



CHEM F111 : General Chemistry

Semester I: AY 2017-18

Lecture-16, 16-02-2018

EXTRA CLASS NOTICE

TUTORIAL SECTION 6

DATE: Friday 16th Feb 2018

TIME: 5.00pm

VENUE: Room No. 3249

TUTORIAL SECTION 10

DATE: Friday 19th Feb 2018

TIME: 5.00pm

VENUE: Room No. 3250

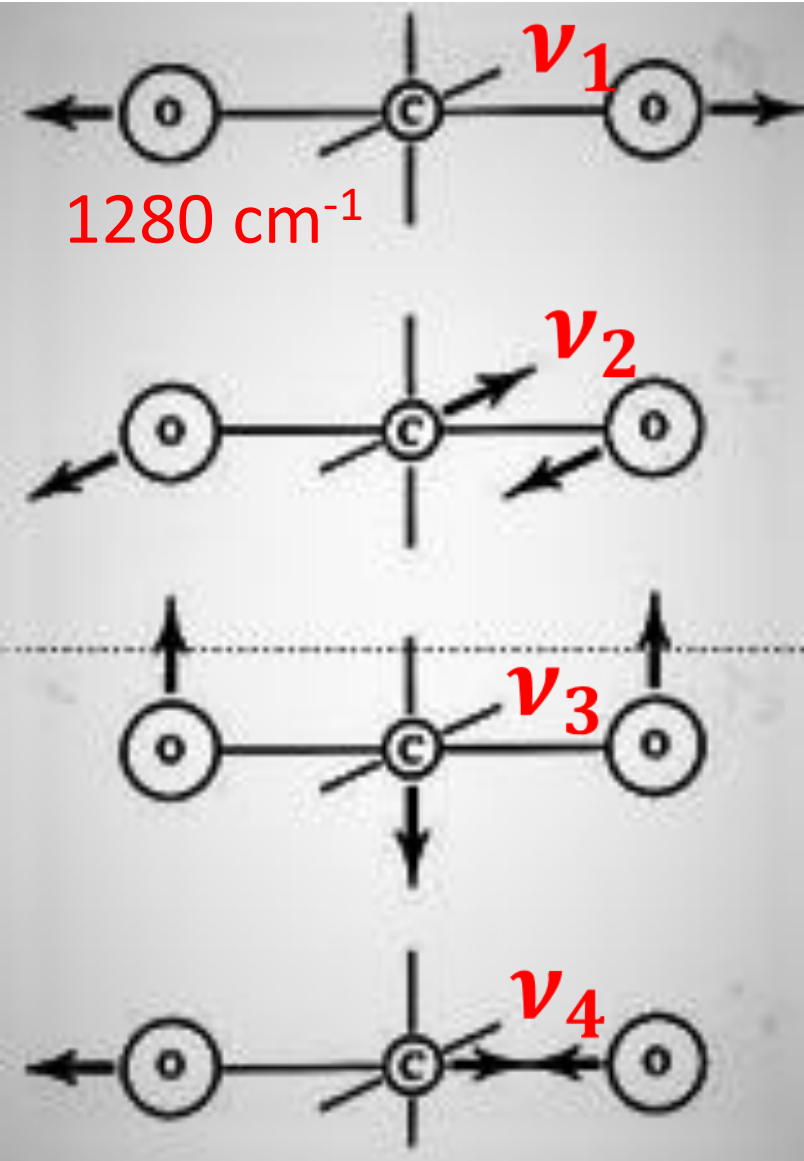
TUTORIAL SECTIONs 7 & 11

DATE: Friday 16th Feb 2018

TIME: 5.15pm

VENUE: Room No. 6101

L-15:Vibrational transitions in CO₂



$$\psi_1(0)\psi_2(0)\psi_3(0)\psi_4(0)$$

$$\nu_2 \& \nu_3 \downarrow 580 \text{ cm}^{-1}$$

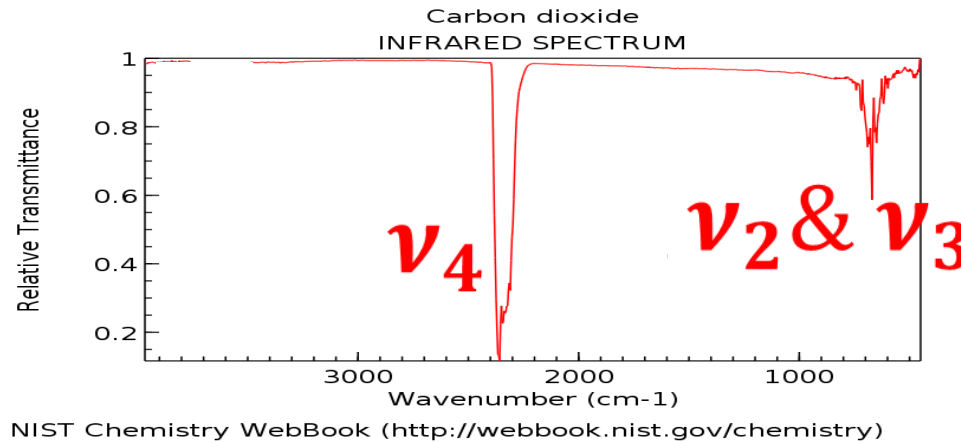
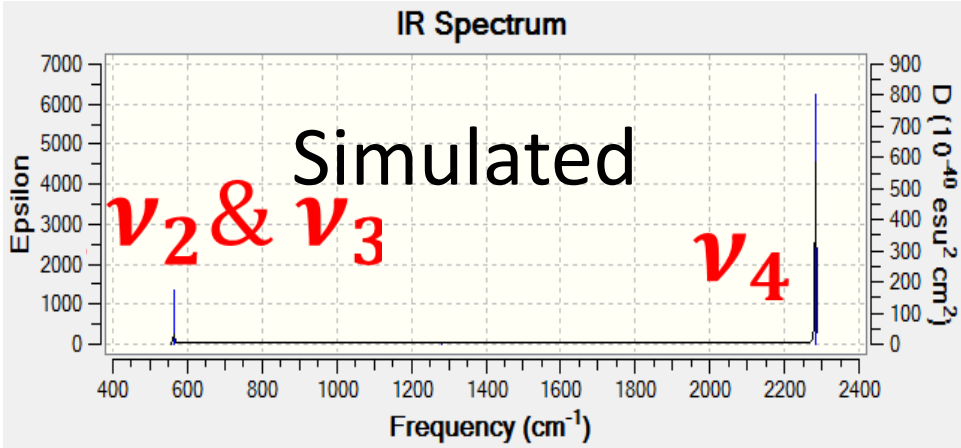
$$\psi_1(0)\psi_2(1)\psi_3(1)\psi_4(0)$$

$$\psi_1(0)\psi_2(0)\psi_3(0)\psi_4(0)$$

$$\nu_4 \downarrow 2200 \text{ cm}^{-1}$$

$$\psi_1(0)\psi_2(0)\psi_3(0)\psi_4(1)$$

$$\Psi_{vib} = \psi_1(\nu_1)\psi_2(\nu_2)\psi_3(\nu_3)\psi_4(\nu_4)$$

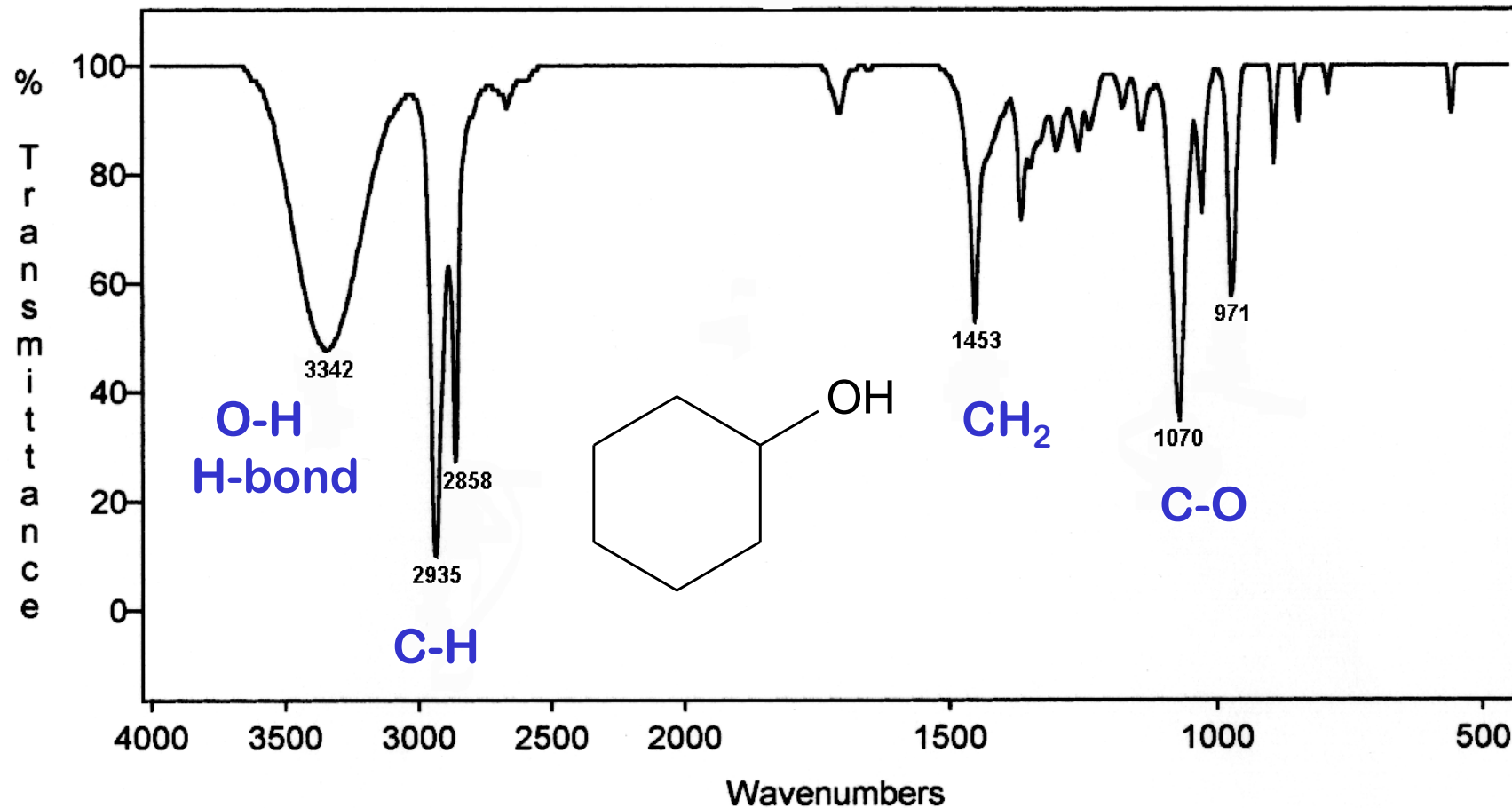


L-15: Interpreting IR spectra

O-H stretching: $\sim 3600\text{ cm}^{-1}$ for alcohols;

broadens and lowers to 3300 cm^{-1} due to H-bonding in alcohols, acids, etc.

How to distinguish between intramolecular and intermolecular H-bonding?



Vibrational Raman



Polarizability must change with some displacement coordinate of vibration (q), $\frac{d\alpha}{dq} \neq 0$

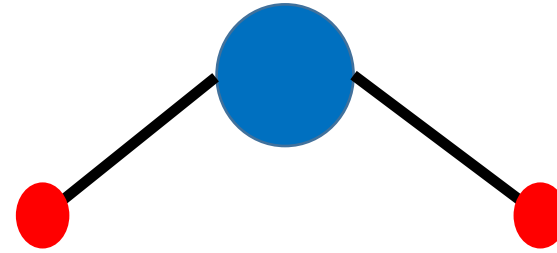
For stretching vibration q is a measure of extension (+ q) and compression (- q) of the bond from equilibrium position.

