Lecture #8 of 12

Prof. Shane Ardo
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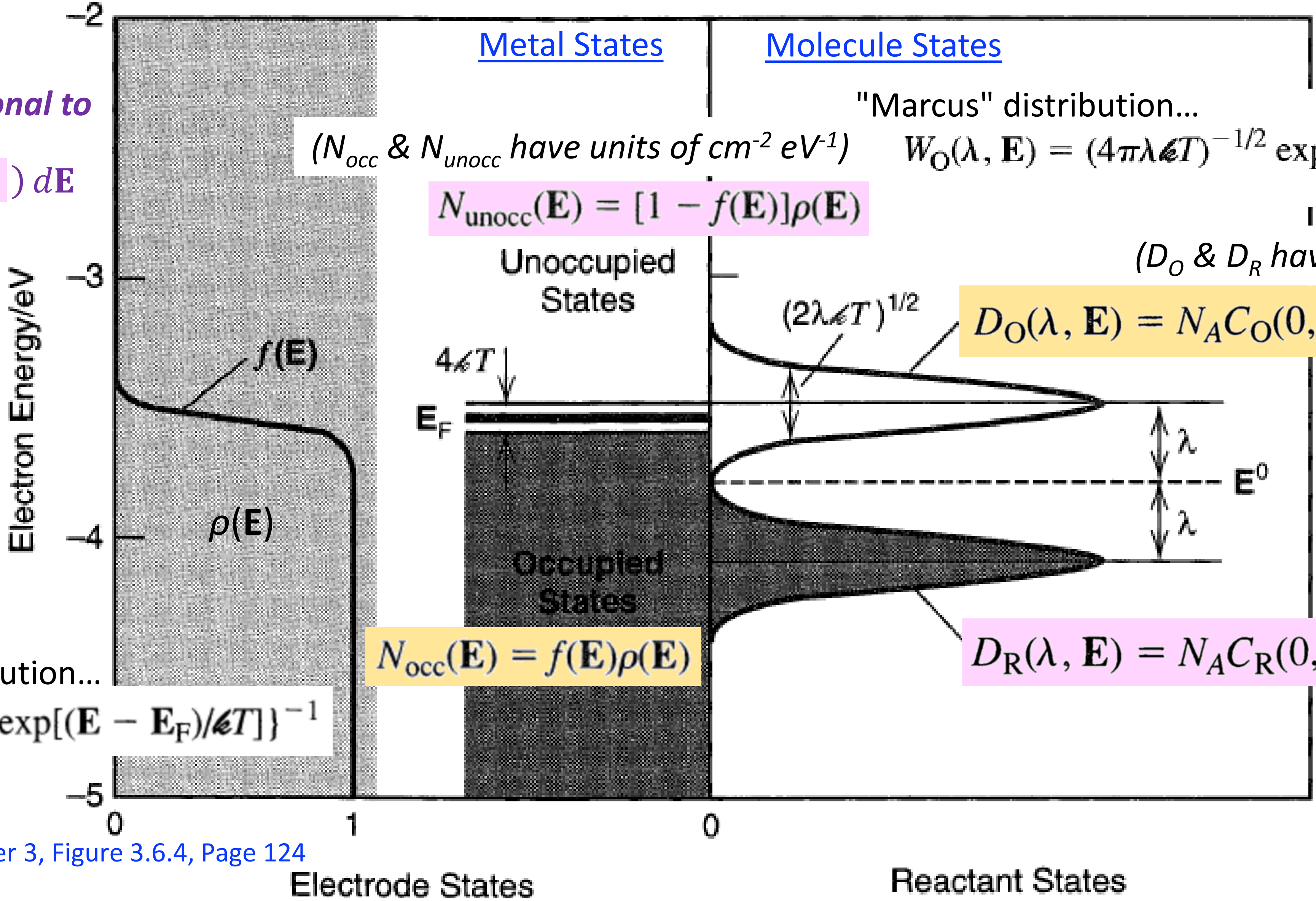
Marcus–Gerischer Theory

ET rate is proportional to

$$\int_{-\infty}^{\infty} (N\ D - N\ D)\, d\mathbf{E}$$



Metal States

Molecule States

"Marcus" distribution…

$$W_{\mathrm{O}}(\lambda, \mathbf{E}) = (4\pi\lambda kT)^{-1/2} \exp\left[-\frac{(\mathbf{E} - \mathbf{E}^0 - \lambda)^2}{4\lambda kT}\right]$$

(N_{occ} & N_{unocc} have units of $cm^{-2}\ eV^{-1}$)

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

(D_O & D_R have units of $cm^{-3}\ eV^{-1}$)

$$D_{\mathrm{O}}(\lambda, \mathbf{E}) = N_A C_{\mathrm{O}}(0, t) W_{\mathrm{O}}(\lambda, \mathbf{E})$$

$$D_{\mathrm{R}}(\lambda, \mathbf{E}) = N_A C_{\mathrm{R}}(0, t) W_{\mathrm{R}}(\lambda, \mathbf{E})$$

