



# **UV-Vis. Molecular Absorption Spectroscopy**

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## UV-Vis. Electronic Spectroscopy

- The interaction of molecules with ultraviolet and visible light may result in absorption of photons. This results in electronic transition, involving valence electrons, from ground state to higher electronic states (called excited states). The promoted electrons are electrons of the highest molecular orbitals HOMO.
- Absorption of ultraviolet and visible radiation in organic molecules is restricted to certain functional groups (known as chromophores) that contain valence electrons of low excitation energy.
- A **chromophore** is a chemical entity embedded within a molecule that absorbs radiation at the same wavelength in different molecules.
- Examples of Chromophores are dienes, aromatics, polyenes and conjugated ketones, etc.

## Types of electronic transitions

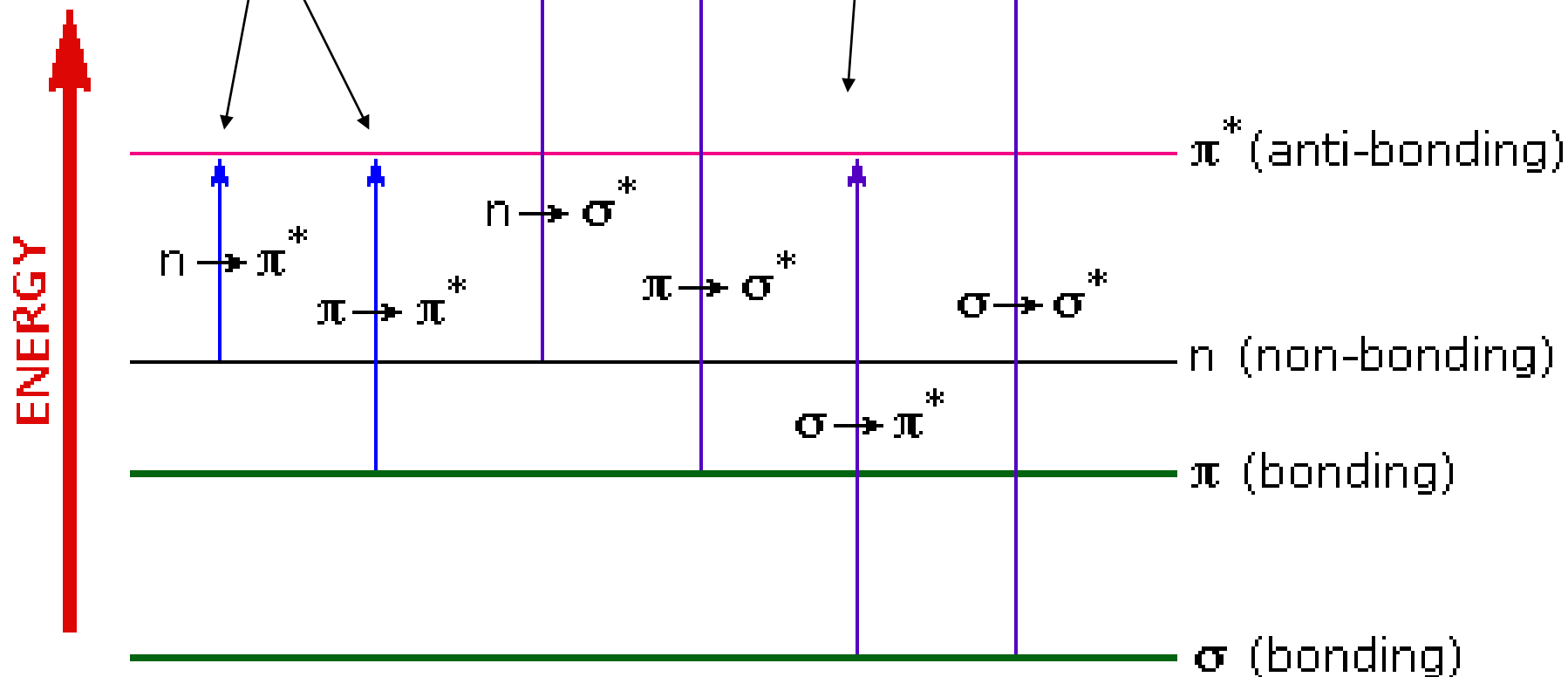
Electronic transitions that can take place are of three types which can be considered as;

- Transitions involving p-, s-, and n-electrons.
- Transitions involving charge-transfer electrons.
- Transitions involving d- and f-electrons in metal complexes.

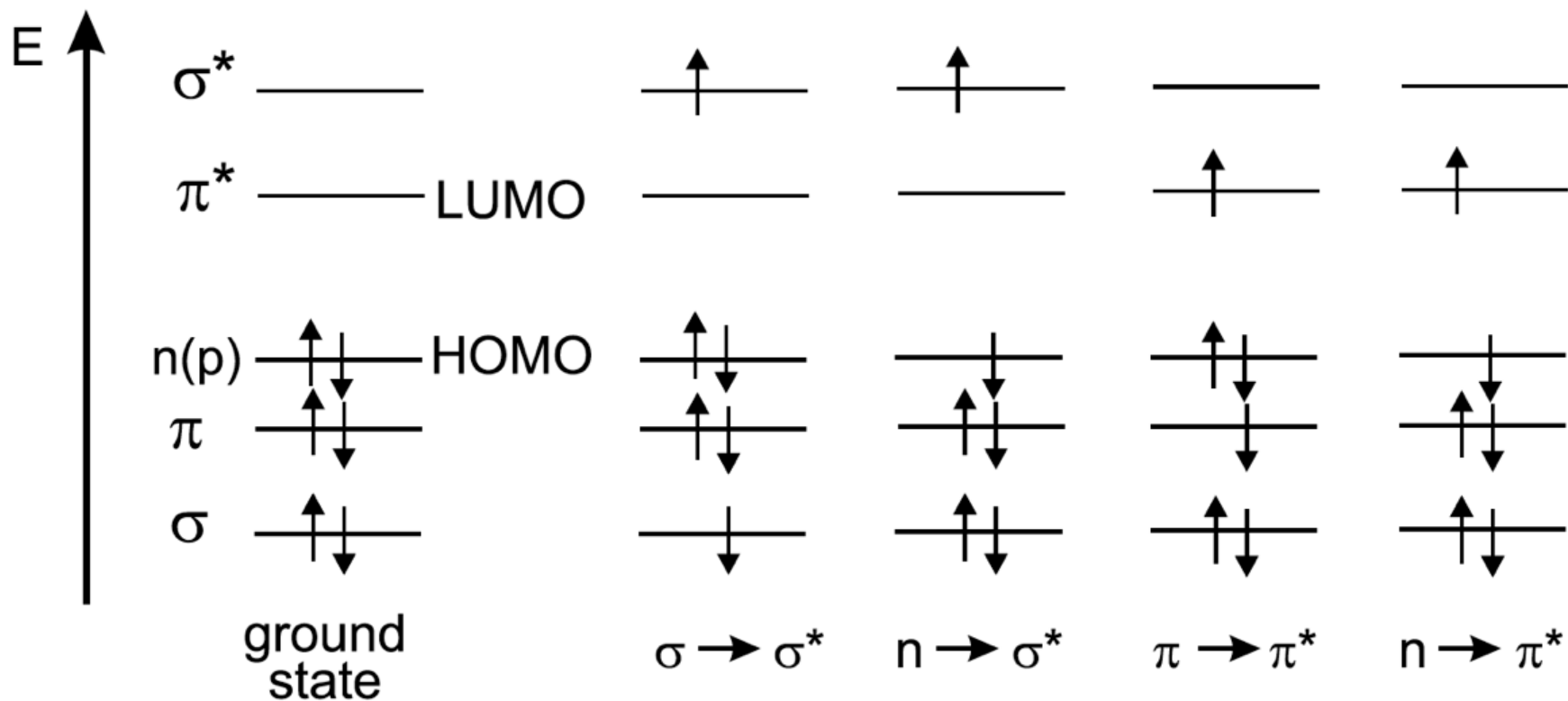
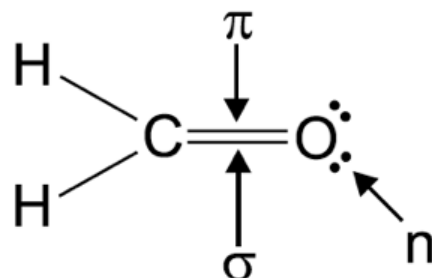
Most absorption spectroscopy of organic molecules is based on transitions of n- or  $\pi$ -electrons to the  $\pi^*$ -excited state. These transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm), and need an unsaturated group in the molecule to provide the  $\pi$ -electrons.

# In vacuum UV or far UV ( $\lambda < 190 \text{ nm}$ )

## In UV/VIS



# For formaldehyde molecule;



## Selection Rules of electronic transitions

Electronic transitions may be allowed or forbidden transitions, as reflected by appearance of an intense or weak band according to the magnitude of  $\epsilon_{\text{max}}$ , and is governed by the following selection rules :

1. Spin selection rule ( $\Delta S = 0$  for the transition to be allowed): there should be no change in spin orientation i. e no spin inversion takes place during these transitions. Thus, S→S, T→T are allowed, but S→T, T→S are forbidden transitions.
2. Laporte (orbital) selection rule ( $\Delta l = \pm 1$ ):
  - If the molecule has a centre of symmetry, transitions within a given set of p- or d-orbitals (i.e. those which only involve a redistribution of electrons within a given subshell) are forbidden.

