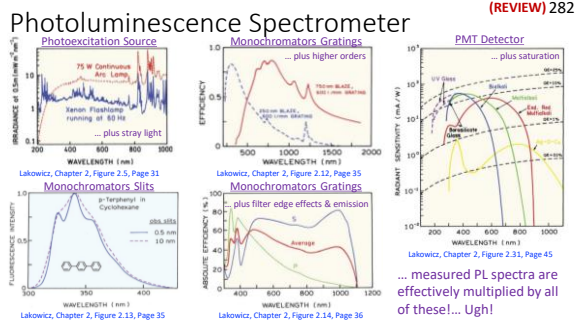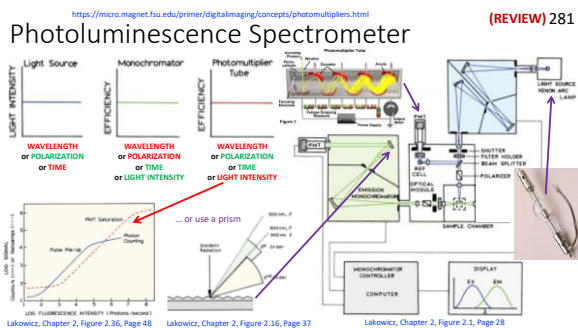# Lecture #12 of 12
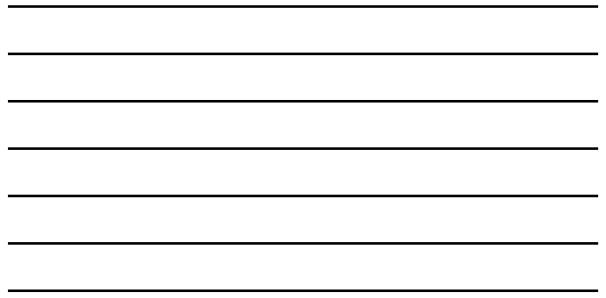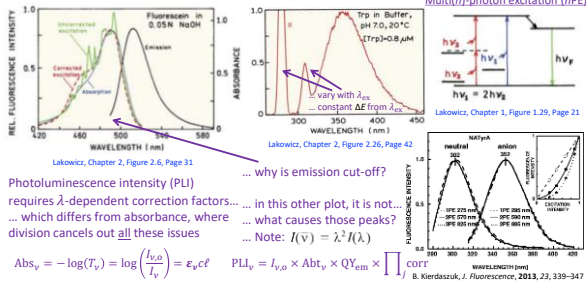### {80 min away from no more lectures... tear}

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

(REVIEW) 281

Photoluminescence Spectrometer

Lakowicz, Chapter 2, Figure 2.36, Page 48   Lakowicz, Chapter 2, Figure 2.16, Page 37   Lakowicz, Chapter 2, Figure 2.1, Page 28

(REVIEW) 282

Photoluminescence Spectrometer

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

Emission & Excitation Spectra

Multi(n)-photon excitation (nPE)

Lakowicz, Chapter 1, Figure 1.29, Page 21

Lakowicz, Chapter 2, Figure 2.26, Page 42

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

... why is emission cut-off?
... in this other plot, it is not...
... what causes those peaks?
... Note: $I(\bar{v}) = \lambda^2 I(\lambda)$

$$\text{Abs}_v = -\log(T_v) = \log\left(\frac{I_{v,o}}{I_v}\right) = \varepsilon_v c\ell \qquad \text{PLI}_v = I_{v,o} \times \text{Abt}_v \times \text{QY}_{em} \times \prod \text{corr}$$
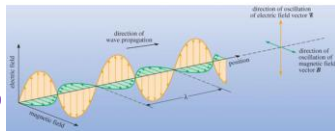
B. Kierdaszuk, *J. Fluorescence*, **2013**, *23*, 339–347

Photon Properties & Conservation Laws

Where does light come from?
Particle Type: Boson
Mass: 0
Charge: 0
Energy: $E = hv = \hbar\omega$
Linear Velocity: $\frac{c}{n} = \left(\frac{\lambda}{n}\right)v = \lambda'v$
Linear Momentum: $p = \frac{h}{\lambda'} = \frac{nhv}{c} \approx 0$
Linear Polarization: $\vec{E}$ and $\vec{B}$

