



Lecture #12 of 12

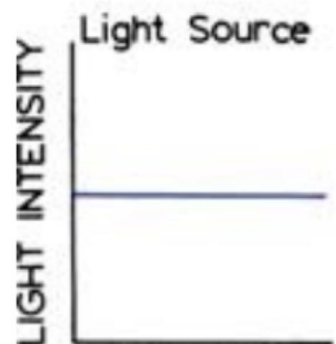
{80 min away from no more lectures... tear}

Prof. Shane Ardo

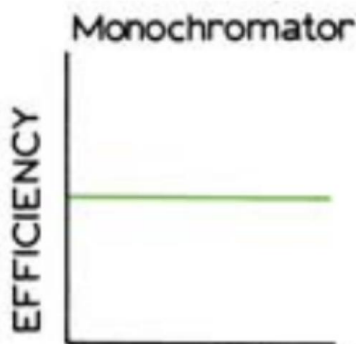
Department of Chemistry

University of California Irvine

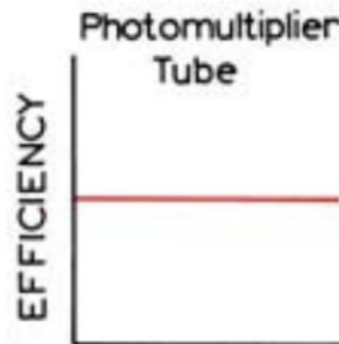
Photoluminescence Spectrometer



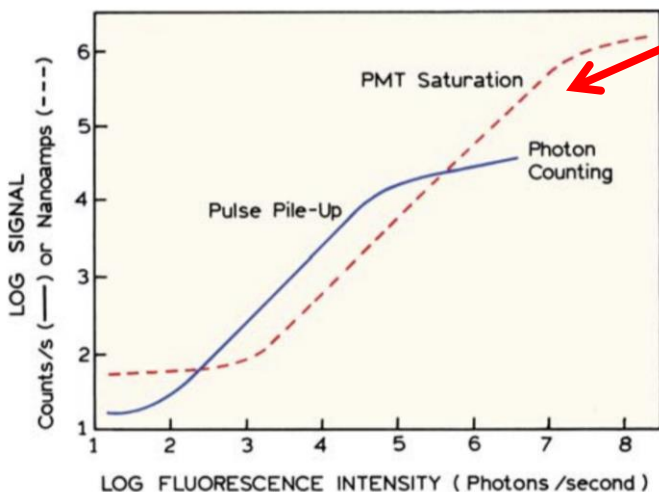
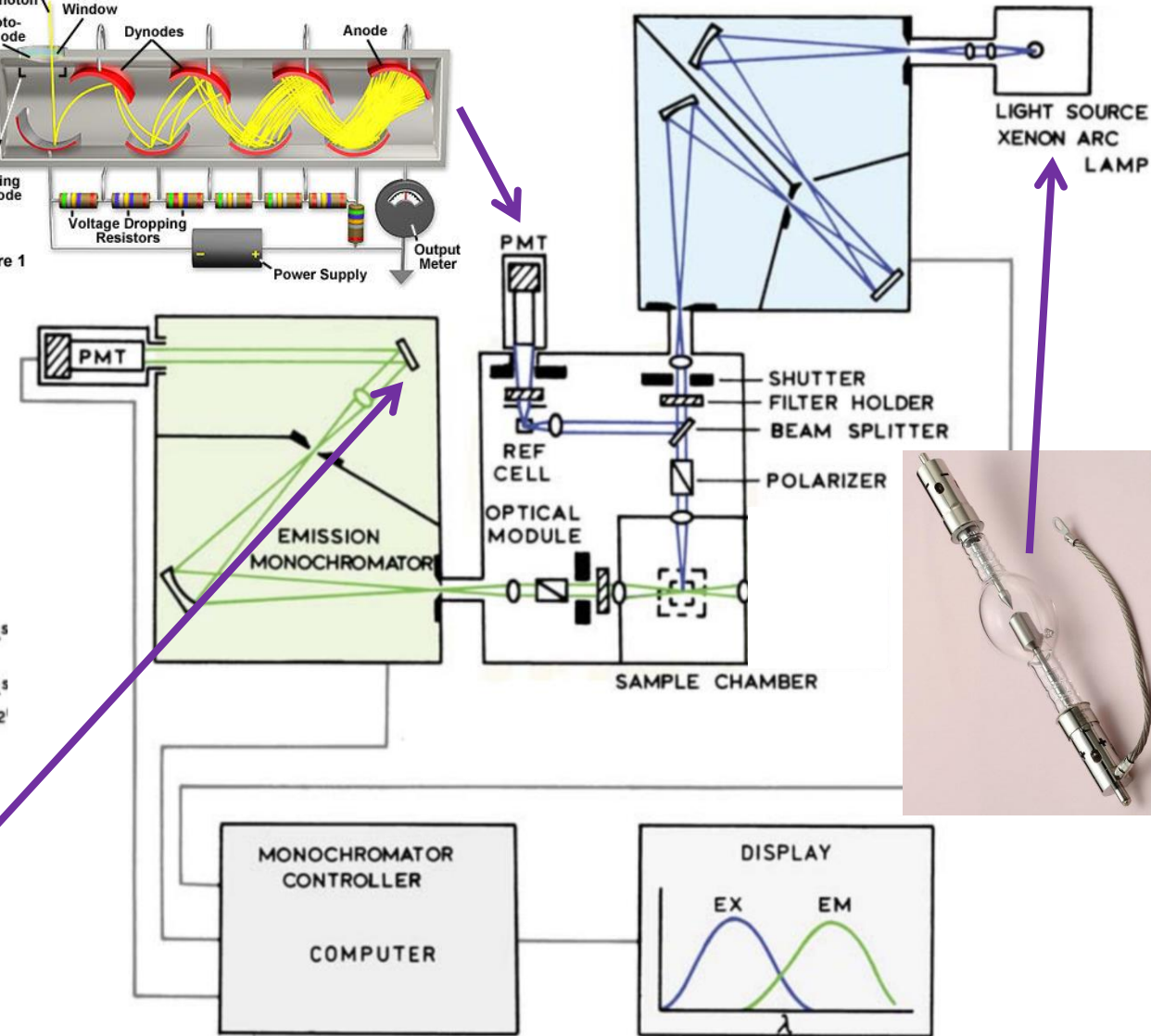
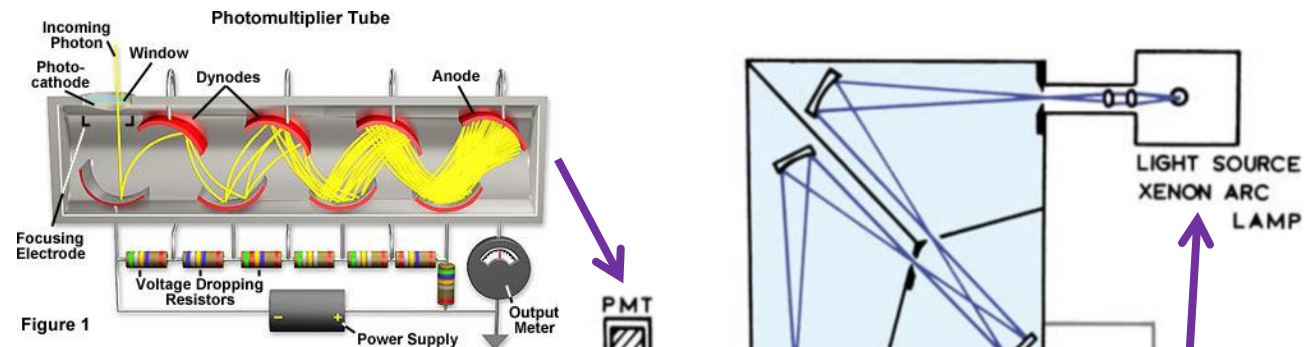
WAVELENGTH
or POLARIZATION
or TIME



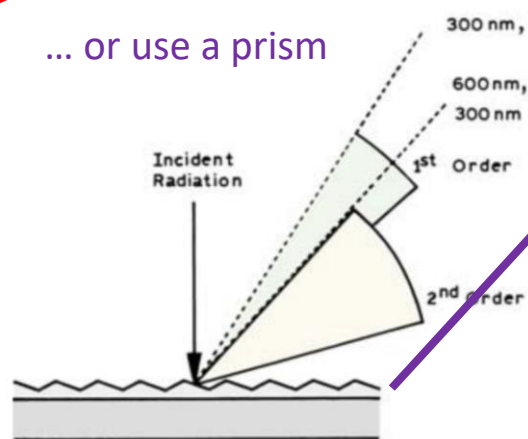
WAVELENGTH
or POLARIZATION
or TIME
or LIGHT INTENSITY



WAVELENGTH
or POLARIZATION
or TIME
or LIGHT INTENSITY



Lakowicz, Chapter 2, Figure 2.36, Page 48

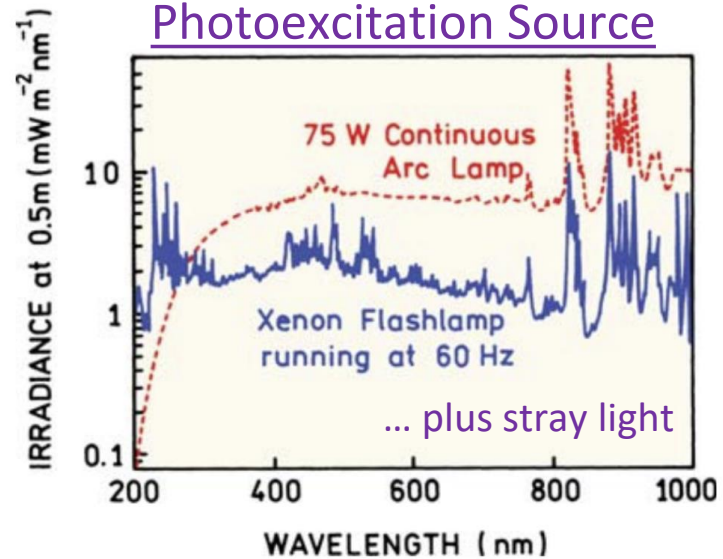


Lakowicz, Chapter 2, Figure 2.16, Page 37

Lakowicz, Chapter 2, Figure 2.1, Page 28

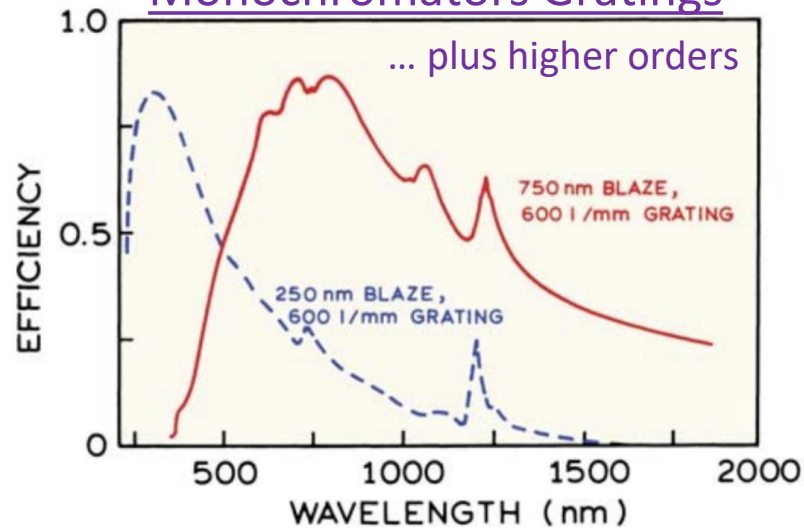
Photoluminescence Spectrometer

Photoexcitation Source



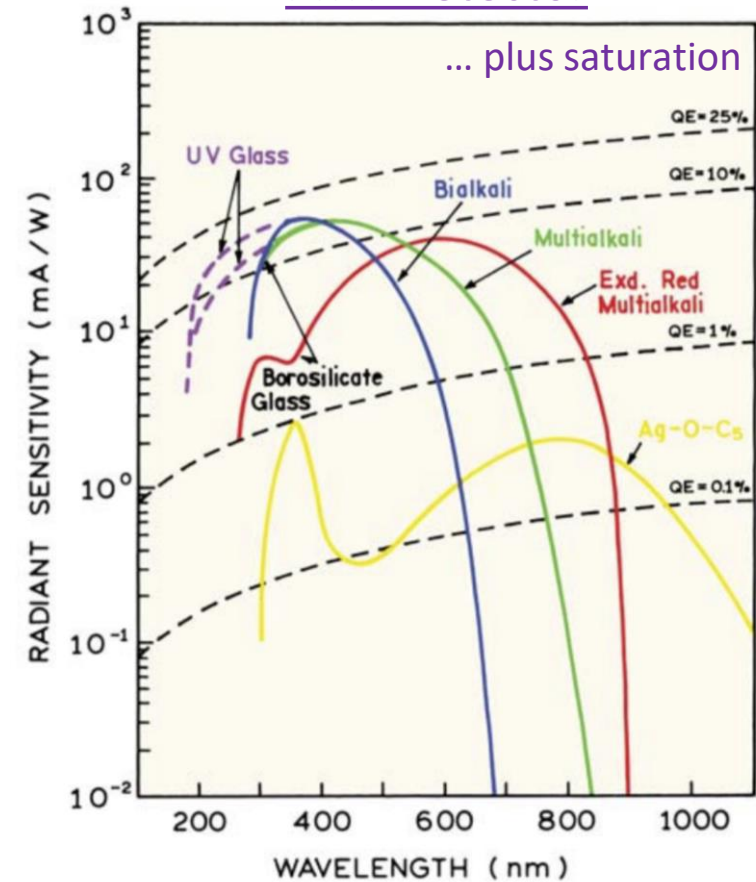
Lakowicz, Chapter 2, Figure 2.5, Page 31

Monochromators Gratings



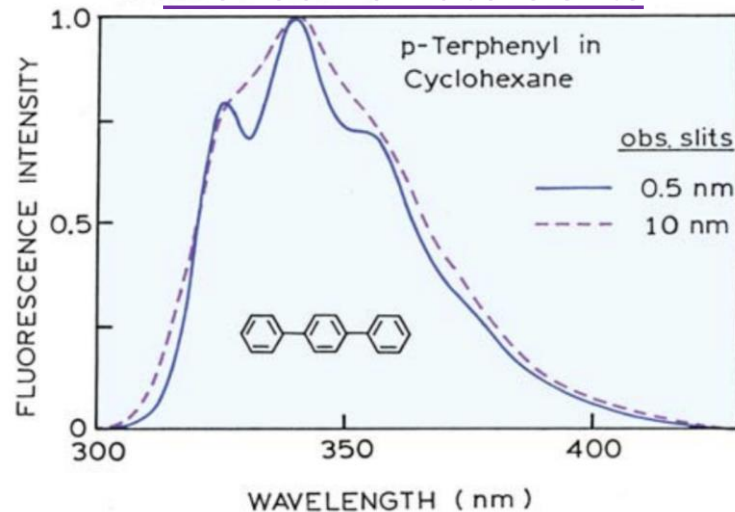
Lakowicz, Chapter 2, Figure 2.12, Page 35

PMT Detector



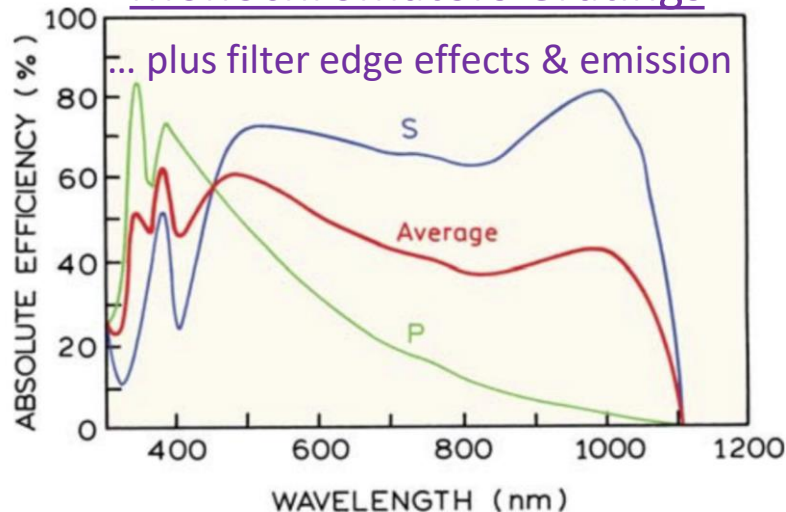
Lakowicz, Chapter 2, Figure 2.31, Page 45

Monochromators Slits



Lakowicz, Chapter 2, Figure 2.13, Page 35

Monochromators Gratings

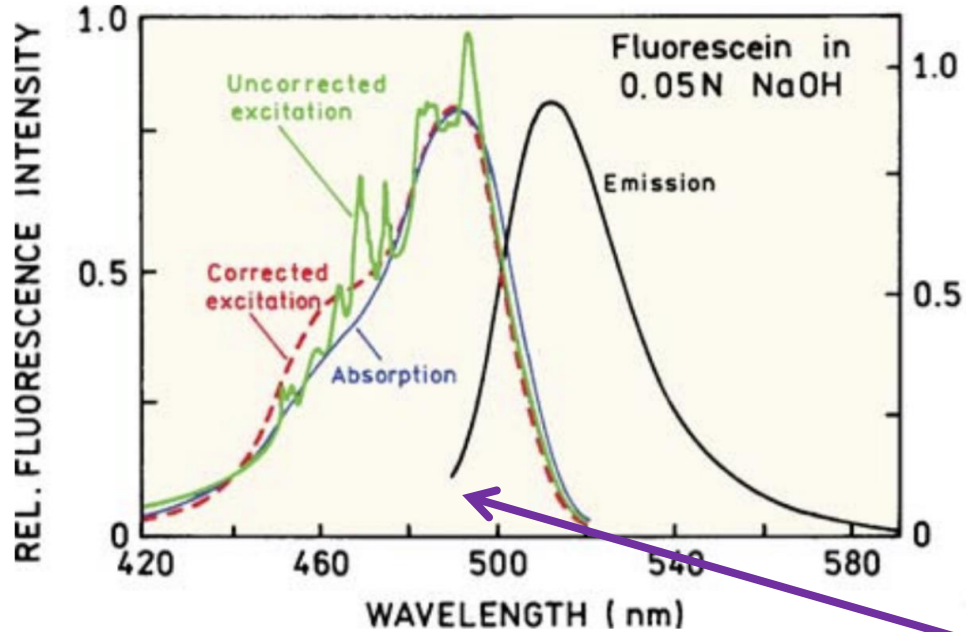


Lakowicz, Chapter 2, Figure 2.14, Page 36

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

Emission & Excitation Spectra

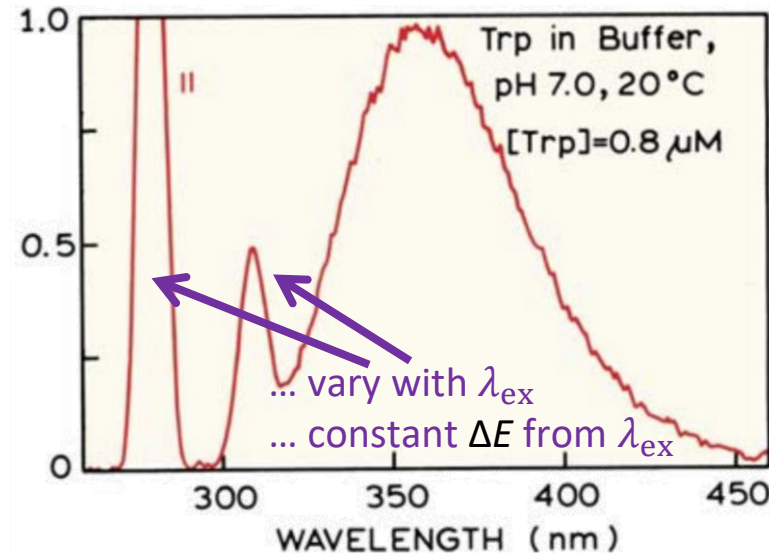
Multi(n)-photon excitation (nPE)



Lakowicz, Chapter 2, Figure 2.6, Page 31

Photoluminescence intensity (PLI) requires λ -dependent correction factors...
 ... which differs from absorbance, where division cancels out all these issues

$$Abs_{\nu} = -\log(T_{\nu}) = \log\left(\frac{I_{\nu,0}}{I_{\nu}}\right) = \epsilon_{\nu} c \ell$$



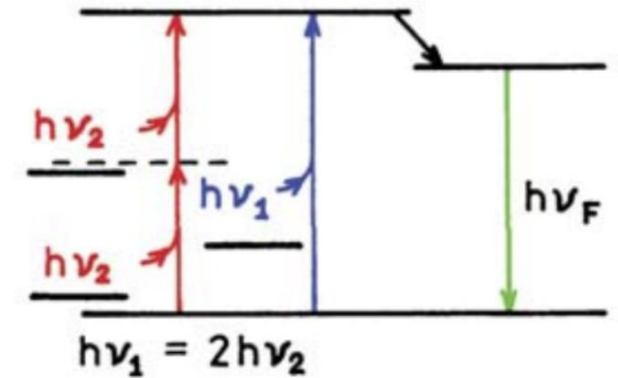
Lakowicz, Chapter 2, Figure 2.26, Page 42

... why is emission cut-off?

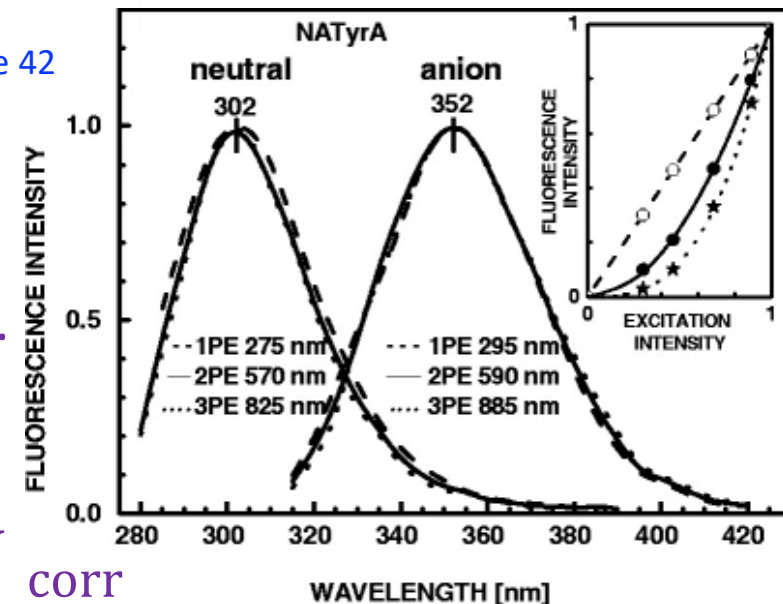
... in this other plot, it is not...

... what causes those peaks?

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



Lakowicz, Chapter 1, Figure 1.29, Page 21



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

$$PLI_{\nu} = I_{\nu,0} \times Abt_{\nu} \times QY_{em} \times \prod_j corr$$

Photon Properties & Conservation Laws

Where does light come from?

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: $p = \frac{h}{\lambda'} = \frac{nh\nu}{c} \approx 0$

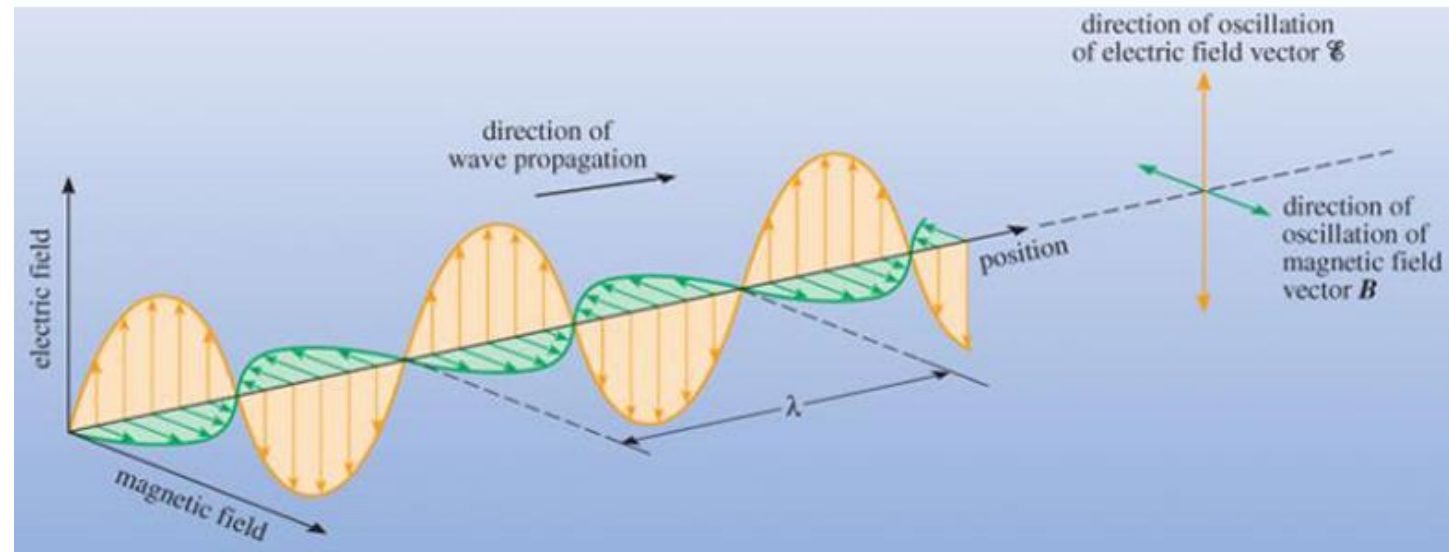
Linear Polarization: \vec{E} and \vec{B}

z-Direction Angular Momentum / Circular Polarization / Chirality / Helicity / Spin: $\pm\hbar = \pm\frac{h}{2\pi}$

Wait... is a light a wave or a particle?