Consider symmetric stretch of CO_2 :

Near equilibrium position, $\frac{d\alpha}{dq} \neq 0$

Raman active

CO₂ is having inversion symmetry (i)



Can we draw any conclusion??

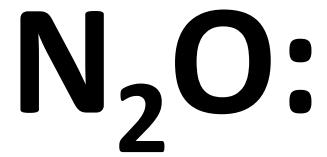
CO₂:

Symmetric stretching: Raman active & IR inactive

Bending: Raman inactive and IR active

Asymmetric stretching: Raman inactive and IR active

Vibrational Raman – more examples



Does not have 'i'

Wavenumber	IR	Raman
589	Active	Inactive?
1285	Active	Active
2224	Active	Active

Conclusion:

1. If a molecule does not exhibit any common lines in Raman and IR-spectra – molecule must have center of symmetry
2. If a molecule does exhibit common transitions in Raman and IR spectrum – molecule does not contain any center of symmetry.

What about SO_2 ??

All three fundamental vibrations are Raman and IR active.

Work out



Assume you are working in a molecular spectroscopy laboratory which is equipped with instruments to perform four major spectroscopic measurement techniques, namely, (i) Rotational spectroscopy, (ii) Rotational Raman spectroscopy, (iii) Vibrational spectroscopy, and (iv) Vibrational Raman spectroscopy. You have been assigned to determine the molecular structure of hydrogen peroxide (H_2O_2). You may know already that H_2O_2 may exist in the form of three different Conformers depending on the dihedral angle ($d_\theta = \angle\text{H-O-O-H}$). Dihedral angles of those three conformers are $d_\theta = 0^\circ$ (Conformer-I), $d_\theta = 80^\circ$ (Conformer-II), and $d_\theta = 180^\circ$ (Conformer-III). You may use any one of the above mentioned spectroscopic techniques to determine the structure of the three conformers. Choice is yours but that should be logical and less complicated. In general, scattering experiment is challenging and complicated compared to techniques based on absorption/transmission mode. You have also recorded vibrational and vibrational Raman spectra of H_2O_2 :

Mode description	Vibration (cm^{-1}), H_2O_2	Raman (cm^{-1}), H_2O_2
ν_1	3607	3606
ν_2	-	1393
ν_3	-	863
ν_4	317	-
ν_5	3608	-
ν_6	1266	-

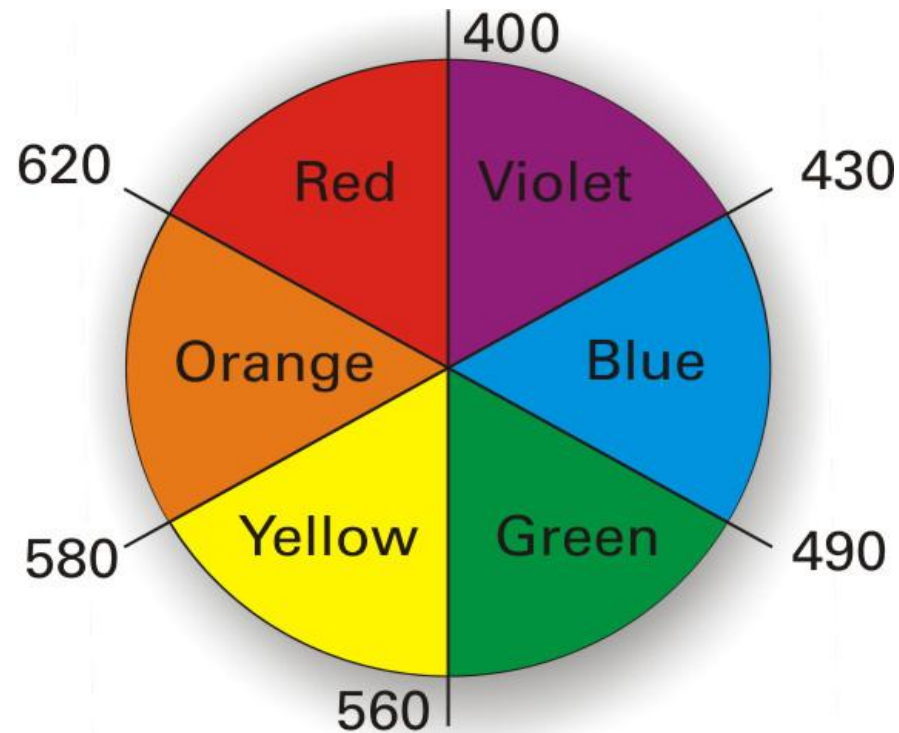
- 1) Identify spectroscopic technique to determine the structure of a) Conformer-I, b) Conformer-II, and c) Conformer-III. Justify your choice .
- 2) Identify possible conformers of H_2O_2 which/those are responsible for the observed vibrational and vibrational Raman spectra. Justify your answer.
- 3) ν_1 and ν_3 modes represent stretching vibration for H_2O_2 molecule. The corresponding transitions in D_2O_2 are 2669 cm^{-1} (ν_1) and 867 cm^{-1} (ν_3). Identify with justification ν_1 and ν_3 modes of H_2O_2 .

Electronic Transitions



Occur in the visible (400 to 700 nm) and ultraviolet (200 to 400 nm) regions of spectrum.

Responsible for the colour of many objects, many photochemical reactions.

