

## Chemistry 475

Molecular Orbital Theory  
and  
Introduction to Spectroscopy

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### Hamiltonian for Polyatomics

Electronic Kinetic Energy      Electron-Electron Repulsion

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_k \frac{\hbar^2}{2m_k} \nabla_k^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{k<l} \frac{Z_k Z_l}{r_{kl}}$$

Nuclear Kinetic Energy      Electron-Nuclear Attraction      Nuclear-Nuclear Repulsion

- Not Solvable exactly
- Relativistic Terms are not shown

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### Born-Oppenheimer Approximation

- Nuclear Motions are much slower than Electronic Motions
- Terms involving Nuclear Motion are constant
  - Fixed internuclear distance
  - Separation of electronic and nuclear terms
- Also used in Vibrational and Rotational Spectroscopy

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## LCAO Approximation

- Assume that near a Nucleus Atomic Orbitals (AOs) are a Good Description of Electron
- Construct Molecular Orbitals (MOs) as Linear Combinations of Atomic Orbitals (LCAO)

$$\psi_{MO} = \frac{1}{N}(c_1\psi_A + c_2\psi_B)$$

Use variational approach and find where  $\frac{\partial E}{\partial c_i} \approx 0$

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## LCAO Approach

- Energy of a Molecular Orbital can be found to be

$$E = \frac{c_1^2 H_{AA} + c_2^2 H_{BB} + 2c_1 c_2 H_{AB}}{c_1^2 + c_2^2 + 2c_1 c_2 S}$$

$$H_{AA} = \int \psi_A \hat{H} \psi_A d\tau < 0$$

*Valence ionization energy.* Approximately equal to energy of AO with small perturbation due to other atom.

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## LCAO Approach

$$H_{AB} = \int \psi_A \hat{H} \psi_B d\tau = \int \psi_B \hat{H} \psi_A d\tau < 0$$

*Resonance integral.* Energy of overlapped electron density being attracted to both nuclei.

$$H_{AB} \approx k \left( \frac{H_{AA} + H_{BB}}{2} \right) S \quad \text{Mulliken}$$

$$S = \int \psi_A \psi_B d\tau$$

*Overlap integral.* Extent to which the AOs involved in the bond overlap.  $0 < S < 1$

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## LCAO Approach

- For each Pair of AO there are two Solutions

$$E = \frac{H_{AA} - H_{BB}}{1 - S} \quad E = \frac{H_{AA} + H_{BB}}{1 + S}$$

$$\psi = \frac{1}{\sqrt{2 - 2S}}(\psi_A - \psi_B) \quad \psi = \frac{1}{\sqrt{2 + 2S}}(\psi_A + \psi_B)$$

**Antibonding**  
MO raised in energy  
relative to AOs

**Bonding**  
MO lowered in energy  
relative to AOs

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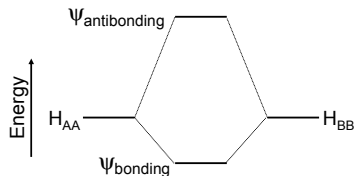
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## LCAO Approach

- Result is two Molecular Orbitals one raised in Energy, one lowered in Energy
  - Antibonding raised more than bonding lowered




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## LCAO Approach

- When Atoms are different the Equations become (with  $H_{AA} > H_{BB}$  and  $S \propto H_{AB}$ )

$$E_{\text{bonding}} = H_{BB} + \frac{H_{AB}^2}{H_{BB} - H_{AA}} \quad \psi_{\text{bonding}} = N(\psi_A + \lambda\psi_B)$$

$$E_{\text{antibonding}} = H_{AA} - \frac{H_{AB}^2}{H_{BB} - H_{AA}} \quad \psi_{\text{antibonding}} = N'(\psi_A - \lambda\psi_B)$$

$$\lambda = \frac{H_{AB}}{(H_{BB} - H_{AA})} < 1 \quad N^2(1 + \lambda^2 + 2\lambda S) = 1$$

(similar equation for N')

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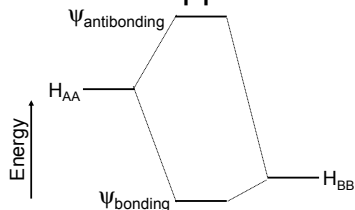
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## LCAO Approach



