1,r_2. Find their representation.

$$\Gamma_1=(2,0,0,2)=A_1+B_2$$

       - Since Γ_1 decomposes into two IRRs, this basis set accounts for 2/3 of the normal vibrational modes.
       - To get the last, we'll need another basis set, but we'll do that later.

     (b) Stretching SALC(s): Apply the projection operator to these normal modes.

$$\hat{P}(A_1)_{r_1}=2(r_1+r_2)\approx r_1+r_2$$
$$\hat{P}(B_2)_{r_1}=2(r_1-r_2)\approx r_1-r_2$$

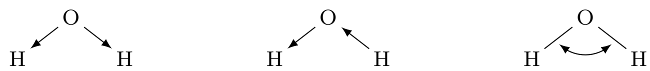
     (c) Bending IRR(s): Label the bending basis (angle between r_1,r_2) $\Delta\theta$. Find its representation.

$$\Gamma_2=(1,1,1,1)=A_1$$

(d) <u>Bending SALC(s)</u>: Apply the projection operator to this normal mode.

$$\hat{P}(A_1)_{\Delta\theta} = 4\Delta\theta \approx \Delta\theta$$

(e) <u>Visualize the normal modes</u>: r_1+r_2 corresponds to a symmetric stretch ν_s, r_1-r_2 corresponds to an asymmetric stretch ν_a, and $\Delta\theta$ corresponds to a bend δ.



(a) a_1 stretch: ν_s. (b) b_2 stretch: ν_a. (c) a_1 stretch: δ.

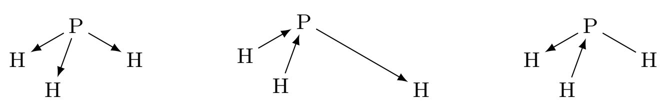
Figure 3.2: H_2O vibrational modes.

(f) <u>Quantum mechanically calculate the stretching frequencies</u>: For H_2O, $\nu_s = 3657\,\text{cm}^{-1}$, $\nu_a = 3756\,\text{cm}^{-1}$, and $\delta = 1595\,\text{cm}^{-1}$.

- Example: PH_3 stretching modes.
  - C_{3v}.
  - $\Gamma_\nu = (3,0,1) = a_1 + e$.
  - Projecting:

$$\hat{P}(A_1)_{r_1} \approx r_1 + r_2 + r_3 \qquad \hat{P}(E)_{r_1} \approx 2r_1 - r_2 - r_3 \qquad \hat{P}(E)_{r_2-r_3} \approx r_2 - r_3$$

  - Drawing:



(a) a_1 stretch. (b) e stretch (1). (c) e stretch (2).

Figure 3.3: PH_3 vibrational modes.

- Note that we don't need Γ_{3N} to derive Γ_ν! We would only need it for Γ_δ, unless Wuttig gives us a bending basis with which to work.
- Some observation on orthogonal projections.
  - Suppose we want to derive $3r_2 - 3r_3$. Since $\hat{P}$ is a linear operator, we can equally well take the difference $\hat{P}(E)_{r_2} - \hat{P}(E)_{r_3}$ and project out $r_2 - r_3$ via $\hat{P}_{r_2-r_3}$ to start.
  - Moreover, I suspect that the projection operator is unitary (i.e., maps orthogonal vectors to orthogonal vectors). At least in this case, notice that r_1 and $r_2 - r_3$ are very much orthogonal (see Figure 3.4), just like their projections.

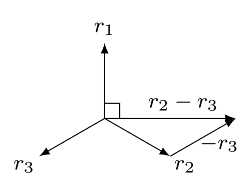


Figure 3.4: Orthogonal stretching basis.

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.

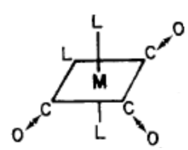
- Bottom line: A vibration will be IR active if it causes a change in the electric dipole moment of a molecule. A fundamental mode will be IR active if the normal mode which is excited belongs to the same representation as any one or several of the Cartesian coordinates.
- What modes are IR active for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

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

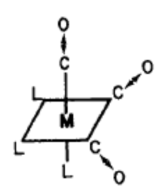
      Since the result of our calculation contains the totally symmetric representation (in its first entry), we know that v_a is allowed.
    - The asymmetric stretch has ground a_1 and excited state b_2. $\hat{\mu}$ is the same as before.

