OUTLINES of Time-Resolved Nonlinear Spectroscopies

Prerequisites:

- Linear spectroscopies: A = cεl Lambert Beer law
- Shrödinger equation
- Born-Oppenheimer Approximation
- Electronic and vibrational molecular levels

We will go through:

- Wavefuction of a damped harmonic oscillator
- Linear and Non Linear Polarization terms in a two level system
- The correlation function
- Natural linewidth and broadening effects on linear spectra: the dephasing.
- Density matrix operator: a statistic ensemble
- Exempla of Time-Resolved Non-Linear experiments

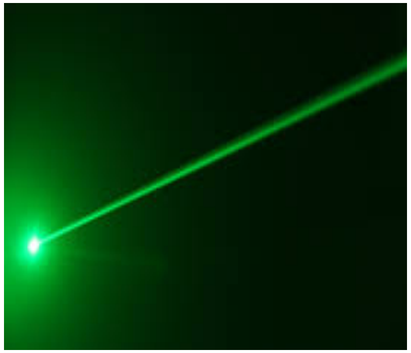
What is SPECTROSCOPY ?

Spectro = image
Scopy= to observe, to see

light – matter interaction

with incoherent and continuous light
(Xe lamp, W lamp)

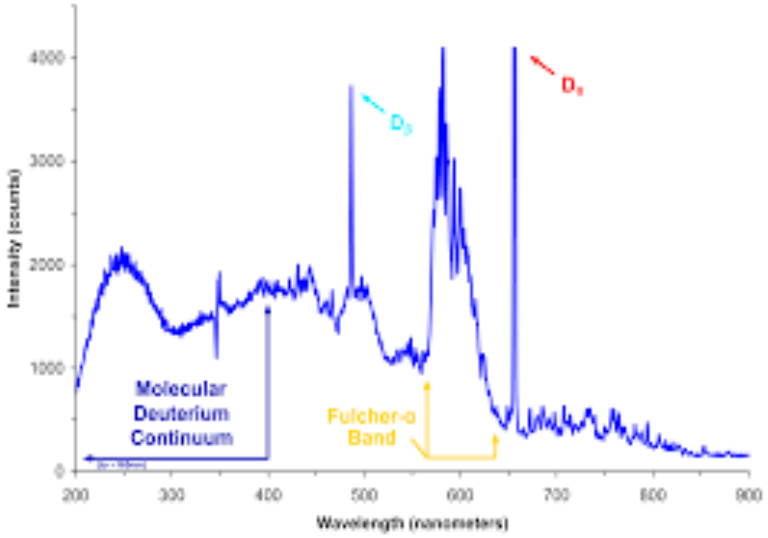
Regime of
weak perturbation



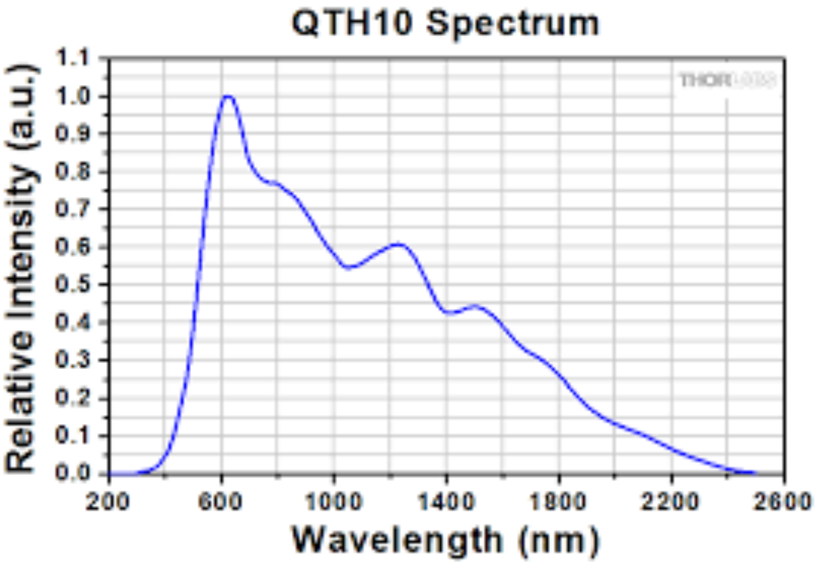
with coherent and pulsed light
(lasers)

