Molecular Photonics

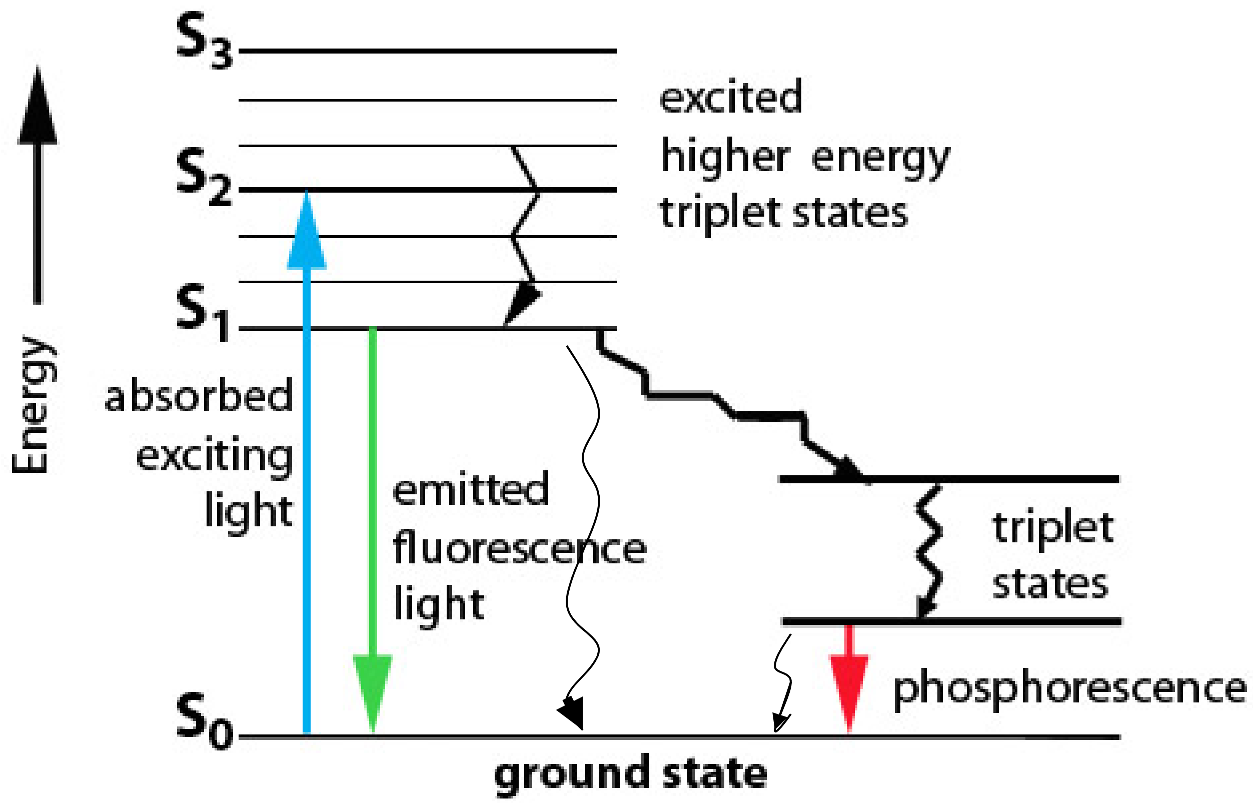
Lecture 2

Outline

- Interaction of light with molecules: polarizability, transition dipole, oscillator strength.
- Frank-Condon principle
- Absorption and emission spectra

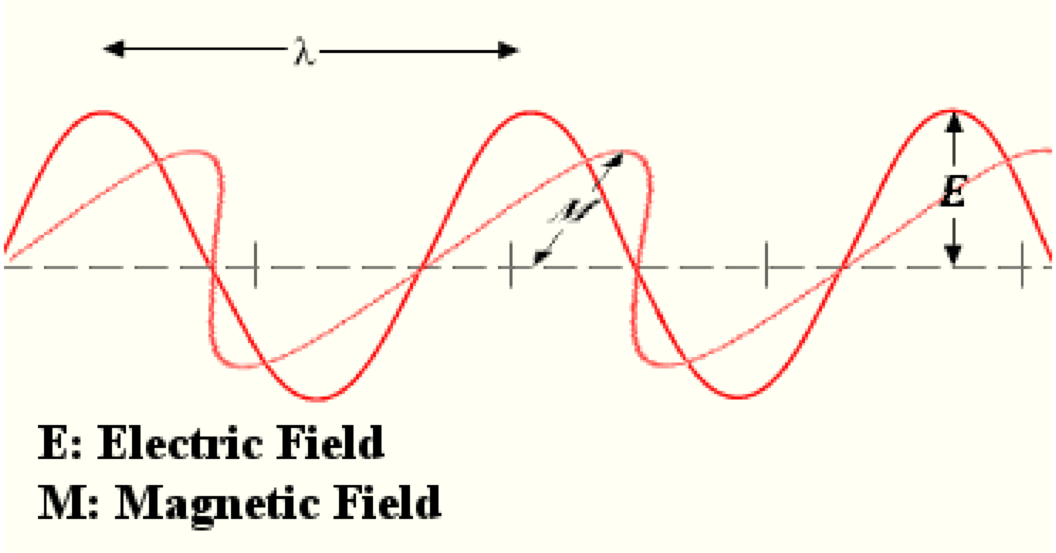
Radiative Transitions: The Absorption and Emission of Light

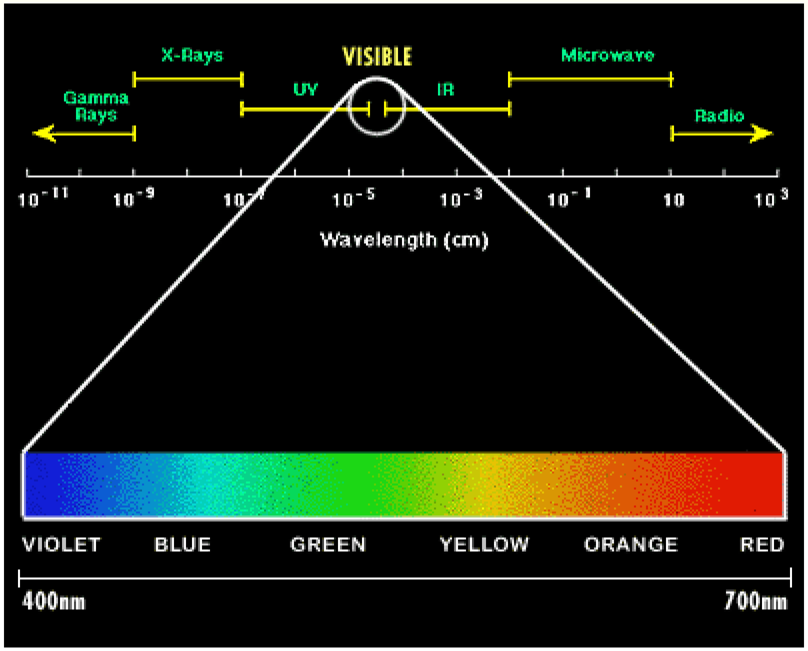
Jablonski Diagram



S_3
S_2
S_1
S_0
Energy
excited
higher energy
triplet states
absorbed
exciting
light
emitted
fluorescence
light
triplet
states
phosphorescence
ground state

Light


λ
E
M
E: Electric Field
M: Magnetic Field

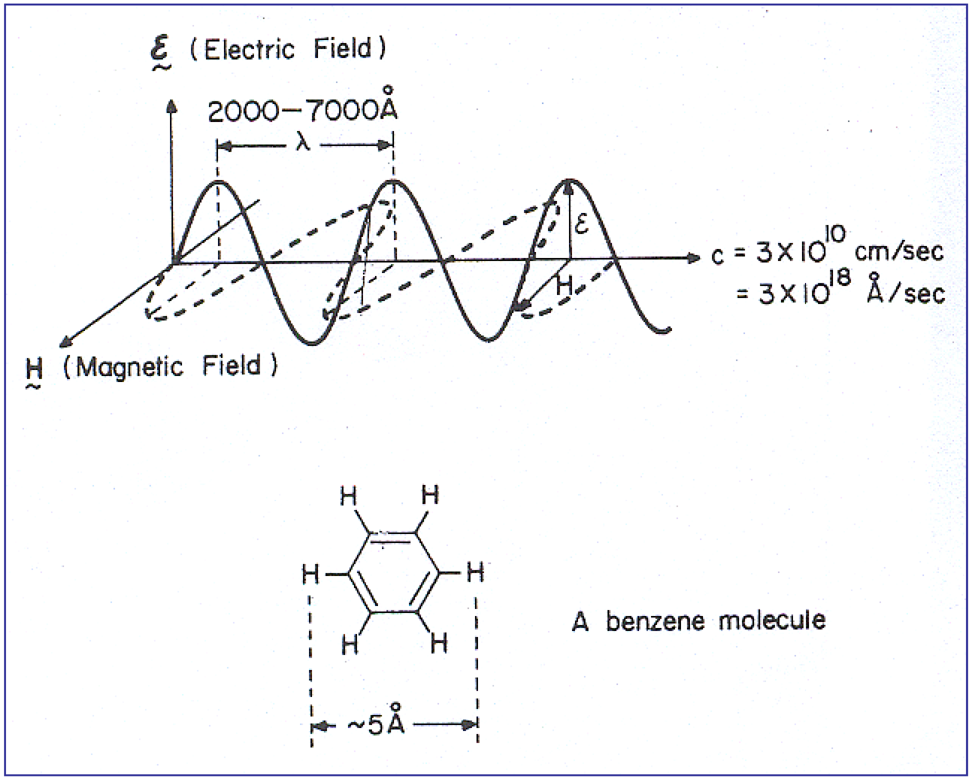

VISIBLE
X-Rays
Microwave
Gamma Rays
UV
IR
Radio
10⁻¹¹
10⁻⁹
10⁻⁷
10⁻⁵
10⁻³
10⁻¹
10
10³
Wavelength (cm)
VIOLET
BLUE
GREEN
YELLOW
ORANGE
RED
400nm
700nm

Pictorial (intuitive) view of light absorption

Not rigorous, but useful

General Representation of Light-Molecule Interaction

Electrons may be set in motion by the oscillating electric field of light, i.e. the excited electron behaves as it were an oscillating dipole



ℰ (Electric Field)
2000–7000Å
λ
ε
H
c = 3×10^10 cm/sec
= 3×10^18 Å/sec
H (Magnetic Field)
H
H
H
H
H
H
~5Å
A benzene molecule

The major force operating on the electrons of a molecule under light is electric field.

The strength of the interaction between an electron and light (electric field) is related directly to the ability of the electron to follow the light wave.

The oscillation of the dipoles corresponds to the movements of electrons in bonds relative to positively charged nuclei, i.e. electrons oscillate about the nuclear framework of the molecule.

Polarizabilty and Transition Dipole Moment

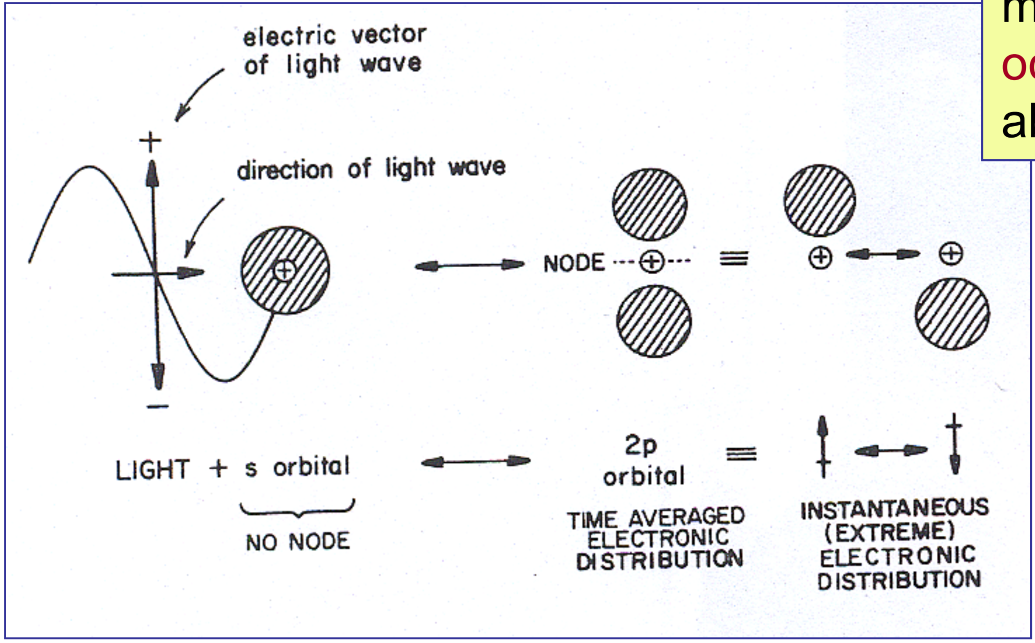
Polarizability (α) is defined as the magnitude of the induced dipole moment (μ_i) generated in a molecule by an electric field $\mathscr{E}$ of unit intensity, i.e.,

$$\alpha = \mu_i/\mathscr{E} \tag{5.4}$$

Initially ($\mathscr{E} = 0$), the electron is held, on the average, at some distance r from the center of "electrical gravity" of the molecule. When $\mathscr{E} > 0$, a displacing force $\mathscr{E}e$ will cause the electron to select a new equilibrium distance different from the original distance by the amount $\delta\mathbf{r}$. The new electronic distribution is related to the induced dipole moment (also called *transition dipole*) by:

$$\mu_i = e\delta\mathbf{r}$$

Nodes and dipole moments have to occur, otherwise no absorption is observed


electric vector of light wave
+
direction of light wave
−
NODE
⊕
≡
⊕
⊕
LIGHT + s orbital
NO NODE
2p orbital
≡
TIME AVERAGED ELECTRONIC DISTRIBUTION
INSTANTANEOUS (EXTREME) ELECTRONIC DISTRIBUTION

According to classical theory,[4,5] f is related to the square of the induced dipole moment μ_i produced by action of a light wave on an electric dipole:

$$\underline{\begin{matrix}\text{Oscillator}\\ \text{strength}\end{matrix}\ f \propto \mu_i^2 = \langle e\mathbf{r}\rangle^2\ \begin{matrix}\text{Transition}\\ \text{dipole moment}\end{matrix}} \tag{5.12}$$

where μ_i is the induced transition dipole moment or *dipole strength* corresponding to the electronic transition. The latter quantity may be set equal to $e\mathbf{r}$, where $\mathbf{r}$ is the dipole length. Quantitatively the expression relating f and μ_i is given by

$$f = \left(\frac{8\pi m_e \bar{\nu}}{3he^2}\right)\mu_i^2 \cong 10^{-5}\,\bar{\nu}|e\mathbf{r}_i|^2 \tag{5.13}$$

where m_e is the mass of the electron, $\bar{\nu}$ is the energy of the transition (in cm^{-1}), h is Planck's constant, and $\mathbf{r}$ is the length (in cm) of the transition dipole (i.e., $e\mathbf{r}$ is the transition dipole moment).

