Lecture #13 of 14

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

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Chemical Kinetics *(let's review* T**W**Th*)*

- T: Continuity of mass, Mass transfer, Nernst–Planck equation, Diffusion, Diffusion coefficient, Migration, Mobility, Convection, Boundary layer

- **W: Mass action, Microscopic reversibility, Förster cube, Square schemes, Rate constants, Activation energies, Transition-state theory, Marcus–Hush theory, Transition-state character, Reorganization energies (outer and inner)**

- Th: Linear free energy relationships, Charge transfer across electrified interfaces, Butler–Volm*er equation, Fermi's golden rule, Solid-state physics, Marcus–Gerischer theory, Rate-determining step, Steady-state & Pre-equilibrium approximations, Langmuir/Frumkin isotherms*

Summary of Key Equations and Equilibrium

$$A \rightleftharpoons B$$
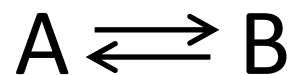
$$\frac{\partial c_{A,z_o}}{\partial t} = \sum_j R_{A,j}$$

(Chemists should be yawning)

$$\bar{\mu}_B^\alpha - \bar{\mu}_A^\alpha = \Delta G^\alpha = \Delta G^{o,\alpha} + RT \ln Q \dots \text{ where } Q = \frac{a_B^\alpha}{a_A^\alpha} = \frac{\gamma_B^\alpha(c_B^\alpha/c_B^{0,\alpha})}{\gamma_A^\alpha(c_A^\alpha/c_A^{0,\alpha})}$$

$$R_{A,f} = -k_f a_A \qquad R_{B,f} = +k_f a_A \qquad k_j \text{ (M/s)... a rate!}$$

$$R_{A,b} = +k_b a_B \qquad R_{B,b} = -k_b a_B \qquad k_j' \text{ (s}^{-1}\text{)... an inverse time constant!}$$

$$\bar{\mu}_i^\alpha = \left(\frac{\partial G^\alpha}{\partial n_i^\alpha}\right)_{T,p,n_{j\neq i}^\alpha} \qquad \frac{\partial c_{A,z_o}^\alpha}{\partial t} = -k_f a_A^\alpha + k_b a_B^\alpha = -k_f' c_A^\alpha + k_b' c_B^\alpha = -\frac{\partial c_{B,z_o}^\alpha}{\partial t}$$
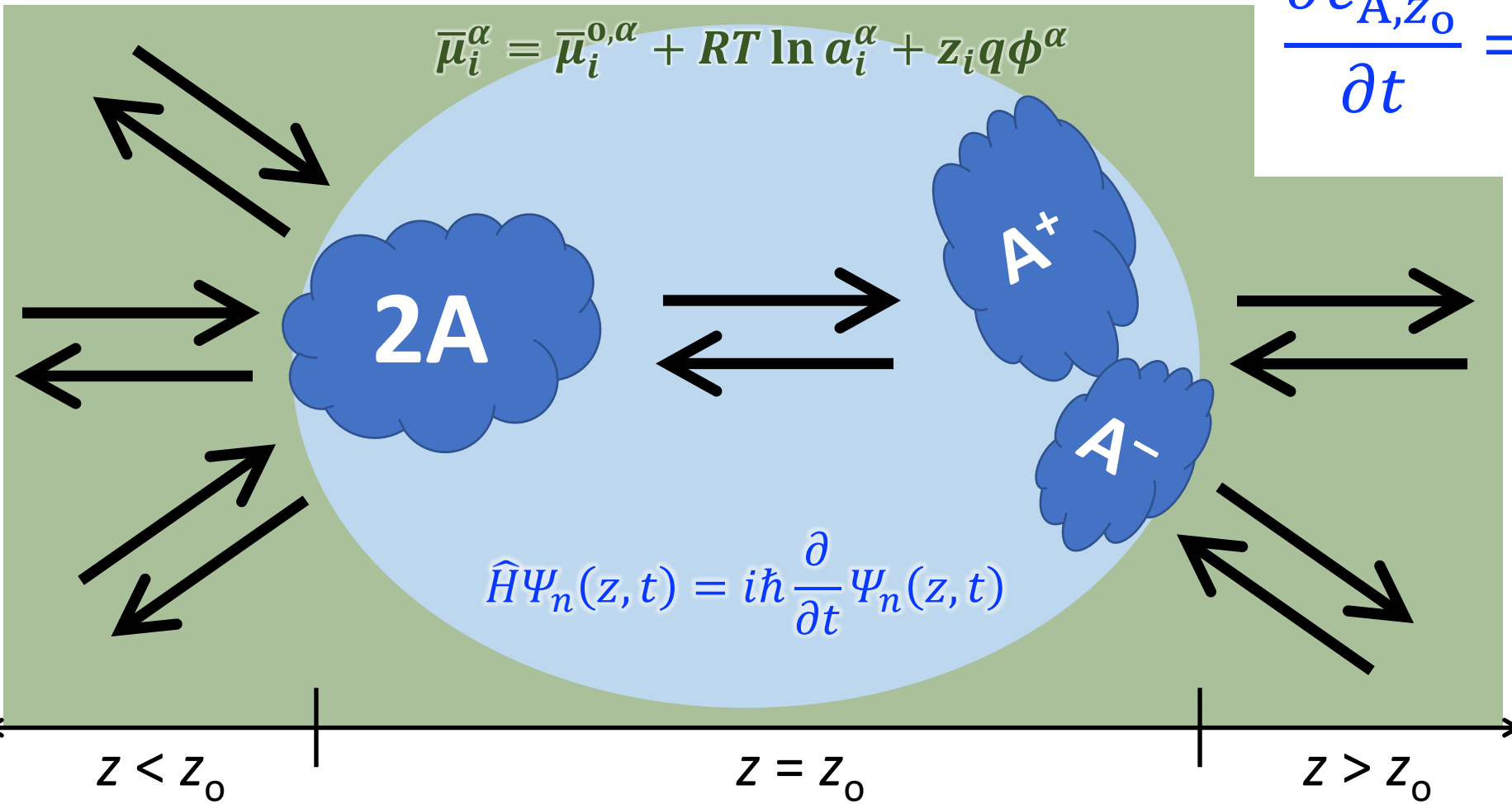
Now, consider the reaction to be at equilibrium (3 ways)... $\Delta G^\alpha = 0 = \Delta G^{o,\alpha} + RT \ln Q$

$$\dots \text{ and so, } \Delta G^{o,\alpha} = -RT \ln K, \text{ with } K = \frac{a_{B,eq}^\alpha}{a_{A,eq}^\alpha} = \frac{\gamma_B^\alpha\left(c_{B,eq}^\alpha/c_B^{0,\alpha}\right)}{\gamma_A^\alpha\left(c_{A,eq}^\alpha/c_A^{0,\alpha}\right)}$$

And also, $\bar{\mu}_B^\alpha - \bar{\mu}_A^\alpha = 0 \dots$ and so, $\bar{\mu}_A^\alpha = \bar{\mu}_B^\alpha \dots$ if that is even helpful

And also, $\frac{\partial c_{A,z_o}^\alpha}{\partial t} = 0 = -\frac{\partial c_{B,z_o}^\alpha}{\partial t} = -k_f a_{A,eq}^\alpha + k_b a_{B,eq}^\alpha \dots$ and so $\frac{k_f}{k_b} = \frac{a_{B,eq}^\alpha}{a_{A,eq}^\alpha} = \frac{\gamma_B^\alpha\left(c_{B,eq}^\alpha/c_B^{0,\alpha}\right)}{\gamma_A^\alpha\left(c_{A,eq}^\alpha/c_A^{0,\alpha}\right)} = K$

Continuity of Mass

$$\bar{\mu}_i^\alpha = \bar{\mu}_i^{o,\alpha} + RT \ln a_i^\alpha + z_i q \phi^\alpha$$

$$\frac{\partial c_{A,z_o}}{\partial t} = \sum_j R_{A,j} - \frac{\partial N_A}{\partial z}$$

$$\hat{H}\Psi_n(z,t) = i\hbar \frac{\partial}{\partial t}\Psi_n(z,t)$$

Note: Adjusting just one variable is difficult… but people, like us, can try
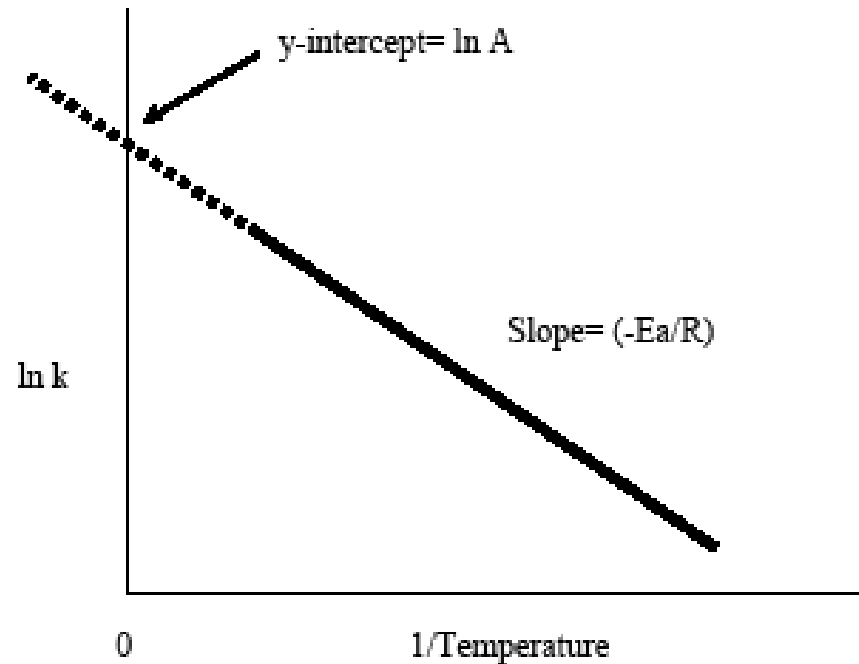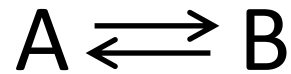
$z < z_o$ $z = z_o$ $z > z_o$

"Jean Piaget, the Swiss psychologist who first studied object permanence in infants, argued that it is one of an infant's most important accomplishments, as, without this concept, objects would have no separate, permanent existence."
– Wiki, Object permanence

Activation Energies

<u>Arrhenius (1889)</u>
empirical rate constant equation

$A \rightleftharpoons B$

$$k_f = Ae^{-\frac{E_a}{RT}}$$ ... **pre-exponential factor**, A, has units of s^{-1}

y-intercept= ln A

ln k

Slope= (-Ea/R)

0   1/Temperature

$A \rightleftharpoons X^{\neq} \rightleftharpoons B$

<u>Eyring–Polanyi–Evans (1930s)</u>
theoretical rate constant equation (from **transition-state theory / activated complex theory**)

$$k_f = \kappa \nu K^{\neq} = \frac{\kappa k_{\mathrm{B}} T}{h} K^{\neq}$$ ... with **transmission coefficient**, κ, and **vibrational frequency**, ν (s^{-1})

... and $R = N_A k_{\mathrm{B}}$ ... and $\frac{\kappa k_{\mathrm{B}} T}{h}$ has units of s^{-1}

$$k_f = \frac{\kappa k_{\mathrm{B}} T}{h} \exp\left(-\frac{\Delta G^{\neq}}{RT}\right) = \frac{\kappa k_{\mathrm{B}} T}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{\Delta H^{\neq}}{RT}\right)$$ ... and so A contains $\Delta S^{\neq}$

... what is the largest predicted pre-exponential factor at 25 °C? **(161 fs)$^{-1}$ = (1.61 x 10^{-13} s)$^{-1}$**

Marcus–Hush Theory

$$\underline{D + A} \rightleftharpoons \underline{D^+ + A^-}$$
$$\quad\; A \qquad\qquad\; B$$

... but how is this a first-order reaction (s⁻¹)?

Marcus–**Hush** (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar} |H_{\mathrm{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\mathrm{AB}}kT}} \exp\left(-\frac{\Delta G_{\mathrm{AB}}^{\neq}}{kT}\right) \quad ... \frac{2\pi|H_{\mathrm{DA}}|^2}{\hbar\sqrt{4\pi\lambda kT}} \text{ has units of s⁻¹}$$

$$A \rightleftharpoons X^{\neq} \rightleftharpoons B$$

Eyring–Polanyi–Evans (1930s)

theoretical rate constant equation (from **transition-state theory / activated complex theory**)

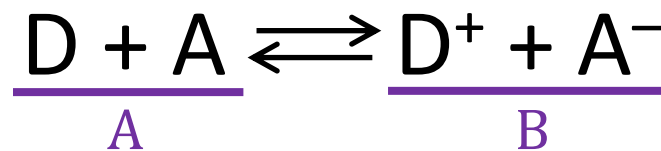$$k_f = \kappa \nu K^{\neq} = \frac{\kappa k_{\mathrm{B}}T}{h} K^{\neq} \quad ... \text{ with } \textbf{transmission coefficient}, \kappa, \text{ and } \textbf{vibrational frequency}, \nu \text{ (s⁻¹)}$$

$$... \text{ and } R = N_A k_{\mathrm{B}} ... \text{ and } \frac{\kappa k_{\mathrm{B}}T}{h} \text{ has units of s⁻¹}$$

$$k_f = \frac{\kappa k_{\mathrm{B}}T}{h} \exp\left(-\frac{\Delta G^{\neq}}{RT}\right) = \frac{\kappa k_{\mathrm{B}}T}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \quad ... \text{ and so } A \text{ contains } \Delta S^{\neq}$$

... what is the largest predicted pre-exponential factor at 25 °C? **(161 fs)⁻¹ = (1.61 x 10⁻¹³ s)⁻¹**

Marcus–Hush Theory

$$D + A \rightleftharpoons D^+ + A^-$$

$$\underbrace{D + A}_{A} \qquad \underbrace{D^+ + A^-}_{B}$$

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{\mathrm{ET}} = \underbrace{\frac{2\pi}{\hbar} |H_{\mathrm{DA}}|^2}_{\substack{\text{quantum adiabatic} \\ \text{electronic coupling}}} \underbrace{\frac{1}{\sqrt{4\pi\lambda_{\mathrm{AB}}kT}} \exp\left(-\frac{\Delta G_{\mathrm{AB}}^{\neq}}{kT}\right)}_{\substack{\text{classical nuclear free-} \\ \text{energy dependence}}}$$

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar} |H_{\mathrm{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\mathrm{AB}}kT}} \exp\left(-\frac{(\lambda_{\mathrm{AB}} + \Delta G_{\mathrm{AB}}^{\mathrm{o}})^2}{4\lambda_{\mathrm{AB}}kT}\right)$$ ... what kind of function is this?

$$\Delta G_{\mathrm{AB}}^{\neq} = \frac{(\lambda_{\mathrm{AB}} + \Delta G_{\mathrm{AB}}^{\mathrm{o}})^2}{4\lambda_{\mathrm{AB}}}$$

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar} |H_{\mathrm{DA}}|^2 \frac{1}{\sqrt{2\pi}\sqrt{2\lambda_{\mathrm{AB}}kT}} \exp\left(-\frac{1}{2}\left(\frac{\Delta G_{\mathrm{AB}}^{\mathrm{o}} - (-\lambda_{\mathrm{AB}})}{\sqrt{2\lambda_{\mathrm{AB}}kT}}\right)^2\right)$$ ... does this help at all?