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

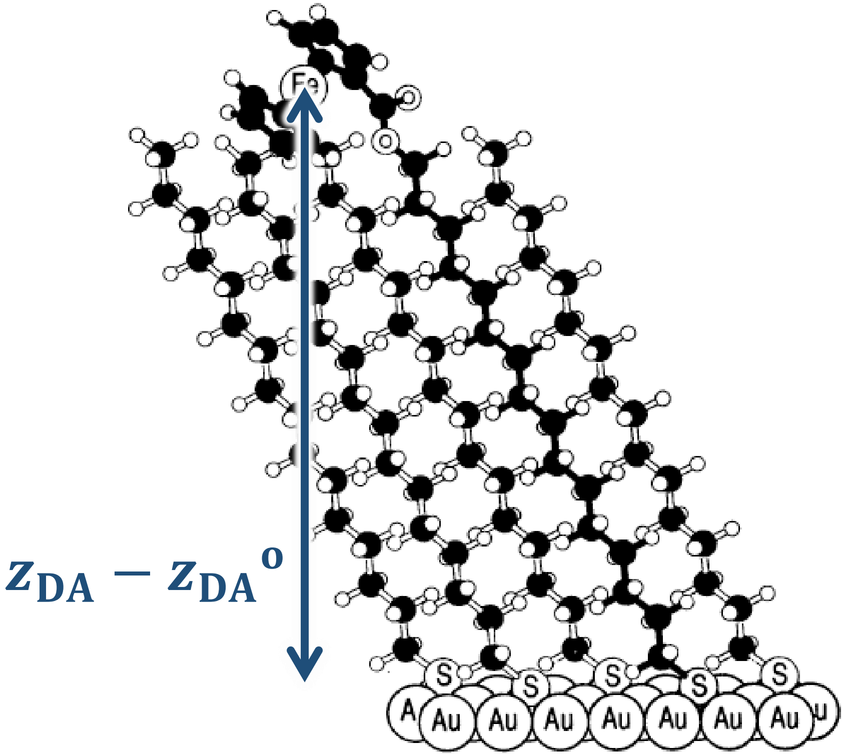
Fermi–Dirac distribution…

$$f(\mathbf{E}) = \{1 + \exp[(\mathbf{E} - \mathbf{E}_{\mathrm{F}})/kT]\}^{-1}$$

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

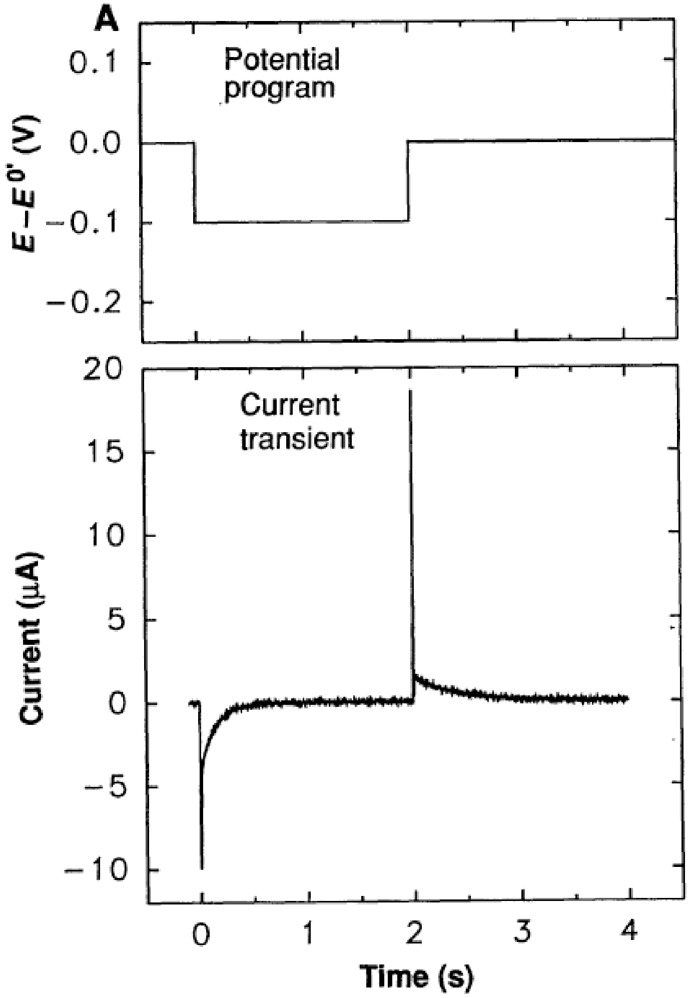
Marcus–Gerischer Theory

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



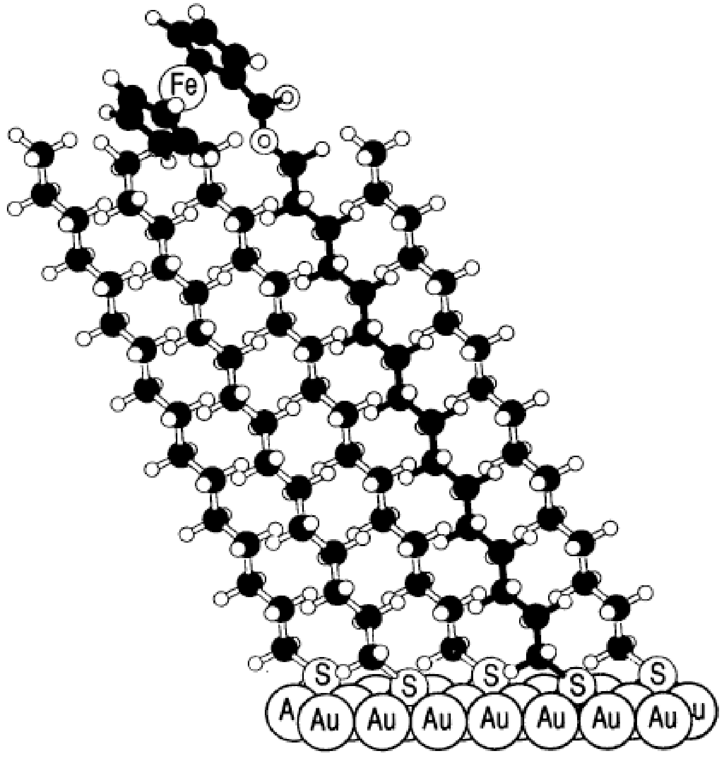
… as an aside… why is the data biphasic for the Current?

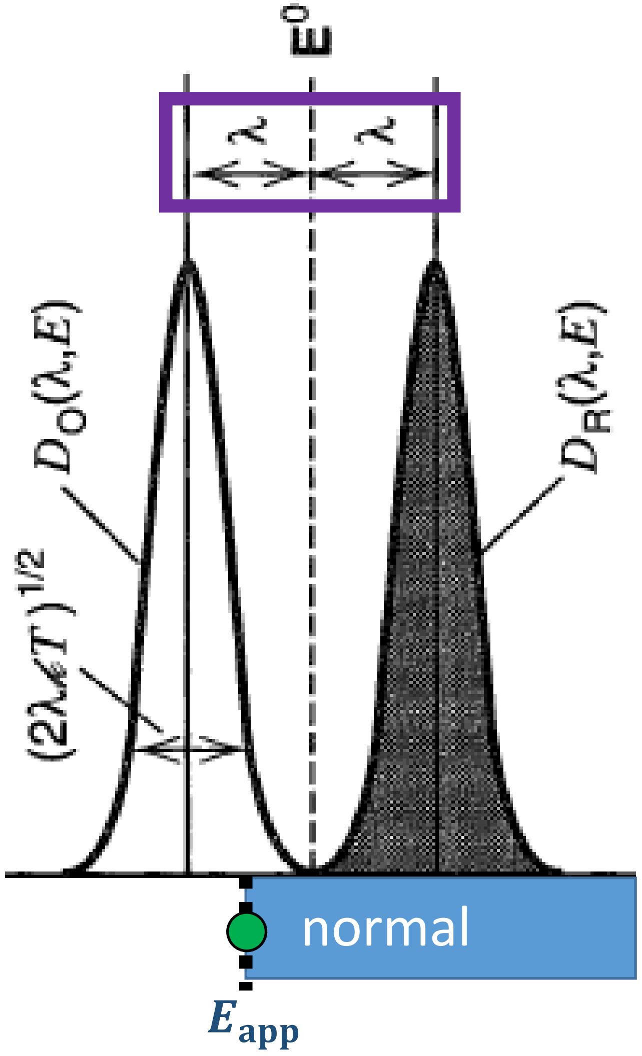
… RC-circuit double layer charging… followed by 1st-order ET kinetics