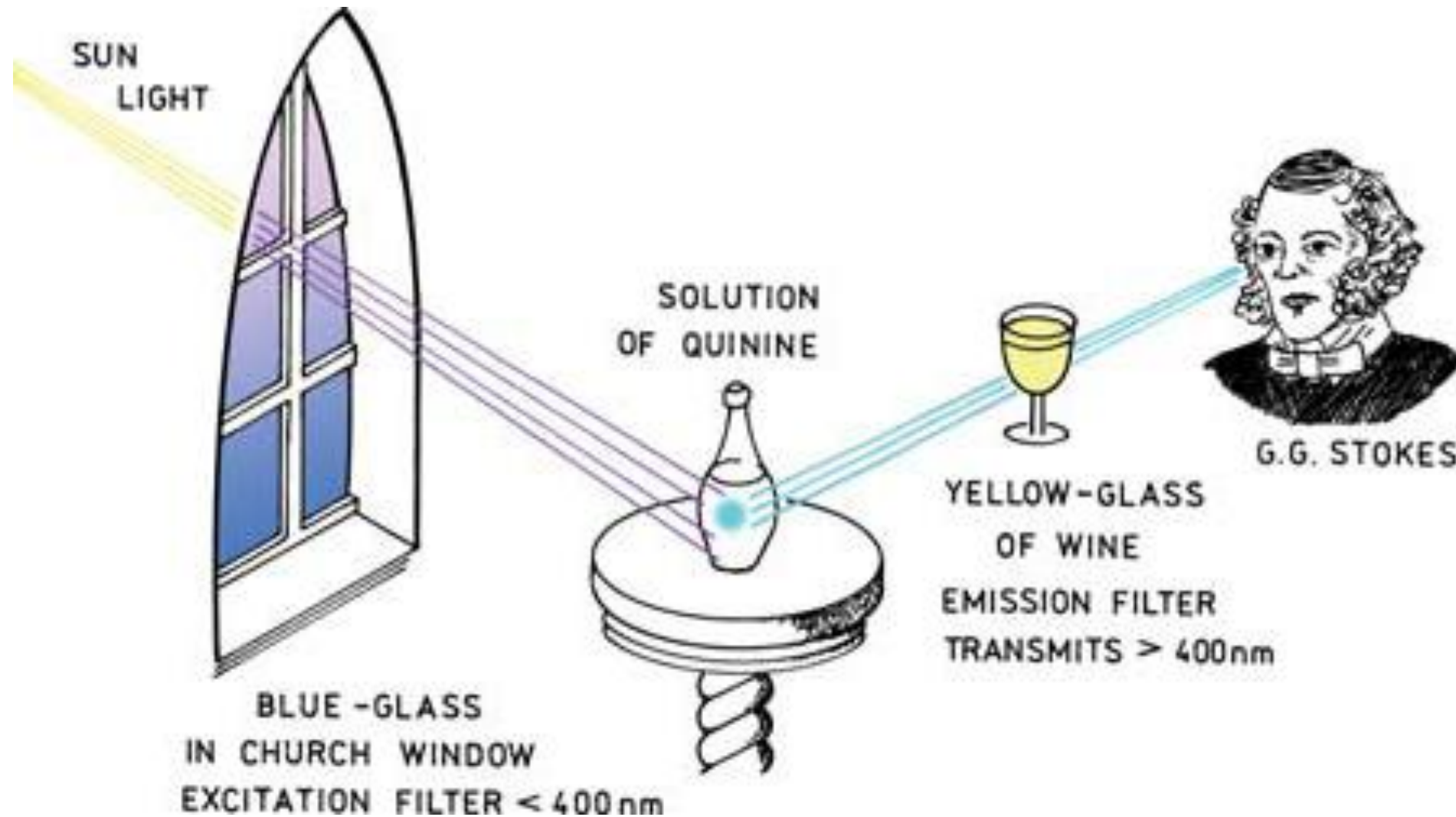


Eye as detector

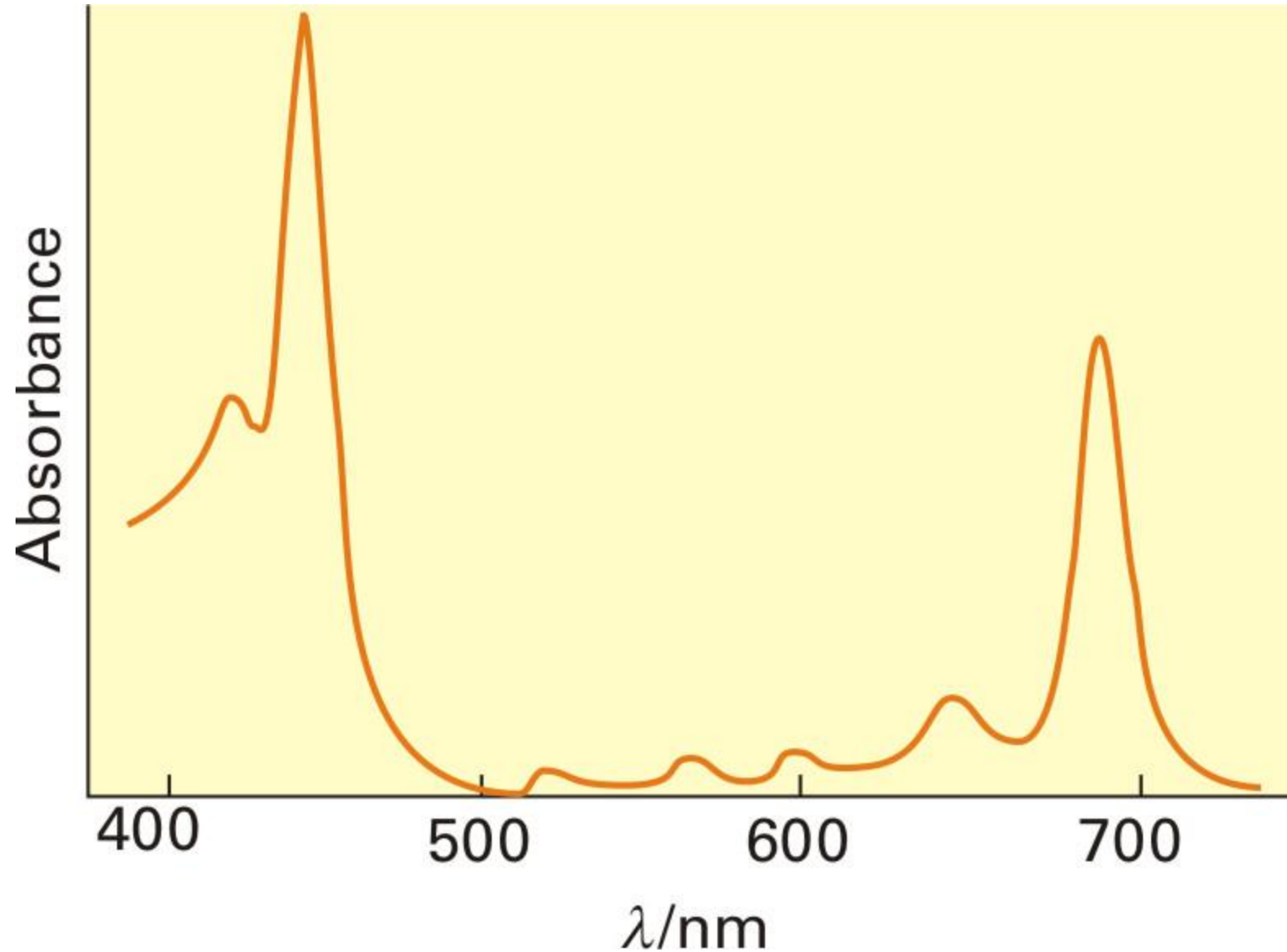
innovate

achieve

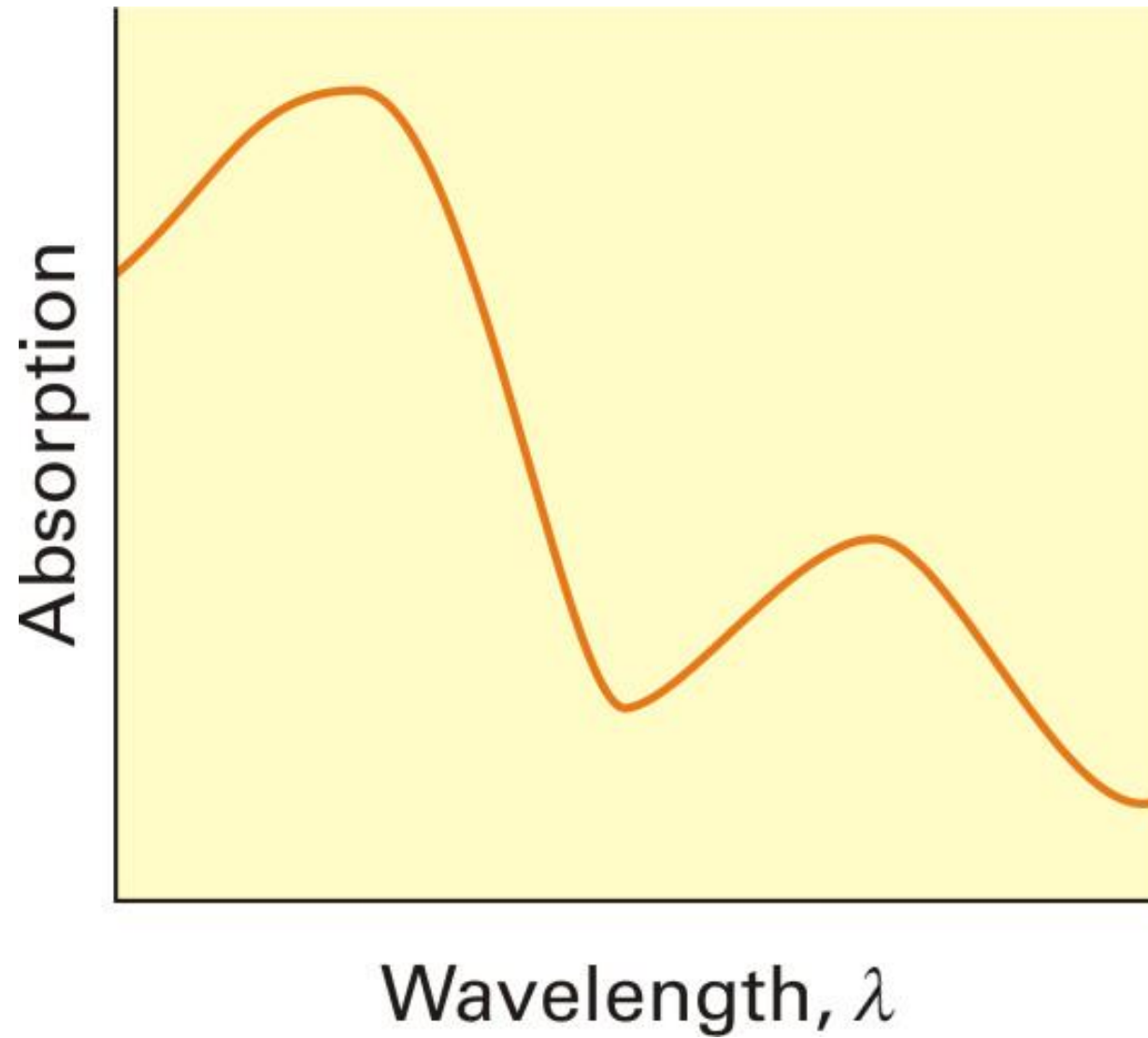
lead



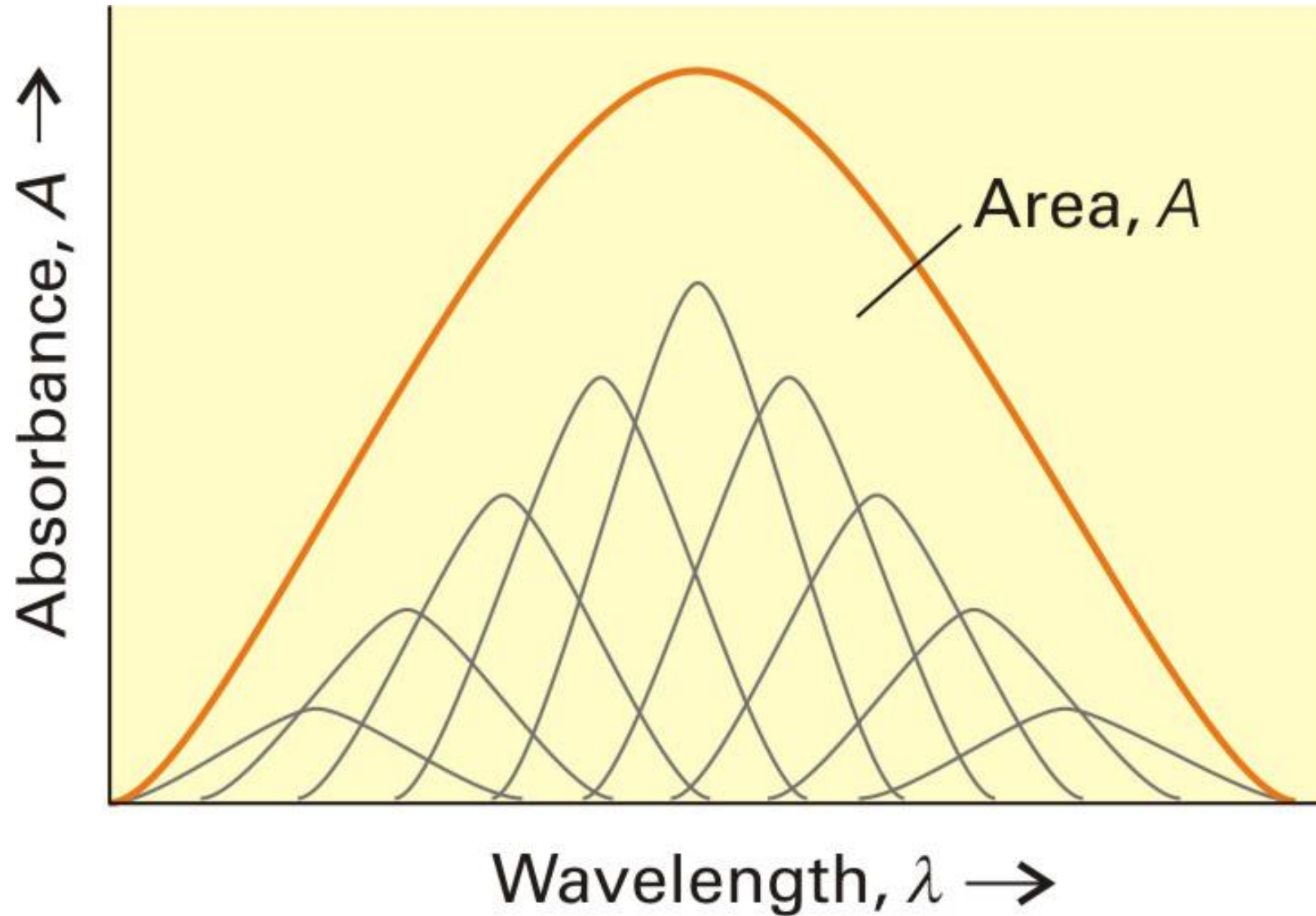
Visible absorption spectrum of chlorophyll



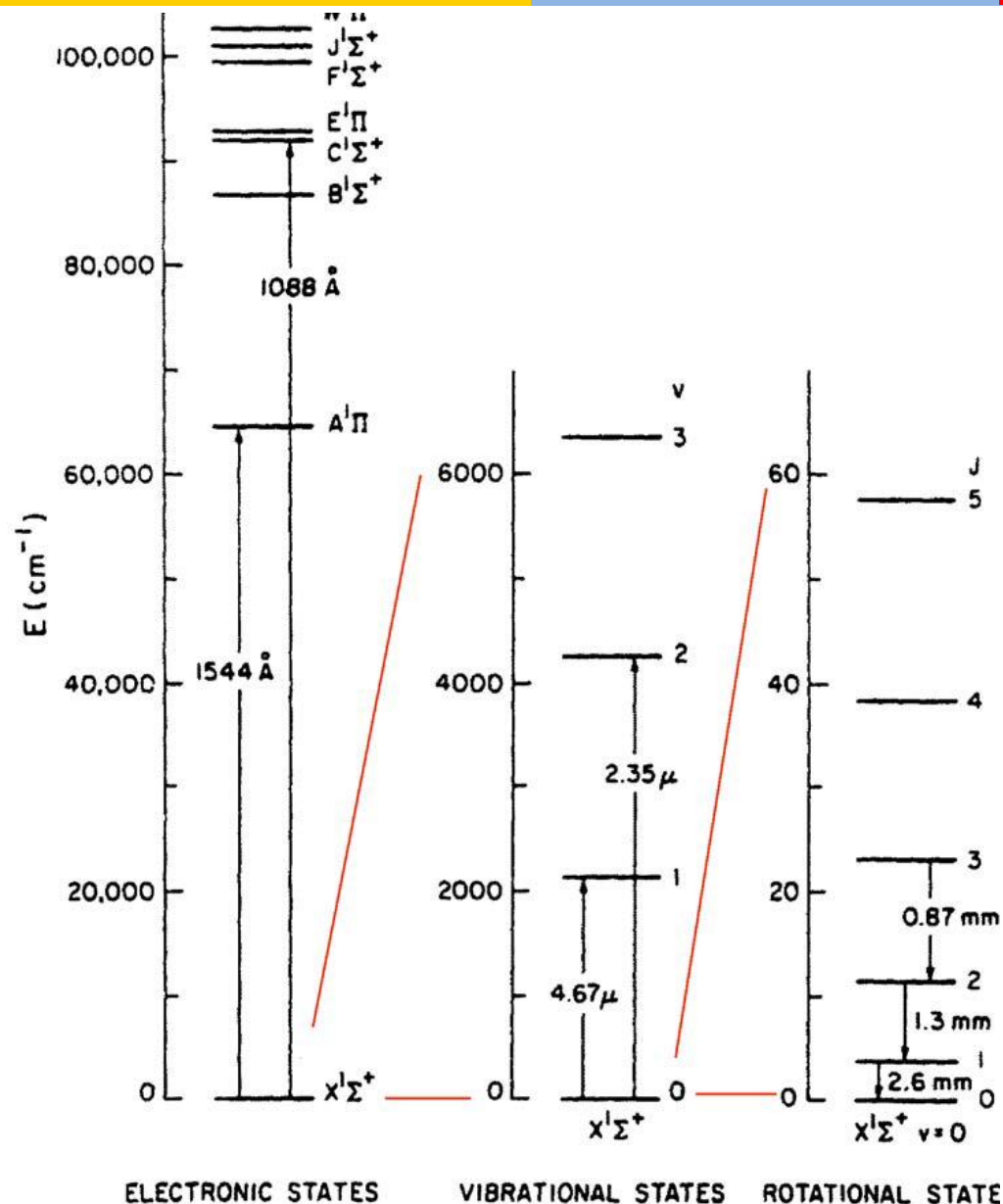
**Electronic absorption spectrum often very broad,
particularly in solution**



Many bands may merge to give a single broad band with unresolved vibrational structure.