Regime of
strong perturbation

Incoherent light sources

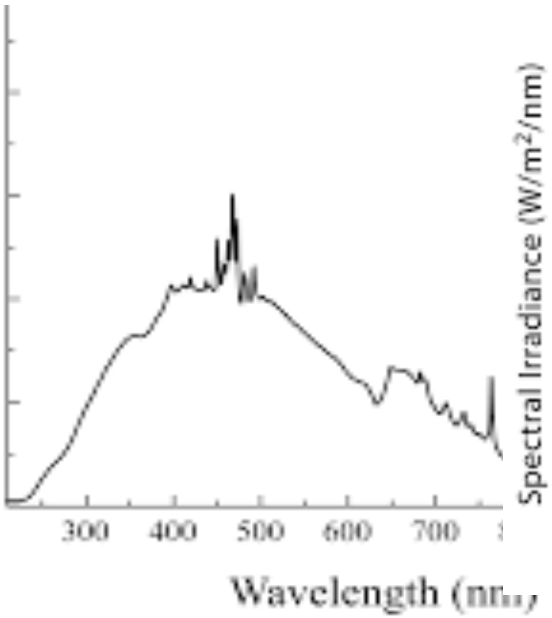


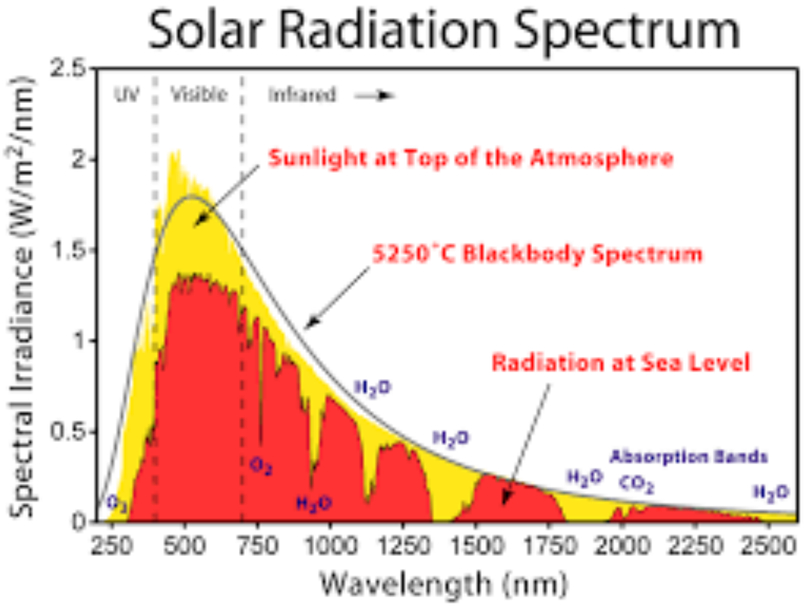
Deuterium lamp in the UV



Tungsten halogen lamp in the VIS

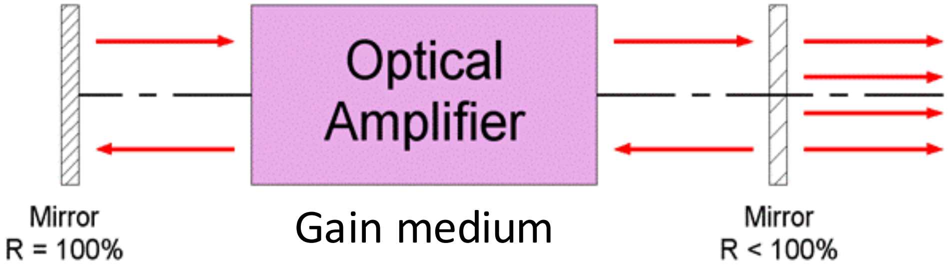
Xe arc spectrum broadband in the VIS





Coherent light sources

- Collimated light: spatial coherence length up to hundred of kilometers
- Very small focus
- Monochromatic emission (L cavity)
- Polarized light
- High intensity



$$n\frac{\lambda}{2} = L$$

Continuous laser *

Gas laser: He-Ne 632 nm

CO$_2$ 10 μm (far-IR)