z-Direction Angular Momentum / Circular Polarization / Chirality / Helicity / Spin: $\pm\hbar = \pm\frac{h}{2\pi}$
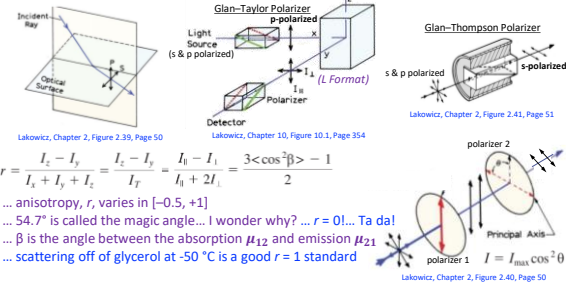
With what matter does light interact?
Fermion Angular Momentum (Orbital, Spin)
Magnitude: $\hbar\sqrt{J(J+1)}$
z-Direction: $m_J\hbar$, $m_J = [-J, J]$ in steps of 1
Multiplicity/Degeneracy, g_J: $2J + 1$

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?

Polarization & Anisotropy

285

Glan–Taylor Polarizer
Glan–Thompson Polarizer

Lakowicz, Chapter 2, Figure 2.39, Page 50
Lakowicz, Chapter 10, Figure 10.1, Page 354
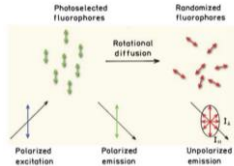Lakowicz, Chapter 2, Figure 2.41, Page 51

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

... 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

$I = I_{max}\cos^2\theta$

Lakowicz, Chapter 2, Figure 2.40, Page 50

Polarization & Anisotropy

9–AS
... in propylene glycol at -52 °C

PL Excitation Spectrum

Lakowicz, Chapter 1, Figure 1.15, Page 13   Lakowicz, Chapter 10, Figure 10.8, Page 360

Perrin equation

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

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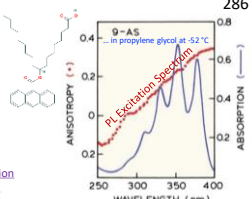
$$\theta = \frac{\eta V}{RT} = 100 \text{ ps at RT}$$

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

... assuming a random orientation of molecules in the dark...   ... and because of this...
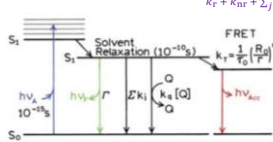where β is the angle between the absorption and emission transitions.   ... r_0 varies in [−0.2, +0.4]

E-S Lifetime & Emission Quantum Yield

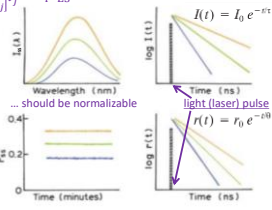Excited-State Lifetime, $\tau_{ES} = \frac{1}{k_r + k_{nr} + \sum_j k_j[Q_j]^{v_j}} = \langle t \rangle = t_{\left(\frac{100}{e}\right)\%}$

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

... R is an actinometer

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

Solvent Relaxation (10^{-10}s)

FRET $k_t = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6$

$I(t) = I_0 e^{-t\tau}$

... should be normalizable   light (laser) pulse

$r(t) = r_0 e^{-t\theta}$

Lakowicz, Chapter 1, Figure 1.14, Page 11

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

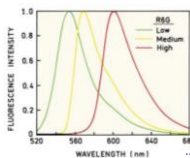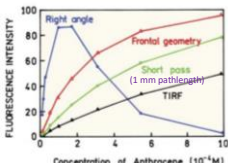Lakowicz, Chapter 1, Figure 1.17, Page 14

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!

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

Right angle   Frontal geometry   Short pass (1 mm pathlength)   TIRF

Lakowicz, Chapter 2, Figure 2.47, Page 56

... what if this effect was not caused by changing concentration...
Lakowicz, Chapter 2, Figure 2.49, Page 57   ... 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?
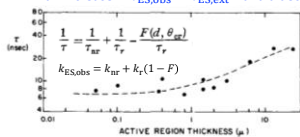 … an increase in $\tau_{ES,obs} = \tau_{ES,ext}$… and a decrease in $\phi_{em,ext}$

$$\frac{1}{\tau} = \frac{1}{\tau_{nr}} + \frac{1}{\tau_r} - \frac{F(d, \theta_{cr})}{\tau_r}$$

$$k_{ES,obs} = k_{nr} + k_r(1 - F)$$

FIG. 2. Recombination lifetime versus active region thickness.
The dots represent experimental data from Ref. 2 correspond-
ing to $x = 0, 5$; the dashed curve has been obtained theoretically
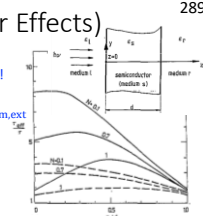(see text).