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

      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.
   - 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 $Mo(CO)_3[P(OCH_3)_3]_3$ 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

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

- 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 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:

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

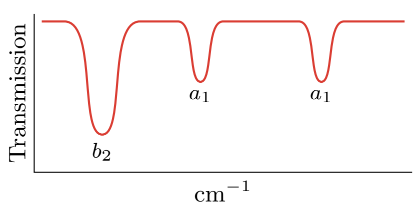
- a_1' is Raman active, e' is both, a_2'' is IR active, and e'' is both.

- 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.

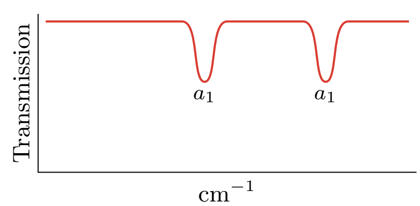
4.3 Special Spectroscopic Bands

10/21:

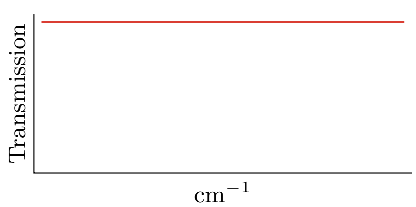
- Calculators that aren't connected to the internet are permitted. Arrive by 9:25. Think of it as a quiz more than an exam — there's only so much you can do in 50 minutes.
- **Polarization**: When electric fields are restricted to a specific direction by filtration.
- Recall H_2O and its vibrational 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.



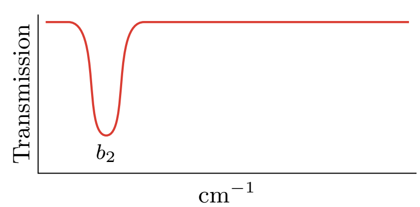
(a) Unpolarized.



(b) z-polarized.



(c) x-polarized.



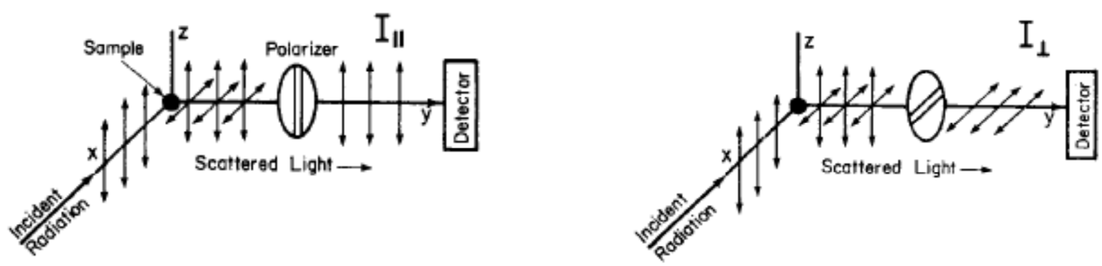
(d) y-polarized.

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.



(a) Parallel scattering. (b) Perpendicular scattering.

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* $\boldsymbol{\rho}$. *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 $v_0 \to v_1$.
- **Combination band**: A band that occurs when more than one vibration is excited by one photon. *Also known as* **combo band**.
  - Example:
    $$\Psi_1(0)\Psi_2(0)\Psi_3(0) \to \Psi_1(1)\Psi_2(1)\Psi_3(0)$$
  - Example:
    $$\Psi_1(0)\Psi_2(0)\Psi_3(0) \to \Psi_1(2)\Psi_2(0)\Psi_3(1)$$
    - 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:
    $$\Psi_1(0)\Psi_2(1)\Psi_3(0) \to \Psi_1(0)\Psi_2(2)\Psi_3(0)$$
  - 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 $1388\,\text{cm}^{-1}$ and $1286\,\text{cm}^{-1}$.
  - 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.