Solid state laser: diode pumped lasers;

Nd:YAG

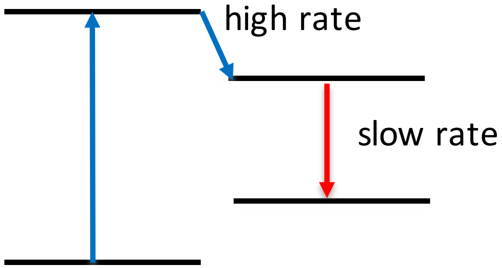
Nd:YVO 1064 nm -> 532 nm.

*light amplification by stimulated emission of radiation

Pulsed laser *

Dye lasers: large gain bandwidth at different wavelengths;

Solid state laser: Ti:Sa around 800 nm.



Focused laser = strong perturbation on matter

$$\vec{E}_{molec} = \frac{1}{4\pi\varepsilon_r\varepsilon_0} \cdot \frac{q}{r^2} = k_{el_r} \int \frac{dq}{r^2}\hat{r}$$ continuous distribution of charge in a dielectric r

Atomic distances: r = 10 Å
Elementary charge: q = 1.6 x 10^{-19} C
$k_{el\ H2O}$ = 1.1 x 10^{8} Nm^2/C^2

Take as example the electric field generated by a H^+ atom in water (acid solution) or a solvated electron e^- in H_2O.

$$\vec{E}_{H^+, e^-_{solv}} = 1.1 \cdot 10^8 \frac{Nm^2}{C^2} \cdot \frac{1.6 \cdot 10^{-19}\ C}{10^{-20}\ m^2} = 1.77 \cdot 10^9 \frac{N}{C}$$

$$I_{Poynting} \propto E_0^2 \sim 10^{18} \frac{W}{m^2} = 10^{18}\ W/m^2$$ Molecular electric field

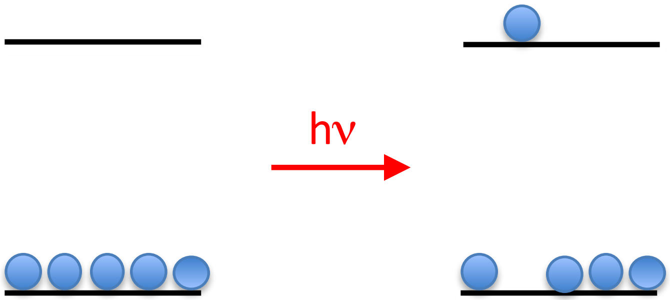
200 nJ/pulse for a 35 fs pulse duration, focalised on a 100 μm spot:

$$\vec{I}_{laser} = \frac{200\ nJ}{35\ fs} = 5.7 \cdot 10^6\ W$$ Average power (higher peak power)

$$\vec{I}_{focus} = \frac{5.7 \cdot 10^6\ W}{\pi(50\ \mu m)^2} \sim 10^{15}\ W/m^2$$ Laser electric field