We can now identify μ_i with an observable quantity related to the quantum mechanical transition moment matrix element or integral, i.e., $\mu \equiv \langle H\rangle$, and produce:

$$\text{Classical} \rightarrow f = \left(\frac{8\pi m_e \bar{\nu}}{3he^2}\right)\langle H\rangle^2 \leftarrow \text{Quantum mechanical} \tag{5.14}$$

Selection rules (everything is about the conservation of momentum)

1. **Spin-forbidden transitions.** *Transitions between states of different multiplicities are forbidden, i.e. singlet–singlet and triplet–triplet transitions are allowed, but singlet–triplet and triplet–singlet transitions are forbidden.*

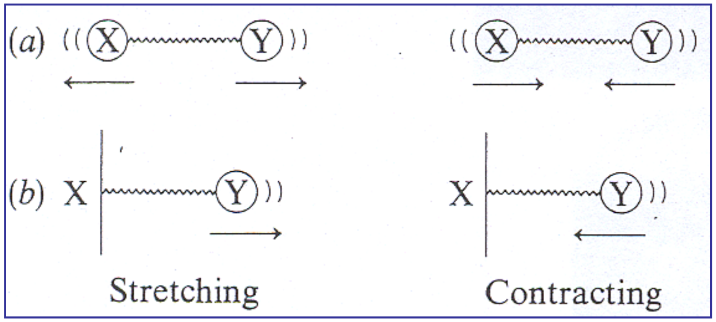
However, there is always a weak interaction between the wavefunctions of different multiplicities via spin–orbit coupling). As a result, a wavefunction for a singlet (or triplet) state always contains a small fraction of a triplet (or singlet) wavefunction; this leads to a small but non-negligible value of the intensity integral during a transition between a singlet state and a triplet state or vice versa. In spite of their very small molar absorption coefficients, such transitions can be effectively observed.

2. **Symmetry-forbidden transitions.** A transition can be forbidden for symmetry reasons. Detailed considerations of symmetry using group theory is needed

It is important to note that a symmetry-forbidden transition can nevertheless be observed because the molecular vibrations cause some departure from perfect symmetry (vibronic coupling). The molar absorption coefficients of these transitions are very small and the corresponding absorption bands exhibit well-defined vibronic bands.

Potential energy curves and surfaces

Harmonic Oscillator

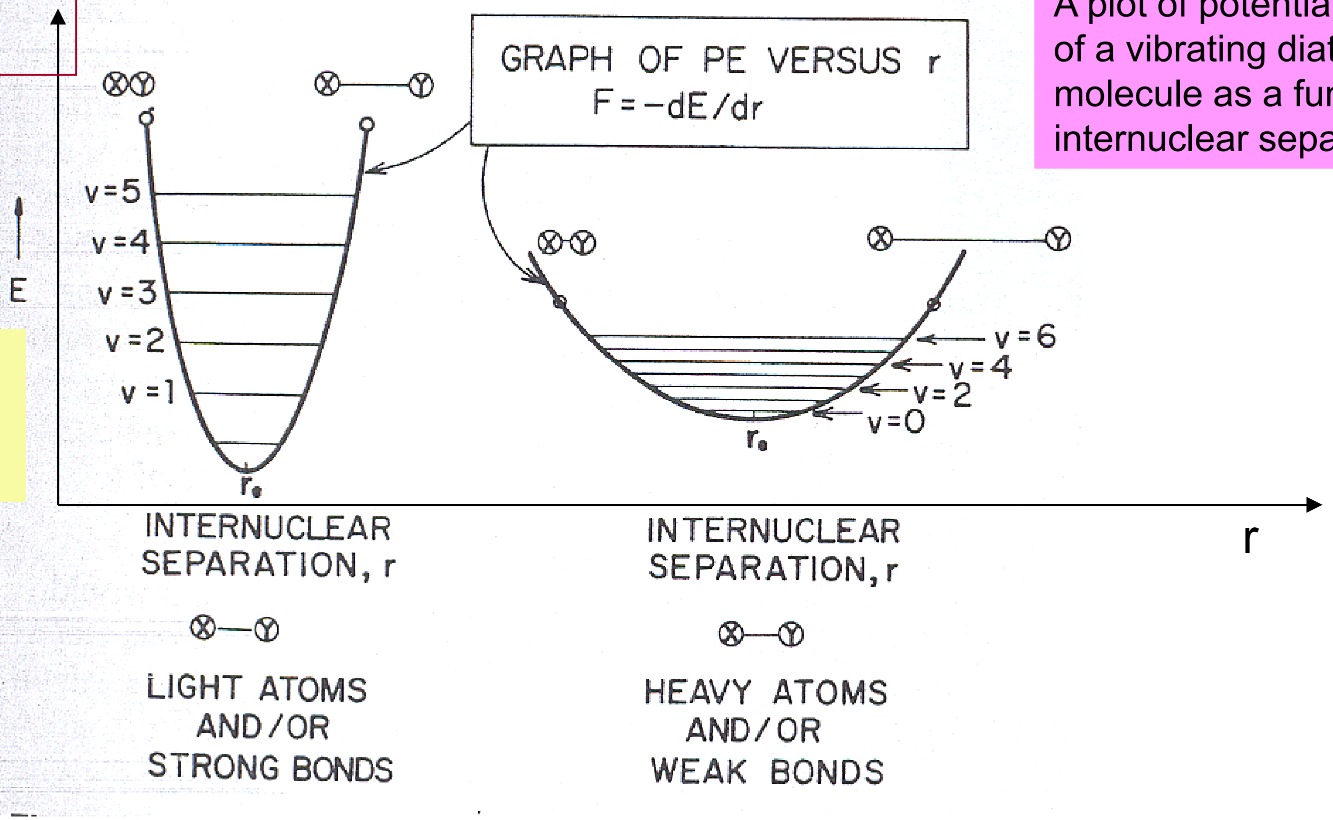


(a)
X
Y
(b)
X
Y
Stretching
Contracting

Harmonic oscillator quantized levels:
$E_v = h\nu(v+1/2)$

The energy levels are quantized: vibrational levels

A plot of potential energy of a vibrating diatomic molecule as a function of internuclear separation



GRAPH OF PE VERSUS r
F = −dE/dr
E
X Y
v=5
v=4
v=3
v=2
v=1
r_e
v=6
v=4
v=2
v=0
INTERNUCLEAR SEPARATION, r
INTERNUCLEAR SEPARATION, r
LIGHT ATOMS AND/OR STRONG BONDS
HEAVY ATOMS AND/OR WEAK BONDS
r

(An)harmonic Oscillator + vibrations

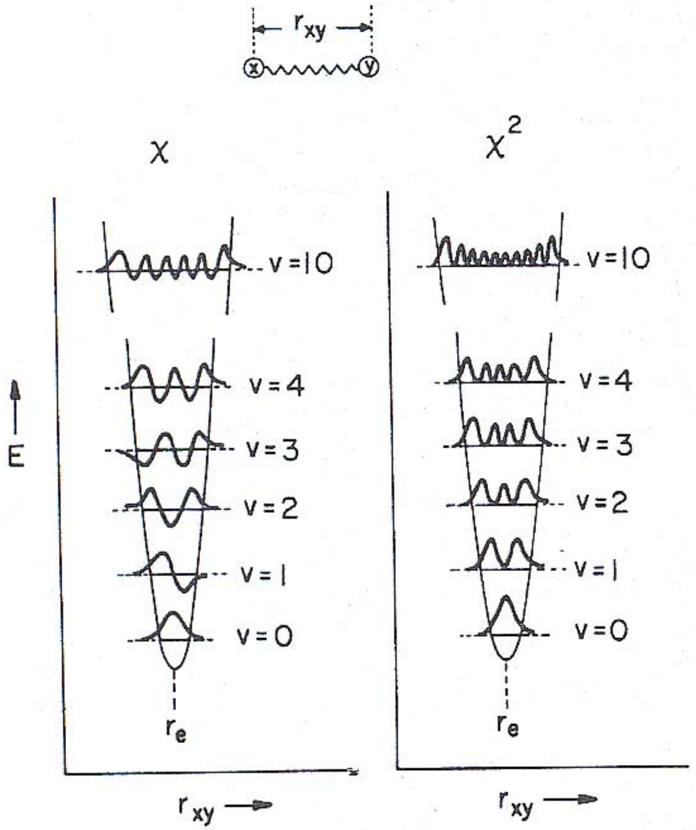
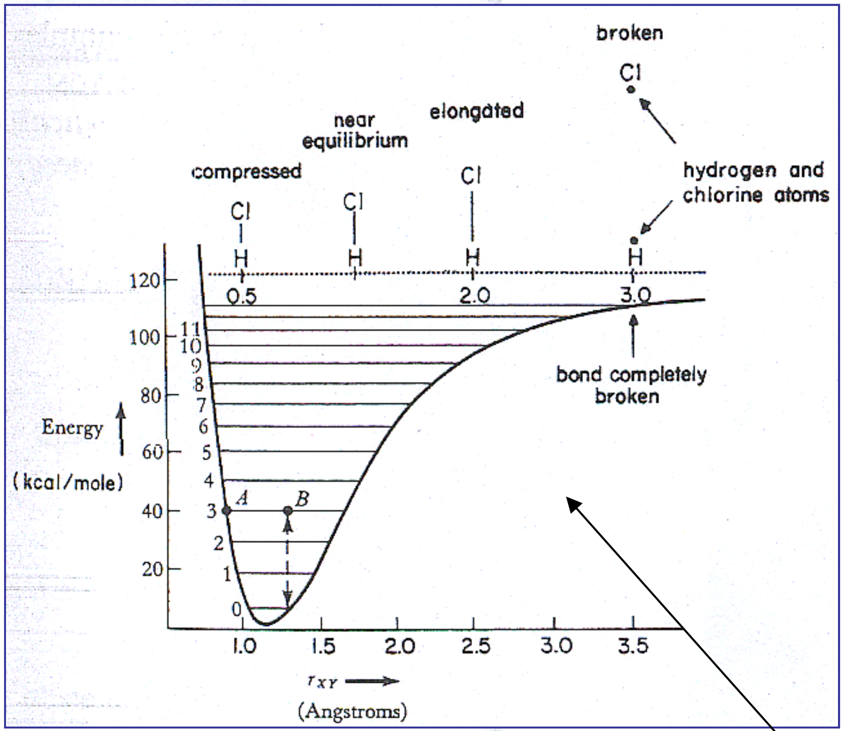


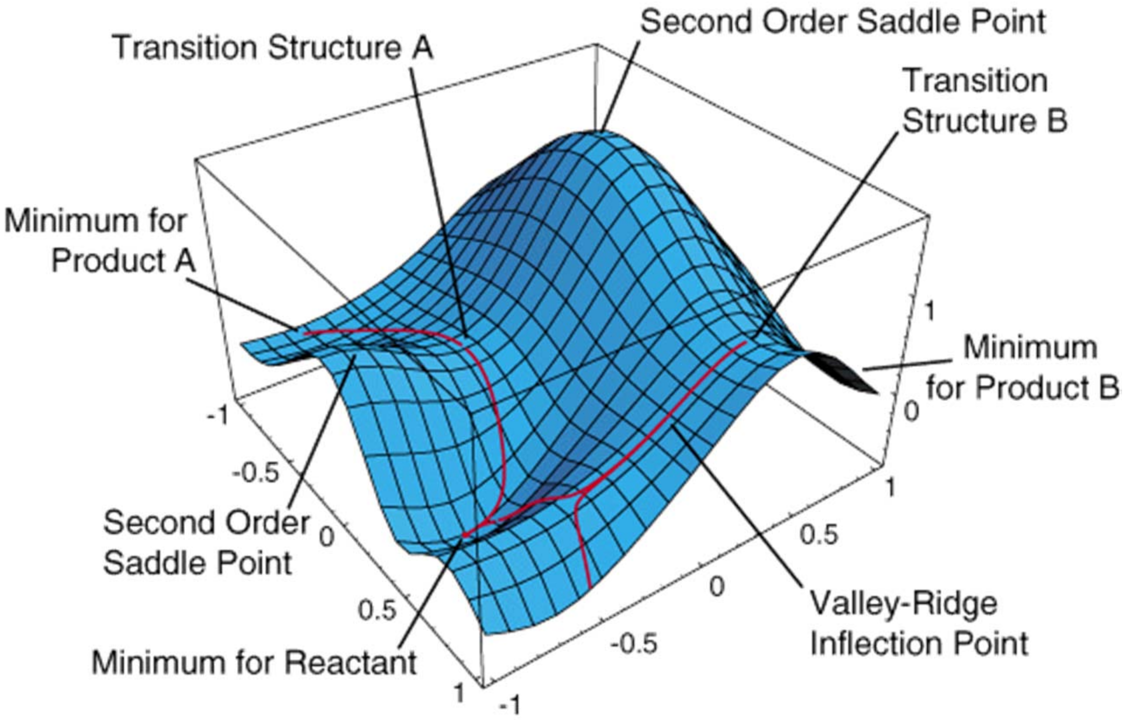
Figure 4.5

Quantum mechanical description of a vibrating molecule. Superimposed on the various levels ($v = 0, 1, 2, \ldots$) are the vibrational eigenfunction (χ)—left-hand curves—and the square of the vibrational eigenfunctions (χ^2). The mathematical sign of the function oscillates from positive to negative values except for the χ of $v = 0$, which is positive everywhere. The positive portions of χ are indicated as portions of the curve above the line representing the energy of the vibrational level. The greater the number of nodes in χ, the greater the kinetic energy of the vibrational level. The values of χ^2 are proportional to the probability of finding the nuclei XY at a corresponding separation r_{xy}.