... I mean, is matter a wave or particle?

... I mean, doesn't everything exhibit wave-like and particle-like properties?



With what matter does light interact?

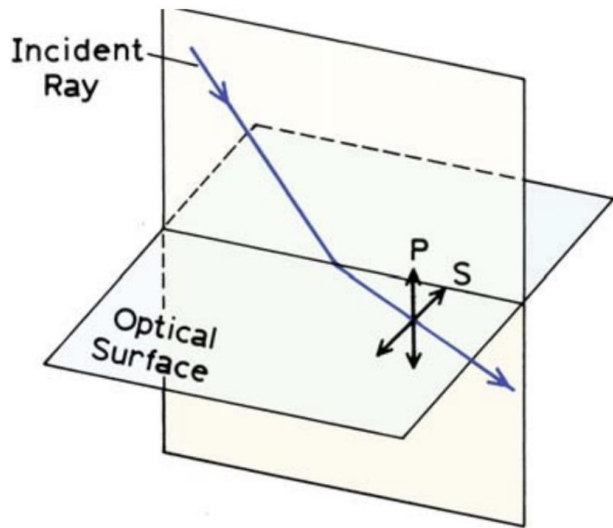
Fermion Angular Momentum (Orbital, Spin)

Magnitude: $\hbar\sqrt{J(J+1)}$

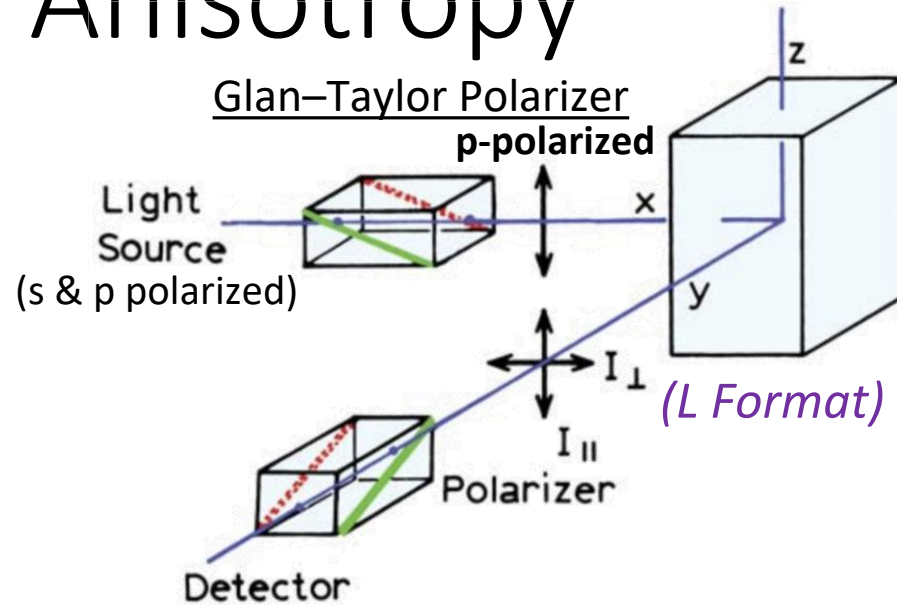
z-Direction: $m_J\hbar$, $m_J = [-J, J]$ in steps of 1

Multiplicity/Degeneracy, $g_J: 2J + 1$

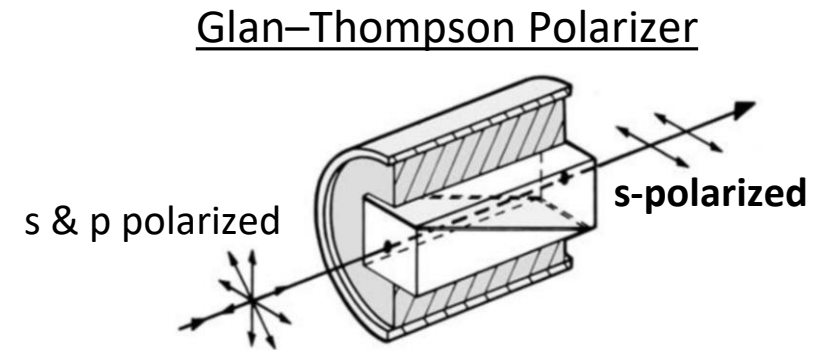
Polarization & Anisotropy



Lakowicz, Chapter 2, Figure 2.39, Page 50



Lakowicz, Chapter 10, Figure 10.1, Page 354



Lakowicz, Chapter 2, Figure 2.41, Page 51

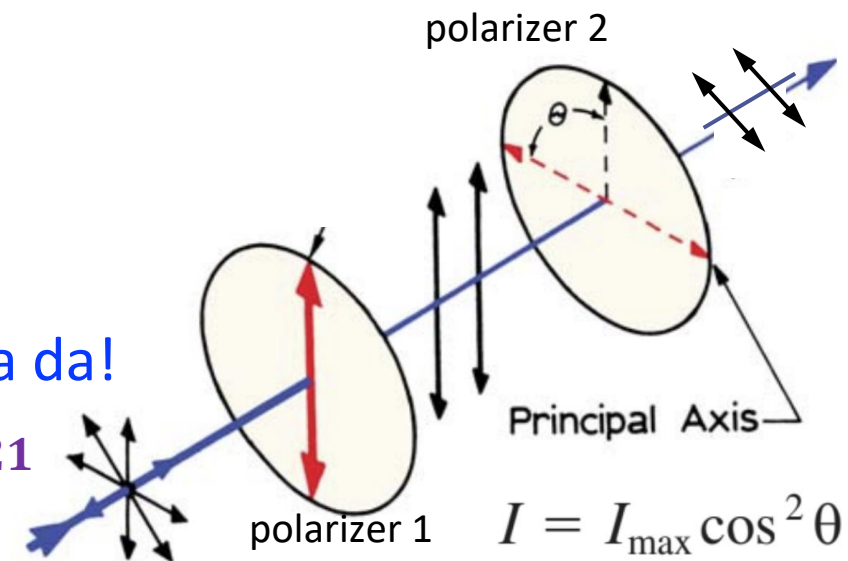
$$r = \frac{I_z - I_y}{I_x + I_y + I_z} = \frac{I_z - I_y}{I_T} = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} = \frac{3\langle \cos^2 \beta \rangle - 1}{2}$$

... anisotropy, r , varies in $[-0.5, +1]$

... 54.7° is called the magic angle... I wonder why? ... $r = 0!$... Ta da!

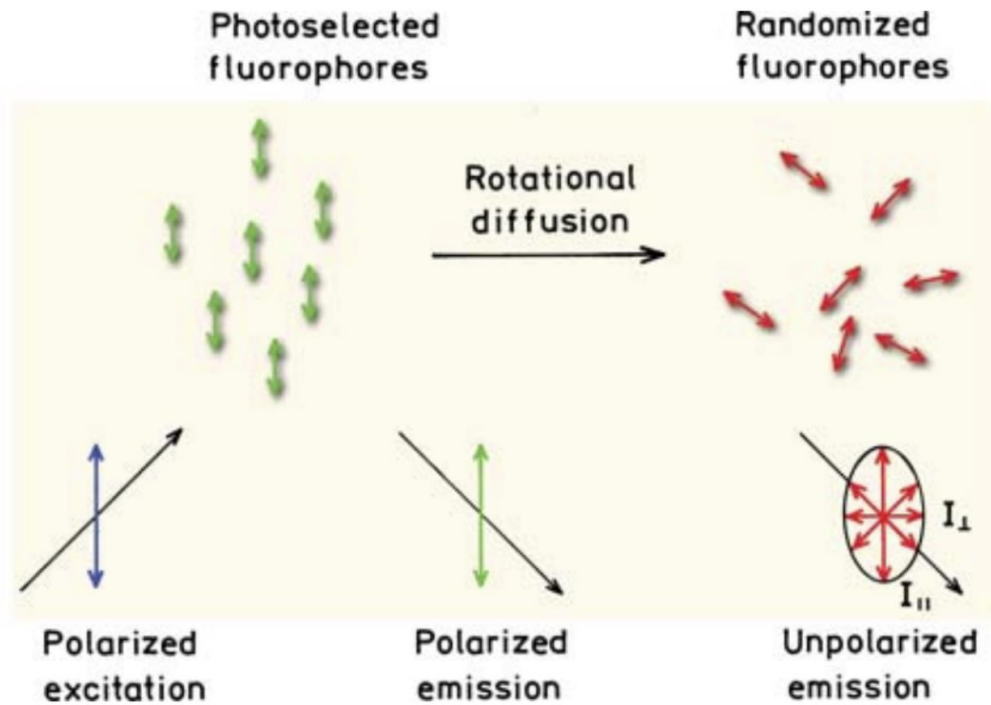
... β is the angle between the absorption μ_{12} and emission μ_{21}

... scattering off of glycerol at -50°C is a good $r = 1$ standard



Lakowicz, Chapter 2, Figure 2.40, Page 50

Polarization & Anisotropy



Lakowicz, Chapter 1, Figure 1.15, Page 13

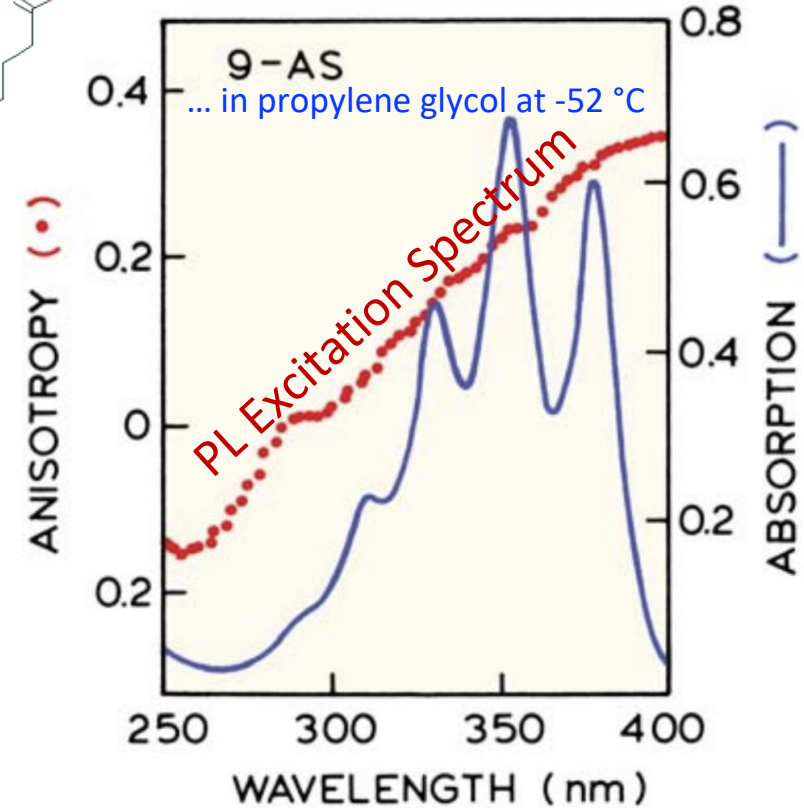
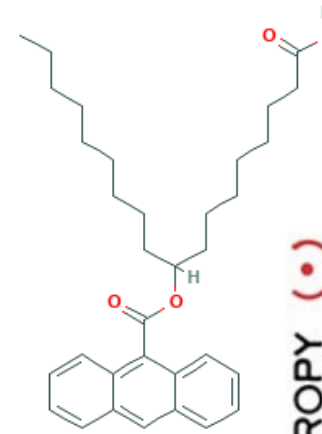
where r_0 is the anisotropy that would be measured in the absence of rotational diffusion, and θ is the rotational correlation time for the diffusion process.

Perrin equation

$$r = \frac{r_0}{1 + (\tau/\theta)}$$

$$r_0 = \frac{2}{5} \left(\frac{3 \cos^2 \beta - 1}{2} \right)$$

... assuming a random orientation of molecules in the dark...
where β is the angle between the absorption and emission transitions.



Lakowicz, Chapter 10, Figure 10.8, Page 360

$$\theta = \frac{\eta V}{RT} \approx 100 \text{ ps at RT}$$

... and because of this...
... r_0 varies in $[-0.2, +0.4]$

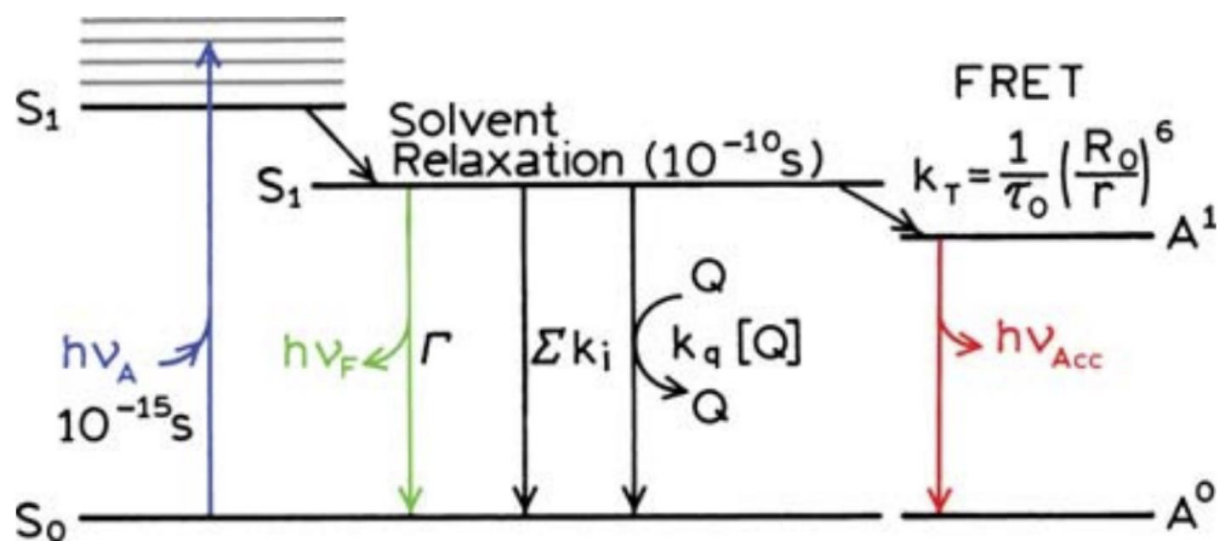
E-S Lifetime & Emission Quantum Yield

Excited-State Lifetime, $\tau_{ES} = \frac{1}{k_r + k_{nr} + \sum_j k_j [Q_j]^{v_j}} = \langle t \rangle = t\left(\frac{100}{e}\right)\%$

$$\phi_{em} = \phi_R \frac{I}{I_R} \frac{Abs_R}{Abs} \frac{n^2}{n_R^2}$$

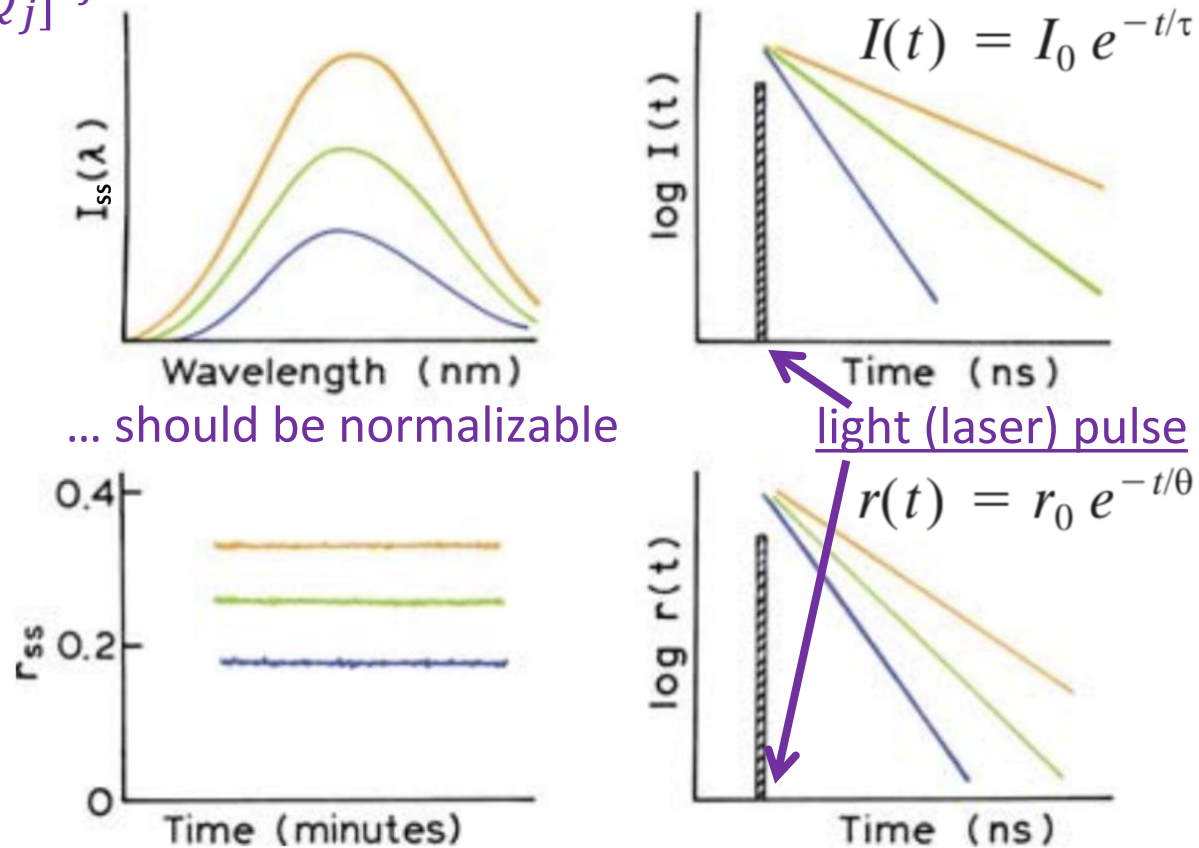
... R is an actinometer

Emission Quantum Yield, $\phi_{em} = \frac{k_r}{k_r + k_{nr} + \sum_j k_j [Q_j]^{v_j}} = k_r \tau_{ES}$



Lakowicz, Chapter 1, Figure 1.14, Page 11

$$I_{SS} = \int_0^{\infty} I_0 e^{-t/\tau} dt = I_0 \tau \quad r_{ss} = \frac{\int_0^{\infty} r(t) I(t) dt}{\int_0^{\infty} I(t) dt}$$



... should be normalizable

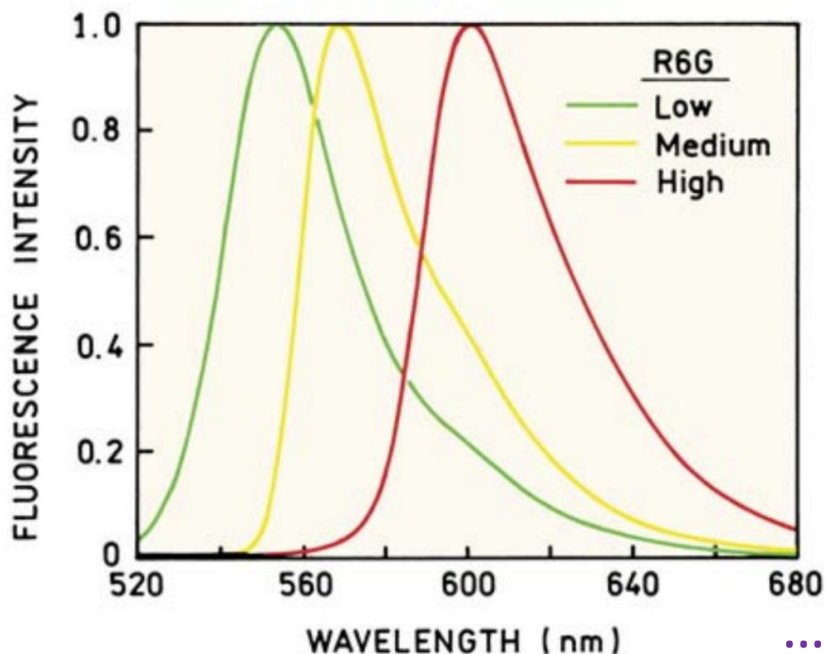
Lakowicz, Chapter 1, Figure 1.17, Page 14

Inner Filter Effects (= Photon Recycling)

... does this also occur in the solid state?... Yep!

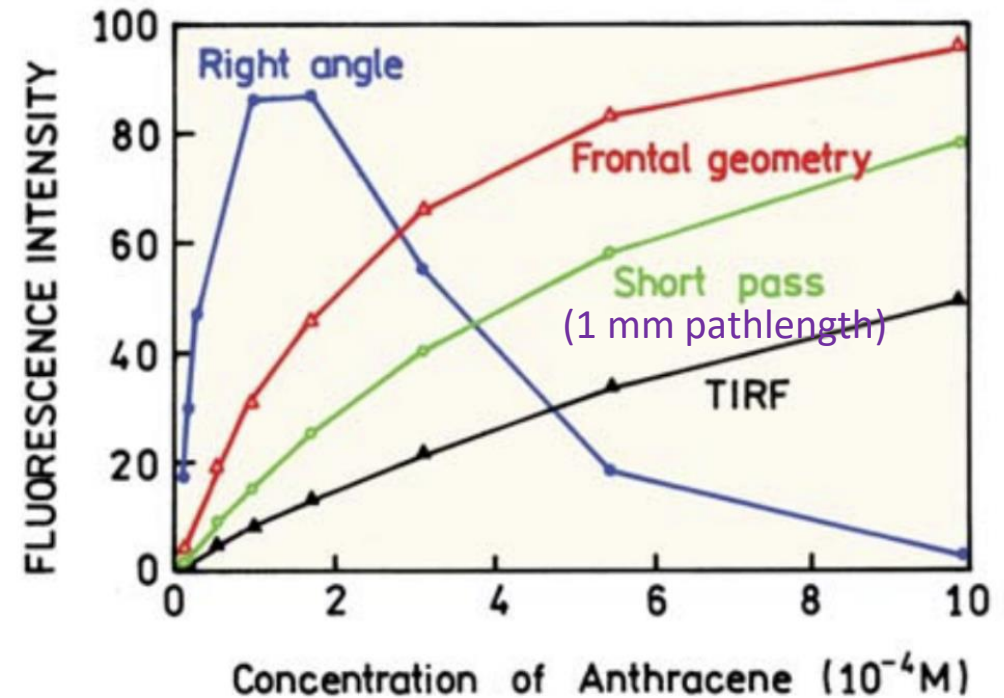
... and not just frozen solutions... but semiconductors?... Yep!

... what is the major observation in this case?... Wait!



Lakowicz, Chapter 2, Figure 2.49, Page 57

So use an optically dilute sample...
 ... how dilute is that?
 ... $A_{\lambda_{ex}} < 0.05!$...
 ... Wow!... That is quite dilute!



Lakowicz, Chapter 2, Figure 2.47, Page 56

... what if this effect was not caused by changing concentration...

... but rather, by changing λ_{ex} ?... it's likely Raman scattering!

Photon Recycling (= Inner Filter Effects)

... does this also occur in the solid state?... Yep!
 ... and not just frozen solutions... but semiconductors?... Yep!
 ... what is the major observation in this case?

... an increase in $\tau_{ES,obs} = \tau_{ES,ext}$... and a decrease in $\phi_{em,ext}$

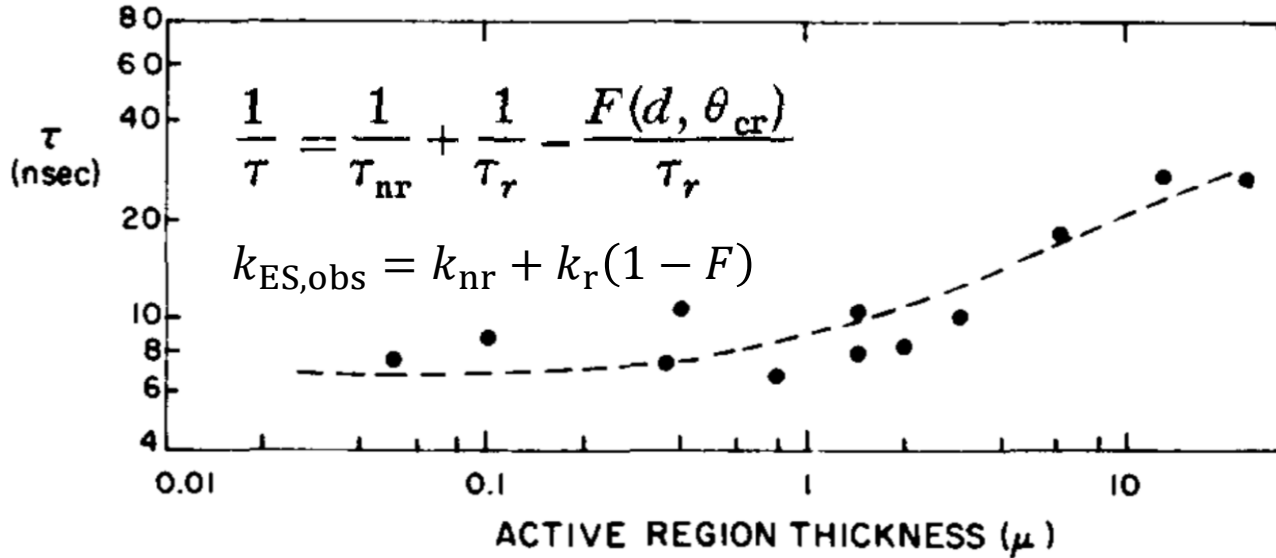


FIG. 2. Recombination lifetime versus active region thickness. The dots represent experimental data from Ref. 2 corresponding to $x = 0.5$; the dashed curve has been obtained theoretically (see text).

