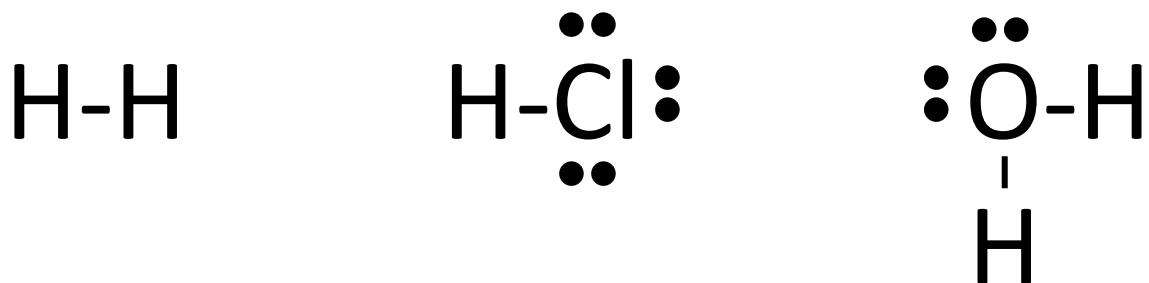


# Molecular Structure and Energy Levels for Polyatomic Molecules

I) Commonly use Lewis Structure approach (localized bonding model)



Helps to understand the stoichiometry and importance of non-bonding electron pairs but not really the geometry

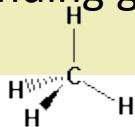
# Molecular Structure and Energy Levels for Polyatomic Molecules

II) Can build upon Lewis Structure approach to develop valence shell electron pair repulsion (VSEPR) model to get geometry:

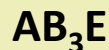
- 1) Ligands and lone pairs act as if they repel each other;
- 2) Lone pair occupies more space than a ligand;
- 3) Space occupied by a ligand increases with its electronegativity and decreases as the electronegativity of the central atom increases;
- 4) Multiply bonded ligands occupy more angular space than singly bonded ligands



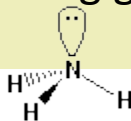
bonding groups: 4  
non-bonding groups: 0



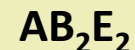
CH<sub>4</sub>  
methane



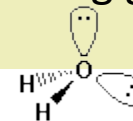
bonding groups: 3  
non-bonding groups: 1



NH<sub>3</sub>  
ammonia



bonding groups: 2  
non-bonding groups: 2



H<sub>2</sub>O  
water

This is still oversimplified: CH<sub>3</sub> radical is flat, not tetrahedral;  
CaF<sub>2</sub> or SrCl<sub>2</sub> are angular, not linear, etc.

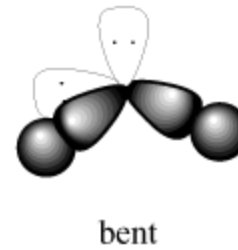
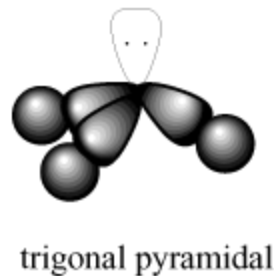
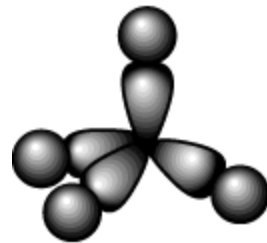
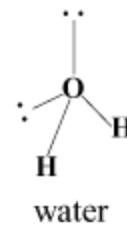
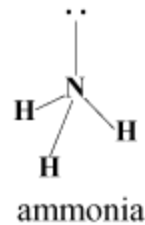
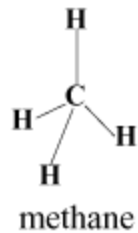
There are many limitations on the localized bonding models

# Molecular Structure and Energy Levels for Polyatomic Molecules

Problem with VSERP: It does not use QM explicitly. The way to correct it is:

III) Valence bond (VB) model developed by Slater and Pauling:

- 1) Atomic orbitals of the same atom are combined into hybrid orbitals
- 2) These localized structures are put together to represent a molecule as an ensemble of separate and independent parts that are still localized in space



# Molecular Structure and Energy Levels for Polyatomic Molecules

Problem with VSEPR: It does not use QM explicitly. The way to correct it is:

III) Valence bond (VB) model developed by Slater and Pauling:

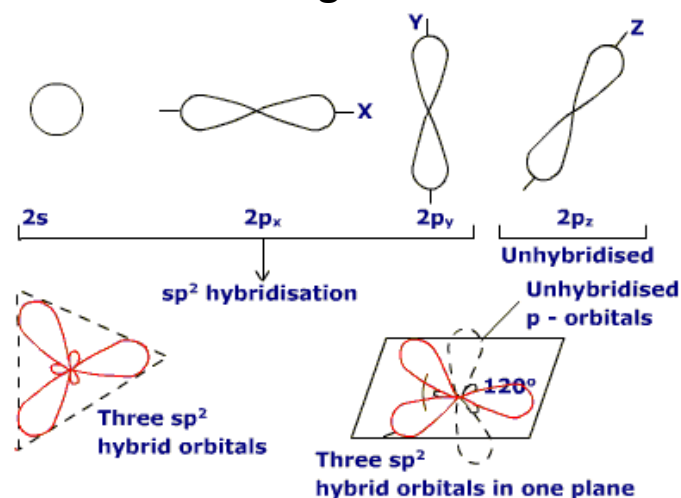
According to this image:

From carbon  $1s^2 2s^2 2p^2$  configuration we can produce  $1s^2 2p_z^1 \psi_a^1 \psi_b^1 \psi_c^1$ , where the last three functions are wavefunctions used in VB model

$$\psi_a = C_1 \phi(2p_x) + C_2 \phi(2s) + C_3 \phi(2p_y)$$

$$\psi_b = C_4 \phi(2p_x) + C_5 \phi(2s) + C_6 \phi(2p_y)$$

$$\psi_c = C_7 \phi(2p_x) + C_8 \phi(2s) + C_9 \phi(2p_y)$$



# Molecular Structure and Energy Levels for Polyatomic Molecules

Problem with VSEPR: It does not use QM explicitly. The way to correct it is:

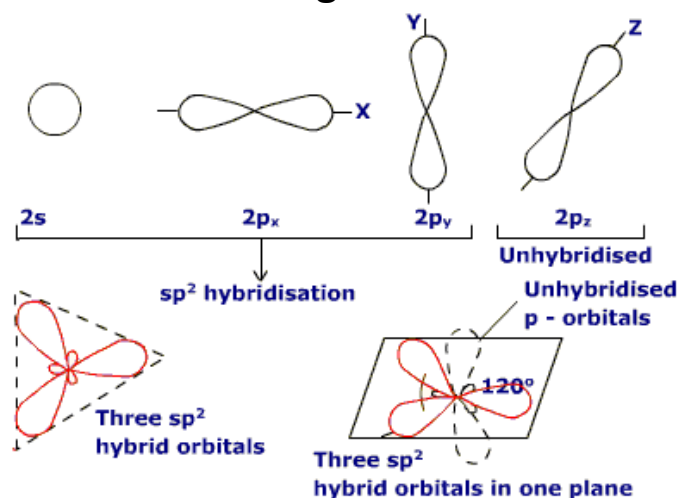
III) Valence bond (VB) model developed by Slater and Pauling:

From geometry considerations, normalization conditions, and based on the fact that centrosymmetric 2s orbital contributes equally to all the hybrid orbitals, can show that

$$\psi_a = C_1\phi(2p_x) + \frac{1}{\sqrt{3}}\phi(2s)$$

$$\psi_b = C_4\phi(2p_x) + \frac{1}{\sqrt{3}}\phi(2s) + C_6\phi(2p_y)$$

$$\psi_c = C_4\phi(2p_x) + \frac{1}{\sqrt{3}}\phi(2s) + C_6\phi(2p_y)$$



# Molecular Structure and Energy Levels for Polyatomic Molecules

III) Valence bond (VB) model developed by Slater and Pauling:

Similarly,  $sp^3$  and  $sp$  hybridization can be treated:

		<b>s/p ratio</b>	<b>Angle</b>
<b>C-C</b>	$sp^3$	1/3	109.4
<b>C=C</b>	$sp^2$	1/2	120
<b>C≡C</b>	$sp$	1/1	180

# Molecular Structure and Energy Levels for Polyatomic Molecules

III) Valence bond (VB) model developed by Slater and Pauling:

For non-equivalent ligands, we follow Henry Bent rules:

- 1) Central atoms that obey octet rule surrounded by a combination of single bonds or electron pairs have tetrahedral geometry and  $sp^3$  hybridization;  
one double bond + a combination of two single bonds or electron pairs -  $sp^2$ ;  
two double bonds or one triple bond + a single bond or electron pair -  $sp$ .
- 2) For multiple ligands:
  - a) atomic s character concentrates in hybrid orbitals directed toward electropositive ligands and p character concentrates in hybrid orbitals directed towards electronegative ligands

Example: trends in  $H_2CO$  and  $F_2CO$  angles

F is more electronegative than H. Thus, hybridization of the C-F yields more p character compared to C-H. The F-C-F angle is smaller than H-C-H

# Molecular Structure and Energy Levels for Polyatomic Molecules

Unlike any of the previous models, molecular orbital (MO) theory considers delocalized bonding model (no localized bonds or building blocks). Structure comes as a result of solving Shroedinger equation with

$$\sigma_{j(\text{molecular orbital})}(k_{\text{electron}\#k}) = \sum_i C_{ij} \phi_{i,\text{atom}}(k)$$

This approach also helps describing the processes involving HOMO and LUMO (frontier orbitals)



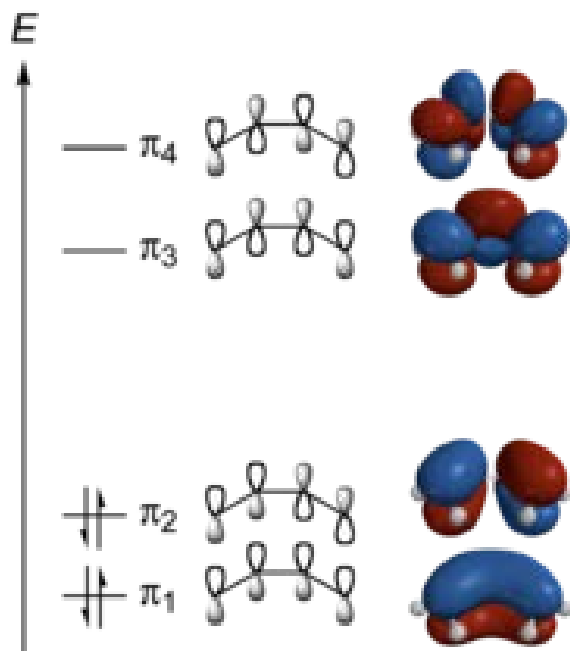
# Molecular Structure and Energy Levels for Polyatomic Molecules

Direct difference between localized and delocalized models is that we can never observe the building blocks for any localized models, only the results of the measurements (such as electron density) for delocalized models. The more complex the process, the easier it is to make a mistake using delocalized models

# Molecular Structure and Energy Levels for Polyatomic Molecules

## Conjugated and Aromatic Molecules – Hückel Model

Use VB model to describe sigma bonding and MO theory to describe the delocalized  $\pi$  electrons.



This semiempirical approach relies on theory and experimental measurement to determine the coefficients of the MO wavefunction. Clearly shows that smallest number of nodes corresponds to the lowest energies.

# Molecular Structure and Energy Levels for Polyatomic Molecules

## Conjugated and Aromatic Molecules – Hückel Model

Can be also used for other aromatics, including benzene. Hückel rules are often used to see if the produced molecule is aromatic (“flat” and “stable”) with  $N$  of  $\pi$  electrons:

- 1) If  $N = 4n + 2$  (like in benzene), this is aromatic;
- 2) If  $N = 4n + 1$ , it is a free radical;
- 3) If  $N = 4n$ , the molecule is very reactive.

Can also compare the energy of similar cyclic and linear conjugated molecules to determine “resonance stabilization energy”

# Molecular Symmetry

Symmetry elements:

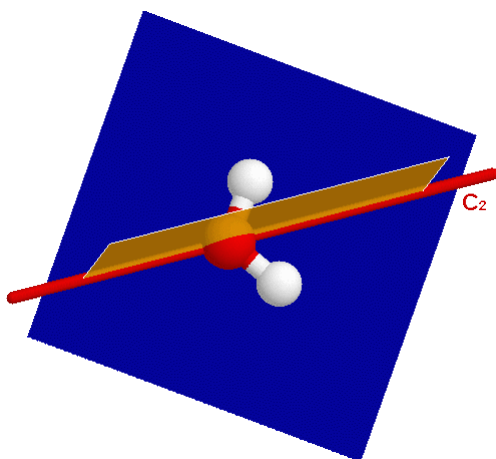
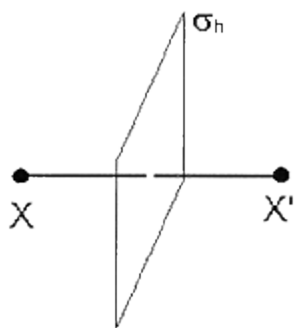
## Table of Elements and Operations