Marcus–Hush Theory

$$D + A \rightleftharpoons D^+ + A^-$$

$$\underline{A} \qquad \underline{B}$$
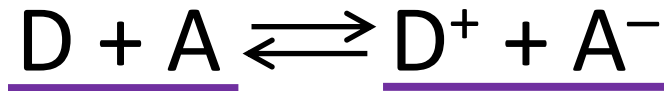
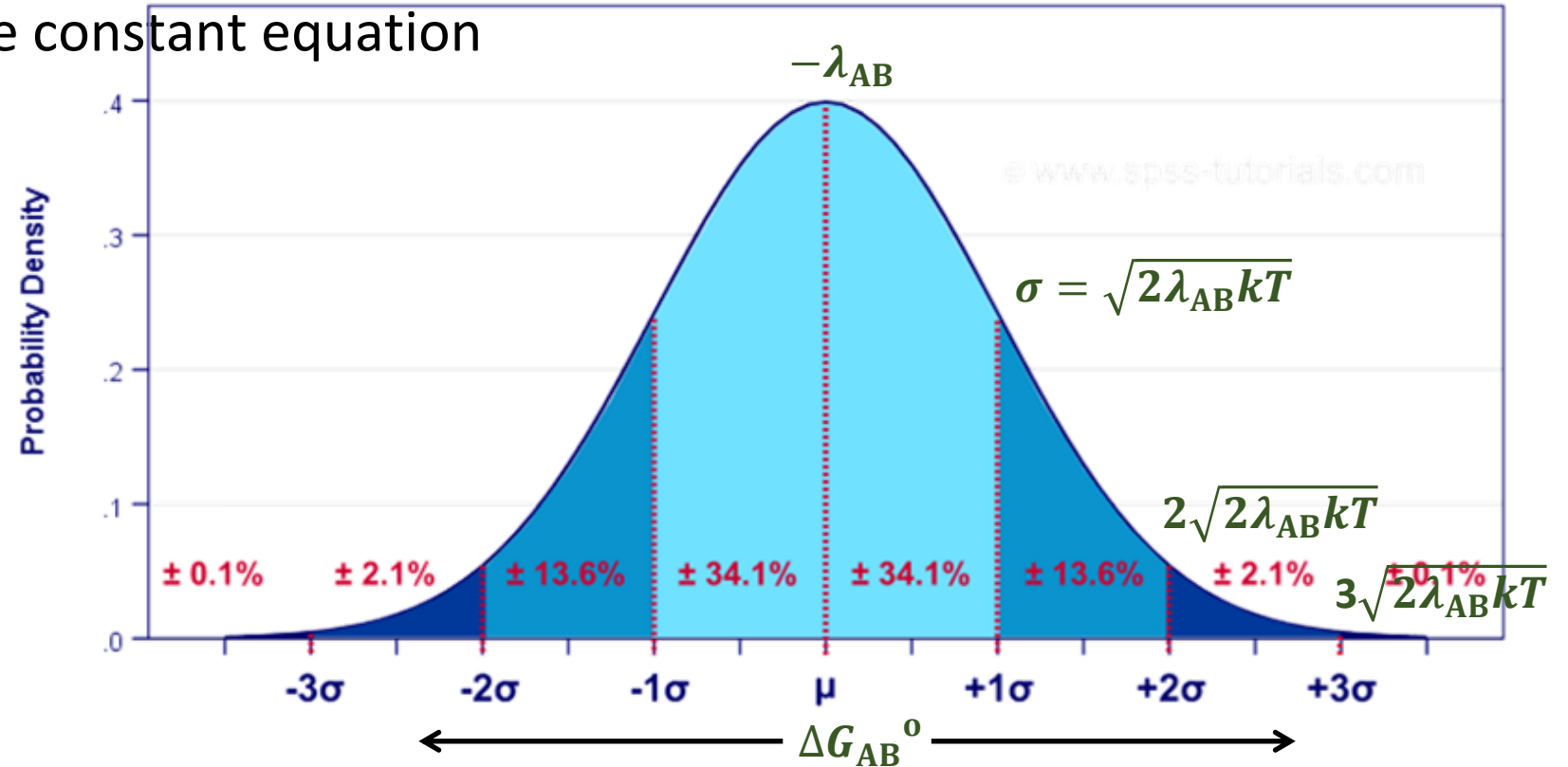**Marcus**–**Hush** (1950s–1960s)

Standard Normal Distribution

$\mu = 0 \mid \sigma = 1$

theoretical (semiclassical) rate constant equation

… wait… the classical component in Marcus electron-transfer theory is a **normal distribution** as a function of standard-state thermodynamic driving force ($\Delta G_{AB}^{\,o}$)?… **Yep!**

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$-\lambda_{AB}$

$\sigma = \sqrt{2\lambda_{AB}kT}$

$2\sqrt{2\lambda_{AB}kT}$

$3\sqrt{2\lambda_{AB}kT}$

± 0.1%   ± 2.1%   ± 13.6%   ± 34.1%   ± 34.1%   ± 13.6%   ± 2.1%   ± 0.1%

-3σ   -2σ   -1σ   μ   +1σ   +2σ   +3σ

$\Delta G_{AB}^{\,o}$

$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{2\pi}\sqrt{2\lambda_{AB}kT}} \exp\left(-\frac{1}{2}\left(\frac{\Delta G_{AB}^{\,o} - (-\lambda_{AB})}{\sqrt{2\lambda_{AB}kT}} \right)^2 \right)$$

… does this help at all?

Charge Transfer across Electrified Interfaces

… aren't these so-called "heterogeneous electron-transfer reactions"?… Sure.

$$e^{-,M} + O \rightleftharpoons R$$

FYI: For each c_O and c_R, electrochemical equilibrium ($j = 0$) is attained via interfacial charge transfer to alter $\Delta\phi^{M|s}$

$$R_O = \frac{\partial c_{O,z_O}}{\partial t} = -k_f c_O + k_b c_R$$

$$j_E = nF\left(-k'_{f,E} c_{O,z_O} + k'_{b,E} c_{R,z_O}\right)$$

… R_O is a rate… with units of M/s (= mol dm^{-3} s^{-1})
… k_j (s^{-1}) is an inverse time constant!

… j_E is a current density… with units of A/cm^2 (= C cm^{-2} s^{-1})
… $k'_{j,E}$ (cm s^{-1}) is a velocity!

… as a specific case choose $E^{o\prime}$… and thus, $j_{E^{o\prime}} = nF\left(-k'_{f,E^{o\prime}} c_{O,z_O} + k'_{b,E^{o\prime}} c_{R,z_O}\right)$

But how does this lead to the Butler–Volmer eqn?…

$$0 = j_{E^{o\prime}} = nF\left(-k'_{f,E^{o\prime}} + k'_{b,E^{o\prime}}\right)$$

$$j_E = j_o\left\{\exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \exp\left(\frac{-\beta F\eta}{RT}\right)\right\}$$

$$k'_{f,E^{o\prime}} = k'_{b,E^{o\prime}} = k^0$$

$$\eta = (E - E_{eq}) = E_{app} = \frac{\Delta G^o}{-nF}$$

… where η (V) is overpotential

… this suggests that we will replace $k'_{j,E}$ velocity rate constants…
… with thermodynamic driving force terms!… But how?… **M–H!**

Charge Transfer across Electrified Interfaces
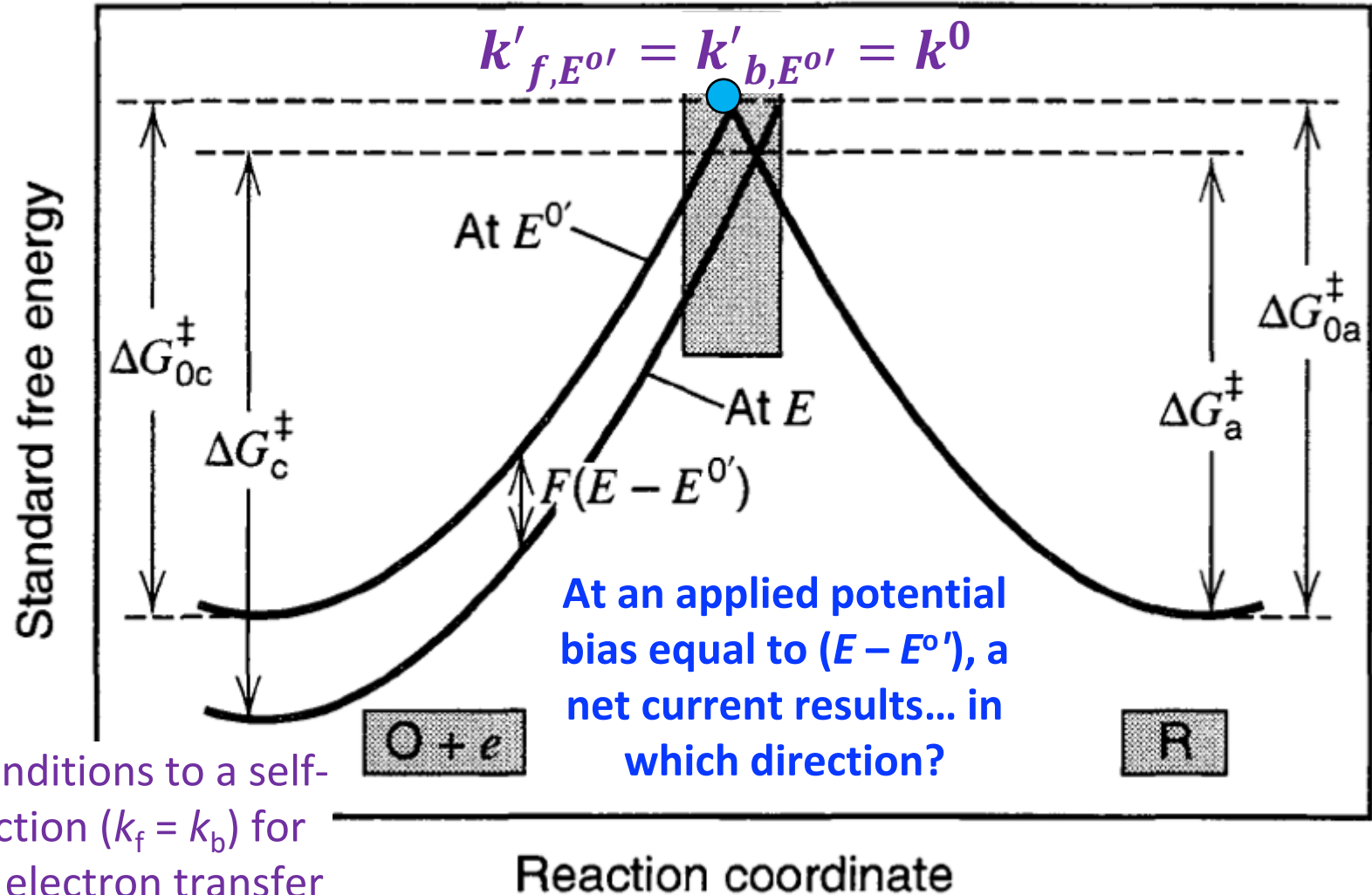
$$e^{-,M} + O \rightleftarrows R$$

Bard & Faulkner, Chapter 3, Figure 3.3.2, Page 95

Key Electrochemical Information

- In electrochemistry, application of a potential, E_{app}, varies the electro-chemical potential of electrons (e^-) in the (M)etal working electrode, $\bar{\mu}_e^M$

- Based on thermodynamics, when written as a reduction reaction, changing $\bar{\mu}_e^M$ alters the free energy **(and also the standard-state free energy)** of the reactants, as $\Delta G_A = \bar{\mu}_e^M + \bar{\mu}_O$ **(and $\Delta G_A^o = \bar{\mu}_e^M + \bar{\mu}_O^o$)**

- *The derivation here assumes that the electrode is inert, e.g. not like battery electrodes*

* analogous conditions to a self-exchange reaction ($k_f = k_b$) for homogeneous electron transfer
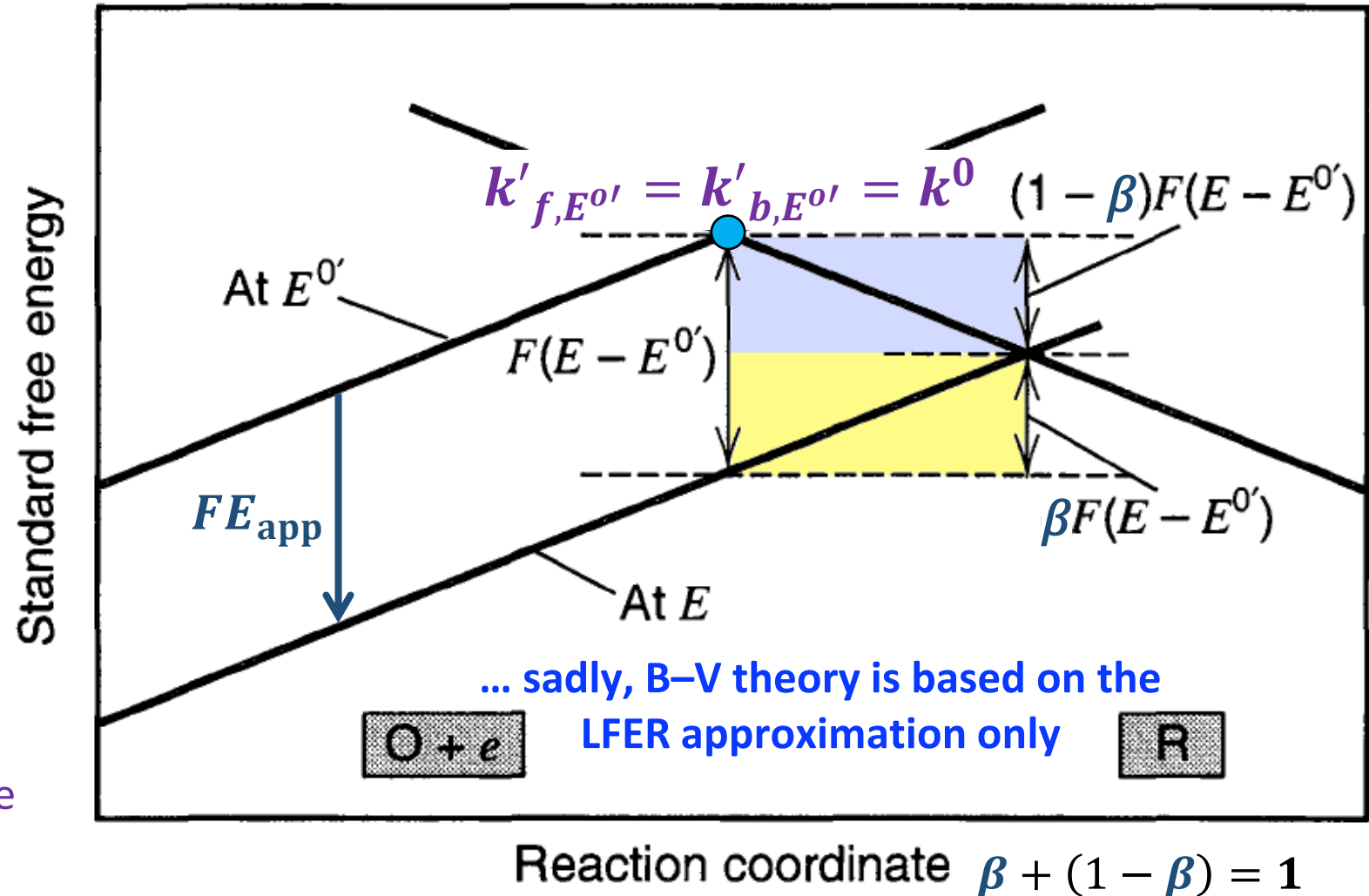
$$k'_{f,E^{o\prime}} = k'_{b,E^{o\prime}} = k^0$$

At $E^{0'}$

At E

$\Delta G_{0c}^{\ddagger}$

$\Delta G_c^{\ddagger}$

$F(E - E^{0'})$

$\Delta G_{0a}^{\ddagger}$

$\Delta G_a^{\ddagger}$

At an applied potential bias equal to ($E - E^{o\prime}$), a net current results... in which direction?

