Lecture #15 of 14

(3: TThF, 5: MT*W*ThF, 4: MT*W*Th, 2: TW<u>Th</u>)

{Okay... let's wrap this up}

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# Photochemistry

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Photochemistry

- **Blackbody radiation, Carnot efficiency limits, Light–Matter interactions, Photon properties, Conservation laws**

- **Jablonski diagram, Internal conversion, Intersystem crossing, Kasha–Vavilov rule, Thexi state, Stokes shift, Luminescence processes**

- **Harmonic oscillator model, Born–Oppenheimer approximation, Franck–Condon principle, Transition dipole moment operator, Selection rules, Spin–orbit coupling, Heavy-atom effect**

- **Photochemical length and time scales, Electromagnetic spectrum**

- **Beer–Lambert law, Absorption coefficient, Einstein coefficients, Oscillator strength, Absorptance, *E–k* diagrams**
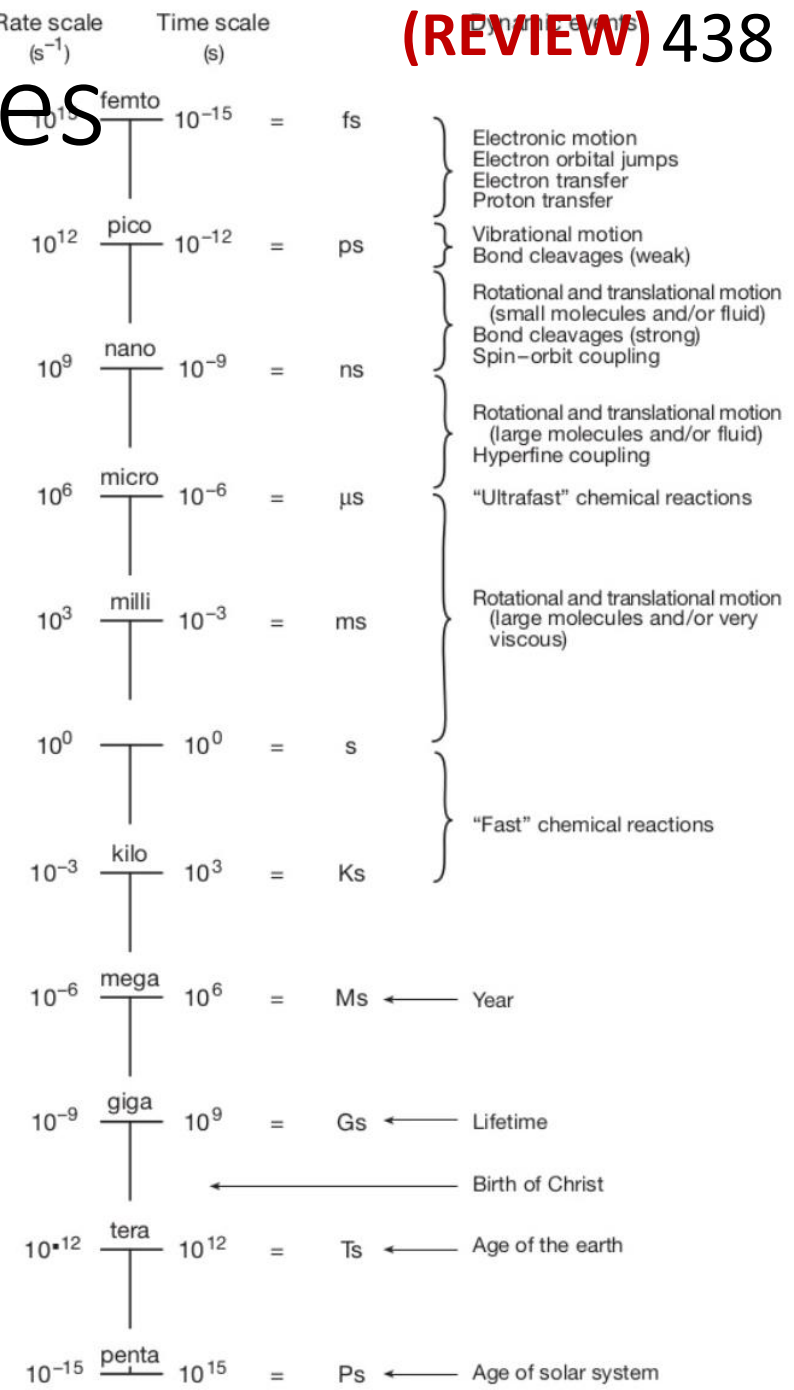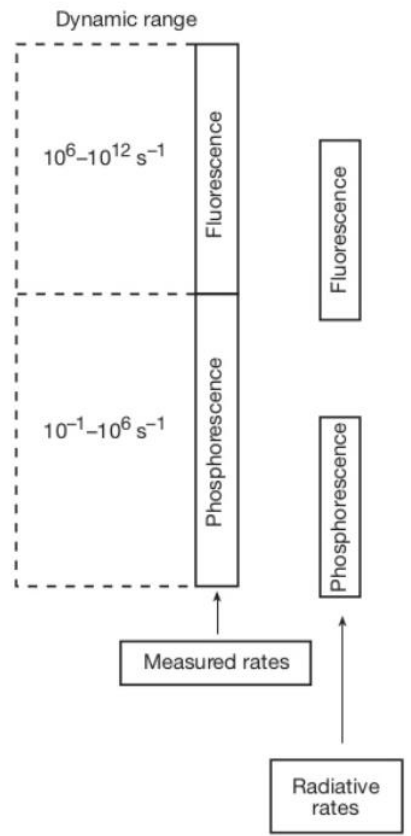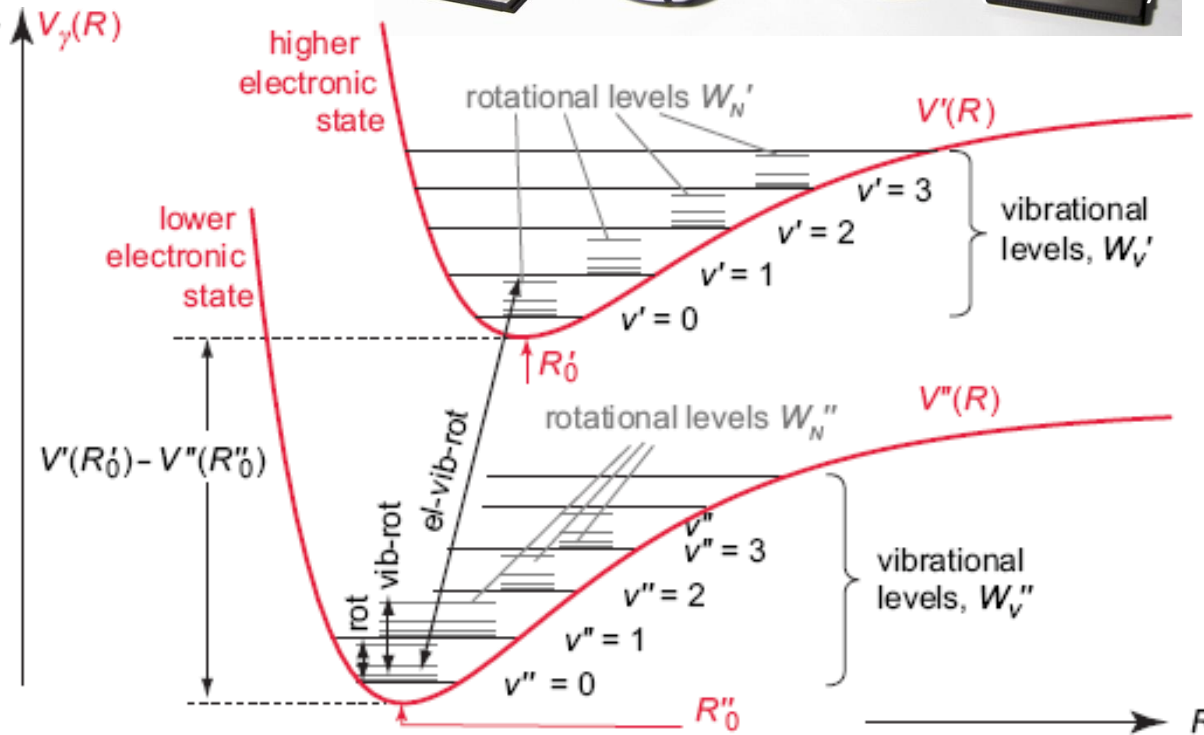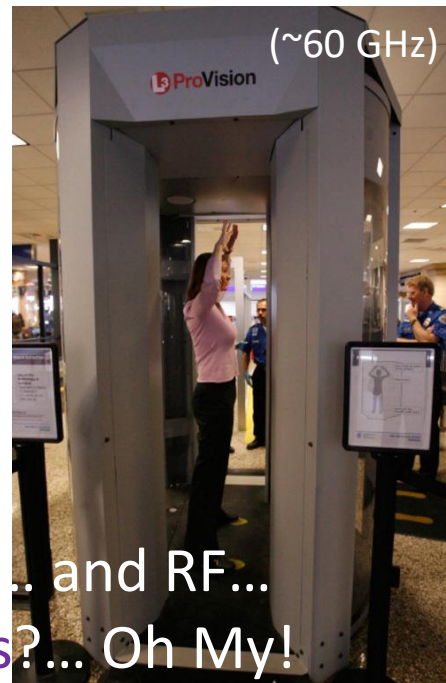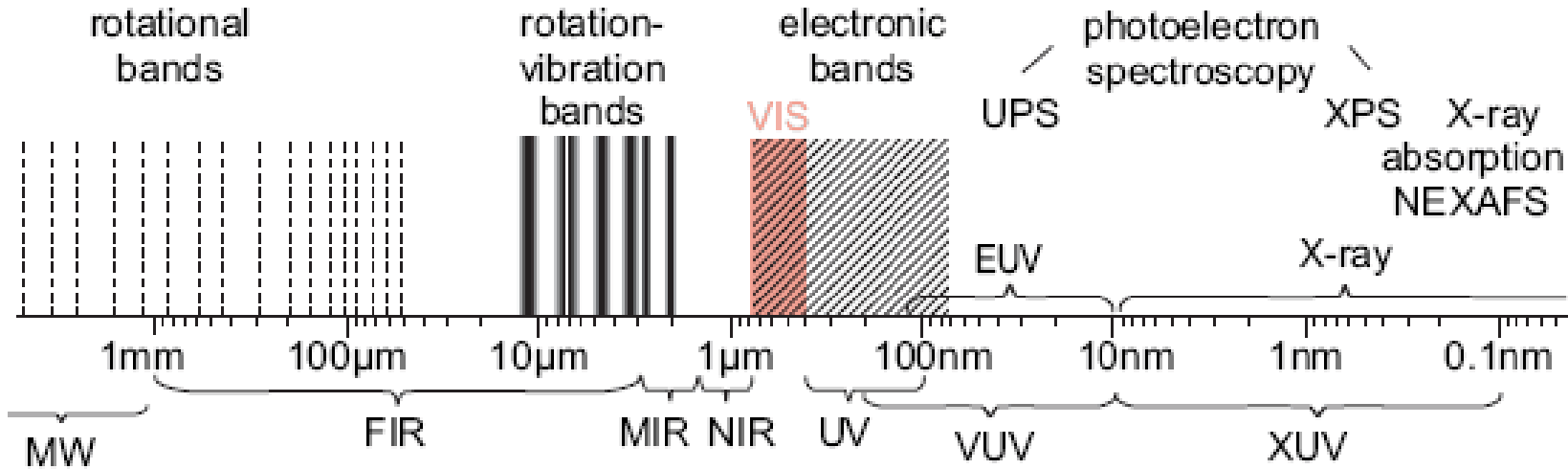
Photochemical Length/Time Scales

