Lecture #10 of 12

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Photophysical Processes

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Today's Critical Guiding Question

What continuity/conservation laws are most important for photophysical processes like absorption and emission of photons… for real this time, again: Part 4?

Photophysical Processes

- Blackbody radiation, Photon properties, Light–Matter interactions, Conservation laws, Einstein coefficients
- Jablonski diagram, Spin multiplicity, Internal conversion, Intersystem crossing, Thexi state, Kasha–Vavilov rule, Stokes shift, PL
- Born–Oppenheimer approximation, Franck–Condon principle, Transition dipole moment operator, Franck–Condon factors, **Beer–Lambert law, Absorption coefficient, Oscillator strength, Absorptance**
- Luminescence processes, **Selection rules, Charge-transfer transitions, Spin–Orbit coupling, Heavy-atom effect, *E*–*k* diagrams**, Jortner energy gap law, Conical intersections, Energy transfer, Exciplex/Excimer
- **Photoluminescence spectrometer, Emission/Excitation spectra, Inner filter effects, Anisotropy, Excited-state lifetime, Emission quantum yield**

Nuclear Terms & F–C Factors

Turro, Chapters 2 and 3

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

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

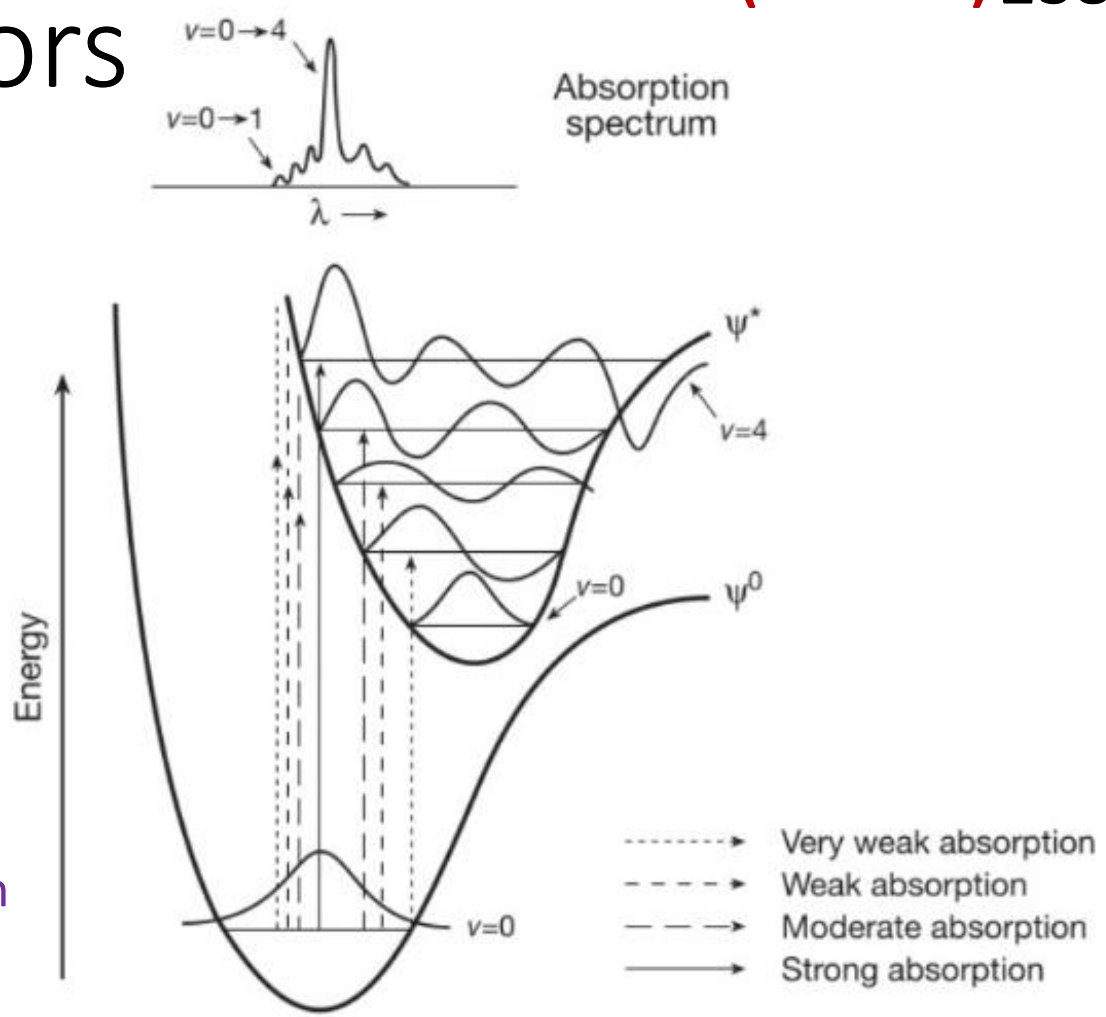
Ψ	$\sim$	$\Psi_0 \chi S$
"True" molecular wave function Exact solution to Eq. 2.1		(orbitals)(nuclei)(spin) Approximate solution to Eq. 2.1

… separable due to the Born–Oppenheimer approximation

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

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

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

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

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

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

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

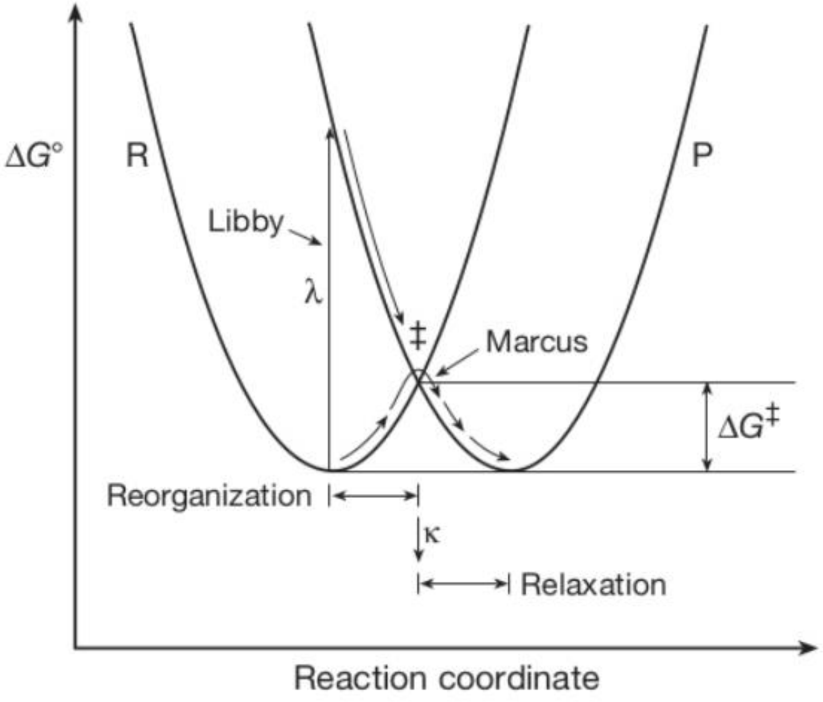
The probability amplitude P for the transition between these two states is given by

$$P = \langle \psi' | \boldsymbol{\mu} | \psi \rangle = \int \psi'^* \boldsymbol{\mu} \psi \, d\tau, \qquad \psi = \psi_e \psi_v \psi_s$$