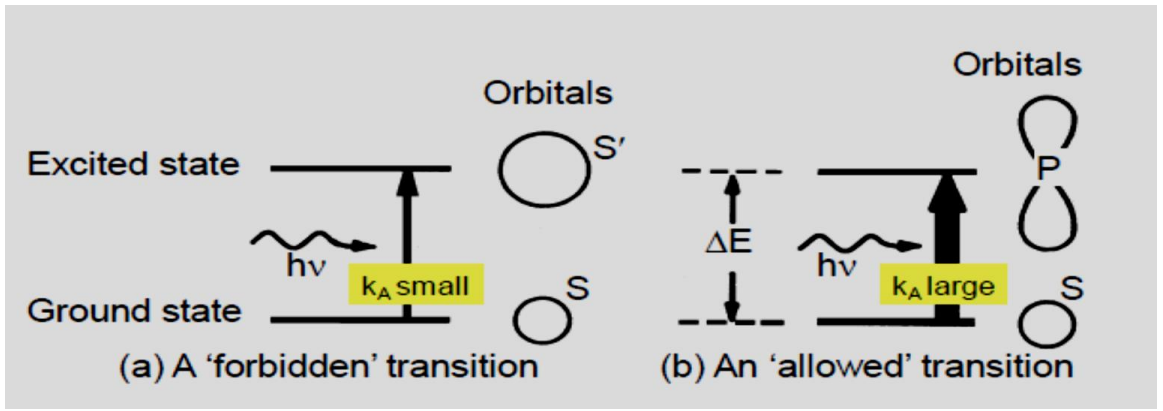
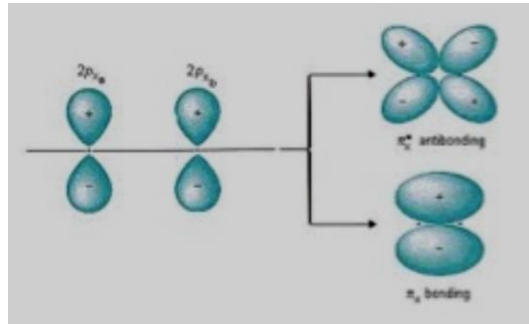
- There must be a change in the parity (symmetry), i.e. transition can occur only between states of opposite parity.


Laporte - allowed transitions:  $g \rightarrow u$  or  $u \rightarrow g$

Laporte - forbidden transitions:  $g \rightarrow g$  or  $u \rightarrow u$

$g$  stands for gerade – compound with a center of symmetry.  $u$  stands for ungerade – compound without a center of symmetry.

Thus,  $s \rightarrow p$ ,  $p \rightarrow d$  are allowed, but  $s \rightarrow s$ ,  $p \rightarrow p$  are forbidden.



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3.  $h\nu = \Delta E$  transition energy (photon matches energy gap between ground and excited state)
  4.  $\Delta \mu \neq 0$  (anisotropic charge displacement)

This selection rule tells us transitions which give no change in dipole moment are forbidden and hence will have almost zero intensity.

### **Selection rules can be relaxed due to:**

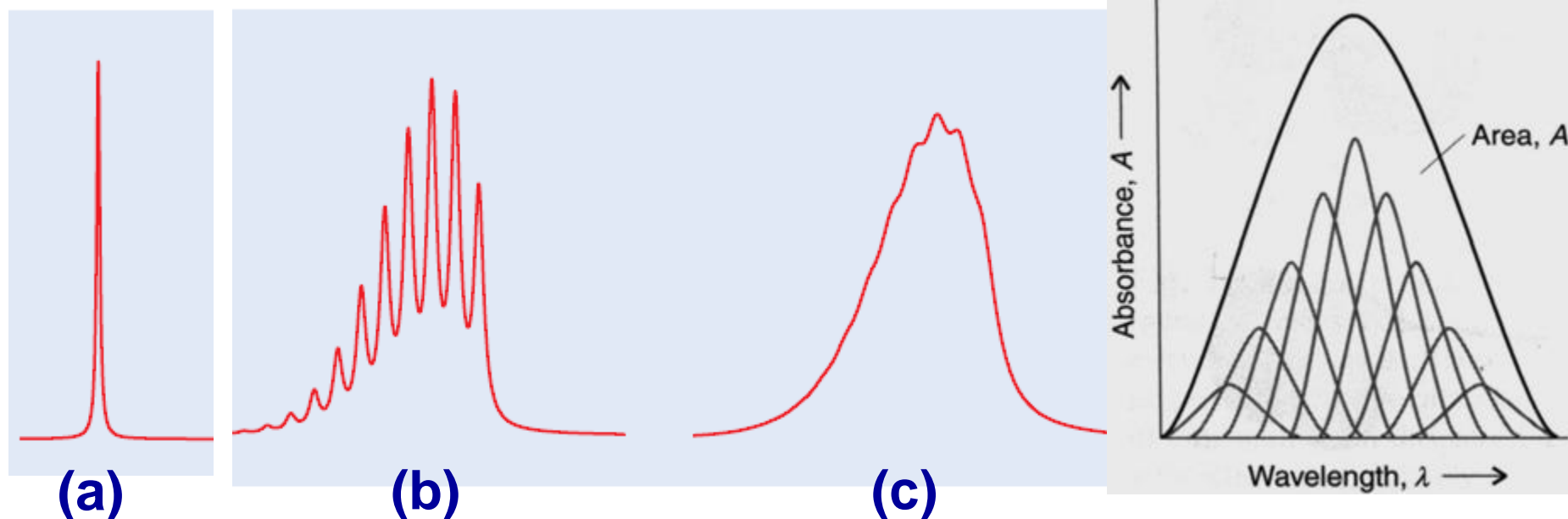
1. Spin-forbidden transitions may be relaxed by spin-orbit coupling effects that make spin a poor quantum number (heavy atom effects).
2. Symmetry-forbidden transitions may be relaxed by coupling of electronic transitions to vibrational transitions (vibronic coupling effect).



## Features of an Electronic Spectrum

- 1. The frequency, wavelength or energy of a transition;** it is related to the energy required to excite an electron (determines the colours of molecules).
- 2. The band width;** it is related to the vibrational excitation that accompanies the electronic transition.
  - *narrow bands:* excited state has similar geometry as the ground state
  - *broad bands:* excited state has different geometry to the ground state
- 3. The band intensity (height or area of a band);** it is related to the number of photons absorbed, and depends on: concentration, optical path length and the transition probability.

# UV-Visible Light Absorption in Polyatomic Molecules



The intensity of absorption for (a) an atom, (b) a diatomic molecule, and (c) a polyatomic molecule.

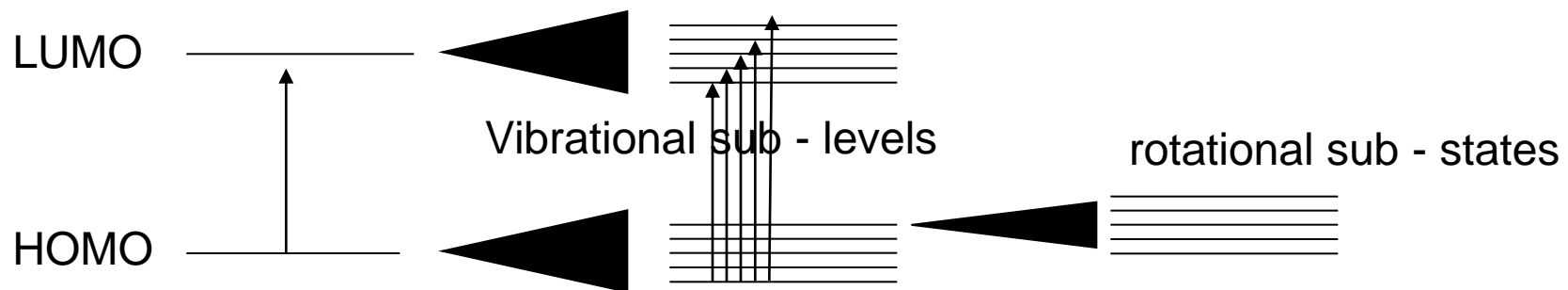
**Spectral lines:** individual transitions between two energy levels.

**Spectral bands:** simultaneous transitions between very close energy levels, thus, represent the sum of many spectral lines.

# Origin of bands in molecular spectra

- Molecules have chemical bonds which are electrons in molecular orbitals.
- Absorption of light photons causes electronic transitions between HOMO and LUMO
- Molecules undergo bond rotations and vibrations. Since different energy sub-levels are occupied at RT and accessible through absorption, many transitions are possible:

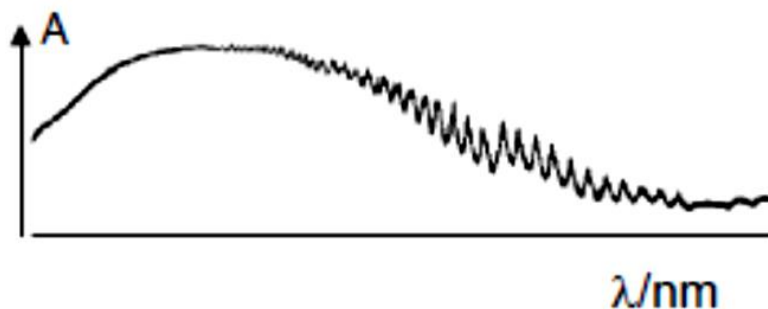
➔ A band is the sum of many lines



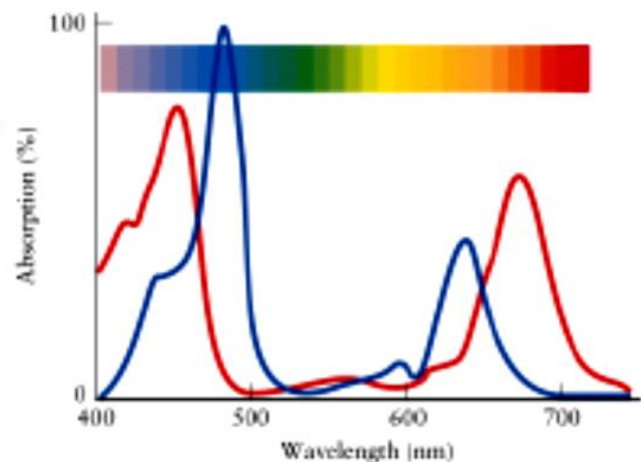
# Examples of electronic transitions for; a diatomic ( $I_2$ ) molecule, and a polyatomic (chlorophyll) molecule.

