Lecture #11 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… <u>for real this time, again: Part 5</u>?

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**

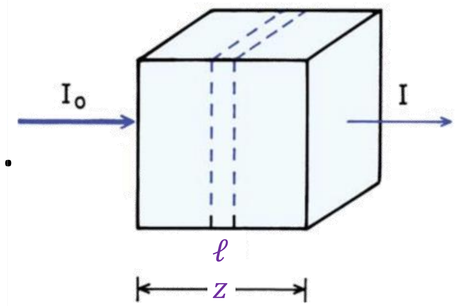
Absorption Coefficient & Beer–Lambert Law

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 $I_{\nu,\text{front}}$ 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 $I_\nu = I_{\nu,\text{o}} e^{-\boldsymbol{\alpha}_\nu \ell}$, 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 linear decadic **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 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}, $\boldsymbol{\sigma}_\nu = \frac{1000\kappa_\nu}{N_\text{A}}$ is the **absorption cross-section** (cm^2)

$\log\left(\frac{I_\nu}{I_{\nu,\text{o}}}\right) = -\boldsymbol{\varepsilon}_\nu c \ell$… 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

Spontaneous Emission

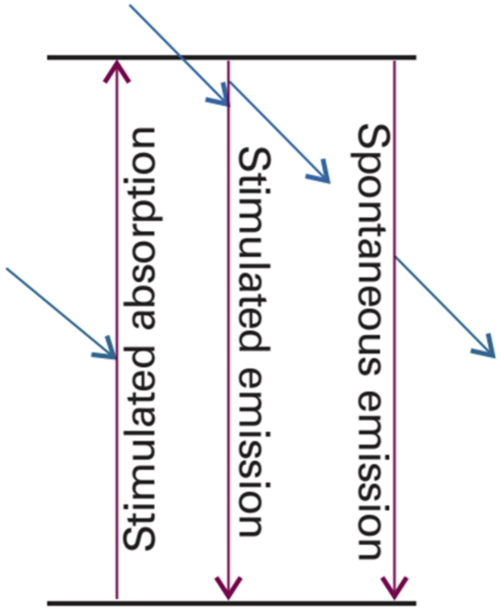
$$\frac{\partial n_1}{\partial t} = A_{21}n_2$$

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…

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

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

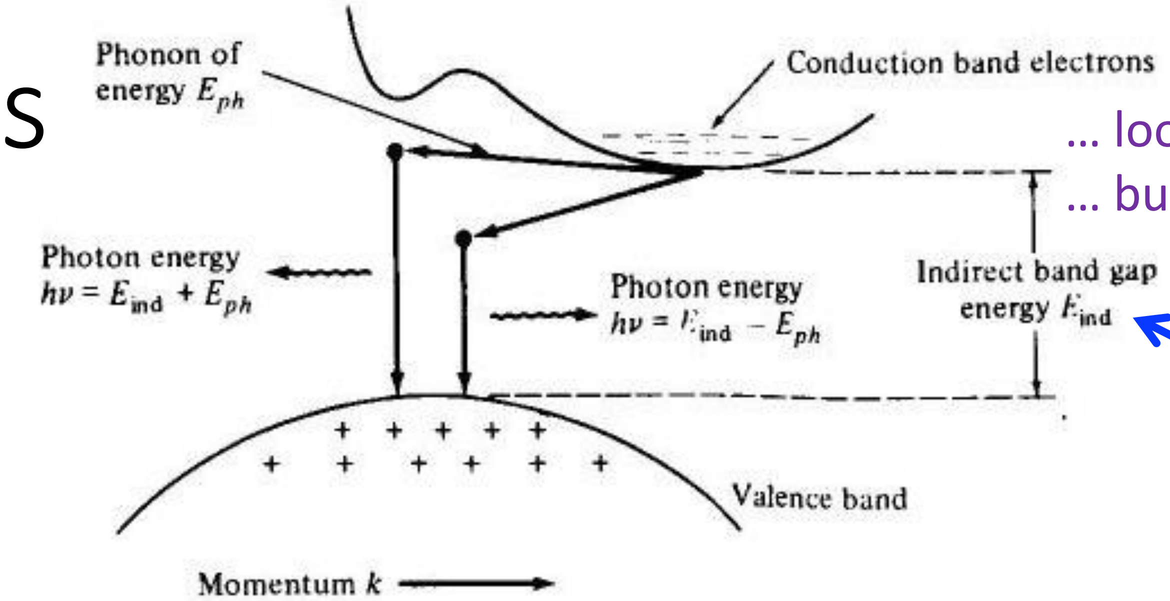
$$\ldots\ A_{21} = \frac{8\pi h\nu^3}{c^3}B_{21} = \frac{16\pi^3\nu^3\mu_{21}^2}{3\varepsilon_0 h c^3}$$

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

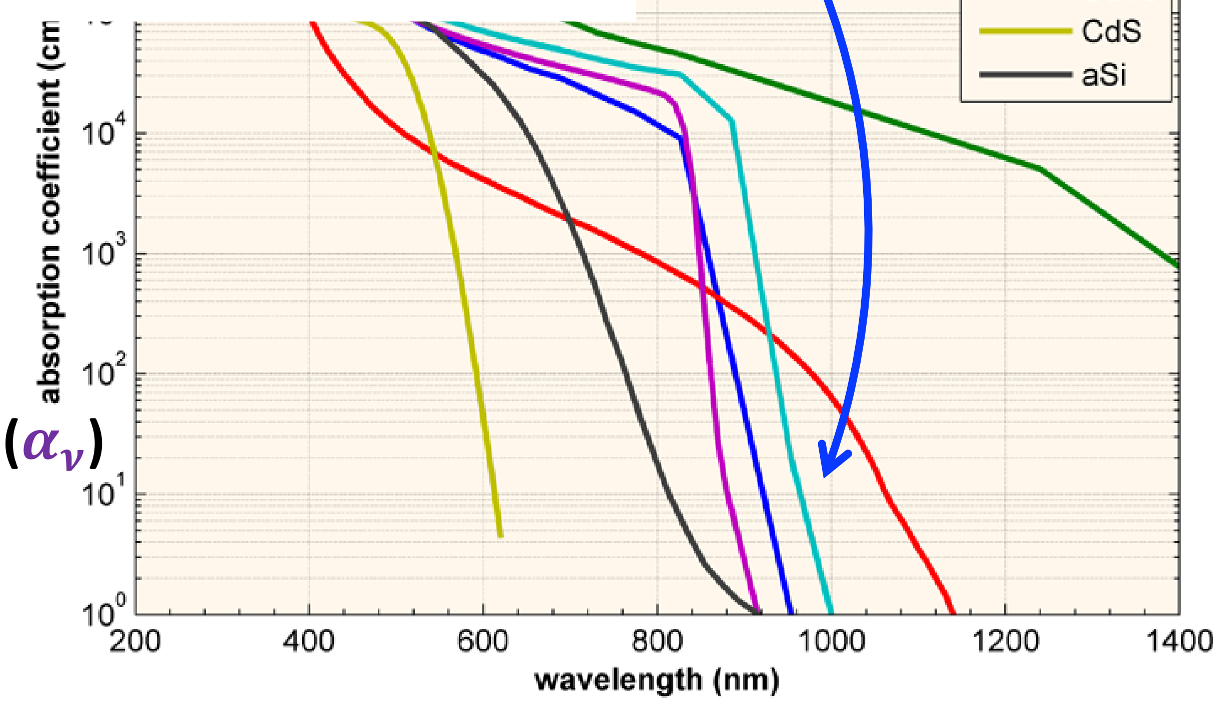
E–*k* Diagrams

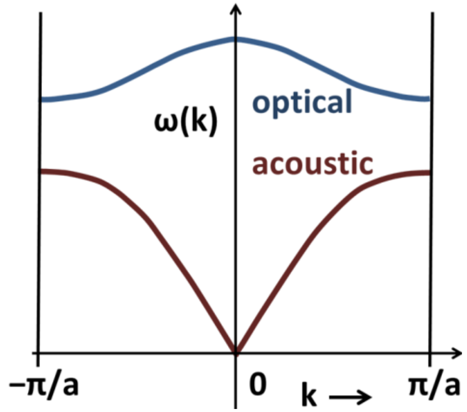
(BRIEFLY; REVIEW)