Element	Operation	Symbol
<a href="#">Identity</a>	<a href="#">Identity</a>	E
<a href="#">Symmetry plane</a>	Reflection in the plane	$\sigma$
<a href="#">Inversion center</a>	Inversion of a point x,y,z to -x,-y,-z	i
<a href="#">Proper axis</a>	Rotation by $(360/n)^\circ$	$C_n$
<a href="#">Improper axis</a>	1. Rotation by $(360/n)^\circ$ 2. Reflection in plane perpendicular to rotation axis	$S_n$

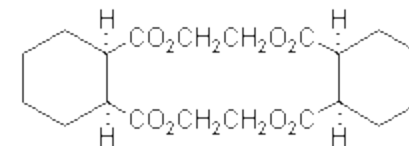
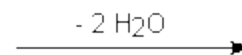
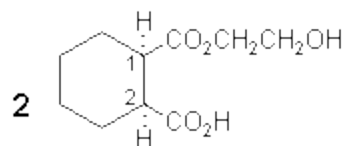
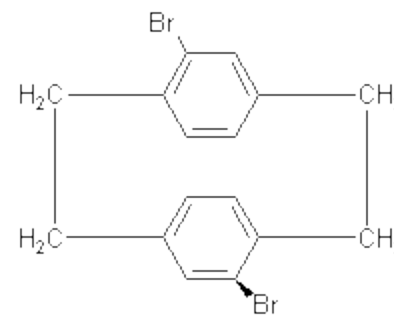
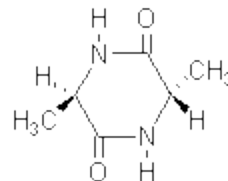
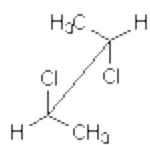
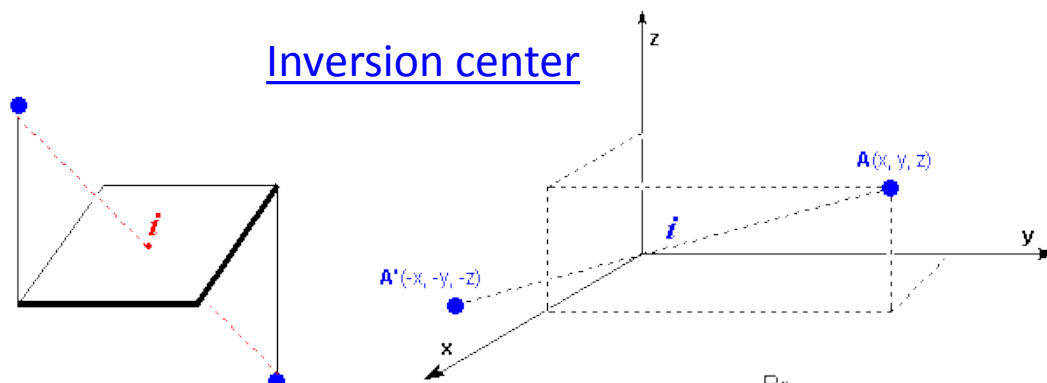
# Molecular Symmetry

Symmetry elements:

## Symmetry plane



## Inversion center



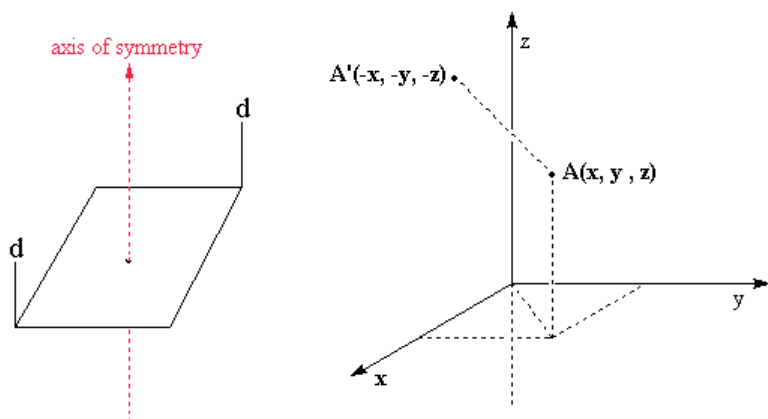
chiral

achiral

# Molecular Symmetry

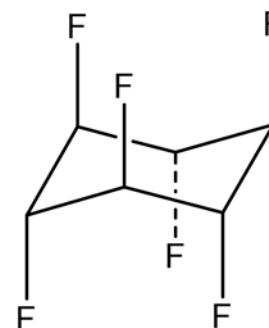
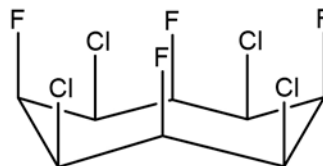
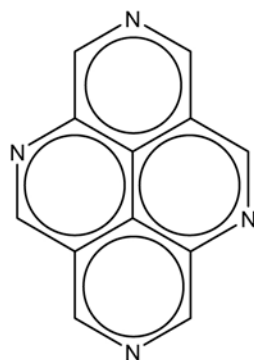
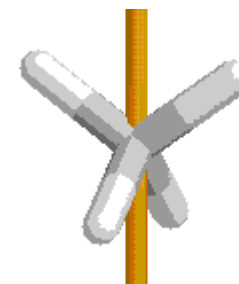
Symmetry elements:

## Proper axis

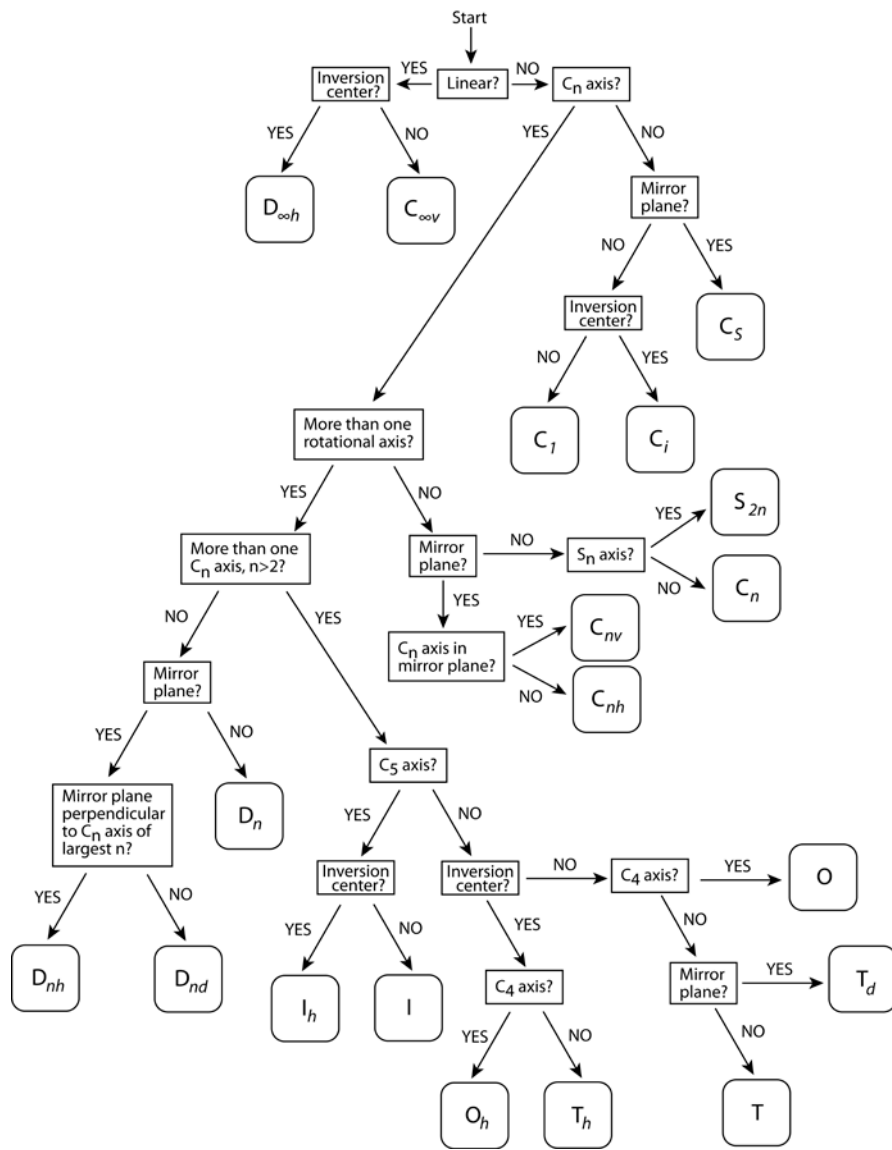


z-axis is also a 2-fold symmetry axis

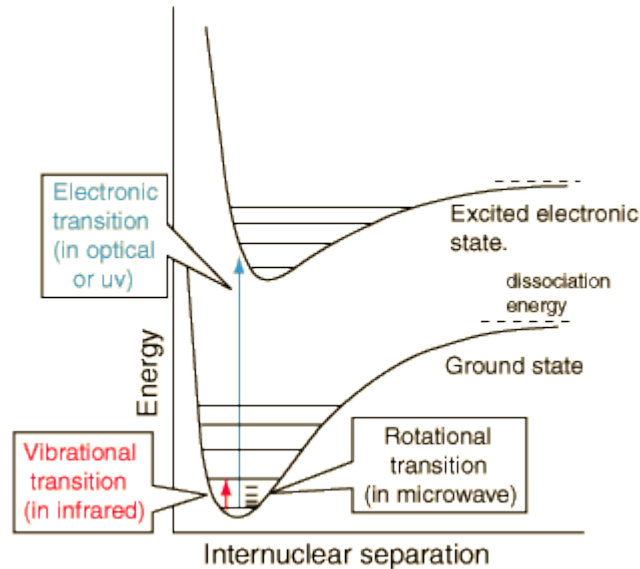
## Improper axis



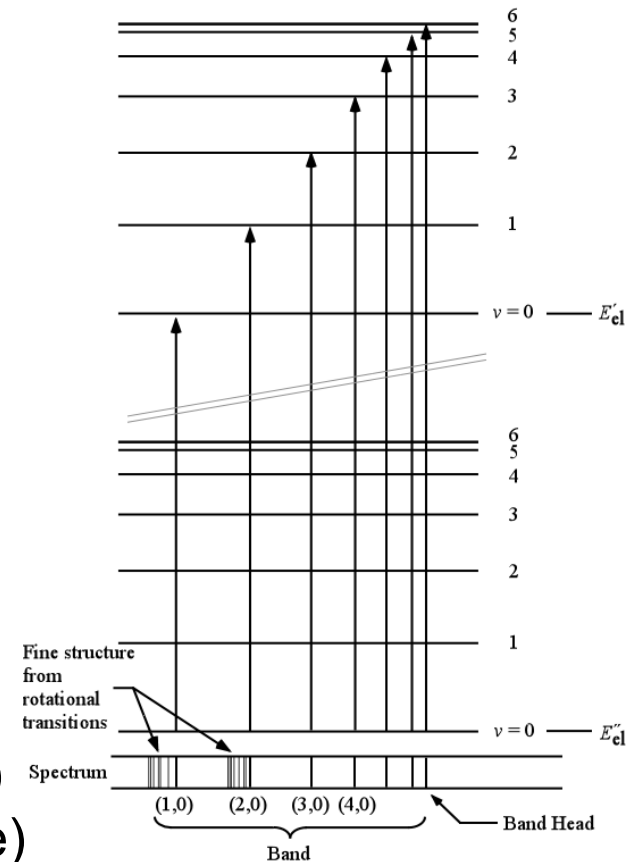
# Molecular Symmetry



# Electronic Spectroscopy for Diatomic Molecule



ELECTRONIC-VIBRATION-ROTATION SPECTRUM OF A DIATOMIC MOLECULE



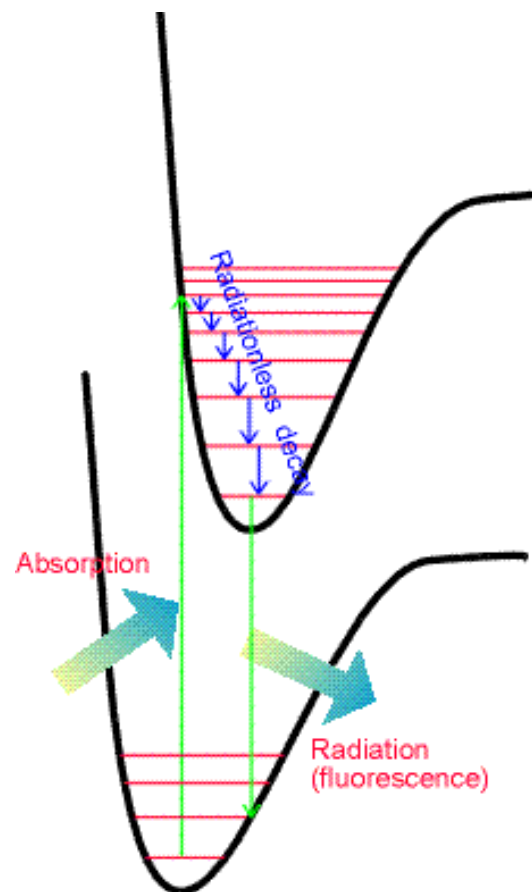
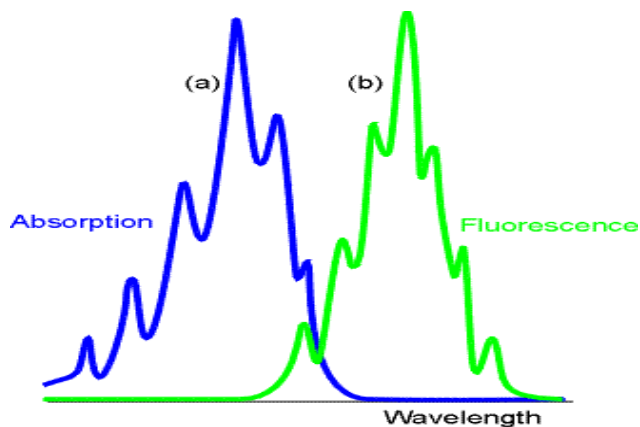
Selection rules for electronic spectroscopy:

- 1)  $\Delta\Lambda = 0, \pm 1$ ;
- 2)  $\Delta S = 0$  (no singlet-triplet transitions allowed)
- 3)  $g \leftrightarrow u$  (the inversion symmetry must change)
- 4)  $\Sigma^+ \leftrightarrow \Sigma^-$  Is not allowed



# Fluorescence

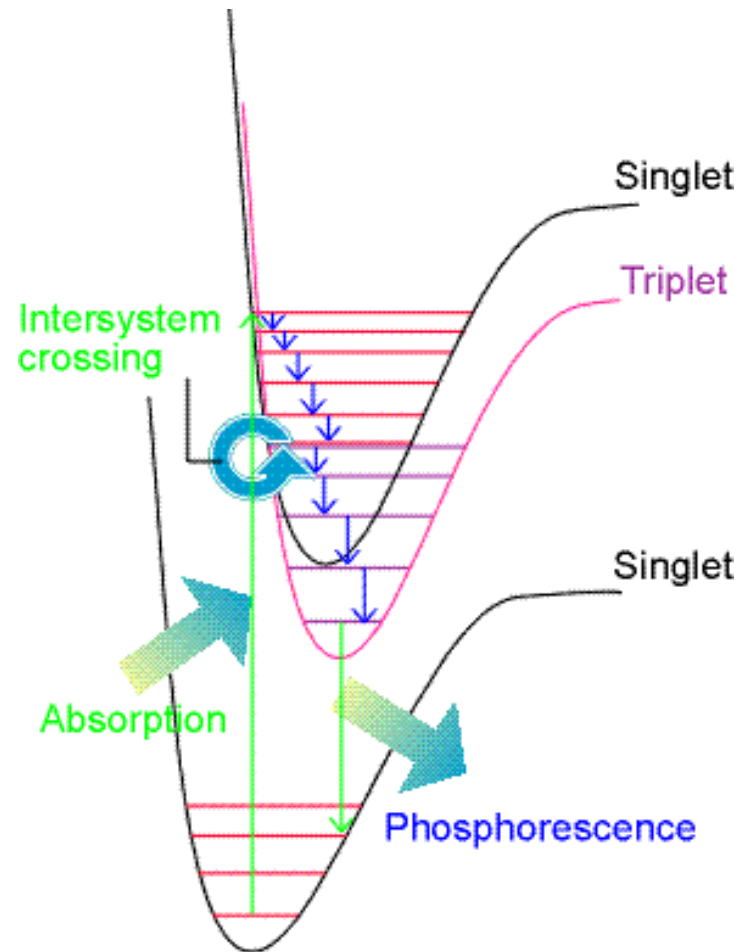
- Direct return to ground state after excitation
- “Fast” process
- Often involves frequency change due to radiationless decay through the upper manifold of states