- Higher energy AO makes larger contribution to  $\Psi_{\text{antibonding}}$
- Lower energy AO makes larger contribution to  $\Psi_{\text{bonding}}$

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## LCAO Approach

- To Have a Strong Bond
  - $H_{BB} - H_{AA}$  must be small (orbital energies must be similar)
  - $S \propto H_{AB}$  must be large (orbital size and the angle between them must match)
- Bonding dominated by Valence Orbitals
- Trends in Bond Strength
  - Down group ( $n$  increases)
  - Across period (!)

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## LCAO Approach

- For bonding  $H_{AB}$  and  $S$  must not equal 0
- From Group Theory

$$\int \psi_A \psi_B d\tau \neq 0 \text{ IFF } \Gamma_A \times \Gamma_B \subset A_{1(g)}$$

$$\int \psi_A \hat{H} \psi_B d\tau \neq 0 \text{ IFF } \Gamma_A \times A_{1(g)} \times \Gamma_B \subset A_{1(g)}$$

- Don't need  $\psi$ 's only how their Symmetry Properties to Evaluate Integrals

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## Group Theory

- Branch of Mathematics concerned with Symmetry
- Basic Descriptors of Symmetry
  - *Symmetry Element*: A geometric figure about which a symmetry operation is performed
  - *Symmetry Operation*: Mathematical description of a physical transformation of an object in space

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## Operations

- Identity ( $\hat{E}$ )
- Proper Rotation ( $\hat{C}_n^m$ )
  - Rotate object by  $2\pi/n$  m times
- Inversion ( $\hat{i}$ )
  - Change sign on all coordinates
- Reflection ( $\hat{\sigma}$ )
  - Types  $\hat{\sigma}_v, \hat{\sigma}_h, \hat{\sigma}_d$
- Improper Rotation ( $\hat{S}_n^m = \hat{\sigma}_h \hat{C}_n^m$ )
  - Rotate by  $2\pi/n$  m times then reflection

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## Symmetry Group

- Set of *Operations* that define an Object
  - Only includes operations that take object into configuration indistinguishable from original
- Properties
  - All binary products (defined right to left) of group members are also in the group
  - Contains identity ( $\hat{E}$ )
  - Associative law of multiplication holds
  - Every member has an inverse ( $\hat{A}^{-1}\hat{A}=\hat{A}\hat{A}^{-1}=\hat{E}$ )
  - Commutative law true only if *Abelian*

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## Symmetry Group

- Define the Order of the Group,  $h$ , as the Number of Operations in the Group
- Define *Classes* of Operations as a Subset of the Group whose Members are *Conjugates*, that is they are related by a Similarity Transformation

$$\hat{P}^{-1}\hat{A}\hat{P} = \hat{B}$$

- Classes consist of operations that perform geometrically equivalent transformations

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## Symmetry Group

- All Functions will behave differently under each Operation but only a small Subset are needed to build all possible Functions
  - This *basis set* called the *irreducible representations* (IRs)
  - IRs are orthogonal
  - Other functions are linear combinations of IRs
- Group's Properties collected in Character Table

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## Character Table

Symmetry (point) group		Operations				
$C_{2v}$		$\hat{E}$	$\hat{C}_2(z)$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}'_v(yz)$	
IRs	$A_1$	1	1	1	1	$z, x^2, y^2, z^2$
	$A_2$	1	1	-1	-1	$xy, R_z$
	$B_1$	1	-1	1	-1	$x, xz, R_y$
	$B_2$	1	-1	-1	1	$y, yz, R_x$

Character of IRs under each symmetry operation

Functions that transform as given IR ( $R_i$  = rotations)

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## Character Table Theorems

- Characters are Representation of Matrix that describes Operation (*Trace*)
  - All operations may be written as matrix multiplication
- Characters of all Operations belonging to same Class are Identical
  - All must have the same trace
- Number of IRs equals Number of Classes in Group