Sun light,
colour vision,
Uv-Vis absorbance …

weak perturbation

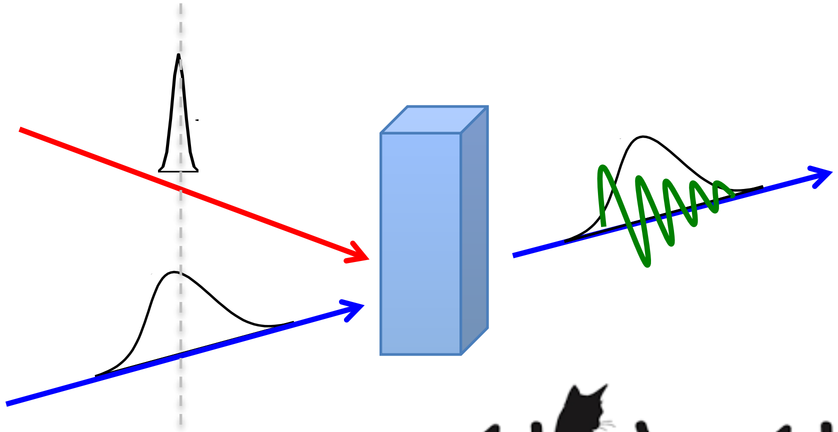


Redistribution of population on quantum states of the system

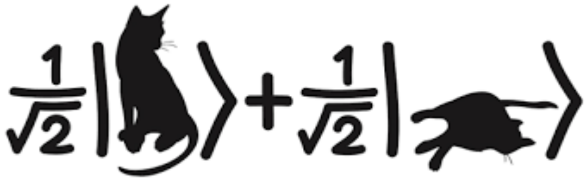
To play with light (change frequency, phase, polarization…) you need non-linear optic effects:

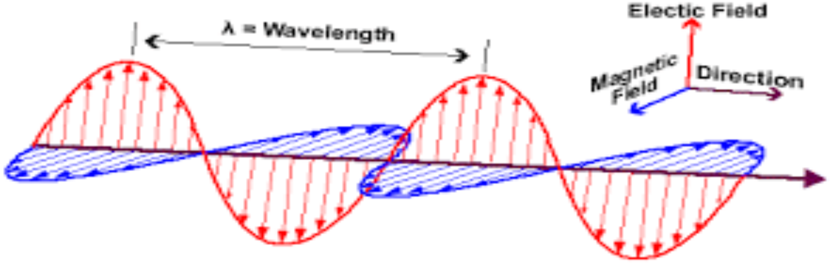
The external electric field couples to the molecular electric field
Quantum states of the system are (temporally) mixed up.

The superposition of states
"answers you" (response signal)
according to "your question" (probe)



strong perturbation





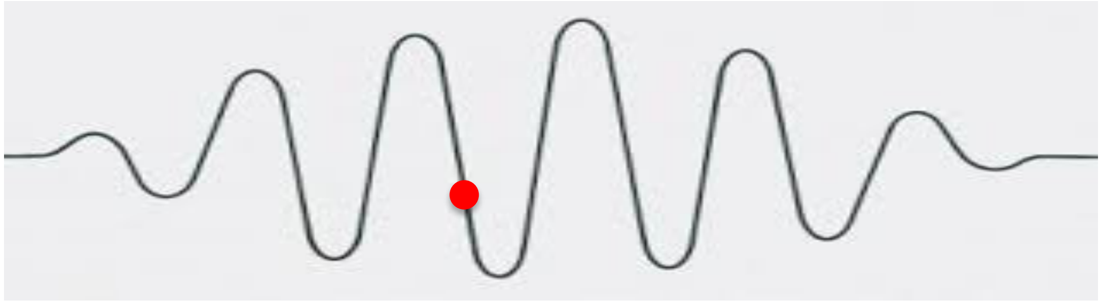
EM field – matter APPROXIMATIONS:

Matter = non-magnetic homogeneous dielectric, with no free-charges and internal currents.

1. We neglect the magnetic part of the EM field.
2. We treat light and matter in the semi-classical approximation.
3. We make use of the moment dipole approximation.

1st Approx.: NEGLECT MAGNETIC FIELD: because you are operating on the electric dipole moment of a (biological) molecule. In some cases you cannot neglect the magnetic contibution and you have to consider both electric and magnetic dipole moments, i.e. lanthanide solid state samples.

2nd Approx.: SEMI-CLASSICAL APPROX: used wavelengths are much longer than molecular dimensions.