Anharmonic oscillator

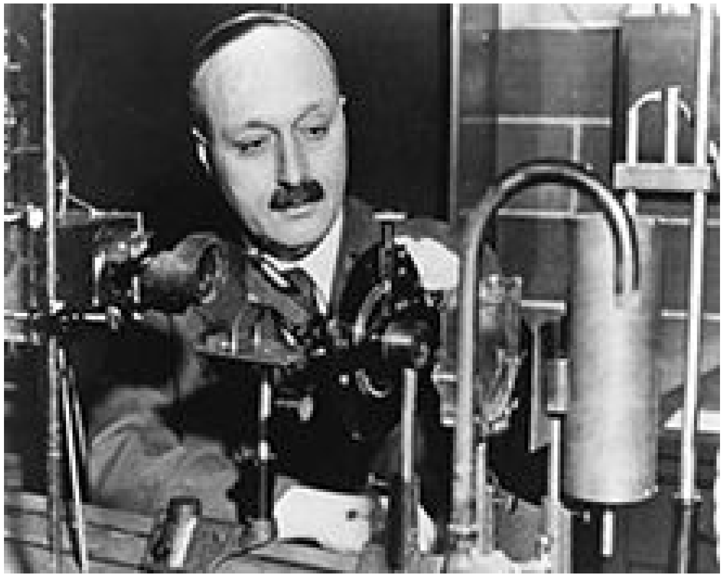
Potential Energy Surfaces


Transition Structure A
Second Order Saddle Point
Transition Structure B
Minimum for Product A
Minimum for Product B
Second Order Saddle Point
Minimum for Reactant
Valley-Ridge Inflection Point
-1
-0.5
0
0.5
1
-1
-0.5
0
0.5
1
0
1

Frank-Condon Principle:

Since electronic motions are much faster than nuclear motion, electronic transitions occur most favorably when the nuclear structure of the initial and final states are most similar

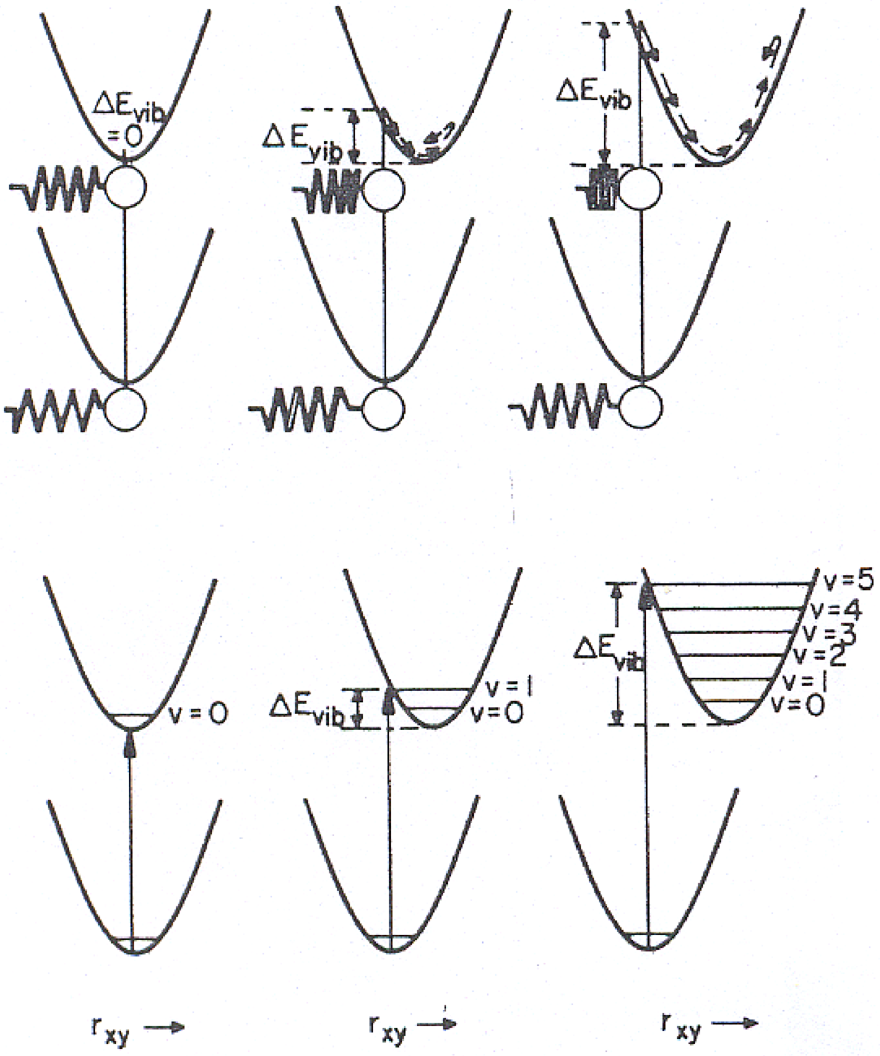
James Franck



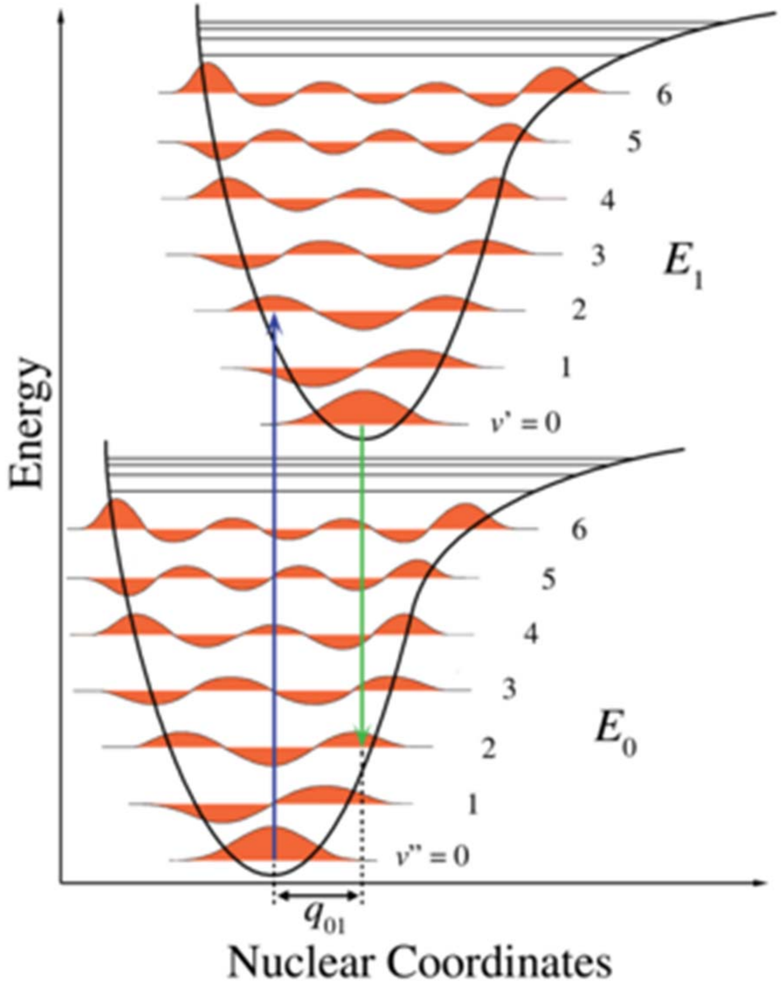
Franck completed his Ph.D. in 1906 and received his venia legendi, or Habilitation, for physics in 1911, both at the University of Berlin, where he lectured and taught until 1918, having reached the position of extraordinarius professor. After World War I, in which he served and was awarded the Iron Cross 1st Class, Franck became the Head of the Physics Division of the Kaiser Wilhelm Gesellschaft for Physical Chemistry. In 1920, Franck became ordinarius professor of experimental physics and Director of the Second Institute for Experimental Physics at the University of Göttingen. While there he worked on quantum physics with Max Born, who was Director of the Institute of Theoretical Physics.

In 1925, Franck received the Nobel Prize in Physics, mostly for his work in 1912-1914, which included the Franck-Hertz experiment, an important confirmation of the Bohr model of the atom. In 1933, after the Nazis came to power, Franck, being a Jew, decided to leave his post in Germany and continued his research in the United States, first at Johns Hopkins University in Baltimore and then, after a year in Denmark, in Chicago. It was there that he became involved in the Manhattan Project during World War II;

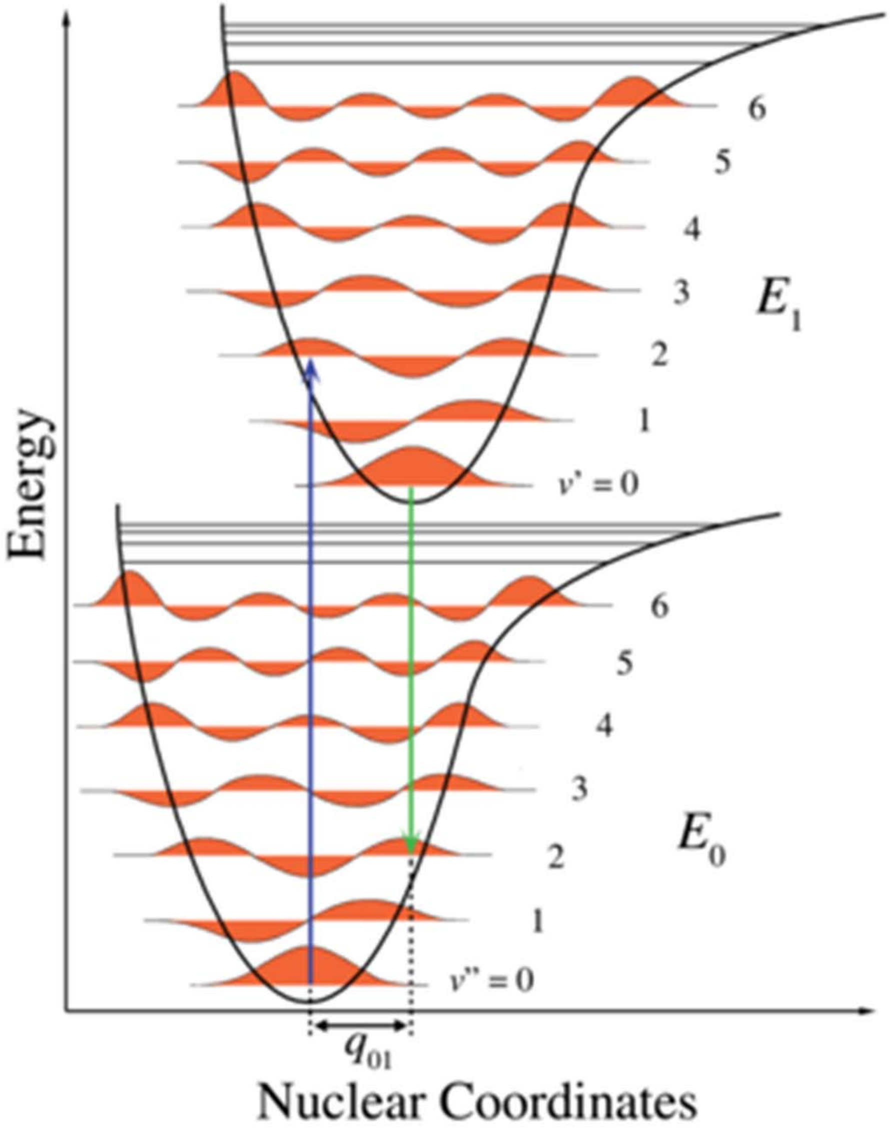
“Vertical” transitions


ΔE_vib =0
ΔE_vib
ΔE_vib
v = 0
ΔE_vib
v = 1
v = 0
ΔE_vib
v = 5
v = 4
v = 3
v = 2
v = 1
v = 0
r_xy →
r_xy →
r_xy →

Think molecules! (curve displacement)


Energy
6
5
4
3
2
1
$v' = 0$
E_1
6
5
4
3
2
1
$v'' = 0$
E_0
q_{01}
Nuclear Coordinates

Radiative transitions


Energy
6
5
4
3
2
1
v' = 0
E_1
6
5
4
3
2
1
v" = 0
E_0
q_{01}
Nuclear Coordinates

Net positive overlap of the wave functions in the initial and final states is given by

Frank-Condon Integral:

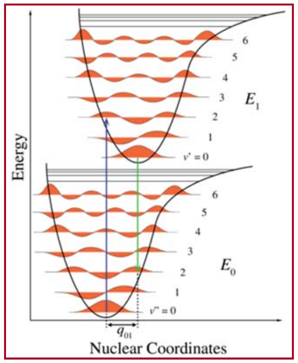
$$\langle \chi_i | \chi_f \rangle$$

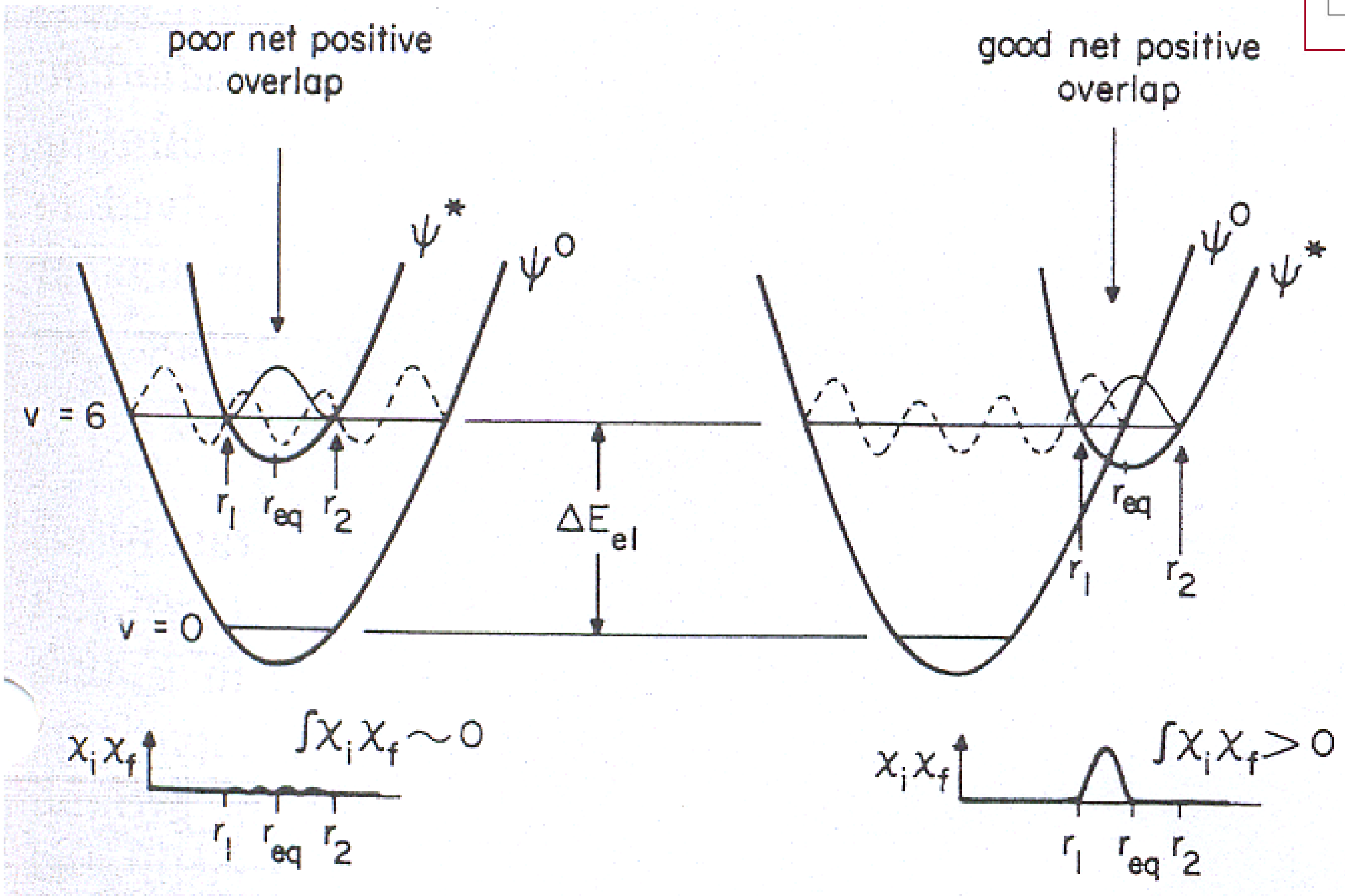
The probability of electronic transition is given by

Frank-Condon factors:

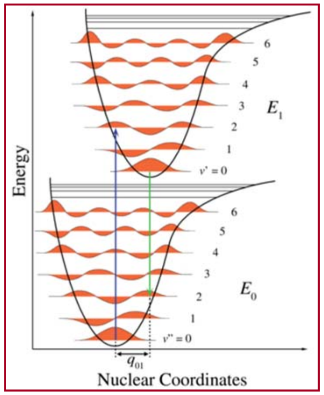
$$\langle \chi_i | \chi_f \rangle^2$$

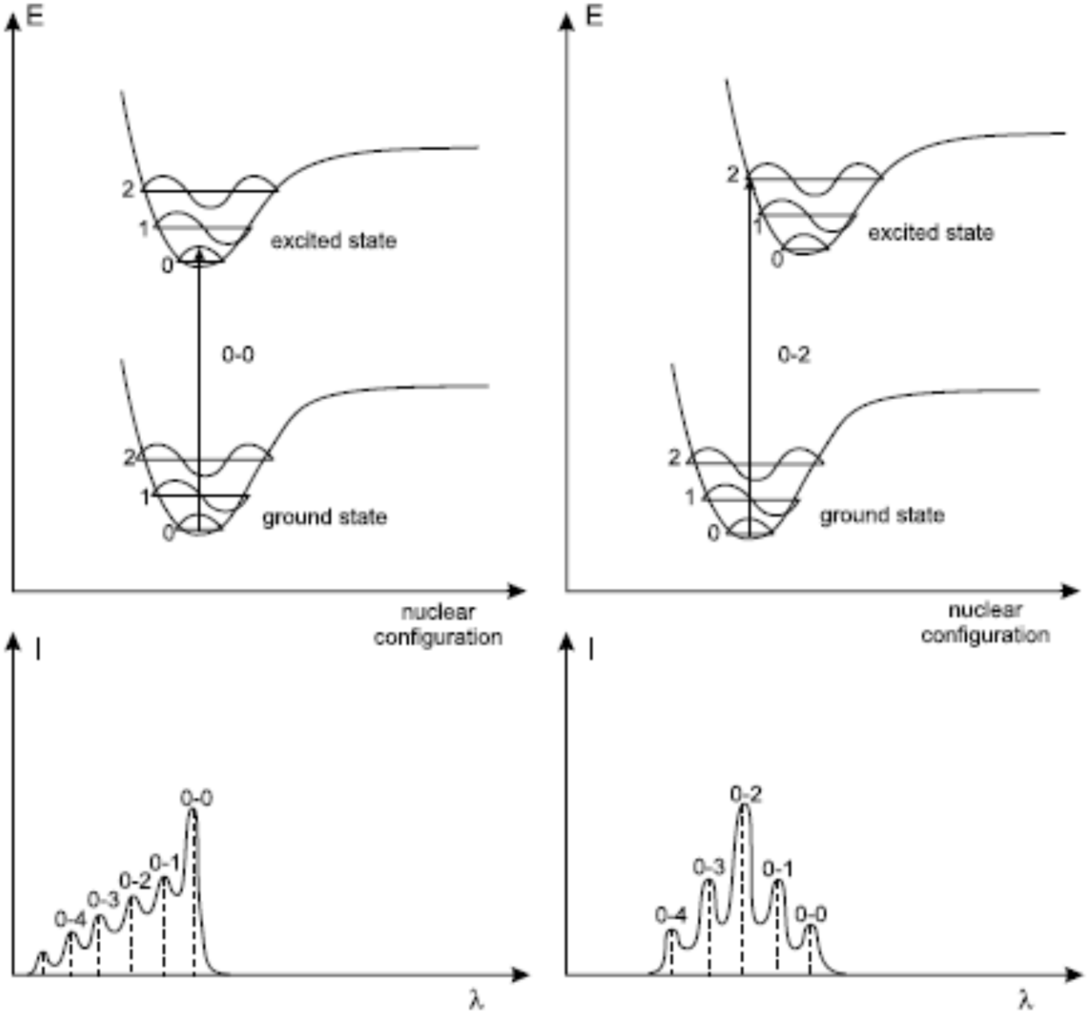
Radiationless transitions


Energy
6
5
4
3
2
1
v' = 0
E_1
6
5
4
3
2
1
v'' = 0
E_0
q_{01}
Nuclear Coordinates

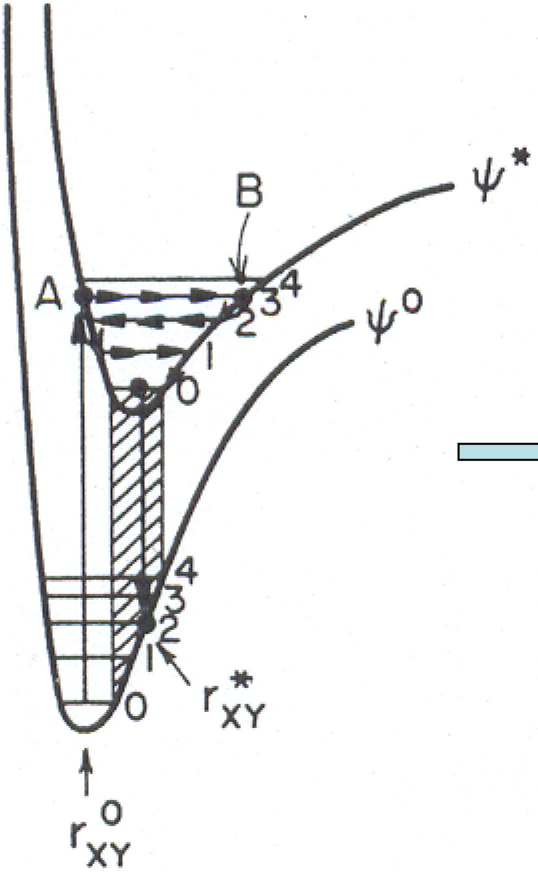

poor net positive overlap
good net positive overlap
ψ^*
ψ^0
ψ^0
ψ^*
v = 6
v = 0
r_1
r_{eq}
r_2
ΔE_{el}
r_{eq}
r_1
r_2
$\chi_i \chi_f$
$\int \chi_i \chi_f \sim 0$
r_1
r_{eq}
r_2
$\chi_i \chi_f$
$\int \chi_i \chi_f > 0$
r_1
r_{eq}
r_2

Absorption

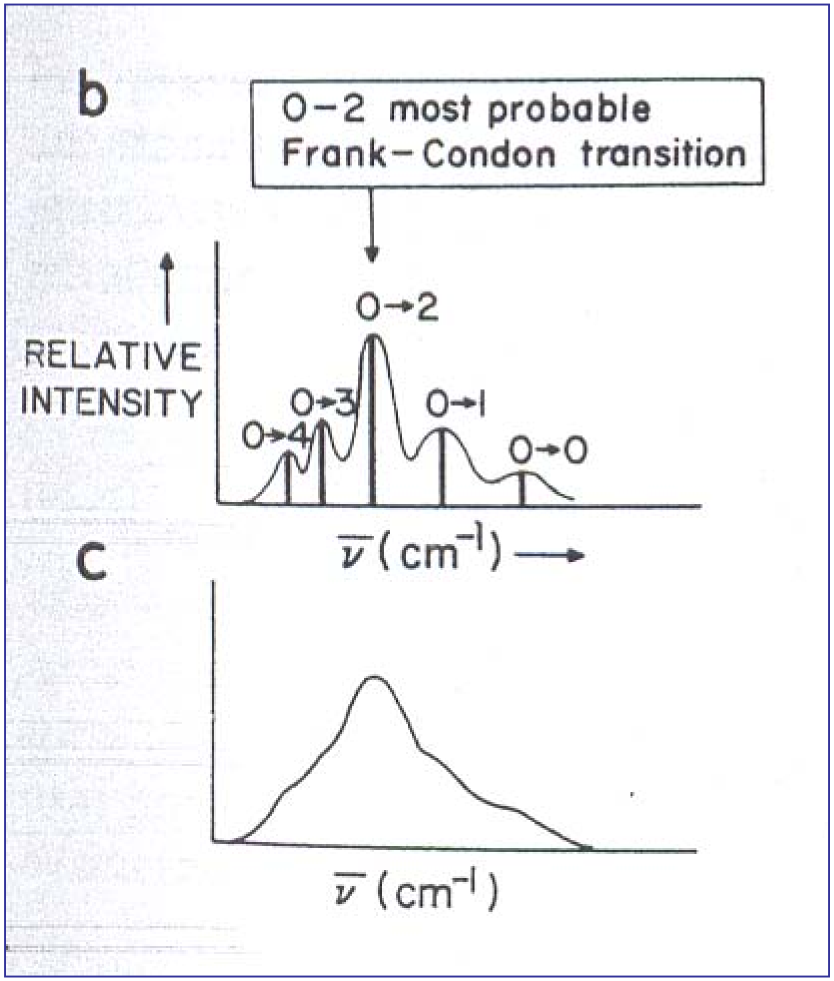

Energy
v' = 0
E_1
v'' = 0
E_0
q_{01}
Nuclear Coordinates


E
2
1
0
excited state
0-0
2
1
0
ground state
nuclear configuration
E
2
1
0
excited state
0-2
2
1
0
ground state
nuclear configuration
I
0-0
0-1
0-2
0-3
0-4
λ
I
0-2
0-3
0-1
0-4
0-0
λ