P. Asbeck, *J. Appl. Phys.*, **1977**, *48*, 820–822

V. Badescu & P. T. Landsberg, *Semicond. Sci. Technol.*, **1993**, *8*, 1267–1276

UCI CHEM267 – Photochemistry, Spring 2023   290

Photochemistry

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University of California Irvine

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?
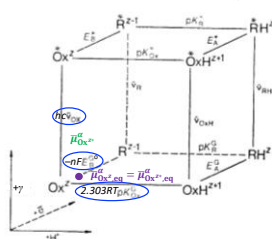
Photochemistry

- **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**

… okay… now let's try this again…

Förster Cube and Square Schemes

(REVIEW) 293

… all of these free energy <u>terms</u> are **standard-state** free energies (ΔG^o)… but what is the actual free energy of the system (ΔG)?

… let's assume that ΔG = 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 <u>or light</u>!

… hopefully this made a little more sense this time around… and if not, <u>WE ARE (NEARLY) OUT OF TIME</u>!

Z. R. Grabowski & W. Rubaszewska, *J. Chem. Soc. Faraday Trans. 1*, **1977**, *73*, 11–28
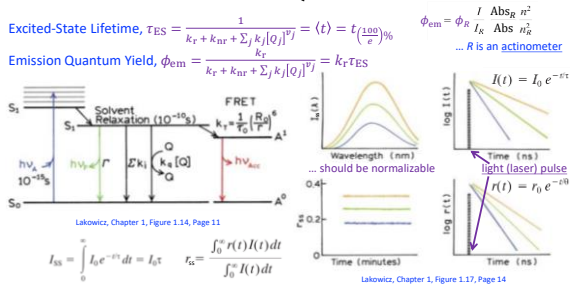

Jablonski Diagram

(REVIEW) 294

<u>Kasha–Vavilov "rule"</u>: 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
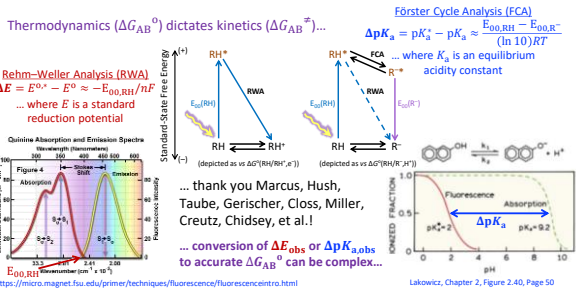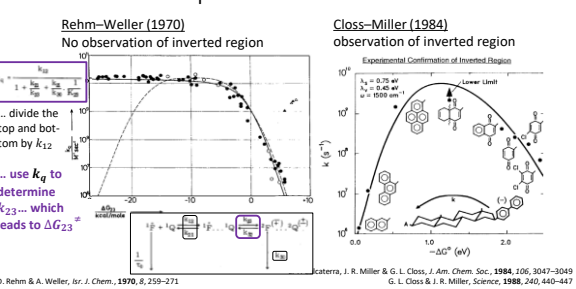

https://micro.magnet.fsu.edu/primer/java/jablonski/jabintro/index.html
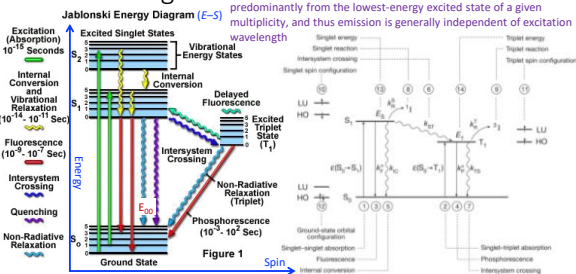
Turro, Chapter 1, Scheme 1.4, Page 17

E-S Lifetime & Emission Quantum Yield

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

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

... R is an <u>actinometer</u>

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

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

$I(t) = I_0 e^{-t/\tau}$

$r(t) = r_0 e^{-t/\theta}$

Lakowicz, Chapter 1, Figure 1.17, Page 14

Excited-State Electron Transfer *vs* Proton Transfer   296

Thermodynamics (ΔG_{AB}^o) dictates kinetics ($\Delta G_{AB}^{\neq}$)...

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)
$\Delta E = E^{o,*} - E^o \approx -E_{00,RH}/nF$
... where E is a standard reduction potential

... 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}^o can be complex...