https://www.e-education.psu.edu/meteo300/node/682
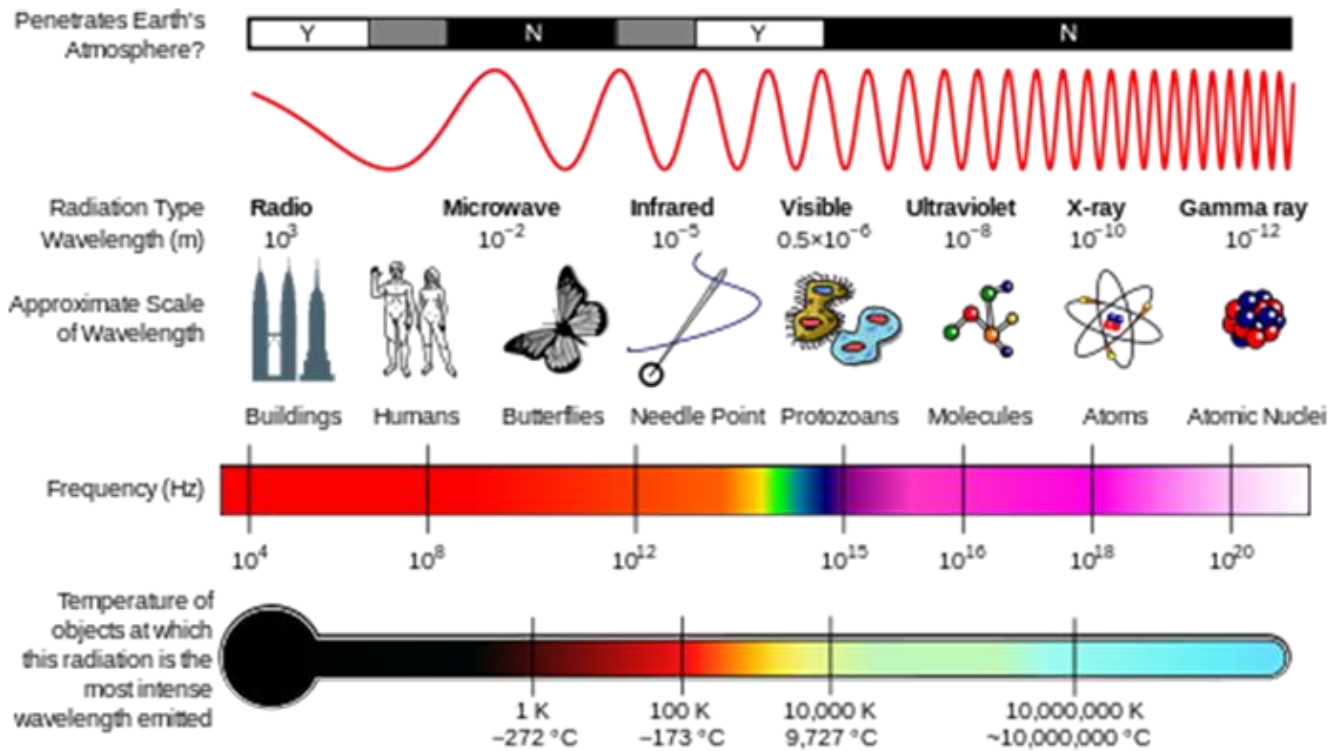
… so how do we probe such fast processes…
… and in each of these regions of the electromagnetic spectrum?

Turro, Chapter 1, Scheme 1.7, Page 36

Electromagnetic spectrum

… what can one do with microwaves?

rotational bands | rotation-vibration bands | electronic bands VIS | photoelectron spectroscopy UPS | XPS | X-ray absorption NEXAFS

EUV | X-ray

1mm | 100µm | 10µm | 1µm | 100nm | 10nm | 1nm | 0.1nm

MW | FIR | MIR NIR | UV | VUV | XUV

(~1.9 GHz)

(~60 GHz)

(~2.45 GHz)

… and what about gamma rays .. and RF…
… and neutrons… and electrons?… Oh My!

W_{vN} $V_\gamma(R)$

higher electronic state

rotational levels W_N'

$V'(R)$

lower electronic state

$v' = 3$
$v' = 2$
$v' = 1$
$v' = 0$

vibrational levels, W_v'

R_0'

$V'(R_0') - V''(R_0'')$

el-vib-rot
vib-rot
rot

rotational levels W_N''

$V''(R)$

$v'' = 3$
$v'' = 2$
$v'' = 1$
$v'' = 0$

vibrational levels, W_v''

R_0''

R

Nuclear Terms & F–C Factors

Turro, Chapters 2 and 3

$$k_{obs} \sim \rho [< \Psi_1 | P'_{1\to2} | \Psi_2 >]^2 \quad \text{Fermi's golden rule}$$

Observed Rate Constant		Zero-point Motion-Limited Rate Constant	"Fully Allowed Rate"
$\underbrace{k_{obs}}_{\text{Prohibition to maximal caused by "selection rules"}}$	$=$	k^0_{max}	$\underbrace{f_{e} \times f_v \times f_S}_{\text{Prohibition factors due to changes in electronic, nuclear, or spin configuration}}$

$$\underbrace{\Psi}_{\substack{\text{"True" molecular wave function} \\ \text{Exact solution to Eq. 2.1}}} \quad \sim \quad \underbrace{\Psi_0 \chi S}_{\substack{\text{(orbitals)(nuclei)(spin)} \\ \text{Approximate solution to Eq. 2.1}}}$$

... separable due to the Born–Oppenheimer approximation

$$k_{obs} = \underbrace{\left[\frac{k^0_{max} < \psi_1 | P_{vib} | \psi_2 >^2}{\Delta E_{12}^2} \right]}_{\text{Vibrational coupling}} \times \underbrace{\left[\frac{< \psi_1 | P_{so} | \psi_2 >^2}{\Delta E_{12}^2} \right]}_{\text{Spin–orbital coupling}} \times \underbrace{\left[< \chi_1 | \chi_2 >^2 \right]}_{\substack{\text{Vibrational overlap} \\ \text{Franck-Condon factors}}}$$

Overlap integral, $S_{12} = \int_{-\infty}^{\infty} \chi_1^*(x) \chi_2(x)\, dx = \langle \chi_1 | \chi_2 \rangle$

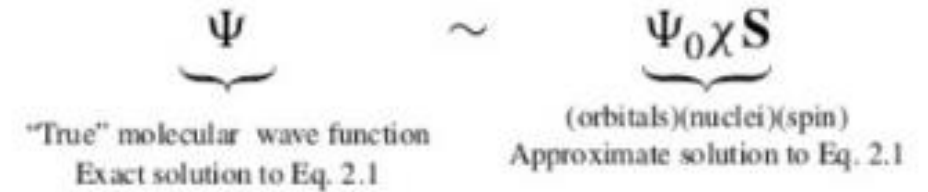Franck–Condon factor, $\langle \chi_1 | \chi_2 \rangle^2$
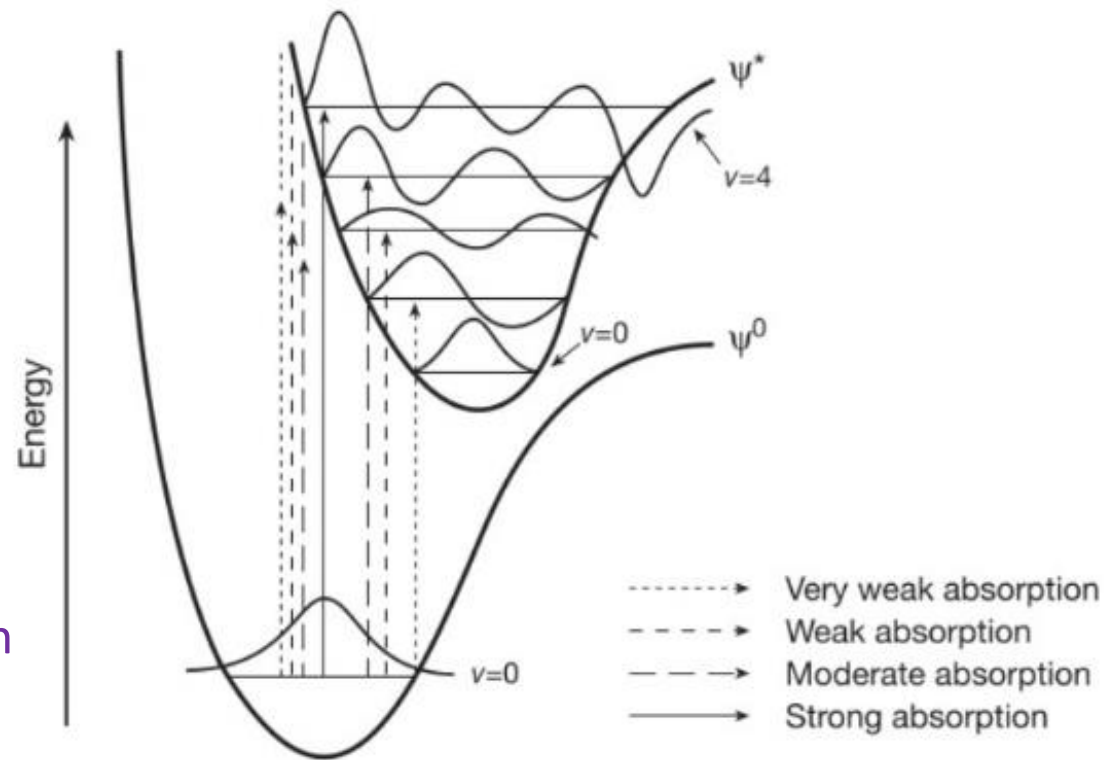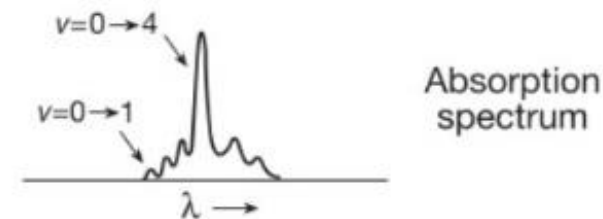
Turro, Chapter 3, Figure 3.3, Page 129