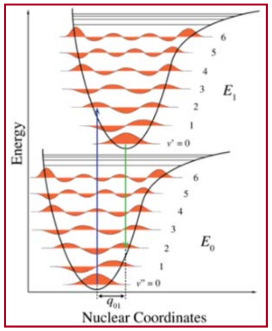
Emission



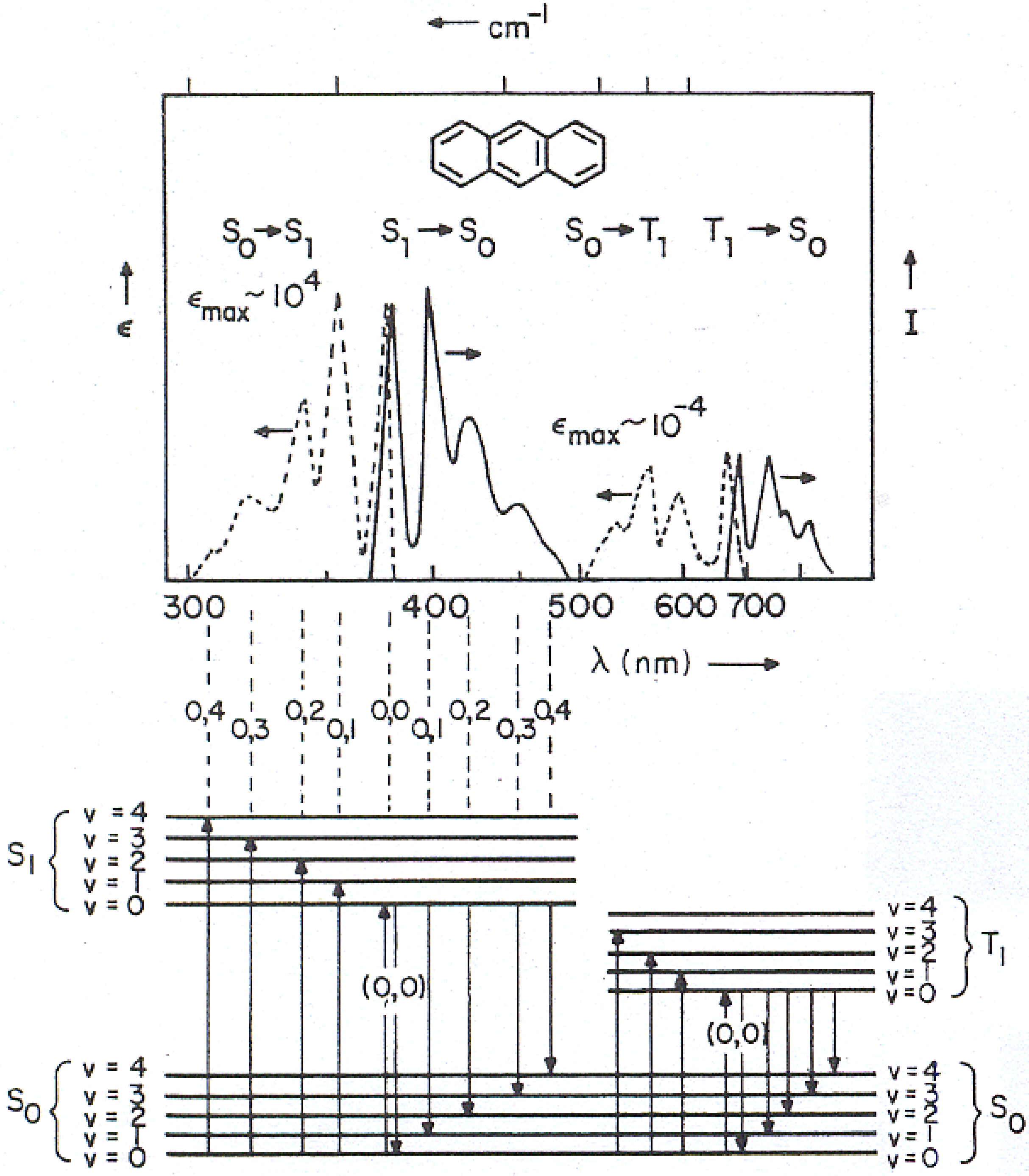
B
ψ*
A
3
4
2
1
0
ψ°
4
3
2
1
0
r*XY
r°XY



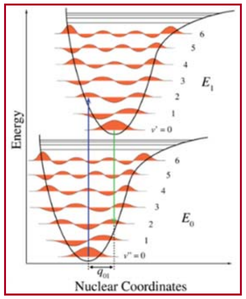
b
0–2 most probable
Frank–Condon transition
RELATIVE INTENSITY
0→2
0→3
0→4
0→1
0→0
ν̄ (cm⁻¹) →
c
ν̄ (cm⁻¹)



Energy
Nuclear Coordinates
E1
E0
6
5
4
3
2
1
v' = 0
6
5
4
3
2
1
v'' = 0
q01

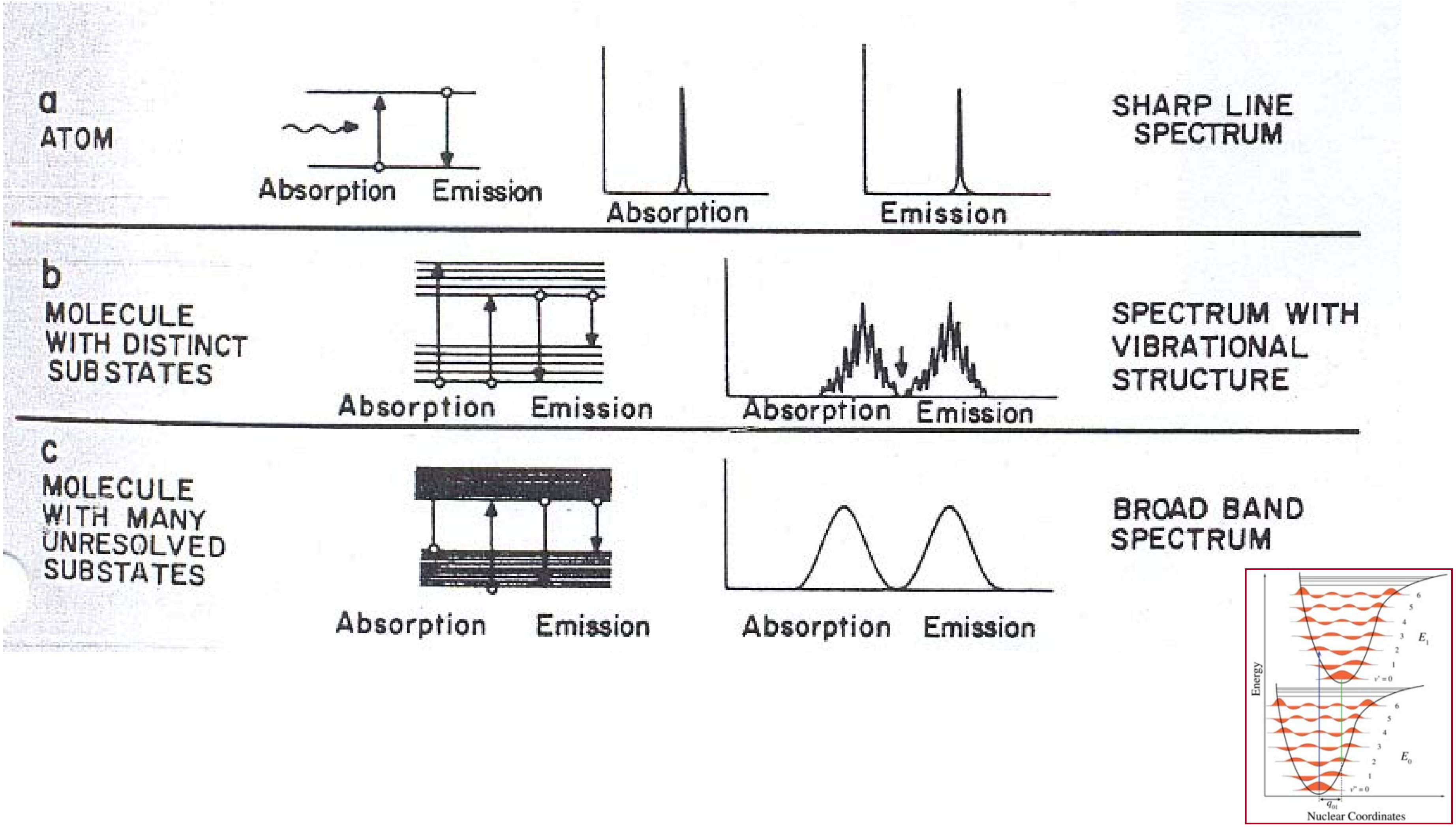


← cm⁻¹
$S_0 \rightarrow S_1$
$S_1 \rightarrow S_0$
$S_0 \rightarrow T_1$
$T_1 \rightarrow S_0$
$\epsilon_{max} \sim 10^4$
$\epsilon_{max} \sim 10^{-4}$
↑ ε
↑ I
300
400
500
600
700
λ (nm) →
0,4
0,3
0,2
0,1
0,0
0,1
0,2
0,3
0,4
S_1
v = 4
v = 3
v = 2
v = 1
v = 0
(0,0)
S_0
v = 4
v = 3
v = 2
v = 1
v = 0
T_1
v = 4
v = 3
v = 2
v = 1
v = 0
(0,0)
S_0
v = 4
v = 3
v = 2
v = 1
v = 0



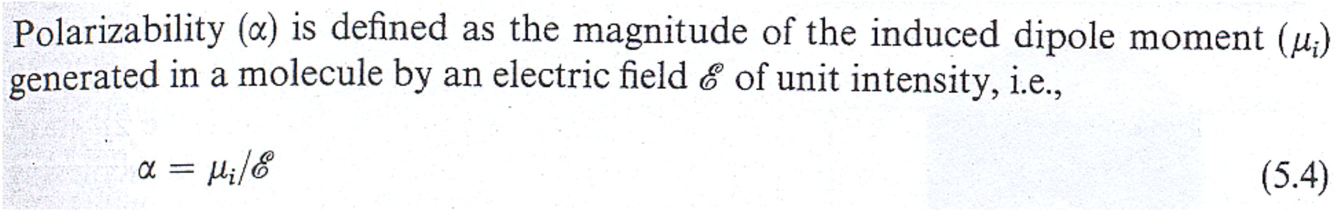
Energy
E_1
E_0
v' = 0
v" = 0
q_{01}
Nuclear Coordinates

Shape of Absorption and Emission Spectra



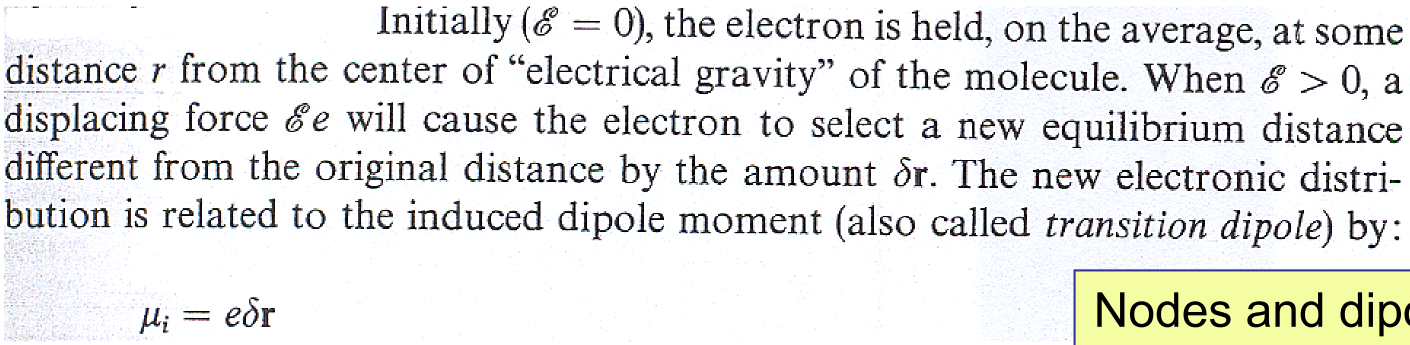
a
ATOM
Absorption
Emission
Absorption
Emission
SHARP LINE SPECTRUM
b
MOLECULE WITH DISTINCT SUBSTATES
Absorption
Emission
Absorption
Emission
SPECTRUM WITH VIBRATIONAL STRUCTURE
c
MOLECULE WITH MANY UNRESOLVED SUBSTATES
Absorption
Emission
Absorption
Emission
BROAD BAND SPECTRUM
Energy
E_1
E_0
$v'=0$
$v''=0$
1
2
3
4
5
6
q_{01}
Nuclear Coordinates

Polarizabilty and Transition Dipole Moment



Polarizability (α) is defined as the magnitude of the induced dipole moment (μ_i) generated in a molecule by an electric field $\mathscr{E}$ of unit intensity, i.e.,

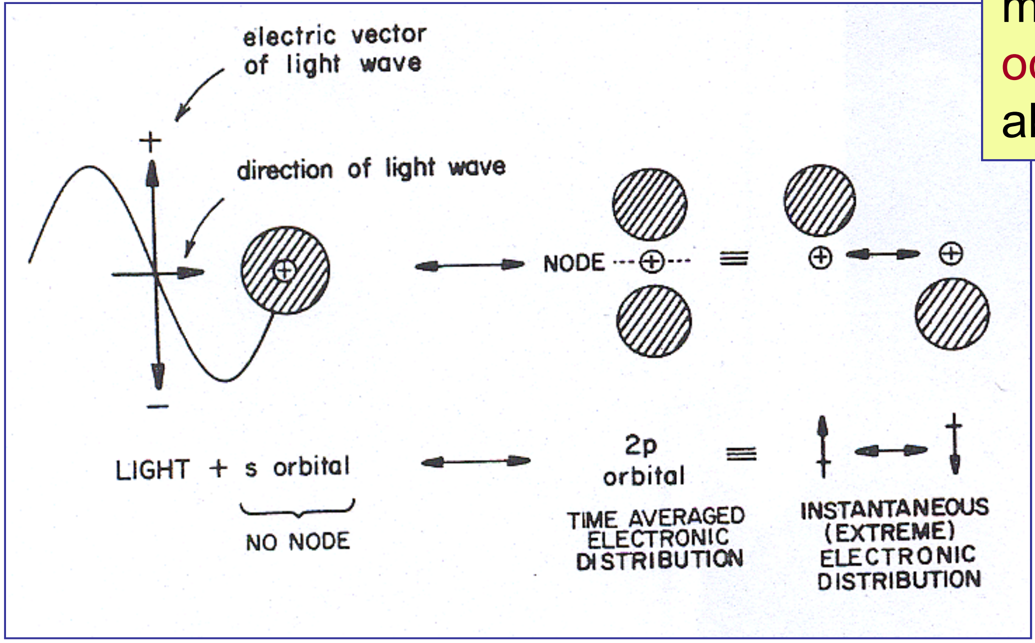
$$\alpha = \mu_i/\mathscr{E} \tag{5.4}$$



Initially ($\mathscr{E} = 0$), the electron is held, on the average, at some distance r from the center of "electrical gravity" of the molecule. When $\mathscr{E} > 0$, a displacing force $\mathscr{E}e$ will cause the electron to select a new equilibrium distance different from the original distance by the amount $\delta\mathbf{r}$. The new electronic distribution is related to the induced dipole moment (also called *transition dipole*) by:

$$\mu_i = e\delta\mathbf{r}$$

Nodes and dipole moments have to occur, otherwise no absorption is observed


electric vector of light wave
+
direction of light wave
−
NODE
≡
LIGHT + s orbital
NO NODE
2p orbital
TIME AVERAGED ELECTRONIC DISTRIBUTION
INSTANTANEOUS (EXTREME) ELECTRONIC DISTRIBUTION

the *theoretical quantity* of the oscillator strength f in the classical theory of light absorption is related to the *experimental* quantity (the extinction coefficient ε of absorption) by the expression:[4]

$$\begin{array}{c}\text{Theoretical oscillator}\\ \text{strength}\end{array} \quad f \equiv 4.3 \times 10^{-9} \int \varepsilon \, d\bar{\nu} \quad \begin{array}{c}\text{Experimental}\\ \text{absorption}\end{array} \tag{5.10}$$

where ε is the experimental extinction coefficient and $\bar{\nu}$ is the energy (in wavenumbers) of the absorption in question.