Vibrational structure of an electronic transition:

- in solutions > broad bands
- in gas phase > resolved vibrational structure.



Absorption spectrum of  $I_2$  molecule in gas phase.



Absorption spectra of chlorophylls a and b, the main pigments in the visible region of the electromagnetic spectrum.

# The vibrational fine structure of electronic transitions in diatomic molecules

## Born–Oppenheimer (BO) approximation

In quantum mechanics, the Born–Oppenheimer (BO) approximation is the assumption that the motion of the atomic nuclei and electrons in a molecule can be separated. In mathematical terms, it allows the wave function of a molecule to be broken into its electronic (vibrational, rotational) and nuclear components.

That is to say:  $E_{\text{total}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{nucl}}$

Where;

$E_{\text{elec}}$ : electronic;  $E_{\text{vib}}$ : vibrational ;  $E_{\text{rot}}$ : rotational; and

$E_{\text{nucl}}$ : nucleus spin, transitional energies.

# TYPES OF MOLECULAR ENERGIES AND BORN-OPPENHEIMER APPROXIMATION

A MOLECULE USUALLY POSSESSES FOUR DIFFERENT TYPES OF ENERGIES. THESE ARE...

- TRANSLATIONAL ENERGY
  - ROTATIONAL ENERGY
  - VIBRATIONAL ENERGY
  - ELECTRONIC ENERGY
- 
- ACCORDING TO BORN-OPPENHEIMER APPROXIMATION, THE TOTAL ENERGY OF A MOLECULE IS THE SUM OF TRANSLATIONAL , ROTATIONAL, VIBRATIONAL AND ELECTRONIC ENERGIES.

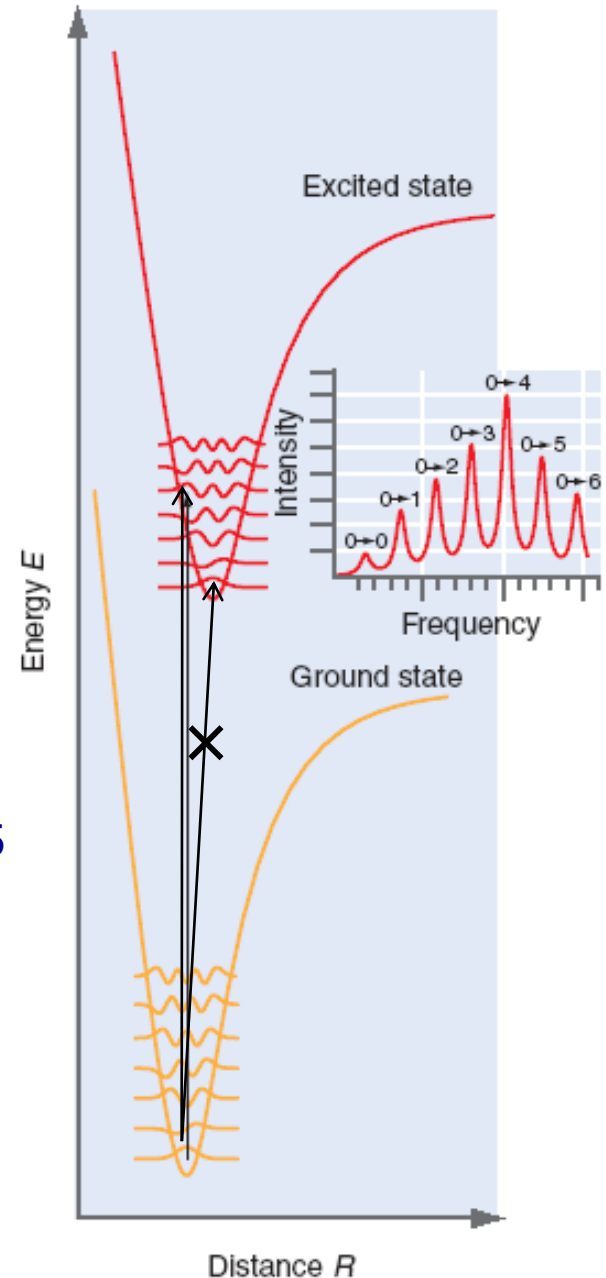
$$E = E_t + E_r + E_v + E_e$$

IT IS FOUND THAT THE TRANSLATIONAL ENERGY IS NEGLEGIBLY SMALL.SO

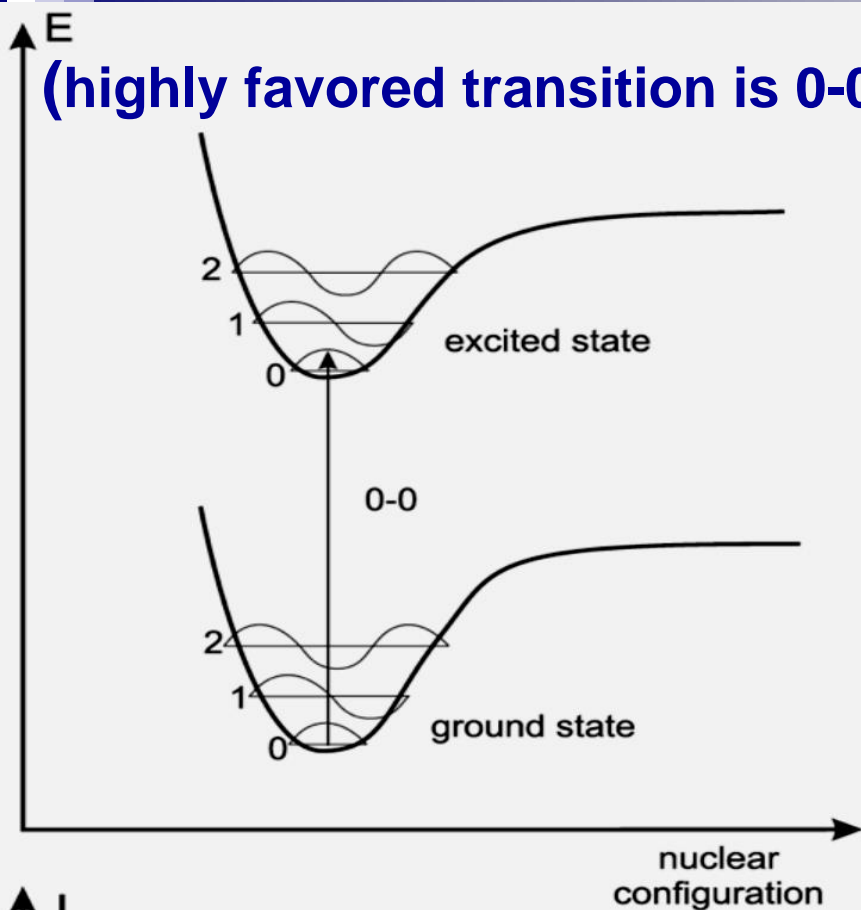
$$E = E_v + E_r + E_e$$

# Frank – Condon (FC) Principle

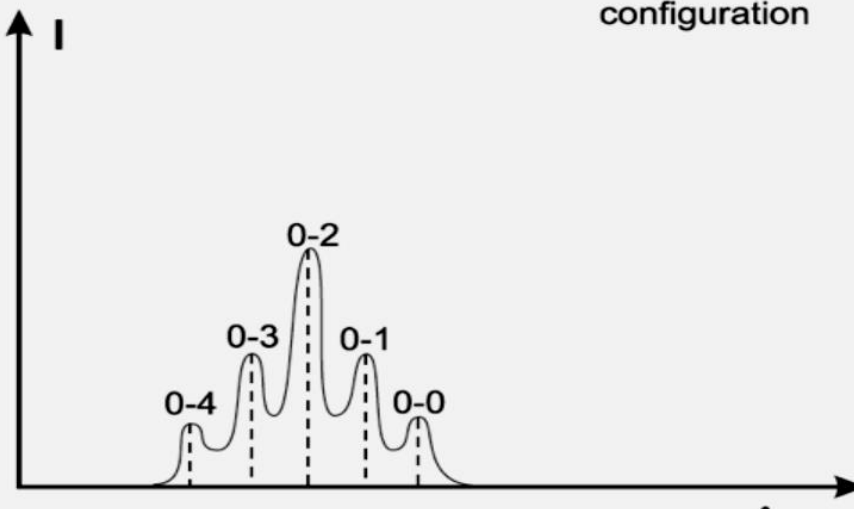
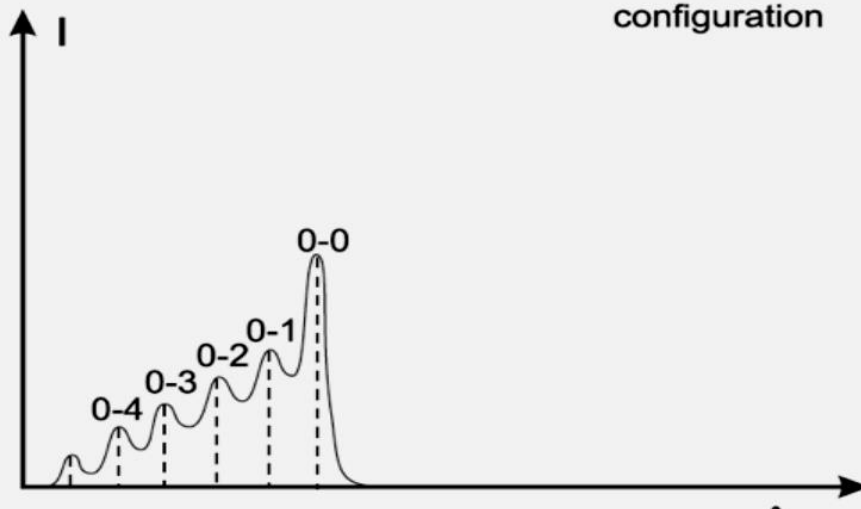
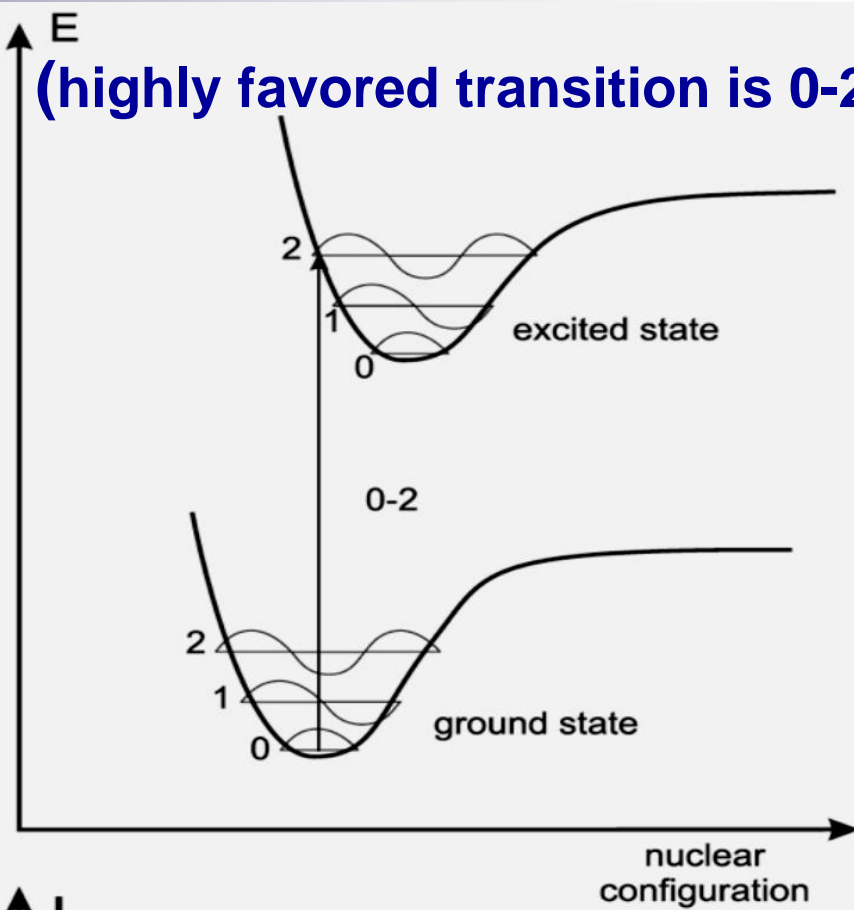
- It states that transitions between electronic states correspond to vertical lines on an energy versus inter-nuclear distance diagram.
  - Electronic transitions occur on a timescale that is very short compared to the vibrational period of a molecule.
  - The electronic transition is fast ( $10^{-15}$  s) with respect to nuclear motions ( $10^{-13}$  s).
- I. e transitions where the position and momentum of the nuclei don't change are favored.