λ >> d

Light → EM field → classical mechanics

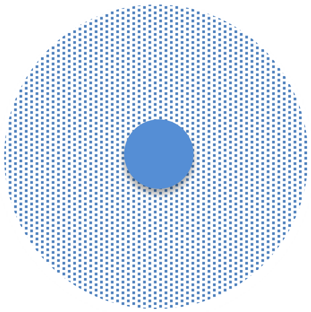
Matter → molecule → quantum mechanics

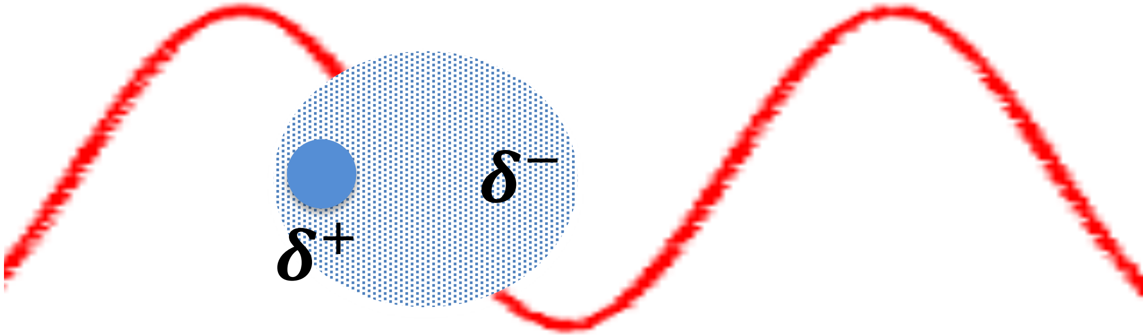
3rd Approx.: DIPOLE APPROX: the spatial oscillating part of the electric field is neglected. Only the time oscillating part is considered, which induces a separation of charge on the molecule at a first approx. considered as a dipole.

$$E = E_0 e^{ikr} e^{-i\omega t} + c.c. = E_0 \left[\cos(\omega t) - i \sin(\omega t)\right] + c.c.$$

$$\boxed{e^x = 1} + x + \frac{1}{2}x^2 + \frac{1}{3}x^3 + \cdots$$

OPTICAL SPECTROSCOPIES → *valence electrons*





Franck-Condon principle → Absorption is a vertical transition where there is the largest overlap between vibrational wavefunctions

Born-Oppheneimer approximation → Nuclear and electronic transition are on different energy and time-scales so that they can be considered independent from each other

N.B.: in optical spectroscopies (UV-VIS-IR) only valence electrons are involved. External electrons react “istantaneously” (10^{-15}-10^{-16} s) to applied E, while massive nuclea are stuck.