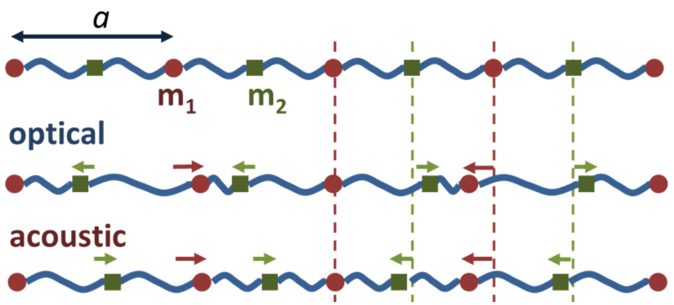
… looks like a Jablonski diagram…
… but showing **linear** momentum



Phonons
Particle Type: Boson
Mass: 0
Charge: 0
Energy: $E = h\nu = \hbar\omega$
Linear Velocity: $\frac{c}{n} = \left(\frac{\lambda}{n}\right)\nu = \lambda'\nu$
Linear Momentum: $p = \frac{h}{\lambda'} = \frac{nh\nu}{c} = h\bar{\nu} = \hbar k$
z Angular Momentum / Spin: $\pm\hbar = \pm\frac{h}{2\pi}$







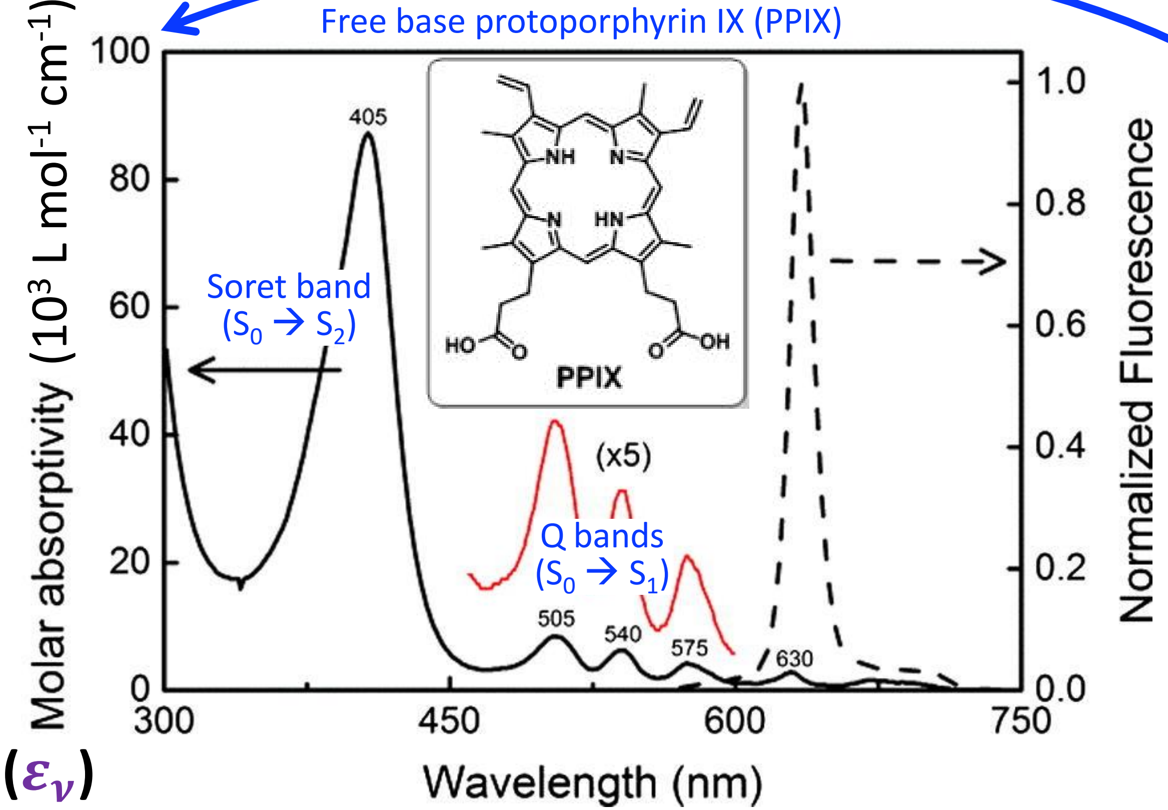
https://en.wikipedia.org/wiki/Phonon

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

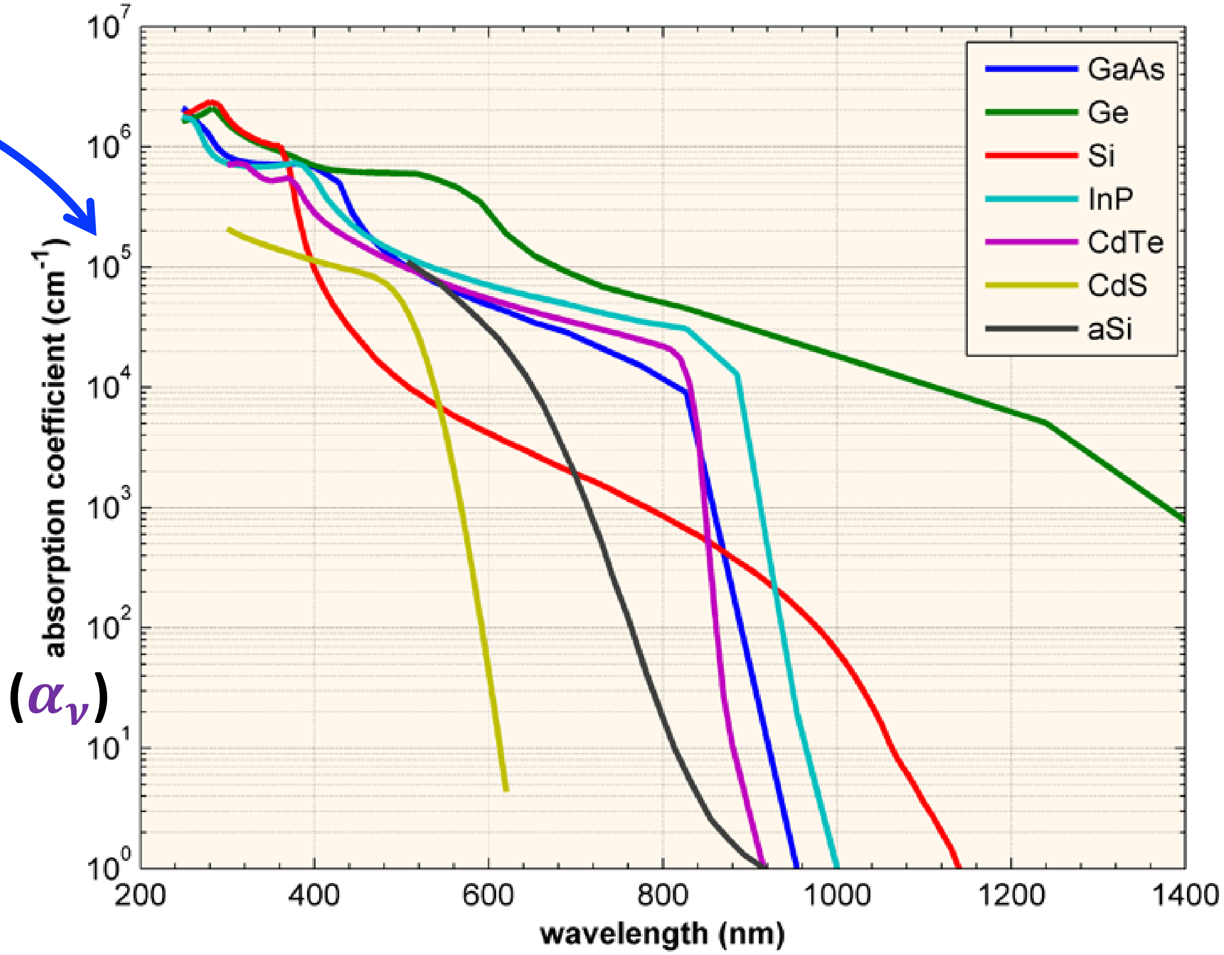
Absorption Coefficient

… 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?