Transition to what vibronic state is most favorable/rapid by absorption?
... and what about by emission?

B–O Approximation, F–C Principle, TDM Operator

- <u>Born–Oppenheimer (B–O) approximation</u>: separability of electronic and nuclear terms in the wavefunction

$$\Psi \sim \Psi_0 \chi \mathbf{S}$$

"True" molecular wave function
Exact solution to Eq. 2.1

(orbitals)(nuclei)(spin)
Approximate solution to Eq. 2.1

- <u>Franck–Condon (F–C) principle</u>: Nuclei are fixed during electron-transfer between orbital *(think Libby)*

- <u>Transition dipole moment (TDM) operator, $\boldsymbol{\mu}$</u>:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_e + \boldsymbol{\mu}_N = -e\sum_i \boldsymbol{r}_i + e\sum_j Z_j \boldsymbol{R}_j.$$

The probability amplitude P for the transition between these two states is given by
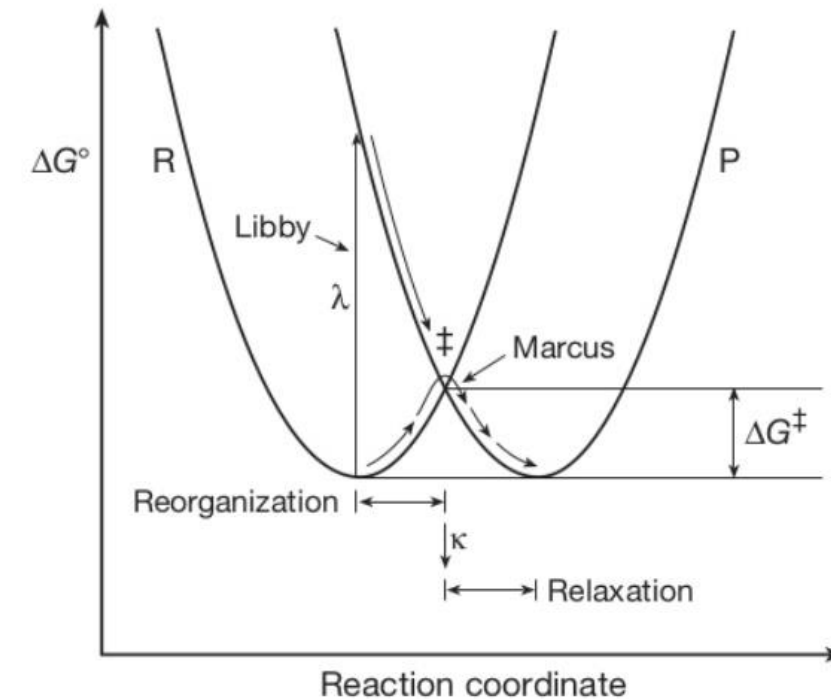
$$P = \langle \psi' | \boldsymbol{\mu} | \psi \rangle = \int \psi'^* \boldsymbol{\mu}\psi \, d\tau, \qquad \psi = \psi_e \psi_v \psi_s$$

$$P = \langle \psi'_e \psi'_v \psi'_s | \boldsymbol{\mu} | \psi_e \psi_v \psi_s \rangle = \int \psi_e'^* \psi_v'^* \psi_s'^* (\boldsymbol{\mu}_e + \boldsymbol{\mu}_N)\psi_e \psi_v \psi_s \, d\tau$$

$$= \int \psi_e'^* \psi_v'^* \psi_s'^* \boldsymbol{\mu}_e \psi_e \psi_v \psi_s \, d\tau + \int \psi_e'^* \psi_v'^* \psi_s'^* \boldsymbol{\mu}_N \psi_e \psi_v \psi_s \, d\tau$$

$$= \underbrace{\int \psi_v'^* \psi_v \, d\tau_n}_{\substack{\text{Franck–Condon} \\ \text{factor}}} \underbrace{\int \psi_e'^* \boldsymbol{\mu}_e \psi_e \, d\tau_e}_{\substack{\text{orbital} \\ \text{selection rule}}} \underbrace{\int \psi_s'^* \psi_s \, d\tau_s}_{\substack{\text{spin} \\ \text{selection rule}}} + \underbrace{\int \psi_e'^* \psi_e \, d\tau_e}_{0} \int \psi_v'^* \boldsymbol{\mu}_N \psi_v \, d\tau_v \int \psi_s'^* \psi_s \, d\tau_s$$
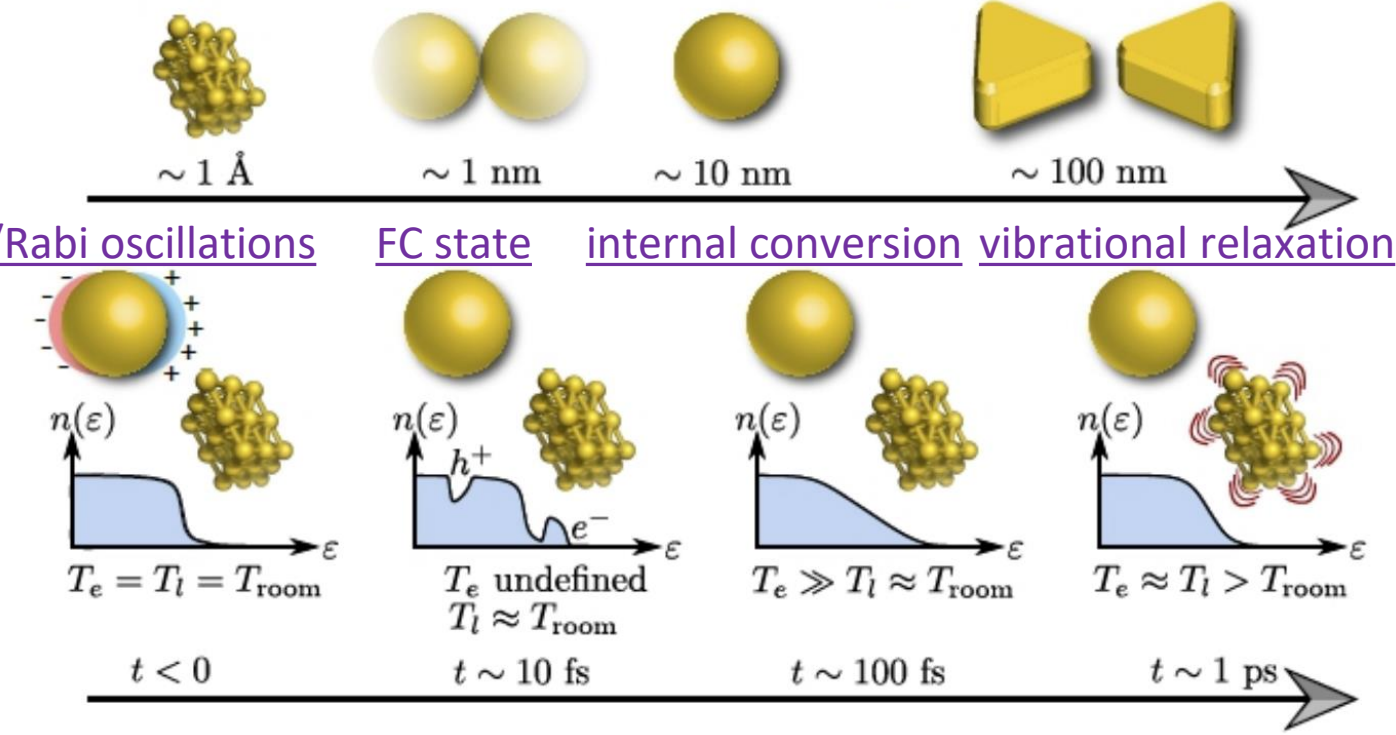
… this factor is 0 when light changes ψ_e Turro, Chapter 7, Figure 7.12, Page 429

Thermally Equilibrated Excited (Thexi) State

Fano/Rabi oscillations   FC state   internal conversion   vibrational relaxation

https://micro.magnet.fsu.edu/primer/techniques/fluorescence/fluorescenceintro.html