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

Lakowicz, Chapter 2, Figure 2.40, Page 50

Rehm–Weller Equation   297

Rehm–Weller (1970)
No observation of inverted region

Closs–Miller (1984)
observation of inverted region

... divide the top and bottom by k_{12}

... use k_q to determine k_{23}... which leads to $\Delta G_{23}^{\neq}$

D. Rehm & A. Weller, *Isr. J. Chem.*, **1970**, 8, 259–271

...caterra, 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

$k_q = \dfrac{k_{12}}{1 + \frac{k_{21}}{k_{23}} + \frac{k_{21}}{k_{23}}\frac{k_{32}}{k_{34}}}$

... this seems to be limited by diffusion...

... divide the top and bottom by k_{12}

... which term is the work term?

... use ΔE, plus light and/or electrostatic work terms, to determine $\Delta G_{23}^{\,o}$

$\Delta G_{23} = 23.06(E(D/D^+) - E(A^-/A) - \frac{e_0^2}{\varepsilon a}) - \Delta E_{0,0}$

D. Rehm & A. Weller, *Isr. J. Chem.*, **1970**, *8*, 259–271
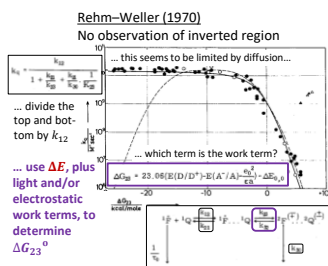
The collisional frequency (Z) of a fluorophore with a quencher is given by

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

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

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

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

where k is Boltzmann's constant, η is the solvent viscosity, and R is the molecular radius. Lakowicz, Chapter 8, Pages 281

Rate-Determining Step (RDS)

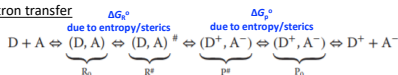$$D + A \rightleftarrows D^+ + A^-$$
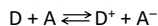
Poisson's Equation (from Gauss's law)

$$\frac{\partial^2 \phi(x)}{\partial x^2} = -\frac{\rho}{\varepsilon} \qquad \mathbf{E} = -\frac{\partial \phi(x)}{\partial x}$$
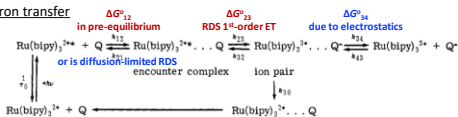
$$\phi(r) = \frac{q}{4\pi\varepsilon r}$$

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

$$D + A \Leftrightarrow \underbrace{(D, A)}_{R_0} \overset{\Delta G_0^{\,o}\;\text{due to entropy/sterics}}{\Leftrightarrow} \underbrace{(D, A)}_{R^\#}{}^{\#} \Leftrightarrow \underbrace{(D^+, A^-)}_{P^\#} \overset{\Delta G_p^{\,o}\;\text{due to entropy/sterics}}{\Leftrightarrow} \underbrace{(D^+, A^-)}_{P_0} \Leftrightarrow D^+ + A^-$$

Excited-state electron transfer

ΔG^o_{12} in pre-equilibrium ΔG^o_{23} RDS 1st-order ET ΔG^o_{34} due to electrostatics

or is diffusion-limited RDS   encounter complex   ion pair

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

$$D + A \overset{①}{\rightleftarrows} (D, A) \overset{②}{\rightleftarrows} (D^+, A^-) \overset{③}{\rightleftarrows} D^+ + A^-$$
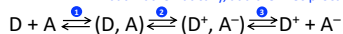
... so how does one determine the **observed** rate constant for 3 reactions **in series**?

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

... 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...

$$\dfrac{1}{k_{f,\text{obs}}} = \dfrac{1}{k_{1f}} + \dfrac{1}{K_1 k_{2f}} + \dfrac{1}{K_1 K_2 k_{3f}} = \dfrac{1}{k_{1f}} + \dfrac{k_{1b}}{k_{1f}k_{2f}} + \dfrac{k_{1b}k_{2b}}{k_{1f}k_{2f}k_{3f}}$$
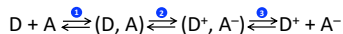
... and for completion, what if 3 (same-order) reactions occur simultaneously, i.e. **in parallel**?

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

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…

$$D + A \overset{\text{①}}{\rightleftharpoons} (D, A) \overset{\text{②}}{\rightleftharpoons} (D^+, A^-) \overset{\text{③}}{\rightleftharpoons} D^+ + A^-$$

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

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

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

… 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

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

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

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

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

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

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

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

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

… conversion of $k_{q,\text{obs}}$ to $\Delta G_{AB}^{\ddagger}$ can be nontrivial

9

Photochemical Length/Time Scales 307

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 308

... what can one do with microwaves?