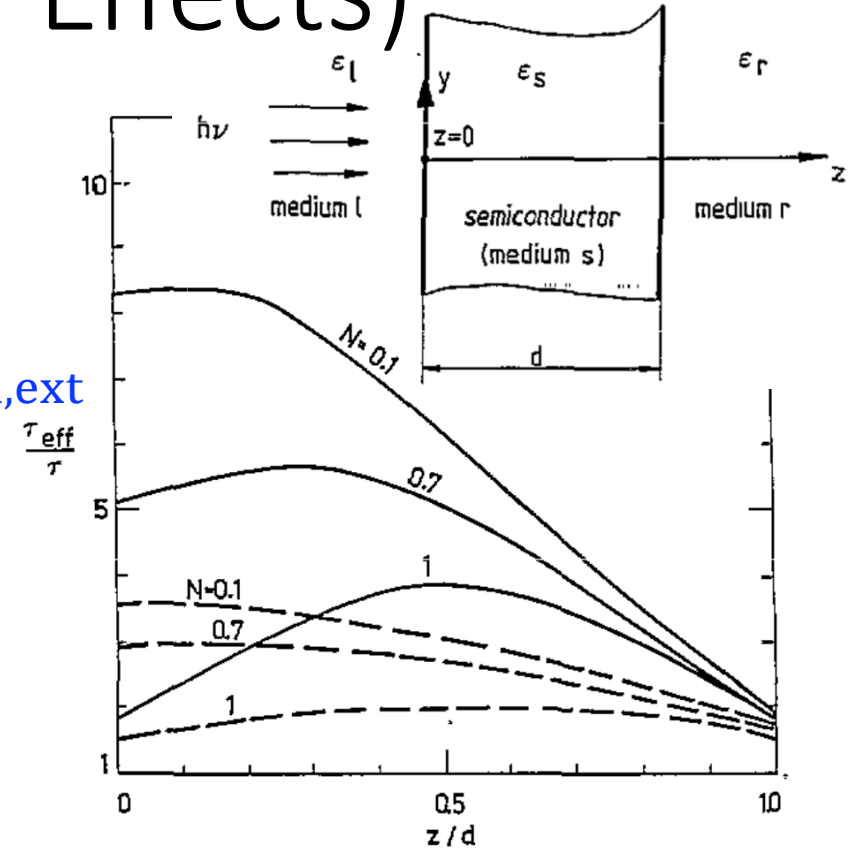


Figure 3. The spatial variation of τ_{eff}/τ calculated from equation (4.17) for different values of the layer thickness d . We considered an ambient temperature of 300 K. Other parameters used: $D_n = 5 \text{ cm}^2 \text{ s}^{-1}$ [18], an overall lifetime $\tau = 7 \text{ ns}$ [11], an average absorption coefficient $\alpha_s = 7000 \text{ cm}^{-1}$ [18], $f = 100 \text{ cm}^{-1}$ [9]. (a) The influence of the relative index of refraction N for the left-hand side of the semiconductor. For the right-hand side $N = 1$ is assumed. Full curves apply for $d = 2 \text{ }\mu\text{m}$ and broken curves for $d = 1 \text{ }\mu\text{m}$.



Photochemistry

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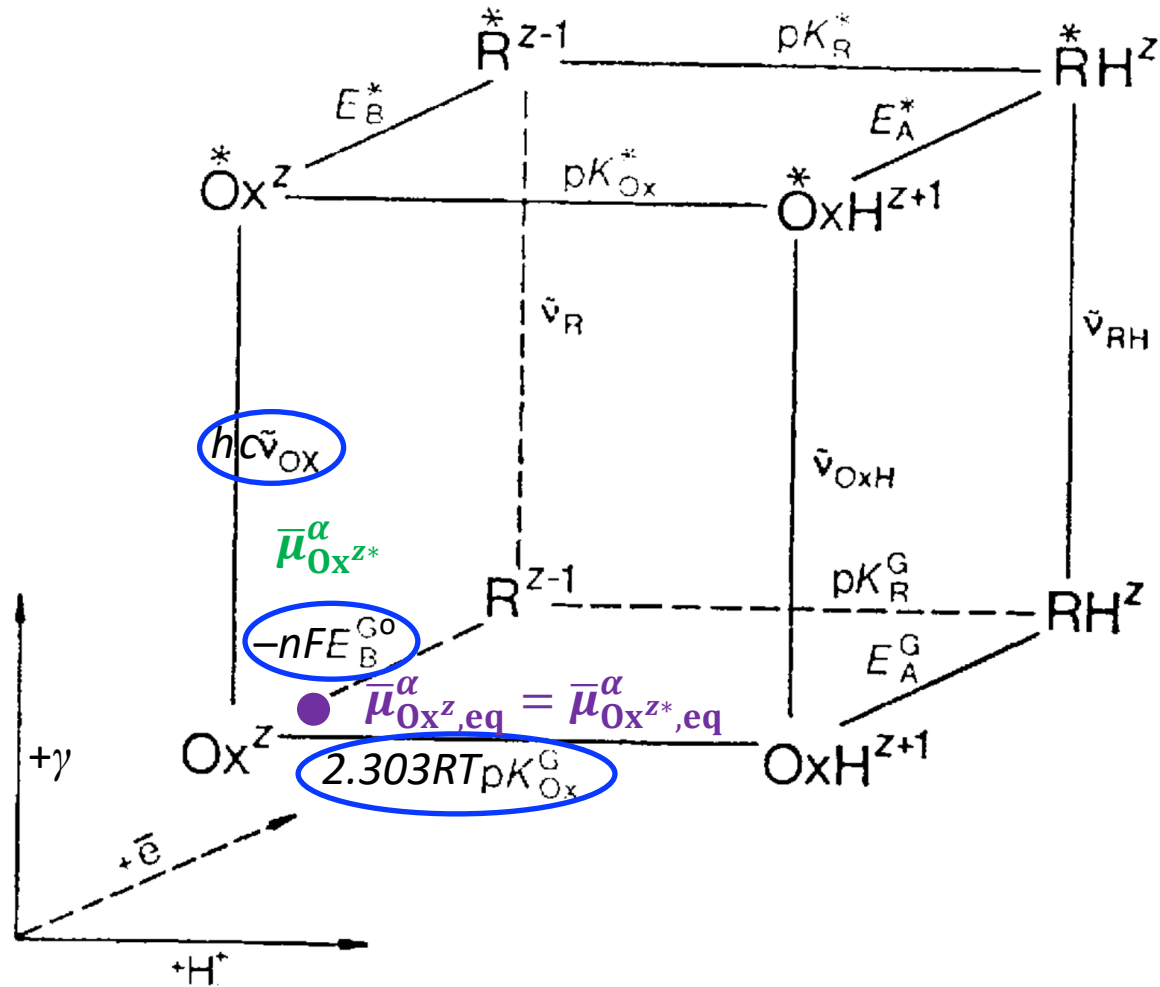
Today's Critical Guiding Question

With knowledge of how to define all rate constants and diffusion coefficients for all continuity/conservation laws that are most important for thermal process and photophysical processes, how can they be used to (i) assess the applicability of Marcus theory for photochemical processes and (ii) predict steady-state photochemical energy conversion efficiencies?

Photochemistry

- **Excited-state electron transfer, Excited-state proton transfer, Förster cycle, Stern–Volmer quenching (Static and Dynamic)**
- **Rehm–Weller equation, Diffusion-limited processes, Electrostatic work terms**
- **Photochemical length scales, Photochemical time scales, Electromagnetic spectrum, Pump–probe transient spectroscopies, General spectroscopic layouts, Neodymium-doped yttrium aluminum garnet (Nd:YAG) laser, Q-switching, Pockels cell, Brewster angle, Titanium-doped sapphire (Ti:sapph) laser, Mode-locking, Delay line**
- **Statistical mechanics distributions, Detailed balance analysis, Photoelectrochemistry, Photoelectrosynthesis, Load line analysis**

Förster Cube and Square Schemes



... all of these free energy terms are **standard-state** free energies (ΔG°)... but what is the actual free energy of the system (ΔG)?

... let's assume that $\Delta G = 0$ (equilibrium)... how could I indicate that on this slide, as a point(s), to depict the majority species present?

... now, how can one **push/pull** this system out of equilibrium?

... recall Le Châtelier's principle... and thus by addition of reactants or removal of products... such as mass or light!

... hopefully this made a little more sense this time around... and if not, **WE ARE (NEARLY) OUT OF TIME!**

Jablonski Diagram

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 (E-S)

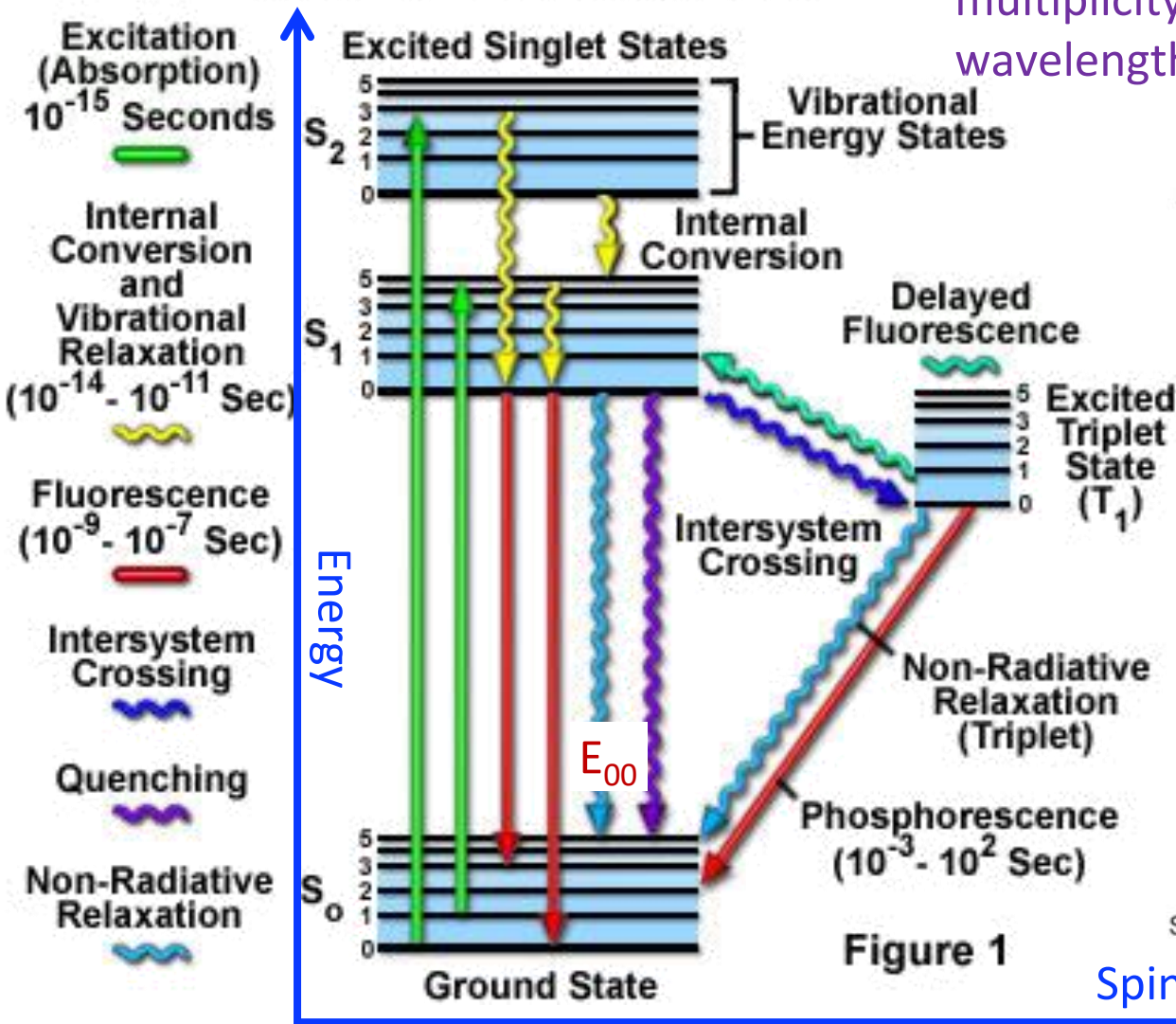
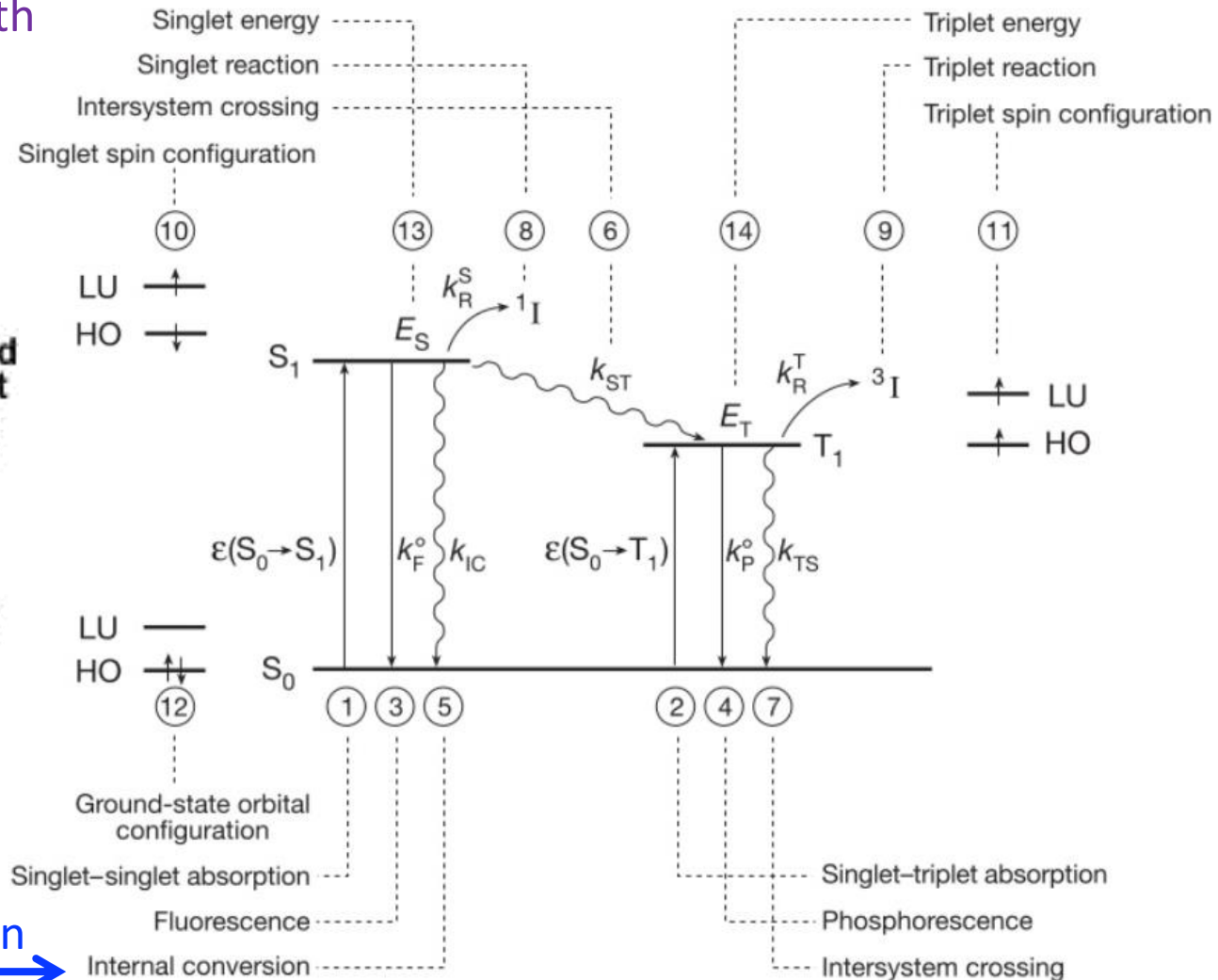


Figure 1

Spin



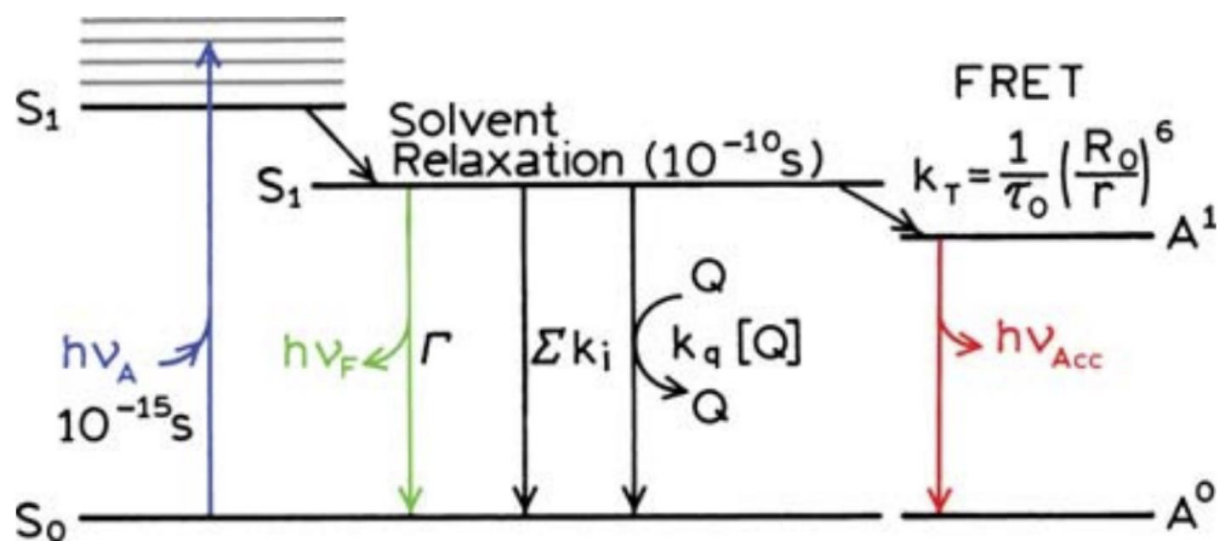
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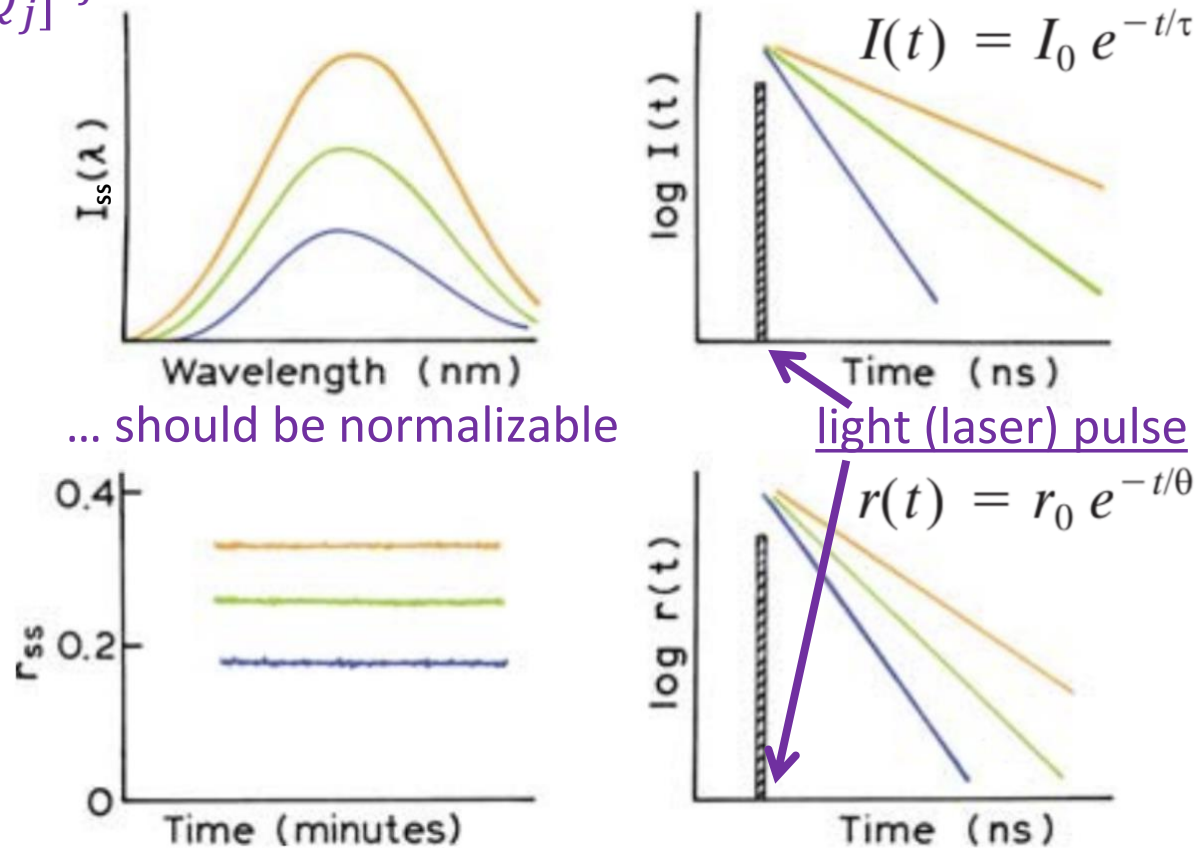
... R is an actinometer

Emission Quantum Yield, $\phi_{em} = \frac{k_r}{k_r + k_{nr} + \sum_j k_j [Q_j]^{v_j}} = k_r \tau_{ES}$



Lakowicz, Chapter 1, Figure 1.14, Page 11

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... should be normalizable

Lakowicz, Chapter 1, Figure 1.17, Page 14

Excited-State Electron Transfer vs Proton Transfer

Thermodynamics (ΔG_{AB}^0) dictates kinetics (ΔG_{AB}^\ddagger)...