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## Character Table Theorems

$$h = \sum_i [\chi_i(\hat{E})]^2$$

*Dimension* of  $i^{\text{th}}$  IR =  $\chi_i(\hat{E})$

$$\text{In } C_{2v} \quad h = (1)^2 + (1)^2 + (1)^2 + (1)^2 = 4$$

$$h = \sum_R [\chi_i(R)]^2$$

Characters of each operation in the IR =  $\chi_i(R)$

$$\text{In } C_{2v} \text{ for } B_2 \quad h = (1)^2 + (-1)^2 + (-1)^2 + (1)^2 = 4$$

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## Character Table Theorems

- Functions which transform as two Different IRs are Orthogonal

$$\sum_R \chi_i(R) \chi_j(R) = 0 \quad \text{for } i \neq j$$

In  $C_{2v}$ :  $B_1 \times B_2$

$$(1)(1) + (-1)(1) + (-1)(-1) + (1)(-1) = 0$$

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## Binary Multiplication

- Can determine Symmetry of a Product of two Functions by simple Multiplication of their Characters for each Operation

$$\chi_{DP}(\hat{R}) = \chi_1(\hat{R})\chi_2(\hat{R})$$

- Example: what is  $A_1 \times A_2$  in  $C_{3v}$ ?
  - Need to have character table for  $C_{3v}$  and then multiply characters of each operation for each IR

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## Binary Multiplication

$C_{3v}$	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$		
$A_1$	1	1	1	z	$x^2+y^2, z^2$
$A_2$	1	1	-1	$R_z$	
E	2	-1	0	(x,y) ( $R_x, R_y$ )	$(x^2-y^2, xy)$ (xz,yz)

	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$
$A_1$	1	1	1
$A_2$	1	1	-1
$A_1 \times A_2$	1	1	-1

In general  $A_{1(g)} \times \Gamma_i = \Gamma_i$

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## Binary Multiplication

- What is  $E \times E$  in  $C_{3v}$  symmetry?

$C_{3v}$	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$
E	2	-1	0
E	2	-1	0
$E \times E$	4	1	0

← Not an irreducible representation!

This reducible representation must be a linear combination of irreducible representations.

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## Reducing Reducible Representations

- Great Orthogonality Theorem
  - $a_i$  = number of times  $i^{\text{th}}$  IR appears in reducible representation
  - $h$  = order of the group
  - $n_i$  = number of operations in class
  - $\chi_{\text{RED}}$  and  $\chi_i$  are characters of each operation

$$a_i = \frac{1}{h} \sum_{\hat{R}} n_i \chi_{\text{RED}}(\hat{R}) \chi_i(\hat{R})$$

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## Reducing Reducible Representations

$C_{3v}$	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$		
$A_1$	1	1	1	z	$x^2+y^2, z^2$
$A_2$	1	1	-1	$R_z$	
E	2	-1	0	$(x,y) (R_x, R_y)$	$(x^2-y^2, xy) (xz, yz)$
E x E	4	1	0		

$$a_{A_1} = \frac{1}{6} ((1)(4)(1) + (2)(1)(1) + (3)(1)(0)) = 1$$

$$a_{A_2} = \frac{1}{6} ((1)(4)(1) + (2)(1)(1) + (3)(0)(-1)) = 1$$

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## Reducing Reducible Representations

$C_{3v}$	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$		
$A_1$	1	1	1	z	$x^2+y^2, z^2$
$A_2$	1	1	-1	$R_z$	
E	2	-1	0	$(x,y) (R_x, R_y)$	$(x^2-y^2, xy) (xz, yz)$
E x E	4	1	0		

$$a_E = \frac{1}{6} ((1)(2)(4) + (2)(-1)(1) + (3)(0)(0)) = 1$$

$$E \times E = A_1 + A_2 + E$$

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## Group Multiplication Tables

- Work out all Possible Direct Products in a Group
  - Symmetric about diagonal
  - $A_{1(g)}$  appear only on diagonal (only direct products that contain  $A_{1(g)}$ )

$C_{3v}$	$A_1$	$A_2$	$E$
$A_1$	$A_1$	$A_2$	$E$
$A_2$	$A_2$	$A_1$	$E$
$E$	$E$	$E$	$A_1+A_2+E$

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## Systematic Derivation of MO Diagrams