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

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

$$= \underbrace{\int \psi'^*_v \psi_v \, d\tau_n}_{\substack{\text{Franck–Condon} \\ \text{factor}}} \underbrace{\int \psi'^*_e \boldsymbol{\mu}_e \psi_e \, d\tau_e}_{\substack{\text{orbital} \\ \text{selection rule}}} \underbrace{\int \psi'^*_s \psi_s \, d\tau_s}_{\substack{\text{spin} \\ \text{selection rule}}} + \underbrace{\int \psi'^*_e \psi_e \, d\tau_e}_{0} \int \psi'^*_v \boldsymbol{\mu}_N \psi_v \, d\tau_v \int \psi'^*_s \psi_s \, d\tau_s$$



Turro, Chapter 7, Figure 7.12, Page 429

Selection Rules

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

Angular Momentum Quantum Numbers

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 factor makes sense based on pictures on previous slides

… but what does $\boldsymbol{\mu}_e$ do to a wavefunction?…

… maybe we don't know, but it better change the angular momentum properly for a photon

… and what are spin wavefunctions?… just symbols!… spin does not appear in $\boldsymbol{\mu}$… it's just math…

… so, the spin wavefunctions only overlap when they are identical… meaning spin does not change

Atomic Selection "rules"

Orbital angular momentum (Laporte "rule"): $\boldsymbol{\Delta l = \pm 1}$… as $l_f = l_i \pm s_{\text{photon}}$

Spin angular momentum (Wigner "rule"): $\boldsymbol{\Delta m_s = 0}$… $\boldsymbol{\mu}$ 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

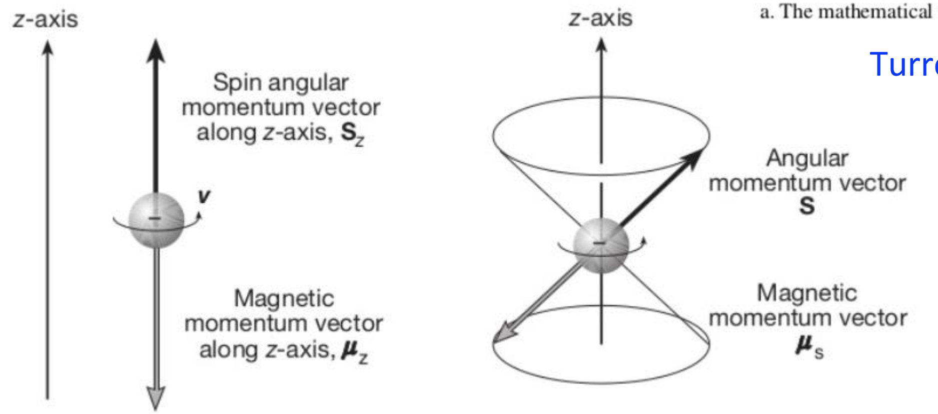
$$= \underbrace{\int \psi_v'^{*} \psi_v \, d\tau_n}_{\text{Franck–Condon factor}} \; \underbrace{\int \psi_e'^{*} \boldsymbol{\mu}_e \psi_e \, d\tau_e}_{\text{orbital selection rule}} \; \underbrace{\int \psi_s'^{*} \psi_s \, d\tau_s}_{\text{spin selection rule}} .$$

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.

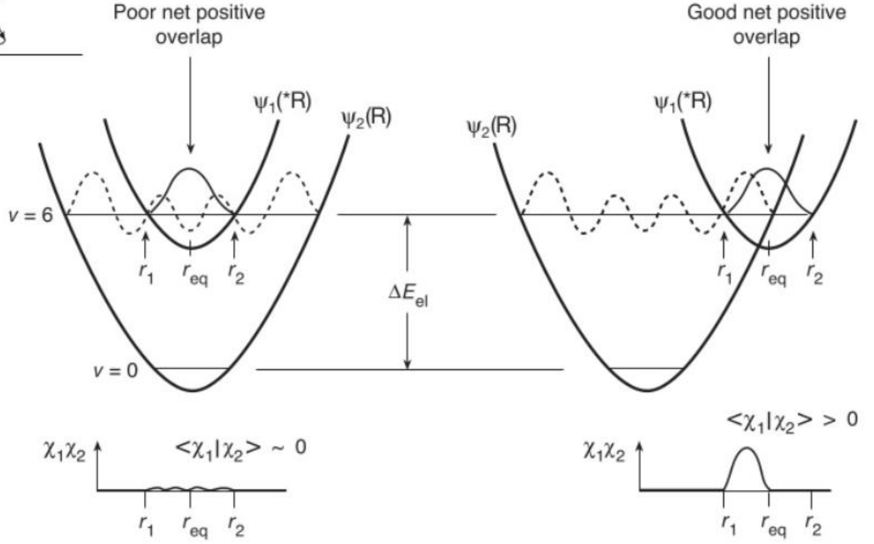
Turro, Chapter 2, Table 2.4, Page 102

… related to spin–orbital coupling…



Turro, Chapter 2, Figure 2.13, Page 99

… related to the F–C factor…



Turro, Chapter 3, Figure 3.5, Page 133

Summary of Atomic Selection "rules"