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

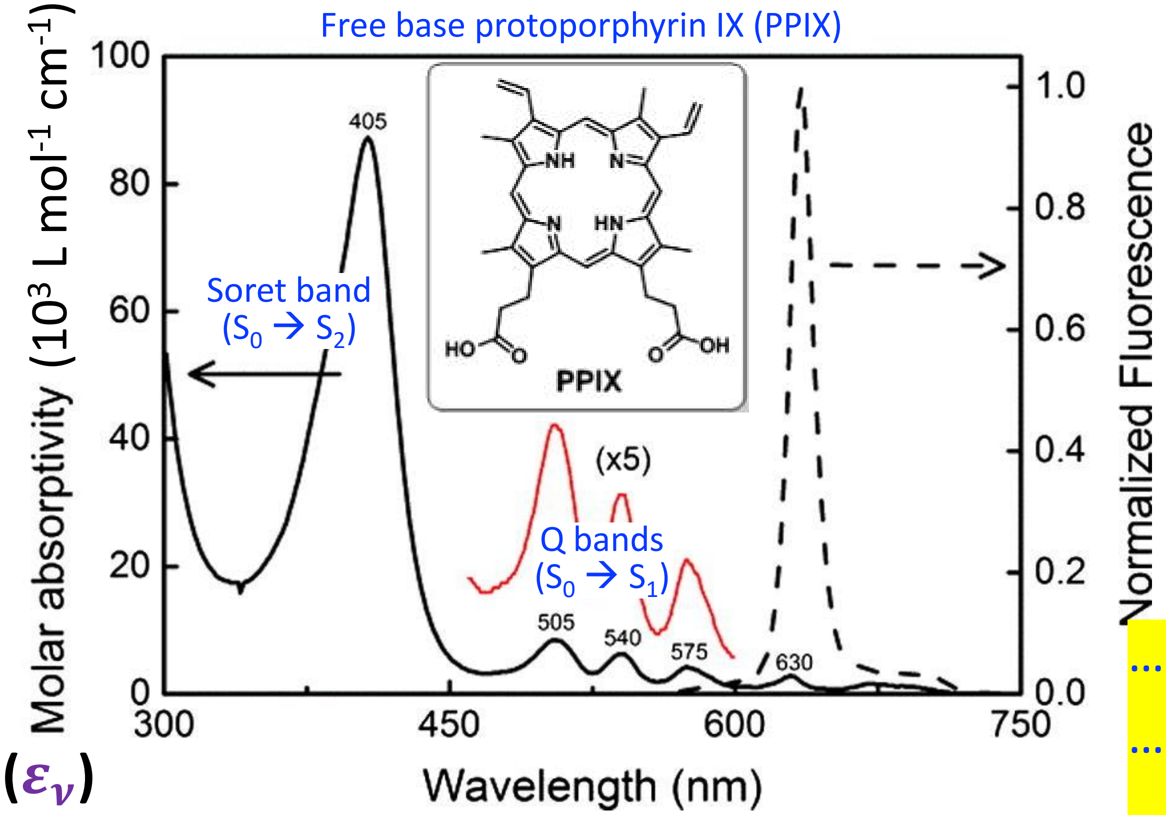


https://www.pveducation.org/pvcdrom/pn-junctions/absorption-coefficient

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



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

… "This plot displays an absorption spectrum"

… "The ordinate is often absorbance, which is dimensionless… and definitely not “a.u.”"

… "Absorbance, A, is directly related to concentration… and so its range is [0, ∞)"

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

… "Photochemists must know **concentrations** (via Abs, A) and **amount of light absorbed** (as Abt, α)"

… assuming $\%R_{\nu,i} = 0$, $\%A_\nu = 100\% - \%T_\nu$

… $\frac{\%A_\nu}{100\%} = 1 - 10^{-\varepsilon_\nu c \ell} = \alpha$ (dimensionless)

… $\boldsymbol{\alpha = 1 - 10^{-A}}$

$$\%\boldsymbol{R_\nu} = \left(\frac{\boldsymbol{n_2 - n_1}}{\boldsymbol{n_2 + n_1}}\right)^{\mathbf{2}}$$

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

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

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

Huang–Rhys Factor

Marcus–Hush (1950s–1960s)

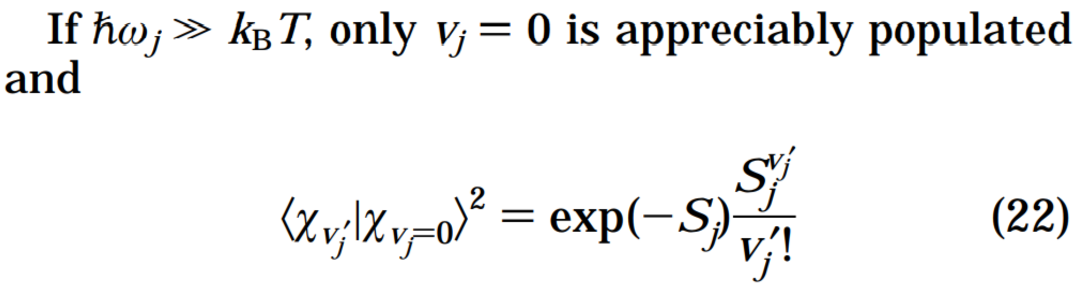
theoretical (semiclassical) rate constant equation

$$\boldsymbol{k}_{\mathbf{ET}} = \frac{2\pi}{\hbar}|H_{\mathrm{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\mathrm{AB}}kT}} \exp\left(-\frac{\Delta G_{\mathrm{AB}}{}^{\neq}}{kT}\right)$$

$$= \nu_{\mathrm{n}}(r)\kappa_{\mathrm{el}}(r)\kappa_{\mathrm{n}}(r)$$

$$= \frac{2\pi}{\hbar}\langle\psi'_{\mathrm{el}}|\hat{H}'|\psi_{\mathrm{el}}\rangle^2\langle\psi'_{\mathrm{vib}}|\psi_{\mathrm{vib}}\rangle^2\delta(E' - E)$$

… separable due to the Born–Oppenheimer approximation



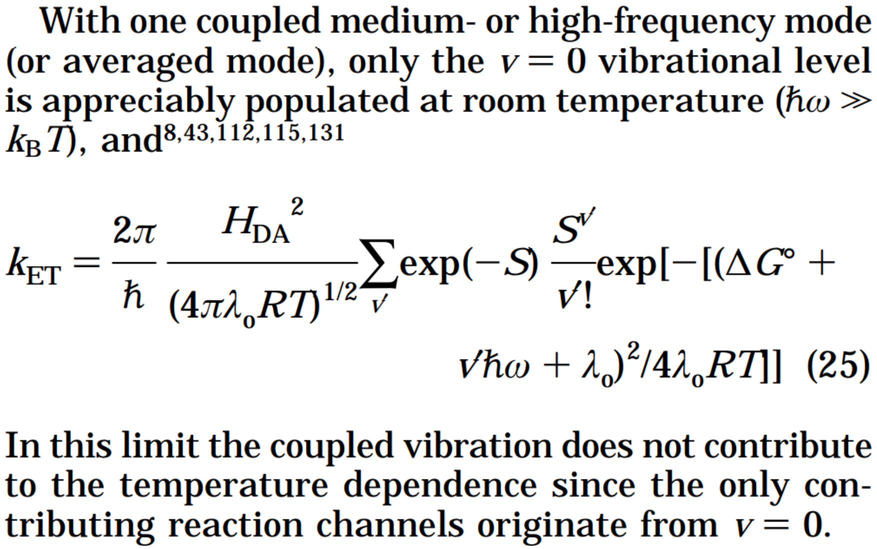
If $\hbar\omega_j \gg k_{\mathrm{B}}T$, only $v_j = 0$ is appreciably populated and

$$\langle\chi_{v_j'}|\chi_{v_j=0}\rangle^2 = \exp(-S_j)\frac{S_j^{v_j'}}{v_j'!} \qquad (22)$$