- Determine Symmetry Properties of all AOs in Molecule or Ion
  - Identify point group of molecule or ion
  - Take central atom's AO symmetry properties directly from character table (IR matches name, e. g.  $p_y$  transforms as  $y$ )
  - Outer atoms need to determine by applying symmetry operations and reducing the resulting reducible representations

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## Systematic Derivation of MO Diagrams

- Use Overlap and Energy Considerations to determine Interactions between AOs
  - Only orbitals with same symmetry can overlap (symmetry and geometry)
  - Orbitals that have similar energies have stronger interactions (electronegativity)
  - While not necessary, construction of ligand SALCs is useful
  - Consider only valence orbitals in most cases

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## Group Theory in MO Theory

- This will be done on the Blackboard
  - Experience has taught me that trying to do this in Power Point causes problems
  - Your understanding is appreciated
- Let me know if you missed Anything

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## Spectroscopy

- For a Transition to be *Allowed* the Transition Moment Integral must be Nonzero:  $\langle \psi_e | \hat{M} | \psi_g \rangle \neq 0$
- It is Equivalent to show that the Following is True:  $\Gamma_e \times \Gamma_M \times \Gamma_g \subset A_{1(g)}$

- Transition Moment Operator can be written:

$$\hat{M} = \hat{M}(\text{electric dipole}) + \hat{M}(\text{magnetic dipole}) + \dots$$

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## Spectroscopy

- *Molecular Term Symbol* describes Electronic State

Multiplicity  
(2S + 1)

6A<sub>1g</sub>

Orbital component  
of wavefunction

- For Electronic Transitions separate Spin and Orbital Parts of Wavefunctions

- Magnetic and electric dipole operators don't affect spin

- So write  $\langle S_e | S_g \rangle \langle \phi_e | \hat{M} | \phi_g \rangle \neq 0$

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## Spectroscopy

$$\langle S_e | S_g \rangle \langle \phi_e | \hat{M} | \phi_g \rangle \neq 0$$

- Spin Selection Rule
  - If  $\Delta S = 0$ , *spin allowed*
  - If  $\Delta S \neq 0$ , *spin forbidden*
- Orbital Selection Rule depends on Symmetry of Dipole Moment Operator
  - Electric dipole operator (x,y,z)
  - Magnetic dipole operator ( $R_x, R_y, R_z$ )

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## Electronic Spectroscopic Methods

- Absorption
  - Electric dipole operator
  - $\epsilon = \epsilon_x + \epsilon_y + \epsilon_z$
- Circular Dichroism
  - Differential absorption of circularly polarized light by optically active substances
  - Magnetic dipole operator
  - $\Delta\epsilon = \epsilon_{\text{left}} - \epsilon_{\text{right}}$
  - “Signed” method (enantiomers, induced CD)

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## Classes of Transitions

- Spin Forbidden, Orbitally Forbidden
  - $\epsilon = \sim 0.01 - \sim 1 \text{ M}^{-1} \text{ cm}^{-1}$
  - Centrosymmetric point groups when ground and excited states have same parity
  - Electric dipole operator transforms with u symmetry, triple direct product  $\not\propto A_{1g}$
  - Parity (Laporte) vs. orbitally forbidden
- Examples:
  - d to d Transitions in transition metal ions
  - Transitions of  $O_2$  in absorbance

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## Classes of Transitions

- Spin Allowed, Orbitally Forbidden
  - $\epsilon = \sim 10 \text{ M}^{-1} \text{ cm}^{-1}$  in high symmetry (parity forbidden)
  - $\epsilon = \sim 100 - 1000 \text{ M}^{-1} \text{ cm}^{-1}$  in low symmetry
- Examples:
  - d to d Transitions of certain metal ions

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## Classes of Transitions

- Spin Allowed, Orbitally Allowed
  - $\epsilon > \sim 10000 \text{ M}^{-1} \text{ cm}^{-1}$
  - Excited states have u symmetry
- Usually Charge Transfer Transitions
  - Optically move electron from one part of molecule to another
  - Energy depends on relative redox properties of donor and acceptor
  - Color of  $\text{PbI}_2$ , etc. from charge transfer