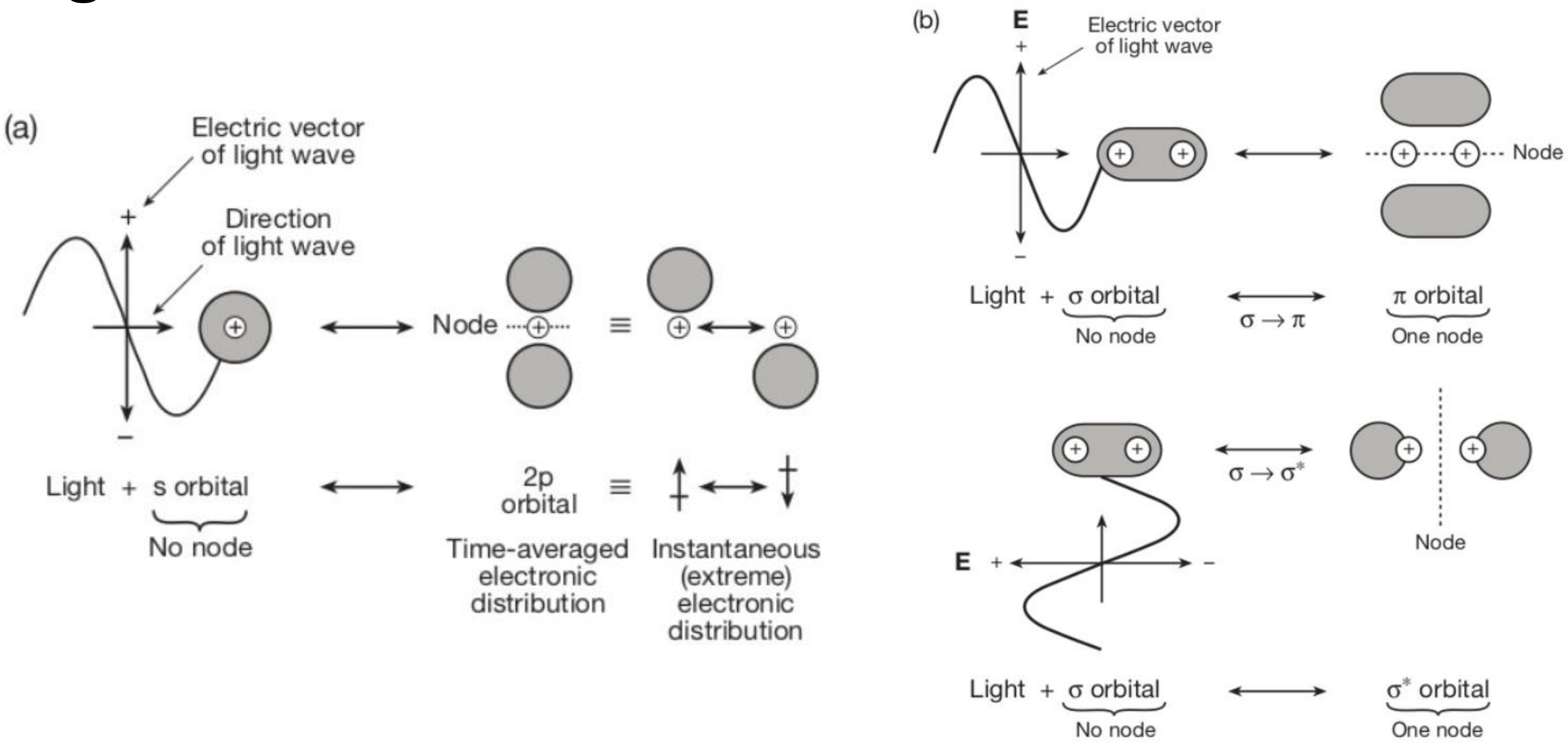
$\boldsymbol{\Delta l = \pm 1}$… as $l_f = l_i \pm s_{\text{photon}}$… $\boldsymbol{\Delta m_s = 0}$… $\boldsymbol{\Delta m_l = 0, \pm 1}$… as $m_{l,f} = m_{l,i} \pm m_{s,\text{photon}}$

Heavy Molecule (Russell–Saunders L–S Coupling) Selection "rules"

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

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

Light–Matter Interactions



Turro, Chapter 4, Figure 4.6, Page 189

Charge-Transfer Transitions & S–O Coupling

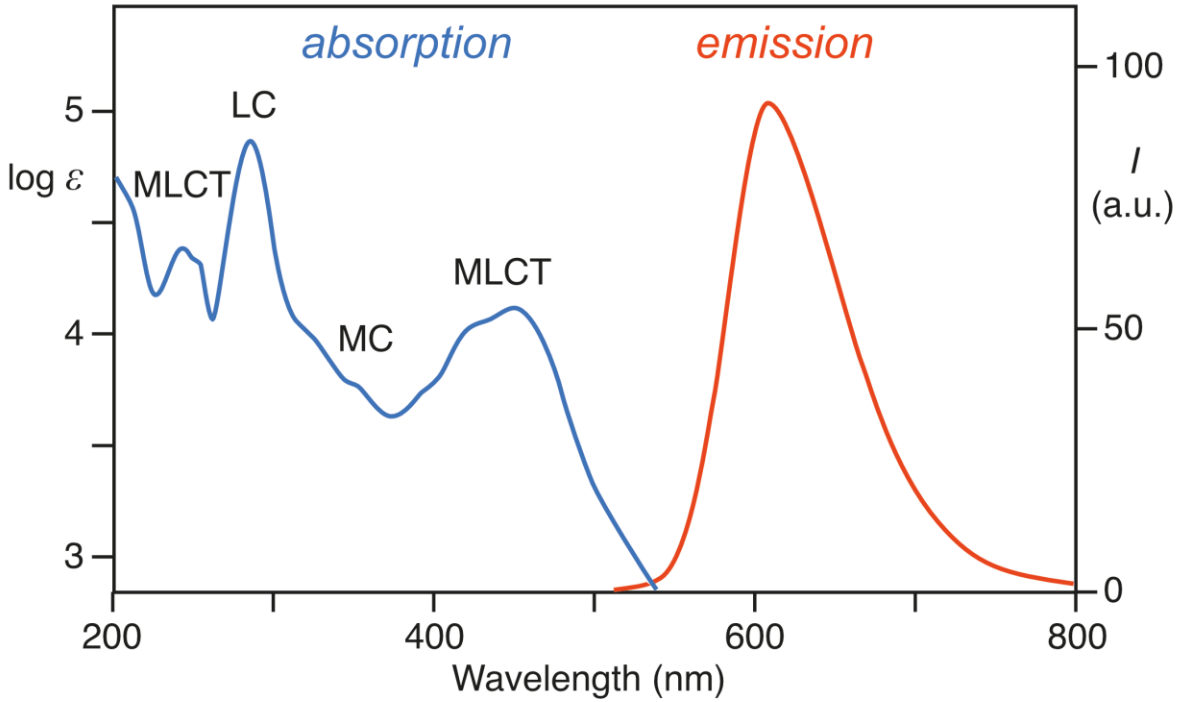
The Hamiltonian for spin–orbit (S–O) coupling results in the heavy-atom effect…