$O + e$

R

Standard free energy

Reaction coordinate

Charge Transfer across Electrified Interfaces

$$e^{-,M} + O \rightleftharpoons R$$

Key Electrochemical Information

Bard & Faulkner, Chapter 3, Figure 3.3.2, Page 95

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- Based on approximations, altering ΔG_A changes all ΔG values on the reaction coordinate relative to the initial ΔG_A, and not along the parabolic/linear shape of the reactant "surface"... **Should it?**

Standard free energy

$$k'_{f,E^{o'}} = k'_{b,E^{o'}} = k^0 \quad (1-\beta)F(E-E^{0'})$$

At $E^{0'}$

$F(E-E^{0'})$

FE_{app}

$\beta F(E-E^{0'})$

At E

... sadly, B–V theory is based on the LFER approximation only

O + e

R

Reaction coordinate

$$\beta + (1-\beta) = 1$$

Butler–Volmer equation

$$e^{-,M} + O \rightleftharpoons R$$

$$j_E = nF\left(k'_{b,E} c_{R,z_O} - k'_{f,E} c_{O,z_O}\right)$$ … for this example, let's assume that $n = 1$…

$$j_E = F k^0 \left\{ c_{R,z_O} \exp\left(\frac{(1-\beta)F(E - E^{O\prime})}{RT}\right) - c_{O,z_O} \exp\left(\frac{-\beta F(E - E^{O\prime})}{RT}\right) \right\}$$

Current–Potential Characteristic

$$j_E = j_o \left\{ \frac{c_{R,z_O}}{c_R^*} \exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \frac{c_{O,z_O}}{c_O^*} \exp\left(\frac{-\beta F\eta}{RT}\right) \right\}$$

$$\eta = \left(E - E_{eq}\right) = E_{app}$$

$$j_o = F k^0 c_R^{*\,\beta} c_O^{*\,(1-\beta)}$$

Current–Overpotential Equation

… c^* means bulk concentration… conversion is trivial using $E_{eq} = E^{O\prime} - \frac{RT}{nF} \ln \frac{c_R^*}{c_O^*}$

$$j_E = j_o \left\{ \exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \exp\left(\frac{-\beta F\eta}{RT}\right) \right\}$$

Butler–Volmer Equation

Tafel Slopes

$$\mathrm{TS_{cath}}^{-1} = \left(\frac{d(\log |j_E|)}{d|\eta|}\right)_{cath} = \frac{-\beta F}{2.303RT}$$

$$\mathrm{TS_{an}}^{-1} = \left(\frac{d(\log j_E)}{d\eta}\right)_{an} = \frac{(1-\beta)F}{2.303RT}$$
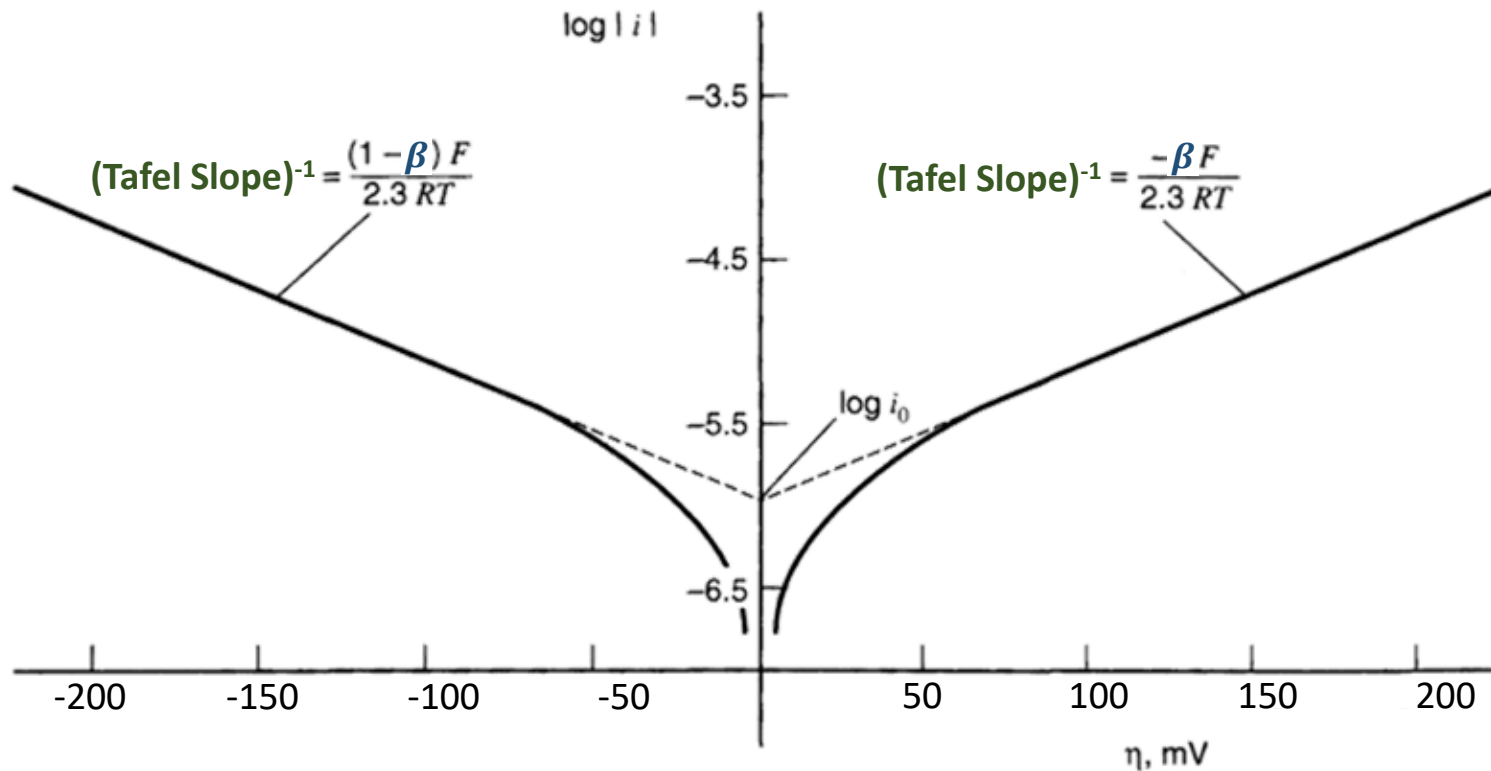
… assuming rapid stirring

Butler–Volmer equation

… let's examine the tradeoff of j_0 and Tafel Slope…

… the latter has units of mV/decade…

… wait, didn't Marcus teach us this should be a parabola?

… then, why is this "potential relationship" so linear?

log | i |

$$(\text{Tafel Slope})^{-1} = \frac{(1-\beta)F}{2.3\,RT}$$

$$(\text{Tafel Slope})^{-1} = \frac{-\beta F}{2.3\,RT}$$

-3.5

-4.5

-5.5

log i_0

-6.5

-200   -150   -100   -50   50   100   150   200

η, mV

Bard & Faulkner, Chapter 3, Figure 3.4.4, Page 103

Quick Quiz: Which catalyst is best?
(A) $j_0 = 10^{-4}$ A cm^{-2}, TS = 120 mV decade^{-1}
(B) $j_0 = 10^{-7}$ A cm^{-2}, TS = 60 mV decade^{-1}

Well, it depends on the desired j_E…

For 1 mA cm^{-2}, (A) is best, but…

For 1 A cm^{-2}, (B) is best…
… because catalyst (A) requires η = 480 mV, while catalyst (B) requires η = 420 mV!

… and neither may be "best" in practice, if they aren't stable or selective for the reaction of interest!

Take-home point: Each current density has a corresponding overpotential!

Fermi's (Second) Golden Rule

$$j_E = nF\left(-\boxed{k'_{f,E}\,c_{O,z_O}} + k'_{b,E}\,c_{R,z_O}\right)$$

k'_j (cm s^{-1})… a velocity!

$$\lambda_{if} = \frac{2\pi}{\hbar}\,|M_{if}|^2\,\rho_f$$

Recall **M–H**… $k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2\frac{1}{\sqrt{4\pi\lambda_{AB}kT}}\exp\left(-\frac{\Delta G_{AB}^{\neq}}{kT}\right)$

Transition probability

Matrix element for the interaction

Density of final states (DoS)

… divide the DoS by c_{i,z_O} …

$D_O(\lambda, \mathbf{E}) = N_A C_O(0, t) W_O(\lambda, \mathbf{E})$

$D_R(\lambda, \mathbf{E}) = N_A C_R(0, t) W_R(\lambda, \mathbf{E})$

$$\mathbf{E} = \mathbf{E}_{F,e^-} = \bar{\mu}_{e^-}$$

(a) Semiconductor | Redox system — Distance x | Density of states

(b) Metal | Redox system — Distance x | Density of states

R. Memming, Chapter 6, Semiconductor Electrochemistry

frequency factor (s^{-1})

$$k_f = \nu \int_{-\infty}^{\infty} \varepsilon_{red}(\mathbf{E}) W_O(\lambda, \mathbf{E}) f(\mathbf{E}) \rho(\mathbf{E})\, d\mathbf{E}$$

proportionality function (cm^3 eV)

$$k_b = \nu \int_{-\infty}^{\infty} \varepsilon_{ox}(\mathbf{E}) W_R(\lambda, \mathbf{E})[1 - f(\mathbf{E})]\rho(\mathbf{E})\, d\mathbf{E}$$

applied potential

$$k'_{f,E,\mathbf{obs}} = \int_{-\infty}^{\infty} k'_{f,\mathbf{E}}\, d\mathbf{E} \qquad k'_{b,E,\mathbf{obs}} = \int_{-\infty}^{\infty} k'_{b,\mathbf{E}}\, d\mathbf{E}$$

energy

$$j_{E,\mathbf{obs}} = nF\left(-\boxed{k'_{f,E,\mathbf{obs}}\,c_{O,z_O}} + k'_{b,E,\mathbf{obs}}\,c_{R,z_O}\right)$$

Marcus–Gerischer Theory

ET rate is proportional to

$$\int_{-\infty}^{\infty} (N\,D - N\,D)\,dE$$

Metal States | Molecule States

(N_{occ} & N_{unocc} have units of cm⁻² eV⁻¹)

"Marcus" distribution…

$$W_O(\lambda, \mathbf{E}) = (4\pi\lambda\hspace{-0.2em}kT)^{-1/2} \exp\left[-\frac{(\mathbf{E} - \mathbf{E}^0 - \lambda)^2}{4\lambda\hspace{-0.2em}kT}\right]$$

$$N_{\text{unocc}}(\mathbf{E}) = [1 - f(\mathbf{E})]\rho(\mathbf{E})$$

(D_O & D_R have units of cm⁻³ eV⁻¹)

$$D_O(\lambda, \mathbf{E}) = N_A C_O(0, t) W_O(\lambda, \mathbf{E})$$

$$N_{\text{occ}}(\mathbf{E}) = f(\mathbf{E})\rho(\mathbf{E})$$

$$D_R(\lambda, \mathbf{E}) = N_A C_R(0, t) W_R(\lambda, \mathbf{E})$$

Fermi–Dirac distribution…

$$f(\mathbf{E}) = \{1 + \exp[(\mathbf{E} - \mathbf{E}_F)/\hspace{-0.2em}kT]\}^{-1}$$

Bard & Faulkner, Chapter 3, Figure 3.6.4, Page 124

Marcus–Gerischer Theory

$$k_{\text{ET}} = \underbrace{\frac{2\pi}{\hbar}\left|H_{\text{DA}}{}^o\right|^2 e^{-2\beta(z_{\text{DA}}-z_{\text{DA}}{}^o)}}_{\text{quantum adiabatic electronic coupling}} \underbrace{\frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}}\exp\left(-\frac{(\lambda_{\text{AB}}+\Delta G_{\text{AB}}{}^o)^2}{4\lambda_{\text{AB}}kT}\right)}_{\text{classical nuclear free-energy dependence}}$$

$$z_{\text{DA}} - z_{\text{DA}}{}^o$$
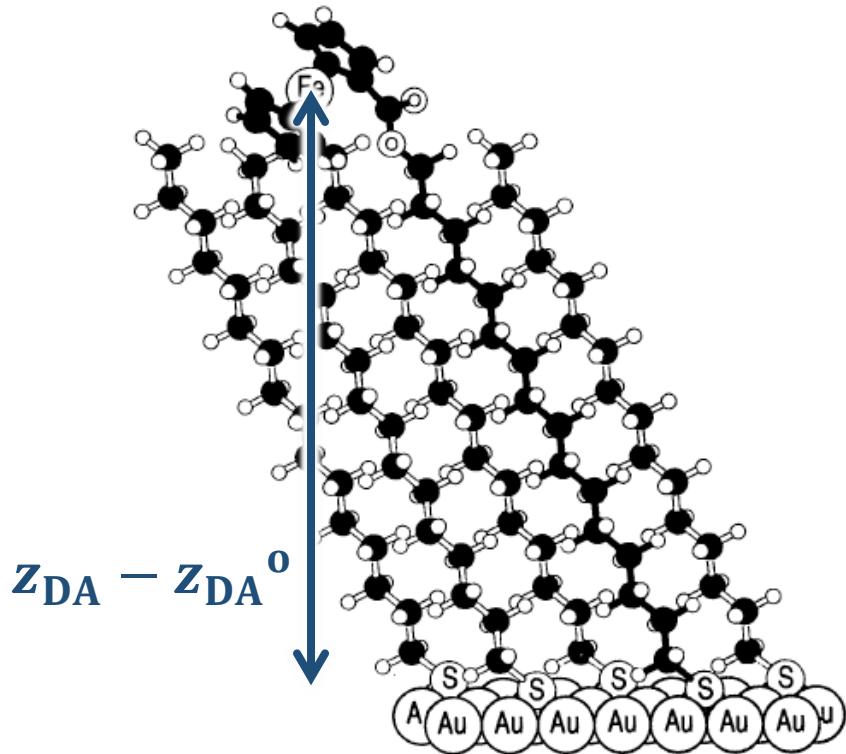
… as an aside… why is the data biphasic for the Current?

… RC-circuit double layer charging… followed by 1st-order ET kinetics
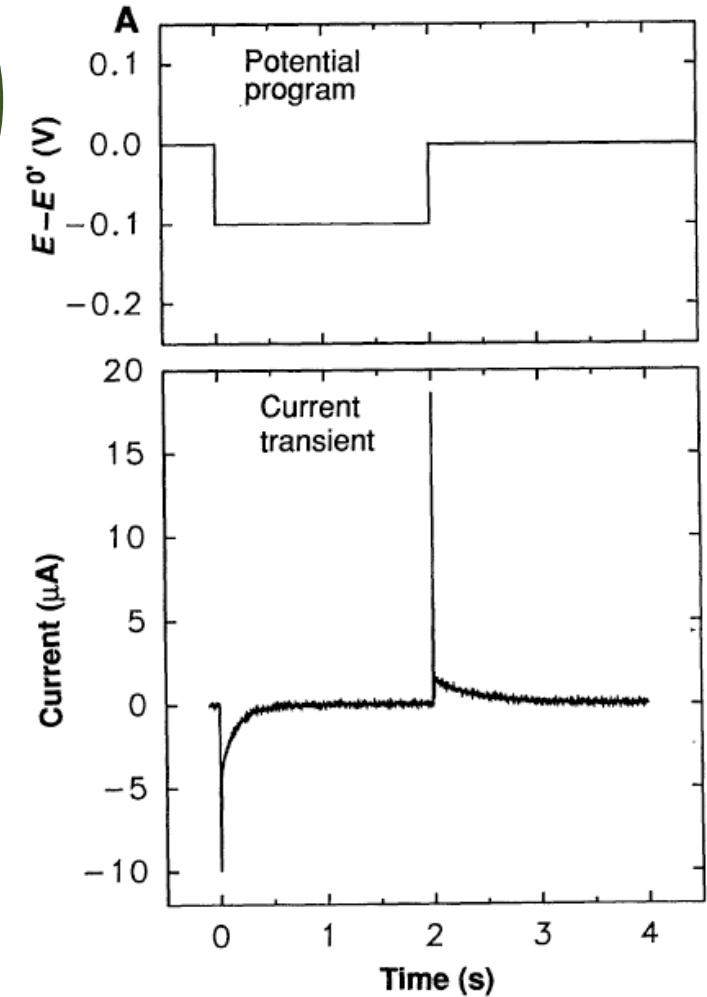
C. E. D. Chidsey, *Science*, **1991**, *251*, 919–922
H. D. Sikes, J. F. Smalley, S. P. Dudek, A. R. Cook, M. D. Newton, C. E. D. Chidsey & S. W. Feldberg, *Science*, **2001**, *291*, 1519–1523