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## Increasing Transition Intensity

- Low Symmetry
  - Removes parity problem
  - Mixes orbitals, but does not affect spin
  - Spin and Laporté forbidden:  $\epsilon$  to  $\sim 10$
  - Spin allowed/Laporté forbidden:  $\epsilon$  to  $\sim 100$
- Vibronic Coupling
  - Dynamic symmetry lowering
  - Very small increase in  $\epsilon$

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## Increasing Transition Intensity

- Mixing of Forbidden Transition with an Allowed Transition
  - Best when transitions have same symmetry and are close in energy
  - Spin-orbit coupling (*double groups*)
  - Spin and Laporté forbidden  $\epsilon$  to  $\sim 20$
  - Spin allowed/Laporté forbidden  $\epsilon$  to  $\sim 1000$

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## Polarization of Absorbance Transitions

- Polarized Light is absorbed only when its **E** Vector is aligned Parallel to correct Axis
- Important in oriented Media (Solids, Liquid Crystals) where x, y, z do not transform in same IR
  - Example: in  $D_{4h}$  z transforms as  $A_{2u}$  and x,y transform as  $E_u$
  - Can be used to assign transitions

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## Polarization of Absorbance Transitions

- Example: In  $D_{4h}$  will the  ${}^3E_g \rightarrow {}^3A_{1u}$  transition be allowed in absorbance? In what polarization?
  - Spin allowed
  - In  $D_{4h}$  electric dipole operator transforms as  $A_{2u}$  (z) and  $E_u$  (x,y)
  - Calculate triple direct products

$$A_{1u} \times A_{2u} \times E_g = A_{1u} \times A_{2g} = E_g$$

$$A_{1u} \times E_u \times E_g = A_{1u} \times (A_{1u} + A_{2u} + B_{1u} + B_{2u}) = A_{1g} + \dots$$

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## Molecular Vibrations

- **Normal Mode:** Simplest Vibrational Motion of a Molecule or Complex Ion
  - Linear molecules:  $3N-5$  normal modes
  - Non-linear molecules:  $3N-6$  normal modes
- The Allowed Energy Levels for Each Normal Mode given by  $E_v = (v + 1/2)\hbar\omega$

– Where

$$\omega = \left(\frac{k}{\mu}\right)^{1/2} \quad \mu = \frac{m_1 \cdot m_2}{m_1 + m_2} \quad v = 0, 1, 2, 3 \dots$$

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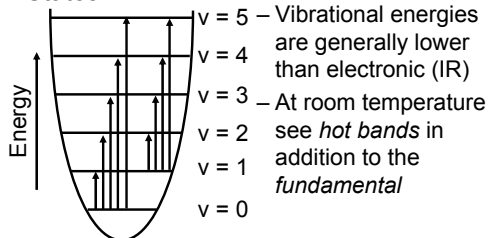
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## Molecular Vibrations

- Result is a Ladder of allowed Vibrational States




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## Vibrational Spectroscopy

- Absorbance Infrared (IR) Spectroscopy
  - Light excites molecular vibrations
- If Laser Excitation is used can get
  - Rayleigh scattering
  - Fluorescence
  - Raman scattering
- Raman Spectroscopy
  - Stokes line ( $\nu = \nu_0 + \nu_v$ )
  - Anti-stokes line ( $\nu = \nu_0 - \nu_v$ ) (too weak to use)

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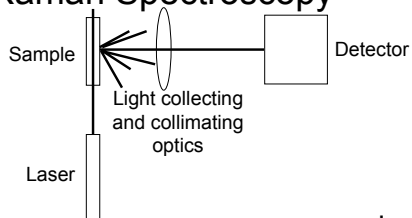
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## Raman Spectroscopy



- Raman Scattering may be polarized  $\rho = \frac{I_{y(II)}}{I_{z(\perp)}}$ 
  - $\rho = 3/4$  are depolarized
  - $0 < \rho < 3/4$  are polarized (must transform as  $A_{1(g)}$ )

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## Vibrational Spectroscopy and Group Theory