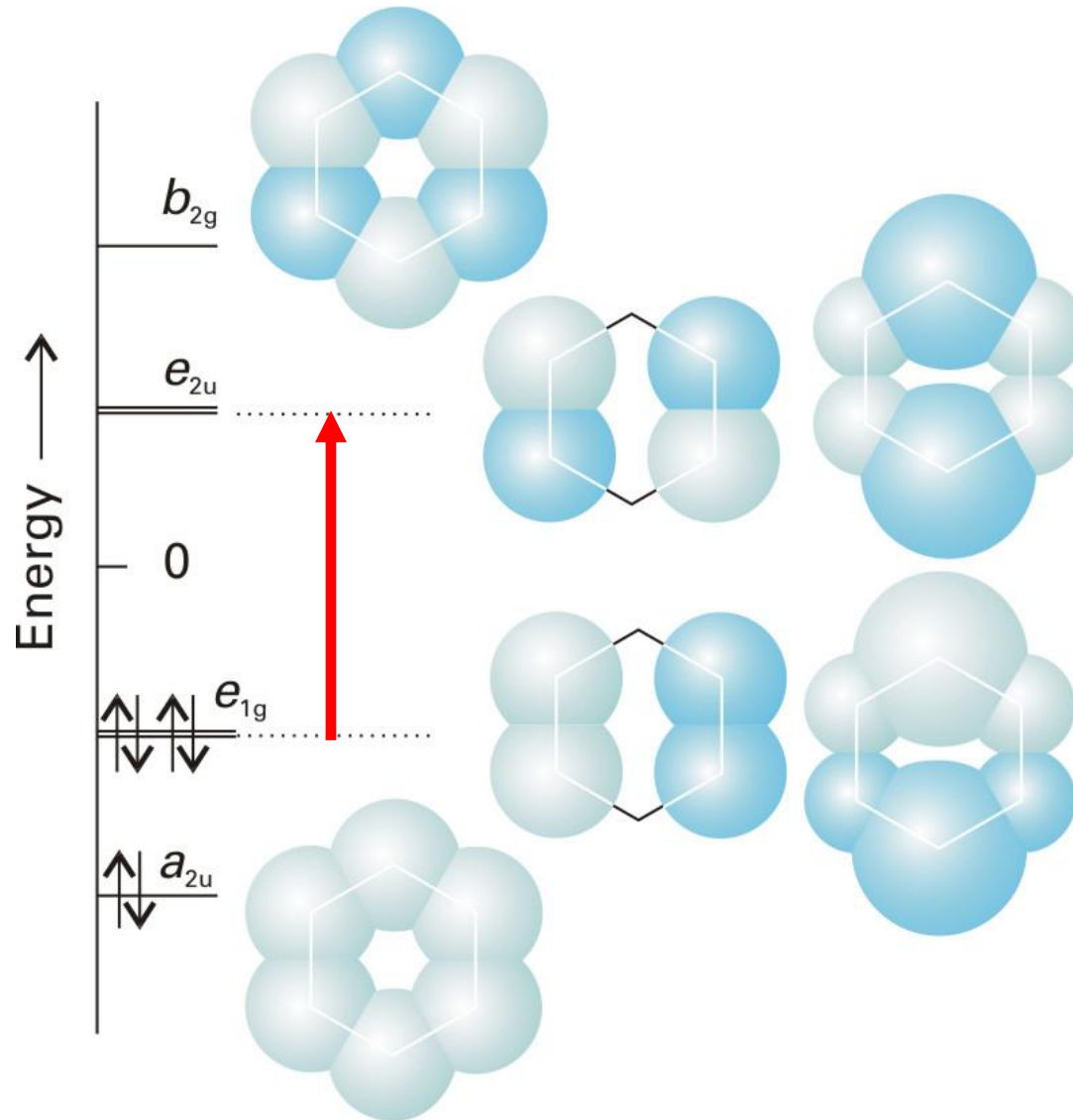
Relative energy states



Consider HCl molecule:

- Rotational energy states: $1 - 10 \text{ cm}^{-1}$
- Vibrational energy separation: 3000 cm^{-1}
- Energies of these states are too different – these transitions will happen independently.
- **Born-Oppenheimer Approx.**
- Combined transitions may only happen if the energy requirement is fulfilled.

States for electronic transitions in molecules



Beer-Lambert Law:



$$\text{Absorbance } A = \log \frac{I_0}{I} = \epsilon [C] l$$

How do we record a spectrum?

Radiation of wavelength 289 nm is passed through 1.00 mm of a solution that contained an aqueous solution of the amino acid tryptophan at a concentration of $0.50 \text{ mmol}^{-1} \text{ dm}^{-3}$. The light intensity is reduced to 54% of its initial value (so $T=0.54$). Calculate the absorbance and the molar absorption coefficient of tryptophan at 280 nm. What would be the transmittance through a cell of thickness 2.00 mm?

$$\epsilon = 5.4 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ mm}^{-1}$$

$$A = 0.27$$

Mixture of two species



$$\text{Absorbance, } A = \log(I_0/I) = \varepsilon [c] l$$

Both the species absorb light.

Individual concentrations of two absorbing species in the mixture can be determined.

Total absorbance at a given wavelength,

$$A = A_A + A_B$$

or

$$A = \varepsilon_A [A]l + \varepsilon_B [B]l$$

Mixture of two species



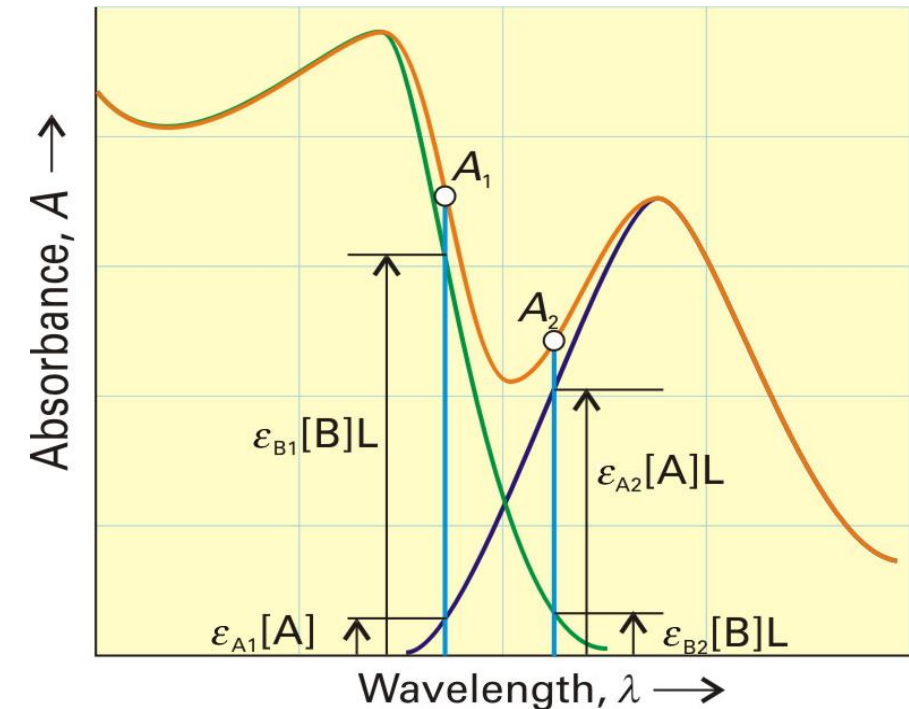
Total absorbance at λ_1 , $A_1 = \epsilon_{A1} [A]l + \epsilon_{B1}[B]l$

Total absorbance at λ_2 , $A_2 = \epsilon_{A2} [A]l + \epsilon_{B2}[B]l$

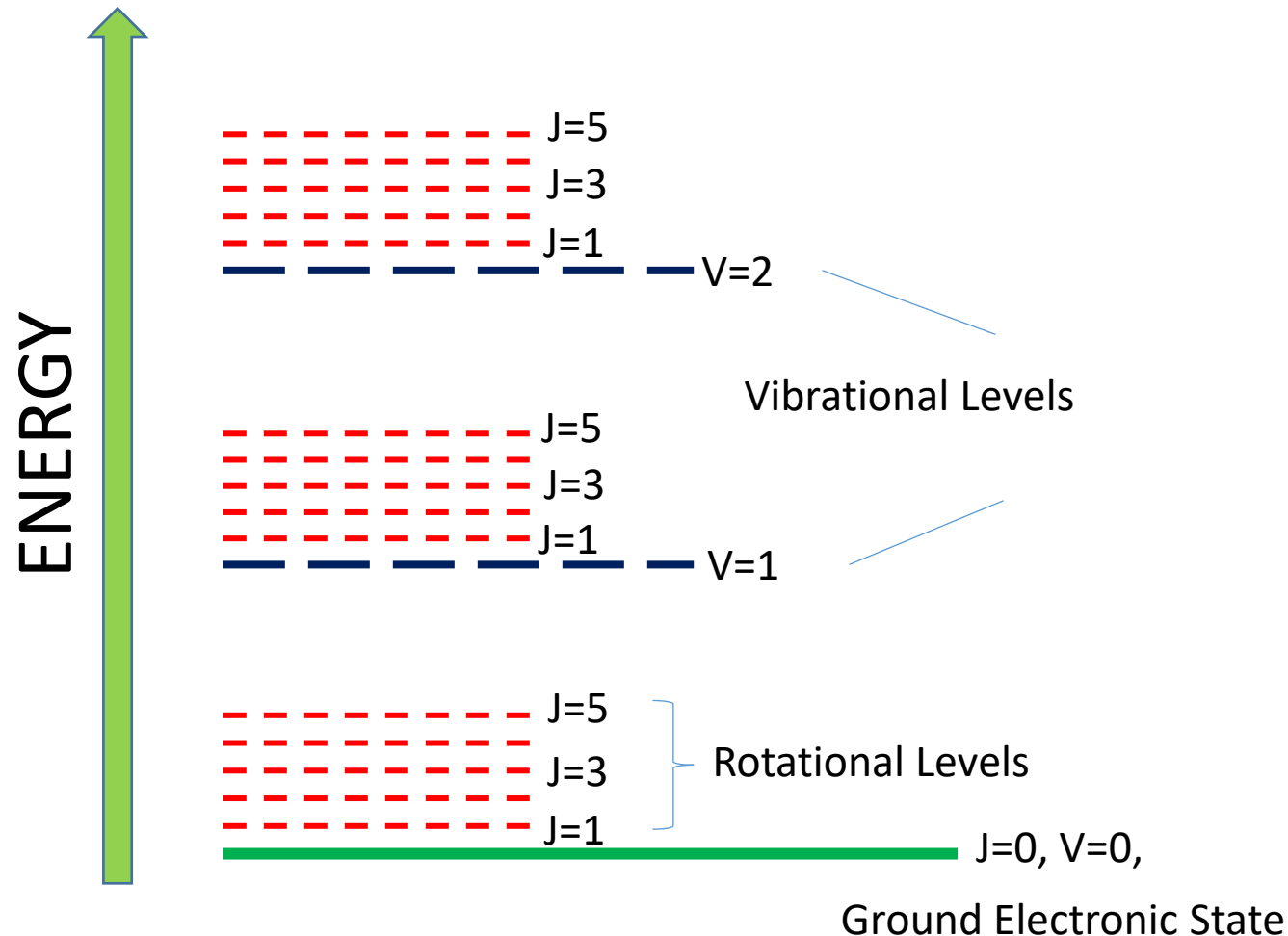
Solving these two equations, find individual concentration of A and B

$$[A] = (\epsilon_{B2} A_1 - \epsilon_{B1} A_2) / (\epsilon_{A1}\epsilon_{B2} - \epsilon_{A2}\epsilon_{B1})l$$

$$[B] = (\epsilon_{A1} A_2 - \epsilon_{A2} A_1) / (\epsilon_{A1}\epsilon_{B2} - \epsilon_{A2}\epsilon_{B1})l$$