Marcus–Gerischer Theory

$\lambda = 0.85$ eV

Marcus–Gerischer Theory

E^0

E_{app}

barrierless

λ = 0.85 eV

C. E. D. Chidsey, *Science*, **1991**, *251*, 919–922
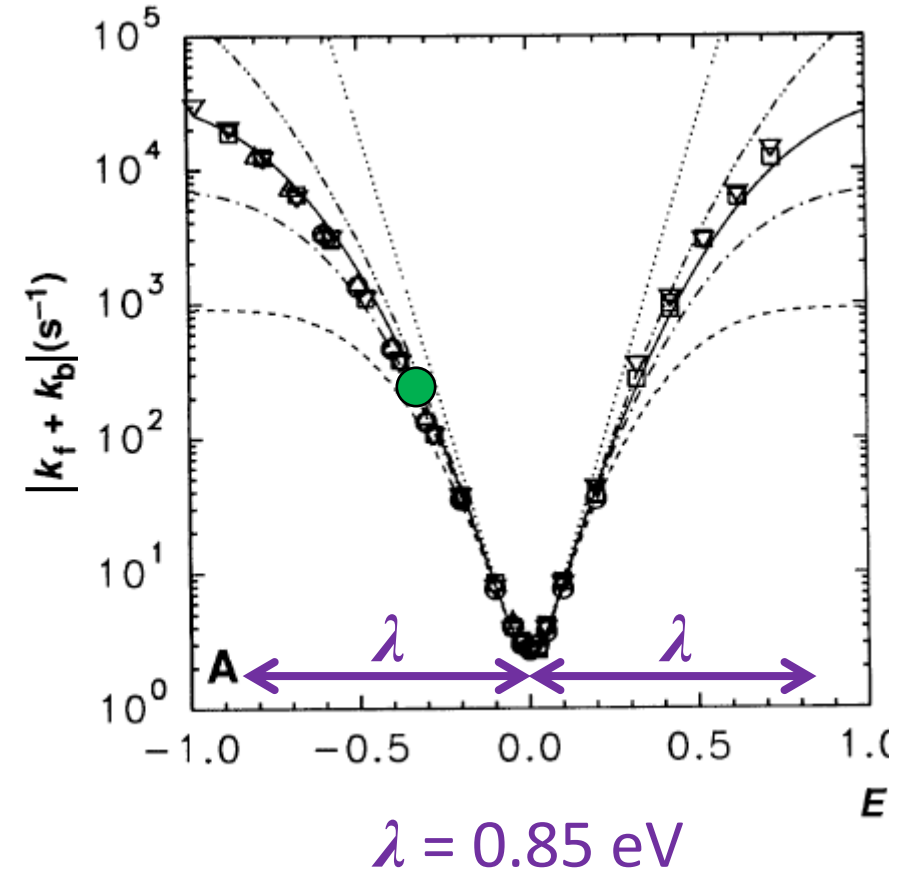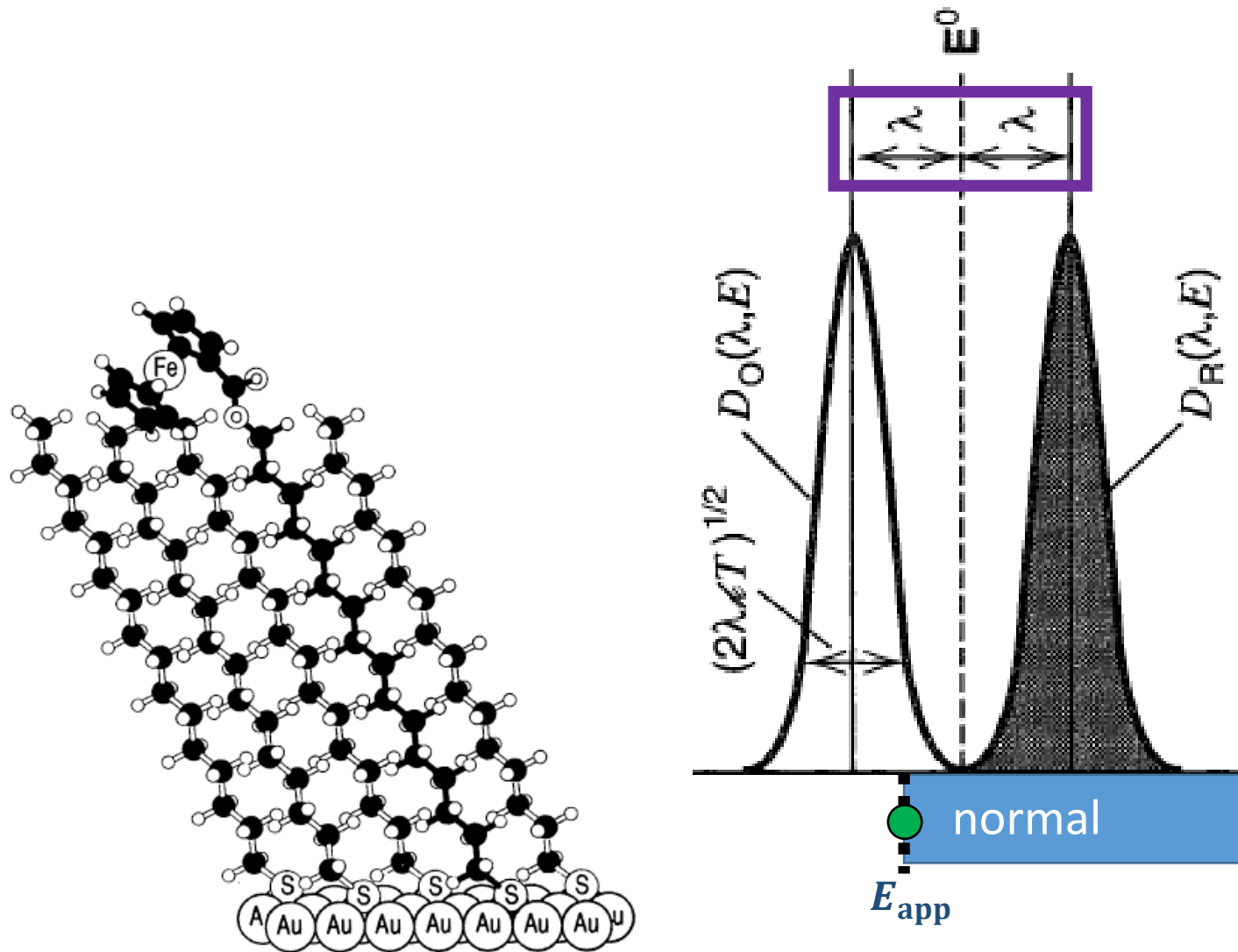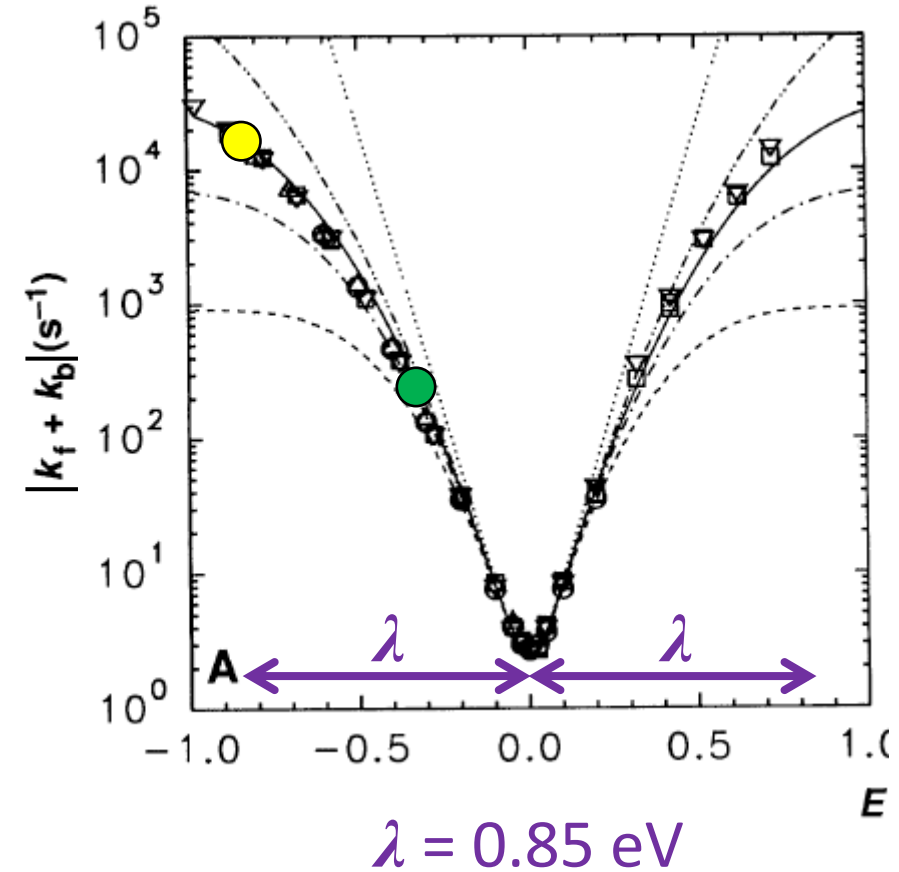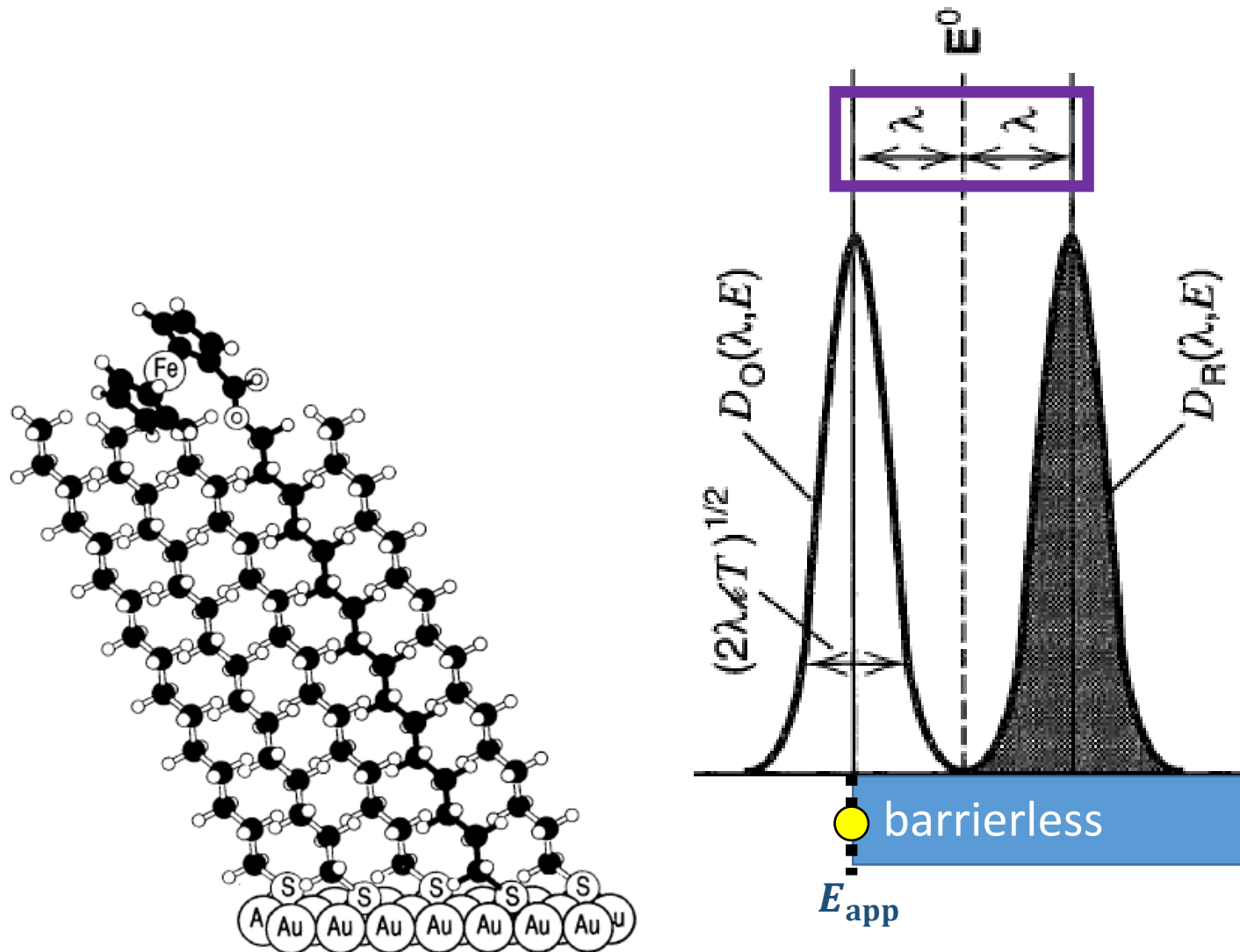
Marcus–Gerischer Theory

- It is easy to sweep/vary the driving force, ΔG_{AB}, by simply changing the electrochemical potential of electrons (e^-) in the <u>(M)etal</u> working electrode, $\bar{\mu}_e^M$, through variations in E_{app}

- **But evidence of the inverted region is a little challenging to clearly observe**

… what if Chidsey had plotted the derivative of his data on the right?

… what do you expect that would have looked like?… a nice Marcus parabola!

… I wish he had done that!