… and it also results in variation in the selection rules…

Total angular momentum: $\boldsymbol{\Delta J = 0, \pm 1}$

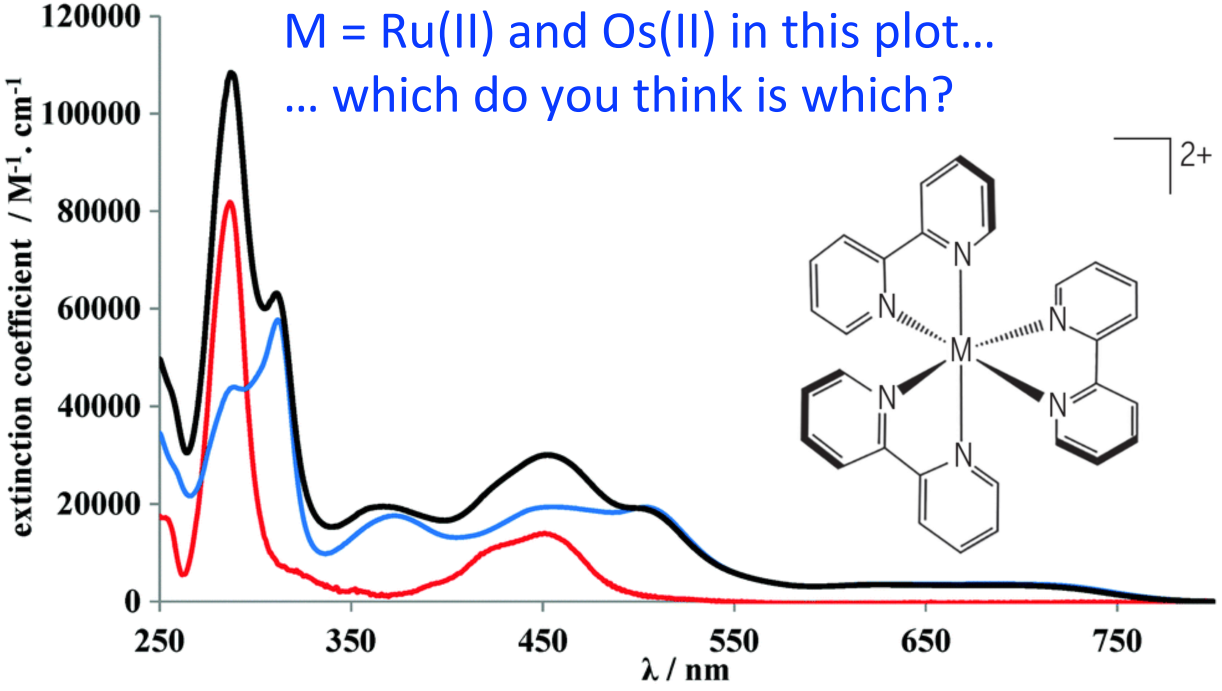
Total z-direction angular momentum: $\boldsymbol{\Delta m_J = 0, \pm 1}$

$$E_{SO} = \boldsymbol{Z^4}\alpha^2 hcR_H \left\{ \frac{j(j+1) - l(l+1) - s(s+1)}{2n^3 l\left(l+\frac{1}{2}\right)(l+1)} \right\}$$



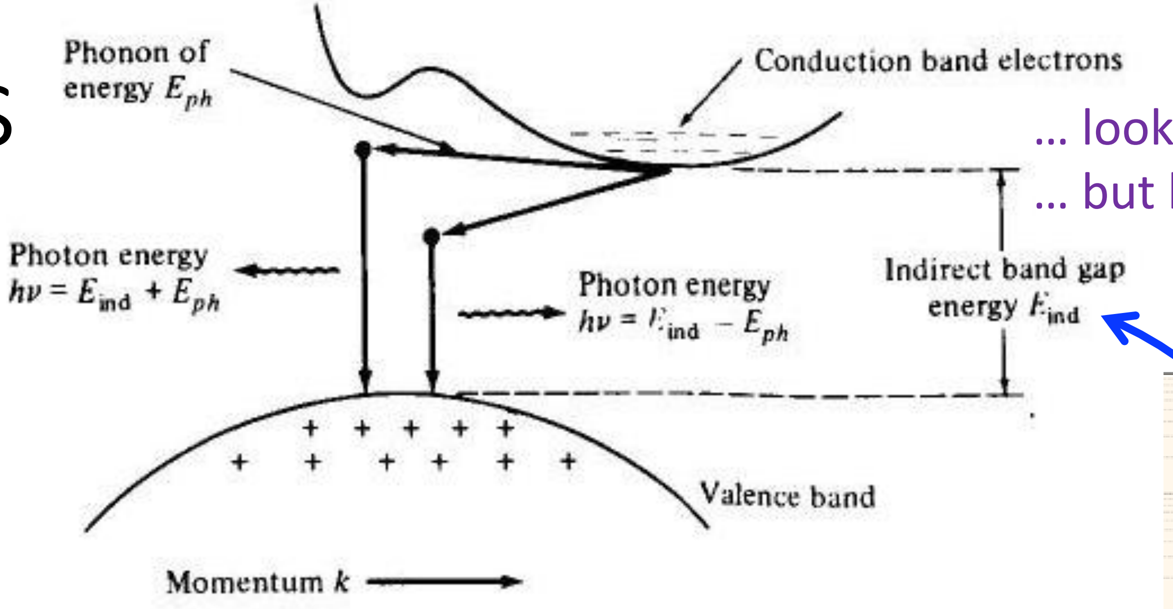
M = Ru(II) and Os(II) in this plot…

… which do you think is which?