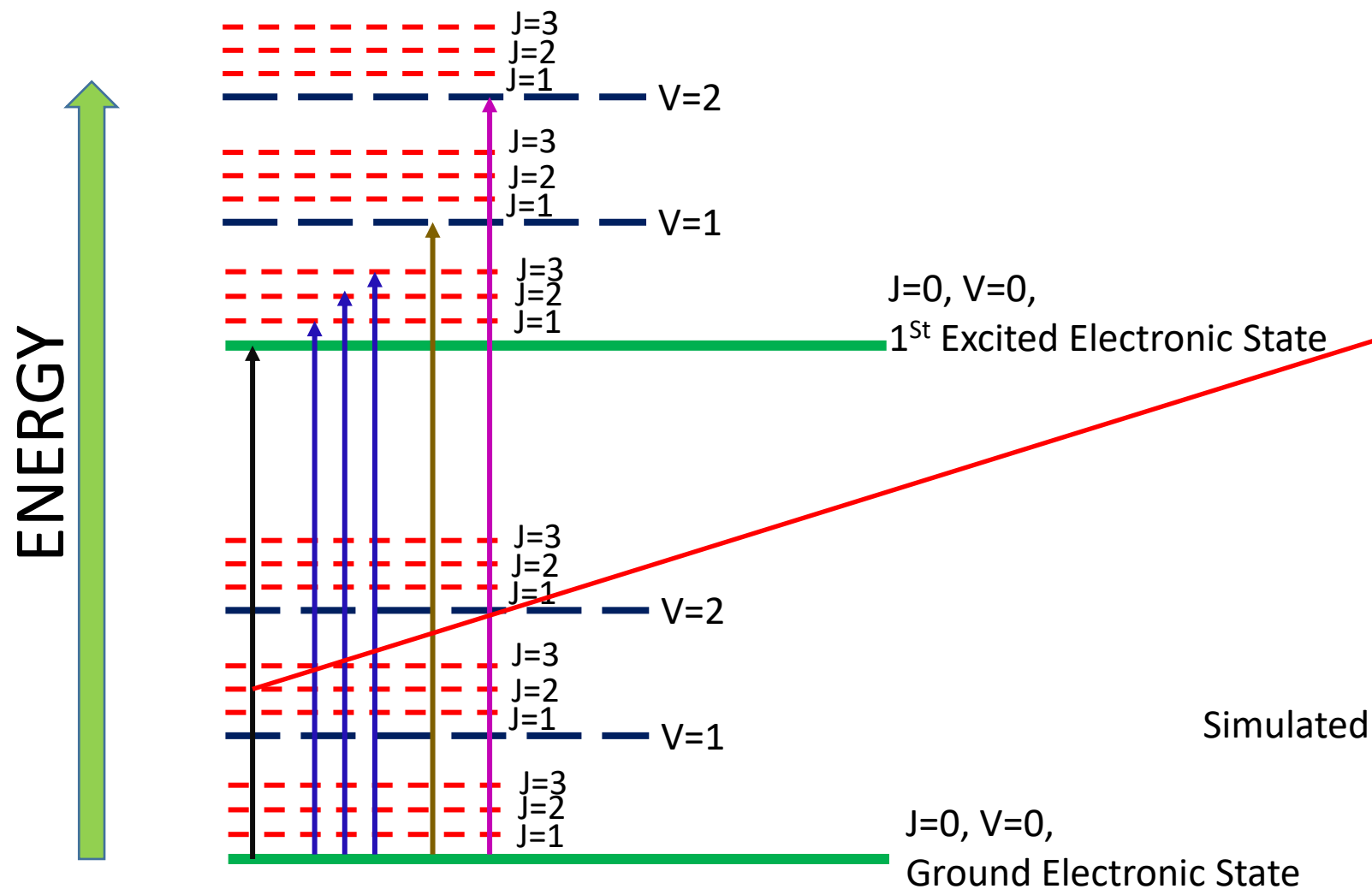


Energy states of a molecule

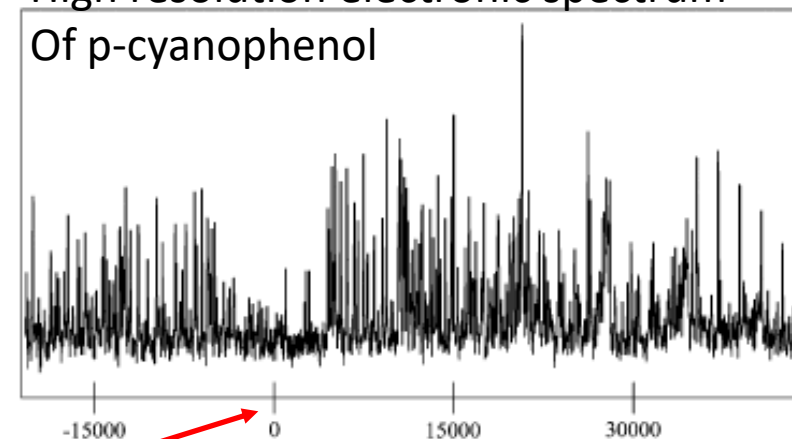


- Vibrational and rotational transitions accompany electronic transitions.
- Vibrational structure can be resolved in gas phase.
- Franck-Condon principle: Since nuclei are very much more massive than electrons, an electronic transition takes place much faster than nuclei can respond – vertical transitions.
- Excitation may occur to more than one vibrational state.

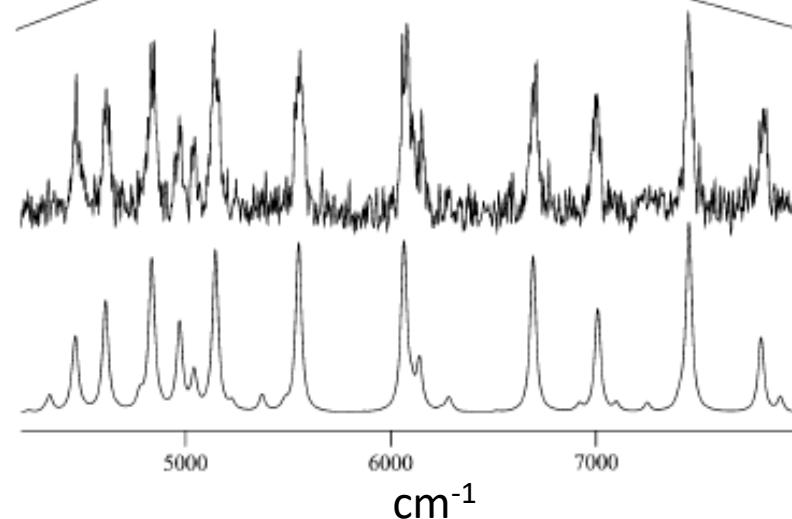
What happen during electronic transitions?



High resolution electronic spectrum
Of p-cyanophenol



Simulated



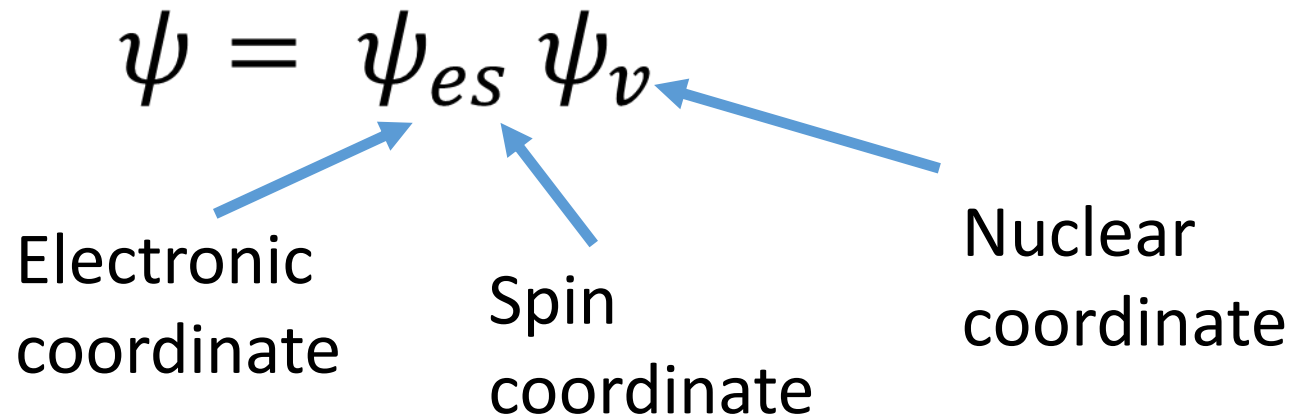
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Transition moments



Transition moment integral: $\int \psi'^* \hat{\mu} \psi d\tau$

Dipole moment operator, $\hat{\mu}$, can be divided into two components. One depends on nuclear coordinates ($\hat{\mu}_n$) and the other depends on electron coordinates ($\hat{\mu}_e$).