(highly favored transition is 0-0)

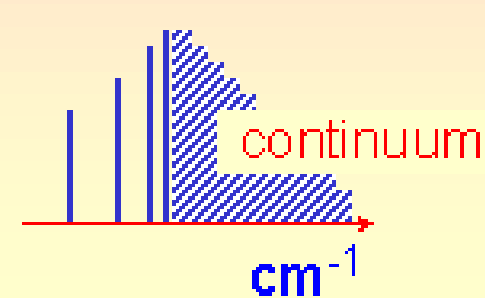
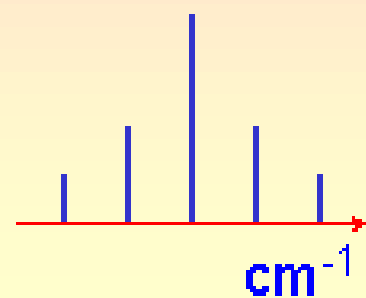
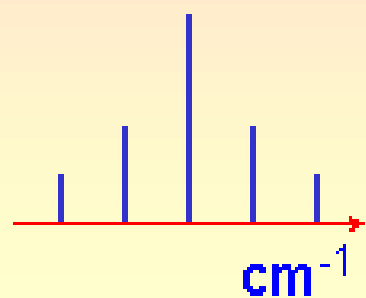
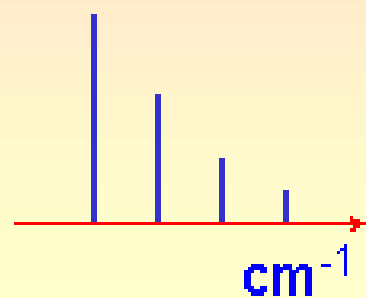
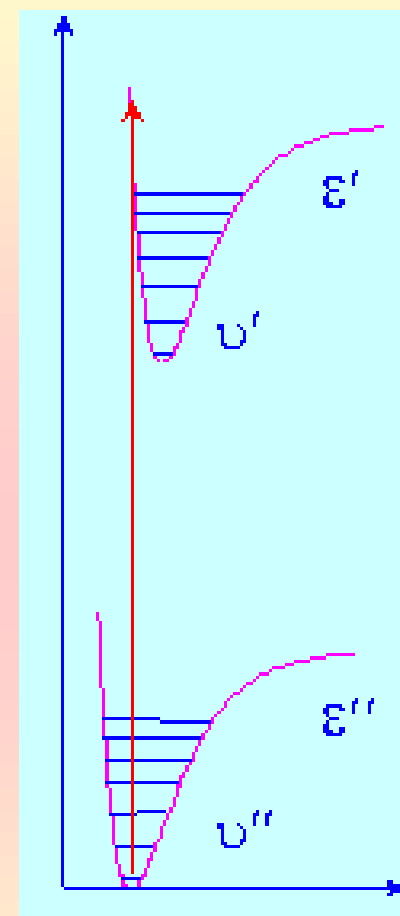
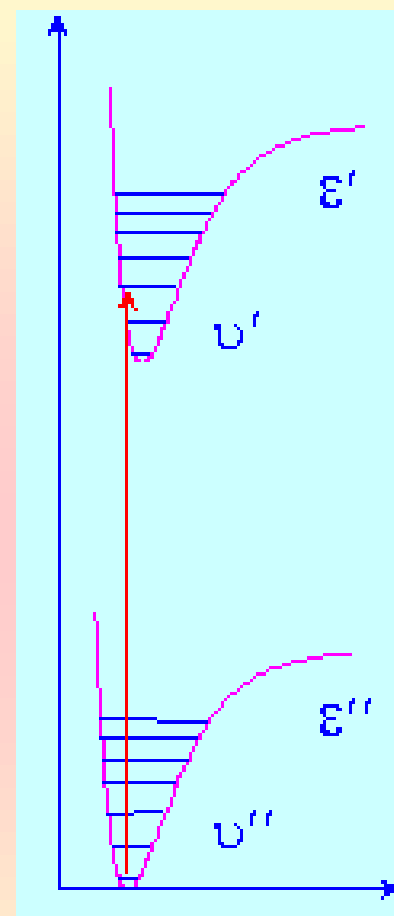
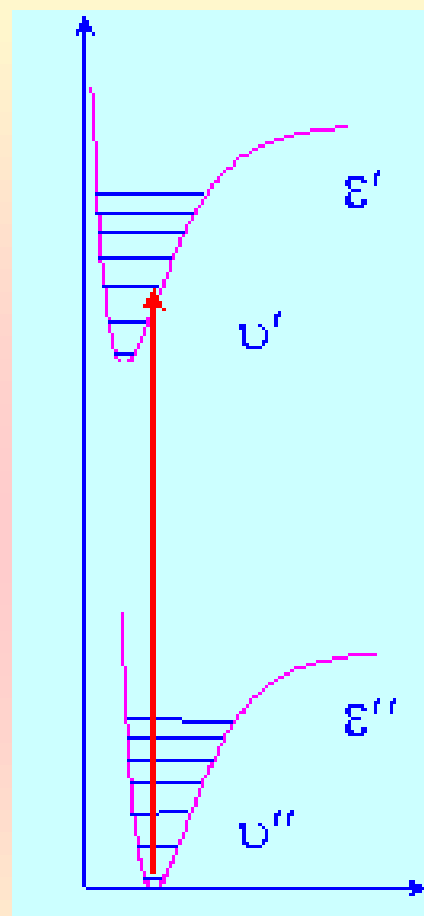
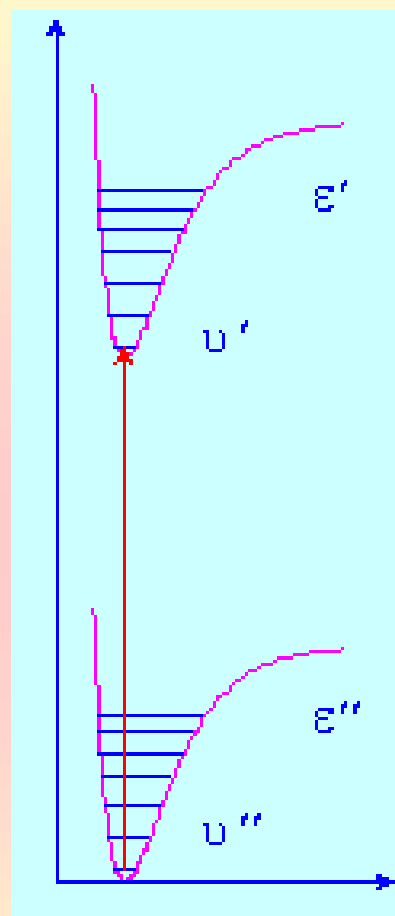


(highly favored transition is 0-2)