Förster Cycle Analysis (FCA)

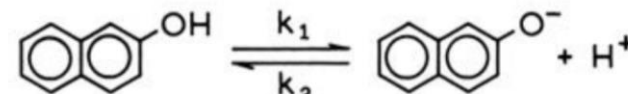
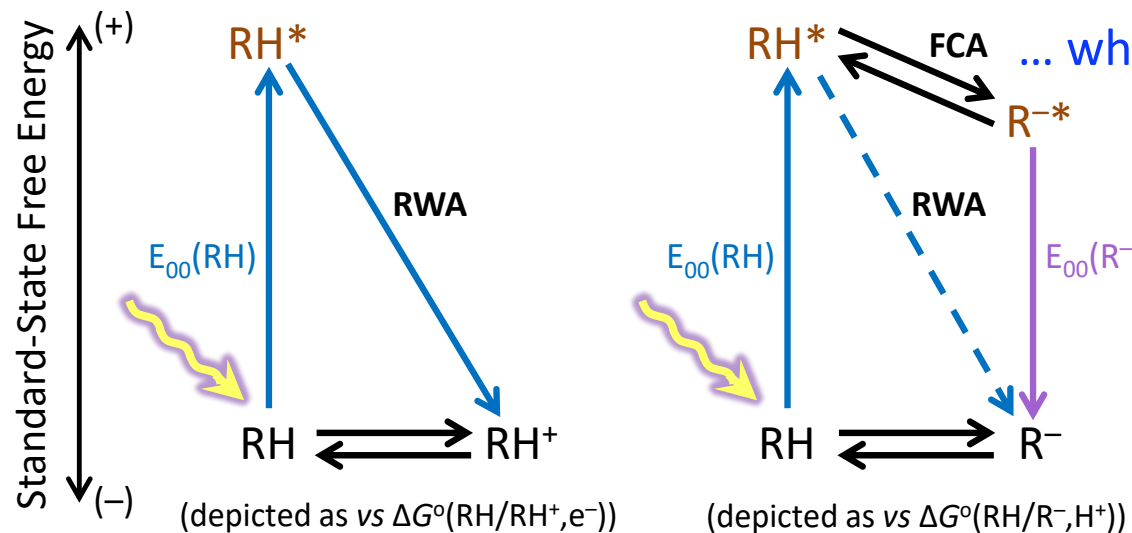
$$\Delta pK_a = pK_a^* - pK_a \approx \frac{E_{00,RH} - E_{00,R^-}}{(\ln 10)RT}$$

... where K_a is an equilibrium acidity constant

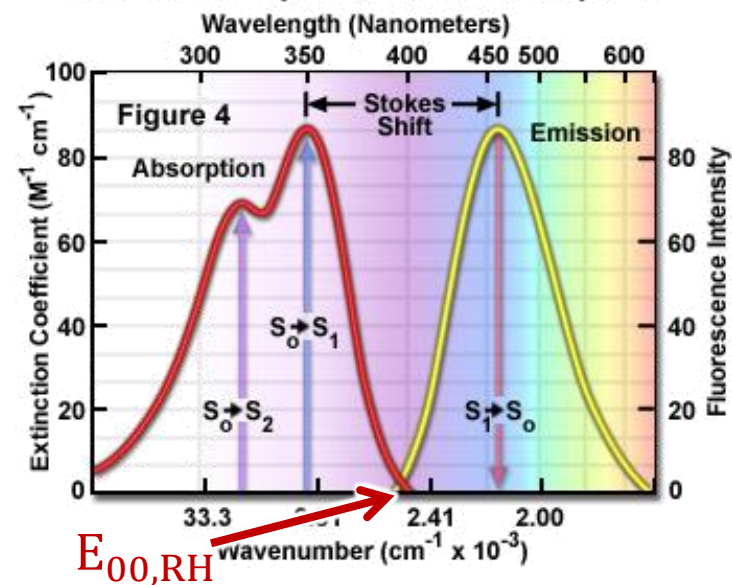
Rehm–Weller Analysis (RWA)

$$\Delta E = E^{0,*} - E^0 \approx -E_{00,RH}/nF$$

... where E is a standard reduction potential

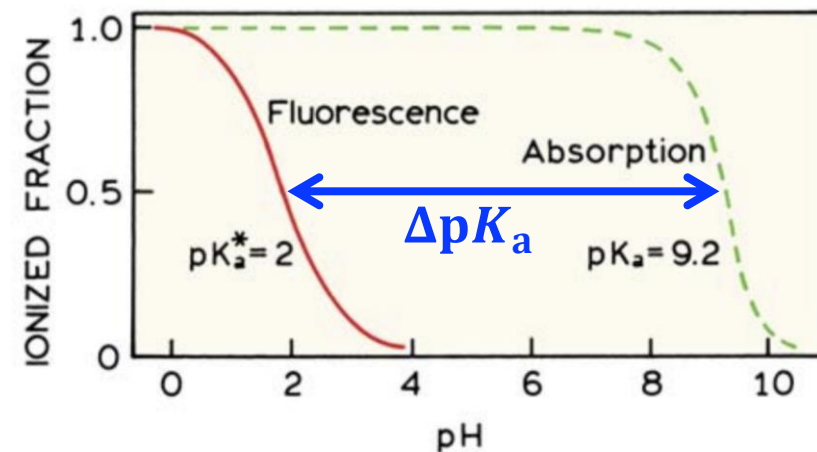


Quinine Absorption and Emission Spectra



... thank you Marcus, Hush, Taube, Gerischer, Closs, Miller, Creutz, Chidsey, et al.!

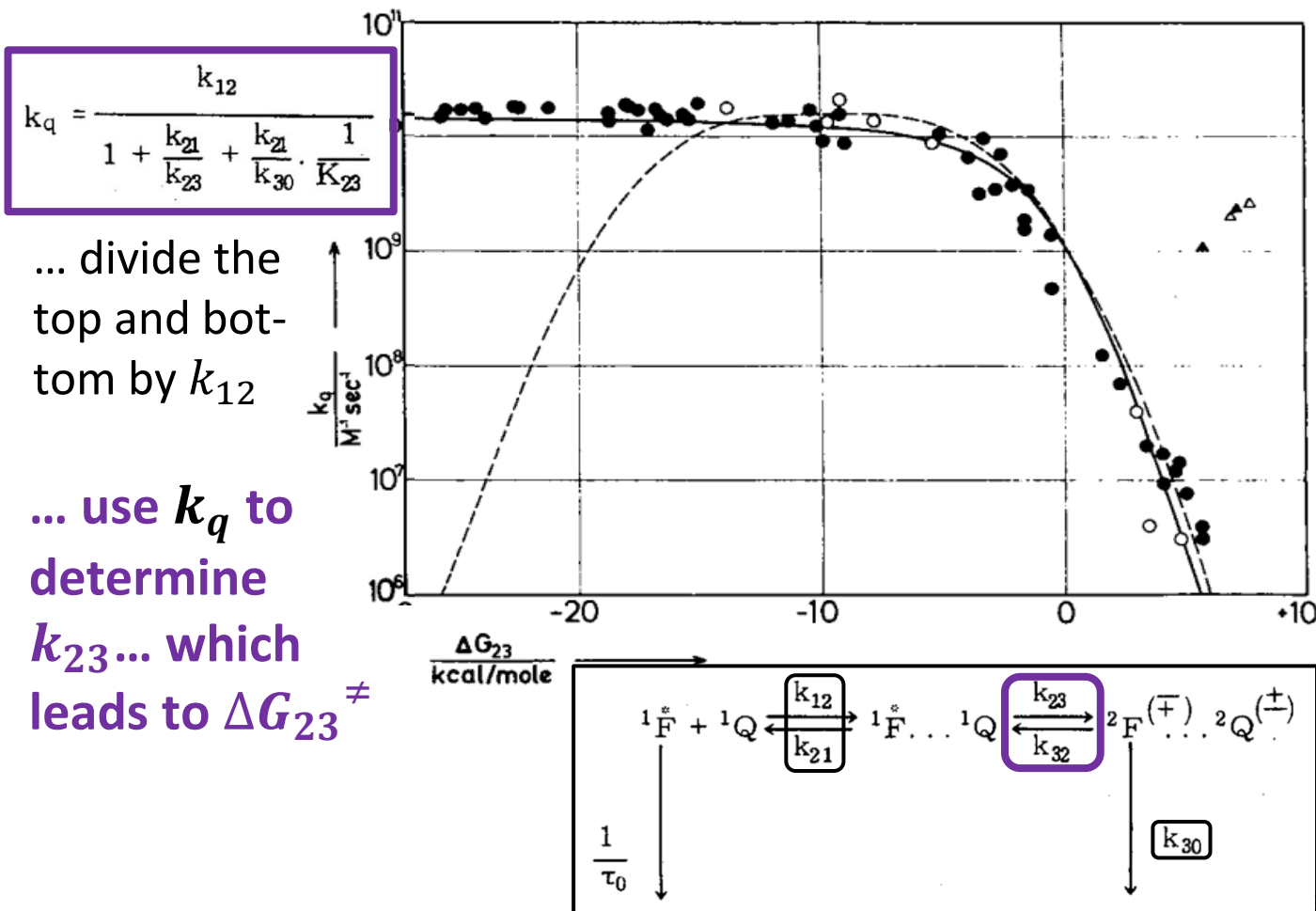
... conversion of ΔE_{obs} or $\Delta pK_{a,obs}$ to accurate ΔG_{AB}^0 can be complex...



Rehm–Weller Equation

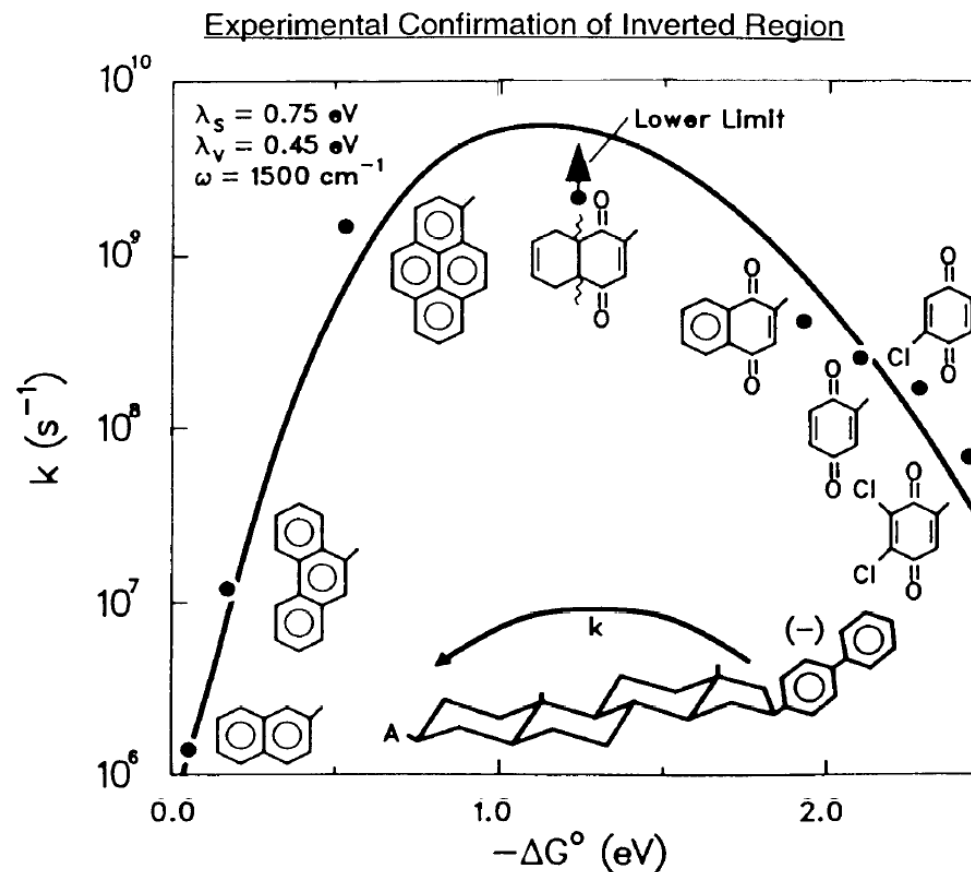
Rehm–Weller (1970)

No observation of inverted region



Closs–Miller (1984)

observation of inverted region



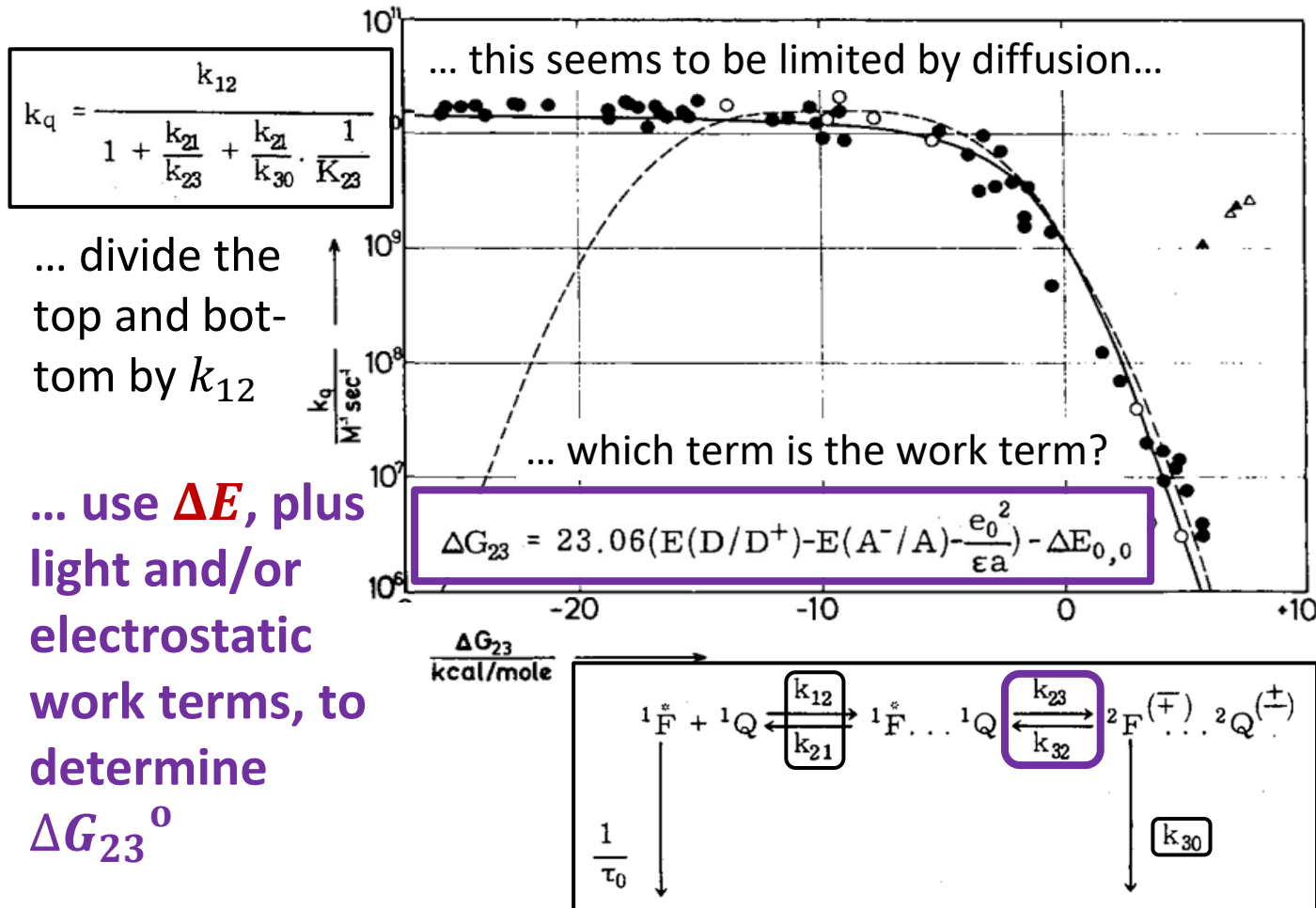
Scaterra, J. R. Miller & G. L. Closs, *J. Am. Chem. Soc.*, **1984**, *106*, 3047–3049

G. L. Closs & J. R. Miller, *Science*, **1988**, *240*, 440–447

Diffusion-Limited Processes & Work Terms

Rehm–Weller (1970)

No observation of inverted region



The collisional frequency (Z) of a fluorophore with a quencher is given by

$$Z = k_0[Q] \quad (8.10)$$

where k_0 is the diffusion-controlled bimolecular rate constant. This constant may be calculated using the Smoluchowski equation:

$$k_0 = 4\pi RDN/1000 = \frac{4\pi N}{1000}(R_f + R_q)(D_f + D_q) \quad (8.11)$$

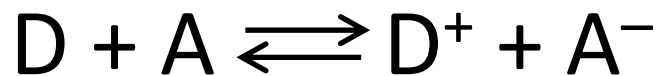
where R is the collision radius, D is the sum of the diffusion coefficients of the fluorophore (D_f) and quencher (D_q), and N is Avogadro's number. The collision radius is generally assumed to be the sum of the molecular radii of the fluorophore (R_f) and quencher (R_q).

obtained from the Stokes-Einstein equation:

$$D = kT/6\pi\eta R \quad (8.13)$$

where k is Boltzmann's constant, η is the solvent viscosity, and R is the molecular radius.

Rate-Determining Step (RDS)



Poisson's Equation (from Gauss's law)

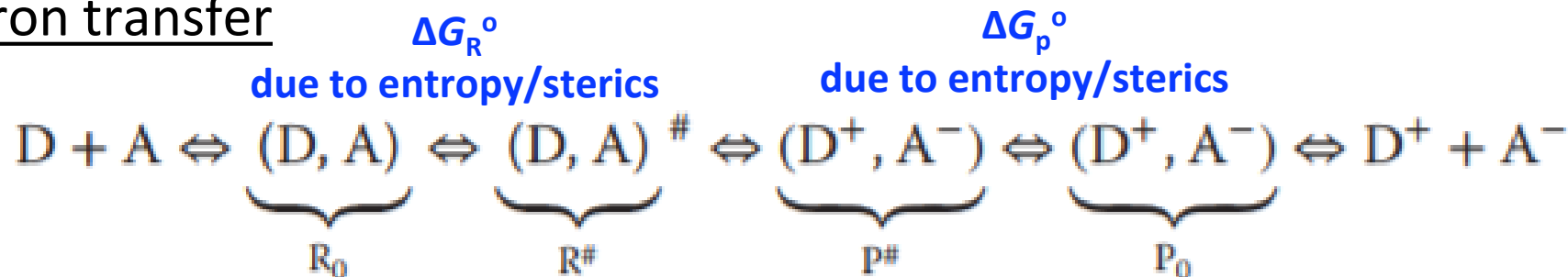
$$\frac{\partial^2 \phi(x)}{\partial x^2} = -\frac{\rho}{\epsilon} \quad E = -\frac{\partial \phi(x)}{\partial x}$$

$$\phi(r) = \frac{q}{4\pi\epsilon r}$$

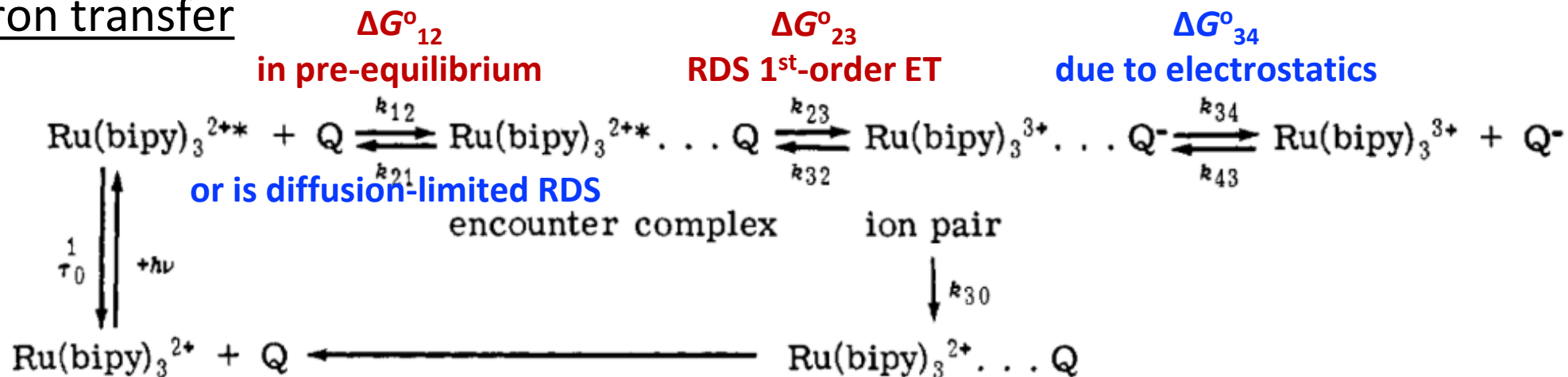
But wait... is this the elementary reaction step for electron transfer between a (D)onor and an (A)cceptor in solution?

Nope!

Ground-state electron transfer



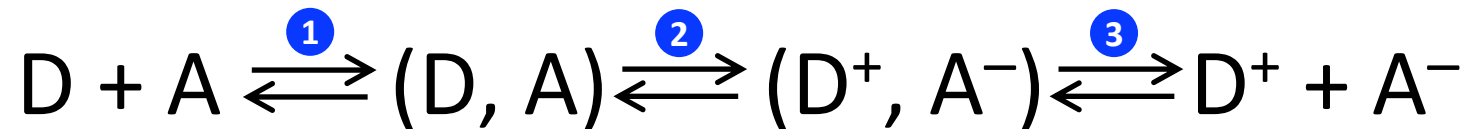
Excited-state electron transfer



RDS: Pre-Equilibrium Approximation

... seemingly totally unrelated... how does one determine the **observed** resistance of 3 resistors in parallel, or 3 capacitors in series? ... it's approximately equal to the smaller one... okay...

but mathematically, add their reciprocals... and reciprocate



... so how does one determine the **observed** rate constant for 3 reactions **in series**?

... it's the same general idea... $\frac{1}{k_{f,obs}} = \frac{1}{k_{1f}} + \frac{1}{k'_{2f}} + \frac{1}{k'_{3f}}$... where $\frac{\partial[D]}{\partial t} = \frac{\partial[A]}{\partial t} = -k_{f,obs}[D][A]$

... except that Step 2 is preceded by Step 1... and Step 3 is preceded by Steps 1 and 2

... and only one of those Steps will dominate the observed rate when it is the slowest step

... so the (pre)ceding steps must be much faster... thus assume they are in equilibrium...

$$\frac{1}{k_{f,obs}} = \frac{1}{k_{1f}} + \frac{1}{K_1 k_{2f}} + \frac{1}{K_1 K_2 k_{3f}} = \frac{1}{k_{1f}} + \frac{k_{1b}}{k_{1f} k_{2f}} + \frac{k_{1b} k_{2b}}{k_{1f} k_{2f} k_{3f}}$$

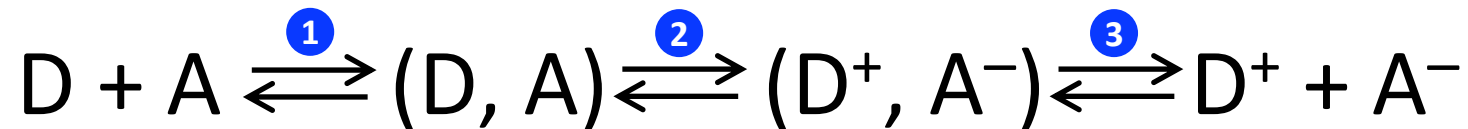
... and for completion, what if 3 (same-order) reactions occur simultaneously, i.e. **in parallel**?

... it's as easy as it seems... $k_{f,obs} = k_{1f} + k_{2f} + k_{3f} = \frac{1}{\tau_{1f}} + \frac{1}{\tau_{2f}} + \frac{1}{\tau_{3f}} = \frac{1}{\tau_{f,obs}}$

RDS: Steady-State Approximation

... but what if we want to determine $\frac{\partial[D^+]}{\partial t} = \frac{\partial[A^-]}{\partial t}$... and some preceding steps are fast?

... when all are fast, **except Step 1**, won't $k_{f,obs} = k_{1f}$ then?... not always...



Assume that the middle steps come and go quickly... so each has a small steady-state conc...

$$\frac{\partial[(D,A)]}{\partial t} = 0 = -k_{2f}[(D,A)] + k_{1f}[D][A] \dots \text{and thus } [(D,A)] = \frac{k_{1f}[D][A]}{k_{2f}}$$

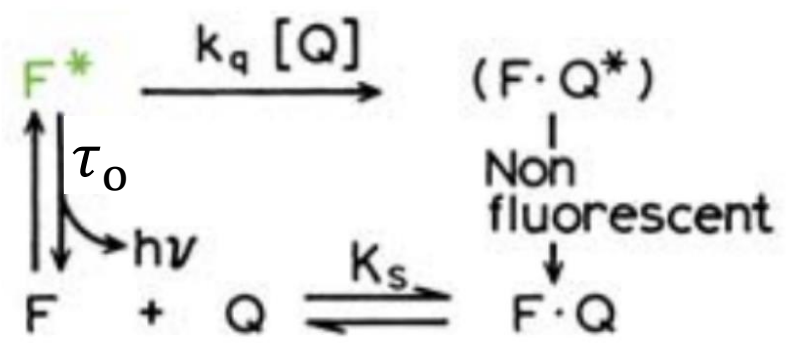
$$\frac{\partial[(D^+,A^-)]}{\partial t} = 0 = -k_{3f}[(D^+,A^-)] + k_{2f}[(D,A)] \dots \text{and thus } [(D^+,A^-)] = \frac{k_{2f}[(D,A)]}{k_{3f}}$$

$$\dots \text{which means that } [(D^+,A^-)] = \frac{k_{1f}k_{2f}[D][A]}{k_{2f}k_{3f}} = \frac{k_{1f}[D][A]}{k_{3f}}$$

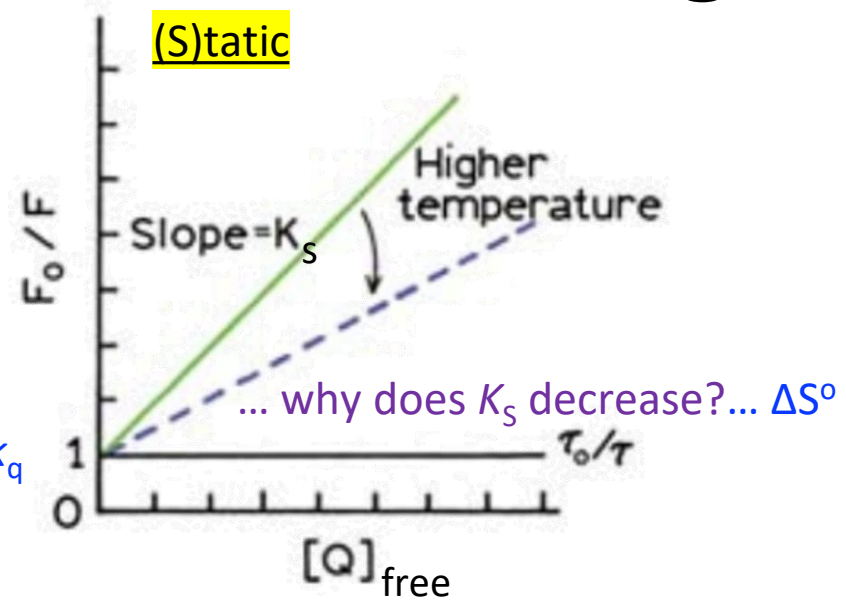
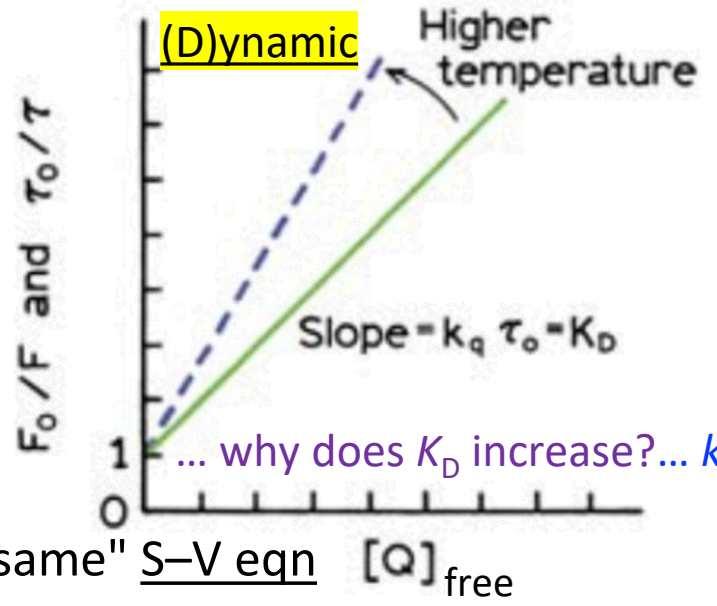
... since $\frac{\partial[D^+]}{\partial t} = \frac{\partial[A^-]}{\partial t} = k_{3f}[(D^+,A^-)]$... this is just equal to $k_{1f}[D][A]$... and $k_{f,obs} = k_{1f}$

... which is what the pre-equilibrium approximation would have predicted too, so... consistent!