Transition moments

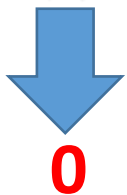


Transition moment integral: $\int \psi'^* \hat{\mu} \psi d\tau$

$$\Rightarrow \int \psi_{e's'}^* \psi_{v'}^* (\hat{\mu}_n + \hat{\mu}_e) \psi_{es} \psi_v d\tau$$

$$\Rightarrow \int \psi_{e's'}^* \psi_{v'}^* \hat{\mu}_n \psi_{es} \psi_v d\tau + \int \psi_{e's'}^* \psi_{v'}^* \hat{\mu}_e \psi_{es} \psi_v d\tau$$

$$\Rightarrow \int \psi_{e's'}^* \psi_{es} d\tau_{es} \int \psi_{v'}^* \hat{\mu}_n \psi_v d\tau_n + \underbrace{\int \psi_{v'}^* \psi_v d\tau_n}_{\text{FCF}} \int \psi_{e's'}^* \hat{\mu}_e \psi_{es} d\tau_{es}$$



0

$$\text{Transition moment integral: } \int \psi_{v'}^* \psi_v d\tau_n \int \psi_e^* \hat{\mu}_e \psi_e d\tau_e \int \psi_{s'}^* \psi_s d\tau_s$$

Franck-Condon Factor

Orbital selection
rule

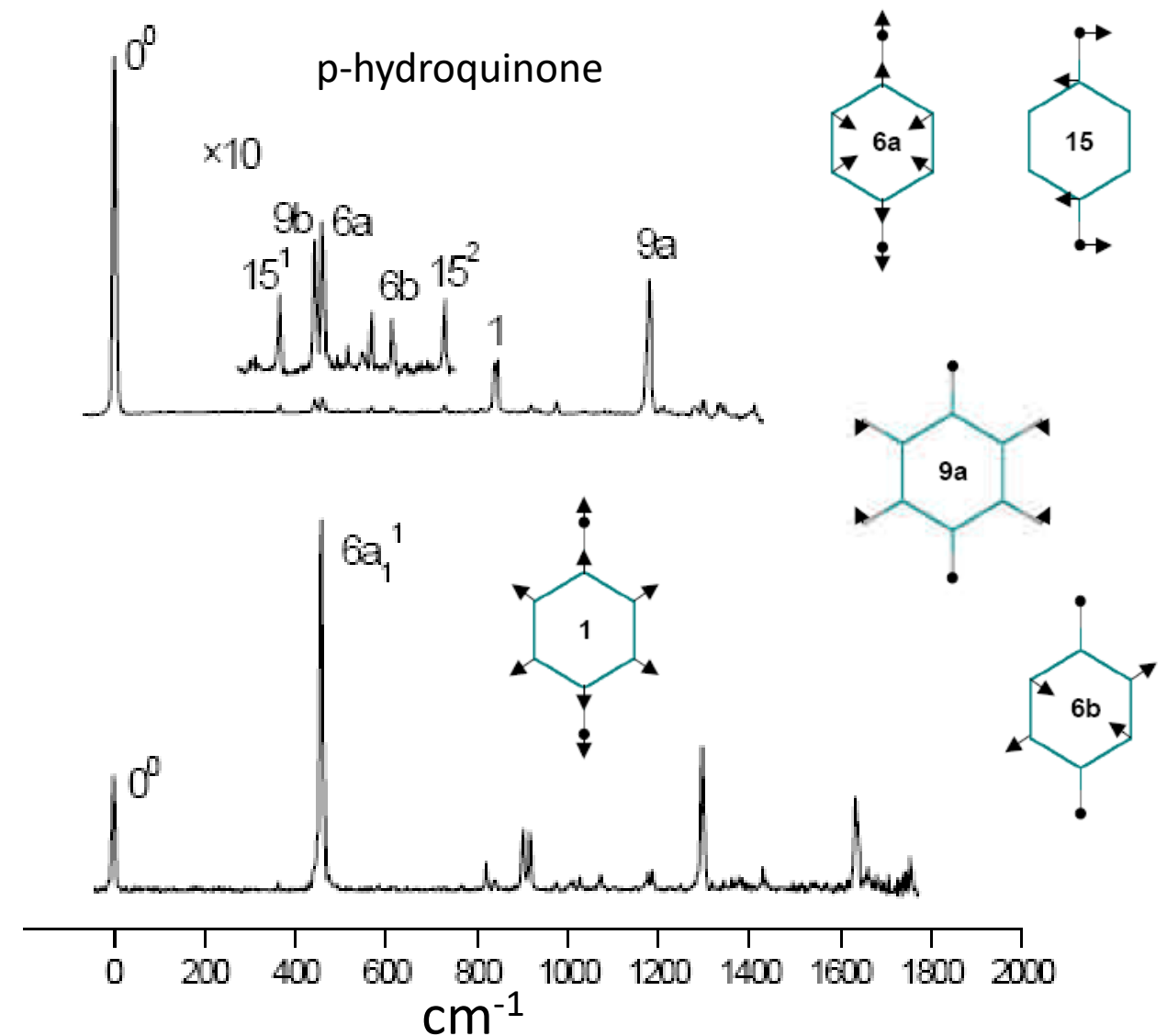
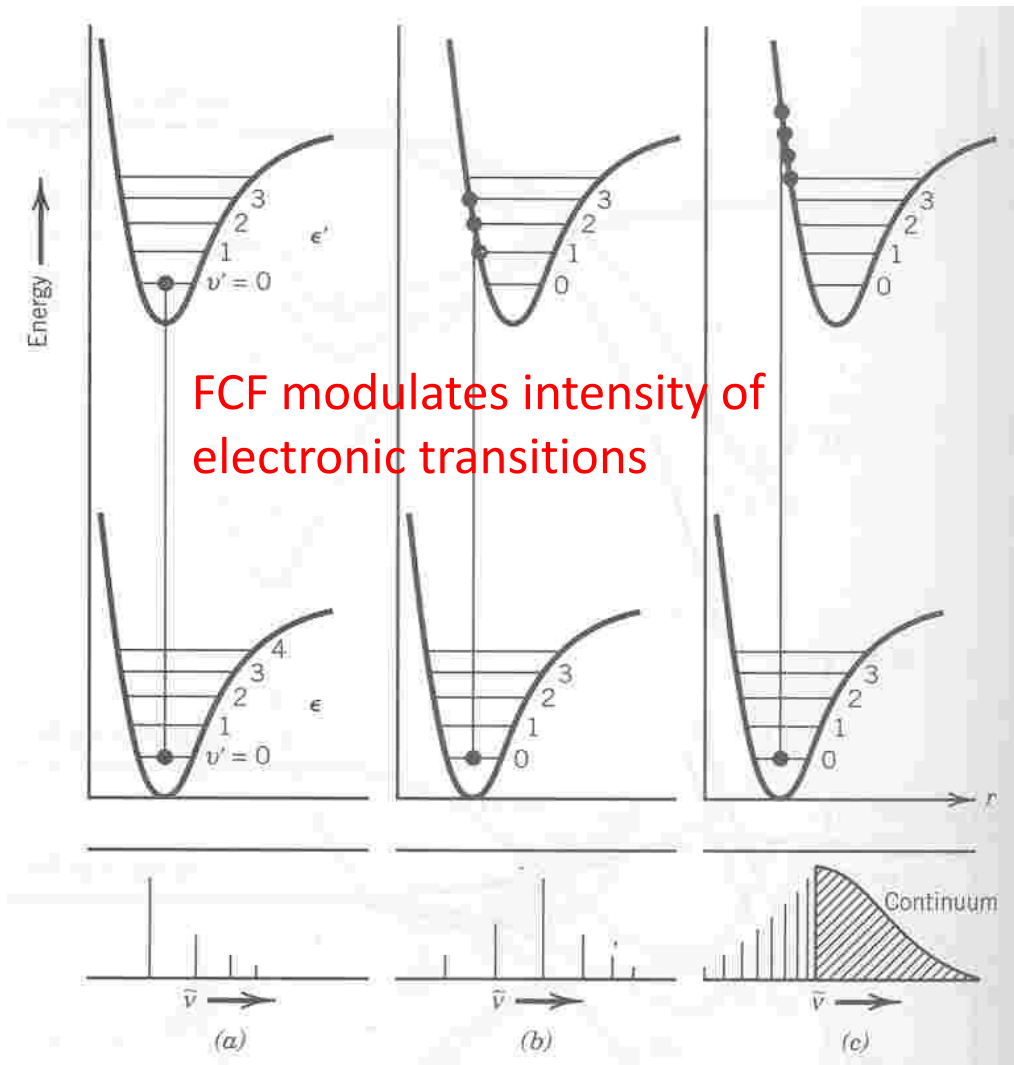
Spin selection
rule

Franck-Condon Factor (FCF)

innovate

achieve

lead

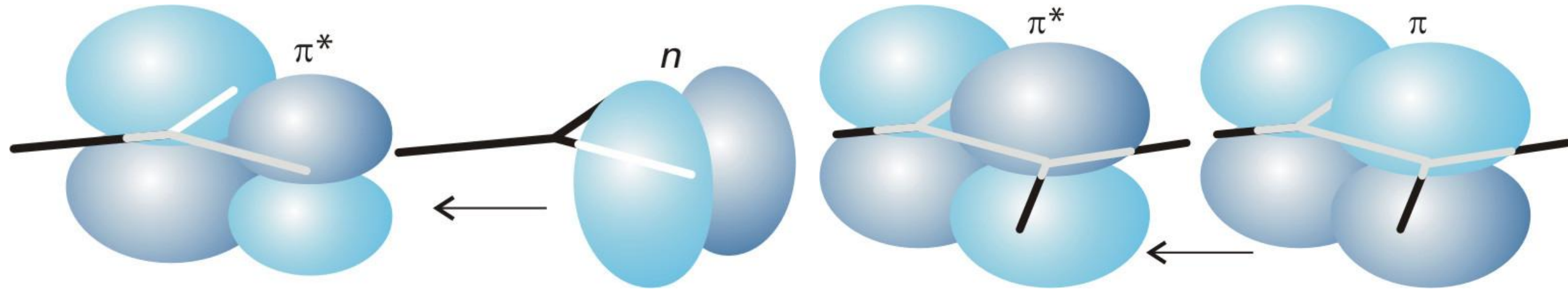


Specific types of transitions

Absorption of photon often related to excitation of electron localized on small group of atoms – chromophore.

n-to- π^* transition in carbonyl (C=O) group (~290 nm)

π -to- π^* transition in C=C (~180 nm)

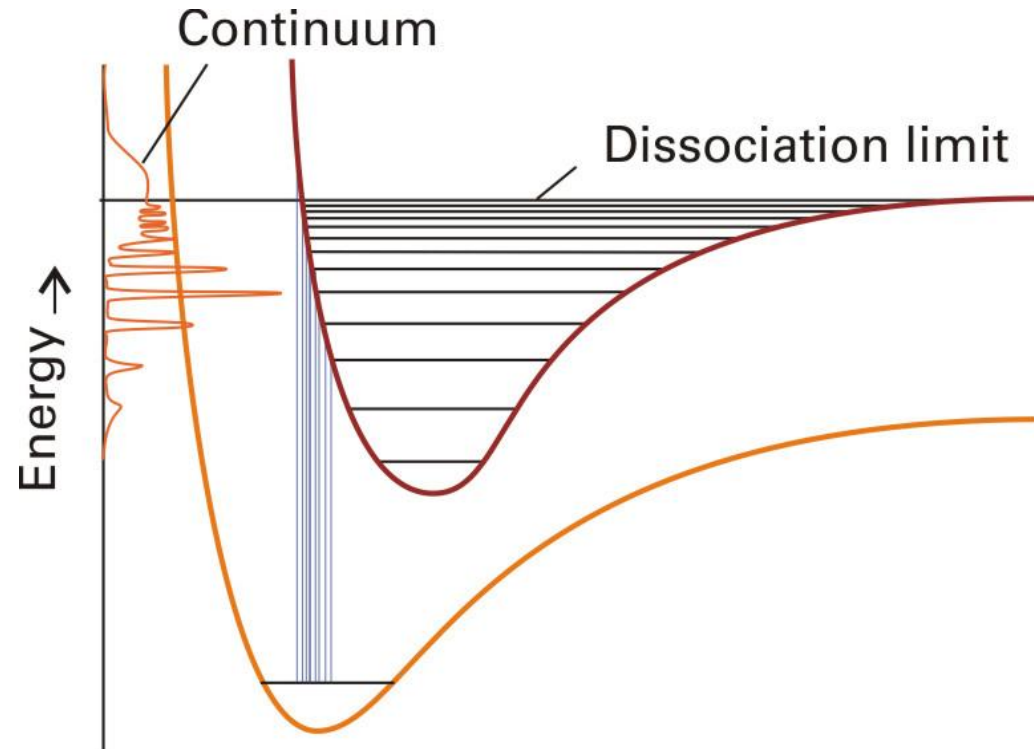


Radiative and non-radiative decay (de-excitation):

Non-radiative:

Disordered thermal motion of surroundings of molecule – internal conversion.

Dissociation or fragmentation.