E^0

$D_O(\lambda, E)$

$D_R(\lambda, E)$

$(2\lambda kT)^{1/2}$

inverted

E_{app}

$|k_f + k_b| (s^{-1})$

A

λ λ

E

$\lambda = 0.85$ eV

C. E. D. Chidsey, *Science*, **1991**, *251*, 919–922
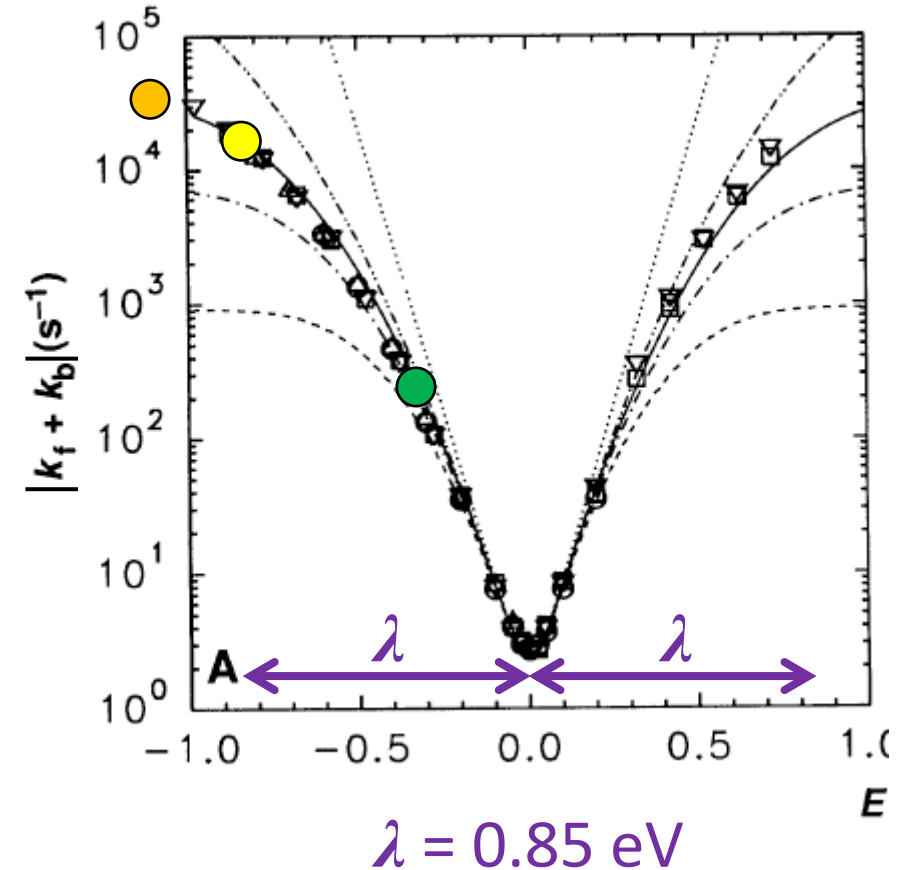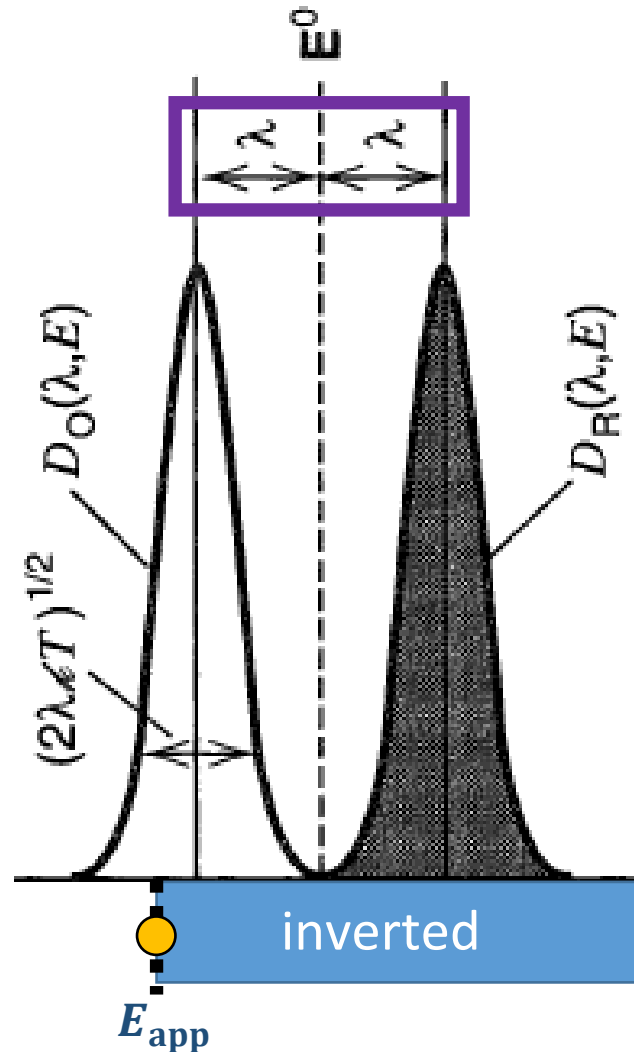
Limiting Processes
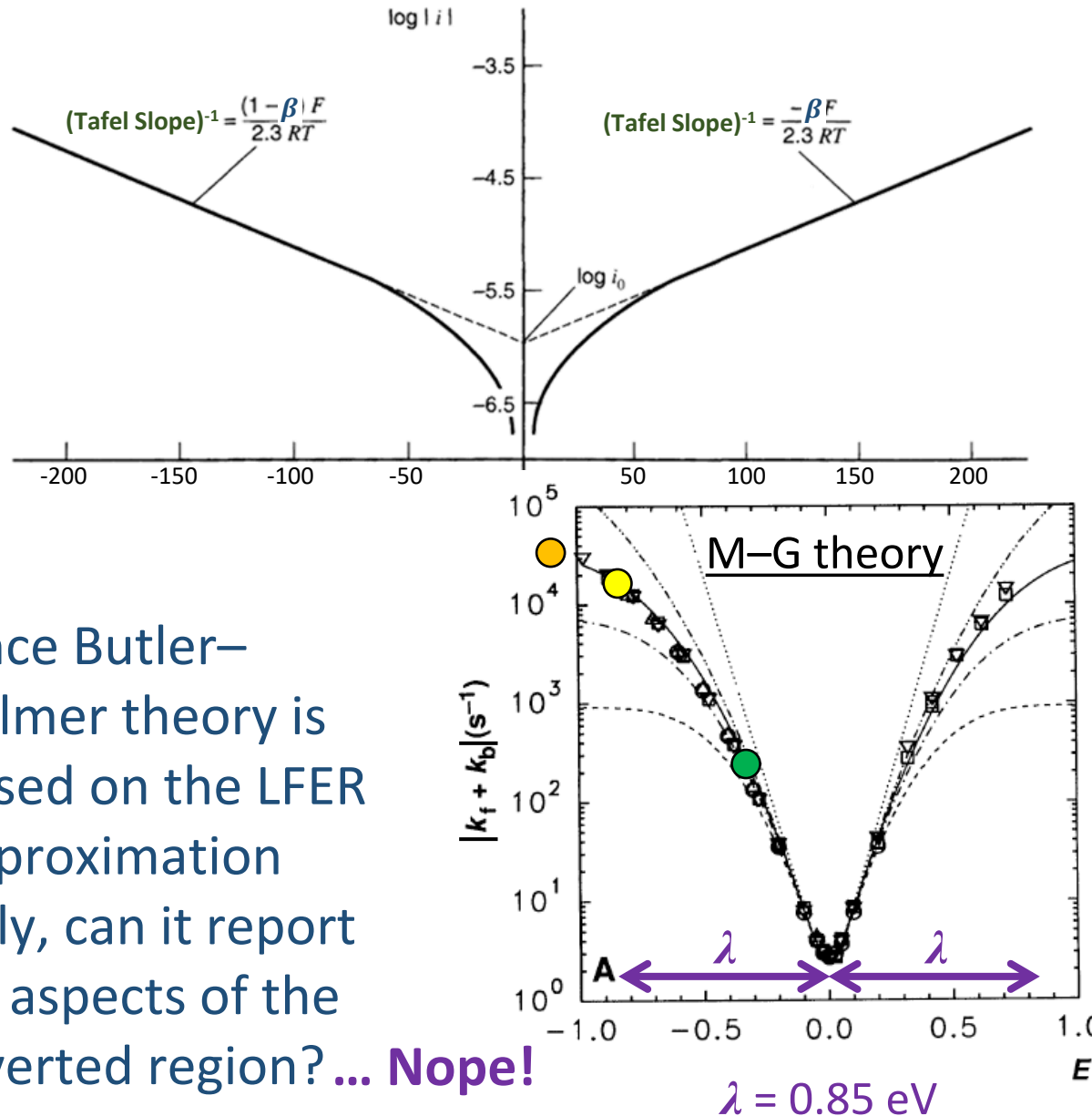
B–V theory
(Current–Overpotential Equation)

$C_{Mn(III)} = 10^{-2}M$
$C_{Mn(IV)} = 10^{-2}M$ (○)
$3 \times 10^{-3}M$ (□)
$10^{-3}M$ (●)

(Tafel Slope)$^{-1} = \dfrac{(1-\beta)F}{2.3\,RT}$

(Tafel Slope)$^{-1} = \dfrac{-\beta F}{2.3\,RT}$

M–G theory

$\lambda = 0.85$ eV

Since Butler–Volmer theory is based on the LFER approximation only, can it report on aspects of the inverted region? **... Nope!**
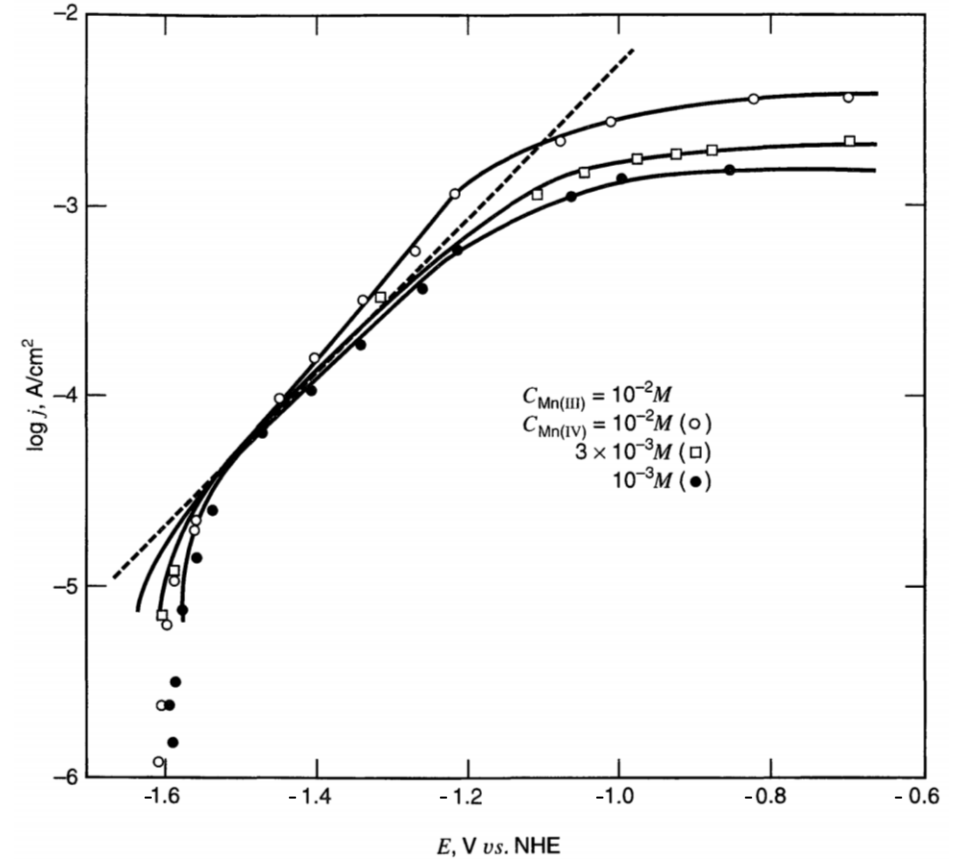
Bard & Faulkner, Chapter 3, Figure 3.4.5, Page 104

... but why do these current densities, j_E, and rate constants, $k'_{j,E,\text{obs}}$, plateau at large overpotential, η? **... Not for the same reasons!**

Marcus–Gerischer Theory

- Use of a semiconductor limits the electronic states to those with (approximately) a single $\mu_{e^-}^o$, which makes analysis of data simpler, i.e. one does not need to consider a distribution of states in the electrode

- **But one cannot alter the driving force, $\Delta G_{AB}{}^o$, by simply changing the electrochemical potential of electrons (e⁻) in the (S)emi(C)onductor working electrode, $\bar{\mu}_e^{SC}$, through variations in E_{app}, because instead that typically changes the concentration of e⁻**
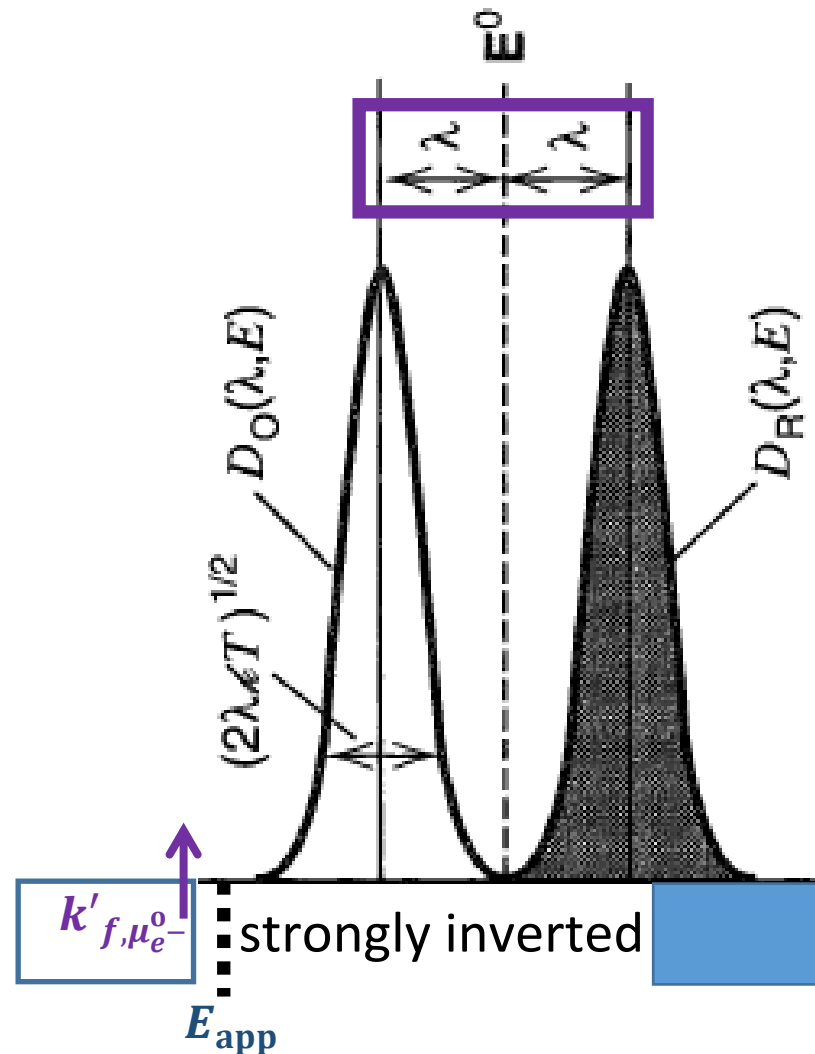
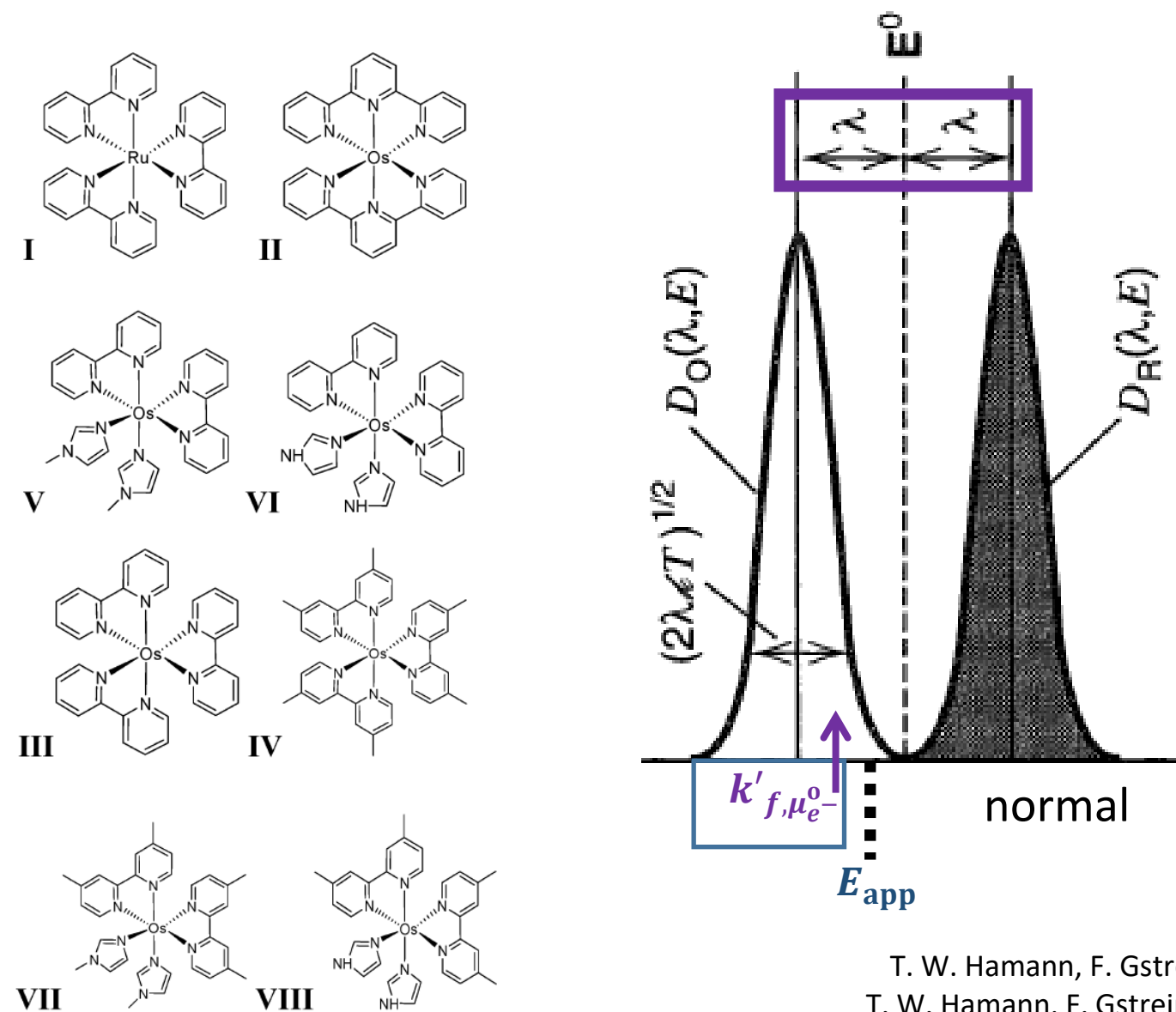How can one use a semiconductor to study the inverted region?