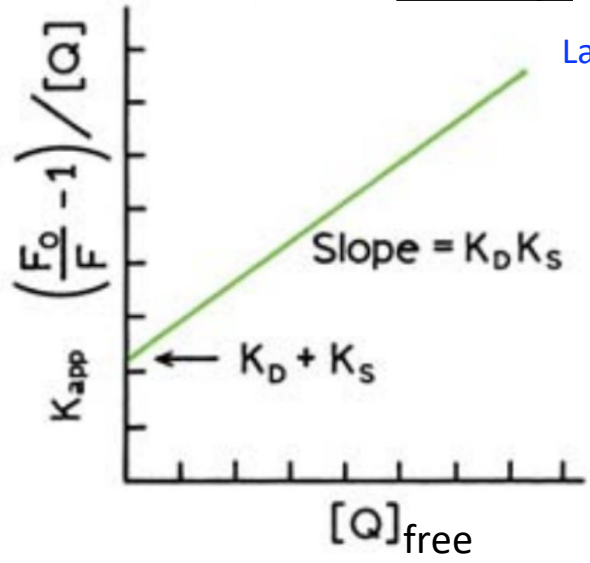
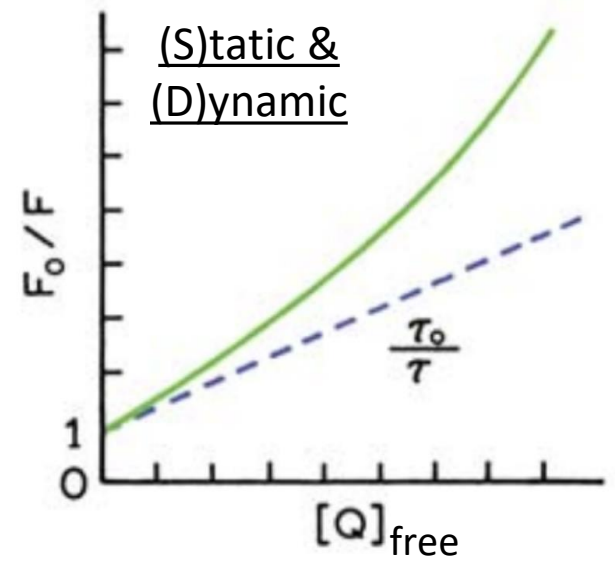
(S)tatic & (D)ynamic Stern–Volmer Quenching



$$K_s = \frac{[F \cdot Q]}{[F][Q]} = \frac{[F]_0 - [F]}{[F][Q]} = \frac{[F]_0}{[F][Q]} - \frac{1}{[Q]}$$



... leads to the "same" S–V eqn



Lakowicz, Chapter 8, Figures 8.1 & 8.2, Pages 280 & 283

$$\frac{\partial c_{F^*}}{\partial t} = f(t) - \left(\frac{1}{\tau_0} + k_q c_Q \right) c_{F^*} = 0 \dots \text{at s.s.}$$

$$\frac{\partial c_{F^*}}{\partial t} = f(t) - \frac{1}{\tau_0} c_{F^*,0} = 0 \dots \text{when } c_Q = 0$$

$$\dots \text{solve for } f(t) \dots \frac{1}{\tau_0} c_{F^*,0} = \left(\frac{1}{\tau_0} + k_q c_Q \right) c_{F^*}$$

$$\dots \text{and simplify to } \underline{\text{S–V eqn}} \dots \frac{c_{F^*,0}}{c_{F^*}} = 1 + k_q \tau_0 c_Q$$

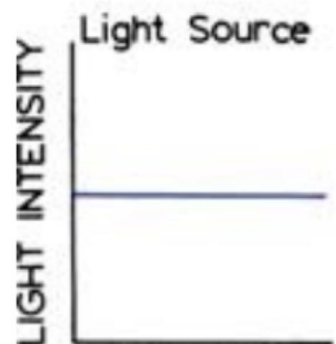
... conversion of $k_{q,obs}$ to ΔG_{AB}^\ddagger can be nontrivial

Today's Critical Guiding Question

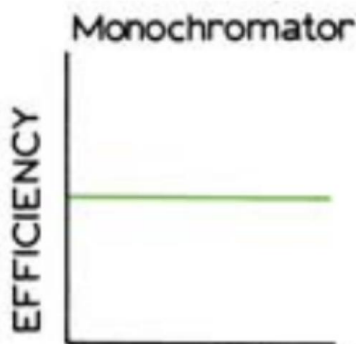
With knowledge of how to define all rate constants and diffusion coefficients for all continuity/conservation laws that are most important for thermal process and photophysical processes, how can they be used to (i) assess the applicability of Marcus theory for photochemical processes and (ii) predict steady-state photochemical energy conversion efficiencies?

DISCUSSION SESSION TOPICS

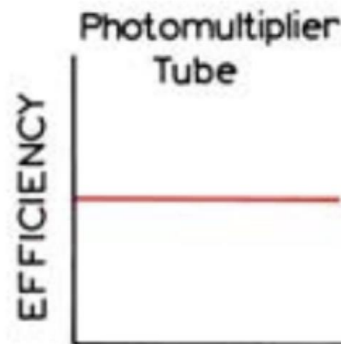
Photoluminescence Spectrometer



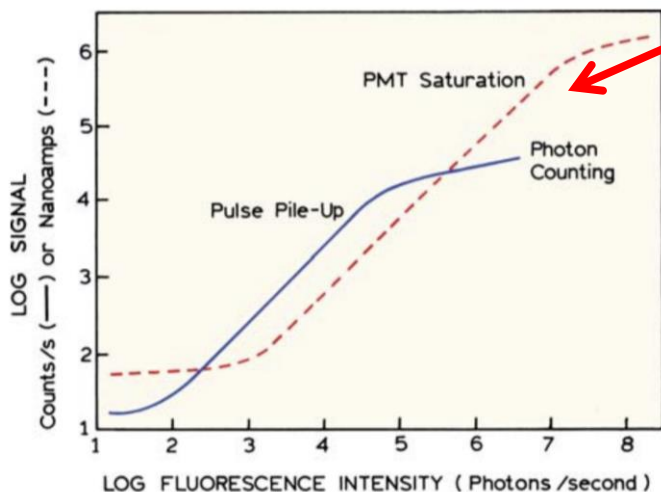
WAVELENGTH
or POLARIZATION
or TIME



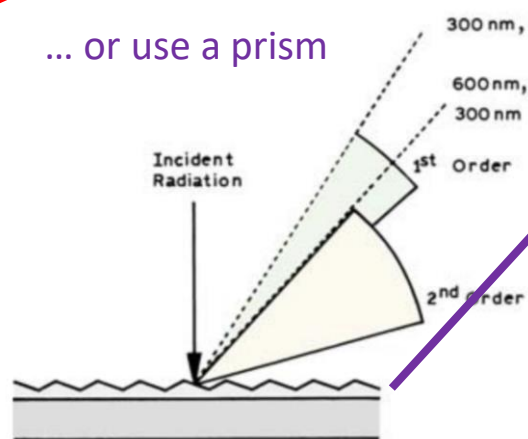
WAVELENGTH
or POLARIZATION
or TIME
or LIGHT INTENSITY



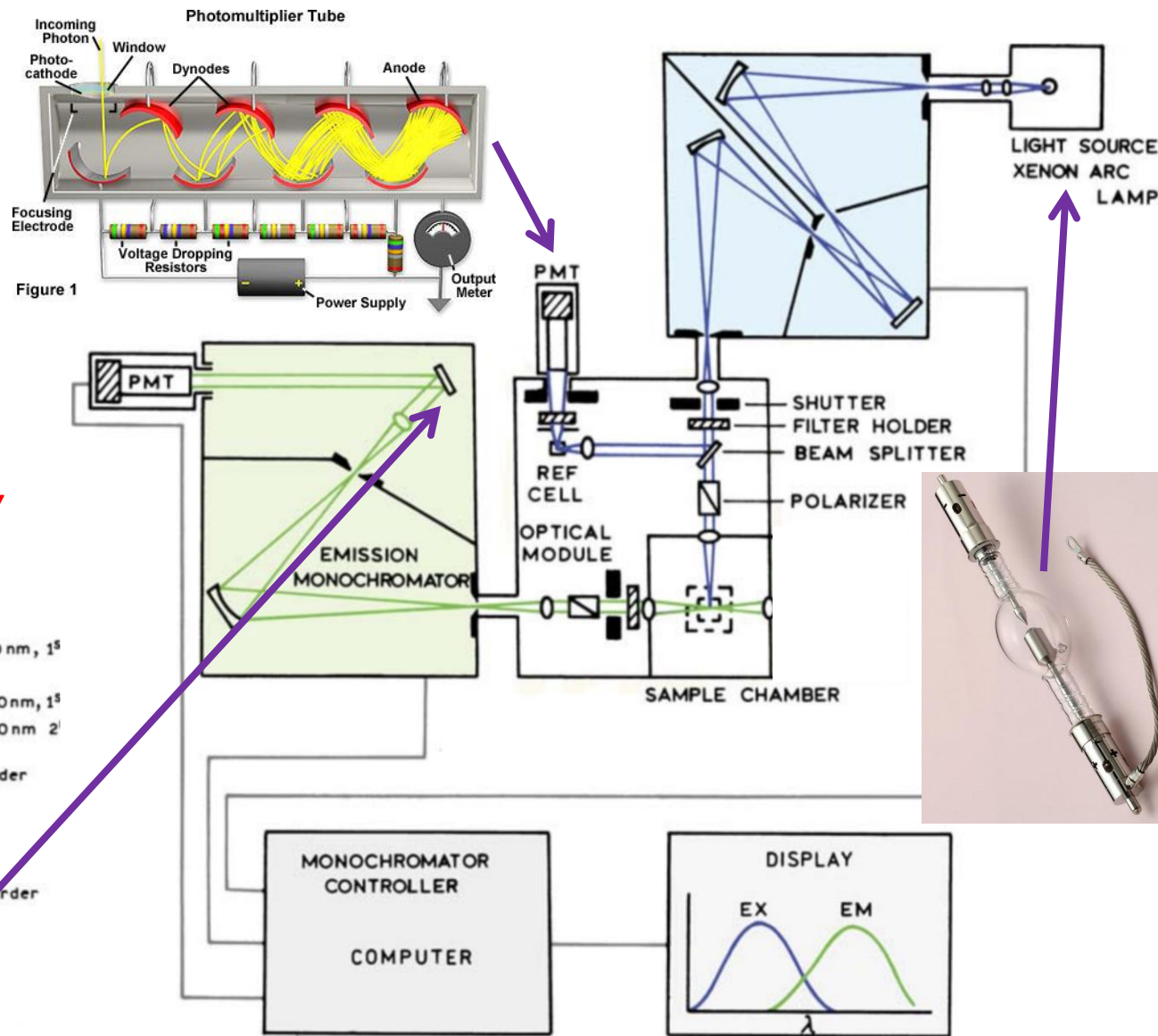
WAVELENGTH
or POLARIZATION
or TIME
or LIGHT INTENSITY



Lakowicz, Chapter 2, Figure 2.36, Page 48



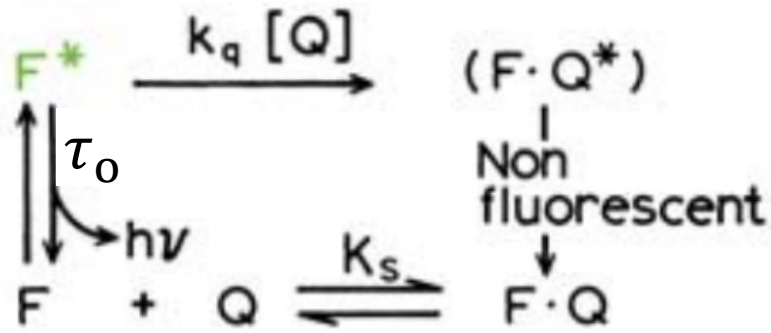
Lakowicz, Chapter 2, Figure 2.16, Page 37



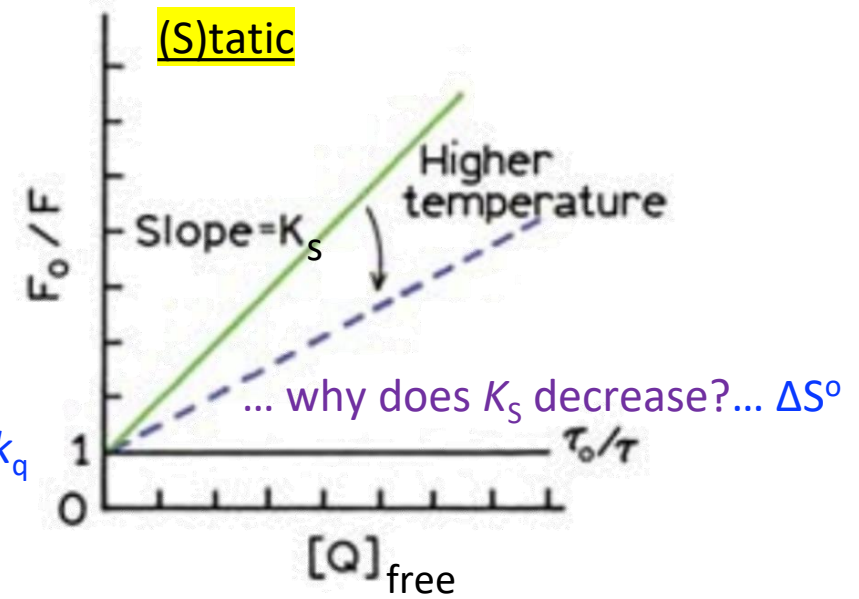
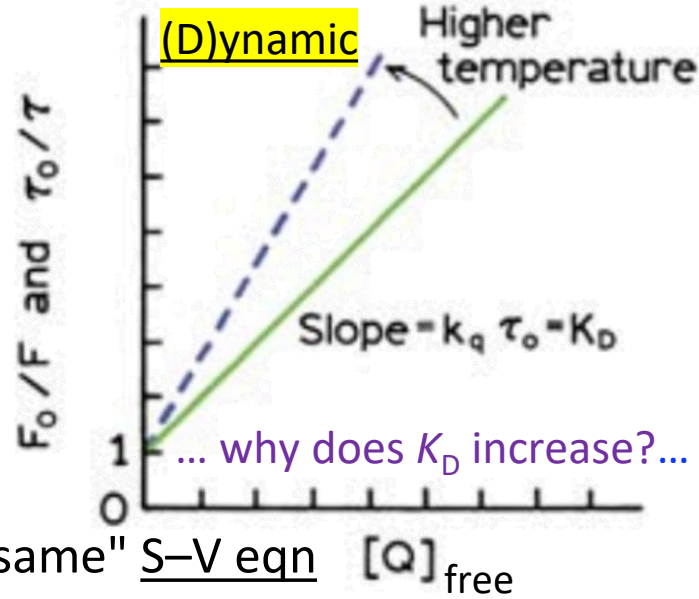
Lakowicz, Chapter 2, Figure 2.1, Page 28



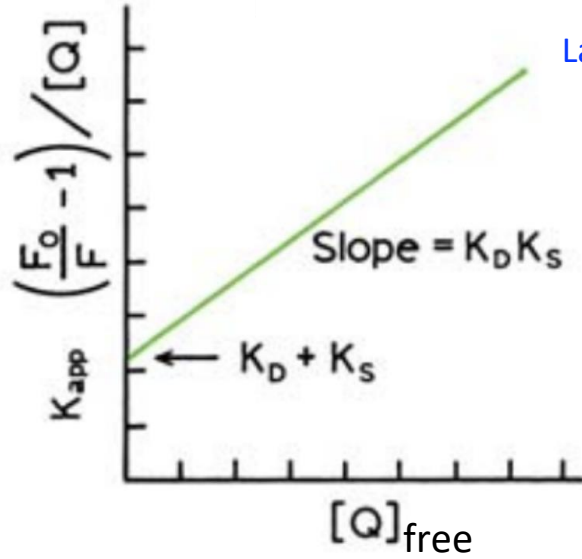
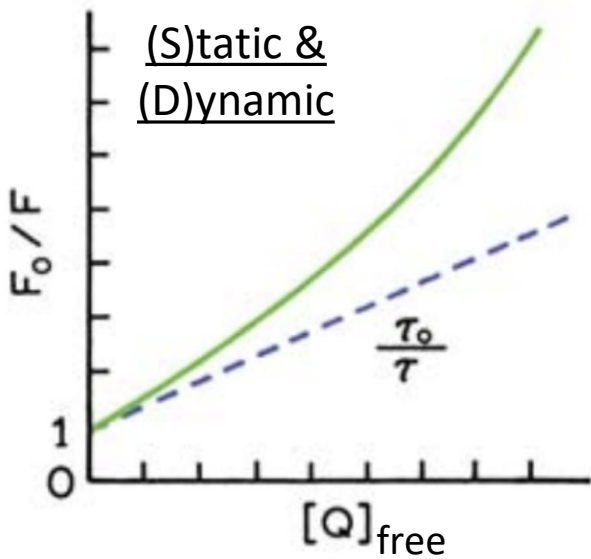
(S)tatic & (D)ynamic Stern–Volmer Quenching



$$K_s = \frac{[F \cdot Q]}{[F][Q]} = \frac{[F]_0 - [F]}{[F][Q]} = \frac{[F]_0}{[F][Q]} - \frac{1}{[Q]}$$



... leads to the "same" S–V eqn



Lakowicz, Chapter 8, Figures 8.1 & 8.2, Pages 280 & 283

$$\frac{\partial c_{F^*}}{\partial t} = f(t) - \left(\frac{1}{\tau_0} + k_q c_Q \right) c_{F^*} = 0 \dots \text{at s.s.}$$

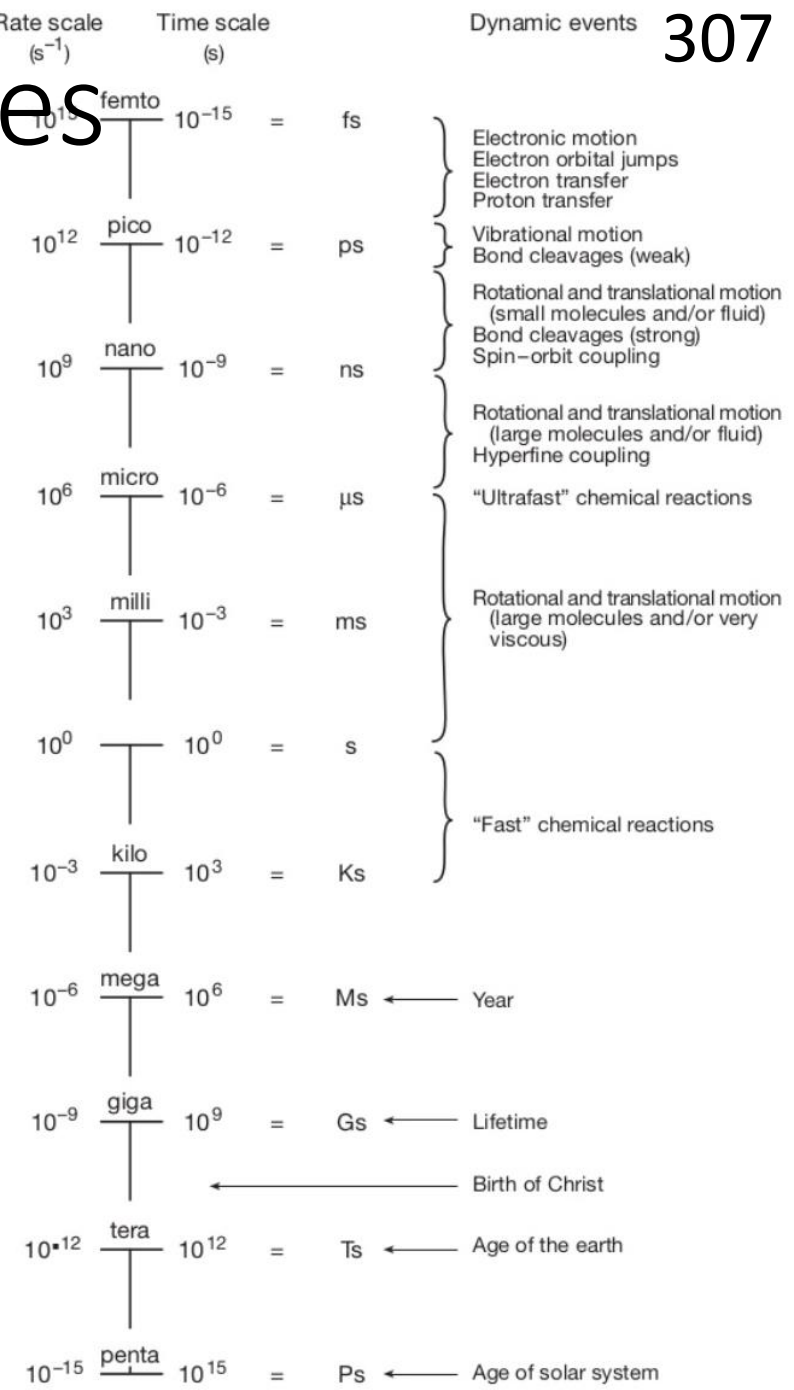
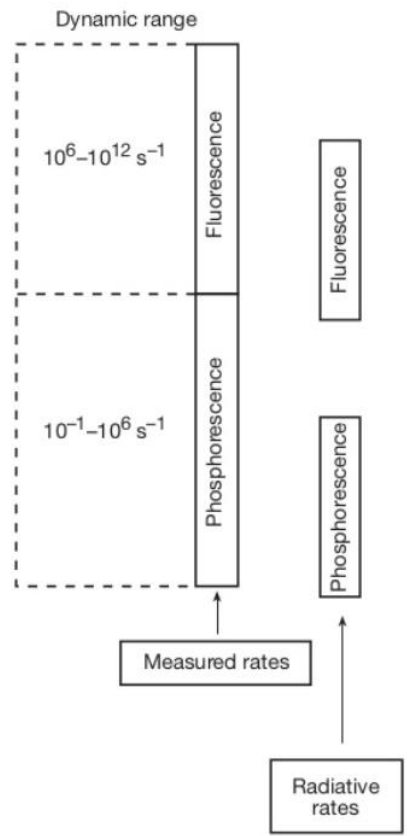
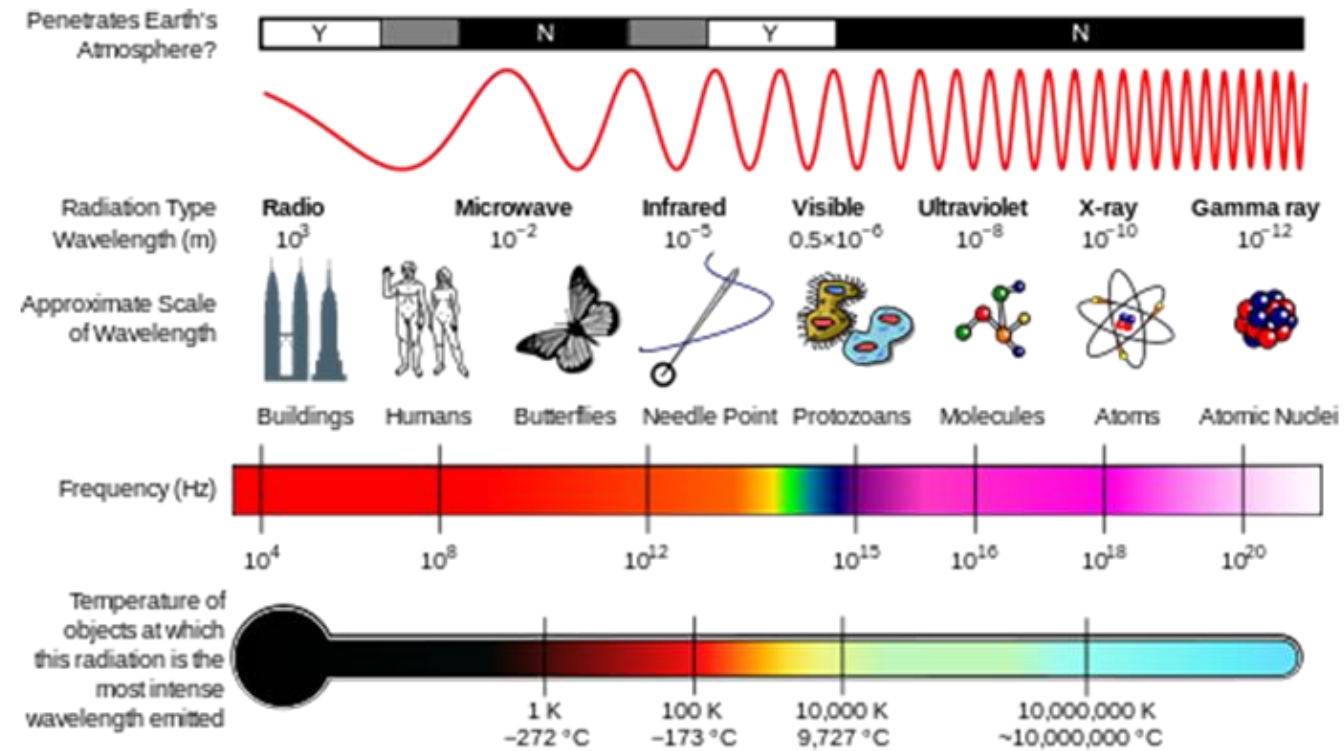
$$\frac{\partial c_{F^*}}{\partial t} = f(t) - \frac{1}{\tau_0} c_{F^*,0} = 0 \dots \text{when } c_Q = 0$$

$$\dots \text{solve for } f(t) \dots \frac{1}{\tau_0} c_{F^*,0} = \left(\frac{1}{\tau_0} + k_q c_Q \right) c_{F^*}$$

$$\dots \text{and simplify to } \underline{\text{S–V eqn}} \dots \frac{c_{F^*,0}}{c_{F^*}} = 1 + k_q \tau_0 c_Q$$