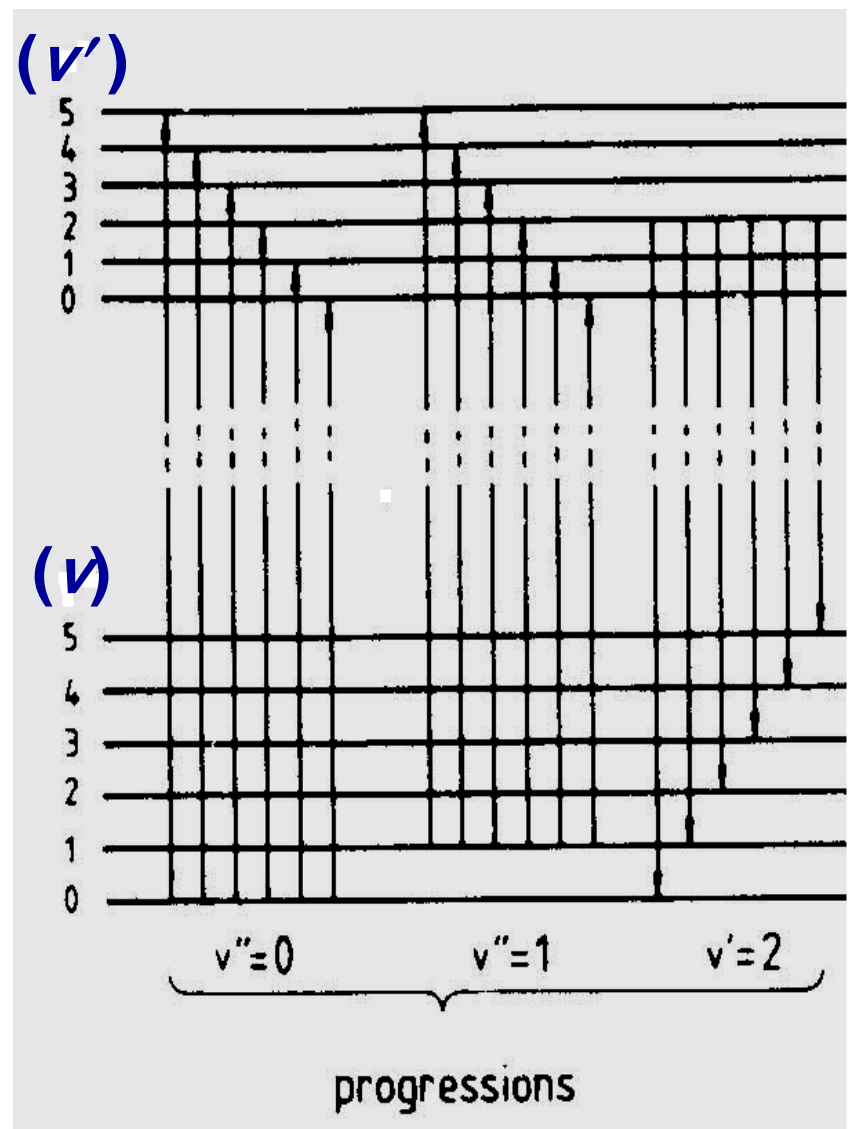


*Frank-Condon principle* governs the relative intensities of transitions between vibrational levels of different electronic states



# Progressions

- Represents a series of bands with a common lower vibrational level (have the same  $\nu$ , for absorption) or a common upper vibrational level (have the same  $\nu'$ , for emission).
- Bands are separated by  $\nu'$  for absorption or  $\nu$  for emission.
- An absorption spectrum reflects the vibrational levels of the electronically excited state.
- An emission spectrum reflects the vibrational levels of the electronic ground state

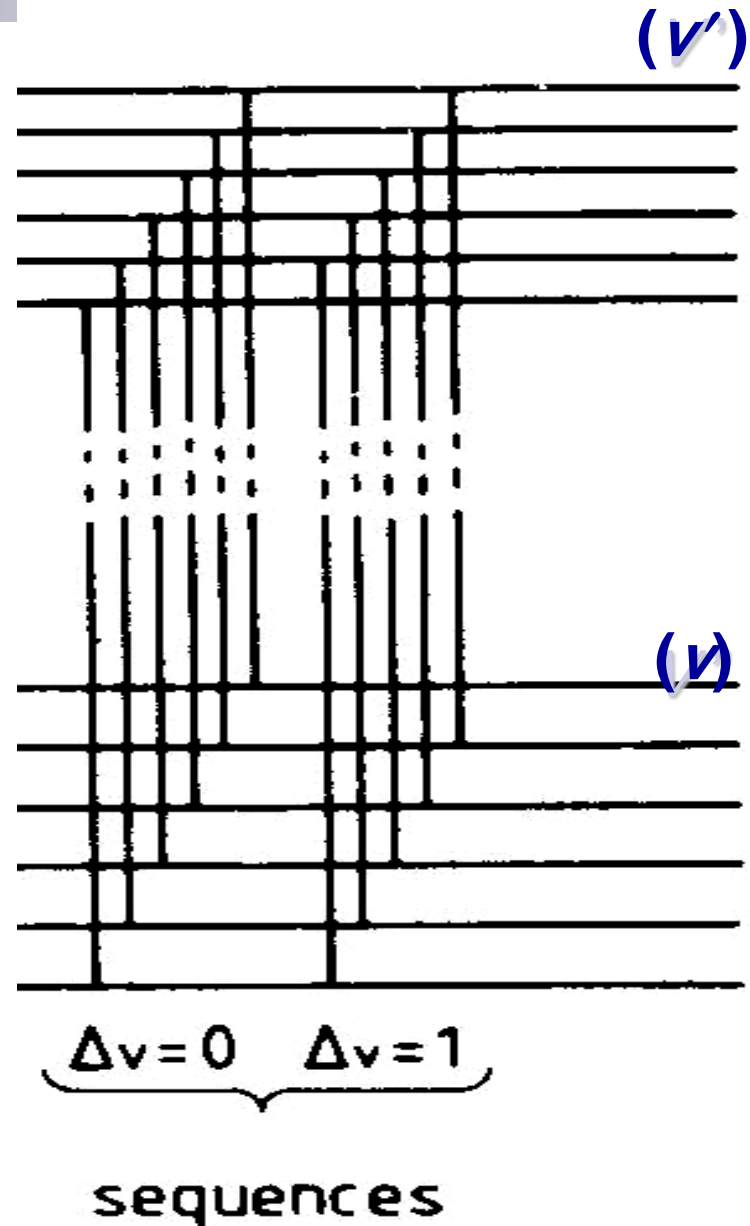


Electronic transitions involving vibrational levels with quantum numbers  $\nu$  and  $\nu'$

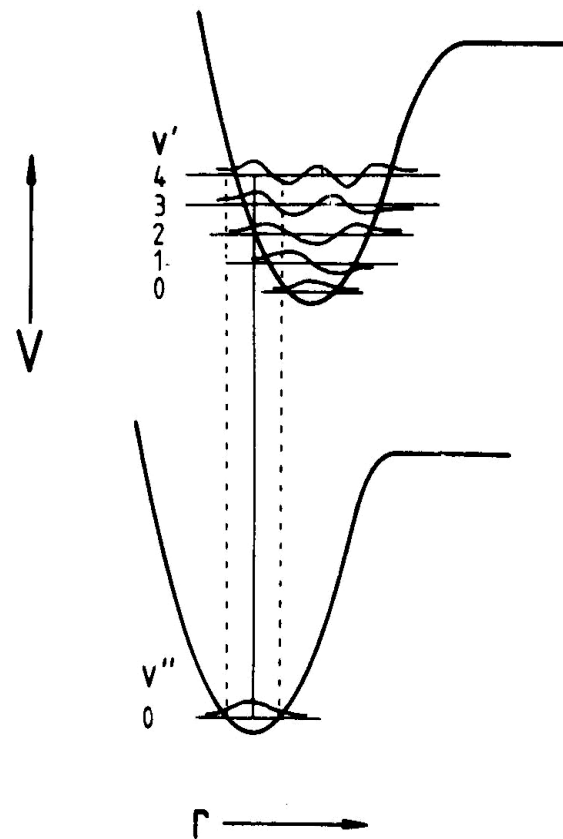
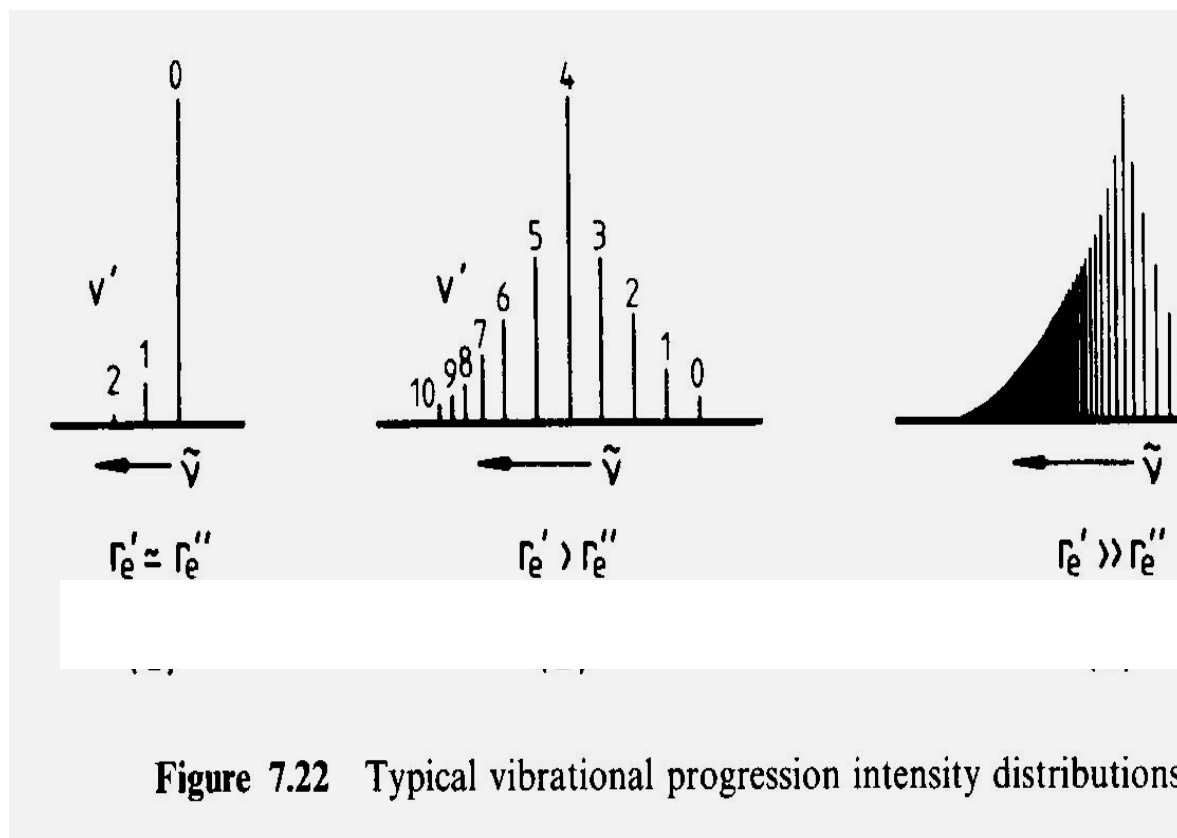
# Sequences

Represents a series of bands separated by  $(\nu' - \nu)$  with  $\Delta\nu$  is constant.