… wait, do molecules and materials undergo the same physical processes and follow the same laws of the Universe?... shocking, isn't it?!?!?!
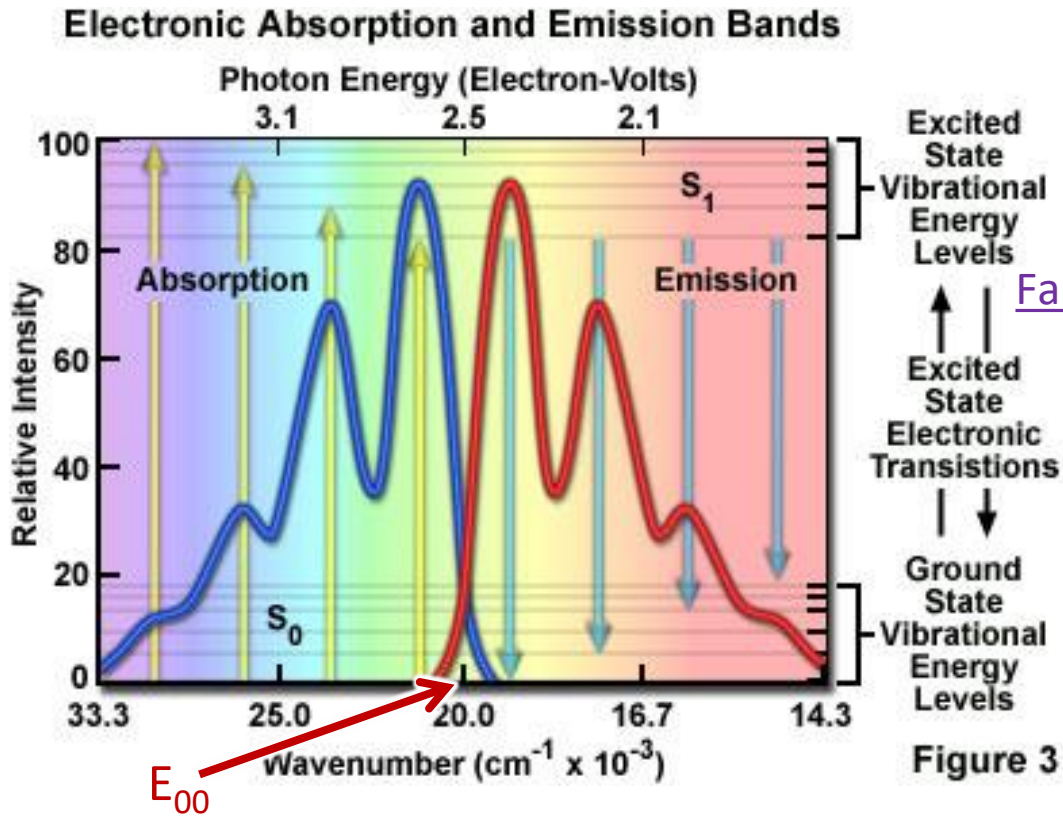
… and why are these spectra plotted as a function of wavenumber… and not wavelength?

… so that you can see the mirror-image "rule"

P. Narang, R. Sundararaman & H. A. Atwater, *Nanophoton.*, **2016**, *5*, 96–111

Jablonski Diagram

REVIEW

Kasha–Vavilov "rule": polyatomic molecular entities **emit and react** predominantly from the lowest-energy excited state of a given multiplicity, and thus emission is generally independent of excitation wavelength
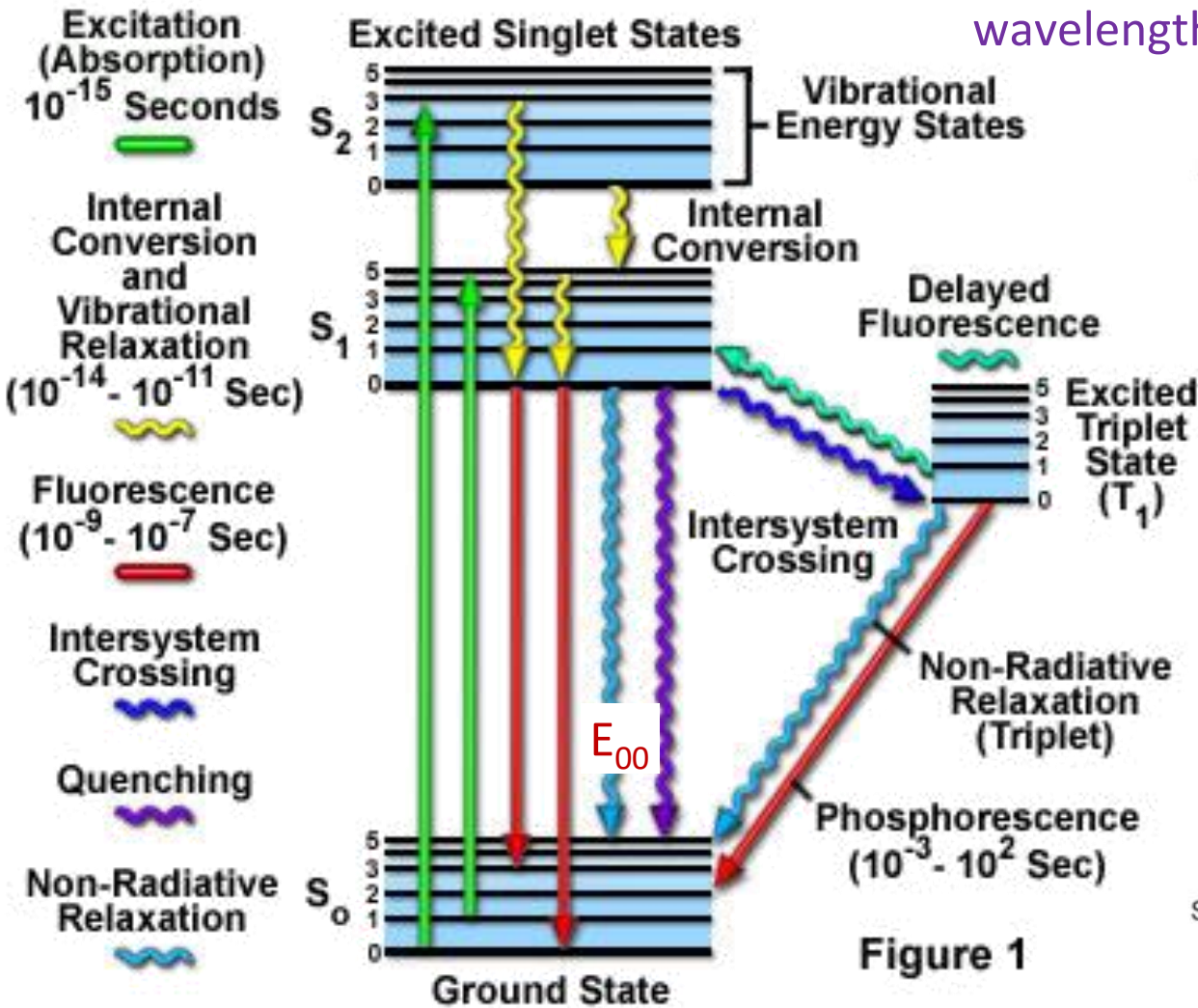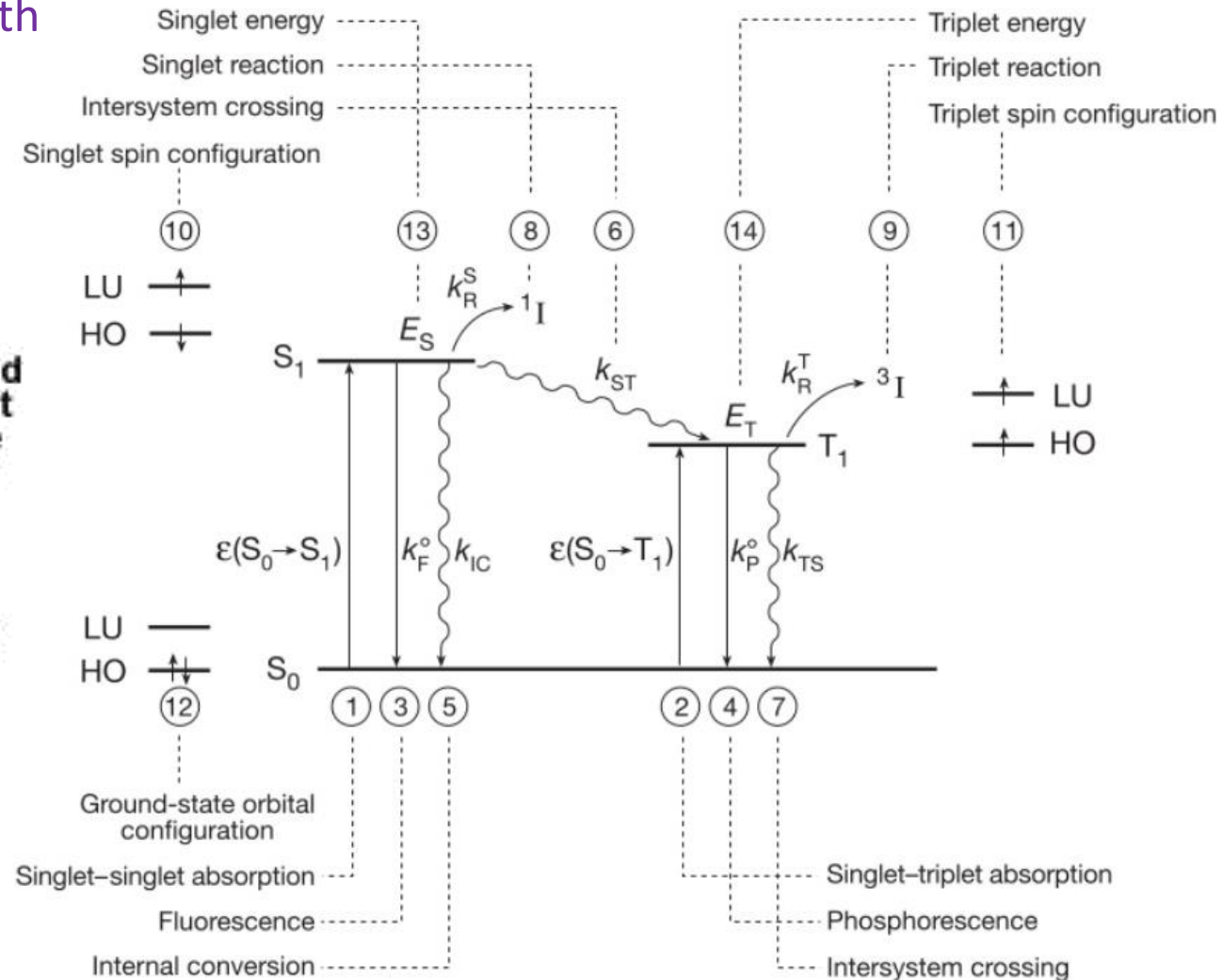