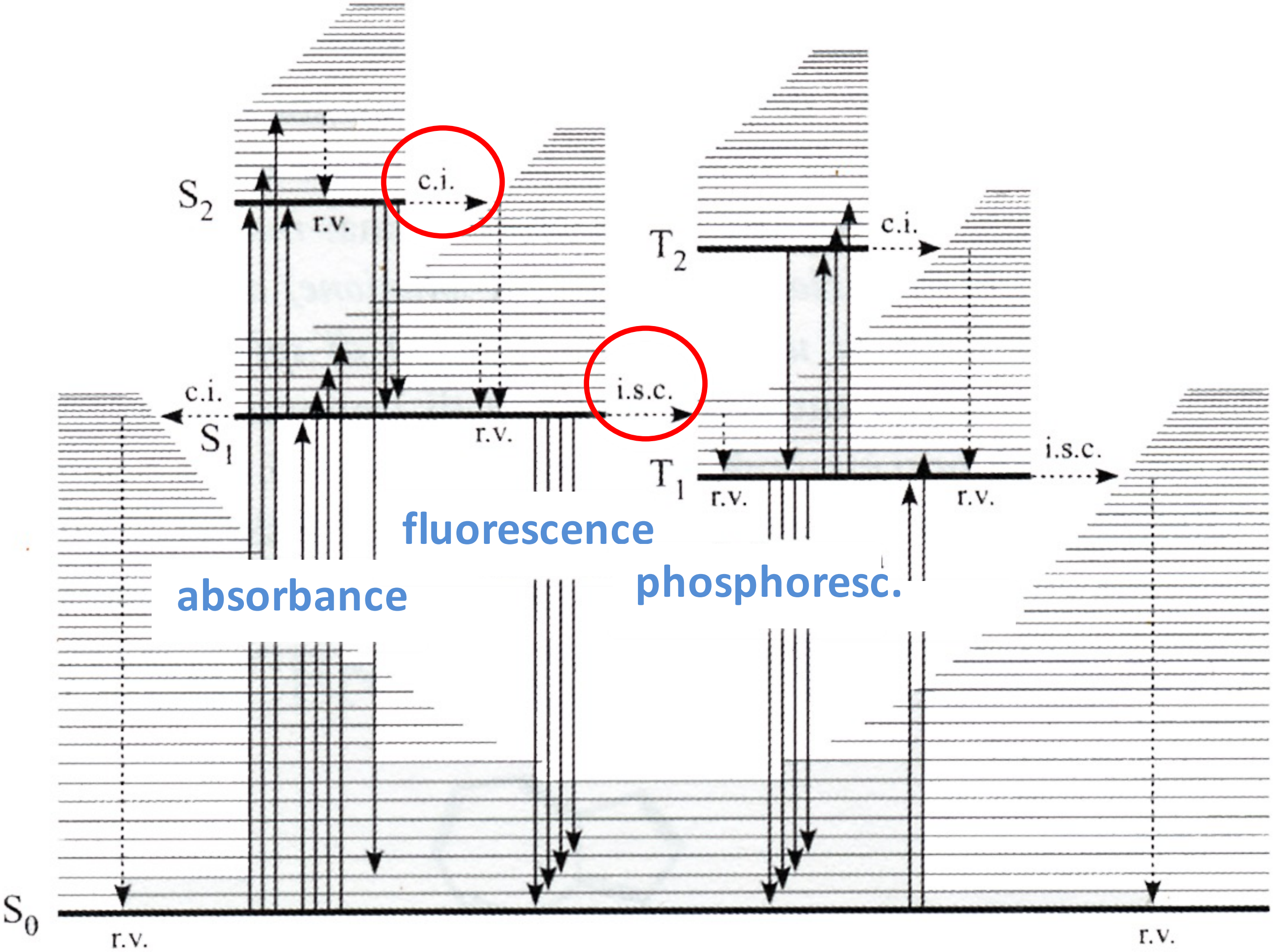
$$\psi = \psi_n \cdot \psi_{el}$$

Horizontal transitions:
Internal Conversion
Inter System Crossing
(out of the B.O. approx – Fermi Golden rule)

Vertical transitions

$$\psi_{el} = \psi_{rot} \cdot \psi_{vibr} \cdot \psi_{el} \cdot \psi_{spin}$$

(B.O. approx – Einstein coefficients)