P. Chen & T. J. Meyer, *Chem. Rev.*, **1998**, *98*, 1439–1477

Fermi's Golden Rule

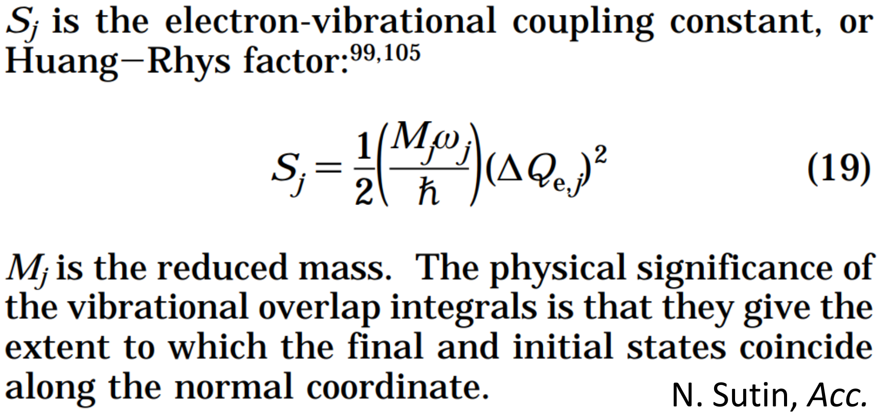
time-dependent perturbation theory



With one coupled medium- or high-frequency mode (or averaged mode), only the $v = 0$ vibrational level is appreciably populated at room temperature ($\hbar\omega \gg k_{\mathrm{B}}T$), and[8,43,112,115,131]

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar}\frac{H_{\mathrm{DA}}{}^2}{(4\pi\lambda_{\mathrm{o}}RT)^{1/2}}\sum_{v'}\exp(-S)\frac{S^{v'}}{v'!}\exp[-[(\Delta G^{\circ} + v'\hbar\omega + \lambda_{\mathrm{o}})^2/4\lambda_{\mathrm{o}}RT]] \quad (25)$$

In this limit the coupled vibration does not contribute to the temperature dependence since the only contributing reaction channels originate from $v = 0$.



S_j is the electron-vibrational coupling constant, or Huang–Rhys factor:[99,105]

$$S_j = \frac{1}{2}\left(\frac{M_j\omega_j}{\hbar}\right)(\Delta Q_{\mathrm{e},j})^2 \qquad (19)$$

M_j is the reduced mass. The physical significance of the vibrational overlap integrals is that they give the extent to which the final and initial states coincide along the normal coordinate.

N. Sutin, *Acc. Chem. Res.*, **1982**, *15*, 275–282

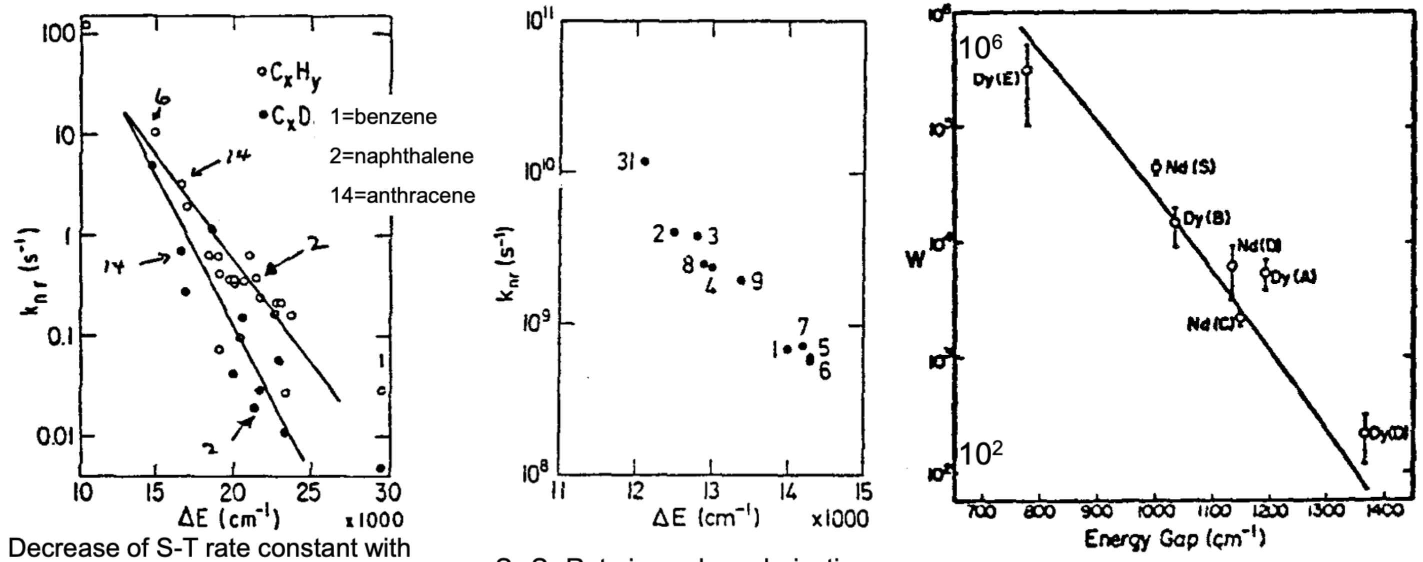
Jortner Energy Gap Law

Jortner Energy Gap Law (1960s–1970s)

theoretical non-radiative rate constant equation

$$W = \frac{C^2\sqrt{(2\pi)}}{\hbar\sqrt{(\hbar\omega_M \Delta E)}} \exp\left(-\gamma\Delta E/\hbar\omega_M\right)$$

Energy gap law data in condensed phase



Decrease of S-T rate constant with energy in aromatics in solid solution at 77K. **Note H-D difference**

S_2-S_1 Rate in azulene derivatives

1 = azulene, 8 = Me-A , 2 = Cl-A

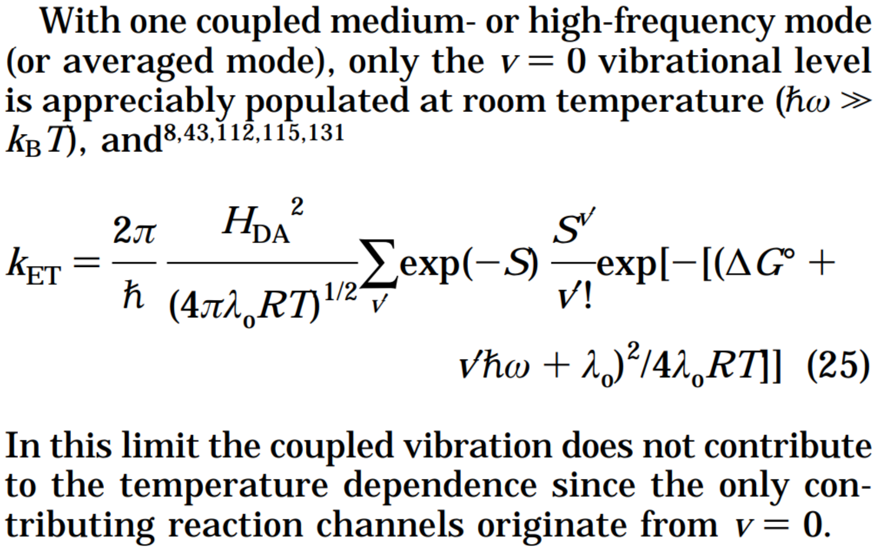
Rare in rare earth ions, $LaCl_3$

https://i.stack.imgur.com/NG6Lt.png

R. Englman & J. Jortner, *Mol. Phys.*, **1970**, *18*, 145–164

Fermi's Golden Rule

time-dependent perturbation theory



With one coupled medium- or high-frequency mode (or averaged mode), only the $v = 0$ vibrational level is appreciably populated at room temperature ($\hbar\omega \gg k_B T$), and[8,43,112,115,131]

$$k_{ET} = \frac{2\pi}{\hbar}\frac{H_{DA}{}^2}{(4\pi\lambda_o RT)^{1/2}}\sum_{v}\exp(-S)\frac{S^v}{v!}\exp[-[(\Delta G^\circ + v\hbar\omega + \lambda_o)^2/4\lambda_o RT]] \quad (25)$$

In this limit the coupled vibration does not contribute to the temperature dependence since the only contributing reaction channels originate from $v = 0$.