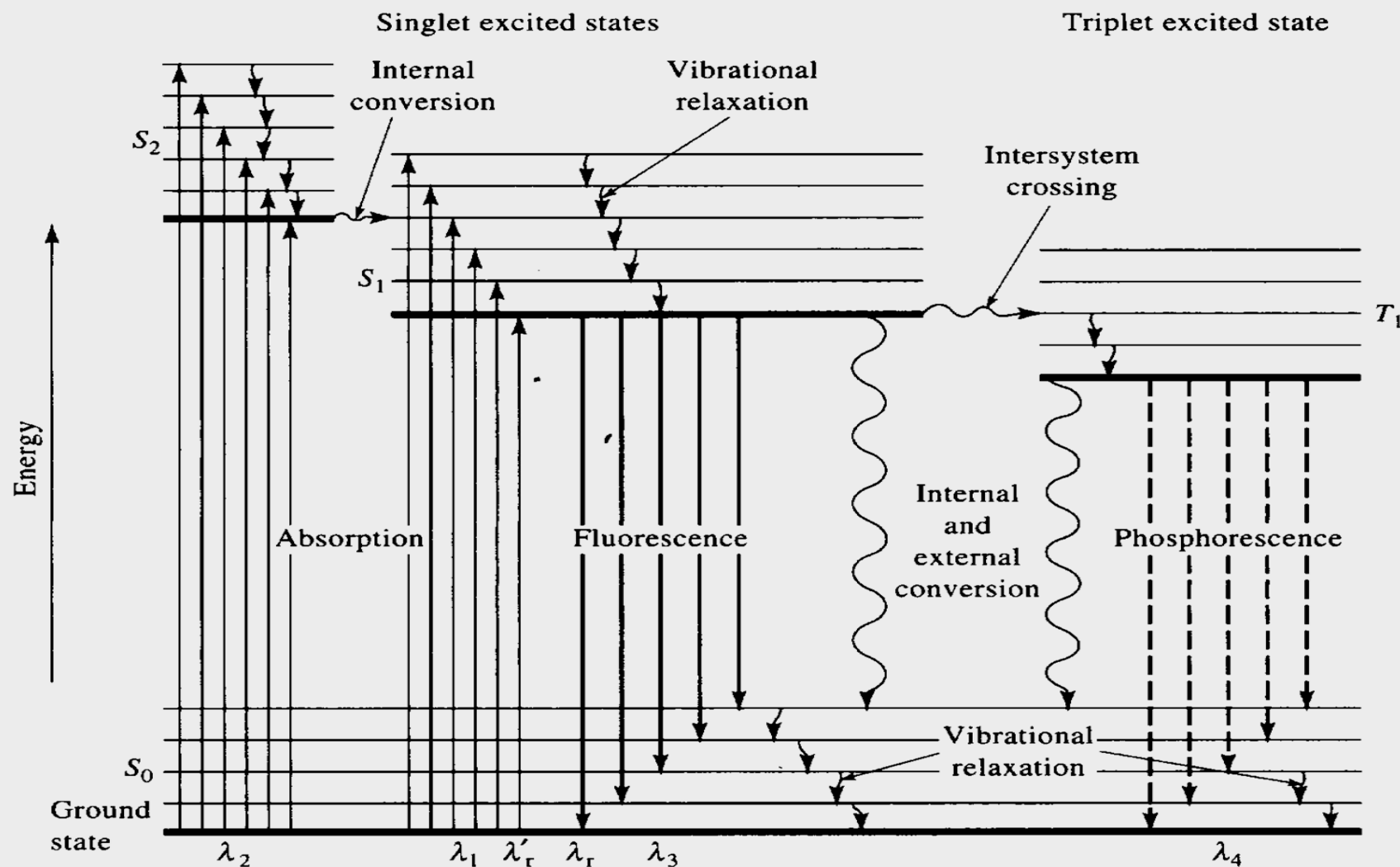
More commonly observed in emission spectra.



# What do the intensity patterns tell us about the allowed transitions?



# Transitions among the ground and excited states (The Jablonski Diagram)



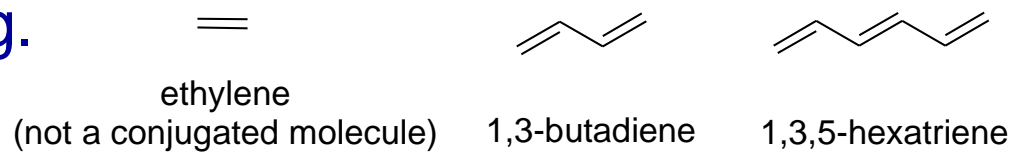
**Figure 15-1** Partial energy diagram for a photoluminescent system.

# Factors affecting electronic transitions:

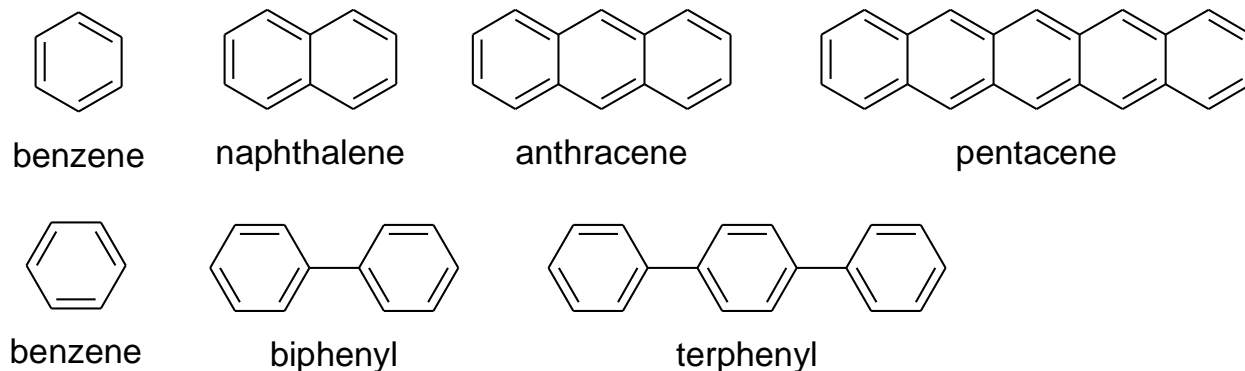
## 1. Molecular structure:

### ■ $\pi$ -Conjugated Molecules

- Numerous examples from organic and biological chemistry (e.g.  $\beta$ -carotene, 11 conjugated double bonds; chromophore responsible for color vision; etc.
- Molecules composed of alternating single and double (or tripl)e bonds e.g.

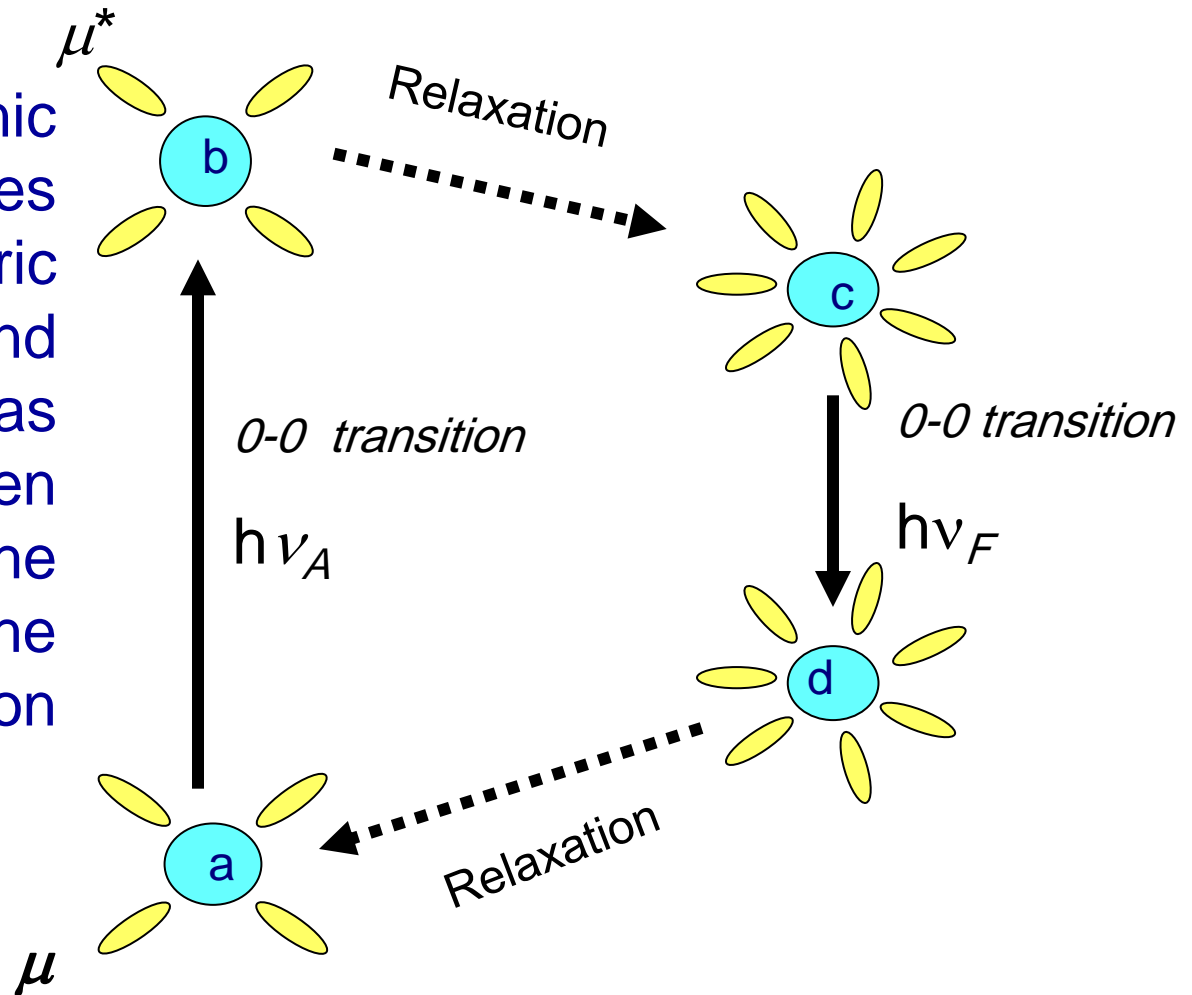


All will have different electronic spectra due to differences in molecular structures.