… oh, now I see it in those spectra… and how the black spectrum is when there is a mixture

E–k Diagrams



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

Phonons

Particle Type: Boson

Mass: 0

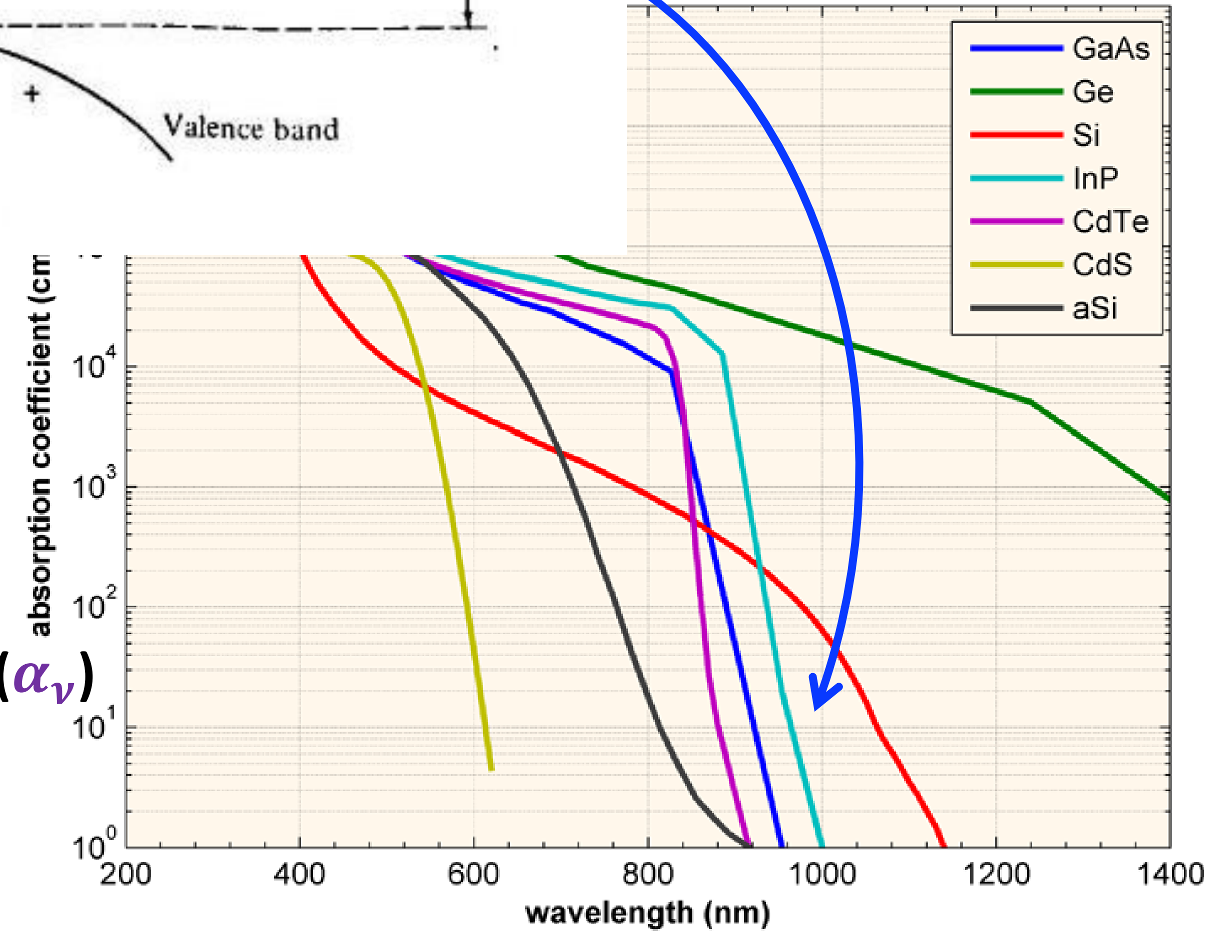
Charge: 0

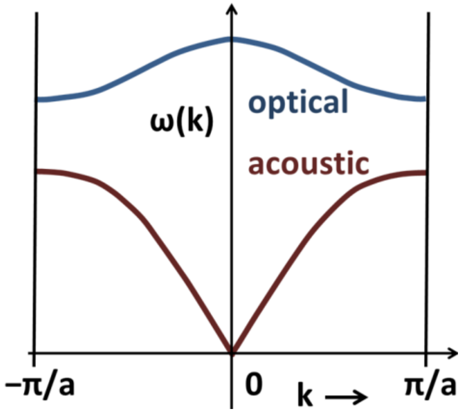
Energy: $\boldsymbol{E} = h\nu = \hbar\boldsymbol{\omega}$

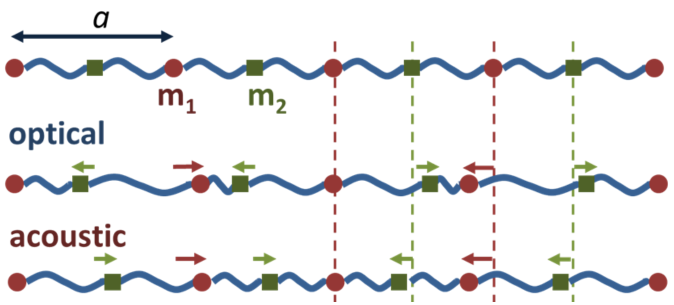
Linear Velocity: $\frac{c}{n} = \left(\frac{\lambda}{n}\right)\nu = \lambda'\nu$

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

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







https://en.wikipedia.org/wiki/Phonon

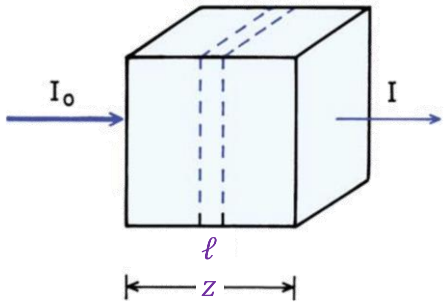
https://www.pveducation.org/pvcdrom/pn-junctions/absorption-coefficient

Absorption Coefficient & Beer–Lambert Law

To describe attenuation of light intensity/power through matter due to absorption only… one writes

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

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



Lakowicz, Chapter 2, Figure 2.52, Page 59

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

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

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

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

$\ln\left(\frac{I_\nu}{I_{\nu,\mathrm{o}}}\right) = -\kappa_\nu c\ell$… where κ_ν is the molar Napierian **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}, $\boldsymbol{\sigma_\nu} = \frac{1000\kappa_\nu}{N_\mathrm{A}}$ is the **absorption cross-section** (cm^2)

$\log\left(\frac{I_\nu}{I_{\nu,\mathrm{o}}}\right) = -\boldsymbol{\varepsilon_\nu} c\ell$… where $\boldsymbol{\varepsilon_\nu}$ is the molar decadic **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

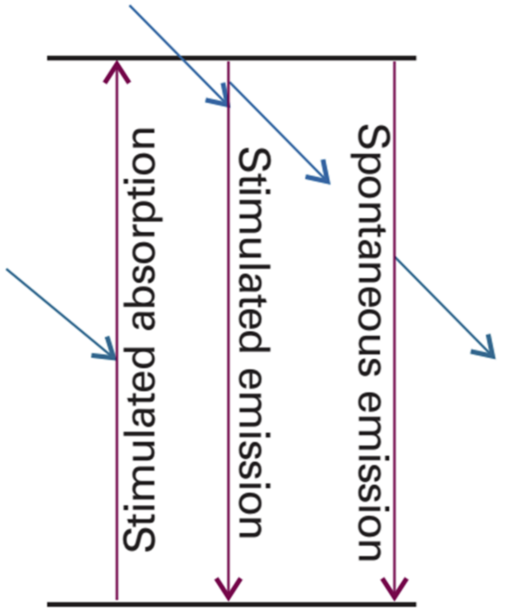
https://goldbook.iupac.org/terms/view/A00037