… also due to weak coupling…

… in the low-temperature limit

N. Sutin, *Acc. Chem. Res.*, **1982**, *15*, 275–282

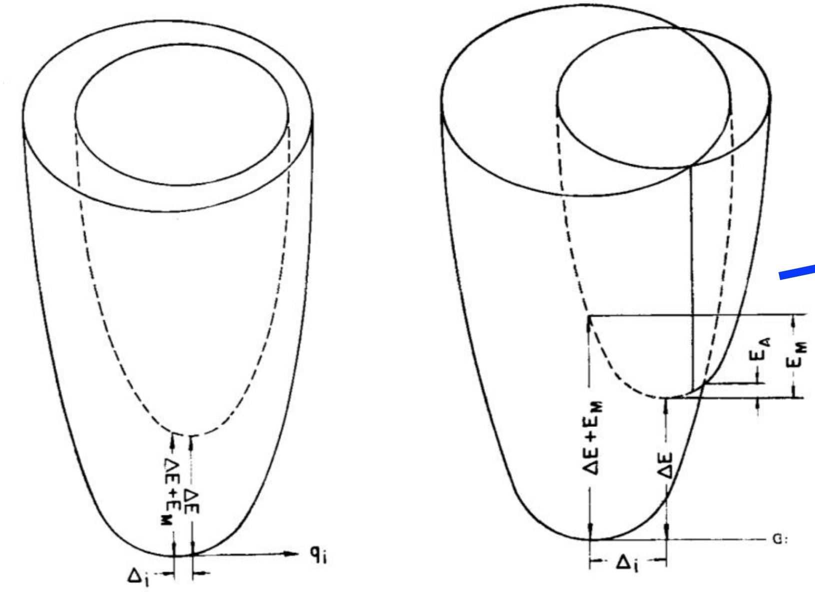
Conical Intersection Curve Crossing

Jortner Energy Gap Law (1960s–1970s)

theoretical non-radiative rate constant equation

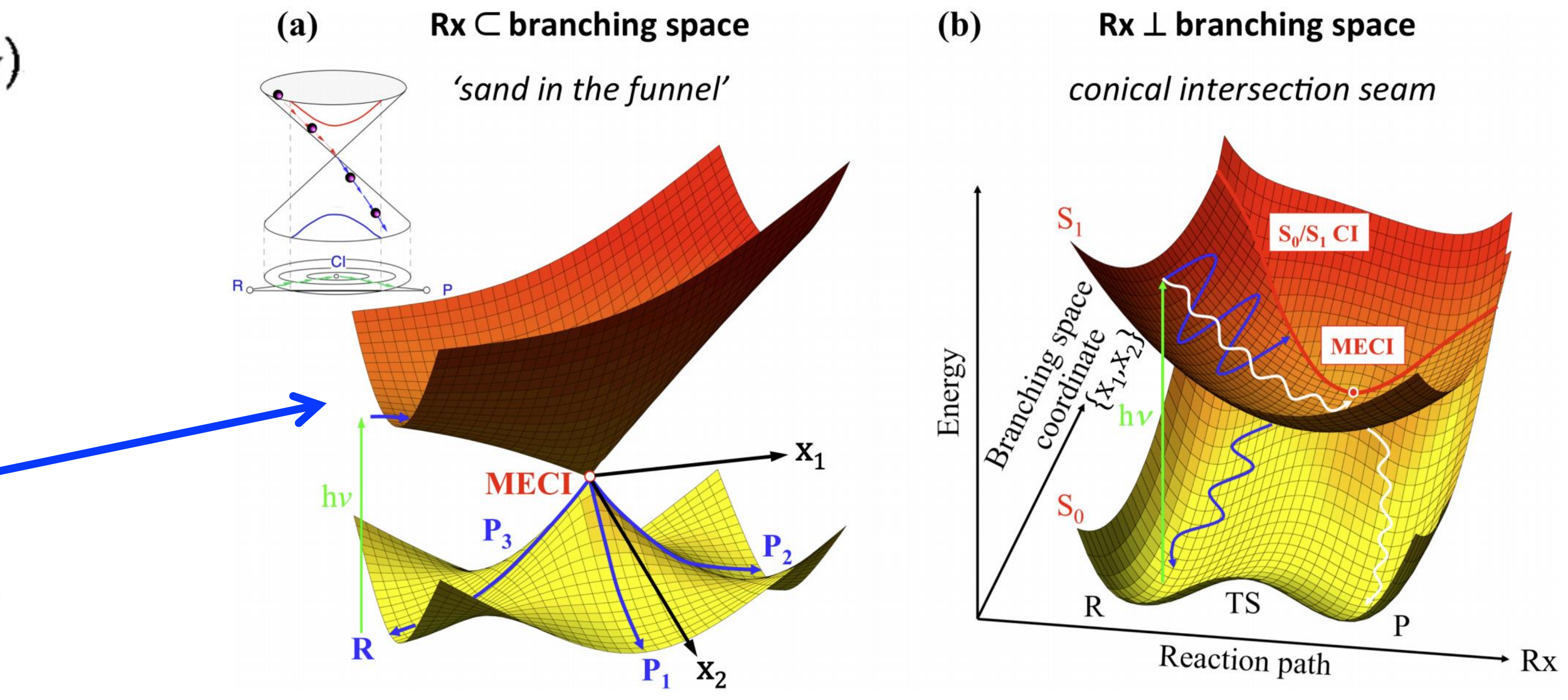
$$W = \frac{C^2\sqrt{(2\pi)}}{\hbar\sqrt{(\hbar\omega_M \Delta E)}} \exp\left(-\gamma \Delta E / \hbar\omega_M\right)$$

weak coupling strong coupling



Conical Intersection

breakdown of the B–O approximation


(a) Rx ⊂ branching space

'sand in the funnel'

(b) Rx ⊥ branching space

conical intersection seam

https://tel.archives-ouvertes.fr/tel-01184241/file/hdr_boggio_final.pdf

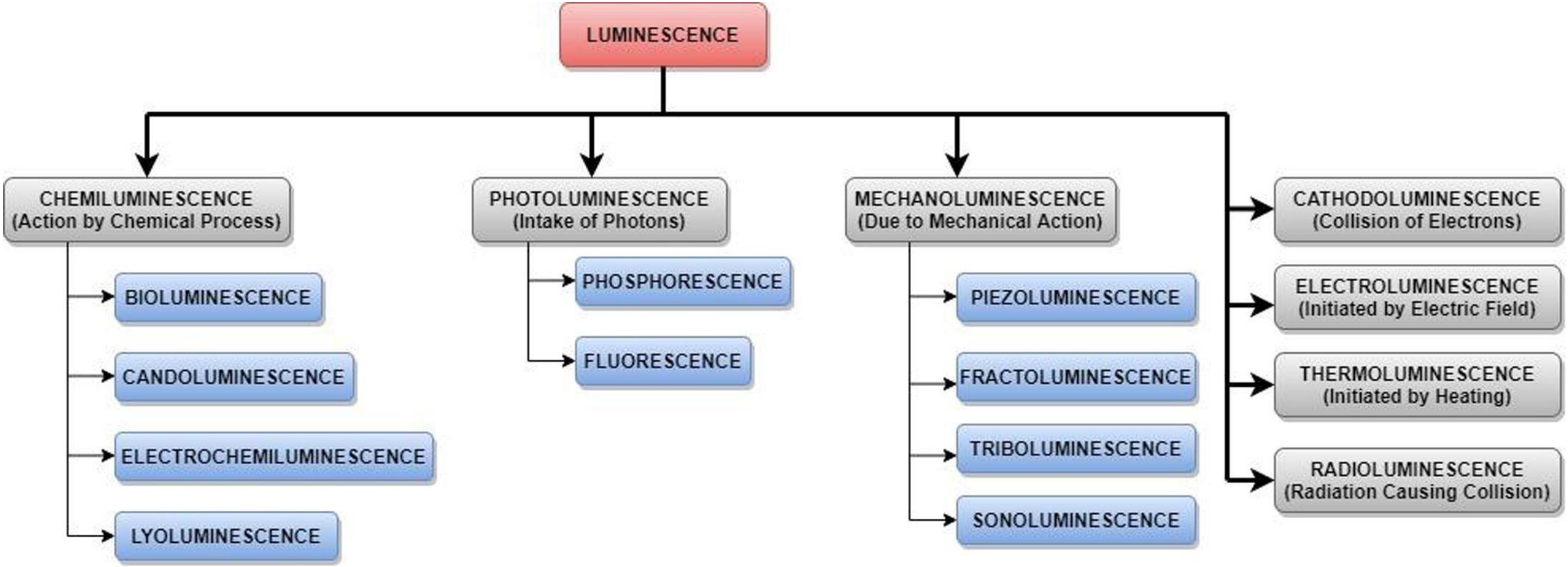
… a conical intersection leads to rapid excited-state deactivation… on the timescale of a bond vibration