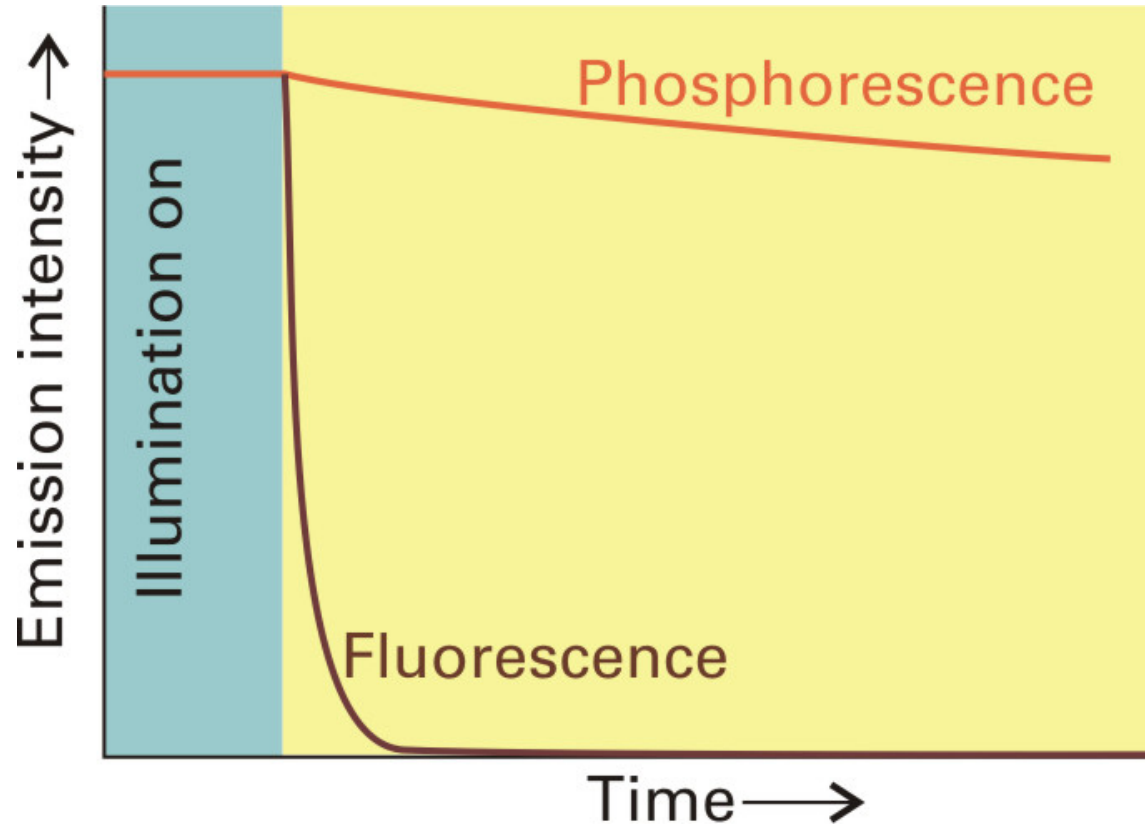


Radiative: De-excitation by photon emission

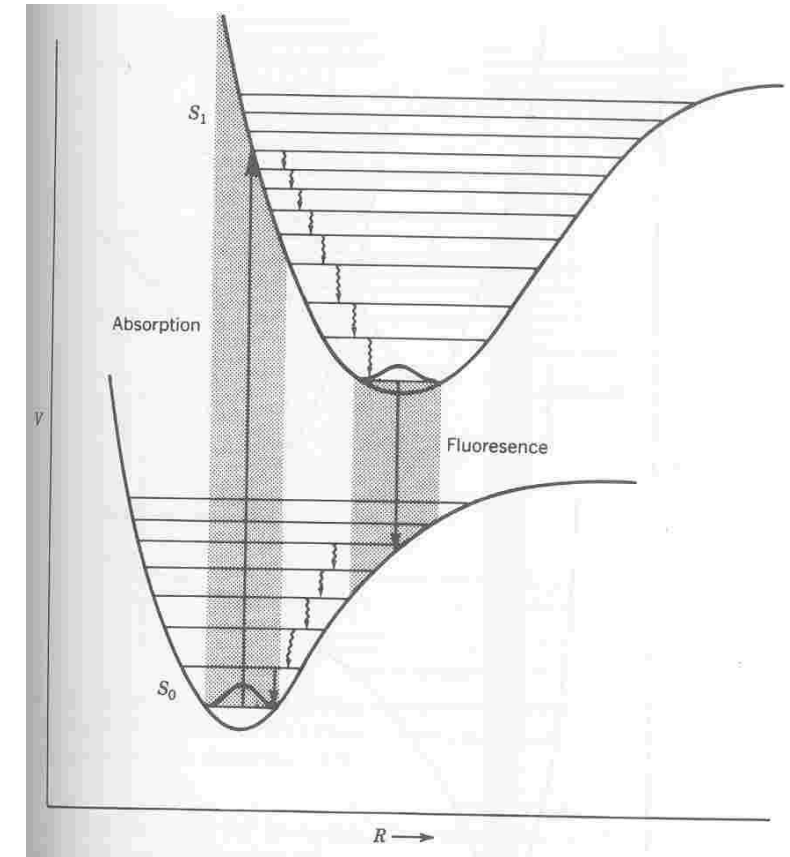
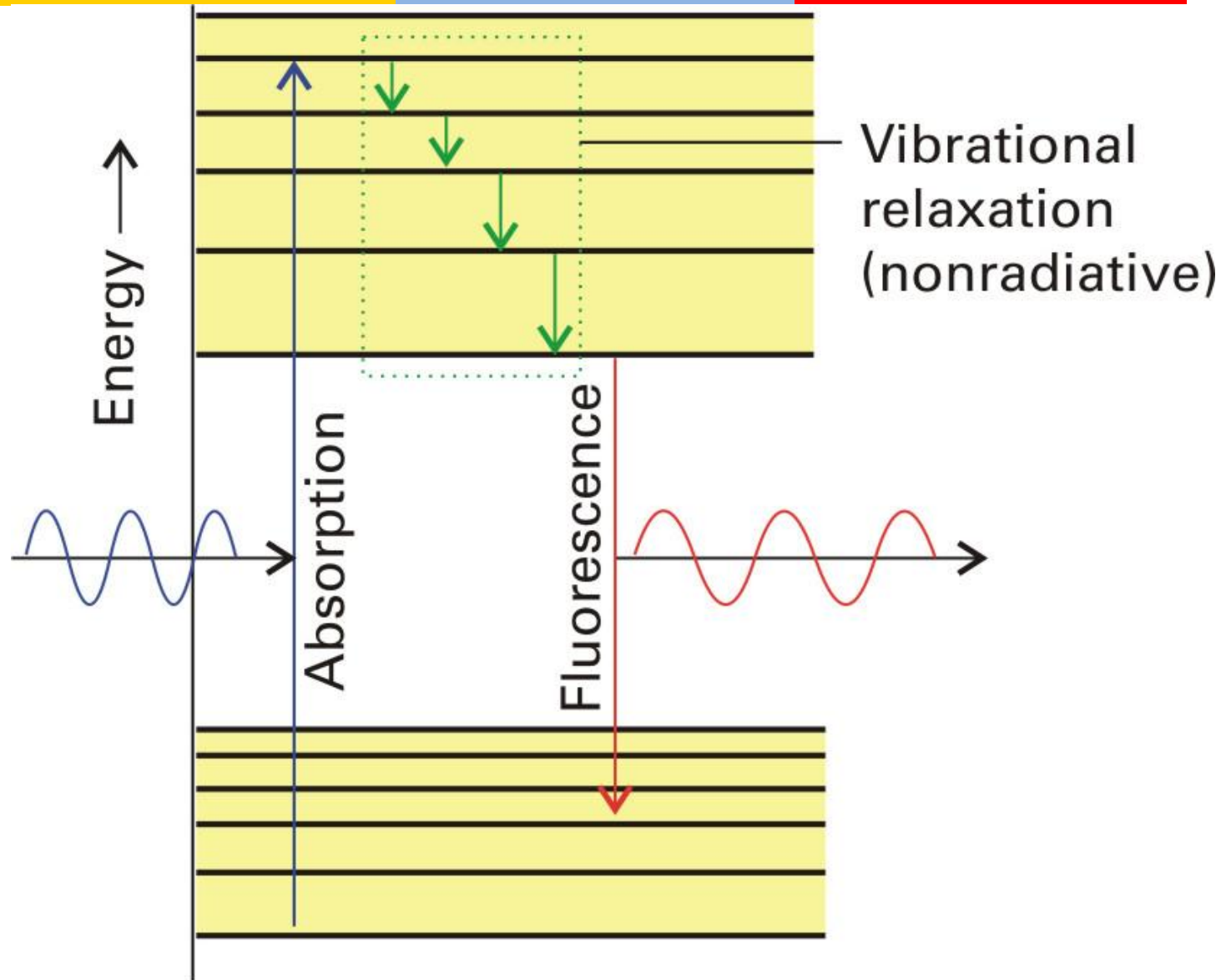


Fluorescence: Emission ceases 'soon' after exciting light is switched off.

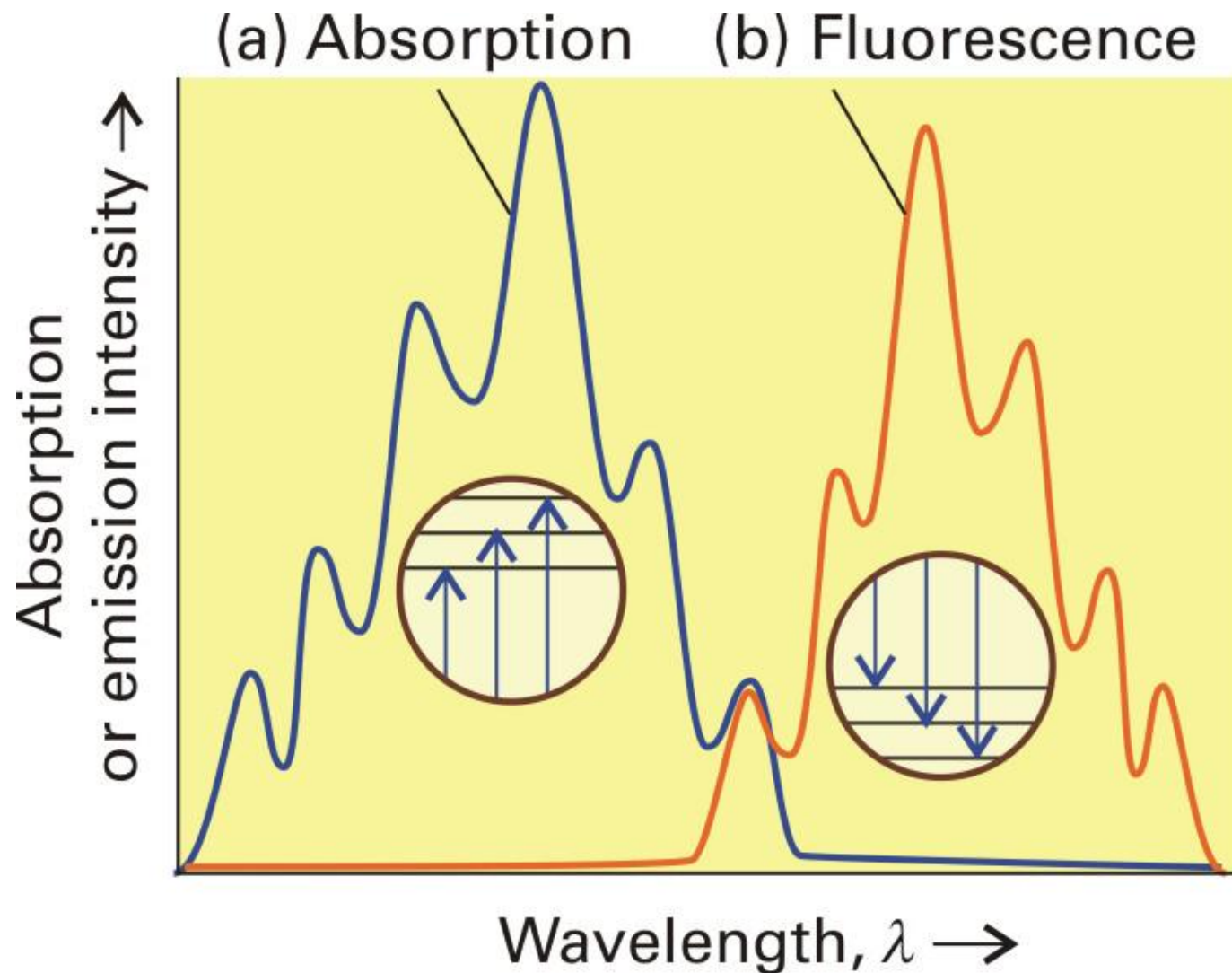
Phosphorescence: Emission persists for 'relatively longer' times.