Think solution studies... vary the molecule!

Marcus–Gerischer Theory
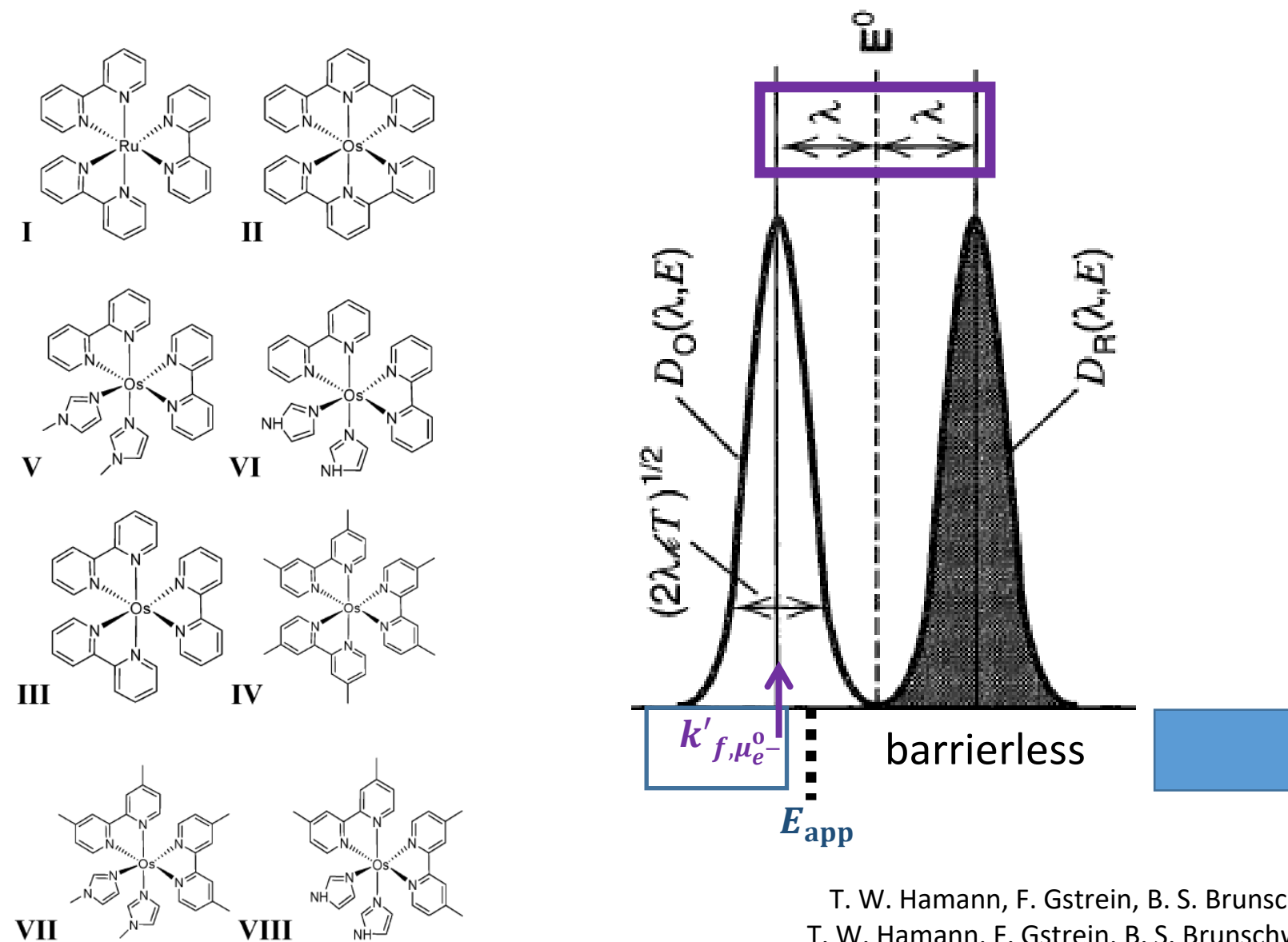
$D_O(\lambda,E)$

$D_R(\lambda,E)$

$(2\lambda kT)^{1/2}$

$k'_{f,\mu_e^{o-}}$

barrierless

E_{app}

T. W. Hamann, F. Gstrein, B. S. Brunschwig & N. S. Lewis, *J. Am. Chem. Soc.*, **2005**, *127*, 7815–7824
T. W. Hamann, F. Gstrein, B. S. Brunschwig & N. S. Lewis, *J. Am. Chem. Soc.*, **2005**, *127*, 13949–13954

I

II

V

VI

III

IV

VII

VIII

Marcus–Gerischer Theory

λ = 0.67 eV
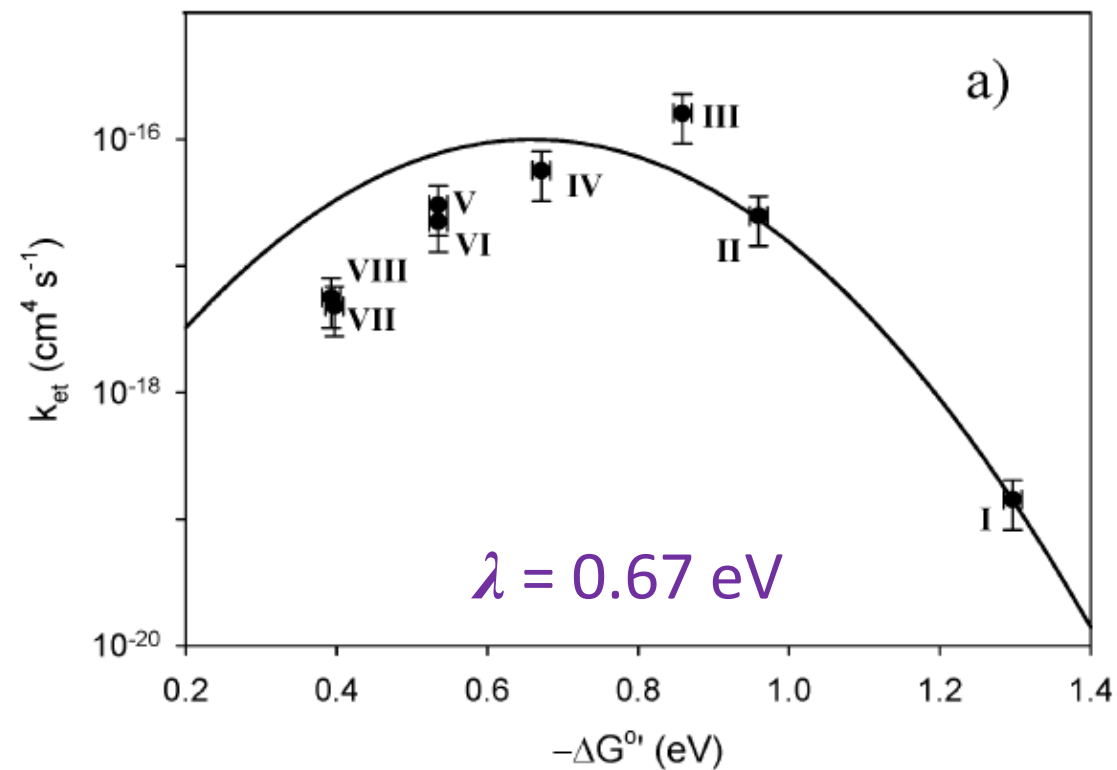
k_{IET} (cm^4 s^{-1})... a second-order rate constant!

T. W. Hamann, F. Gstrein, B. S. Brunschwig & N. S. Lewis, *J. Am. Chem. Soc.*, **2005**, *127*, 7815–7824
T. W. Hamann, F. Gstrein, B. S. Brunschwig & N. S. Lewis, *J. Am. Chem. Soc.*, **2005**, *127*, 13949–13954

Photochemistry

Straight into Groups!

Quiz(zes) Time!

Prof. Shane Ardo

Department of Chemistry

University of California Irvine

Photochemistry

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

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

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

- Photochemical length and time scales, Electromagnetic spectrum

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

Förster Cube and Square Schemes
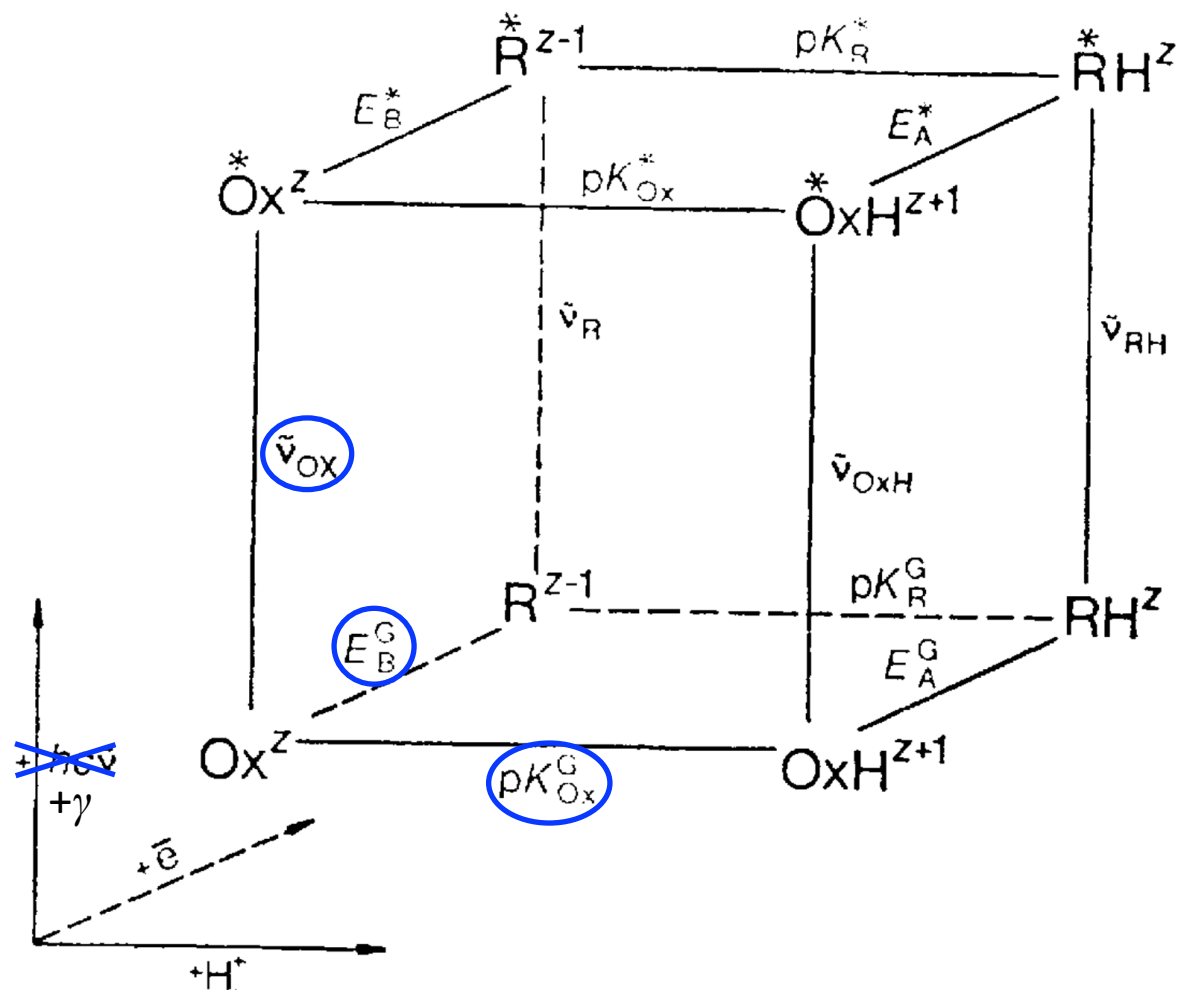
Questions to ponder…

In this figure, what do the thermodynamic parameters E, pK, and $\bar{v}$ represent?

$E = E^o$ (standard-state <u>reduction</u> potential)

pK = pK_a = $-\log K_a$ (acid <u>dissociation</u> constant)

$\bar{v} = \dfrac{1}{\lambda}$ (<u>wave</u>number)

How are they related?

ln 10

Redox: $E^o = -\Delta G^o/nF$

Acidity: pK_a = $-\log K_a$ = $\Delta G^o/(2.303RT)$

Light: $hc\bar{v} = \dfrac{hc}{\lambda} = h\nu$ = E_{photon}

What is the reference state for each?

$E^o(H^+(aq)/H_2) = 0$; p$K_a(H^+(aq)) = 0$; 0

… before we add light… let's backtrack a bit…

… first we must understand dark thermal processes…

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

Blackbody Radiation

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

($T \approx 5790$ K)

SUN

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

EARTH

($T \approx 290$ K)

High T

Experiment and Planck's theory

Classical theory

$I \propto \dfrac{T}{\lambda^4}$

Low T

I (Intensity of emission)

λ
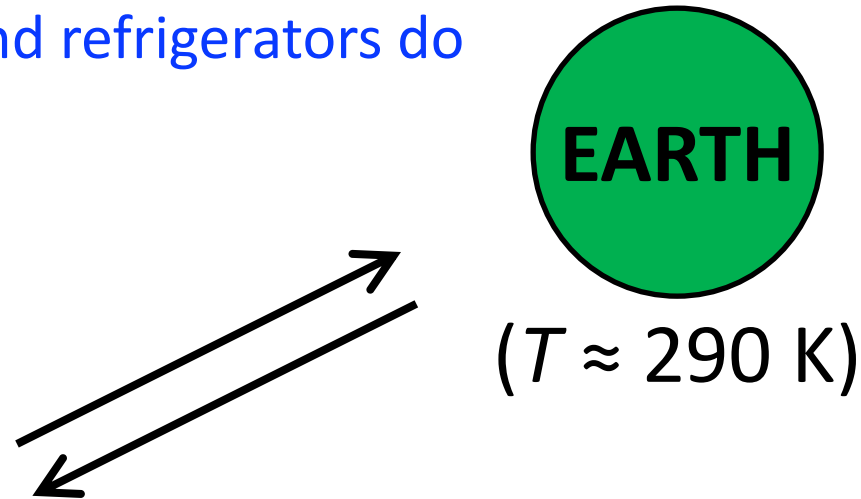
UNIVERSE
($T \approx 3$ K)

… if any two bodies are that the same temperature   Turro, Chapter 4, Figure 4.1, Page 171
… 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
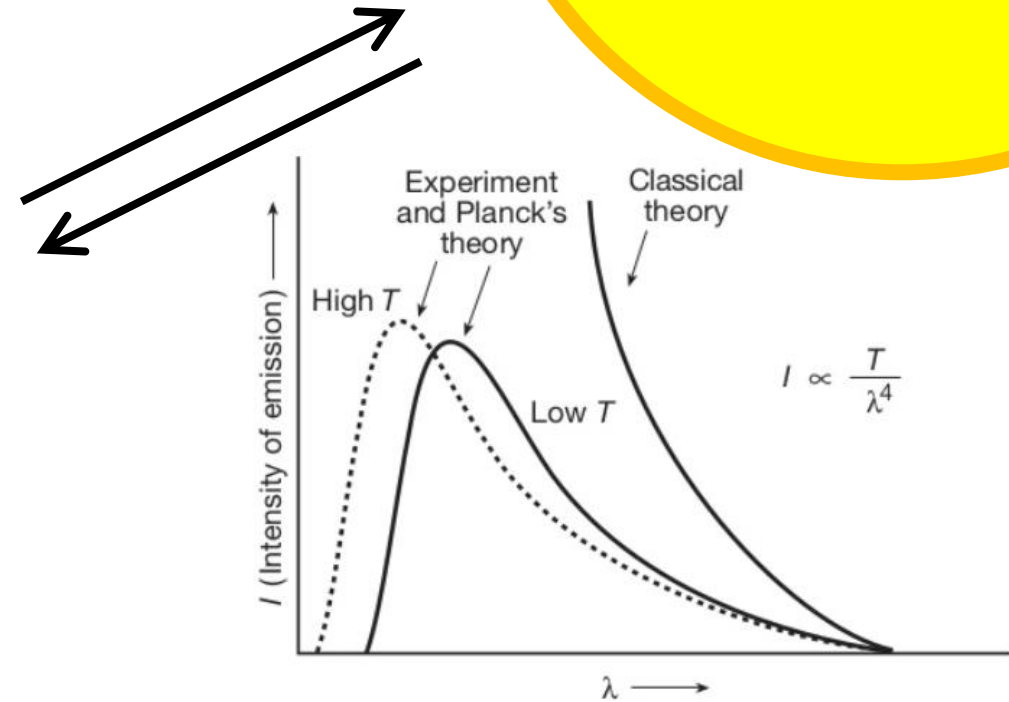
Photon Properties & Conservation Laws

Where does light come from?