Experimentally, $\int \varepsilon \, d\bar{\nu}$ is the quantity of area under a curve of the molecular extinction coefficient plotted against wavenumber

According to classical theory,[4,5] f is related to the square of the induced dipole moment μ_i produced by action of a light wave on an electric dipole:

$$\underline{\begin{array}{c}\text{Oscillator}\\ \text{strength}\end{array}\ f \propto \mu_i^2 = \langle e\mathbf{r}\rangle^2\ \begin{array}{c}\text{Transition}\\ \text{dipole moment}\end{array}} \qquad (5.12)$$

where μ_i is the induced transition dipole moment or *dipole strength* corresponding to the electronic transition. The latter quantity may be set equal to $e\mathbf{r}$, where $\mathbf{r}$ is the dipole length. Quantitatively the expression relating f and μ_i is given by

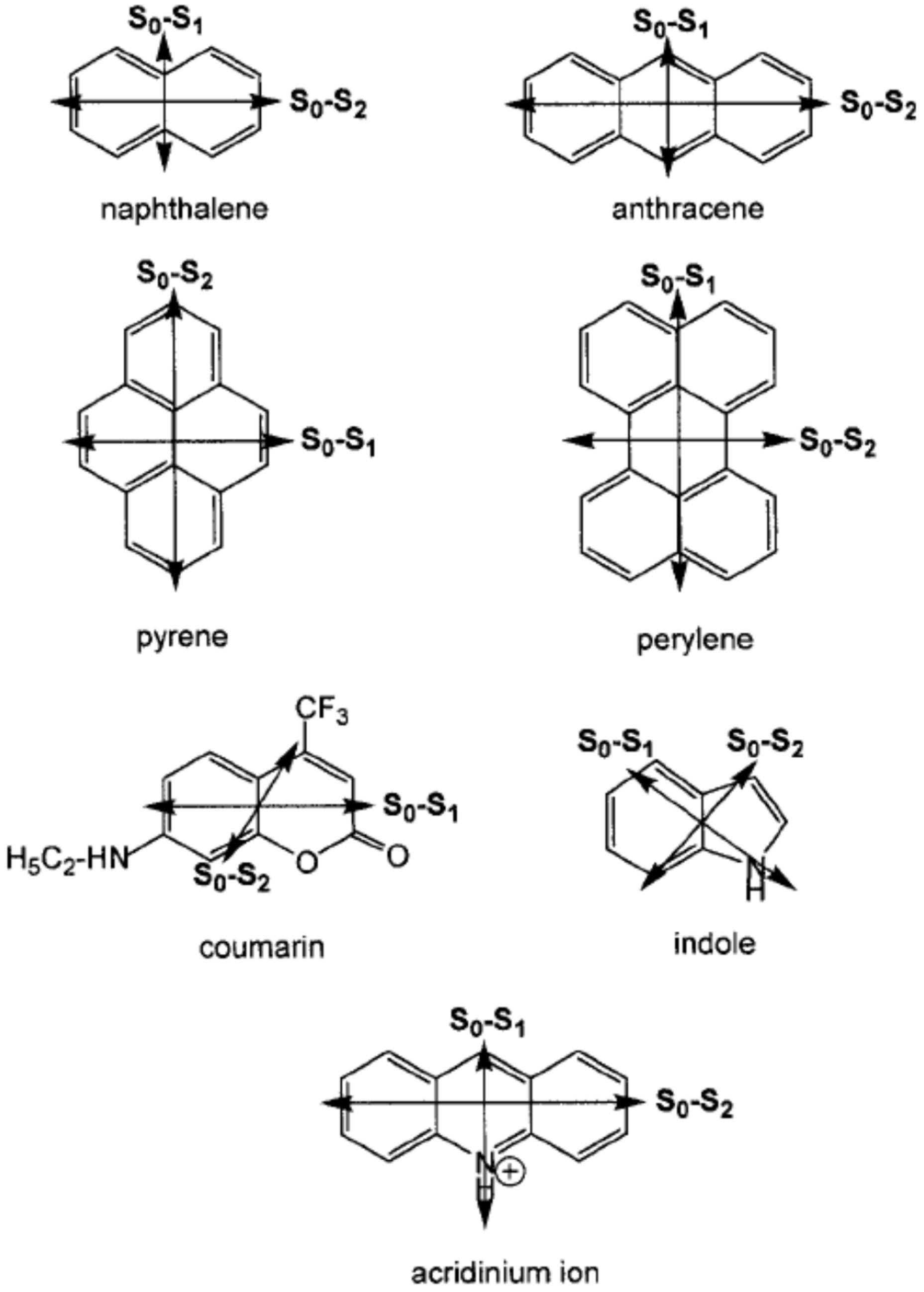
$$f = \left(\frac{8\pi m_e \bar{v}}{3he^2}\right)\mu_i^2 \cong 10^{-5}\,\bar{v}\,|e\mathbf{r}_i|^2 \qquad (5.13)$$

where m_e is the mass of the electron, $\bar{v}$ is the energy of the transition (in cm^{-1}), h is Planck's constant, and $\mathbf{r}$ is the length (in cm) of the transition dipole (i.e., $e\mathbf{r}$ is the transition dipole moment).

We can now identify μ_i with an observable quantity related to the quantum mechanical transition moment matrix element or integral, i.e., $\mu \equiv \langle H\rangle$, and produce:

$$\text{Classical} \rightarrow f = \left(\frac{8\pi m_e \bar{v}}{3he^2}\right)\langle H\rangle^2 \leftarrow \text{Quantum mechanical} \qquad (5.14)$$

Transition Dipoles



naphthalene

anthracene

pyrene

perylene

coumarin

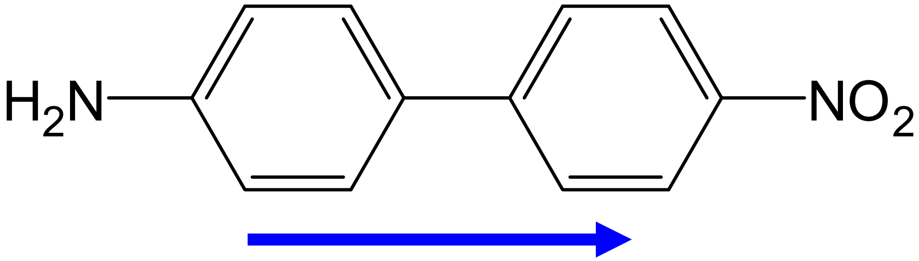
indole

acridinium ion

S_0-S_1
S_0-S_2
CF_3
H_5C_2-HN
O
N
H
+

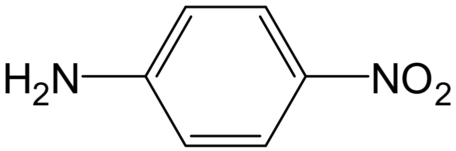
Fig. 2.3. Examples of molecules with their absorption transition moments.

4-AMINO-4'-NITROBIPHENYL

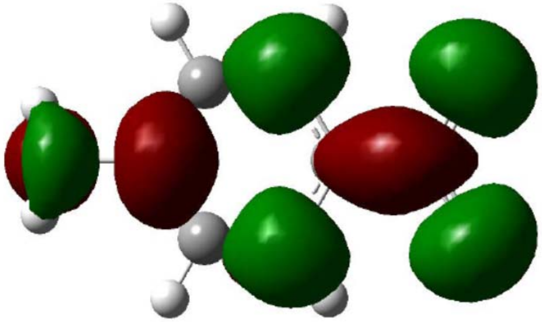


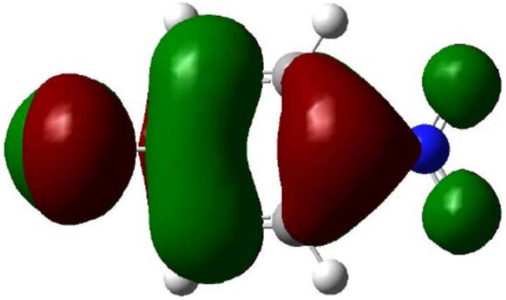
DIPOLES:

Ground state dipole (S_0)	**6 Debye**
Transition dipole (S_1)	**16 Debye**

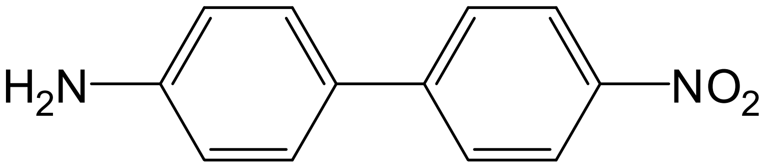


LUMO

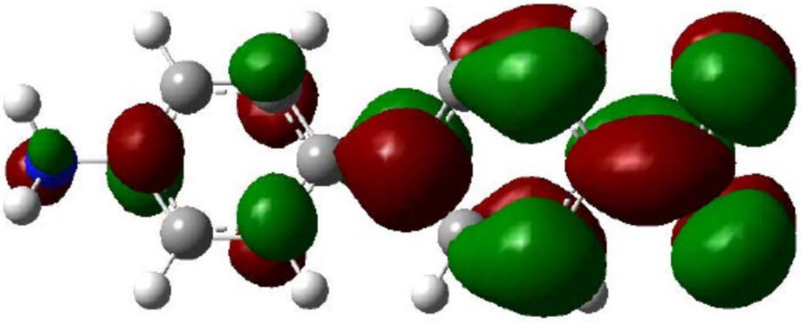


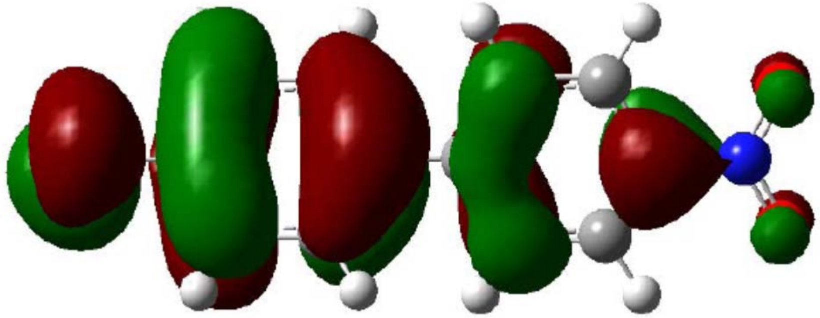


HOMO



LUMO

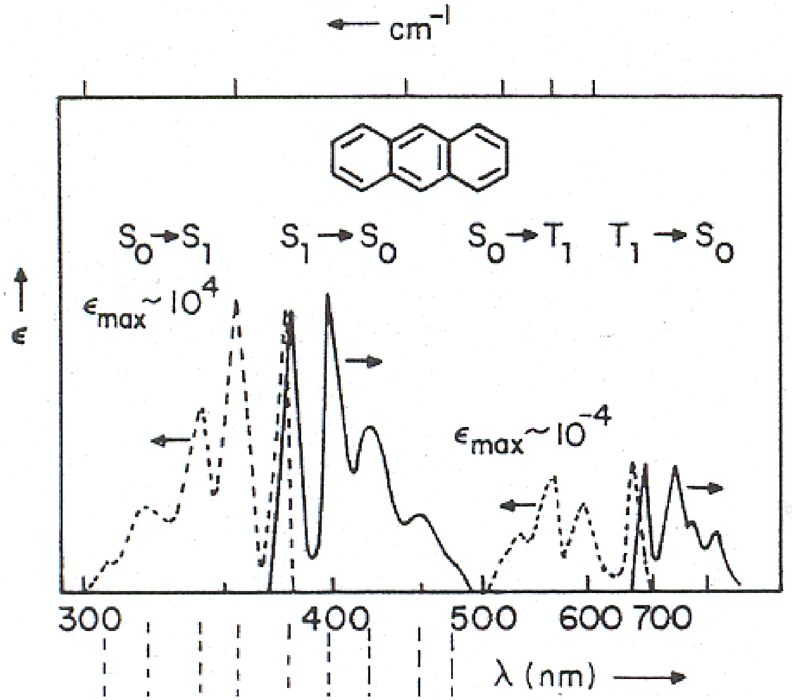




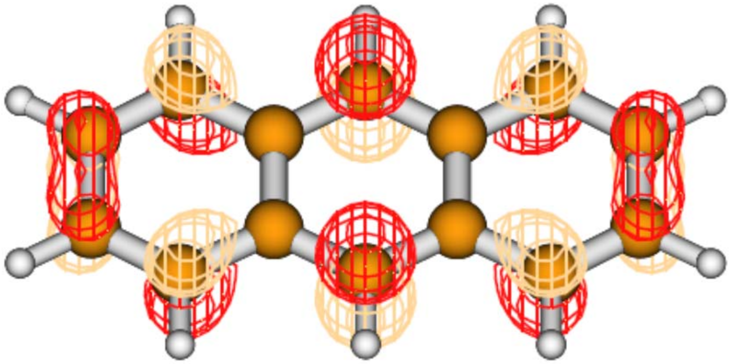
HOMO

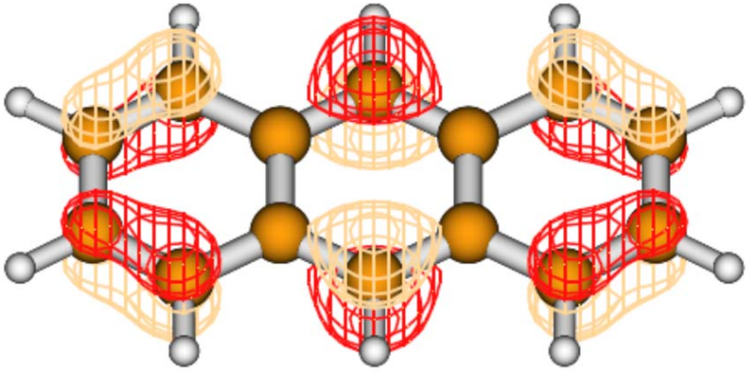
Experimentally Observed Absorption and Emission