Jablonski Energy Diagram

Figure 1

https://micro.magnet.fsu.edu/primer/java/jablonski/jabintro/index.html

Turro, Chapter 1, Scheme 1.4, Page 17

Selection Rules

$$\underbrace{\int \psi_v'^* \psi_v \, d\tau_n}_{\substack{\text{Franck–Condon} \\ \text{factor}}} \underbrace{\int \psi_e'^* \boldsymbol{\mu}_e \psi_e \, d\tau_e}_{\substack{\text{orbital} \\ \text{selection rule}}} \underbrace{\int \psi_s'^* \psi_s \, d\tau_s}_{\substack{\text{spin} \\ \text{selection rule}}}$$

<u>Angular Momentum Quantum Numbers</u>
Photon… *which came from matter*: $s = 1, m_s = \pm 1$
Electron (Orbital): $l, m_l = [-l, l]$ in steps of 1
Electron (Spin): $s = \frac{1}{2}, m_s = \left[-\frac{1}{2}, \frac{1}{2} \right]$

… well these are just overlaps… and so the more overlap, the more favorable a transition…
… the F–C (nuclear vibrational) factor makes sense *based on pictures on the previous slides*
… but what does $\boldsymbol{\mu}_e$ do to a wavefunction?… it uses $\vec{\mathrm{E}}$ to make it coincide with an unoccupied orbital…
　　and even if we didn't know, it better *change the angular momentum during photon annihilation*
… and what are spin wavefunctions?… just symbols!… spin does not fall out of $\boldsymbol{\mu}$… it's just math…
　　so, the spin wavefunctions only overlap when they are identical… meaning *spin does not change*

… simplified systems… <u>(Angular Momentum) Atomic Selection "rules"</u>
Orbital angular momentum (<u>Laporte "rule"</u>): $\boldsymbol{\Delta l = \pm 1}$… as $l_f = l_i \pm s_{\text{photon}}$
Spin angular momentum (<u>Wigner "rule"</u>): $\boldsymbol{\Delta m_s = 0}$… $\boldsymbol{\mu}_e$ does not act on spin
Orbital *z*-direction angular momentum: $\boldsymbol{\Delta m_l = 0, \pm 1}$… as $m_{l,f} = m_{l,i} \pm m_{s,\text{photon}}$
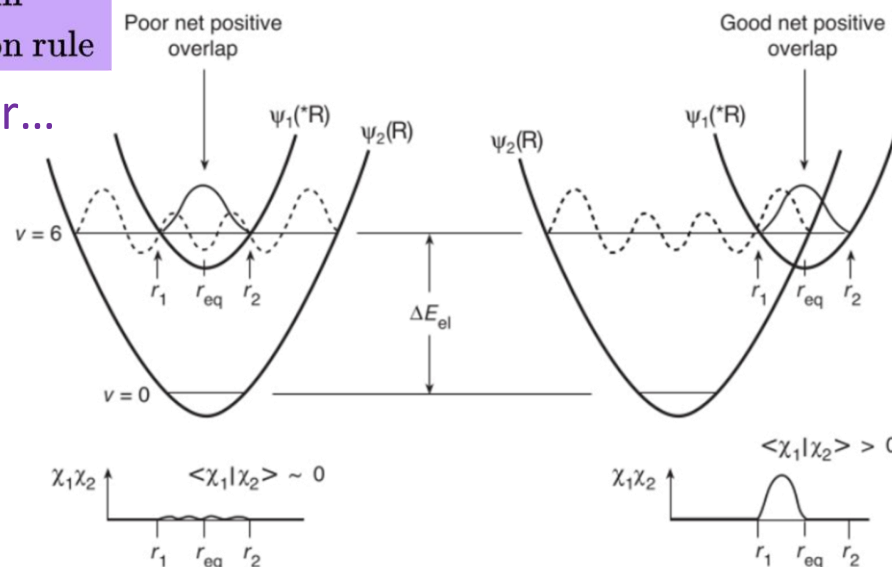… the allowed 0 option can be envisioned as two vectors that are opposite in one direction
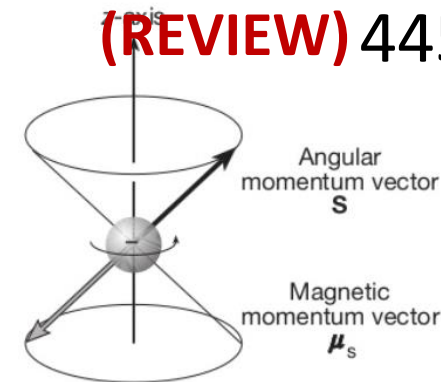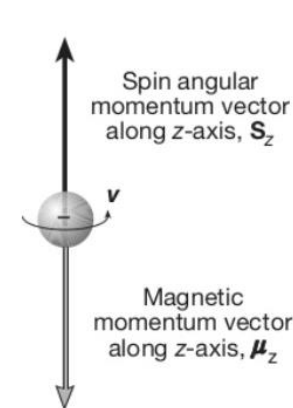
Selection Rules

$$\underbrace{\int \psi_v'^* \psi_v \, d\tau_n}_{\substack{\text{Franck–Condon} \\ \text{factor}}} \underbrace{\int \psi_e'^* \boldsymbol{\mu}_e \psi_e \, d\tau_e}_{\substack{\text{orbital} \\ \text{selection rule}}} \underbrace{\int \psi_s'^* \psi_s \, d\tau_s}_{\substack{\text{spin} \\ \text{selection rule}}}$$

… related to spin–orbital coupling…

… related to the F–C factor…

Turro, Chapter 2, Figure 2.13, Page 99

Turro, Chapter 3, Figure 3.5, Page 133

State	State Symbol	M_s	Magnetic Energy (E_z)	Spin Function	Vector Representation
Doublet	D_+	$+1/2$	$+(1/2)g\mu_e\mathbf{H}_z$	α	
Doublet	D_-	$-1/2$	$-(1/2)g\mu_e\mathbf{H}_z$	β	
Singlet	S	0	0	$\alpha\beta - \beta\alpha$	
Triplet	T_+	$+1$	$+(1)g\mu_e\mathbf{H}_z$	$\alpha\alpha$	
Triplet	T_0	0	0	$\alpha\beta + \beta\alpha$	
Triplet	T_-	-1	$-(1)g\mu_e\mathbf{H}_z$	$\beta\beta$	

a. The mathematical normalizing factor is not shown for the spin function.

… simplified systems… Summary of Atomic Selection "rules"   Turro, Chapter 2, Table 2.4, Page 102

$\Delta l = \pm 1$, since $l_f = l_i \pm s_{\text{photon}}$ … $\Delta m_s = 0$ … $\Delta m_l = 0, \pm 1$, since $m_{l,f} = m_{l,i} \pm m_{s,\text{photon}}$

Heavy Molecule (Russell–Saunders L–S Coupling) Selection "rules" … for linear oscillating photon $\vec{\mathrm{E}}$

Total angular momentum: $\Delta J = 0, \pm 1$ … and $\Delta S = 0$ … and $\Delta L = 0, \pm 1$

Total z-direction angular momentum: $\Delta m_J = 0, \pm 1$ … and **0**'s are there for the reason before

Selection Rules

$$\underbrace{\int \psi_e'^* \psi_e \, d\tau_e}_{0} \int \psi_v'^* \boldsymbol{\mu}_N \psi_v \, d\tau_v \int \psi_s'^* \psi_s \, d\tau_s$$

When light does not change ψ_e...
... this factor is non-zero... and the other factor is 0
This means that the photon absorption event...
... is nuclear... and is not electronic

Summary of Nuclear Selection "rules"
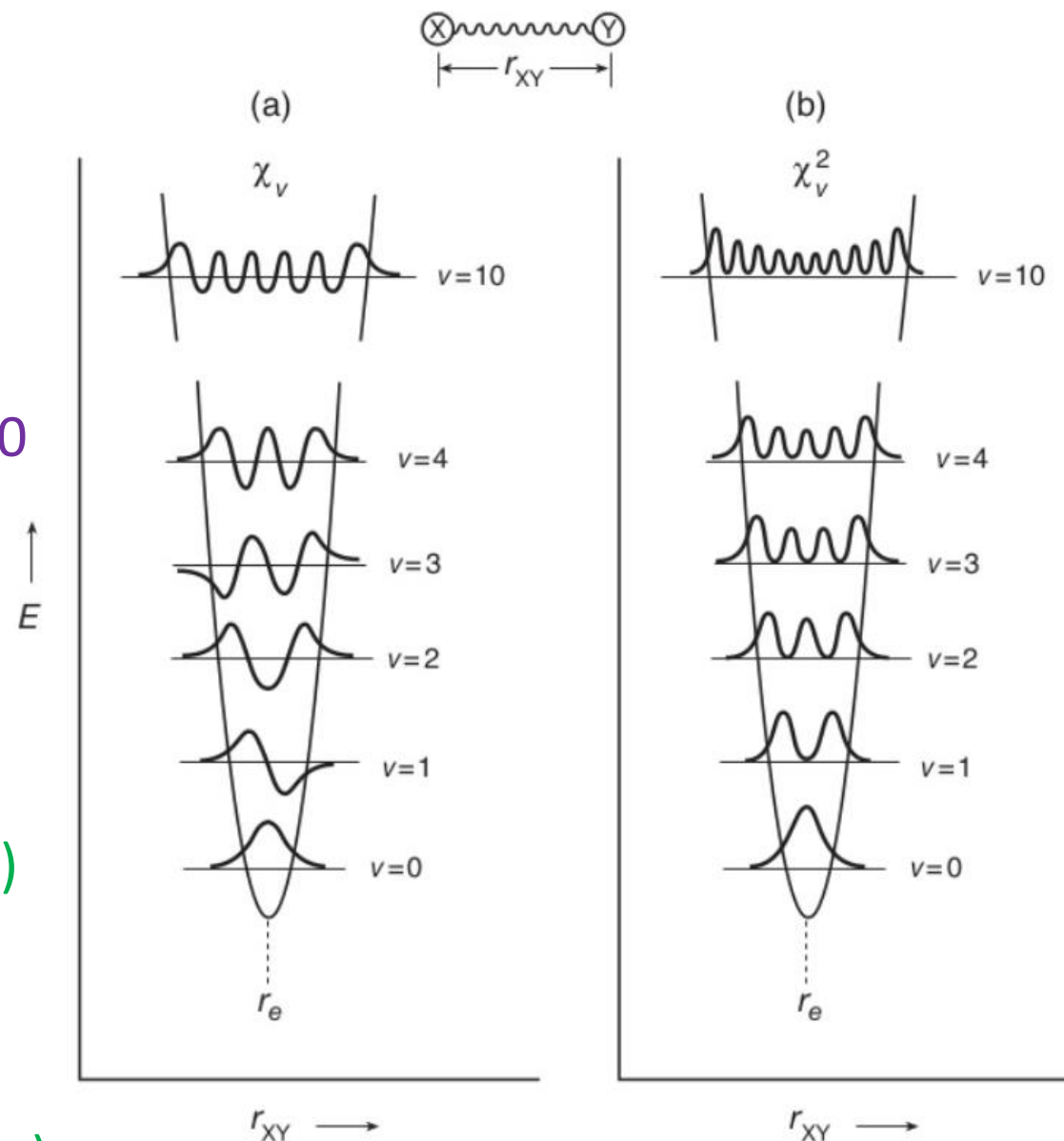Vibrational (Harmonic Oscillator):
$$\Delta v = \pm 1 \text{ (change in dipole)}$$
Vibrational (Harmonic Oscillator) <u>Scattering</u>:
$$\Delta v = \pm 1 \text{ (polarizable)}$$
Rotational (Rigid Rotor Spherical Harmonics):
$$\Delta J = \pm 1 \text{ (permanent dipole)}$$