... conversion of $k_{q,obs}$ to ΔG_{AB}^\ddagger can be nontrivial

Photochemical Length/Time Scales

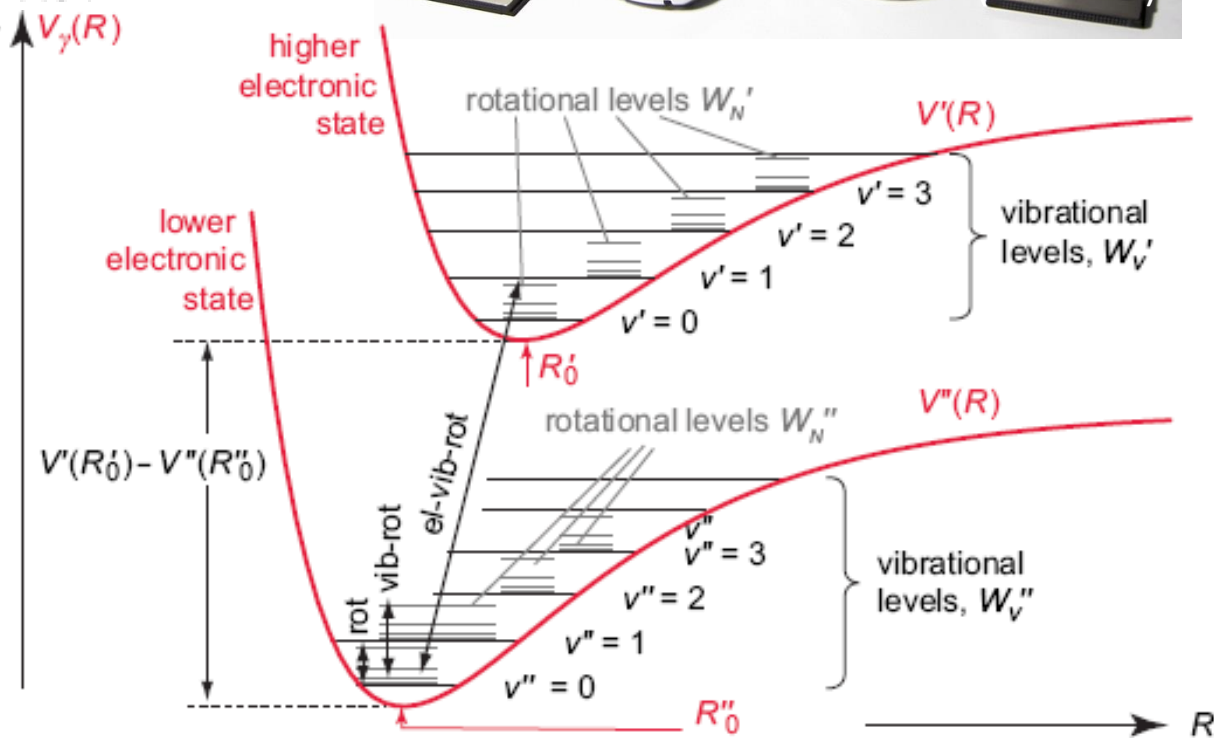
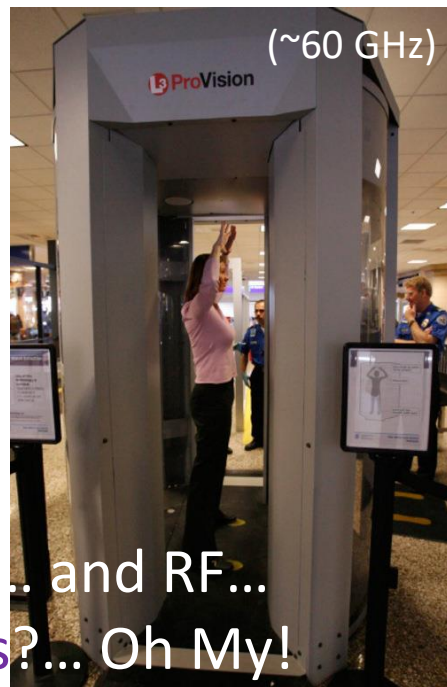
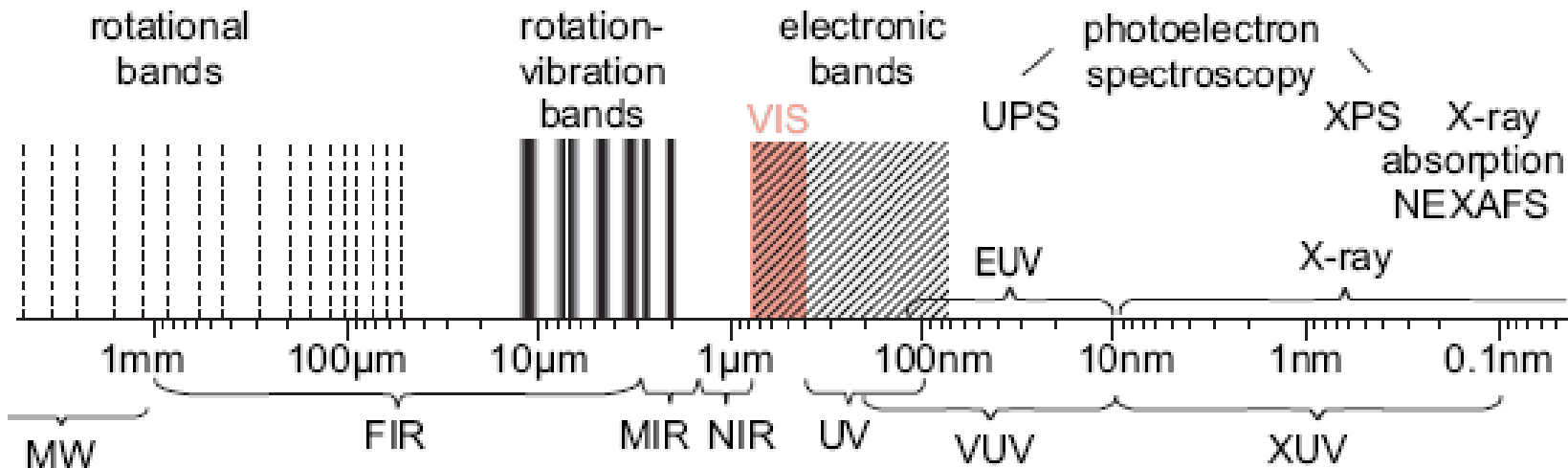


<https://www.e-education.psu.edu/meteo300/node/682>

... so how do we probe such fast processes...
 ... and in each of these regions of the electromagnetic spectrum?

Electromagnetic spectrum

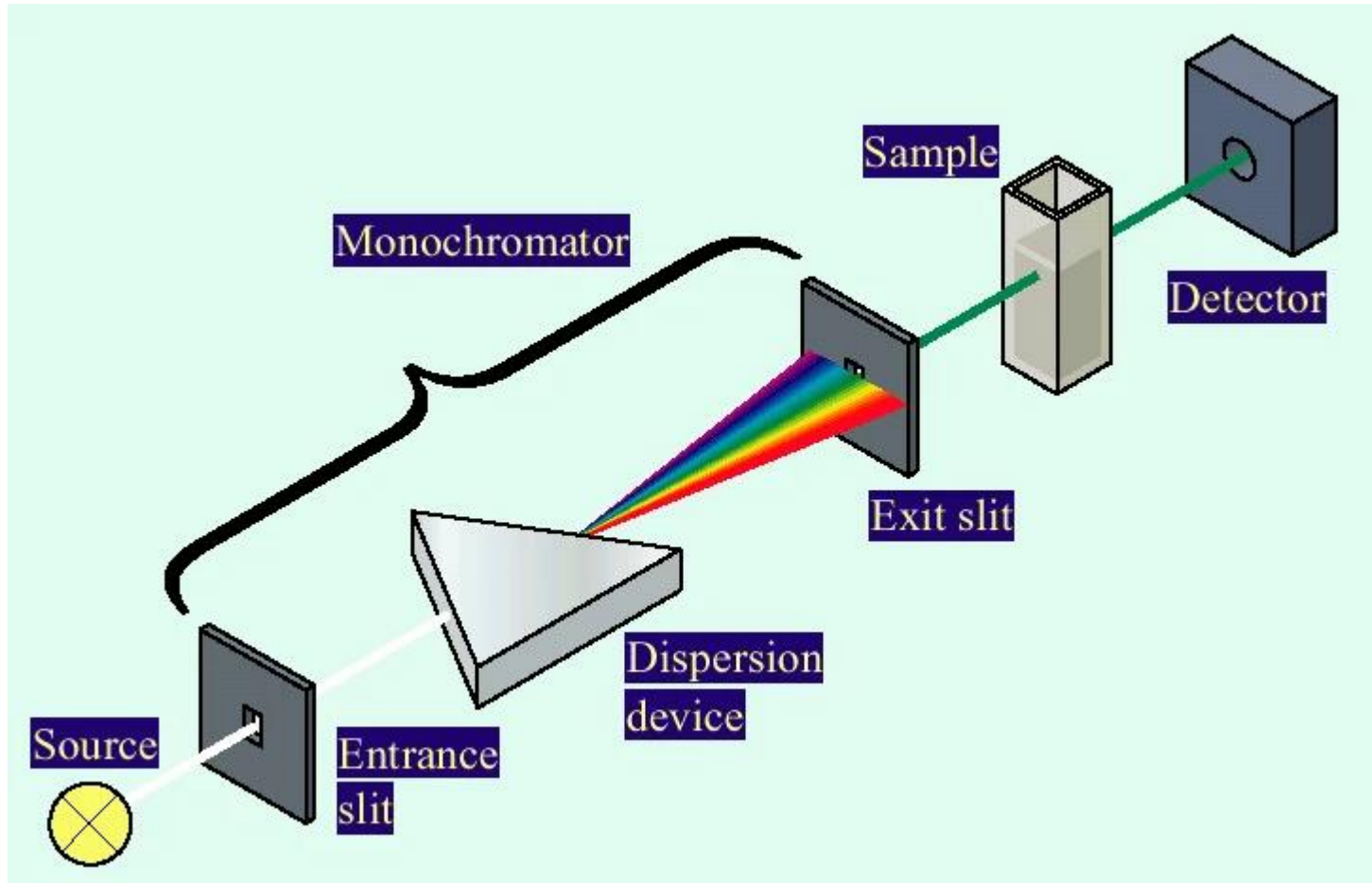
... what can one do with microwaves?



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

Pump-Probe Transient Spectroscopies

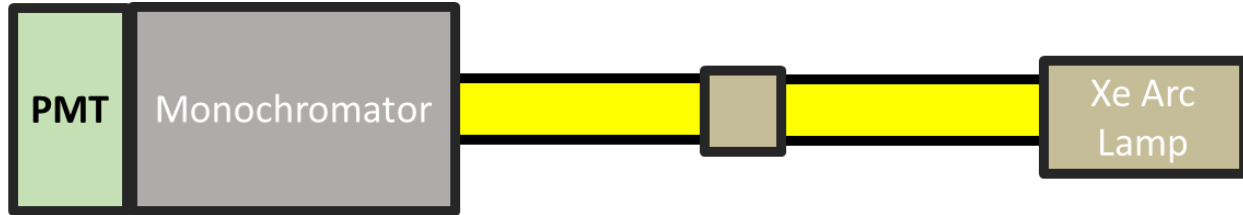
... probing seems reasonably straightforward...
 ... but how does one pump? ...



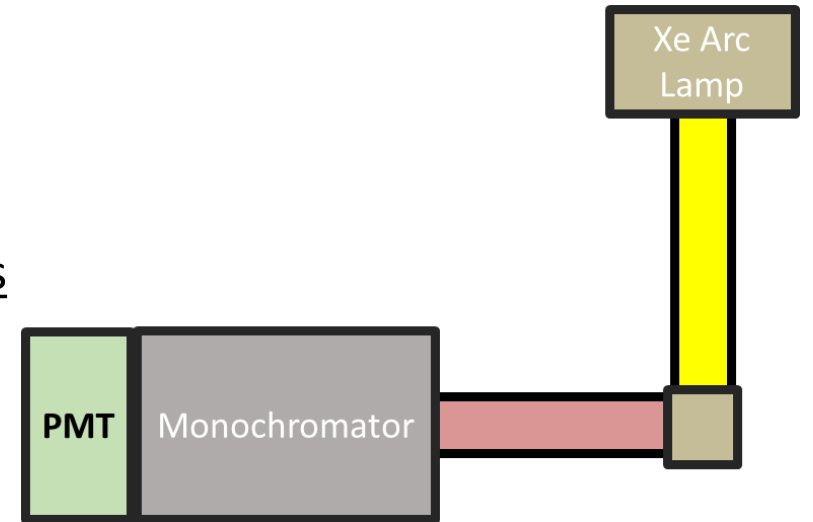
... No... not Reebok Pumps...
 ... pump with a laser!
 ... whose pulse width is generally...
 ... ultrafast @ ~ 10 fs (10^{-15} s)
 ... or just fast @ ~ 5 ns (10^{-9} s)...
 ... let's start with "just fast"...

General Spectroscopic Layouts

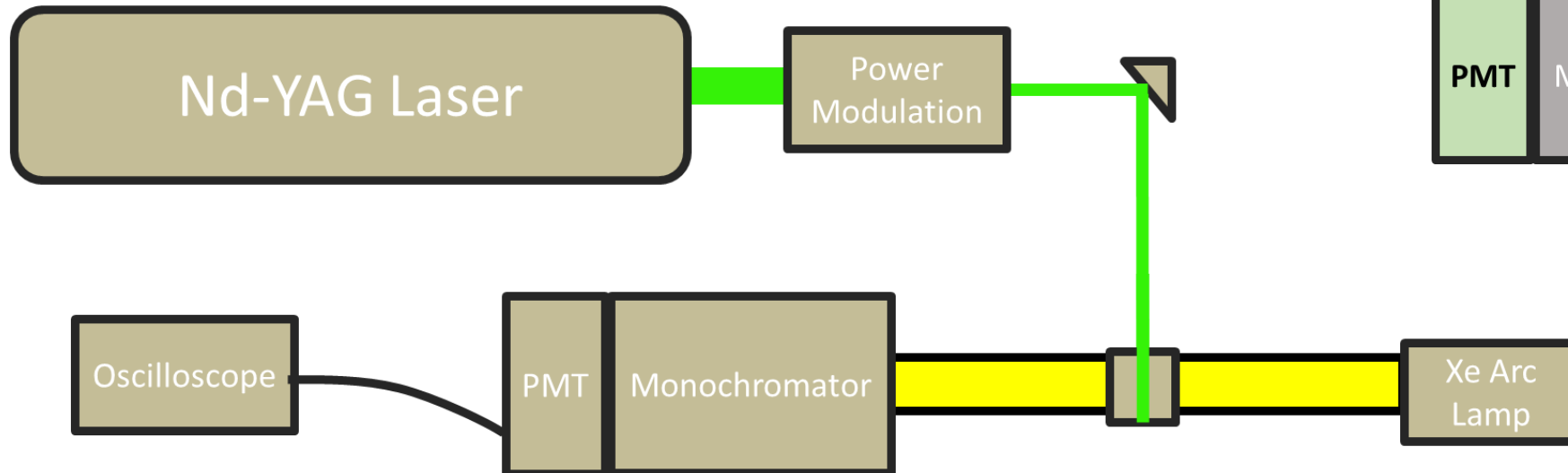
Electronic Absorption Spectroscopy



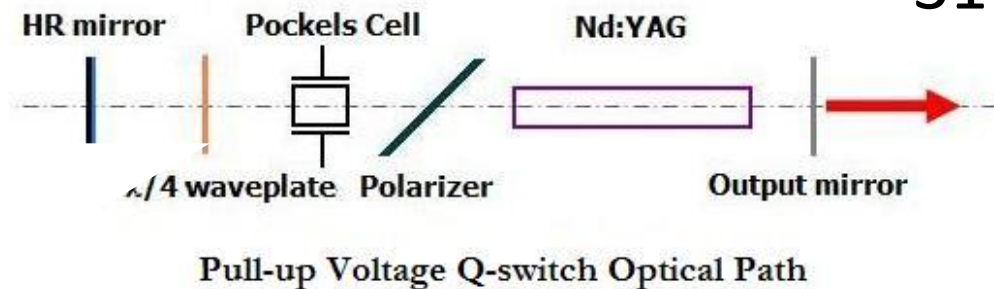
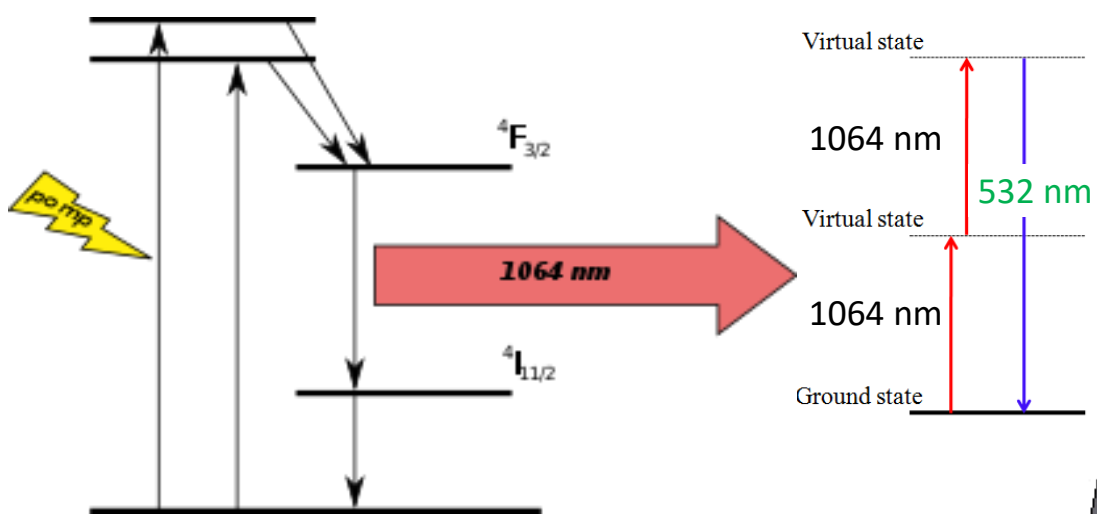
Steady-state Photoluminescence Spectroscopy



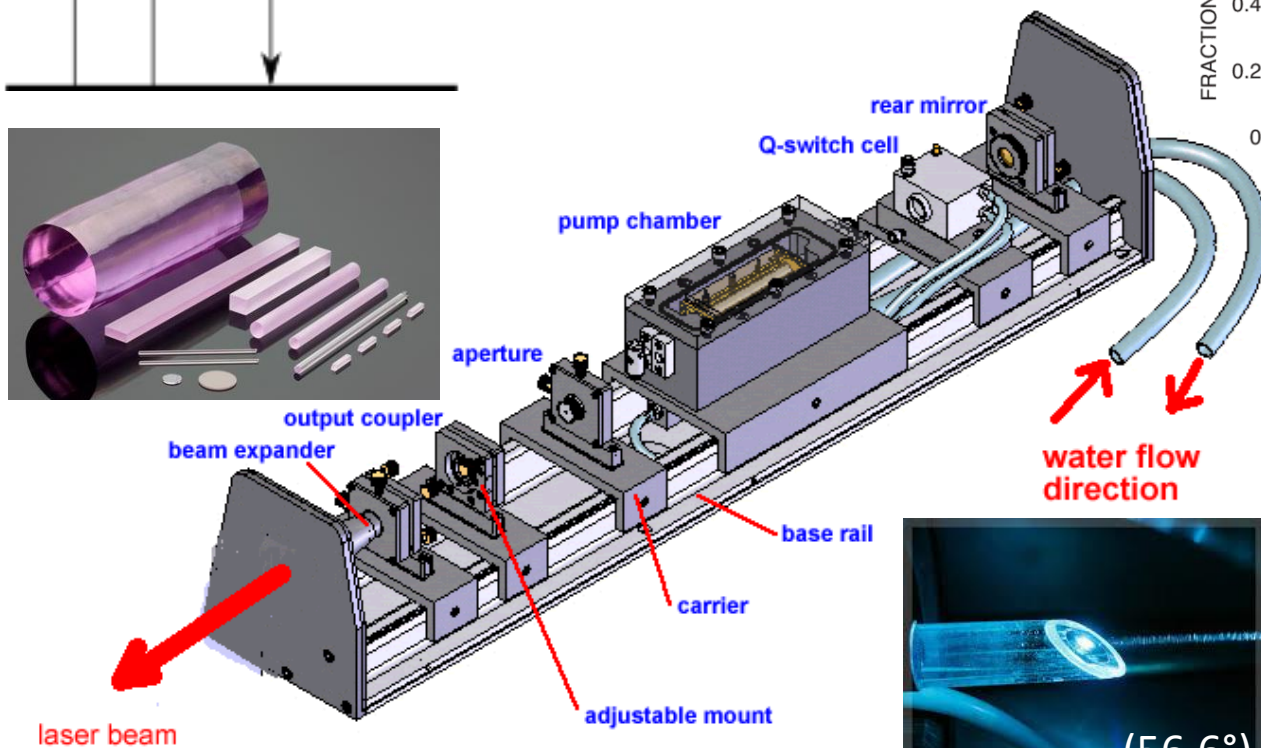
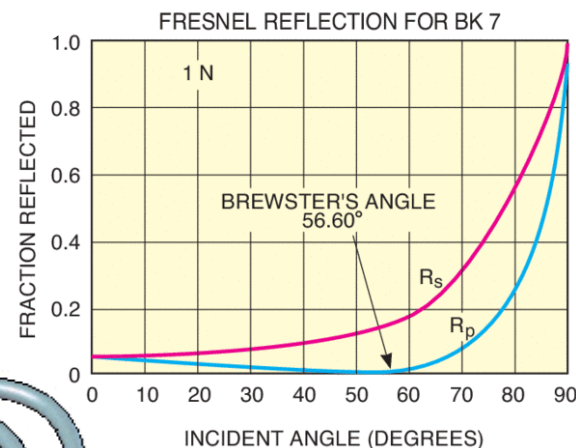
Transient Absorption / Time-Resolved Photoluminescence Spectroscopies