Anthracene case

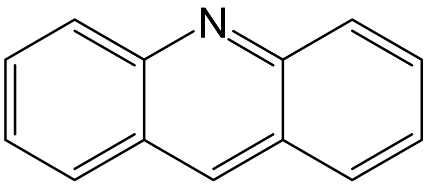


LUMO

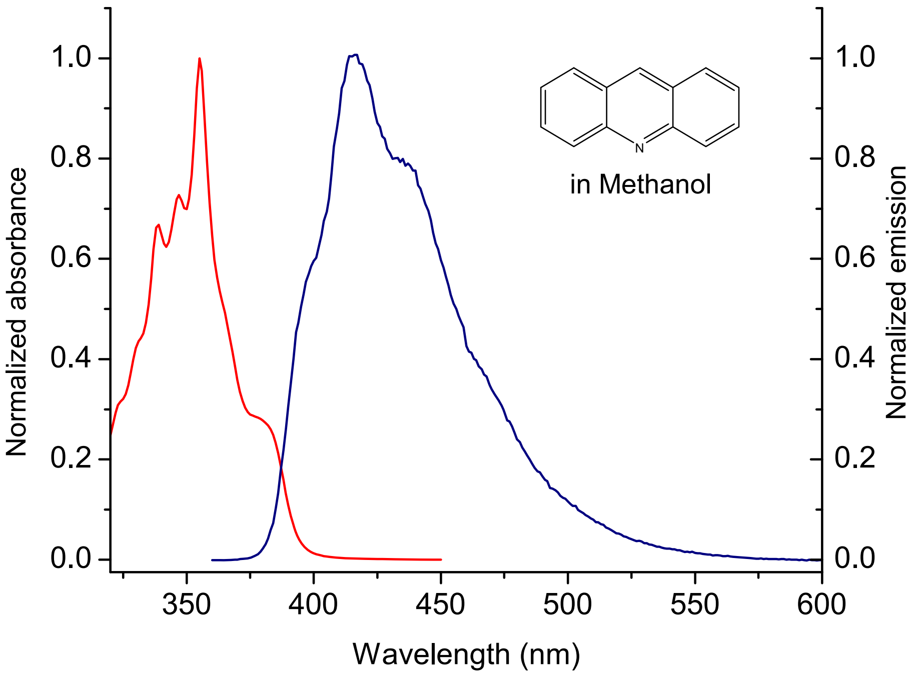




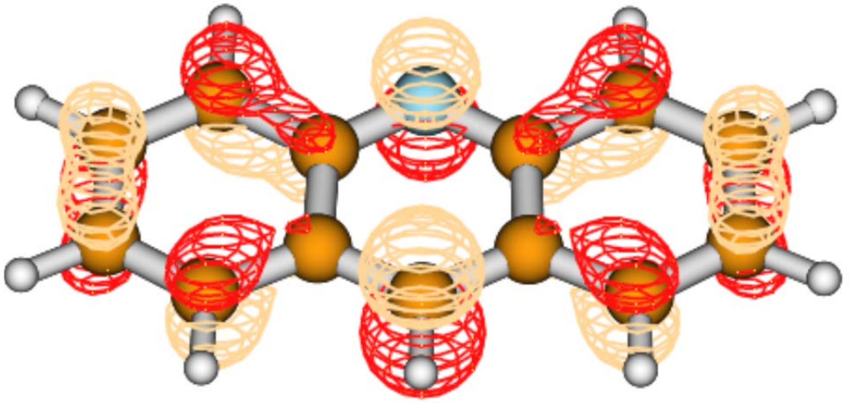
HOMO

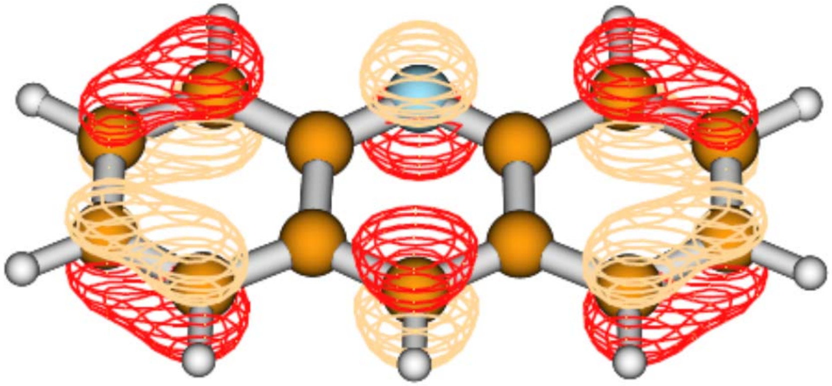


Acridine case

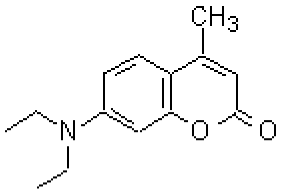


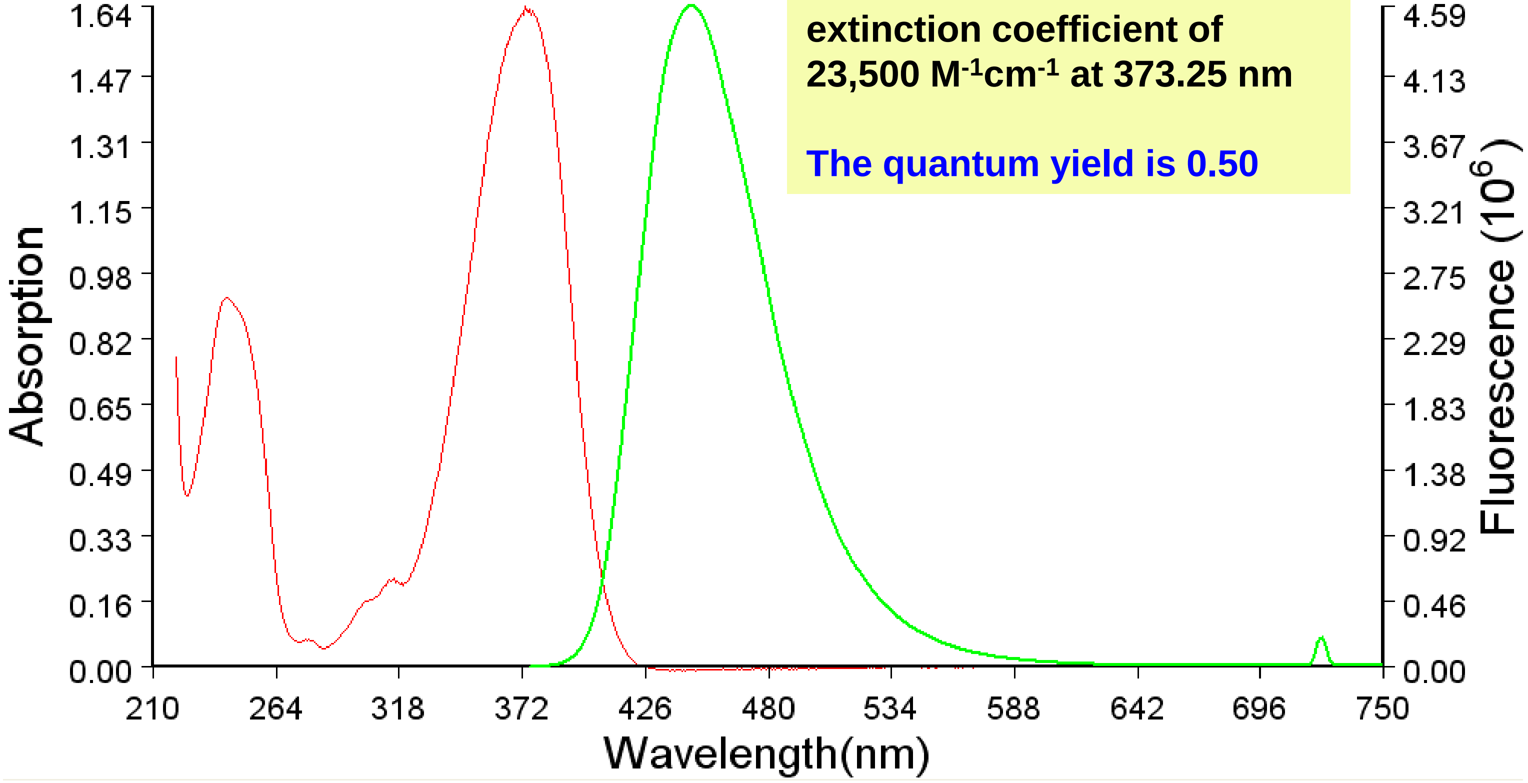
LUMO





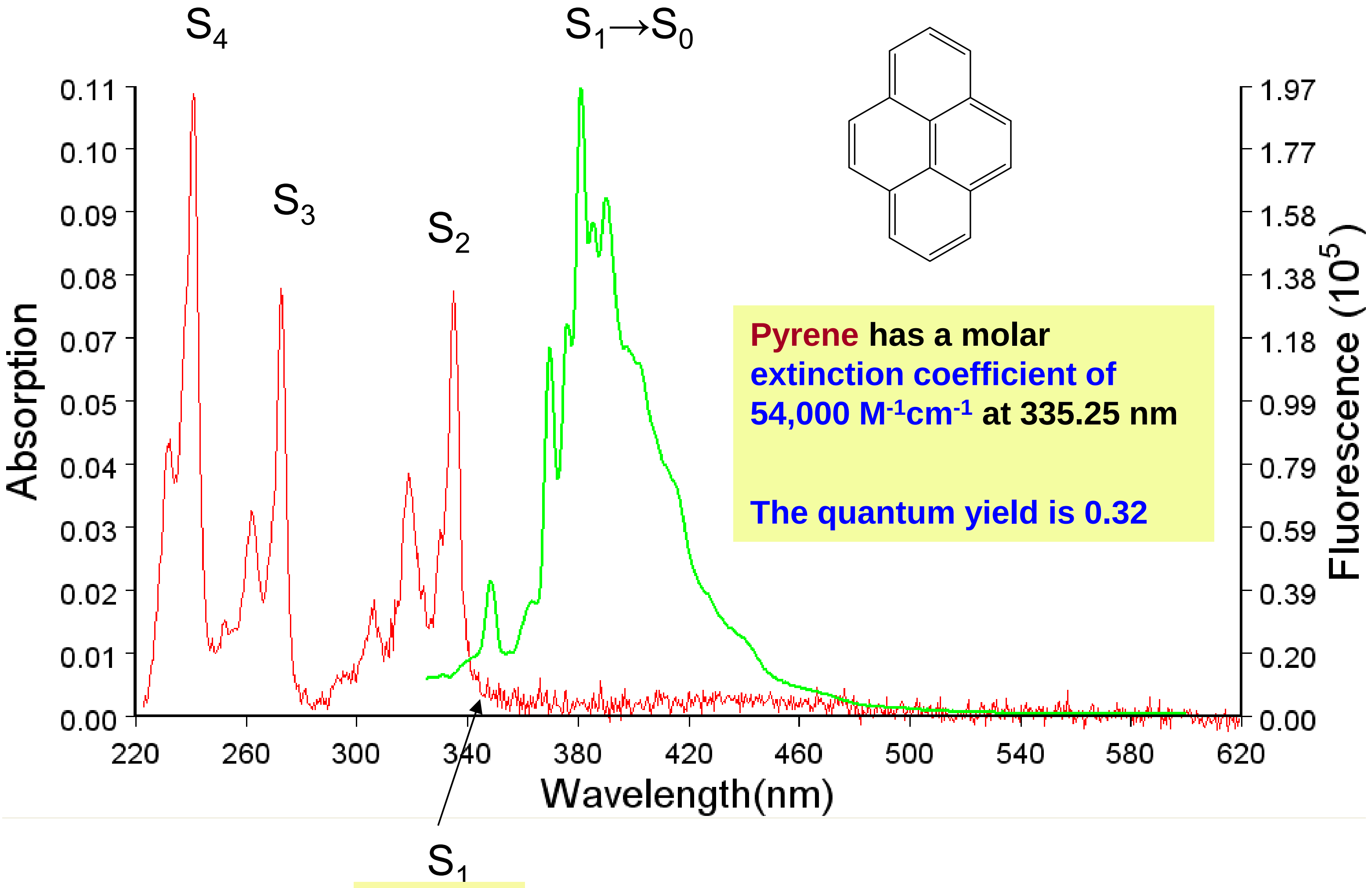
HOMO





Coumarin 1 has a molar extinction coefficient of 23,500 $M^{-1}cm^{-1}$ at 373.25 nm