Particle Type: Boson

Mass: 0

Charge: 0

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

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

Linear Momentum: $p = \dfrac{h}{\lambda'} = \dfrac{nh\nu}{c} \approx 0$

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

direction of oscillation of electric field vector $\mathcal{E}$

direction of wave propagation

direction of oscillation of magnetic field vector B

electric field

magnetic field

position

λ

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

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?
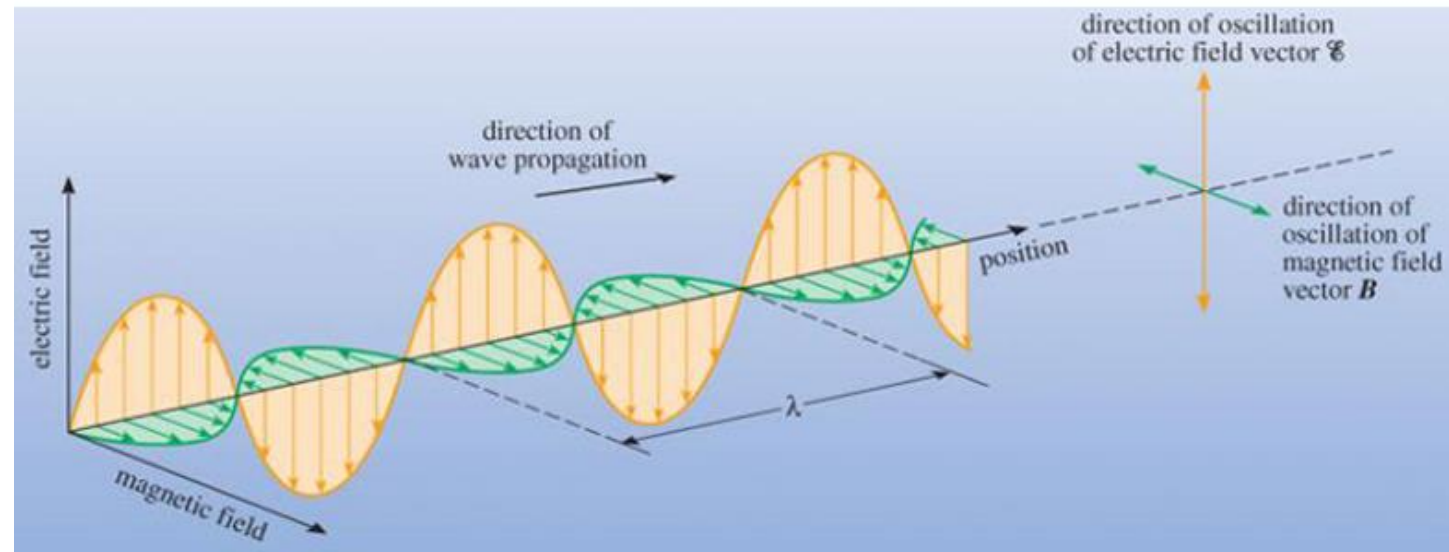
Fermion Angular Momentum (Orbital, Spin)

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

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

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

Light–Matter Interactions

$$\frac{\partial c_{A,z_o}}{\partial t} = \sum_j R_{A,j} - \frac{\partial \mathbf{N}_A}{\partial z}$$

Fonash, Chapter 4, Figure 4.2, Page 125

What value of j have we considered thus far?   **≥2**
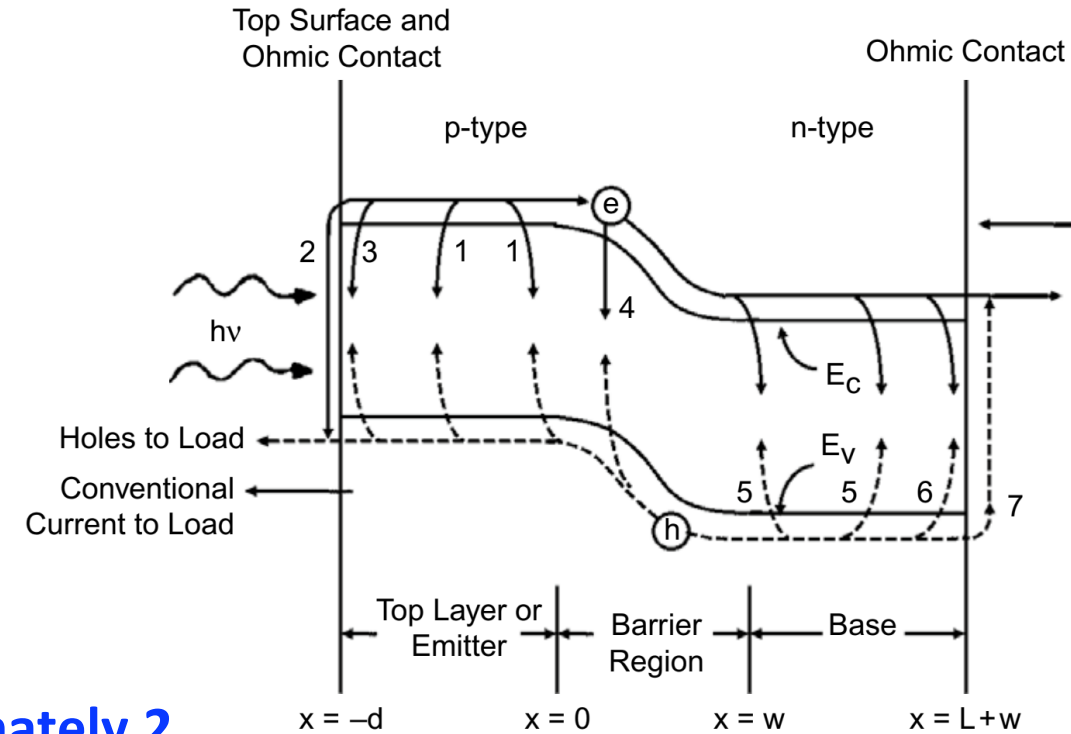
How large is j for actual systems?   **Quite large, likely!**

What is the smallest value that j can be?   **3… but approximately 2**
                                             … stimulated emission is tiny

Given a box at temperature, T, by what processes can heat be transferred to something inside it?
Okay, now what if inside the box was a vacuum?

(Blackbody) radiation only! $A + h\nu_{BB} \rightleftharpoons A^*$

… at a microscopically reversible **equilibrium**, rate is equal to "**%A(ν)** x PhotonFlux(ν), integrated over ν"
… $\bar{\mu}_A = \bar{\mu}_{A^*}$ … with additional (sun)light absorption, $\bar{\mu}_A < \bar{\mu}_{A,eq}$ and $\bar{\mu}_{A^*} > \bar{\mu}_{A^*,eq}$ = <u>useful work</u>!

Light–Matter Interactions

Turro, Chapter 4, Page 184

Total force exerted on an electron by a light wave

$$\mathbf{F} = e\mathbf{E} + \frac{e[\mathbf{H}v]}{c}$$

Electrical force

Magnetic force

$c_{light} = 3 \times 10^{18}$ nm s^{-1}
$v_{electron} = 10^{15} - 10^{16}$ nm s^{-1}
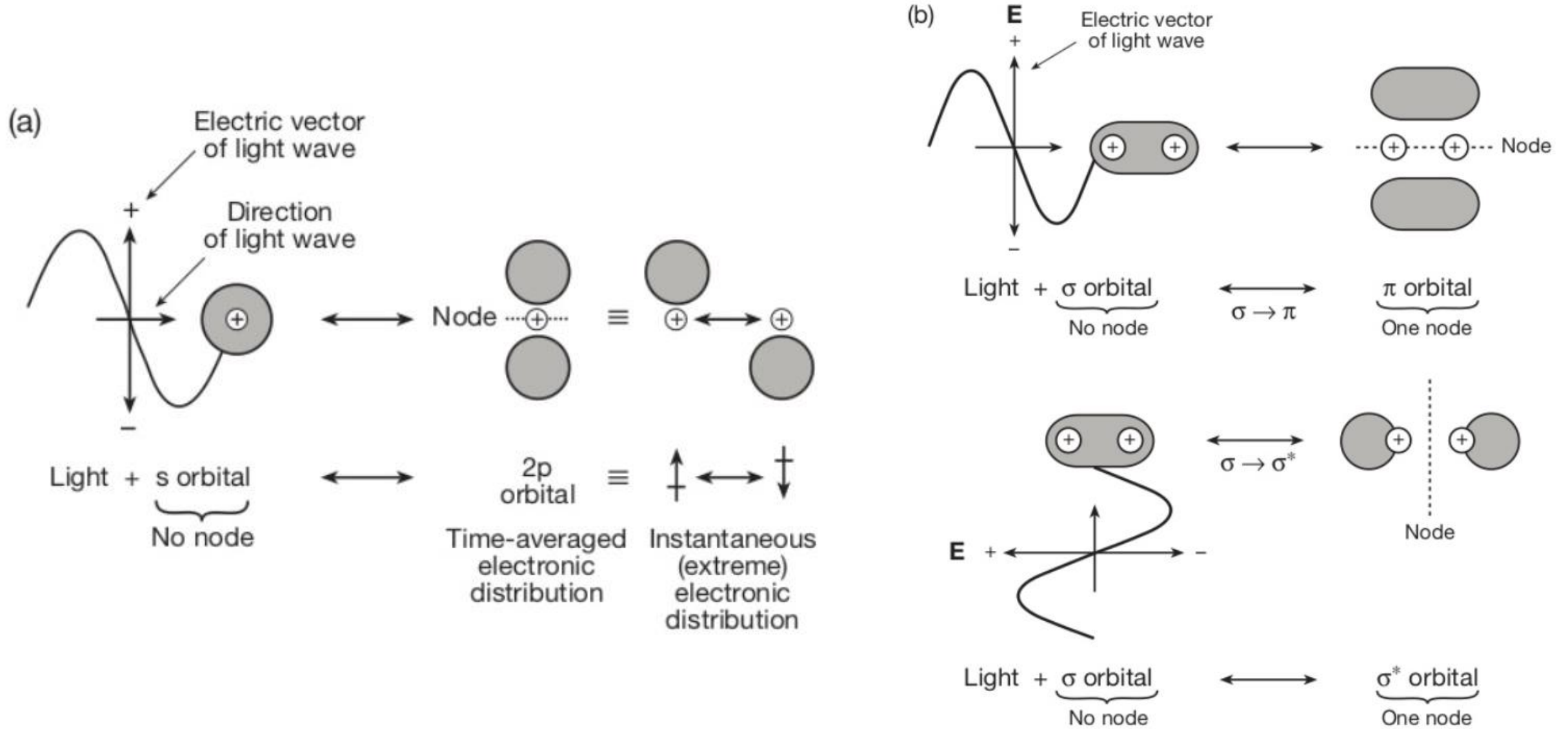$v_{nuclei} = 10^{13} - 10^{14}$ nm s^{-1}
… so which term dominates the resonant response to light?