Einstein Coefficients & Oscillator Strength

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

… is the rate constant for emission equal to that of absorption? **… No way!**

… but Absorption = –Stimulated Emission… but ≠ Spontaneous Emission



Atkins, Chapter 13, Figure 13.5, Page 434

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

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

Consider all possible reactions to be at equilibrium…

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

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

$$\ldots\ A_{21} = \frac{8\pi h\nu^3}{c^3} B_{21} = \frac{16\pi^3 \nu^3 \mu_{21}^2}{3\varepsilon_0 h c^3}$$

R. C. Hilborn, *Am. J. Phys.*, **1982**, *50*, 982–986
R. C. Hilborn, arXiv:physics/0202029

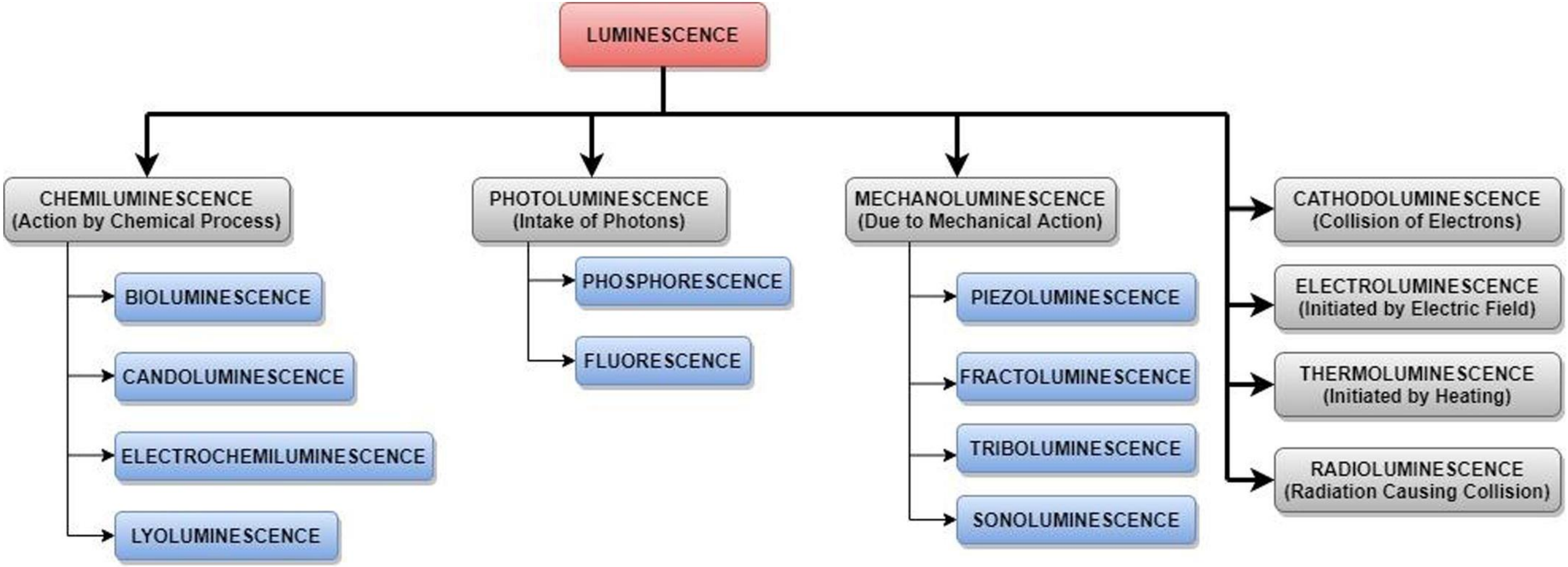
Today’s Critical Guiding Question

What continuity/conservation laws are most important for photophysical processes like absorption and emission of photons… for real this time, again: Part 4?

DISCUSSION SESSION TOPICS

Luminescence Processes

… Photo… and Chemi… and Mechano… Oh My!



https://www.sciencedirect.com/science/article/pii/S2214785321017272

… well I guess it makes sense… it's just conservation of energy… and momentum, of course…

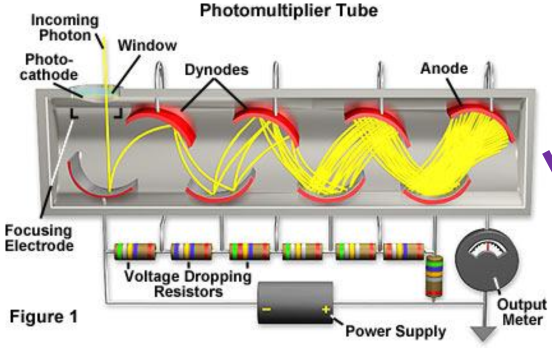
https://micro.magnet.fsu.edu/primer/digitalimaging/concepts/photomultipliers.html