(1.9 GHz)

(~60 GHz)

(~2.45 GHz)

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

Pump–Probe Transient Spectroscopies 309

... 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)...
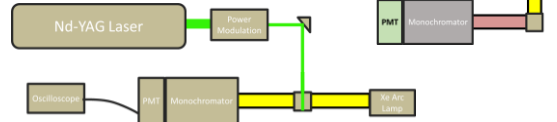... let's start with "just fast"...

General Spectroscopic Layouts

Electronic Absorption Spectroscopy

Steady-state Photoluminescence Spectroscopy

Transient Absorption / Time-Resolved Photoluminescence Spectroscopies

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

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:Al$_2$O$_3$) Ultrafast Laser

(light travels ~1 foot in 1 nanosecond)

... look!... no slits!

(this is a tiny blip on Abs)

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

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

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)
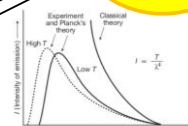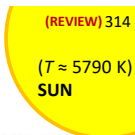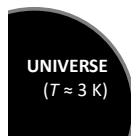
Blackbody Radiation

(REVIEW) 314

($T \approx 5790$ K)
SUN

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

EARTH
($T \approx 290$ K)

UNIVERSE
($T \approx 3$ 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

Turro, Chapter 4, Figure 4.1, Page 171

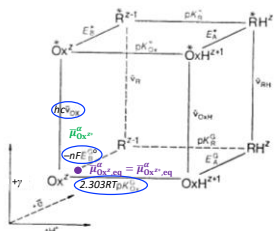**... okay... now let's try this again...**

Förster Cube and Square Schemes

(REVIEW) 315

... all of these free energy <u>terms</u> are **standard-state** free energies (ΔG^o)... 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 <u>or light</u>!

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

Z. R. Grabowski & W. Rubaszewska, *J. Chem. Soc. Faraday Trans. 1*, **1977**, *73*, 11–28

E-S Lifetime & Emission Quantum Yield

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

$\phi_{em} = \phi_R \dfrac{I}{I_R} \dfrac{\text{Abs}_R}{\text{Abs}} \dfrac{n^2}{n_R^2}$

... R is an <u>actinometer</u>

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

$I(t) = I_0\, e^{-t/\tau}$

FRET $k_T = \frac{1}{\tau_0}\left(\frac{R_0}{r}\right)^6$

Solvent Relaxation (10^{-10}s)

... should be normalizable

light (laser) pulse

$r(t) = r_0\, e^{-t/\theta}$

Lakowicz, Chapter 1, Figure 1.14, Page 11

$I_{SS} = \int\limits_0^\infty I_0 e^{-t/\tau}\, dt = I_0 \tau$ $r_{SS} = \dfrac{\int_0^\infty r(t) I(t)\, dt}{\int_0^\infty I(t)\, dt}$

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?

<u>Boltzmann distribution</u>

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

... 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!

<u>Fermi–Dirac distribution</u>

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

... fermions (half-integer spin particles)... e.g. <u>electrons</u>
... 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

<u>Bose–Einstein distribution</u>

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

... bosons (integer spin particles)... e.g. <u>photons</u>
... 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
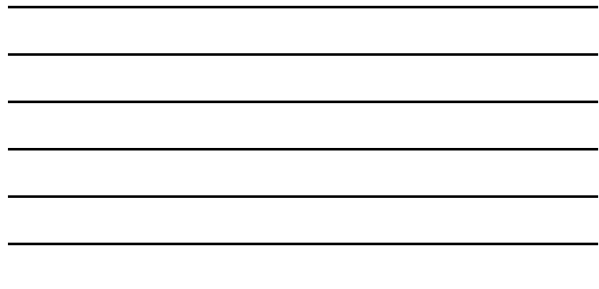
Detailed-Balance Analysis
... thank you Shockley, Queisser, Henry, De Vos, Pauwels, Würfel, Ross, Hsiao, Bolton, et al.!