Turro, Chapter 2, Figure 2.6, Page 76

Absorption Coefficient & Beer–Lambert Law
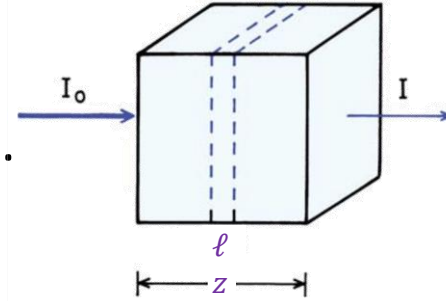
To describe attenuation of light intensity/power through matter <u>due to absorption only</u>… one writes

$\frac{\partial I_\nu}{\partial z} = -\boldsymbol{\alpha_\nu} I_\nu$… where $\boldsymbol{\alpha_\nu}$ is the <u>linear</u> <u>Napierian</u> **absorption coefficient** (cm^{-1})

Rearranging to $\frac{\partial I_\nu}{I_\nu} = -\boldsymbol{\alpha_\nu} \partial z$, and integrating from $I_{\nu,\text{front}}$ to $I_{\nu,\text{back}}$ over ℓ leads to…

$\ln\left(\frac{I_{\nu,\text{back}}}{I_{\nu,\text{front}}}\right) = -\boldsymbol{\alpha_\nu}\ell$… or $I_\nu = I_{\nu,\text{o}} e^{-\alpha_\nu \ell}$, where $I_\nu = I_{\nu,\text{back}}$ and $I_{\nu,\text{o}} = I_{\nu,\text{front}}$

Lakowicz, Chapter 2, Figure 2.52, Page 59

… where $T_\nu = \frac{I_\nu}{I_{\nu,\text{o}}}$ (transmittance) and $A_\nu = -\log(T_\nu) = \log\left(\frac{I_{\nu,\text{o}}}{I_\nu}\right)$ (absorbance)

… but the **absorption coefficient** can take on many forms/units… sorry…

$\log\left(\frac{I_\nu}{I_{\nu,\text{o}}}\right) = -a_\nu \ell$… where a_ν is the <u>linear</u> <u>decadic</u> **absorption coefficient** (cm^{-1}) *[not often used]*

$\ln\left(\frac{I_\nu}{I_{\nu,\text{o}}}\right) = -\kappa_\nu c\ell$… where κ_ν is the <u>molar</u> <u>Napierian</u> **absorption coefficient** (M^{-1} cm^{-1}) *[n. o. u.]*

… since M^{-1} cm^{-1} = L mol^{-1} cm^{-1} = dm^3 mol^{-1} cm^{-1}, $\boldsymbol{\sigma_\nu} = \frac{1000\kappa_\nu}{N_A}$ is the **absorption <u>cross-section</u>** (cm^2)

$\log\left(\frac{I_\nu}{I_{\nu,\text{o}}}\right) = -\boldsymbol{\varepsilon_\nu} c\ell$… where $\boldsymbol{\varepsilon_\nu}$ is the <u>molar</u> <u>decadic</u> **absorption coefficient** (M^{-1} cm^{-1})… finally!…

… leading to the **Beer–Lambert law**… $A_\nu = \boldsymbol{\varepsilon_\nu} c\ell$… a succinct and well-known equation in the end

Einstein Coefficients & Oscillator Strength

Oscillator strength (f_{12}): integrated strength of an absorption band relative to a completely

... is emission the microscopically reversible opposite of absorption? **... Nope!** allowed transition

Absorption = –Stimulated Emission... but not Spontaneous Emission
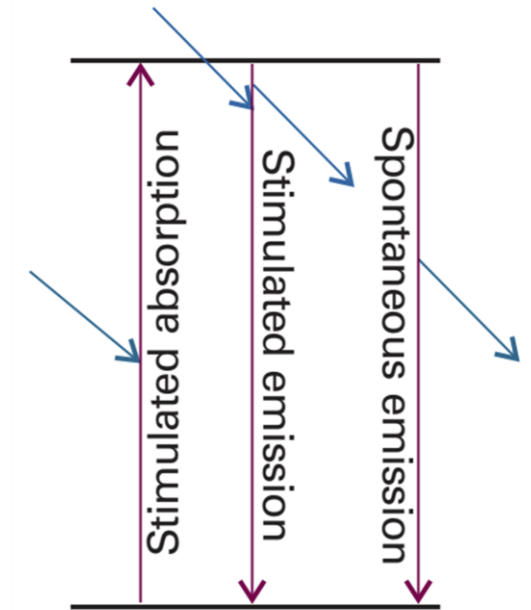
Spontaneous Emission

$$\frac{\partial n_1}{\partial t} = A_{21} n_2$$

Positive Absorption = Stimulated Absorption

$$\frac{\partial n_1}{\partial t} = -B_{12} n_1 \rho(\nu)$$

Negative Absorption = Stimulated Emission

$$\frac{\partial n_1}{\partial t} = B_{21} n_2 \rho(\nu)$$

Atkins, Chapter 13, Figure 13.5, Page 434

Consider all possible reactions to be at equilibrium...

$$\frac{\partial n_1}{\partial t} = -\frac{\partial n_2}{\partial t} = 0 = A_{21} n_2 + B_{21} n_2 \rho(\nu) - B_{12} n_1 \rho(\nu) \dots g_1 B_{12} = g_2 B_{21} = \frac{g_1 c \sigma_{12}}{h\nu} = \frac{g_1 e^2 f_{12}}{4\varepsilon_0 m_e h\nu}$$

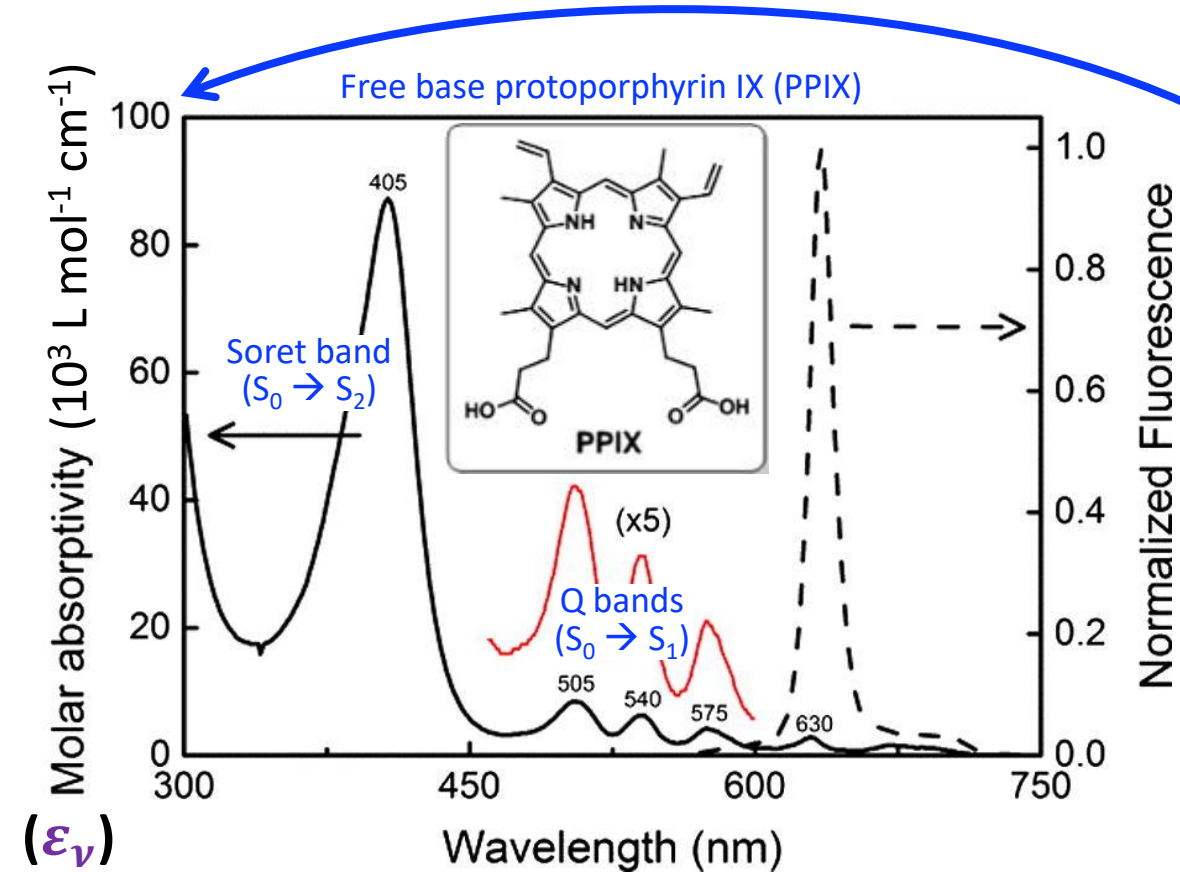... where $\rho(\nu)$ is an irradiance... in units of energy per volume per frequency, ν