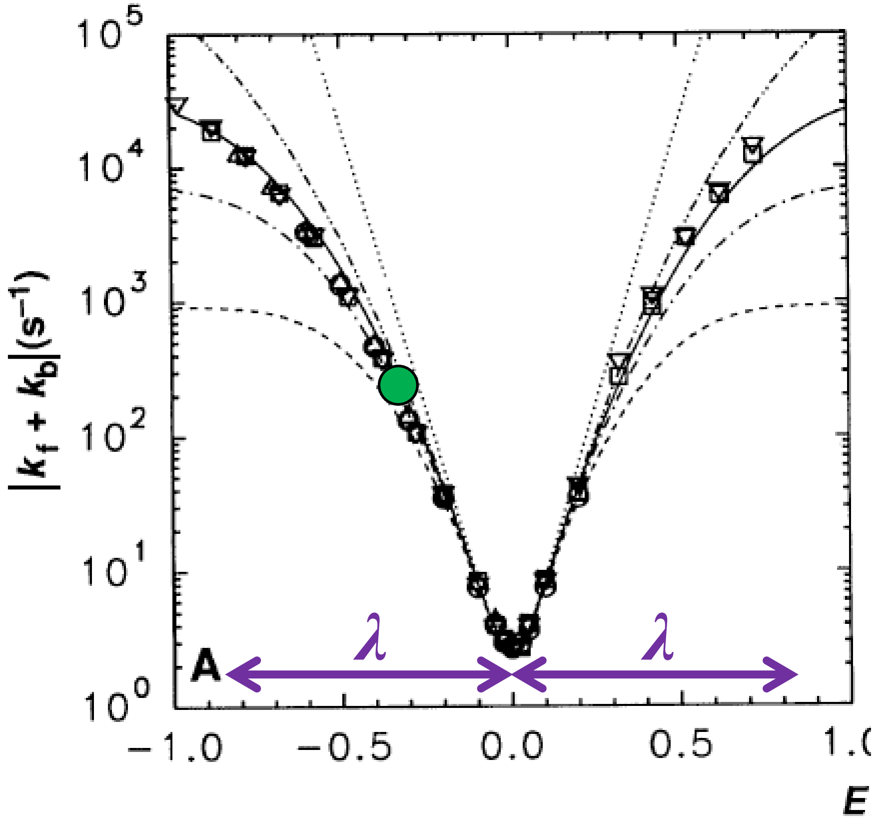


C. E. D. Chidsey, *Science*, **1991**, *251*, 919–922
H. D. Sikes, J. F. Smalley, S. P. Dudek, A. R. Cook, M. D. Newton, C. E. D. Chidsey & S. W. Feldberg, *Science*, **2001**, *291*, 1519–1523