- Normal Mode Symmetry and the Atomic Motions found using Group Theory
  - Define a displacement vector on each atom (treat total as a single entity)
  - Determine reducible representation
  - Reduced reducible representation
  - Remove translations and rotations
  - Determine atomic motions

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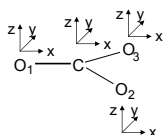
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## Vibrational Spectroscopy

- Consider  $\text{CO}_3^{2-}$ 
  - Symmetry:  $D_{3h}$
  - Displacement vector defined as



- Treat displacement vector as a single function in the point group

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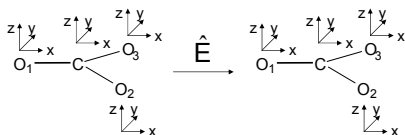
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## Vibrational Spectroscopy

- Generate the Reducible Representation
  - Operations that exchange vectors on different atoms do not contribute
- Operations
  - E nothing changes,  $\chi = 12$




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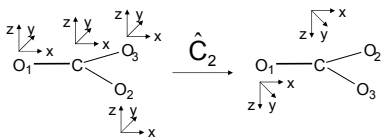
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## Vibrational Spectroscopy

- $C_2$  interchanges vectors on two atoms, and flips two atoms



- Two z components become -z, two y components become -y, two x components don't change,  $\chi = -2$

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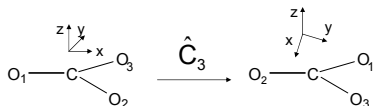
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## Vibrational Spectroscopy

- Operations  $\sigma_h$ ,  $\sigma_v$  are similar
- Operations  $C_3$  and  $S_3$  are Special
  - Interchange components on central atom
  - Linear combinations of old components




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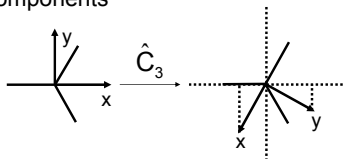
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## Vibrational Spectroscopy

- Under  $C_3$  z Component doesn't change, x and y Components are mixed
  - Rewrite new vector in terms of original components




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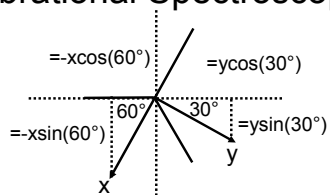
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## Vibrational Spectroscopy



$$x' = -x\cos(60^\circ) + y\cos(30^\circ) = -\frac{1}{2}x + \frac{\sqrt{3}}{2}y$$

$$y' = -x\sin(60^\circ) + y\sin(30^\circ) = -\frac{\sqrt{3}}{2}x + \frac{1}{2}y$$

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## Vibrational Spectroscopy

- Rewrite Equations in Matrix Form

$$\begin{matrix} x \\ y \\ z \end{matrix} \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

- Trace of this matrix is 0
- Character of  $C_3$  is 0

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## Vibrational Spectroscopy

- $S_3$  Operation is Similar to  $C_3$ 
  - x and y Coordinates same as  $C_3$
  - z Changes sign
  - Character of  $S_3 = -2$
- Complete Reducible Representation of Displacement Vectors is

	E	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$2\sigma_v$
$\Gamma$	12	0	-2	4	-2	2

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## Vibrational Spectroscopy

- Reduces to  $A_1' + A_2' + 3E' + 2A_2'' + E''$
- Predict 6 Normal Modes
  - Too many modes (12) found
  - Three are translations (x, y, z)  $\Rightarrow A_2'' + E'$
  - Three are rotations ( $R_x, R_y, R_z$ )  $\Rightarrow A_2' + E''$
- Remove these from Result
  - Gives:  $A_1' + 2E' + A_2''$

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## Vibrational Spectroscopy

- To be an Allowed Normal Mode must
  - Transform as x, y or z for IR
  - Transform as quadratic (e.g. xy,  $x^2-y^2$ ,  $z^2$ ) for Raman
- In  $D_{3h}$ :  $A_2''$  and  $E'$  allowed in IR,  $A_1'$  and  $E'$  are allowed in Raman
  - Observed: 3 peaks in IR, and 3 in Raman
  - Two  $E'$  transitions appear in both

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