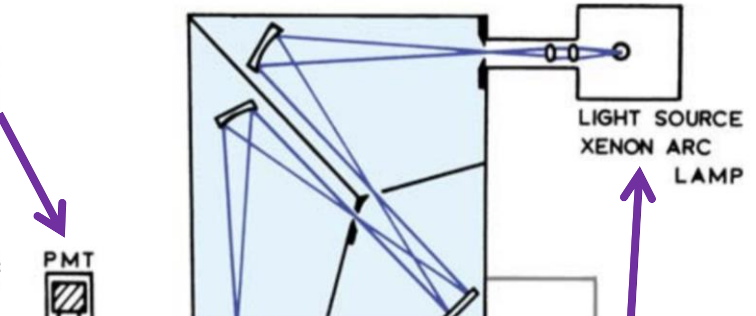
Photoluminescence Spectrometer

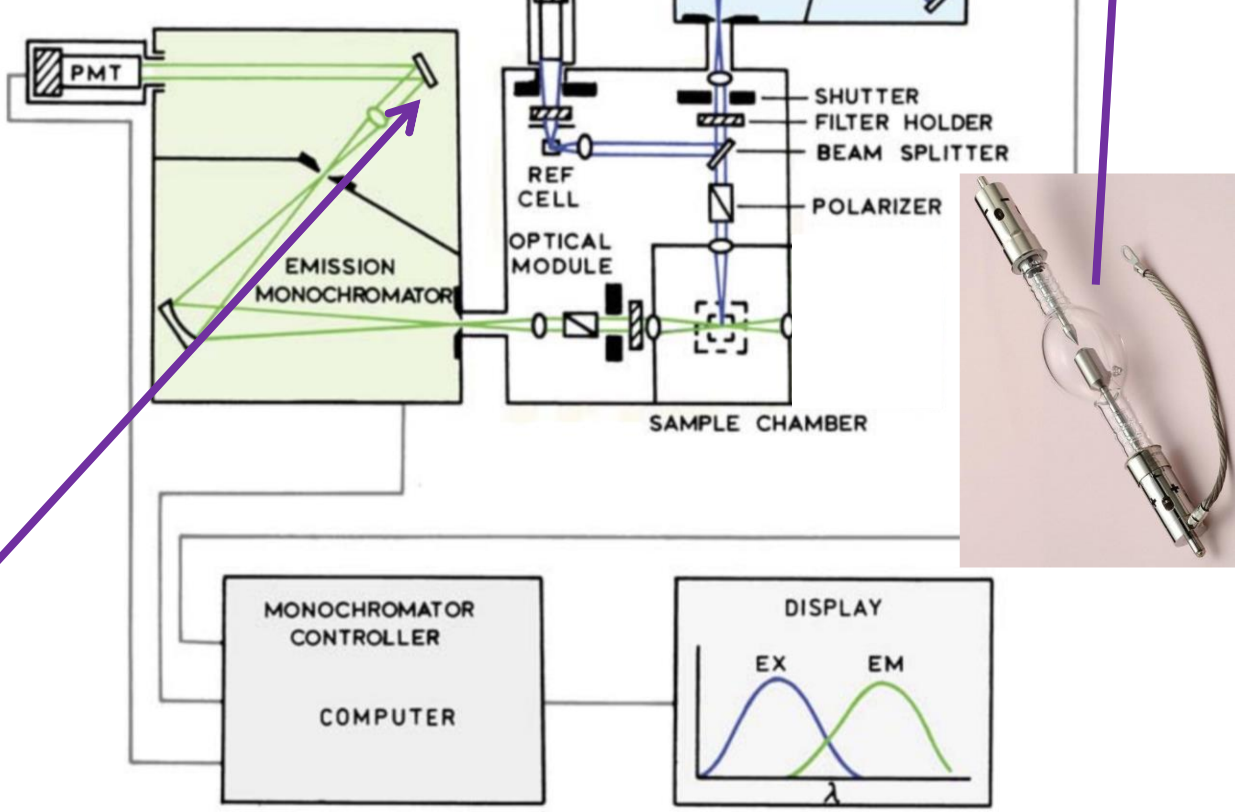
WAVELENGTH or POLARIZATION or TIME

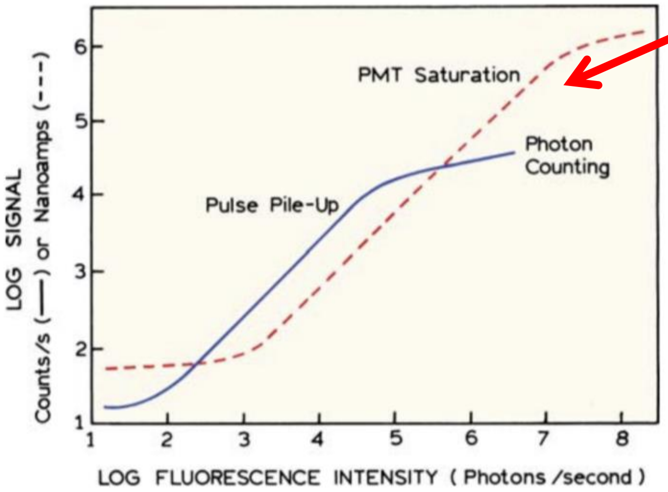
WAVELENGTH or POLARIZATION or TIME or LIGHT INTENSITY