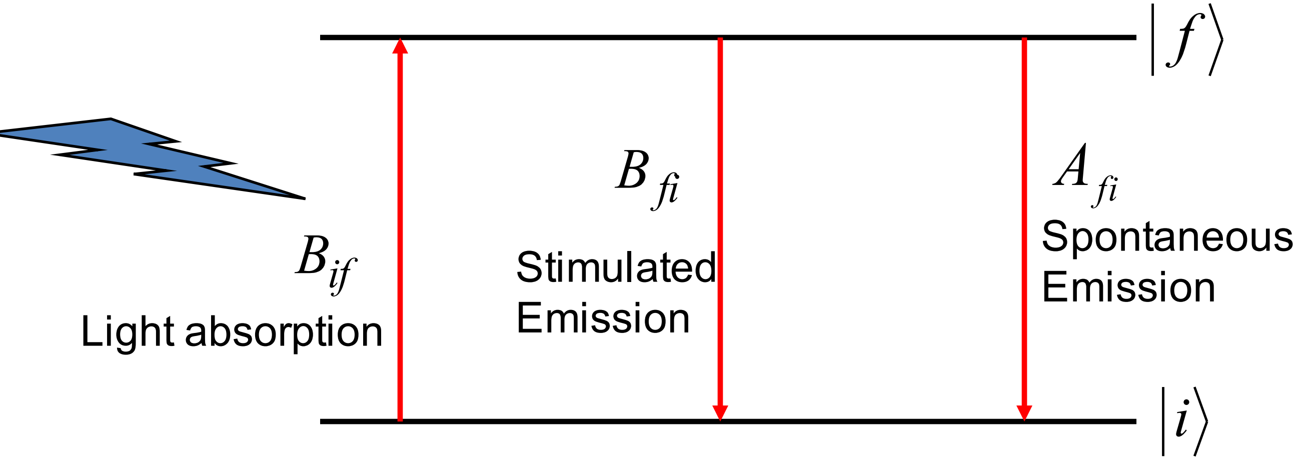
fluorescence
absorbance
phosphoresc.

Absorbance 10^{-16}-10^{-15} s
Fluorescence 10^{-12}-10^{-6} s
Phosphoresc. 10^{-6}-1 s

Vibrational relax. 10^{-12} s

I.C. 10^{-14}-10^{-11} s
I.S.C. 10^{-12}-10^{-4} s

Einstein coefficients for radiative transitions



$|f\rangle$

$|i\rangle$

B_{if}

Light absorption

B_{fi}

Stimulated Emission

A_{fi}

Spontaneous Emission

$$\frac{dN_f}{dt} = B_{if}\rho(\nu)N_i$$

$$-\frac{dN_f}{dt} = B_{fi}\rho(\nu)N_f + A_{fi}N_f$$

$$B_{if}\rho(\nu)N_i = B_{fi}\rho(\nu)N_f + A_{fi}N_f$$

$$\rho(\nu) = \frac{A_{fi}/B_{fi}}{\frac{B_{if}}{B_{fi}}e^{h\nu/kT} - 1}$$

$$\boxed{\begin{array}{c} A_{fi} \propto \nu^3 \\ B_{fi} = B_{if} \end{array}}$$

Kasha rule

$$\rho(\nu) = \frac{8\pi h\nu^3/c^3}{e^{h\nu/kT} - 1}$$

Spectral density of black body radiation

Reminder on the FERMI Golden rule:

Bohr frequency condition

$$k_{if} = \frac{2\pi}{\hbar} < \phi_f \chi_f | \mu_e \cdot \mu_N | \phi_i \chi_i >^2 \underline{\delta(E_f - E_i)}$$

Dirac delta =1

Horizontal transition possible only when Ef=Ei

$$< \phi_f | \mu_e | \phi_i >^2 \underline{< \chi_f | \chi_i >^2} + < \chi_f | \mu_N | \chi_i >^2 \underline{< \phi_f | \phi_i >^2}$$

Superposition integral of 2 vibrational wavefunctions of 2 different electronic excited state They are not part of the same basis set: not orthogonal!!!

Electronic wavefunctions of the same electronic hamiltonian: part of the same basis set and orthogonal = 0 !!!!

$$k_{if} = \frac{2\pi}{\hbar} < \phi_f | \mu_e | \phi_i >^2 \underline{< \chi_f | \chi_i >^2} \; \rho_E$$