Marcus–Gerischer Theory



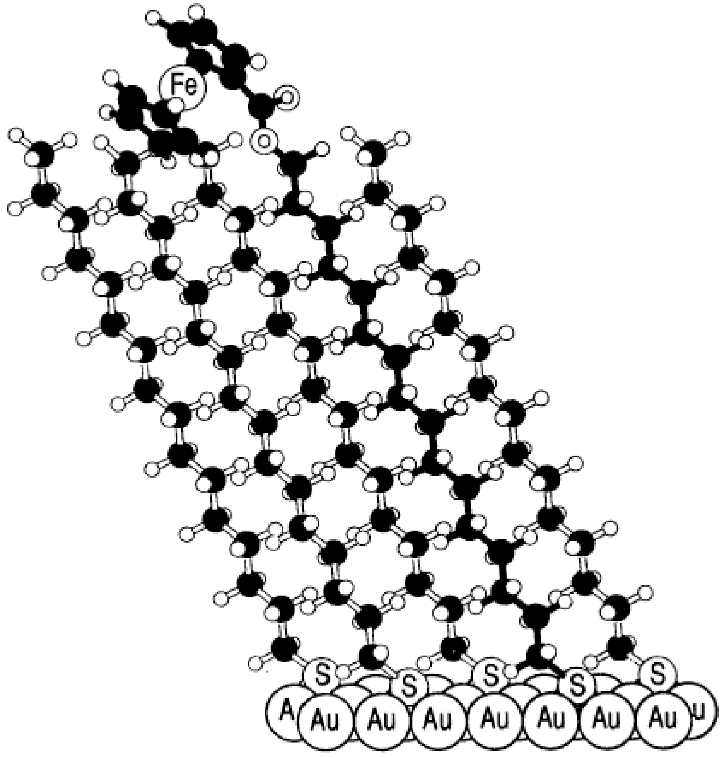


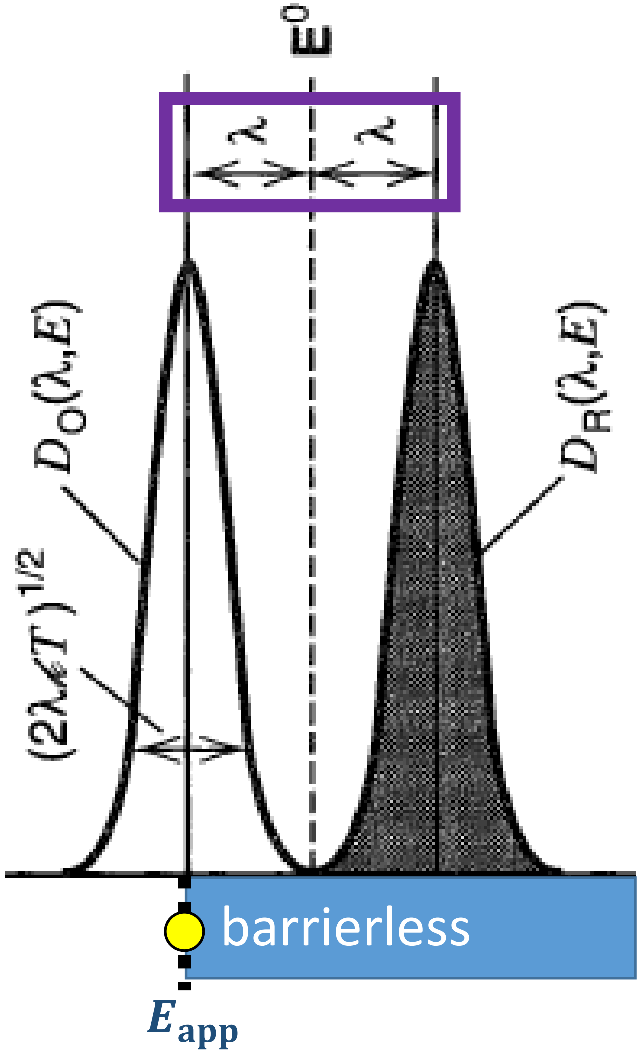


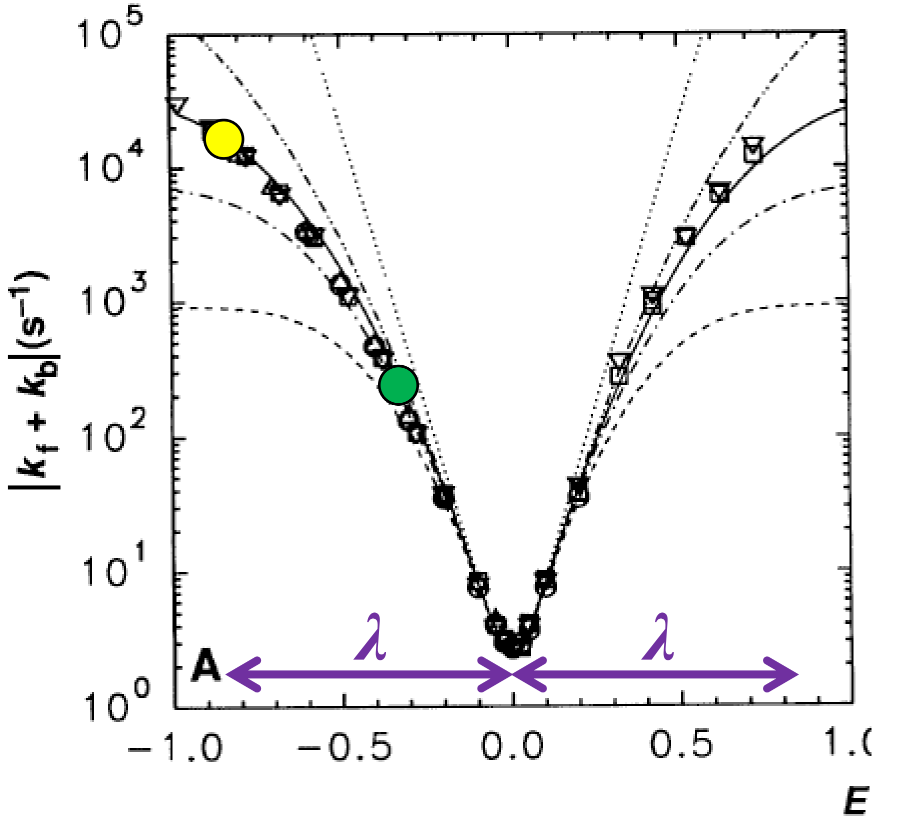
λ = 0.85 eV

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

Marcus–Gerischer Theory







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 (M)etal working electrode, $\bar{\mu}_e^{M}$, through variations in E_{app}

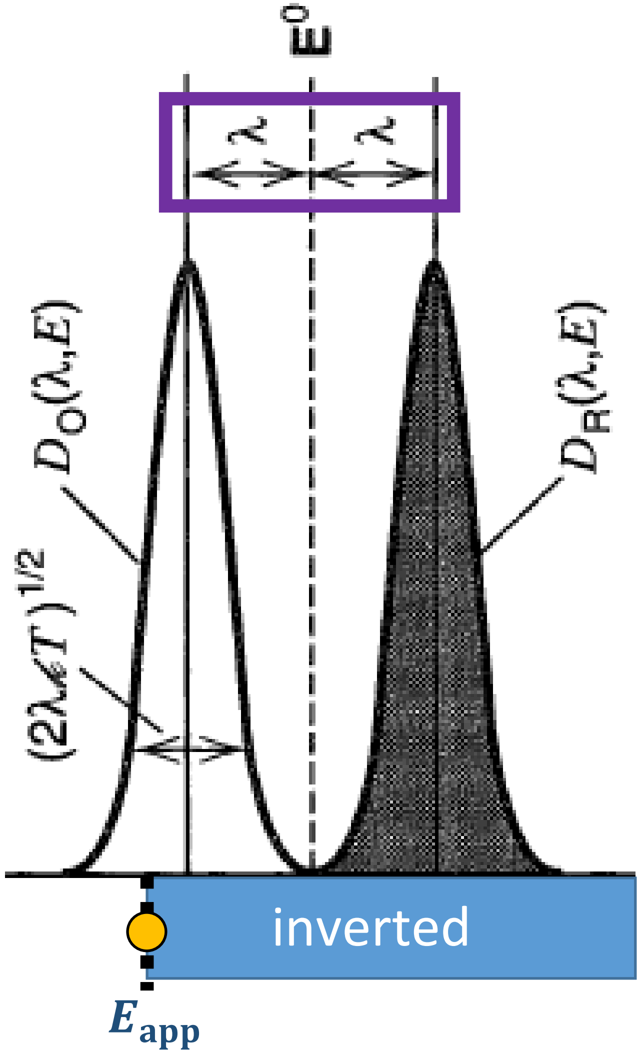
- **But evidence of the inverted region is a little challenging to clearly observe**