Nd:YAG ($\text{Nd:Y}_3\text{Al}_5\text{O}_{12}$) Laser



Pull-up Voltage Q-switch Optical Path

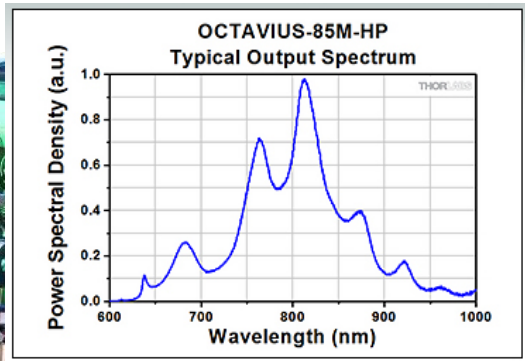
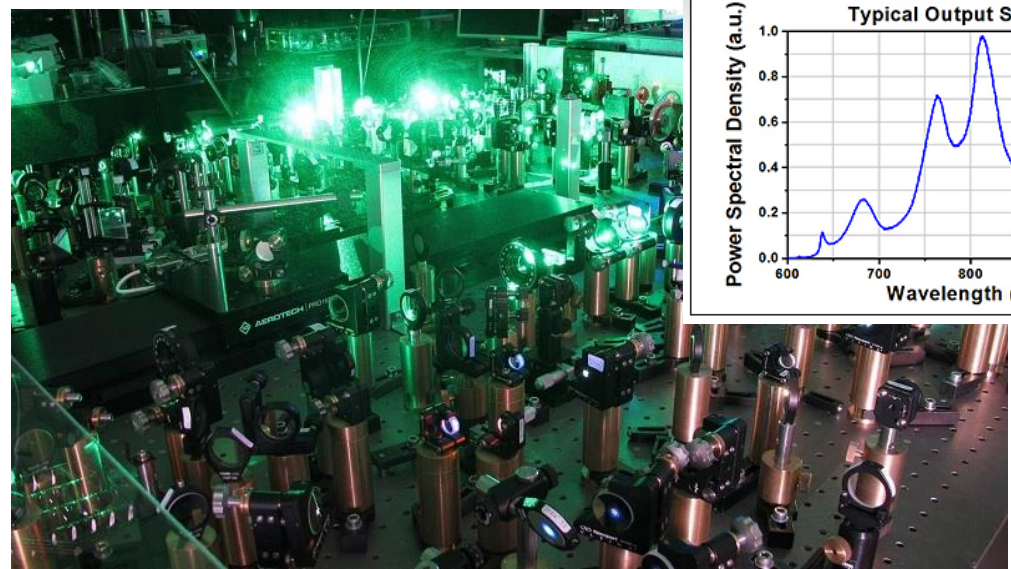


Key Features

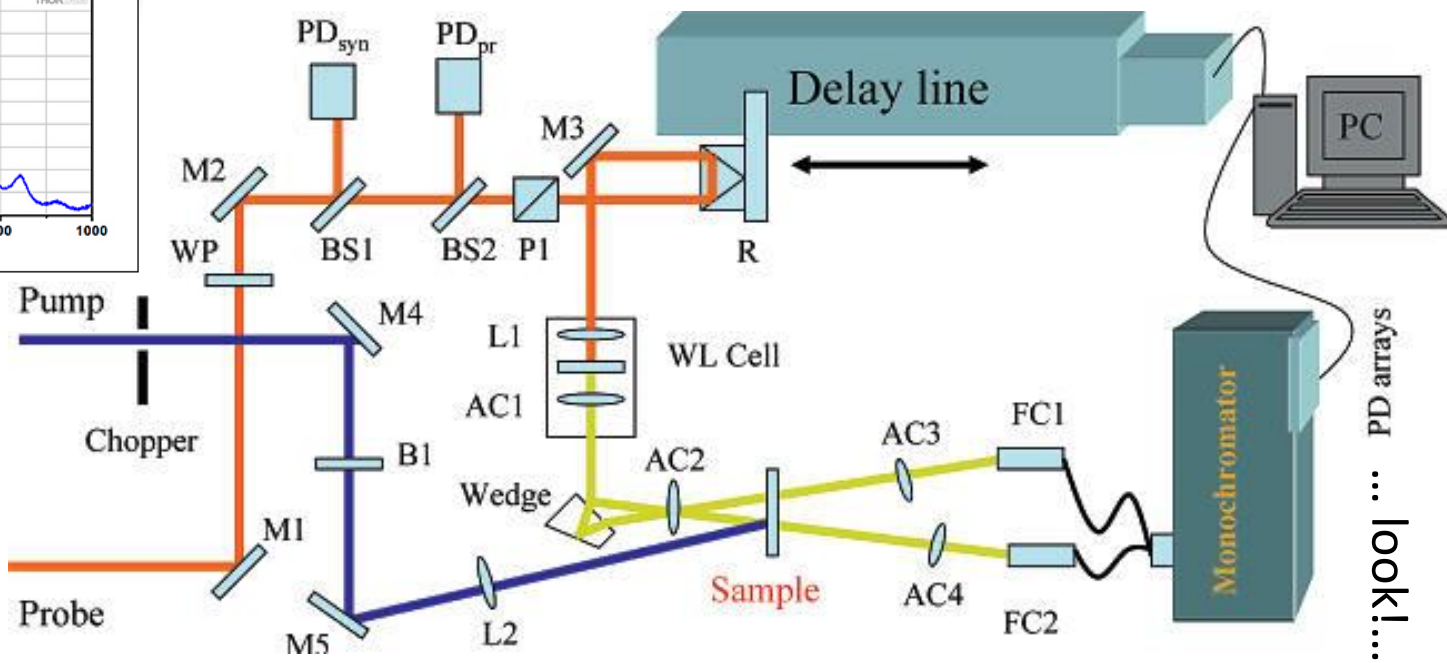
- ~ 5 ns fwhm pulses; fundamental line: 1064 nm
- white light source serves as the probe
- oscilloscope records PMT readout every ~ 1 ns
- need to average data from many laser pulses
- a single wavelength is measured per laser pulse



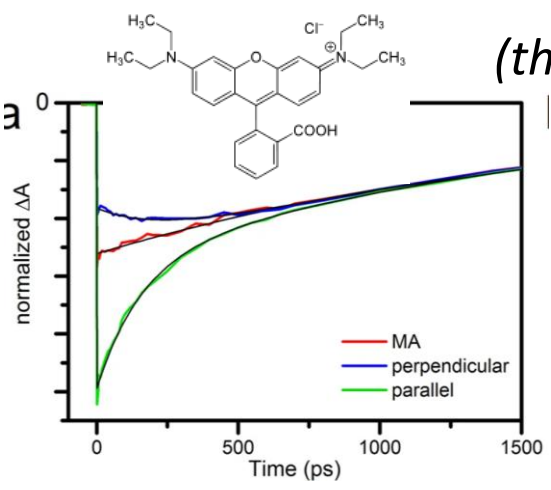
(Ti)tanium:(Sapph)ire (Ti:Al₂O₃) Ultrafast Laser



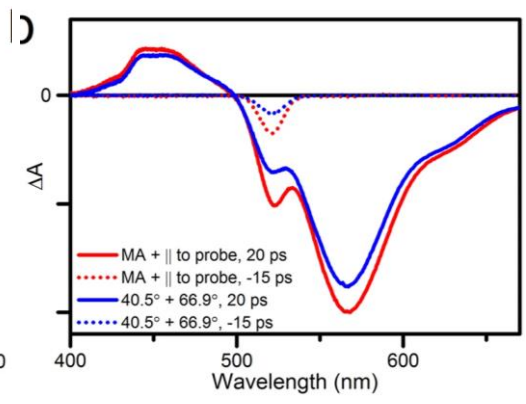
(light travels ~1 foot in 1 nanosecond)



... look!... no slits! PD arrays



(this is a tiny blip on Abs)



Key Features

- 10 – 100 fs fwhm pulses; fundamental line: broad, ~800 nm
- laser serves as both the pump and the probe
- delay line allows one to probe out to ~5 ns
- each laser pulse allows one to measure a single time point
- use an array of detectors to measure entire spectrum per pulse
- measuring photoluminescence requires stimulated emission

... which of these likely took longer to measure?

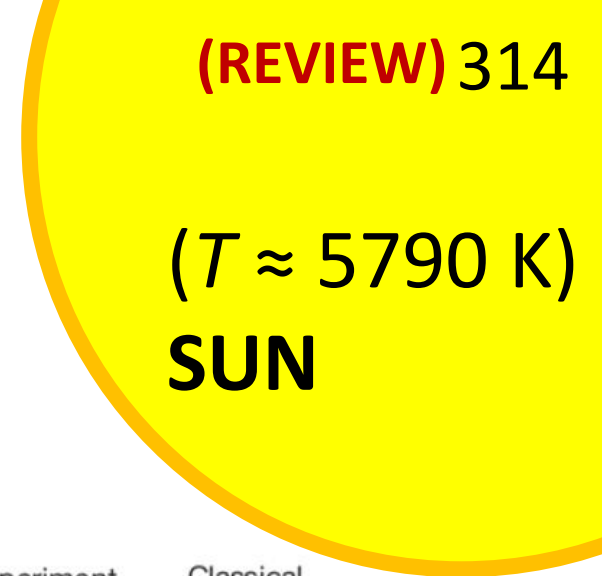
Today's Critical Guiding Question

With knowledge of how to define all rate constants and diffusion coefficients for all continuity/conservation laws that are most important for thermal process and photophysical processes, how can they be used to (i) assess the applicability of Marcus theory for photochemical processes and (ii) predict steady-state photochemical energy conversion efficiencies?... now for part (ii)

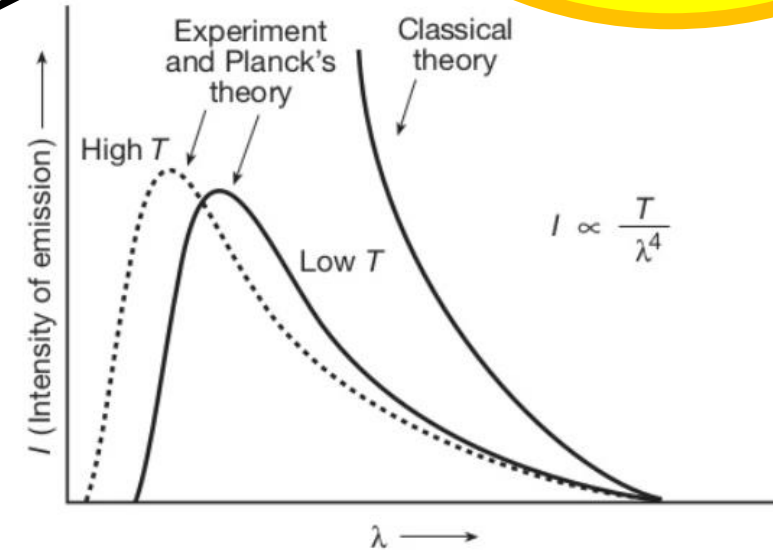
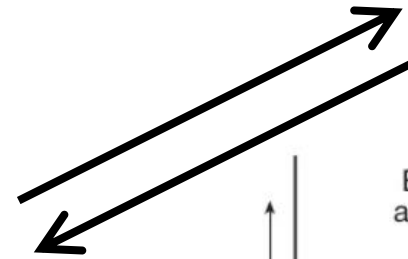
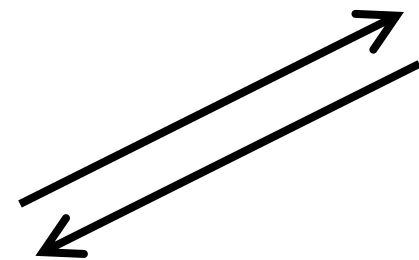
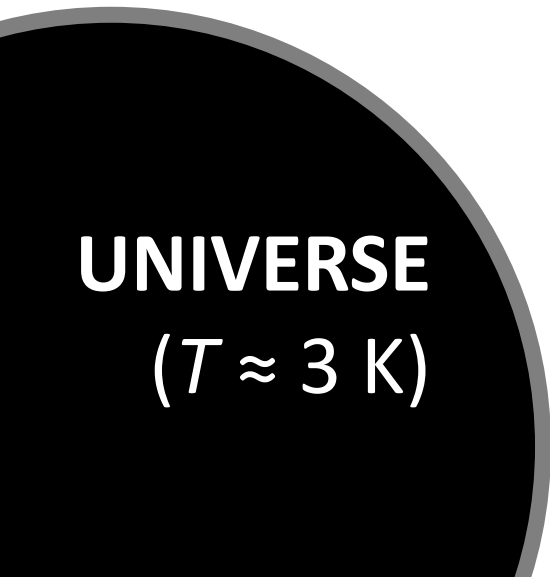
Blackbody Radiation

$$\text{Carnot efficiency limit, } \eta = \frac{w}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

... light-driven processes between two blackbodies
... interconvert energy and work,
like heat engines and refrigerators do

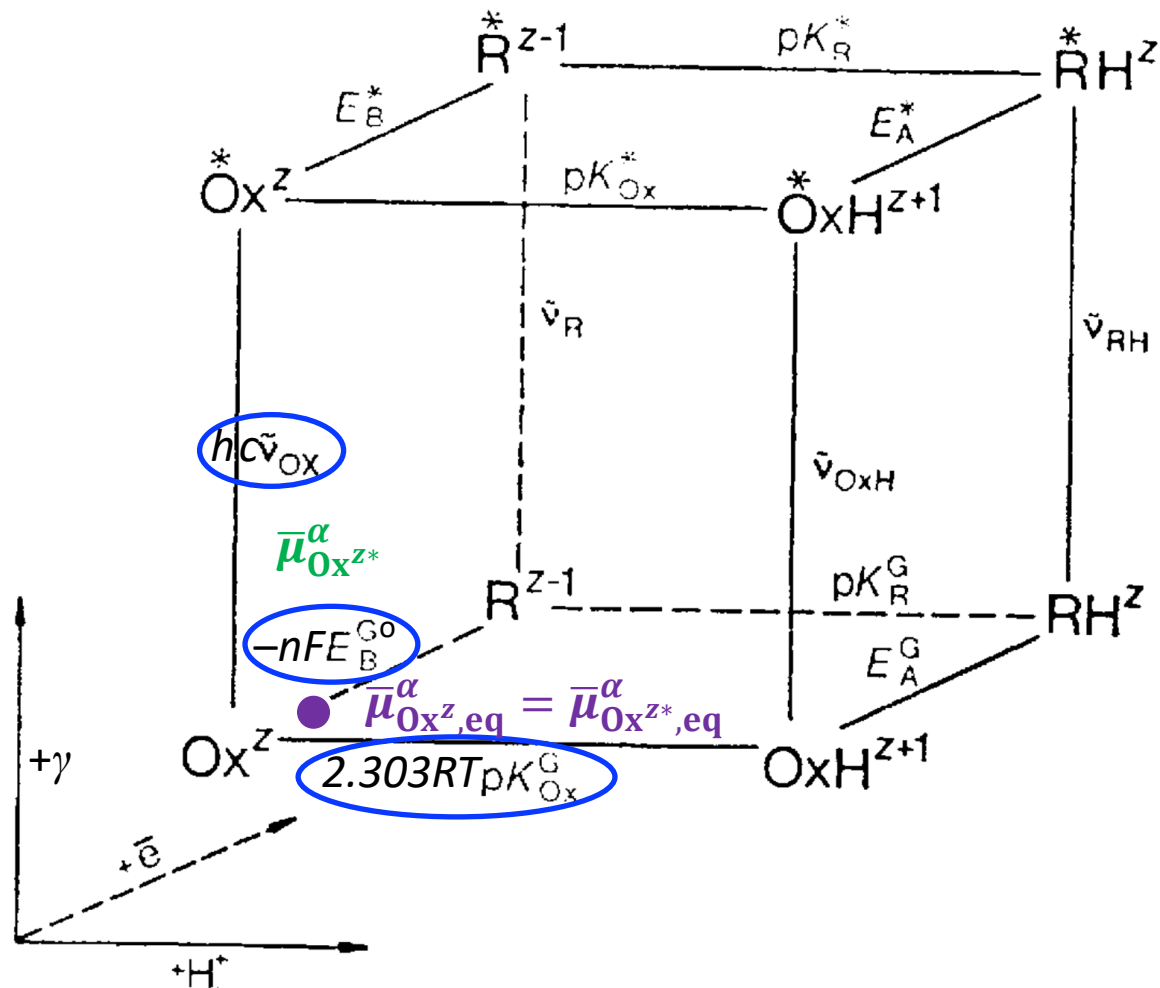


($T \approx 290$ K)



... if any two bodies are that the same temperature
... and they only interact via radiation, i.e., photons (e.g., not chemical)
... then no work can be performed due to these photon exchanges
... and electrochemical potentials do not change due to them

Förster Cube and Square Schemes



... all of these free energy terms are **standard-state** free energies (ΔG°)... but what is the actual free energy of the system (ΔG)?

... let's assume that $\Delta G = 0$ (equilibrium)... how could I indicate that on this slide, as a point(s), to depict the majority species present?

... now, how can one **push/pull** this system out of equilibrium?

... recall Le Châtelier's principle... and thus by addition of reactants or removal of products... such as mass or light!

... hopefully this made a little more sense this time around... and if not, **WE ARE (NEARLY) OUT OF TIME!**

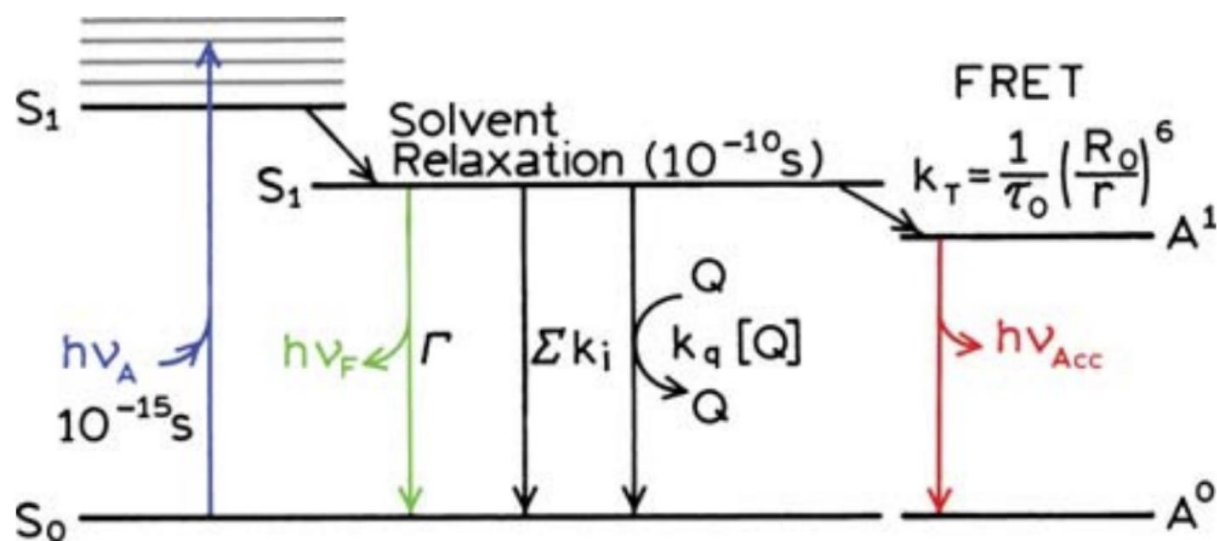
E-S Lifetime & Emission Quantum Yield

Excited-State Lifetime, $\tau_{ES} = \frac{1}{k_r + k_{nr} + \sum_j k_j [Q_j]^{v_j}} = \langle t \rangle = t\left(\frac{100}{e}\right)\%$

$$\phi_{em} = \phi_R \frac{I}{I_R} \frac{Abs_R}{Abs} \frac{n^2}{n_R^2}$$

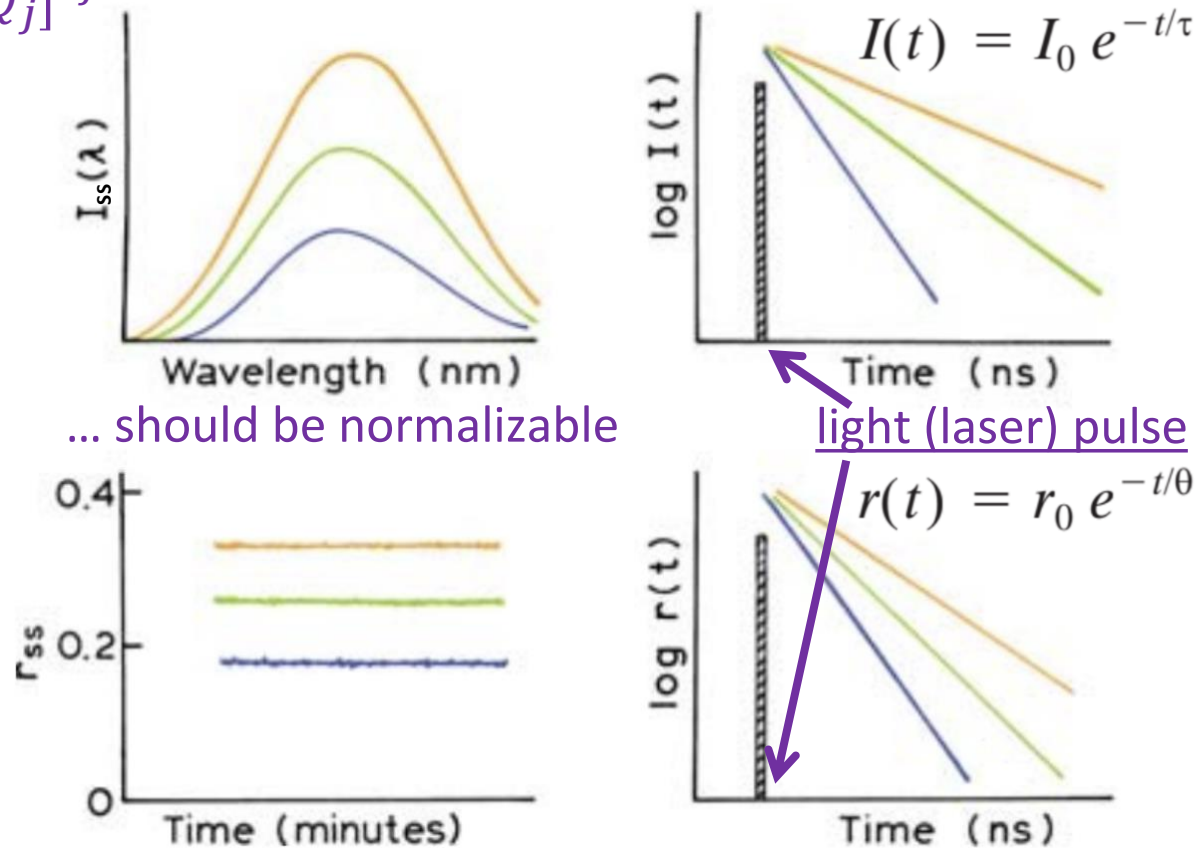
... R is an actinometer

Emission Quantum Yield, $\phi_{em} = \frac{k_r}{k_r + k_{nr} + \sum_j k_j [Q_j]^{v_j}} = k_r \tau_{ES}$



Lakowicz, Chapter 1, Figure 1.14, Page 11

$$I_{SS} = \int_0^{\infty} I_0 e^{-t/\tau} dt = I_0 \tau \quad r_{ss} = \frac{\int_0^{\infty} r(t) I(t) dt}{\int_0^{\infty} I(t) dt}$$



... should be normalizable

Lakowicz, Chapter 1, Figure 1.17, Page 14

Statistical Mechanics Distributions

Given a set of energy levels, E_i , what is the probability, P_i , that each is occupied at equilibrium?

Boltzmann distribution

$$P_i(E_i) = \frac{n_i}{g_i} = \frac{1}{e^{(E_i - \mu)/kT}}$$

- ... thermal ensemble that maximizes free energy
- ... when species are far enough apart that...
- ... effects due to quantum interactions are small

- ... or the other way around...
- ... given an occupancy of energy levels, n_i ...
- ... and assuming quasi-equilibrium...
- ... what is the chemical potential, μ ?...
- ... that can be used to perform useful work
- ... so... how does one determine n_i ?
- ... chemical kinetics!

Fermi–Dirac distribution

$$P_i(E_i) = \frac{n_i}{g_i} = \frac{1}{e^{(E_i - \mu)/kT} + 1}$$

- ... fermions (half-integer spin particles)... e.g. electrons
- ... wavefunction is *antisymmetric* with particle exchange
- ... which results in the Pauli exclusion principle
- ... F–D stats approach M–B stats at high T or small n_i

Bose–Einstein distribution

$$P_i(E_i) = \frac{n_i}{g_i} = \frac{1}{e^{(E_i - \mu)/kT} - 1}$$

- ... bosons (integer spin particles)... e.g. photons
- ... wavefunction is *symmetric* with particle exchange
- ... which results in no limit on quantum state occupancy
- ... B–E stats approach M–B stats at high T or small n_i

Detailed-Balance Analysis

... thank you Shockley, Queisser,
Henry, De Vos, Pauwels, Würfel,
Ross, Hsiao, Bolton, et al.!