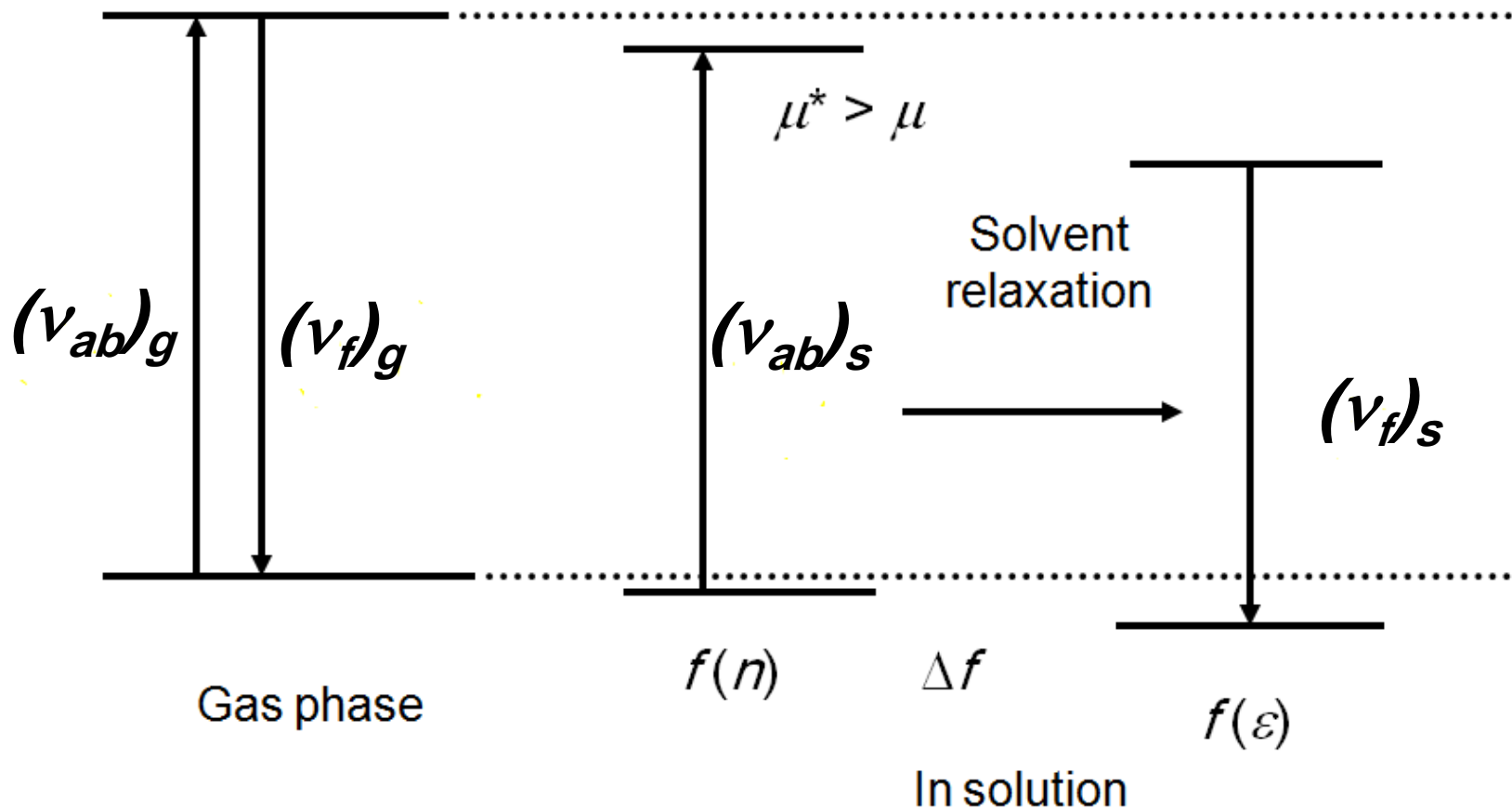


## 2. General solvent effects

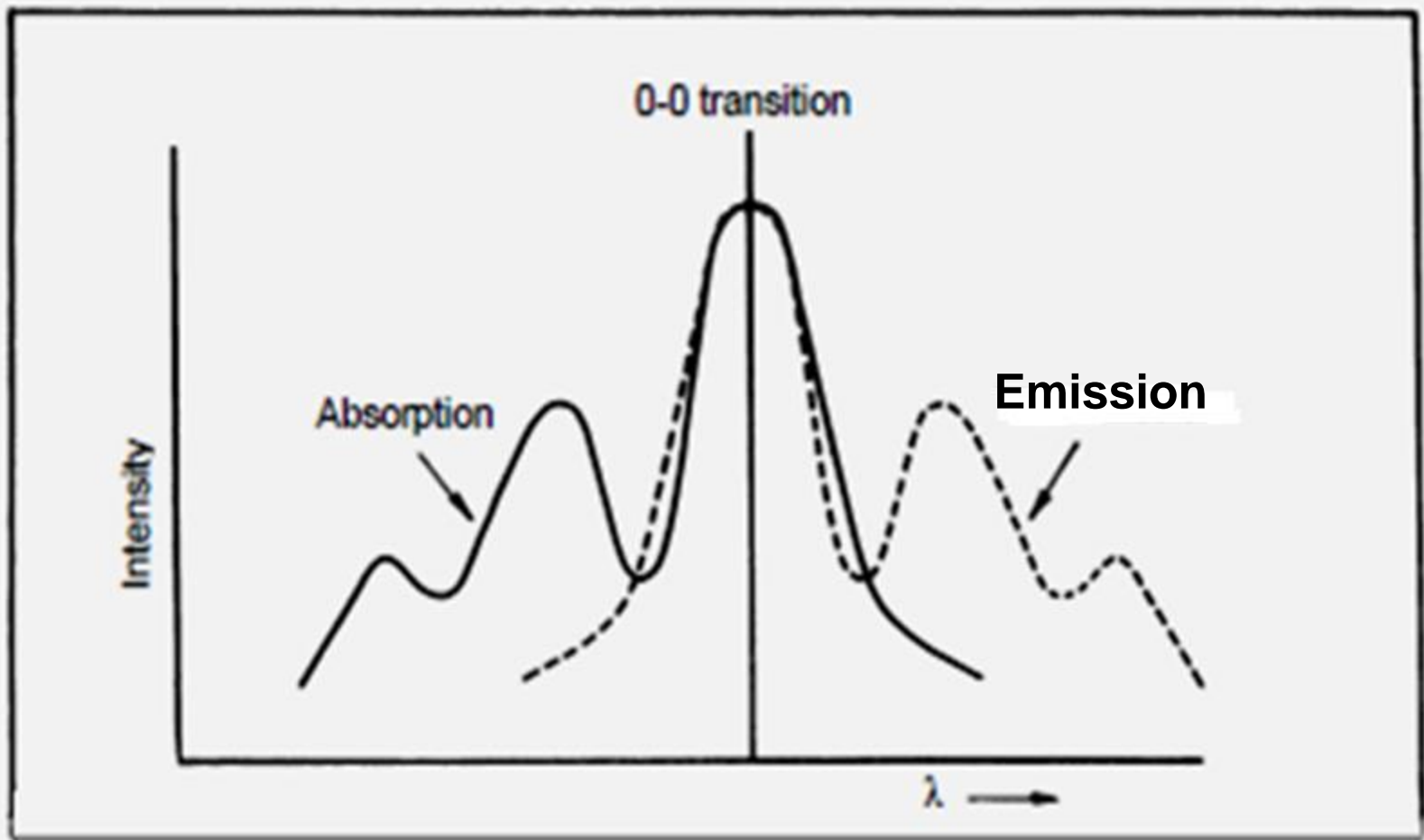
Solvents affect electronic spectra due to changes of their polarity (dielectric constant,  $f(\epsilon)$ , and refractive index,  $f(n)$ ) as well as hydrogen bonding, by changing the probability and the energy of both absorption and emission



Solvents affect electronic spectra through their ability to stabilize ground and excited states differently, thereby changing the probability and the energy of both absorption and emission