From P. Atkins, Physical Chemistry

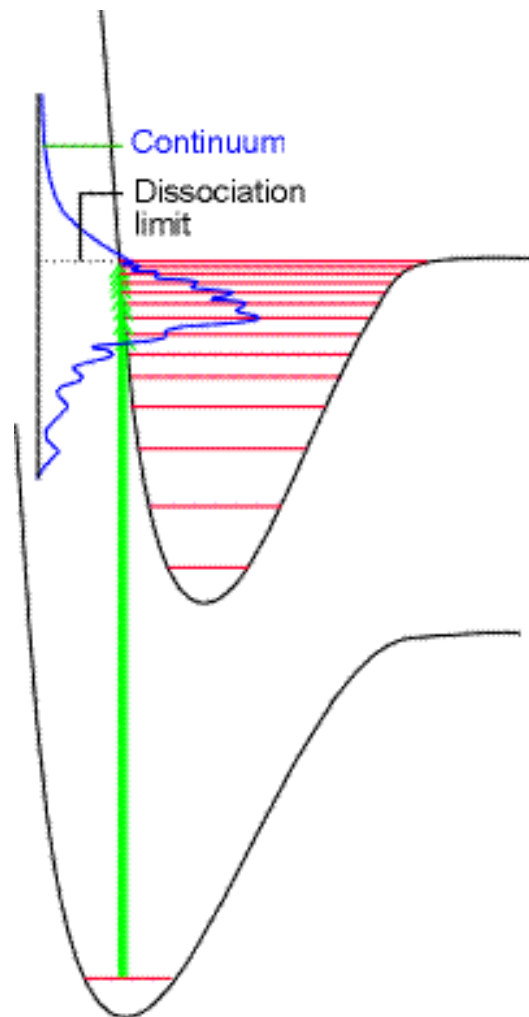
# Phosphorescence

- Emission after absorption
- Requires intersystem crossing
  - Often singlet-to-triplet change of state
  - Must have low-lying triplet state
    - Example: aromatic molecules
- Persists much longer than fluorescence



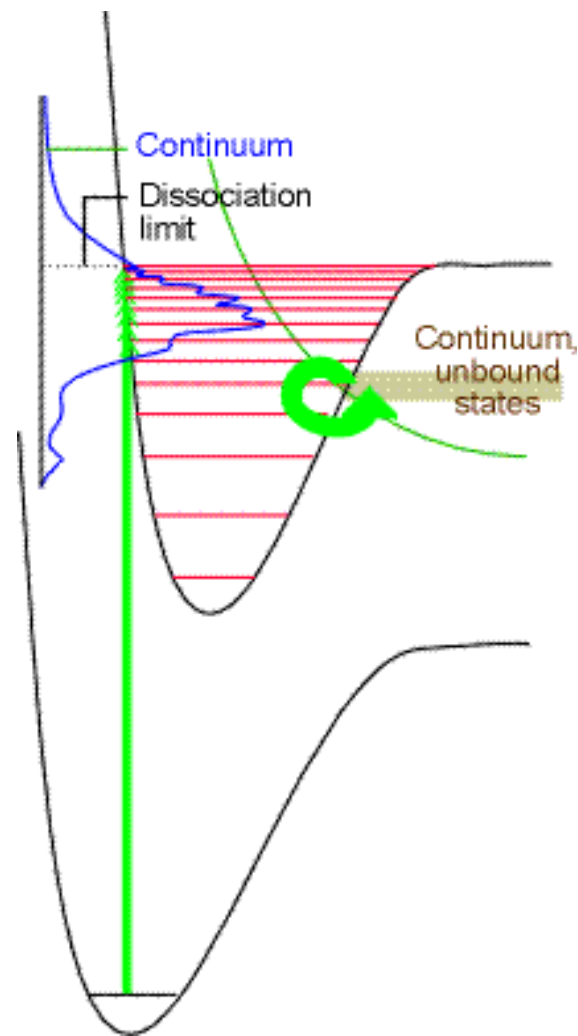
# Effect of continuum states

- The spectrum is discrete only if the energy structure is discrete
- Above a certain energy, transitions are into the continuum states
  - Gives a continuous energy absorption as a function of frequency



# Dissociation and Predissociation

- Unbound states have an effect on spectroscopy
- Absorption that puts the molecule in an unbound state results in **dissociation**
- Sometimes coupling of an unbound state to a bound state causes the appearance of continuum absorption -- **predissociation**



From P. Atkins, Physical Chemistry