… diatomic species with $\Delta m_s = 0$ obey the non-crossing "rule"… where $H_{\mathrm{DA}} \neq 0$, and Jortner is relevant

R. Englman & J. Jortner, *Mol. Phys.*, **1970**, *18*, 145–164

Luminescence Processes

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

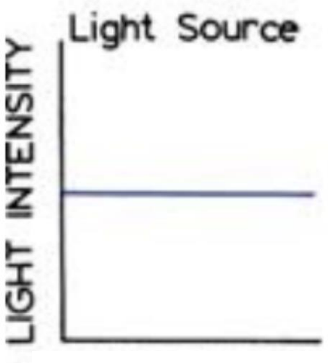


https://www.sciencedirect.com/science/article/pii/S2214785321017272

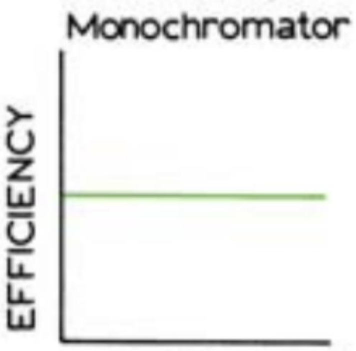
… well I guess it makes sense… it's just conservation of energy… and momentum, of course…

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

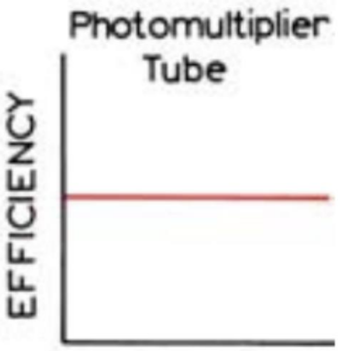
Photoluminescence Spectrometer



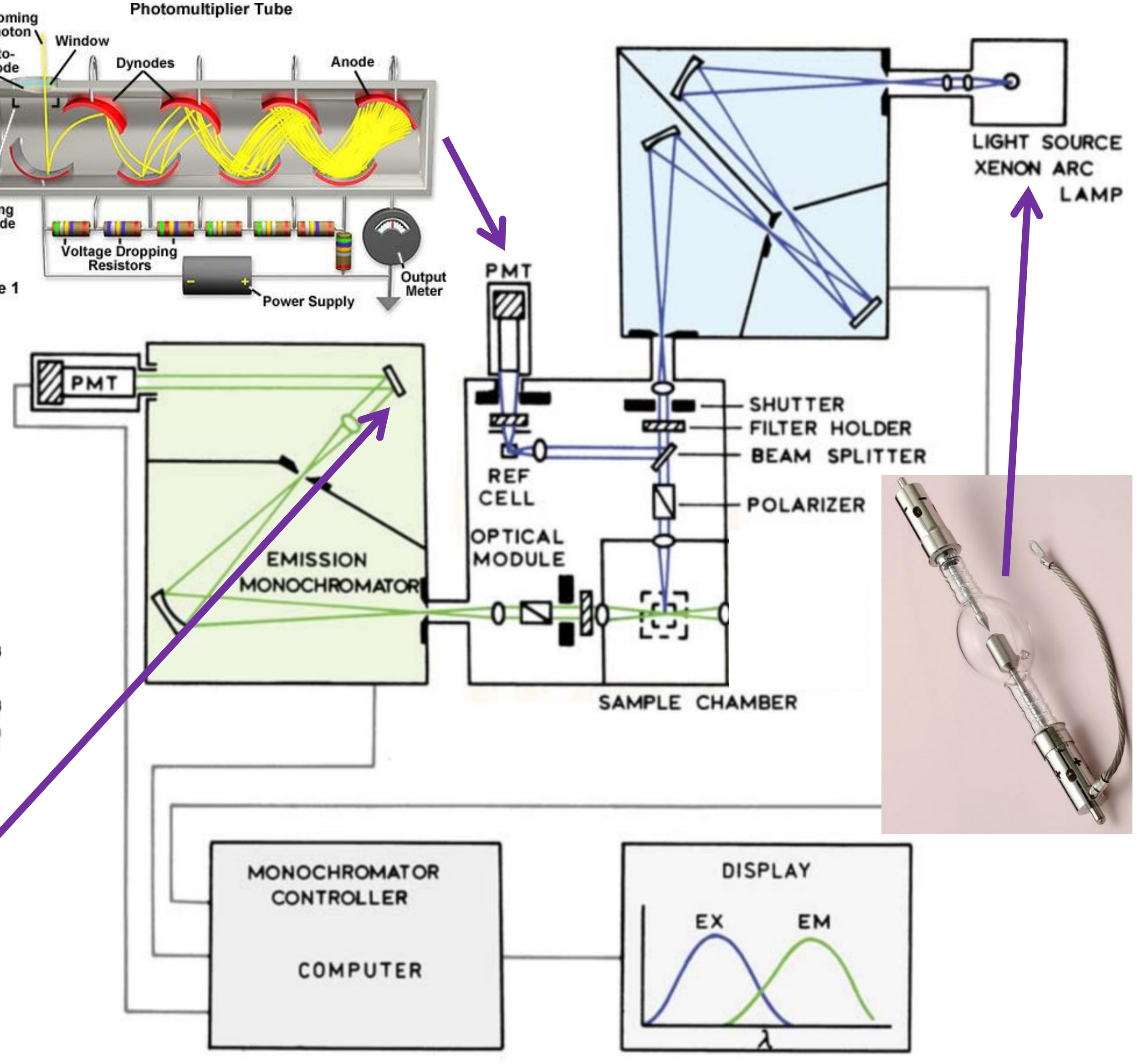
WAVELENGTH
or POLARIZATION
or TIME

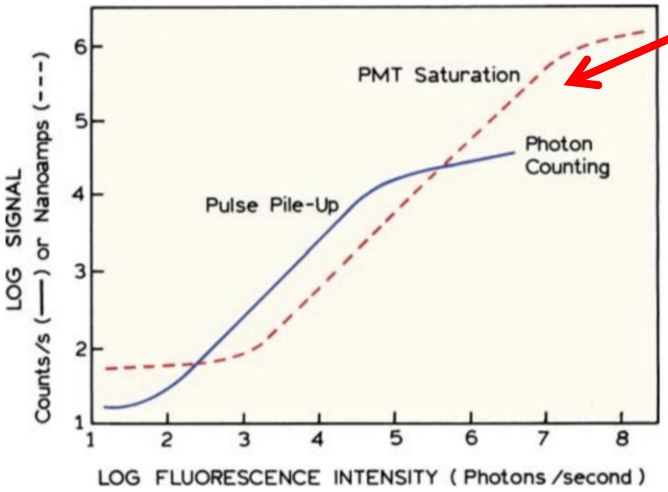


WAVELENGTH
or POLARIZATION
or TIME
or LIGHT INTENSITY



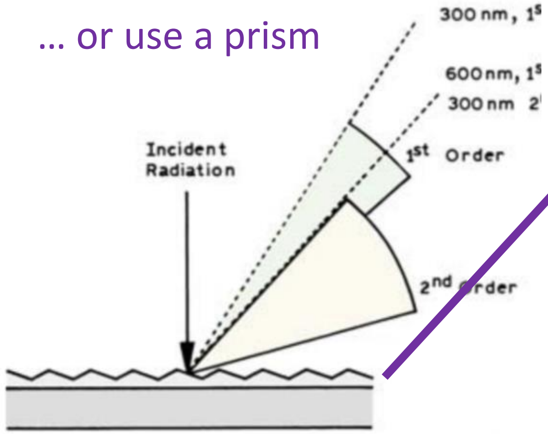
WAVELENGTH
or POLARIZATION
or TIME
or LIGHT INTENSITY