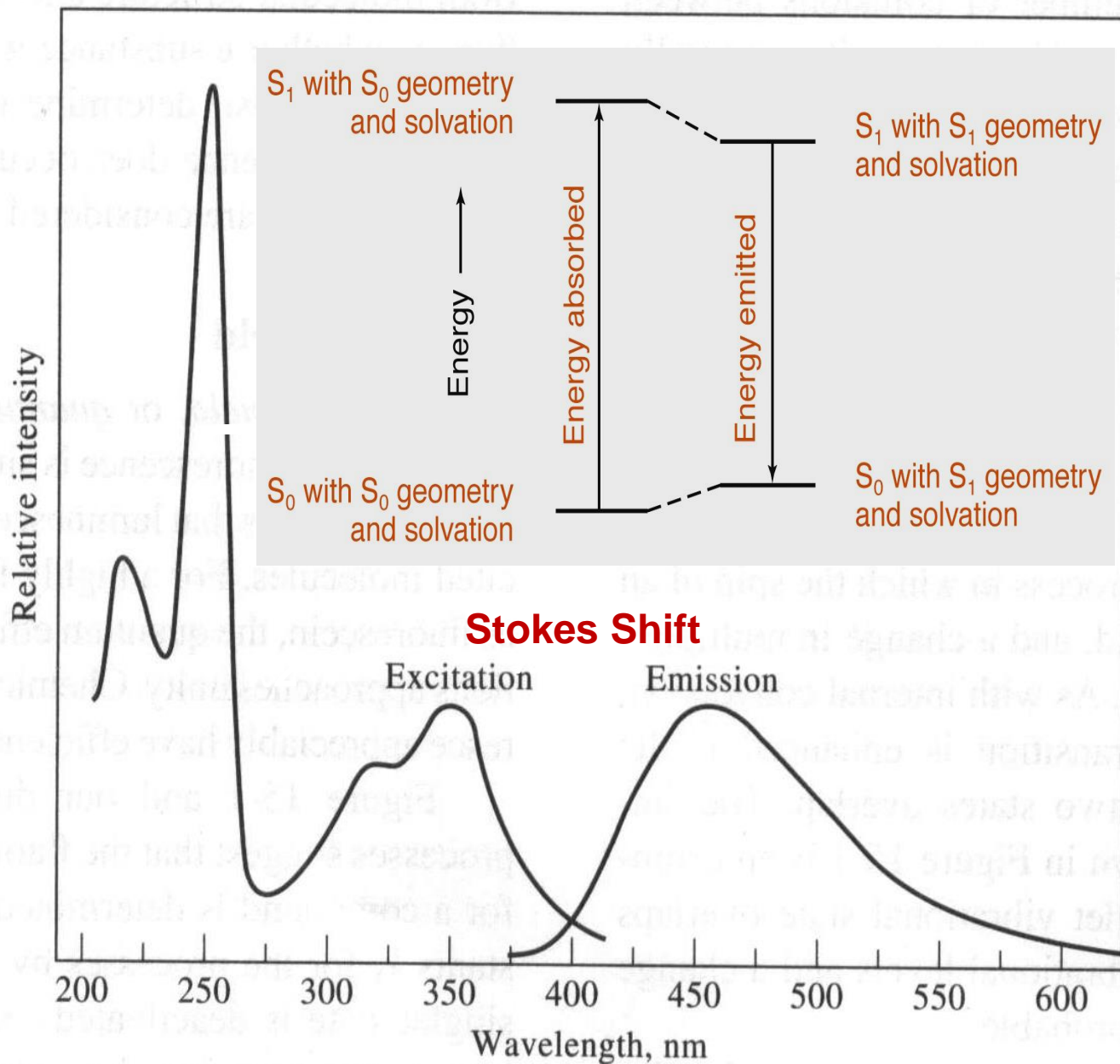




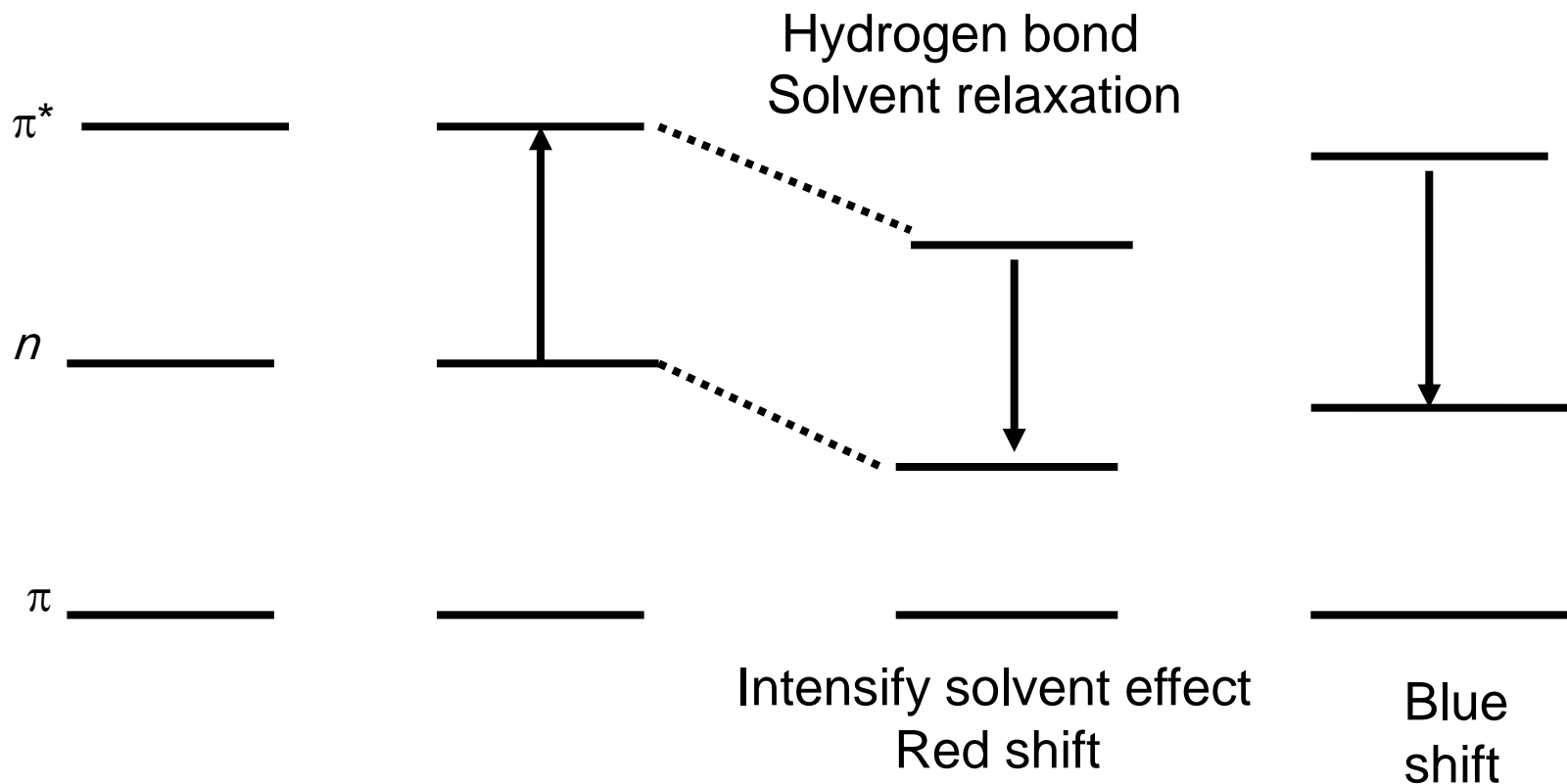


**Figure 2** Idealised absorption and emission spectra

Diagram showing why the transitions do not exactly overlap and there will be a Stokes shift.



# ● Effects on $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition



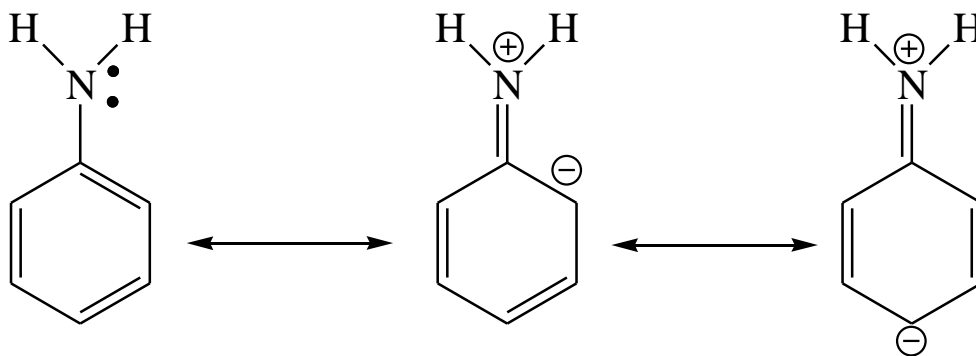
In  $n \rightarrow \pi^*$  transitions as the solvent polarity increases. Solvation stabilizes the nonbonding pair (blue shift).

In  $\pi \rightarrow \pi^*$  transitions as the solvent polarity increases. Solvation stabilizes  $\pi^*$ , which is often more polar than  $\pi$  (red shift).

### 3- Viscosity and pH Effects:

- increasing viscosity leads to increasing of band intensity and formation of vibrational structures of bands due to decreasing of molecular collisions.
- Electronic transitions are pH dependent for compounds with acidic or basic substituents.

Changes in pH influence the degree of ionization, which, in turn, may affect the extent of conjugation or the aromaticity of the compound.



**resonance forms of aniline more resonance forms stabilize excited state**

## Terms describing UV-Vis. absorptions

1. Chromophores: functional groups that is responsible for electronic transitions (Group will have a characteristic  $\lambda_{\max}$  and  $\epsilon_{\max}$ ). Molecular structure or environment can influence  $\lambda_{\max}$  and  $\epsilon$ .
2. Auxochromes: substituents with unshared pair of electrons like OH, NH, SH ..., when attached to  $\pi$  chromophore they generally move the absorption max. to longer  $\lambda$ .
3. Bathochromic shift: shift to longer  $\lambda$ , (red shift).
4. Hypsochromic shift: shift to shorter  $\lambda$ , (blue shift).
5. Hyperchromic effect: increase in  $\epsilon_{\max}$  of a band.
6. Hypochromic effect: decrease in  $\epsilon_{\max}$  of a band.