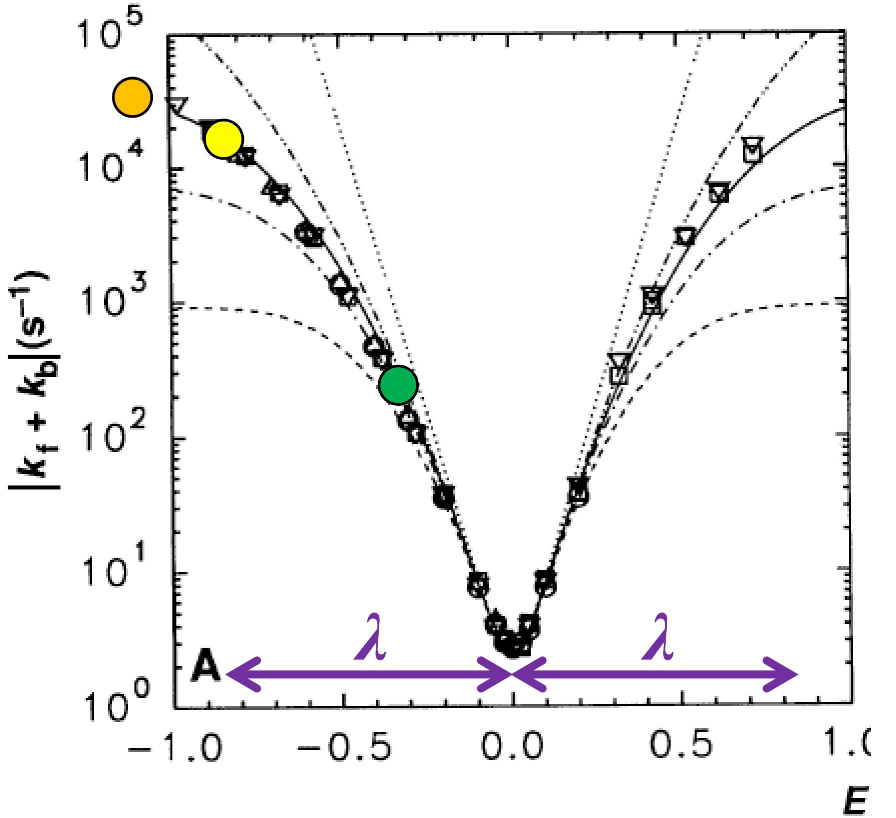
… what if Chidsey had plotted the derivative of his data on the right?

… what do you expect that would have looked like?

… a nice Marcus parabola!

… I wish he had done that!