Lakowicz, Chapter 2, Figure 2.36, Page 48

… or use a prism

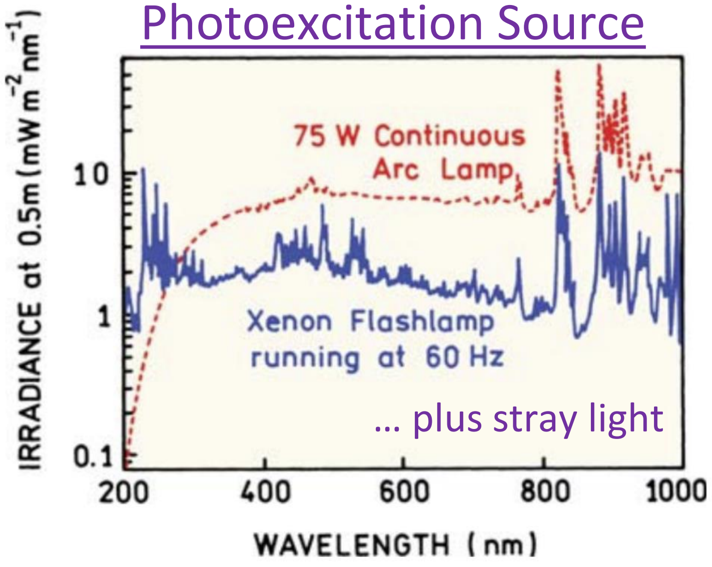


Lakowicz, Chapter 2, Figure 2.16, Page 37

Lakowicz, Chapter 2, Figure 2.1, Page 28

Photoluminescence Spectrometer

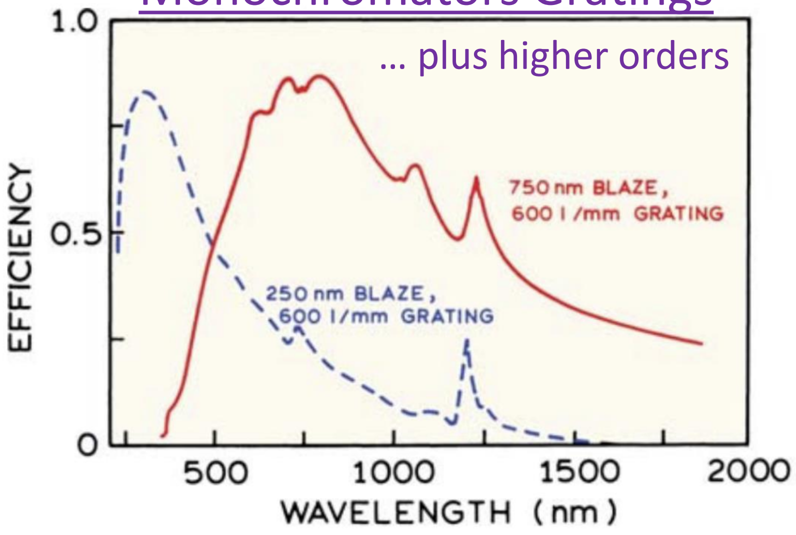
Photoexcitation Source



… plus stray light

Lakowicz, Chapter 2, Figure 2.5, Page 31

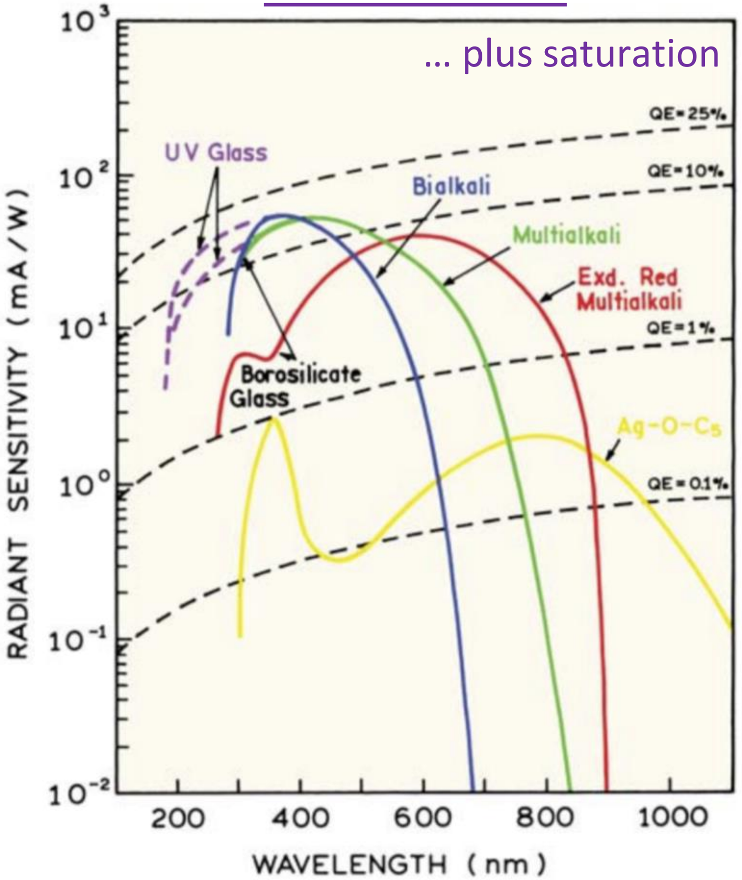
Monochromators Gratings



… plus higher orders

Lakowicz, Chapter 2, Figure 2.12, Page 35

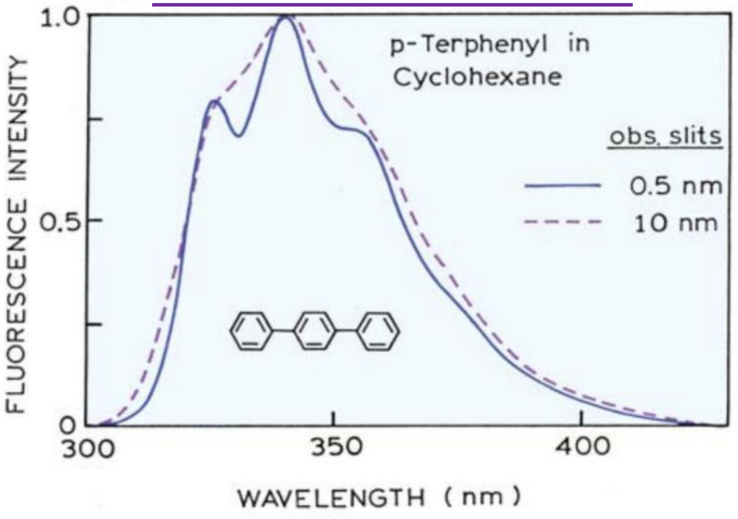
PMT Detector



… plus saturation

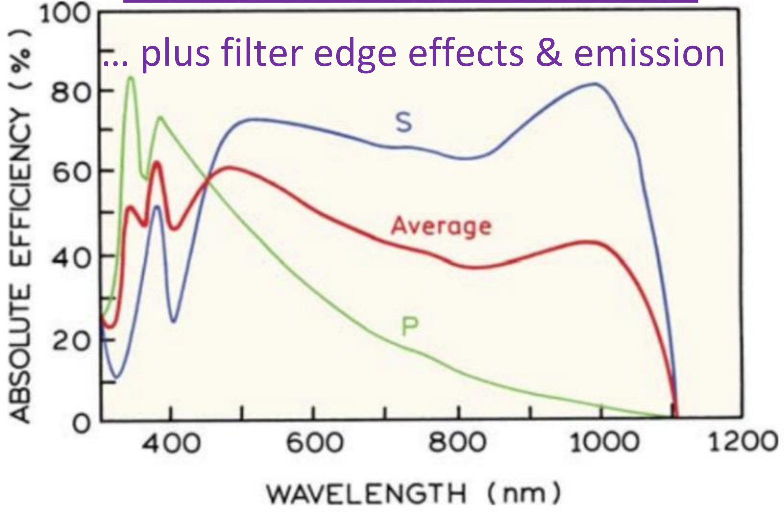
Lakowicz, Chapter 2, Figure 2.31, Page 45