In more concrete chemical terms, the oscillation of the dipoles corresponds to the movements of electrons in bonds relative to positively charged nuclei in matter; that is, electrons oscillate about the nuclear framework of molecules.
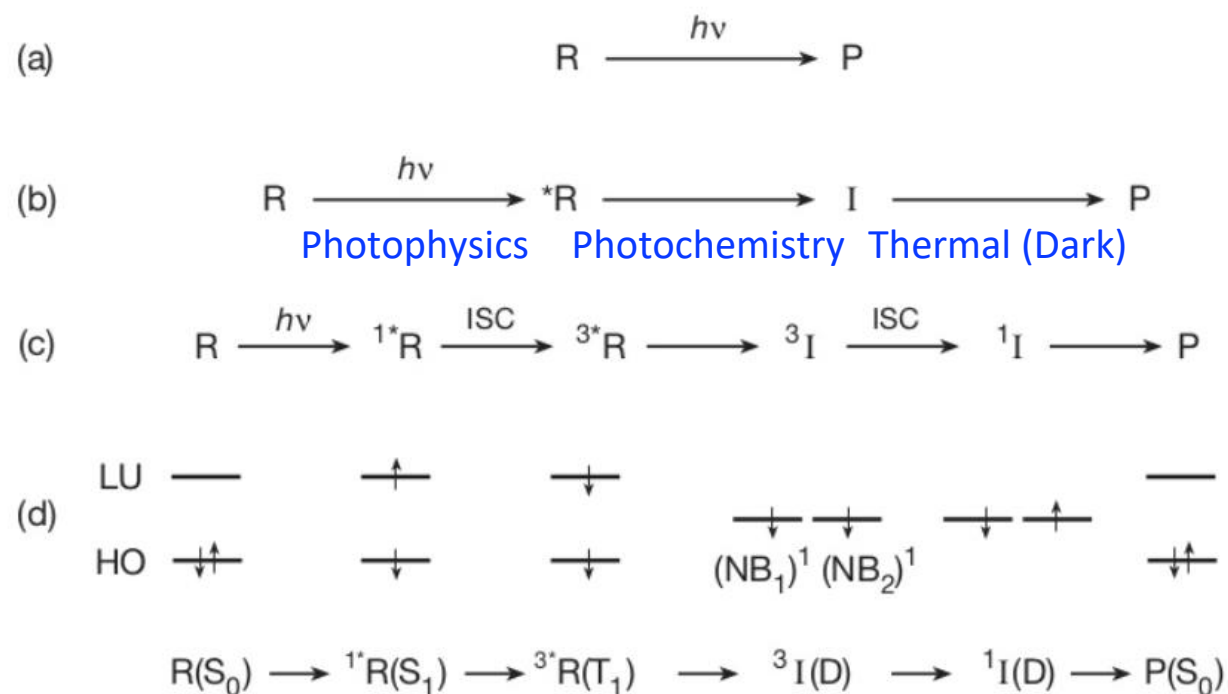
Turro, Chapter 1, Scheme 1.7, Page 36
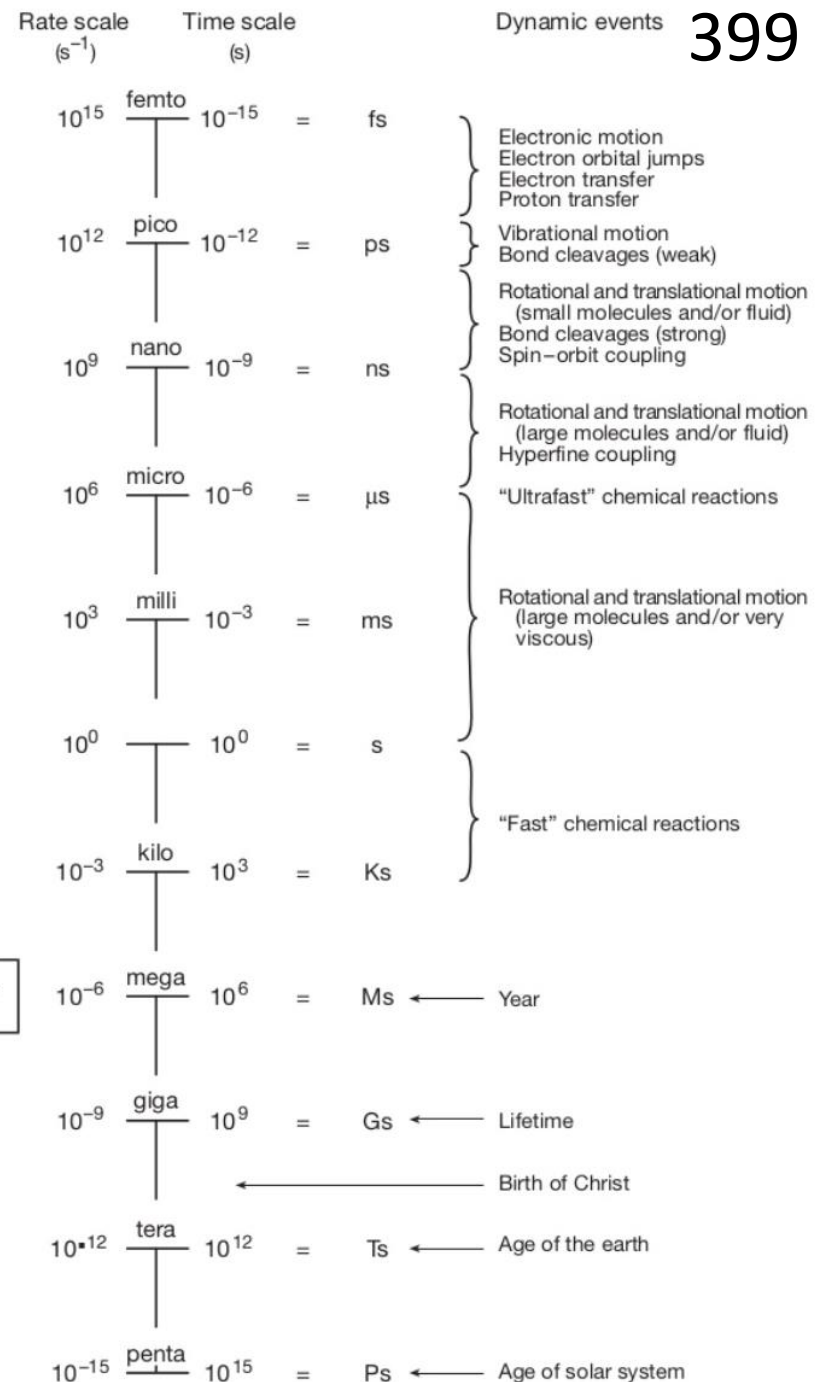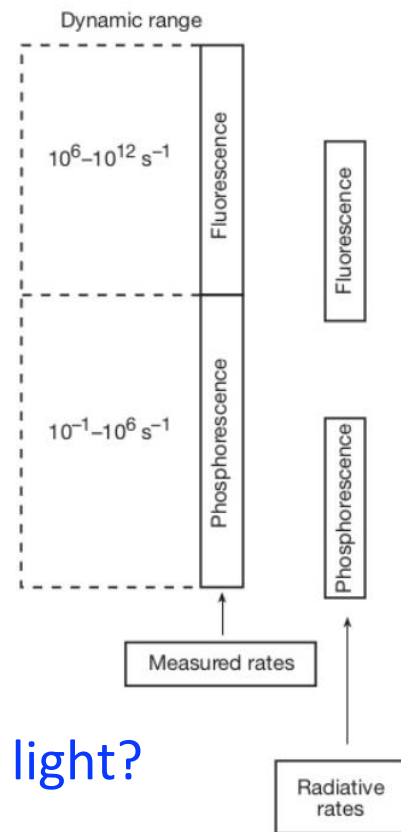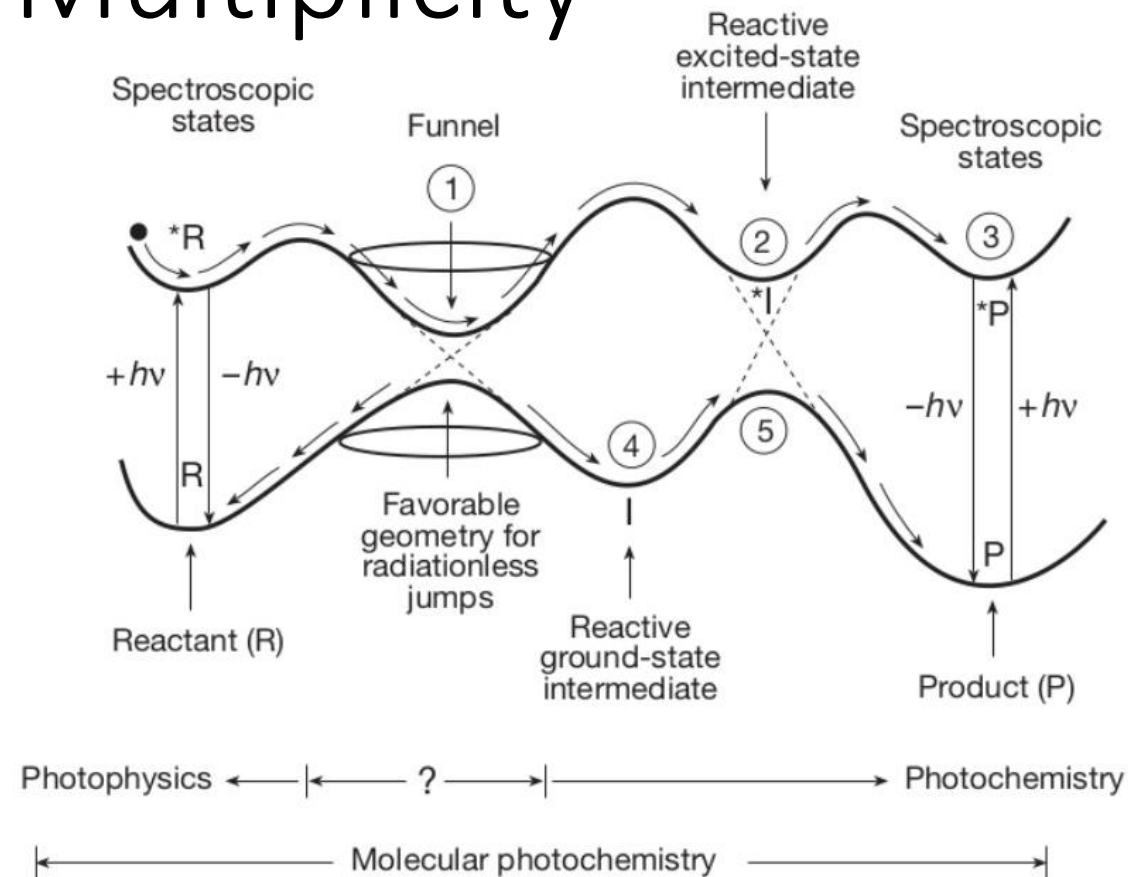
Light–Matter Interactions

Jablonski Diagram & Spin Multiplicity

(a) $R \xrightarrow{hv} P$

(b) $R \xrightarrow{hv} *R \longrightarrow I \longrightarrow P$

Photophysics   Photochemistry   Thermal (Dark)

(c) $R \xrightarrow{hv} {}^{1*}R \xrightarrow{ISC} {}^{3*}R \longrightarrow {}^{3}I \xrightarrow{ISC} {}^{1}I \longrightarrow P$

(d)

$R(S_0) \longrightarrow {}^{1*}R(S_1) \longrightarrow {}^{3*}R(T_1) \longrightarrow {}^{3}I(D) \longrightarrow {}^{1}I(D) \longrightarrow P(S_0)$

Scheme 1.3   Exemplar paradigm for an organic photochemical reaction that proceeds through a triplet state.

Turro, Chapter 1, Scheme 1.3, Page 13

Turro, Chapter 1, Scheme 1.5, Page 21

… Angular Momentum Energy Degeneracy, g_J: $2J + 1$
… when $J = 0$, $g_J = 1$… sounds like a "Singlet (S or ^{1}X)"
… when $J = 1$, $g_J = 3$… sounds like a "Triplet (T or ^{3}X)"

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

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

Turro, Chapter 1, Scheme 1.4, Page 17
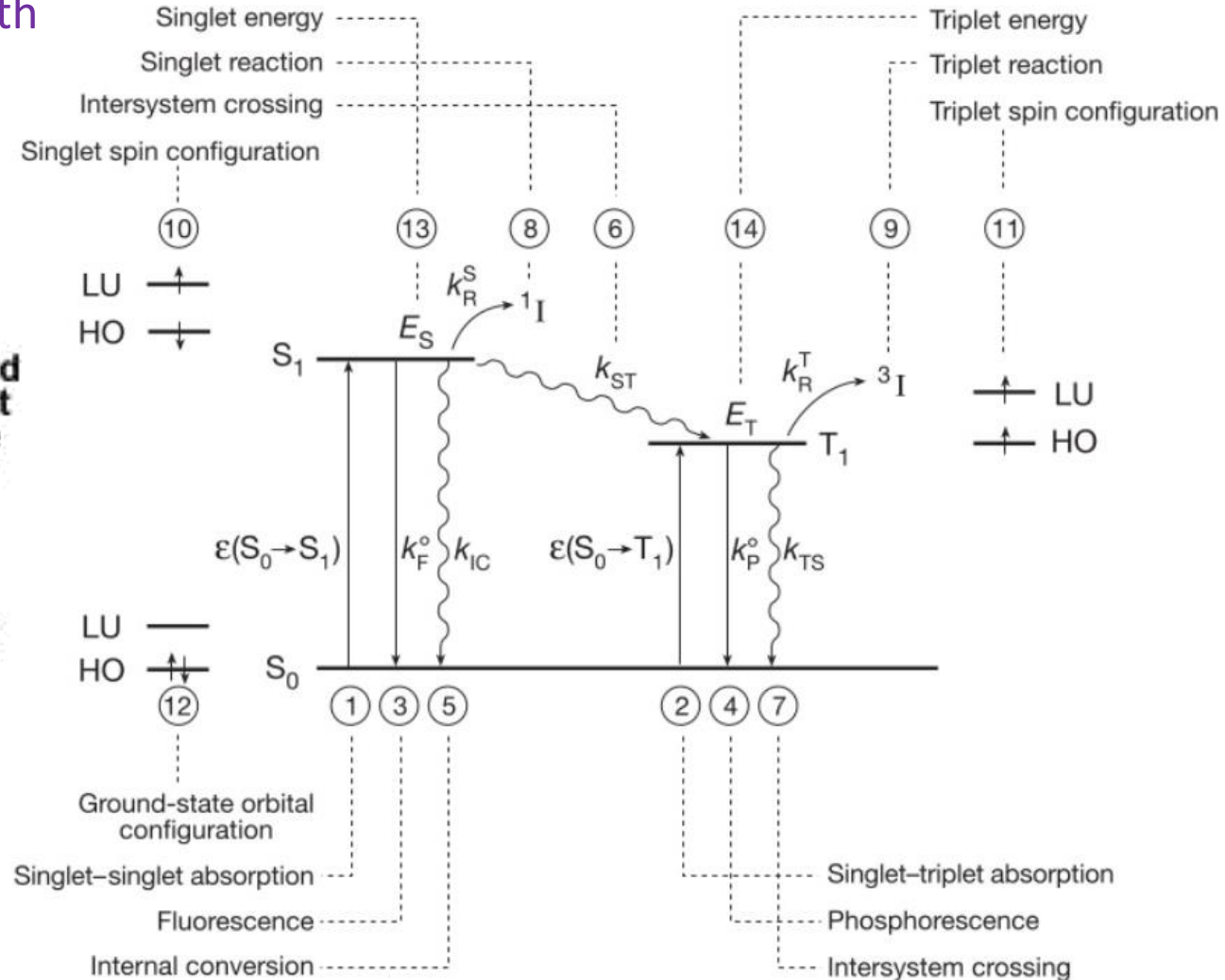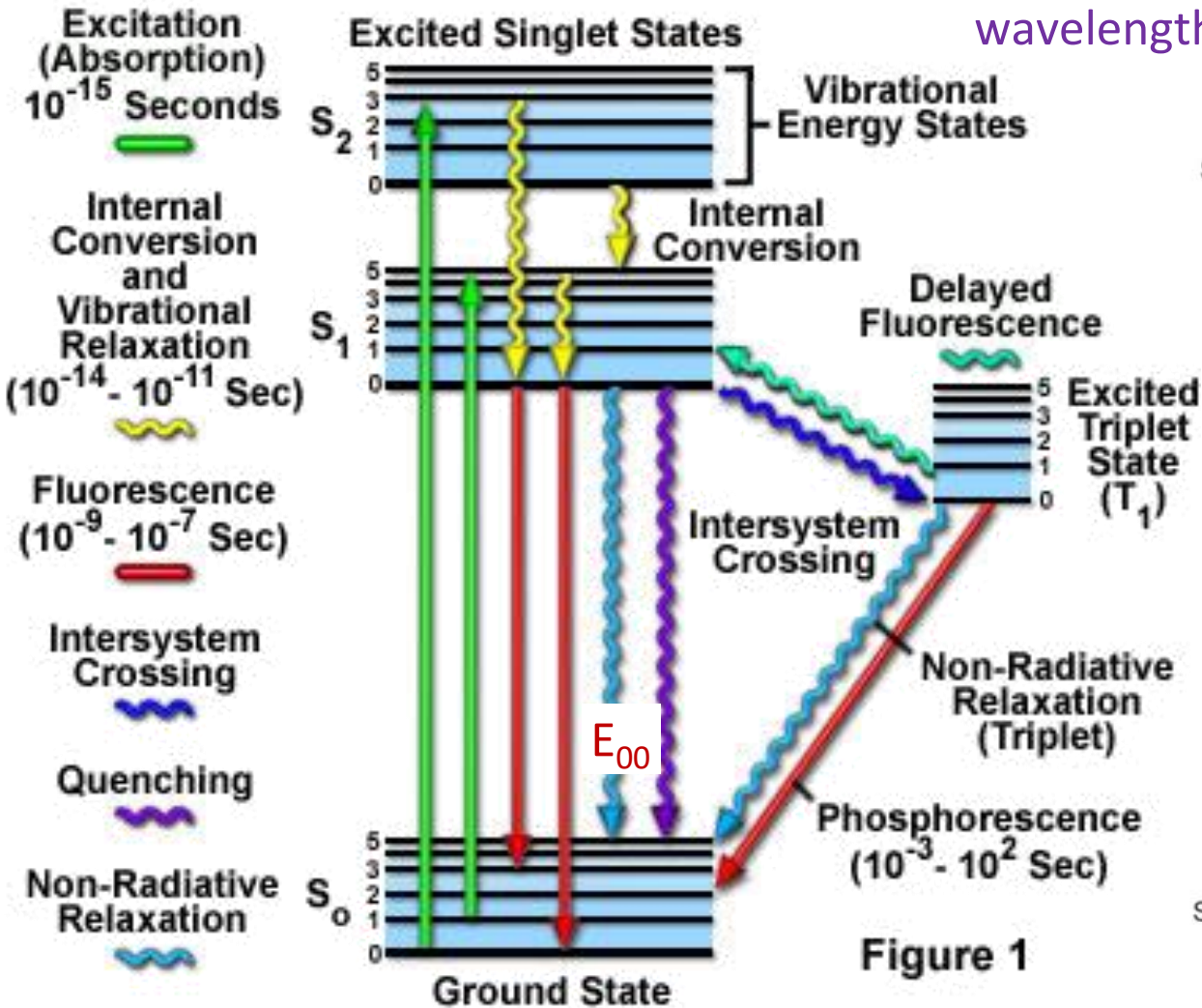
Photochemistry *(summary for today)*

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