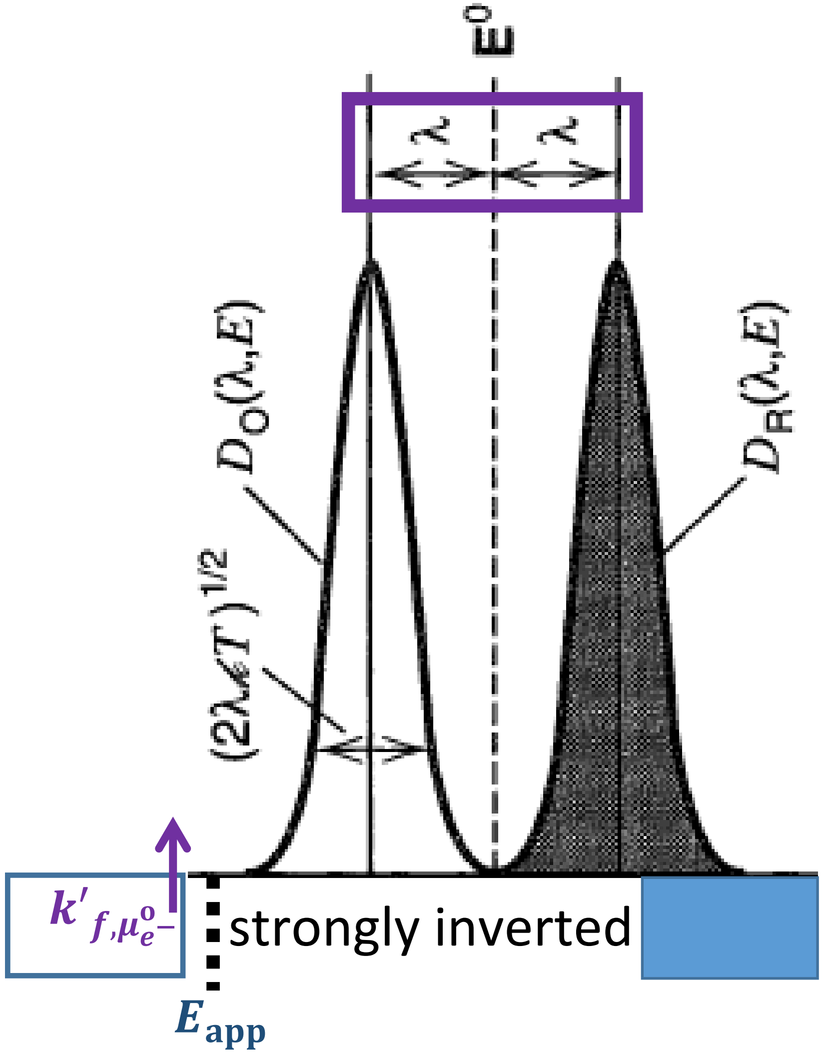
λ = 0.85 eV

… anyway… why is λ so small in water? **… think about the metal!**

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

Marcus–Gerischer Theory

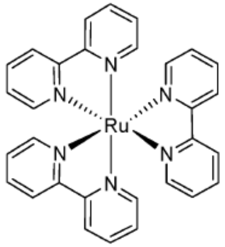
- Use of a semiconductor limits the electronic states to those with (approximately) a single $\mu_{e^-}^{o}$, which makes analysis of data simpler, i.e. one does not need to consider a distribution of states in the electrode
- **But one cannot alter the driving force, $\Delta G_{AB}{}^{o}$, by simply changing the electrochemical potential of electrons (e⁻) in the <u>(S)emi(C)onductor</u> working electrode, $\overline{\mu}_e^{SC}$, through variations in E_{app}, because instead that 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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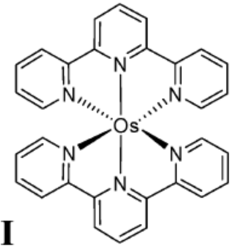
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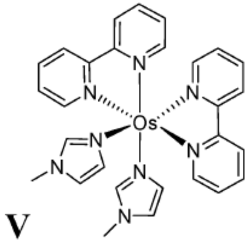
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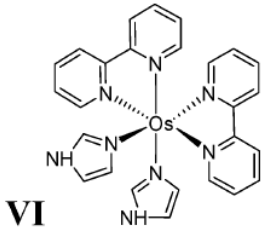
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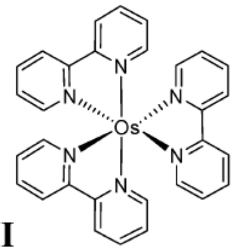
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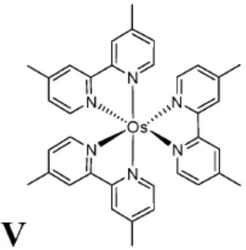
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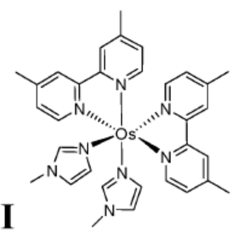
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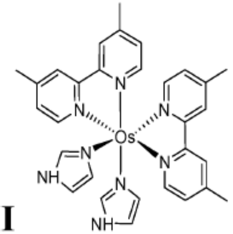
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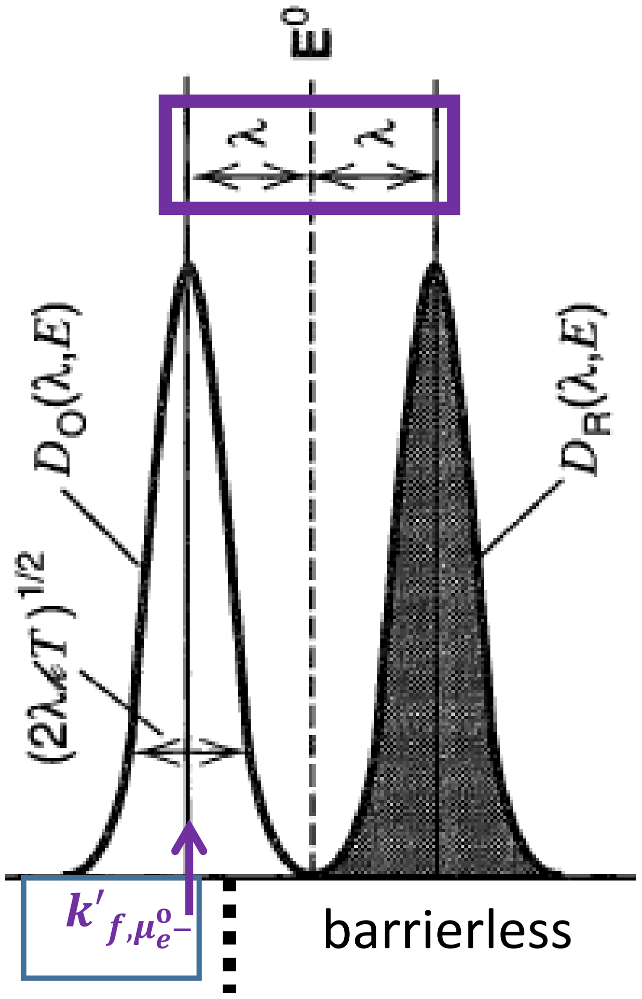


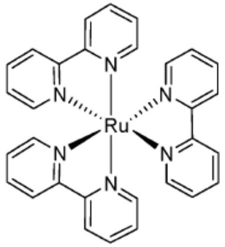
$k'_{f,\mu_{e^-}^{\mathrm{o}}}$

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

Marcus–Gerischer Theory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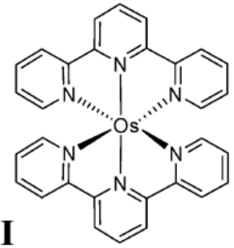
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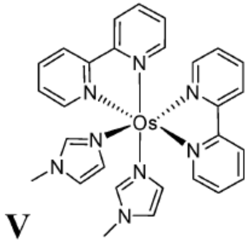
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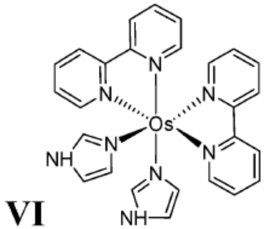
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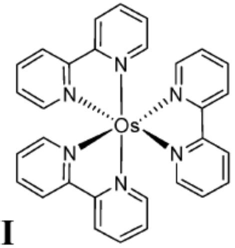
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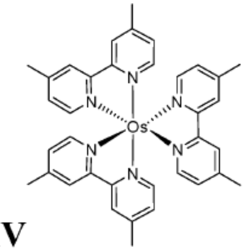
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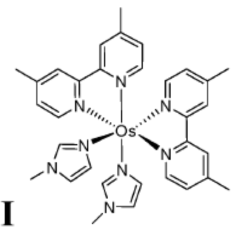
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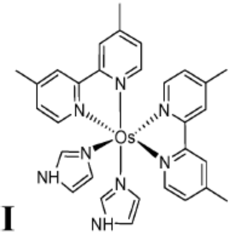
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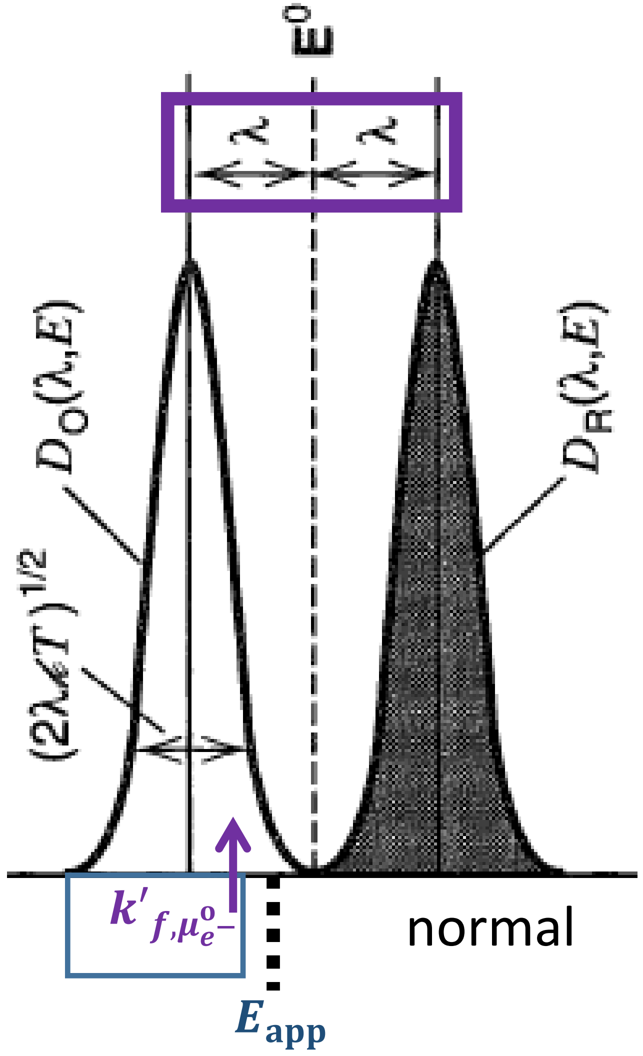