R. C. Hilborn, *Am. J. Phys.*, **1982**, *50*, 982–986
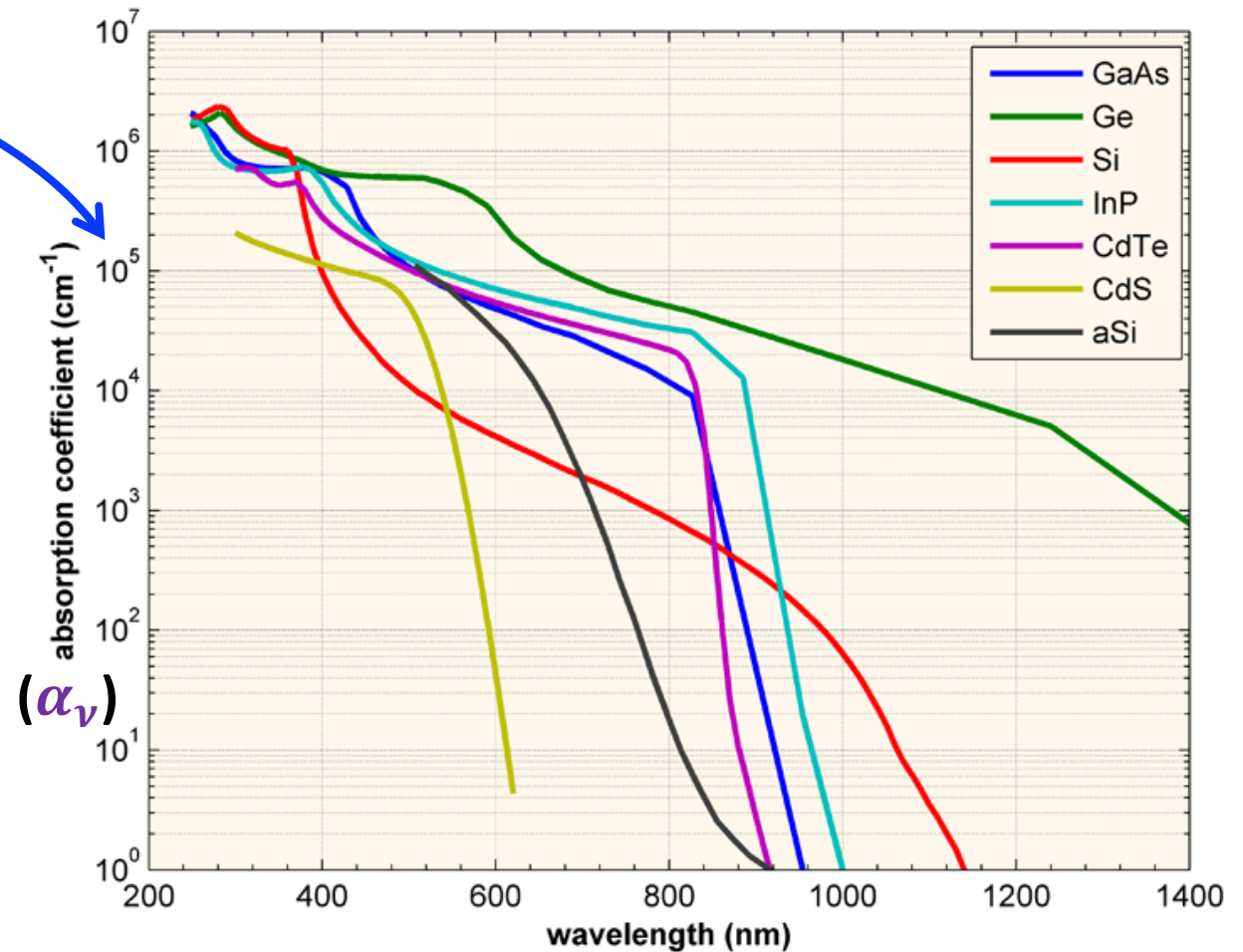R. C. Hilborn, arXiv:physics/0202029 $\dots A_{21} = \frac{8\pi h \nu^3}{c^3} B_{21} = \frac{16\pi^3 \nu^3 \mu_{21}^2}{3\varepsilon_0 h c^3}$

Absorption Coefficient

… what is the name of each absorption coefficient?… and how do we compare them?
… well, what is the concentration in a metal?… Maybe 1 M-ish?

Free base protoporphyrin IX (PPIX)

Soret band
$(S_0 \rightarrow S_2)$

Q bands
$(S_0 \rightarrow S_1)$

(ε_ν)

https://www.sciencedirect.com/science/article/pii/S0009261417301756

(α_ν)

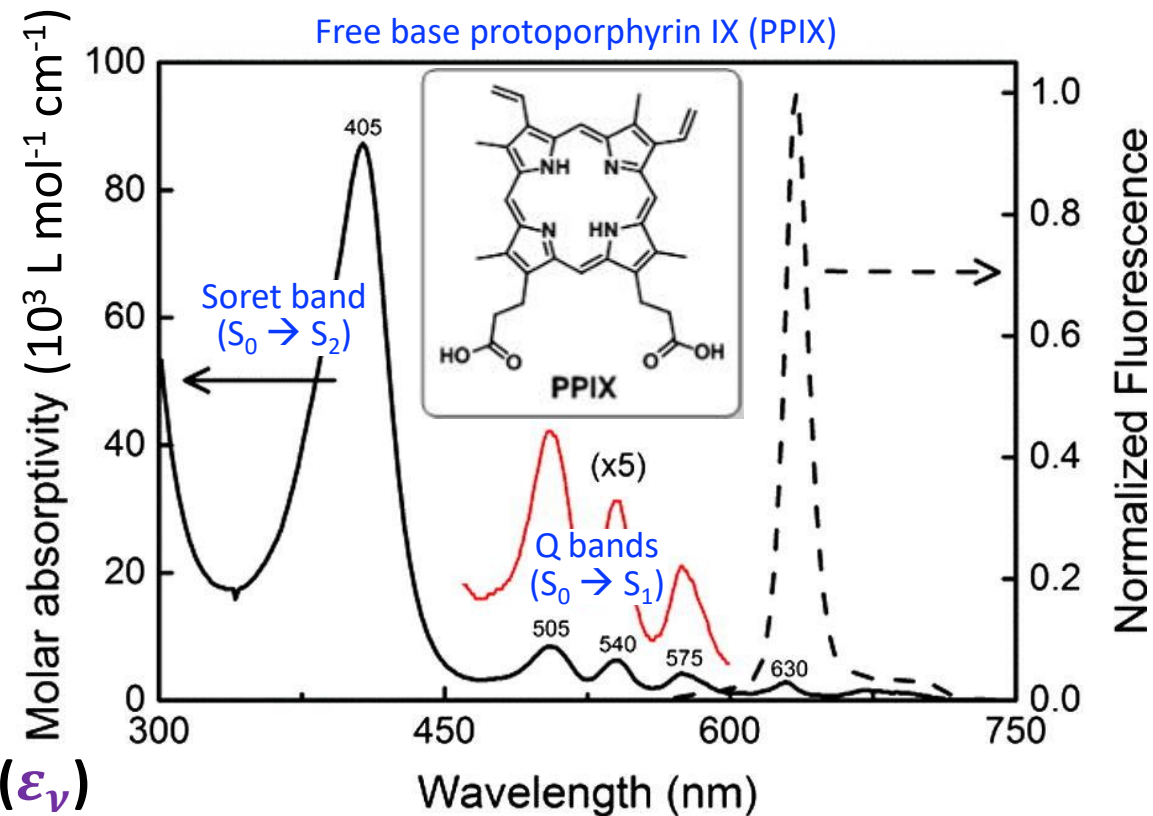https://www.pveducation.org/pvcdrom/pn-junctions/absorption-coefficient

Absorption *vs* Absorbance *vs* Absorptance

… let's use each in a sentence, okay?

… For example, "I do not understand the difference between A., A., and A.?"… Ha! j/k

Free base protoporphyrin IX (PPIX)

Soret band
$(S_0 \rightarrow S_2)$

PPIX

Q bands
$(S_0 \rightarrow S_1)$

(ε_ν)

Molar absorptivity (10^3 L mol^{-1} cm^{-1})

Normalized Fluorescence

Wavelength (nm)

https://www.sciencedirect.com/science/article/pii/S000926141730175 6

… "This plot displays an <u>absorption</u> spectrum"

… "The ordinate is often <u>absorbance</u>, which is dimensionless… and definitely not "a.u.""