... at equilibrium in the dark, meaning $\sum_i \nu_i \mu_i = 0$, photochemical converters absorb and emit radiation from and to the blackbody surroundings with equal fluxes, Φ_j , to (G)enerate and (R)ecombine excited-state species, $\Phi_{\text{Grad,eq}} = \frac{4\pi}{c^2} \int_{E_g/h}^{\infty} \alpha_{\nu} \nu^2 e^{-h\nu/kT} d\nu = \Phi_{\text{Grad}} = -\Phi_{\text{Rrad,eq}}$... in units of $\text{mol cm}^{-2} \text{s}^{-1}$

... when an additional continuous source/sink of light is introduced, e.g. the Sun/Universe, the photochemical converters are no longer at equilibrium, meaning $\Delta\mu_{\text{ES}} \neq 0$ and $\Delta n_{\text{ES}} \neq 0$... in the presence of sunlight, Φ_{Gsolar} , at steady-state one has $\Phi_{\text{Rrad}} = \Phi_{\text{Rrad,eq}} e^{\Delta\mu_{\text{ES}}/kT} = -(\Phi_{\text{Grad}} + \Phi_{\text{Gsolar}})$

... non-radiative processes occur in parallel to these photophysical processes, both in the dark and in the light, with $\Phi_{\text{Gnonrad,eq}} = \Phi_{\text{Grad,eq}} \left(\frac{1 - \phi_{\text{em}}}{\phi_{\text{em}}} \right) = \Phi_{\text{Gnonrad}}$ and $\Phi_{\text{Rnonrad}} = \Phi_{\text{Rrad,eq}} \left(\frac{1 - \phi_{\text{em}}}{\phi_{\text{em}}} \right) e^{\Delta\mu_{\text{ES}}/kT}$

... max. useful work is $\Delta\mu_{\text{ES}} (= -FV_{\text{oc}})$ when $\Phi_{\text{Grad,eq}} + \Phi_{\text{Gnonrad,eq}} + \Phi_{\text{Gsolar}} + \Phi_{\text{Rrad}} + \Phi_{\text{Rnonrad}} = 0$

... useful work occurs by additional reversible (productive) quenching processes, Φ_{Rwork} , which result in a decreased value of $\Delta\mu_{\text{ES}}$ as $\Phi_{\text{Rwork}} = \Phi_{\text{Grad,eq}} \left(\frac{1}{\phi_{\text{em}}} \right) (1 - e^{\Delta\mu_{\text{ES}}/kT}) + \Phi_{\text{Gsolar}}$

... this leads to $j = j_0 (1 - e^{qV/kT}) + j_{\text{ph}}$... which is the photodiode eqn... but is purely thermodynamic!

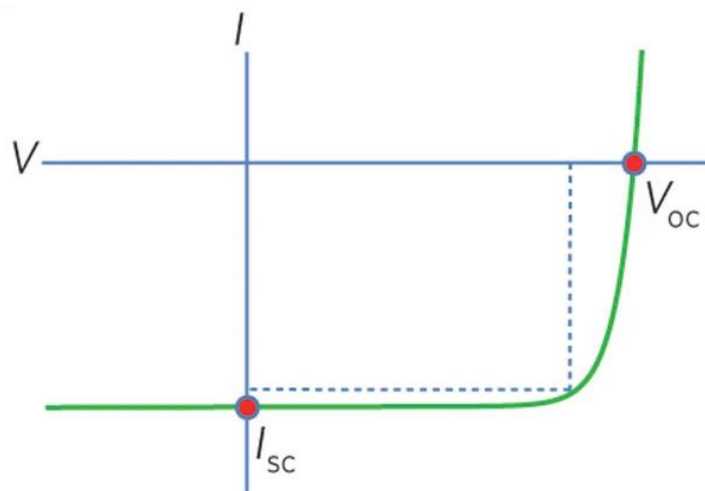
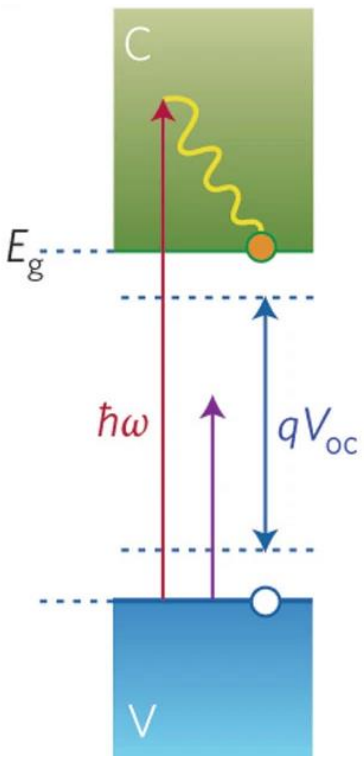
Photoelectrochemistry

... thank you Shockley, Queisser, **(BRIEFLY)** 319
Henry, De Vos, Pauwels, Würfel,
Ross, Hsiao, Bolton, et al.!

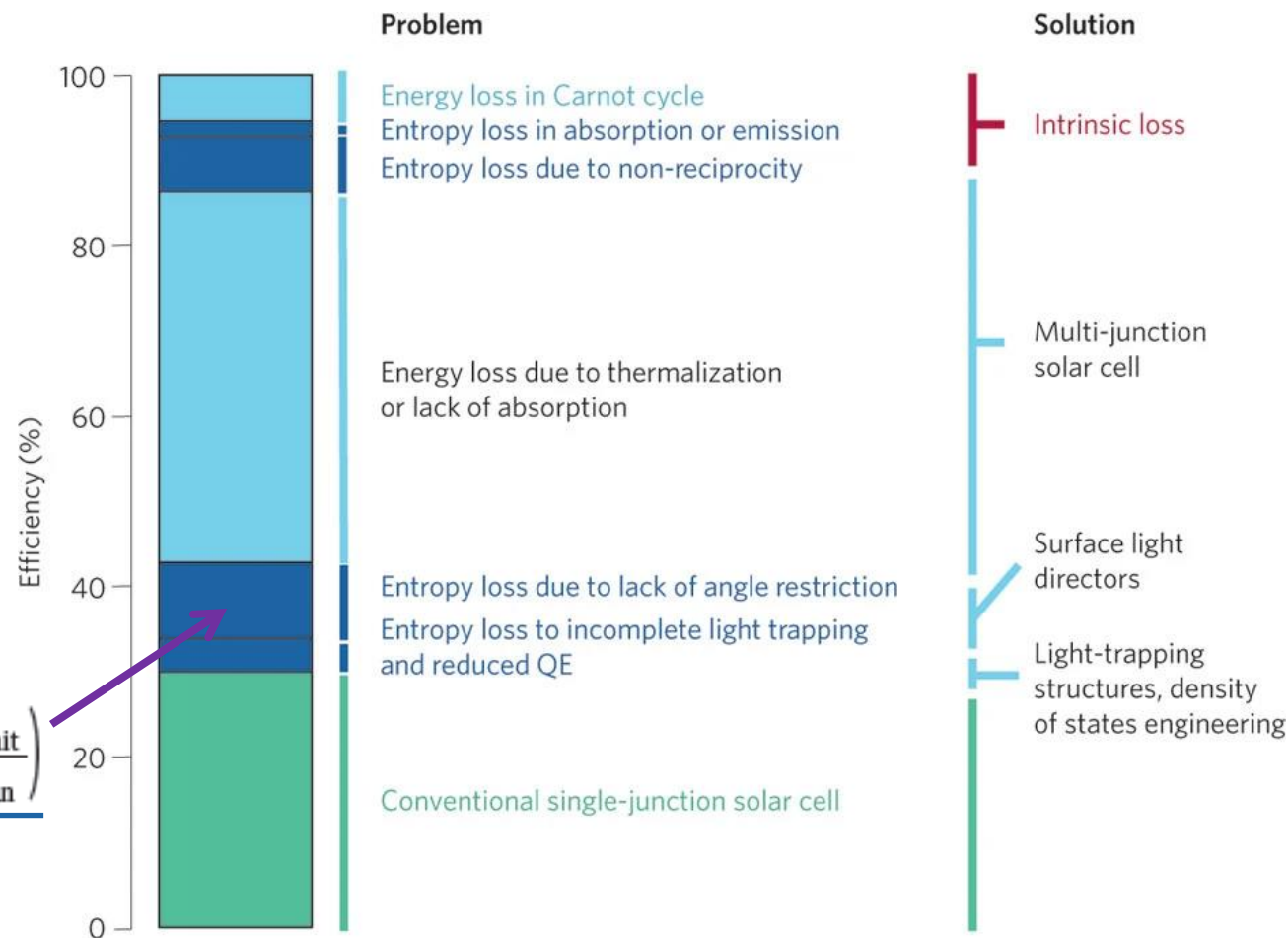
... the key relation between current density, j , and potential, V ...

$$j = j_0(1 - e^{qV/kT}) + j_{ph}$$

... where $I_{sc} = j_{ph} \times A$ and V_{oc} is V when $j = 0$



$$qV_{oc} = E_g \left(1 - \frac{T}{T_{sun}} \right) - kT \left[\ln \left(\frac{\Omega_{emit}}{\Omega_{sun}} \right) + \ln \left(\frac{4n^2}{I} \right) - \ln(QE) \right]$$



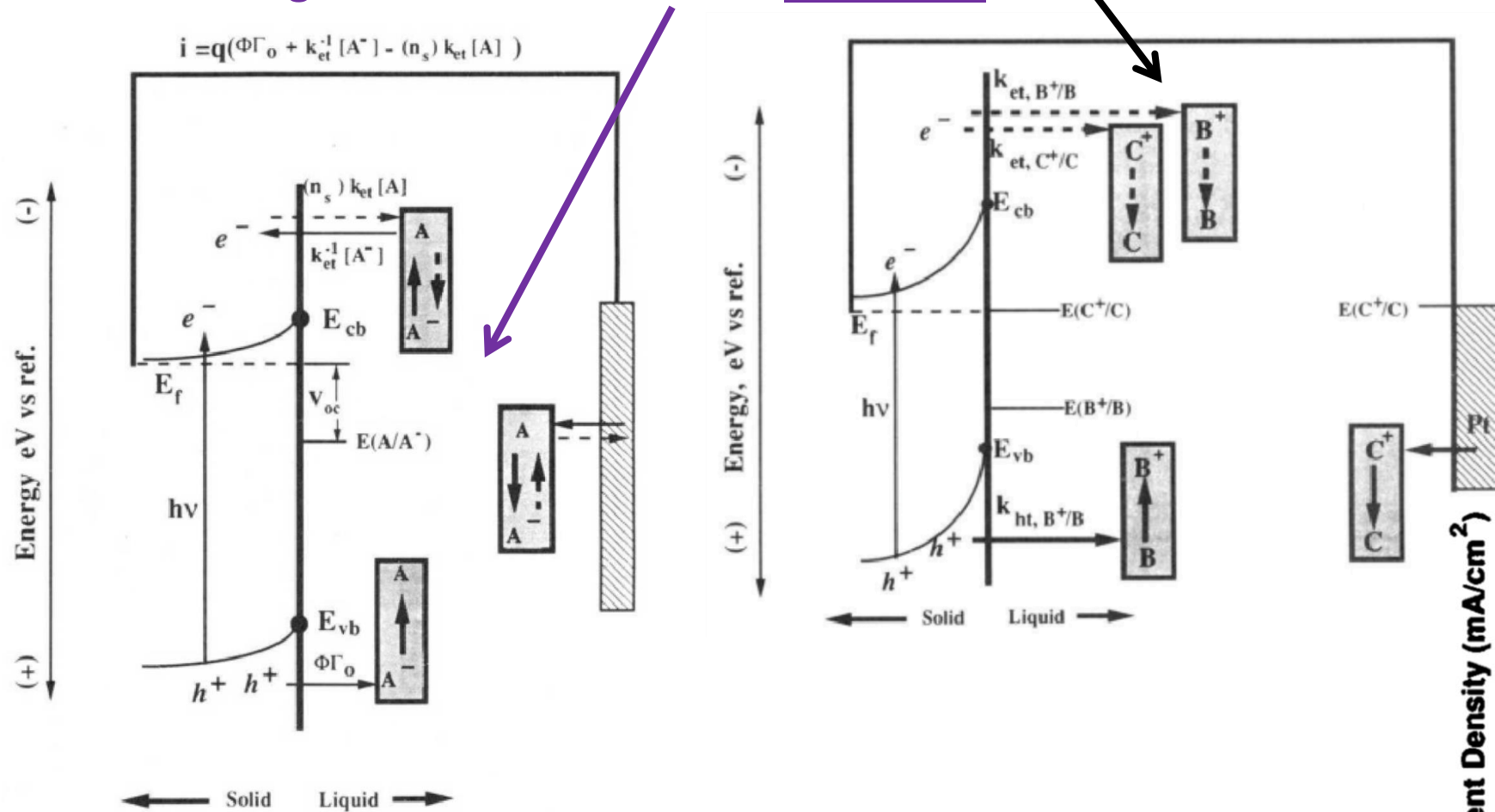
... the goal is to have a large value for V_{oc} ($\Delta\mu_i$)... and then a large value for I_{sc} will follow

Photoelectrosynthesis

... thank you Shockley, Queisser, **(BRIEFLY)** 320 Henry, De Vos, Pauwels, Würfel, Ross, Hsiao, Bolton, et al.!

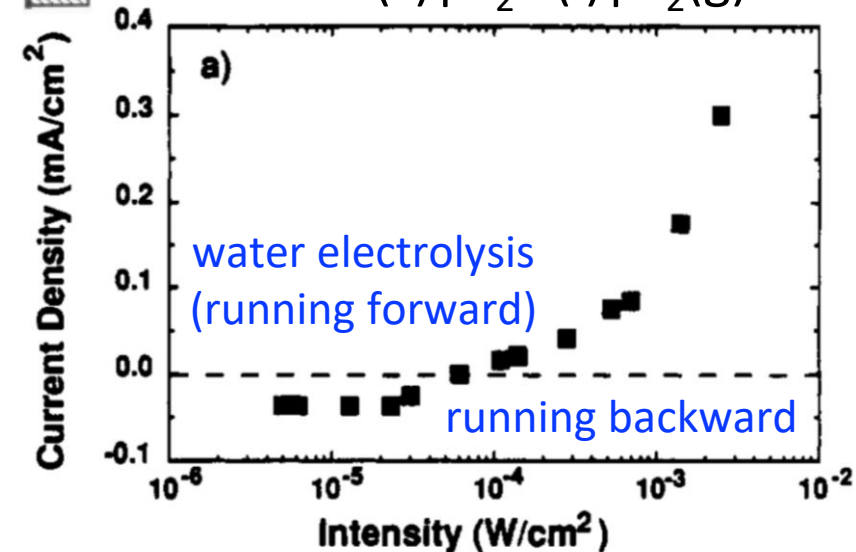
... versus Regenerative Photoelectrochemistry

... thank you Marcus, Hush, Taube, Gerischer, Closs, Miller, Creutz, Chidsey, et al.!



... this generates electricity... one aims to maximize power = $j \times V$

WE: $SrTiO_3(s) | H_2O(l) | O_2(g)$
 CE: $Pt(s) | H_2O(l) | H_2(g)$

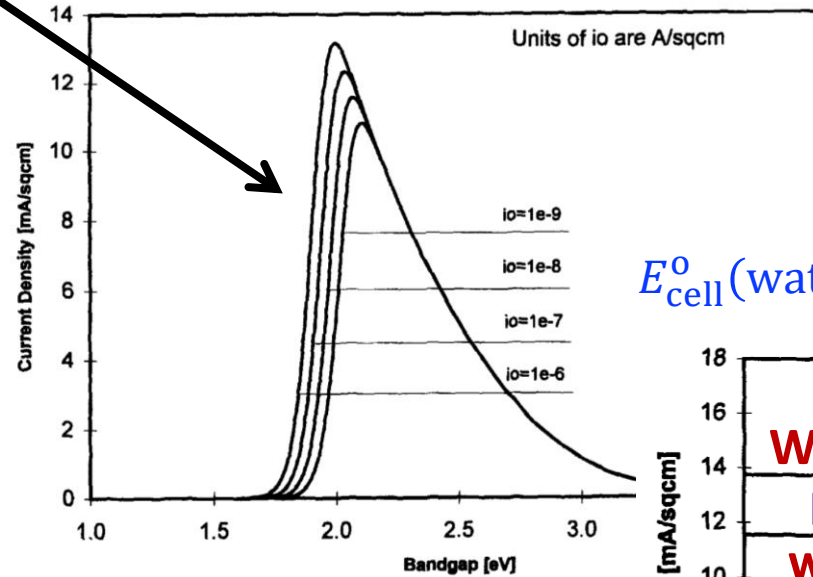
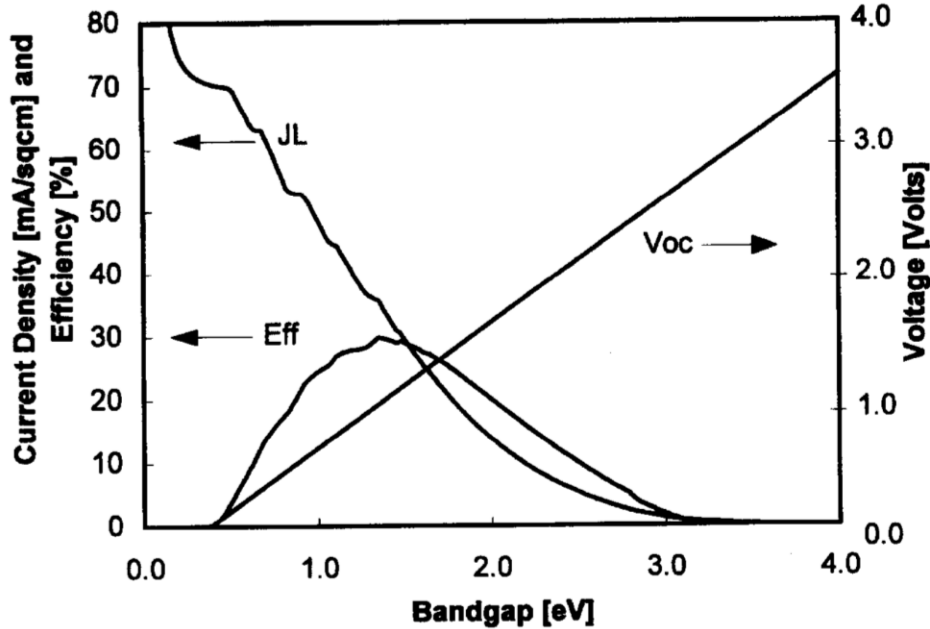


Load Line Analysis

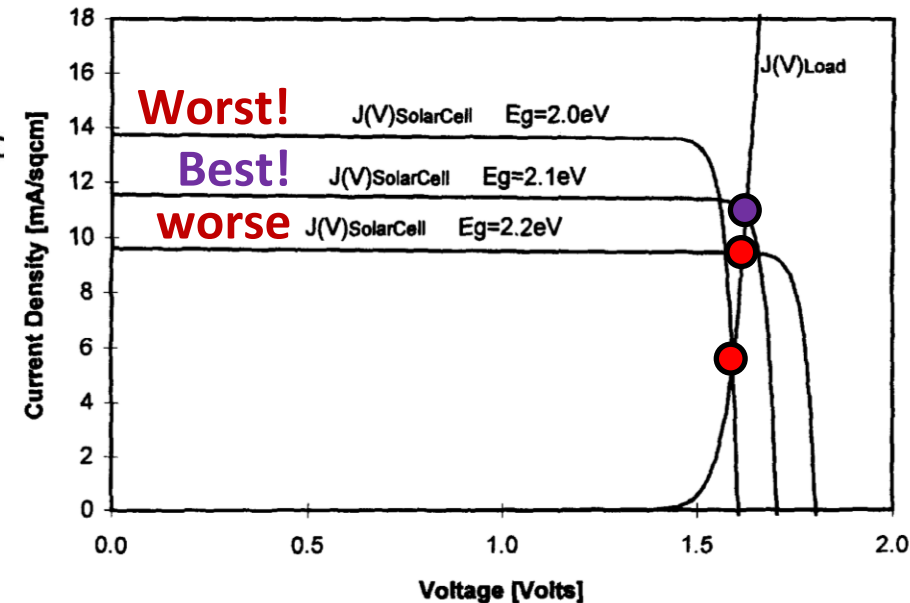
... thank you Shockley, Queisser, **(BRIEFLY)** 321 Henry, De Vos, Pauwels, Würfel, Ross, Hsiao, Bolton, et al.!

... photogenerated j vs. V data (power curve)...
 ... must be current matched with required j vs. V' data (load curve)...
 ... and there is a minimum value of $V = \Delta G/nF$ to form products

... thank you Marcus, Hush, Taube, Gerischer, Closs, Miller, Creutz, Chidsey, et al.!

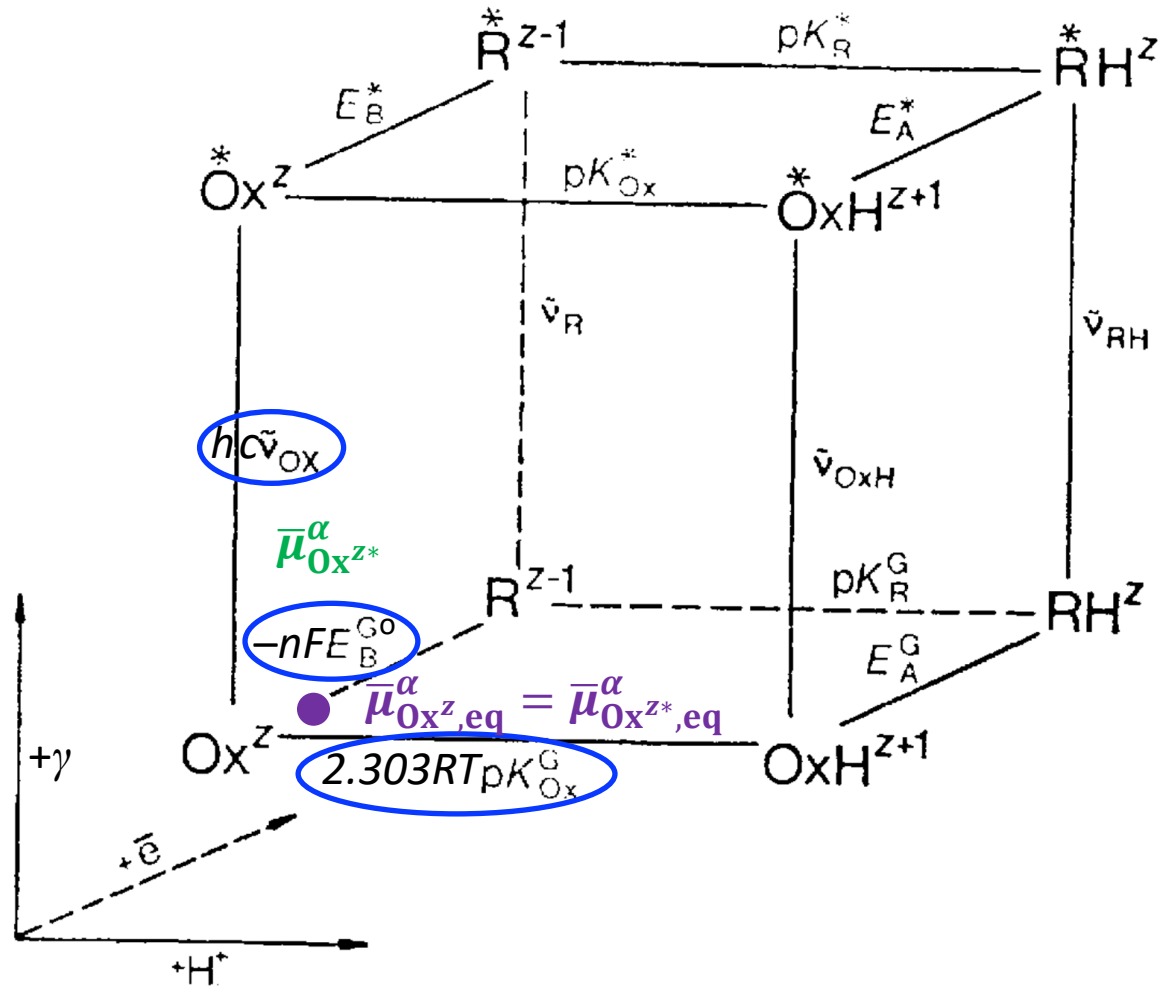


$$E_{\text{cell}}^{\circ}(\text{water electrolysis}) = -1.23 \text{ V}$$



... this generates electricity... one aims to maximize power = $j \times V$

Förster Cube and Square Schemes



... all of these free energy terms are **standard-state** free energies (ΔG°)... but what is the actual free energy of the system (ΔG)?

... let's assume that $\Delta G = 0$ (equilibrium)... how could I indicate that on this slide, as a point(s), to depict the majority species present?

... now, how can one **push/pull** this system out of equilibrium?

... recall Le Châtelier's principle... and thus by addition of reactants or removal of products... such as mass or light!

... hopefully this made a little more sense this time around... and if not, **WE ARE OUT OF TIME!**

Today's Critical Guiding Question

With knowledge of how to define all rate constants and diffusion coefficients for all continuity/conservation laws that are most important for thermal process and photophysical processes, how can they be used to (i) assess the applicability of Marcus theory for photochemical processes and (ii) predict steady-state photochemical energy conversion efficiencies?... now for part (ii)

Photochemistry

- Excited-state electron transfer, Excited-state proton transfer, Förster cycle, Stern–Volmer quenching (Static and Dynamic)
- Rehm–Weller equation, Diffusion-limited processes, Electrostatic work terms
- Photochemical length scales, Photochemical time scales, Electromagnetic spectrum, Pump–probe transient spectroscopies, General spectroscopic layouts, Neodymium-doped yttrium aluminum garnet (Nd:YAG) laser, Q-switching, Pockels cell, Brewster angle, Titanium-doped sapphire (Ti:sapph) laser, Mode-locking, Delay line
- Statistical mechanics distributions, Detailed balance analysis, Photoelectrochemistry, Photoelectrosynthesis, Load line analysis

ALL DONE!...

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