Fluorescence



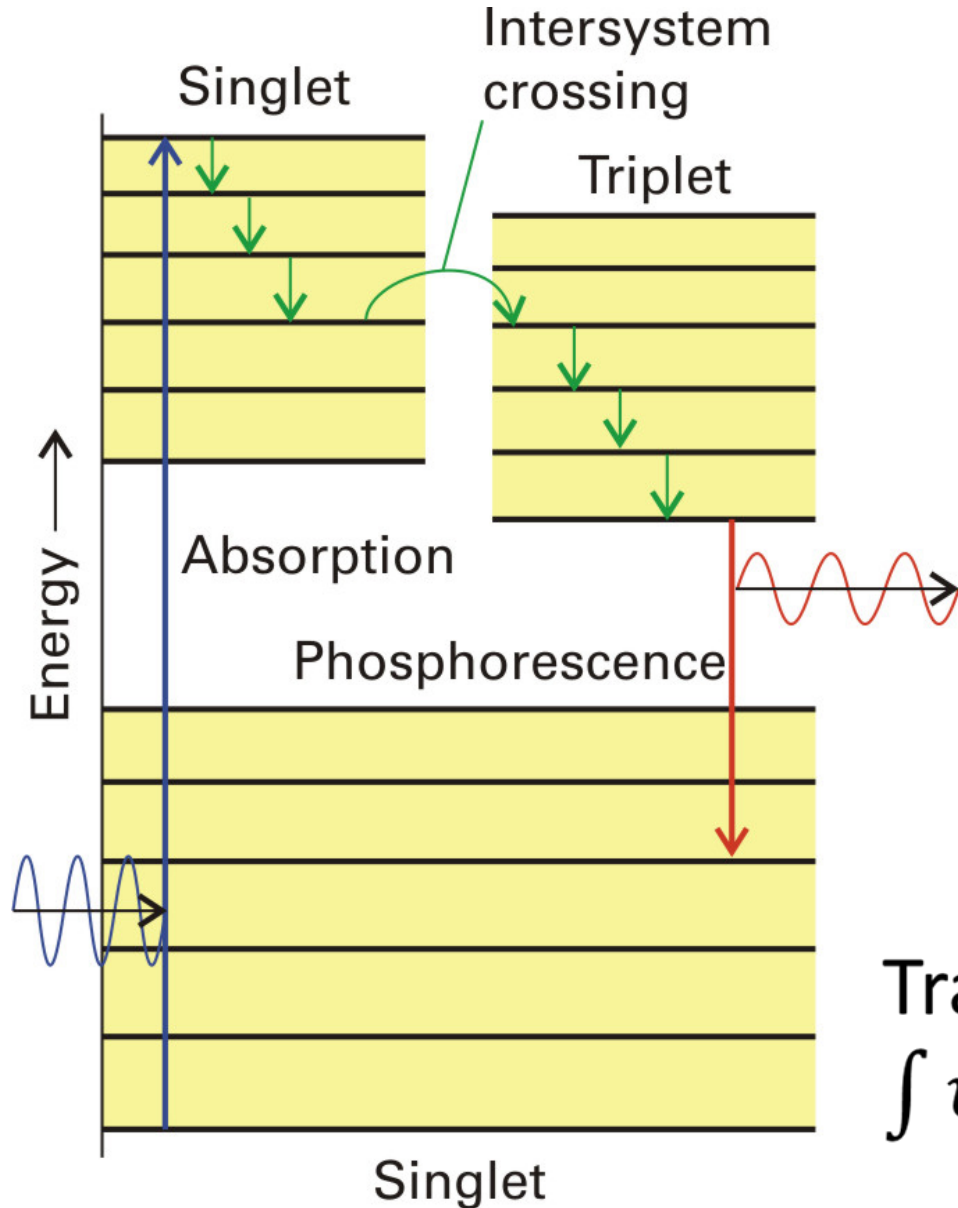
Absorbance and Fluorescence



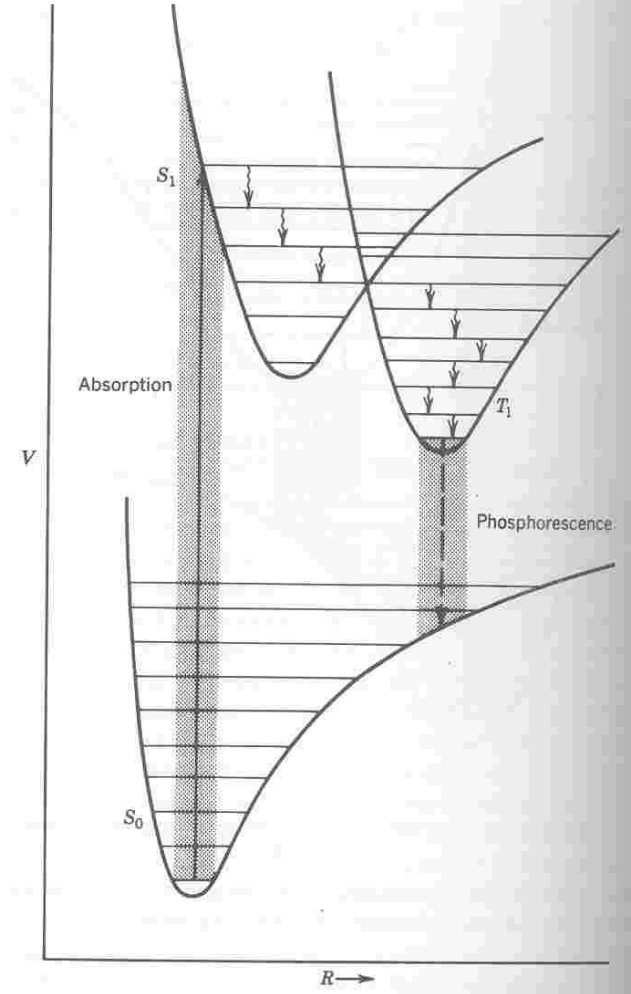
Absorbance: Provides information about the ground state of the molecule.

Fluorescence: Provides information about the excited state of the molecule.

Phosphorescence



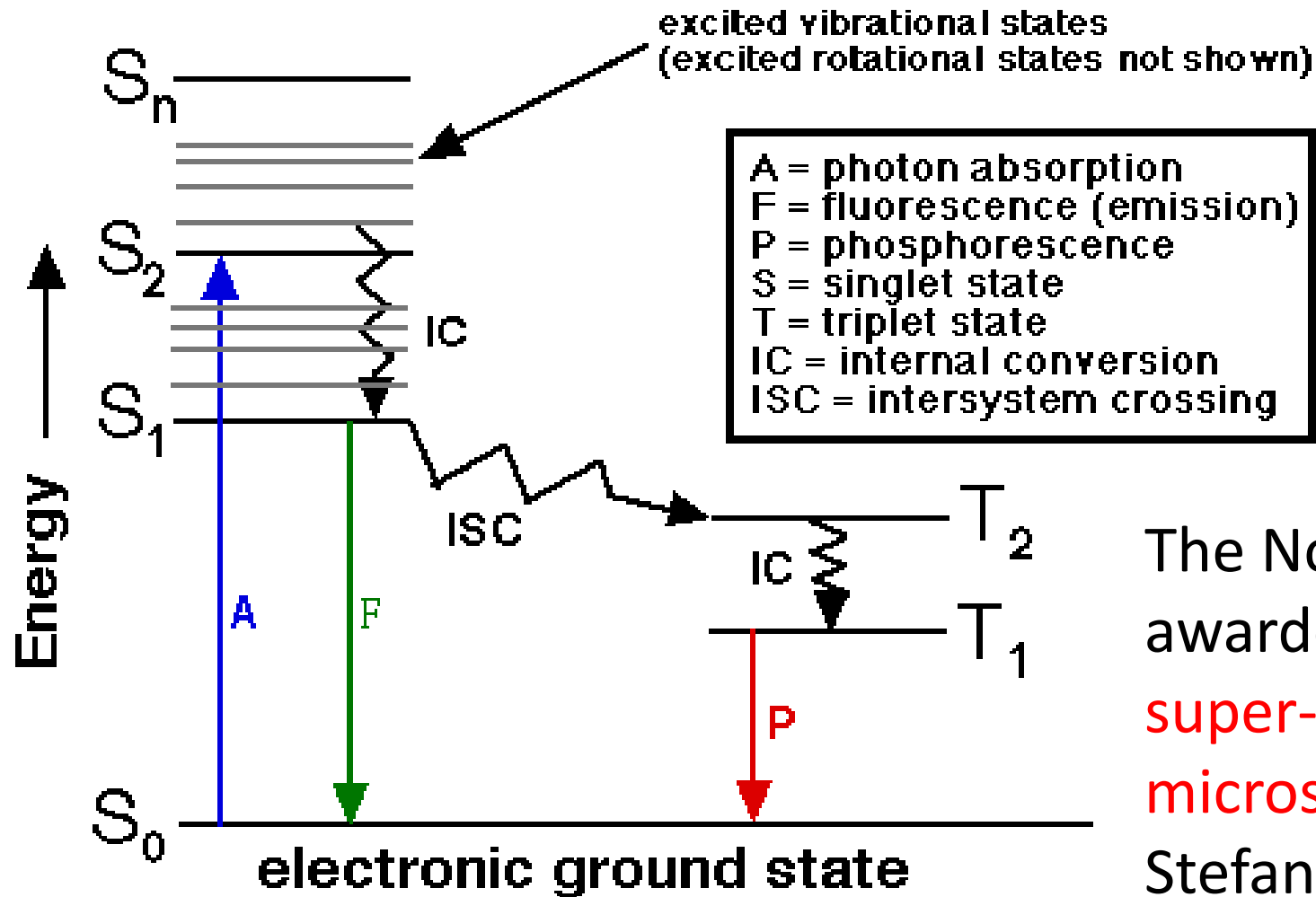
- Phosphorescence:
- Intensity is very weak
 - Time lag



Transition moment integral:

$$\int \psi_v^*, \psi_v d\tau_n \int \psi_e^* \hat{\mu}_e \psi_e d\tau_e \int \psi_s^*, \psi_s d\tau_s$$

Jablonski Diagram



Professor Ahmed Zewail received Nobel Prize in Chemistry for “his studies of transition states of chemical reactions using femtosecond spectroscopy” (1999).

The Nobel prize in chemistry 2014 was awarded “for the development of super-resolved fluorescence microscopy” to Prof. Eric Betzig, Prof. Stefan W. Hell, and Prof. William E. Moerner.