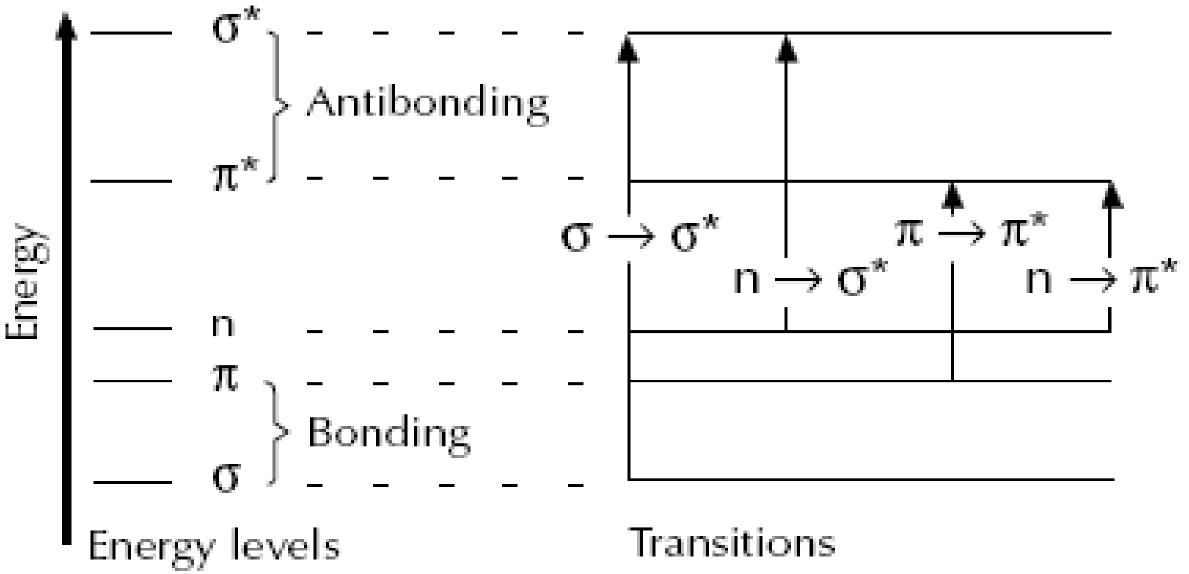
Franck Condon horizontal factor

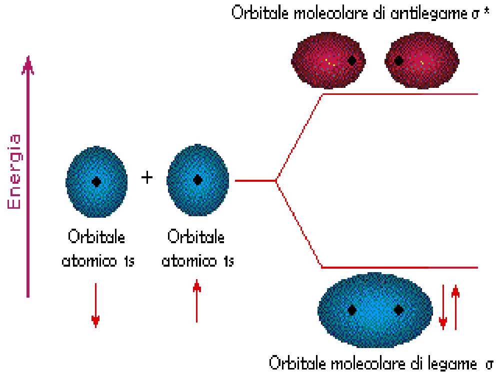
Molecular orbital (MO=LCAO) transitions

Molecular orbital simmetry: σ, n, π

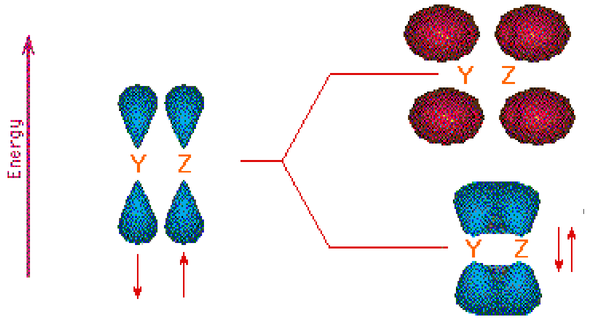
LUMO

HOMO





Transition intensity depends on the charge redistribution, i.e. intensity of induced dipole moment



Electronic selection rules

1. Induced dipole moment $\mu \neq 0$
2. Spin conservation before and after photon arrival: $\Delta S_{TOT} = 0$
3. Transitions within a shell (p,d..) are forbidden: ΔL =+/-1

$$\widehat{\mu_{if}} = \int \psi_f \hat{\mu} \psi_i dV \neq 0$$ Transition moment

Transitions:

$\sigma \rightarrow \sigma^*$ transitions of C-C, C-H saturated bond (deep UV)

$\pi \rightarrow \pi^*$ insaturated bonds or conjugated system (VIS)

$n \rightarrow \sigma^*$

$n \rightarrow \pi^*$typical in the presence of lone pair of ethero atoms C=O, N=N, C=N…

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