... at equilibrium in the dark, meaning $\sum_i v_i \mu_i = 0$, 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, $\Phi_{G_{rad},eq} = \dfrac{4\pi}{c^2} \int_{E_g/h}^{\infty} \alpha_v v^2 e^{-hv/kT}\, dv = \Phi_{G_{rad}} = -\Phi_{R_{rad},eq}$... in units of mol cm^{-2} 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 $\Delta\mu_{ES} \neq 0$ and $\Delta n_{ES} \neq 0$... in the presence of sunlight, $\Phi_{G_{solar}}$, at steady-state one has $\Phi_{R_{rad}} = \Phi_{R_{rad},eq} e^{\Delta\mu_{ES}/kT} = -\left(\Phi_{G_{rad}} + \Phi_{G_{solar}}\right)$

... non-radiative processes occur in parallel to these photophysical processes, both in the dark and in the light, with $\Phi_{G_{nonrad},eq} = \Phi_{G_{rad},eq}\left(\dfrac{1 - \phi_{em}}{\phi_{em}}\right) = \Phi_{G_{nonrad}}$ and $\Phi_{R_{nonrad}} = \Phi_{R_{rad},eq}\left(\dfrac{1 - \phi_{em}}{\phi_{em}}\right) e^{\Delta\mu_{ES}/kT}$

... max. useful work is $\Delta\mu_{ES}$ (= $-FV_{oc}$) when $\Phi_{G_{rad},eq} + \Phi_{G_{nonrad},eq} + \Phi_{G_{solar}} + \Phi_{R_{rad}} + \Phi_{R_{nonrad}} = 0$
... useful work occurs by additional reversible (productive) quenching processes, $\Phi_{R_{work}}$, which result in a decreased value of $\Delta\mu_{ES}$ as $\Phi_{R_{work}} = \Phi_{G_{rad},eq}\left(\dfrac{1}{\phi_{em}}\right)\left(1 - e^{\Delta\mu_{ES}/kT}\right) + \Phi_{G_{solar}}$
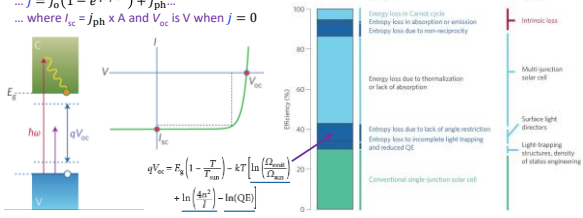... this leads to $j = j_o\left(1 - e^{qV/kT}\right) + j_{ph}$... which is the photodiode eqn.... but is purely thermodynamic!

Photoelectrochemistry

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

… $j = j_o\left(1 - e^{qV/kT}\right) + j_{ph}$…

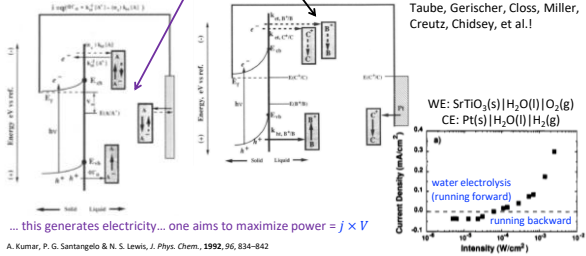… where $I_{sc} = j_{ph}$ x A and V_{oc} is V when $j = 0$

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

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

A. Polman & H. A. Atwater, *Nat. Mater.*, **2012**, *11*, 174–177

Photoelectrosynthesis

… *versus* Regenerative Photoelectrochemistry

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

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

water electrolysis (running forward)

running backward

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

A. Kumar, P. G. Santangelo & N. S. Lewis, *J. Phys. Chem.*, **1992**, *96*, 834–842

Load Line Analysis

… 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

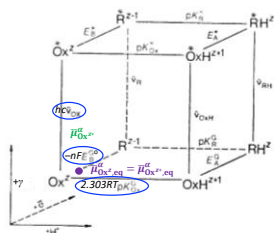… thank you Marcus, Hush, Taube, Gerischer, Closs, Miller, Creutz, Chidsey, et al.!

$E^\ominus_{cell}$(water electrolysis) $= -1.23$ V

Worst!

Best!

worse

… this generates electricity… one aims to maximize power = $j \times V$
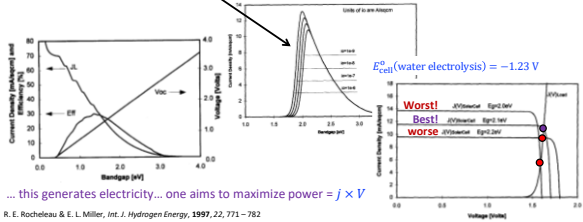
R. E. Rocheleau & E. L. Miller, *Int. J. Hydrogen Energy*, **1997**, *22*, 771 – 782

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Photochemistry

324

- **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!

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