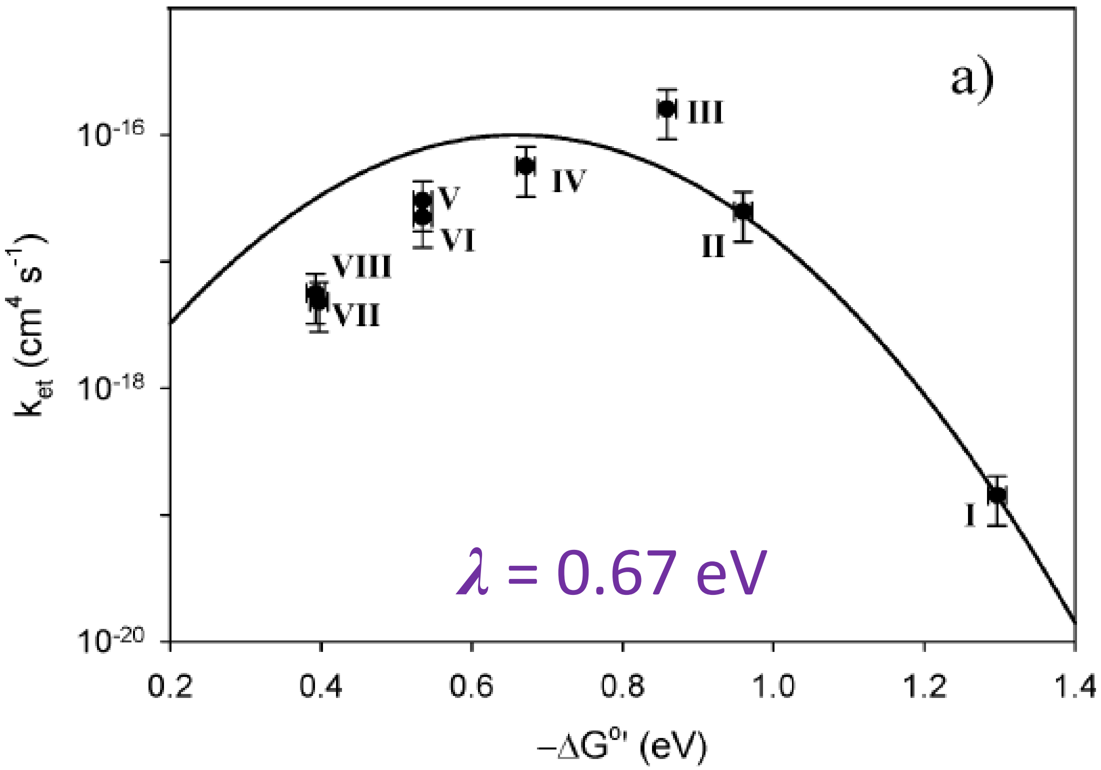

$\boldsymbol{k}_{\mathbf{IET}}$ (cm^4 s^{-1})… a second-order rate constant!

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

Photophysical Processes

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Today’s Critical Guiding Question

What continuity/conservation laws are most important for photophysical processes like absorption and emission of photons… <u>for real this time: Part 2</u>?

Photophysical Processes

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

Blackbody Radiation

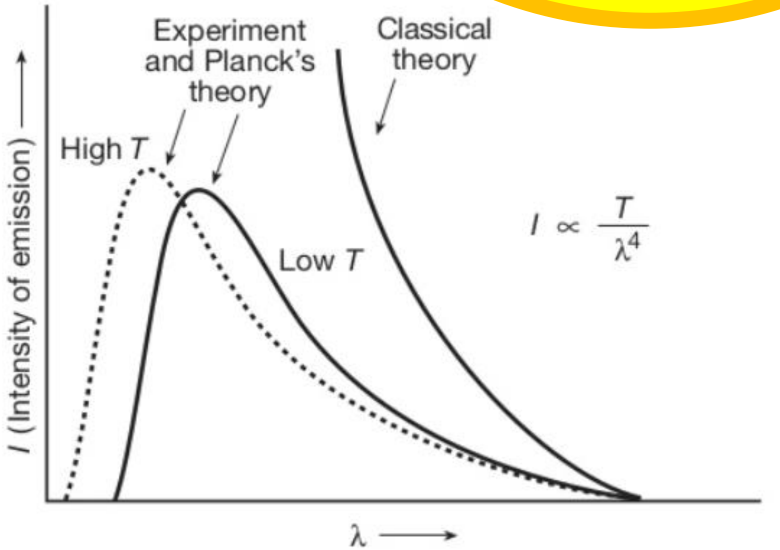
Carnot efficiency limit, $\eta = \frac{w}{Q_\mathrm{H}} = \frac{Q_\mathrm{H} - Q_\mathrm{C}}{Q_\mathrm{H}} = 1 - \frac{Q_\mathrm{C}}{Q_\mathrm{H}} = 1 - \frac{T_\mathrm{C}}{T_\mathrm{H}}$

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

($T \approx 5790$ K)
SUN

EARTH
($T \approx 290$ K)

UNIVERSE
($T \approx 3$ K)



Turro, Chapter 4, Figure 4.1, Page 171

… 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

Photon Properties & Conservation Laws

Where does light come from?