The quantum yield is 0.50

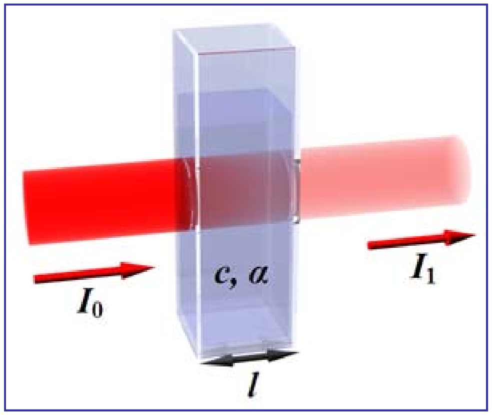


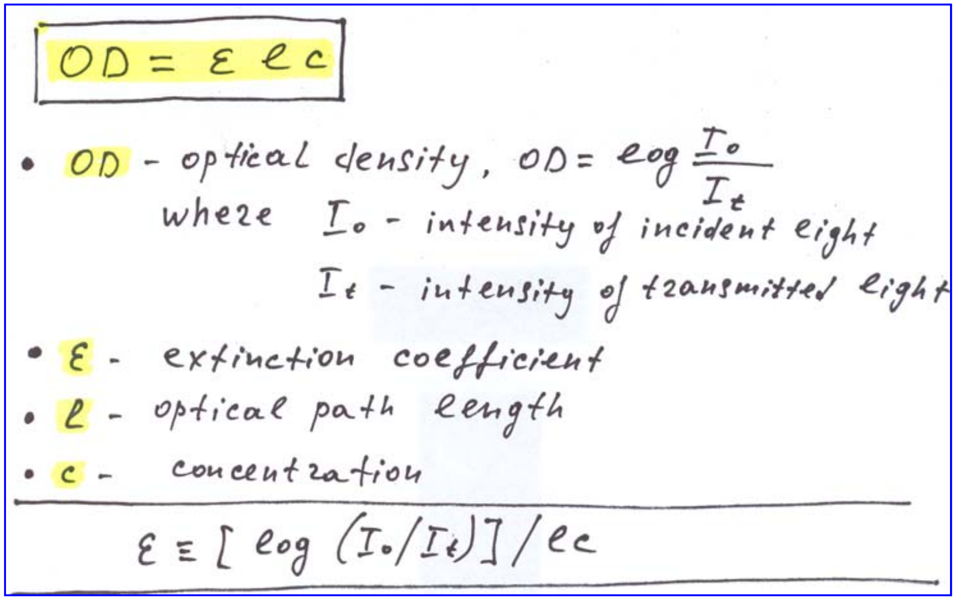
Pyrene has a molar extinction coefficient of 54,000 $M^{-1}cm^{-1}$ at 335.25 nm

The quantum yield is 0.32

Very weak

Absorption: Beer-Lambert Law

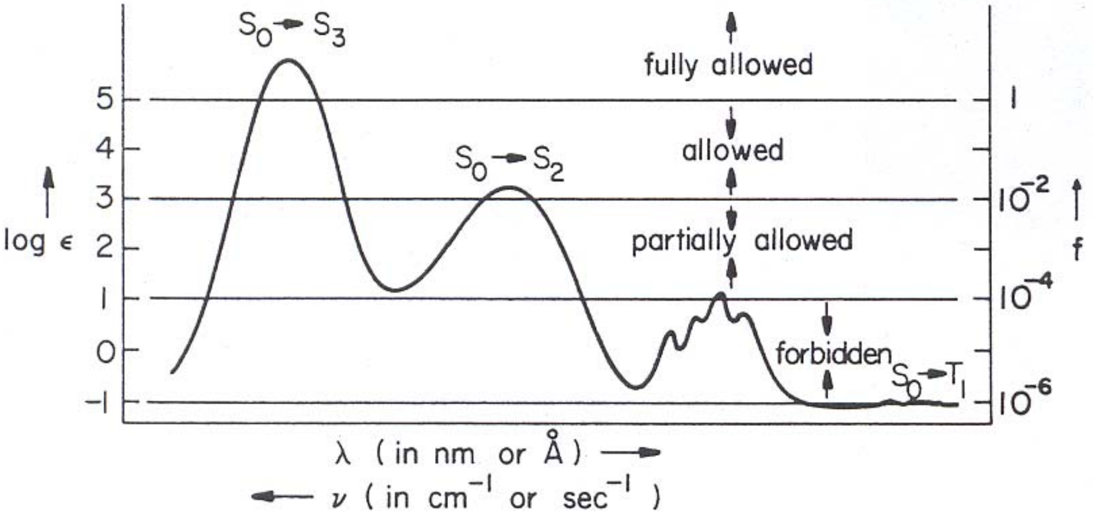


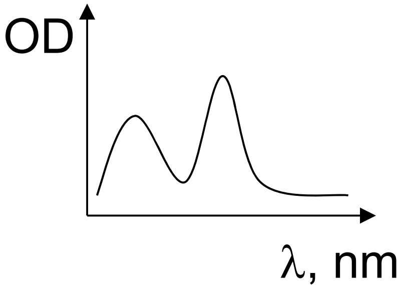


$\boxed{OD = \varepsilon l c}$

- OD - optical density, $OD = \log \frac{I_o}{I_t}$
  where I_o - intensity of incident light
  I_t - intensity of transmitted light
- ε - extinction coefficient
- l - optical path length
- c - concentration

$\varepsilon \equiv [\log (I_o/I_t)]/lc$



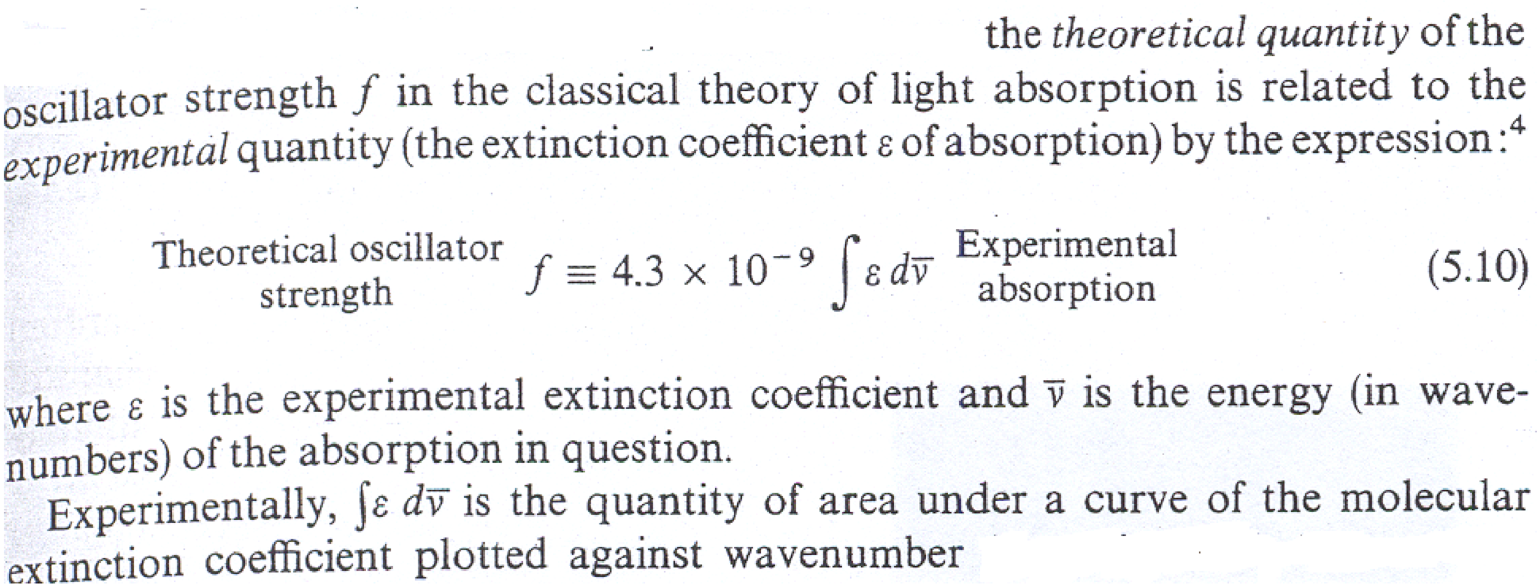


Allowed and Forbidden

- The net moment should be conserved: spin multiplicity cannot change (S-T is forbidden)
- Transition dipole cannot be zero, if zero – transition forbidden
- Symmetry: if HOMO and LUMO have the same symmetry, no net change in transition dipole – forbidden, if they are of wildly different symmetry, so we change orbital momentum upon transition – forbidden.
- Frank-Condon overlap should be significant

Forbidden is never 100% forbidden. Various factors can relax it

f – measure of “allowedness”
Perfectly allowed transition: f ~ 1



the *theoretical quantity* of the oscillator strength f in the classical theory of light absorption is related to the *experimental* quantity (the extinction coefficient ε of absorption) by the expression:[4]

$$\text{Theoretical oscillator strength} \quad f \equiv 4.3 \times 10^{-9} \int \varepsilon \, d\bar{\nu} \quad \text{Experimental absorption} \tag{5.10}$$

where ε is the experimental extinction coefficient and $\bar{\nu}$ is the energy (in wavenumbers) of the absorption in question.

Experimentally, $\int \varepsilon \, d\bar{\nu}$ is the quantity of area under a curve of the molecular extinction coefficient plotted against wavenumber

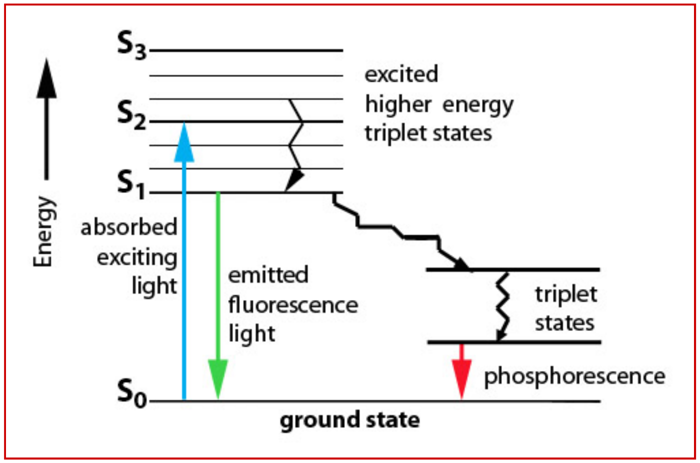
Sir George Gabriel Stokes

In 1852, in his famous paper on the change of wavelength of light, he described the phenomenon of fluorescence, as exhibited by fluorspar and uranium glass, materials which he viewed as having the power to convert invisible ultra-violet radiation into radiation of longer wavelengths that are visible. The Stokes shift, which describes this conversion, is named in Stokes' honor.

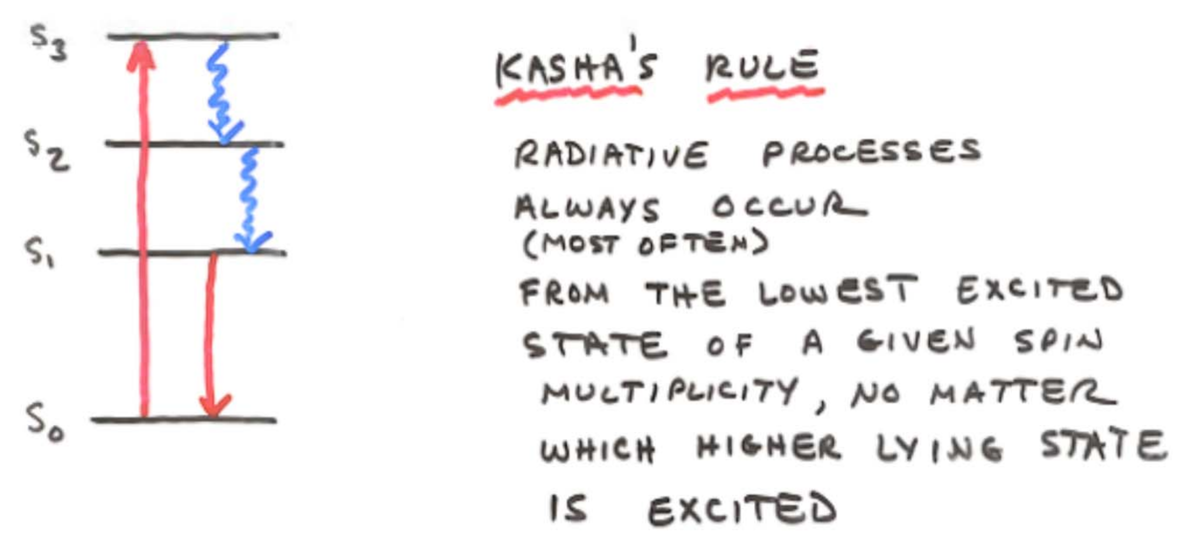
In his first paper, Stokes called the observed phenomenon dispersive reflexion, but in a footnote, he wrote '*I confess I do not like this term. I am almost inclined to coin a word, and call the appearance fluorescence, from fluorspar, as the analogous term opalescence is derived from the name of a mineral*'.

Fluorescence

The Fluorescence Quantum Yield, Φ_F, is defined as the ratio of the number of photons emitted to the number of photons absorbed.



Energy
S_3
S_2
S_1
S_0
excited higher energy triplet states
absorbed exciting light
emitted fluorescence light
triplet states
phosphorescence
ground state



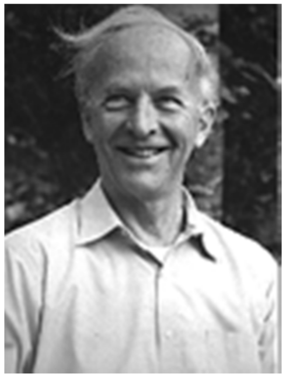
KASHA'S RULE

RADIATIVE PROCESSES ALWAYS OCCUR (MOST OFTEN) FROM THE LOWEST EXCITED STATE OF A GIVEN SPIN MULTIPLICITY, NO MATTER WHICH HIGHER LYING STATE IS EXCITED

Vavilov's Law: Φ_F is independent of the energy of the initially excited state (excitation wavelength). This follows from Kasha's rule.

Fluorescence lifetime.

Practical guide on QY determination: S. Fery-Forgues and D. Lavabre, Journal of Chemical Education 1999, *76*, 1260



Michael Kasha (born December 6, 1920) is an American physical chemist and molecular spectroscopist who is one of the original founders of the Institute of Molecular Biophysics at Florida State University (FSU). Born in Elizabeth, NJ to a family of Ukrainian immigrants, he earned his Ph.D. in chemistry from University of California at Berkeley in 1945, working with renowned physical chemist G.N. Lewis. He is a Distinguished University Research Professor at FSU. He is an elected member of both the National Academy of Sciences and the American Academy of Arts & Sciences, as well as the International Academy of Quantum Molecular Science.

The research in his molecular spectroscopy laboratory has maintained a strong tradition of the discovery and elucidation of excitation mechanisms, with particular application to photochemical and biophysical problems. His most important achievements include identifying triplet states as source of phosphorescence emission, formulating the Kasha rule on fluorescence, and his work on singlet molecular oxygen.

Terminology

- Emission – general term
- Fluorescence – from singlet states
- Phosphorescence – from triplet states
- Luminescence – general for emission of photons