… "<u>Absorbance</u>, A, is directly related to concentration… and so its range is $[0, \infty)$"

… "<u>Absorptance</u>, α, is the fraction (or percentage) of light absorbed… it goes well with T (or $\%T$)"

… "Photochemists must know **concentrations** (via <u>Abs</u>, A) and **amount of light absorbed** (as <u>Abt</u>, α)"
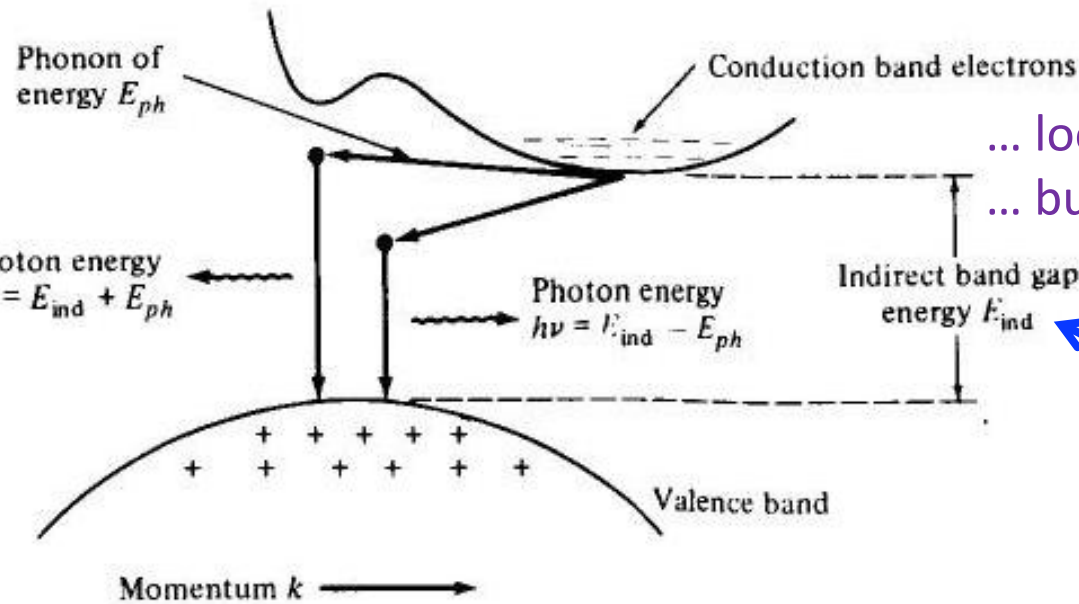
$$\%R_\nu = \left(\frac{n_2 - n_1}{n_2 + n_1} \right)^2$$

$$\%T_\nu = \left(100\% - \%R_{\nu,\text{front}} \right) 10^{-\varepsilon_\nu c \ell} - \%R_{\nu,\text{back}}$$

$$\%T_\nu = \left(100\% - \%R_{\nu,\text{front}} \right) e^{-\alpha_\nu \ell} - \%R_{\nu,\text{back}}$$

… and based on the Fresnel equations, for light with normal incidence… $\%A_\nu + \%T_\nu + \%R_{\nu,\text{total}} = 100\%$

E–k Diagrams

... looks like a Jablonski diagram...
... but based on **linear** momentum

Phonon of energy E_{ph}

Conduction band electrons

Photon energy $h\nu = E_{ind} + E_{ph}$

Photon energy $h\nu = E_{ind} - E_{ph}$

Indirect band gap energy E_{ind}

Valence band
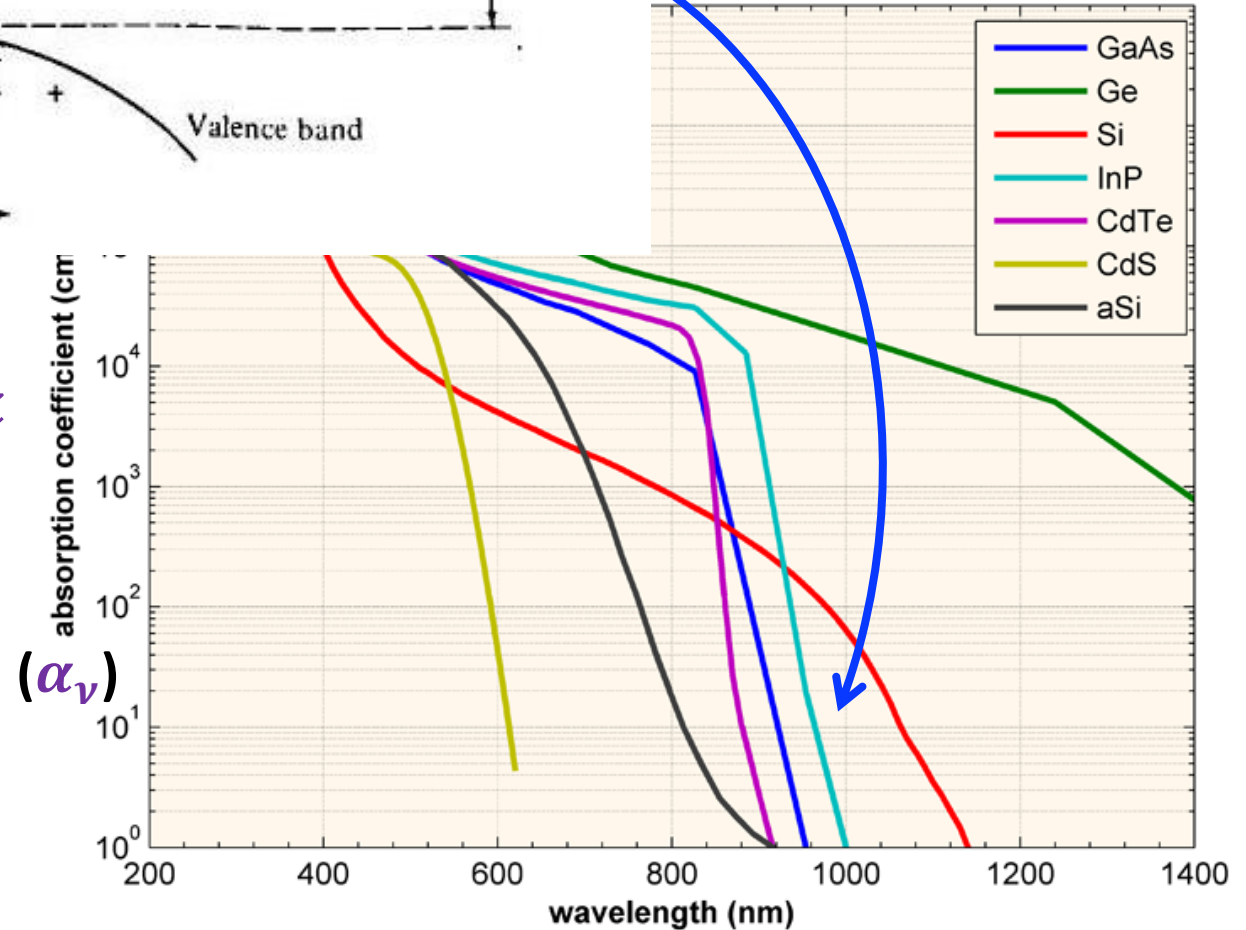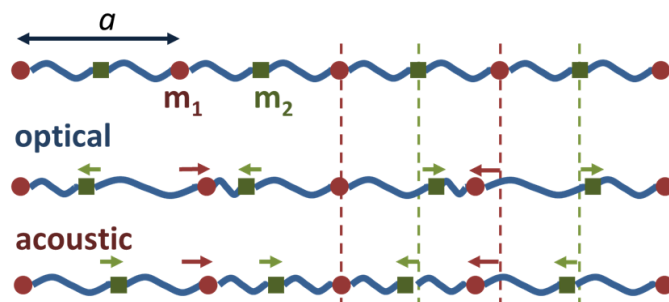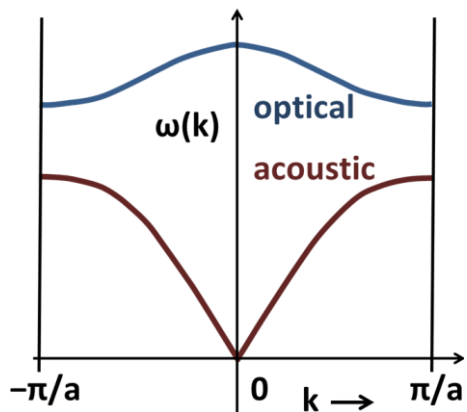
Momentum k

Phonon

Particle Type: Boson

Mass: 0

Charge: 0

Energy: $E = h\nu = \hbar\omega$

Linear Velocity: $\dfrac{c}{n} = \left(\dfrac{\lambda}{n}\right)\nu = \lambda'\nu$

Linear Momentum: $p = \dfrac{h}{\lambda'} = \dfrac{nh\nu}{c} = h\bar{\nu} = \hbar k$

z Angular Momentum / Spin: $\pm\hbar = \pm\dfrac{h}{2\pi}$

$\omega(k)$ optical acoustic

$-\pi/a$　0　$k \rightarrow$　π/a

a m_1 m_2 optical acoustic

(α_ν)

	GaAs
	Ge
	Si
	InP
	CdTe
	CdS
	aSi

absorption coefficient (cm)

wavelength (nm)

https://www.pveducation.org/pvcdrom/pn-junctions/absorption-coefficient

Photochemistry *(summary for today)*

- **Blackbody radiation, Carnot efficiency limits, Light–Matter interactions, Photon properties, Conservation laws**

- **Jablonski diagram, Internal conversion, Intersystem crossing, Kasha–Vavilov rule, Thexi state, Stokes shift, Luminescence processes**

- **Harmonic oscillator model, Born–Oppenheimer approximation, Franck–Condon principle, Transition dipole moment operator, Selection rules, Spin–orbit coupling, Heavy-atom effect**

- **Photochemical length and time scales, Electromagnetic spectrum**

- **<u>Beer–Lambert law, Absorption coefficient, Einstein coefficients, Oscillator strength, Absorptance, *E–k* diagrams</u>**

Paper Time!

Photochemistry *(let's review* TWTh*)*

- T: Blackbody radiation, Carnot efficiency limits, Light–Matter interactions, Photon properties, Conservation laws

- **W: Jablonski diagram, Internal conversion, Intersystem crossing, Kasha–Vavilov rule, Thexi state, Stokes shift, Luminescence processes, Harmonic oscillator model, Born–Oppenheimer approximation, Franck–Condon principle, Transition dipole moment operator, Selection rules, Spin–orbit coupling, Heavy-atom effect, Photochemical length and time scales, Electromagnetic spectrum**

- Th: Beer–Lambert law, Absorption coefficient, Einstein coefficients, Oscillator strength, Absorptance, E–k diagrams

ALL DONE!...

... THANKS SO MUCH FOR TAKING PART IN THIS (RATHER) NEW COURSE!

Take-home messages:
(1) Some chemists know a lot of physics;
(2) Physicists (you!) now know a lot of Chemistry;
(3) Who wants to switch to a Ph.D. in Chemistry?

Final Exam Time!