WAVELENGTH or POLARIZATION or TIME or LIGHT INTENSITY



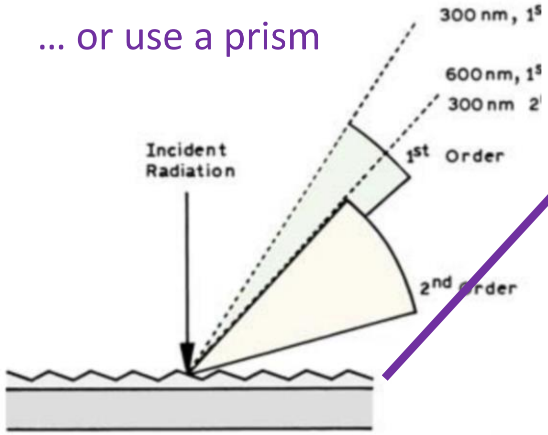






Lakowicz, Chapter 2, Figure 2.36, Page 48

… or use a prism

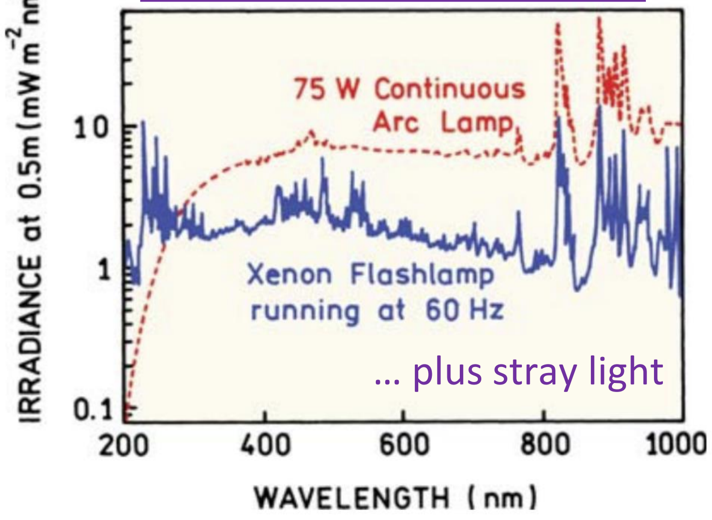


Lakowicz, Chapter 2, Figure 2.16, Page 37

Lakowicz, Chapter 2, Figure 2.1, Page 28

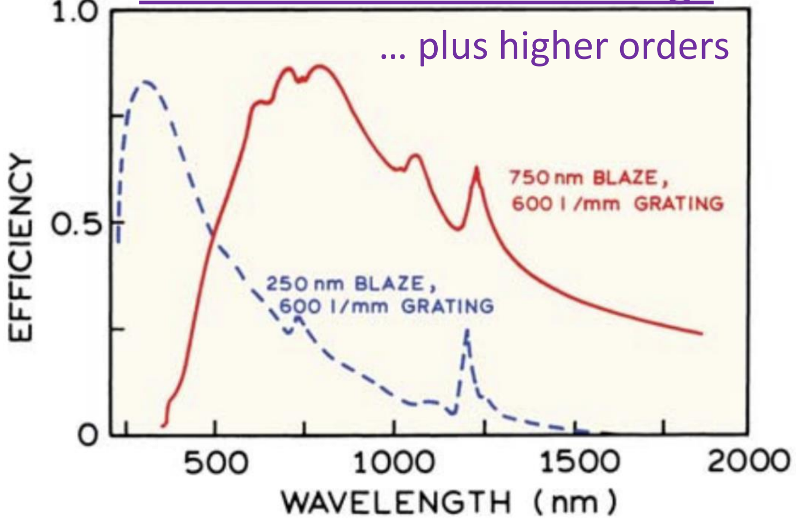
Photoluminescence Spectrometer

Photoexcitation Source



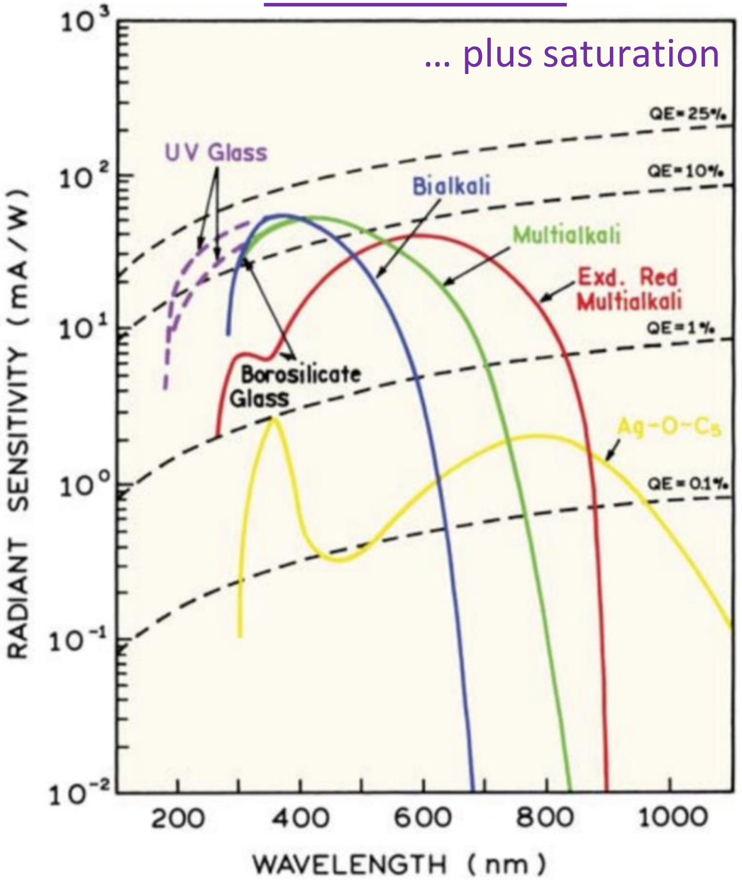
Lakowicz, Chapter 2, Figure 2.5, Page 31

Monochromators Gratings



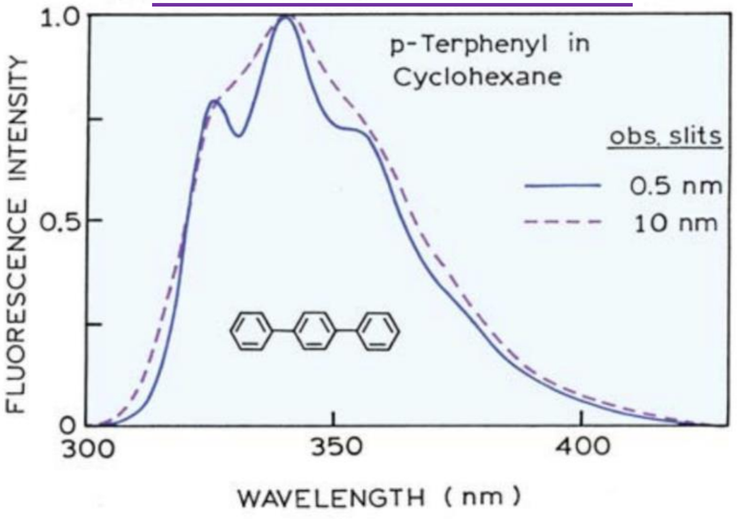
Lakowicz, Chapter 2, Figure 2.12, Page 35

PMT Detector



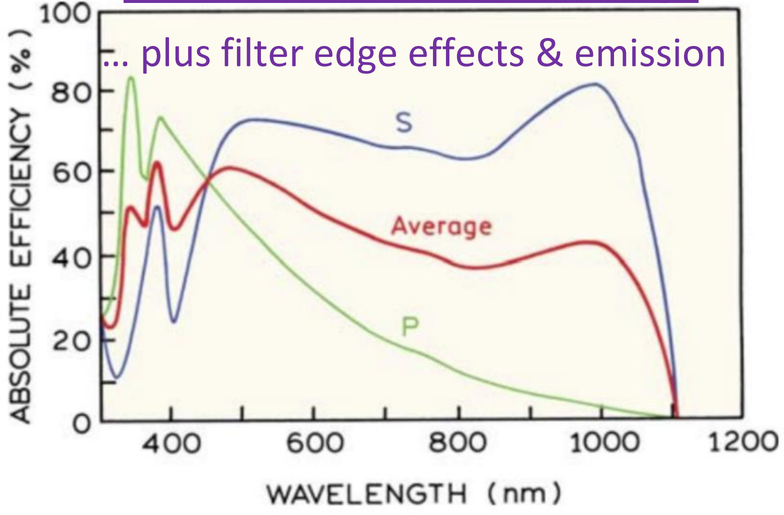
Lakowicz, Chapter 2, Figure 2.31, Page 45

Monochromators Slits



Lakowicz, Chapter 2, Figure 2.13, Page 35

Monochromators Gratings



Lakowicz, Chapter 2, Figure 2.14, Page 36

… measured PL spectra are effectively multiplied by all of these!… Ugh!