Monochromators Slits



Lakowicz, Chapter 2, Figure 2.13, Page 35

Monochromators Gratings



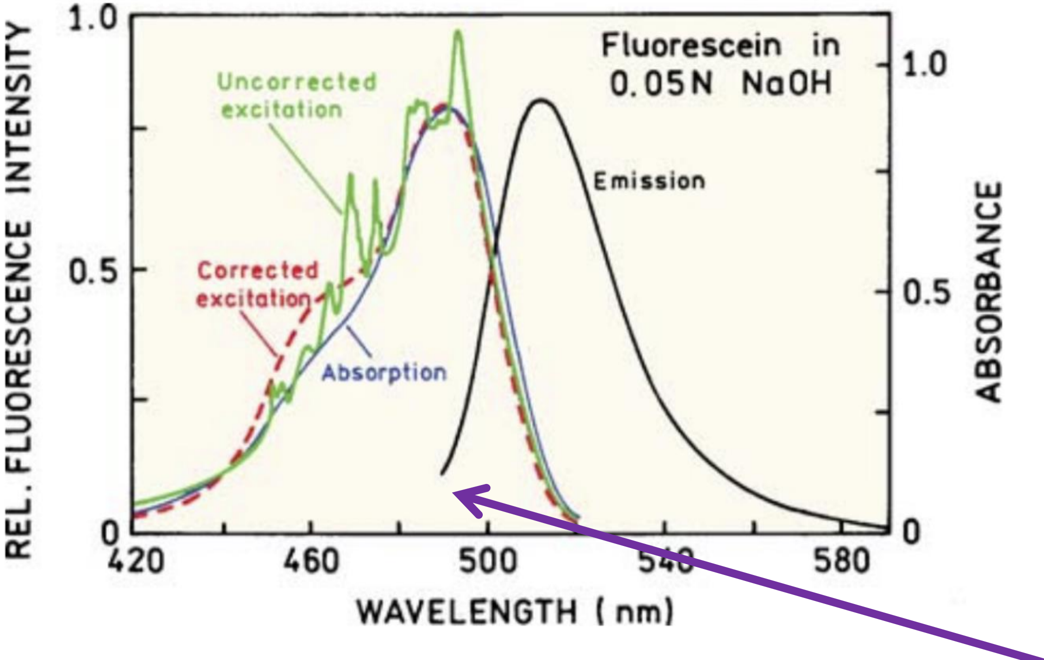
… plus filter edge effects & emission

Lakowicz, Chapter 2, Figure 2.14, Page 36

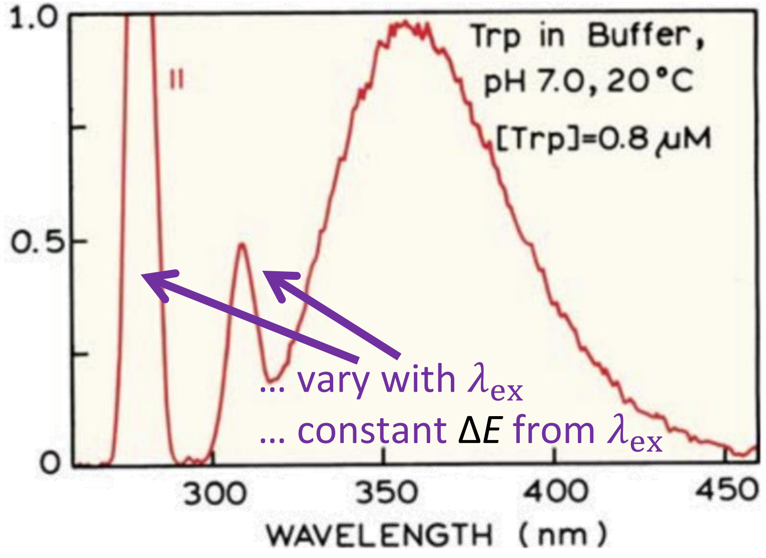
… measured PL spectra are effectively multiplied by all of these!… Ugh!

(BRIEFLY)

Emission & Excitation Spectra



Lakowicz, Chapter 2, Figure 2.6, Page 31

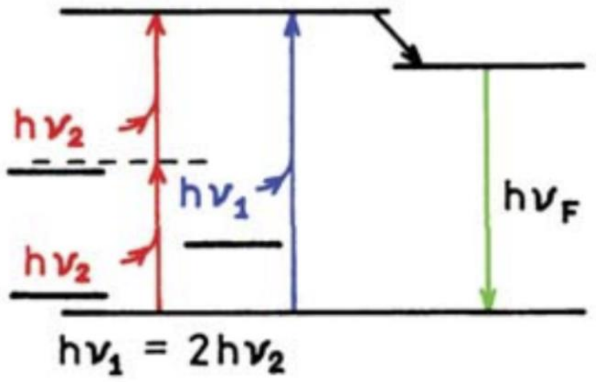


… vary with λ_{ex}

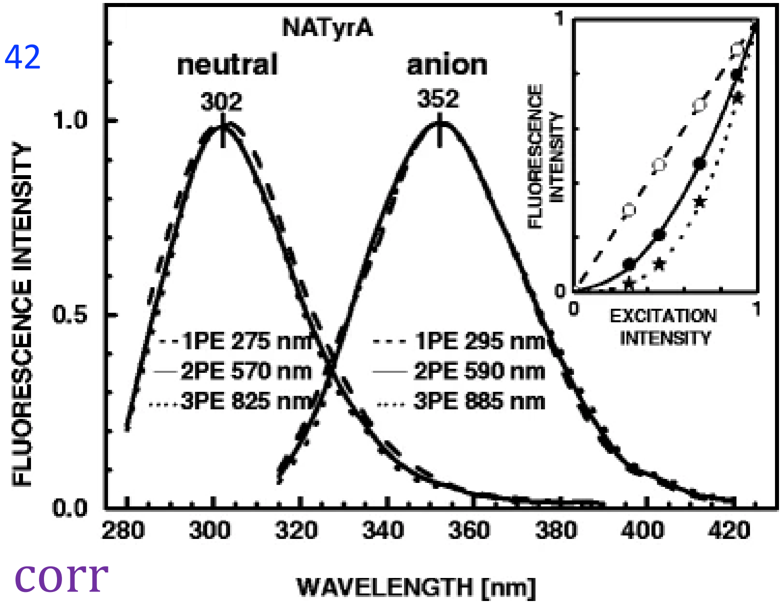
… constant ΔE from λ_{ex}

Lakowicz, Chapter 2, Figure 2.26, Page 42

Multi(*n*)-photon excitation (*n*PE)



Lakowicz, Chapter 1, Figure 1.29, Page 21



B. Kierdaszuk, *J. Fluorescence*, **2013**, *23*, 339–347

… why is emission cut-off?

Photoluminescence intensity (PLI) requires λ-dependent correction factors…

… which differs from absorbance, where division cancels out all these issues

… in this other plot, it is not…

… what causes those peaks?

… Note: $I(\bar{\nu}) = \lambda^2 I(\lambda)$

$$\mathrm{Abs}_\nu = -\log(T_\nu) = \log\left(\frac{I_{\nu,\mathrm{o}}}{I_\nu}\right) = \boldsymbol{\varepsilon}_\nu c\ell$$

$$\mathrm{PLI}_\nu = I_{\nu,\mathrm{o}} \times \mathrm{Abt}_\nu \times \mathrm{QY}_{\mathrm{em}} \times \prod_j \mathrm{corr}$$

Today's Critical Guiding Question

What continuity/conservation laws are most important for photophysical processes like absorption and emission of photons… <u>for real this time, again: Part 5</u>?

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**