Particle Type: Boson

Mass: 0

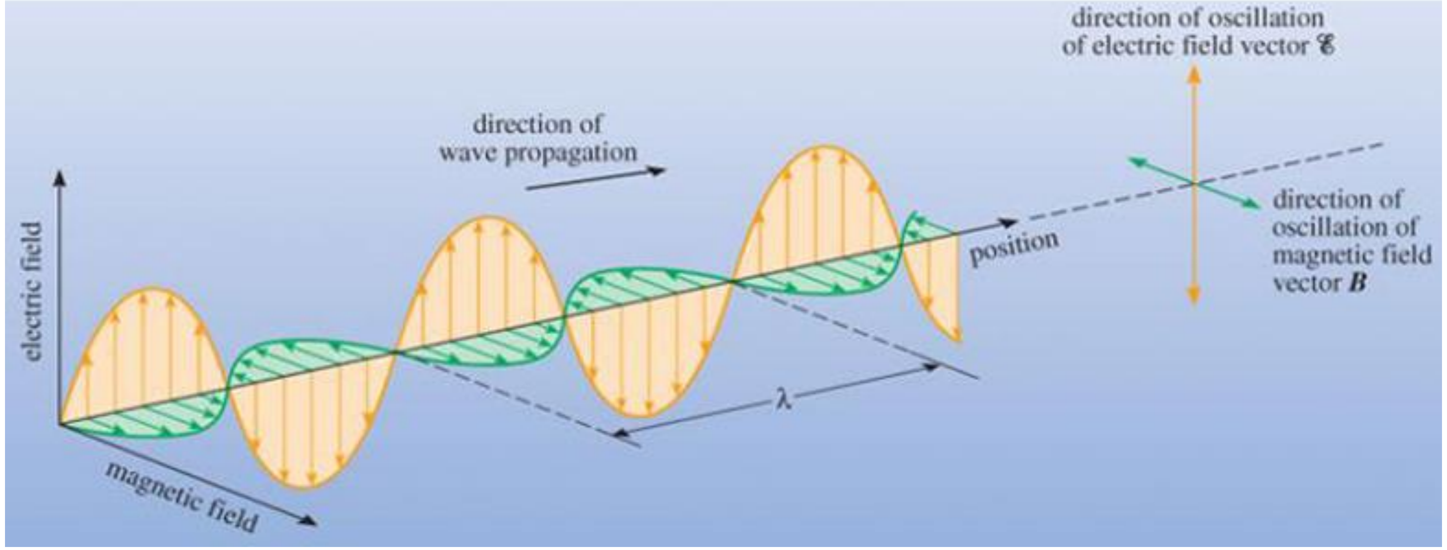
Charge: 0

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: $\vec{\mathrm{E}}$ and $\vec{\mathrm{B}}$



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: $2J + 1$

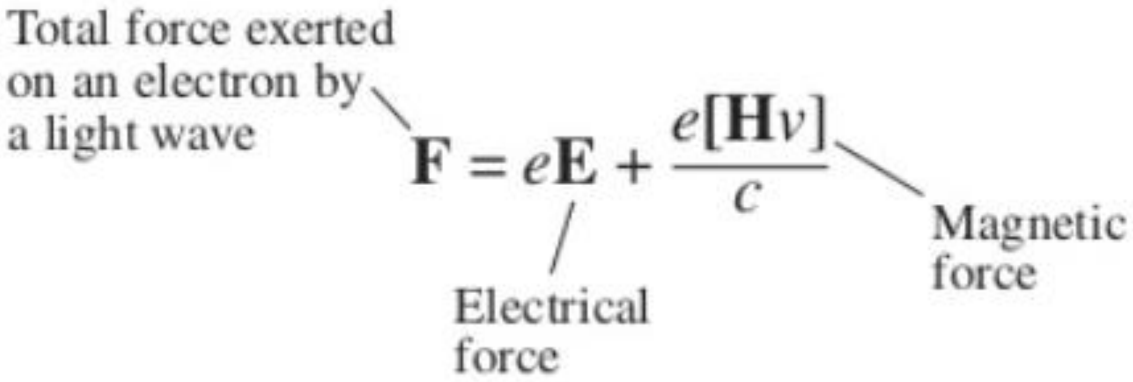
Wait… is a light a wave or a particle?

… I mean, is matter a wave or particle?

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

Light–Matter Interactions

Turro, Chapter 4, Page 184



Total force exerted on an electron by a light wave

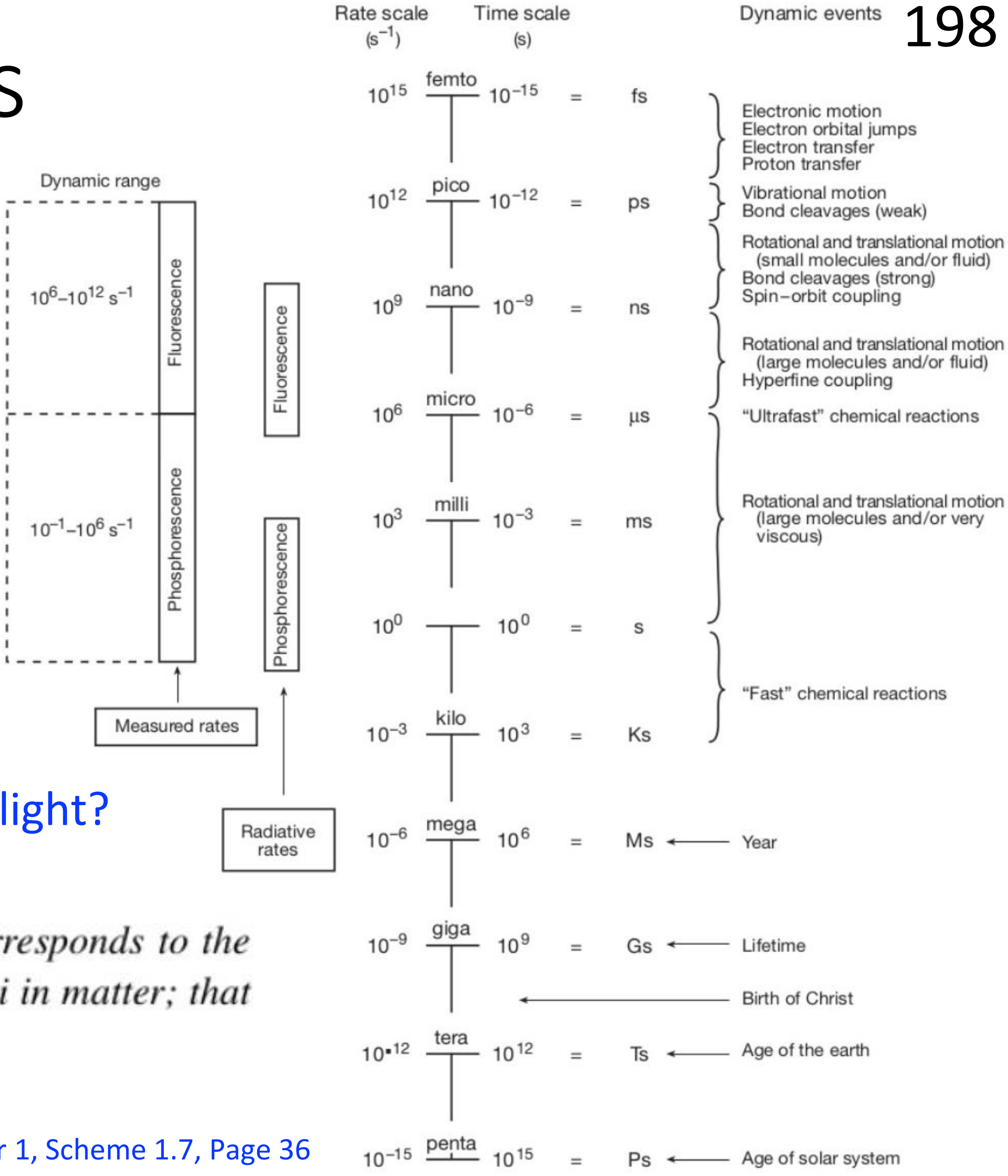
$$\mathbf{F} = e\mathbf{E} + \frac{e[\mathbf{H}\nu]}{c}$$

Electrical force

Magnetic force

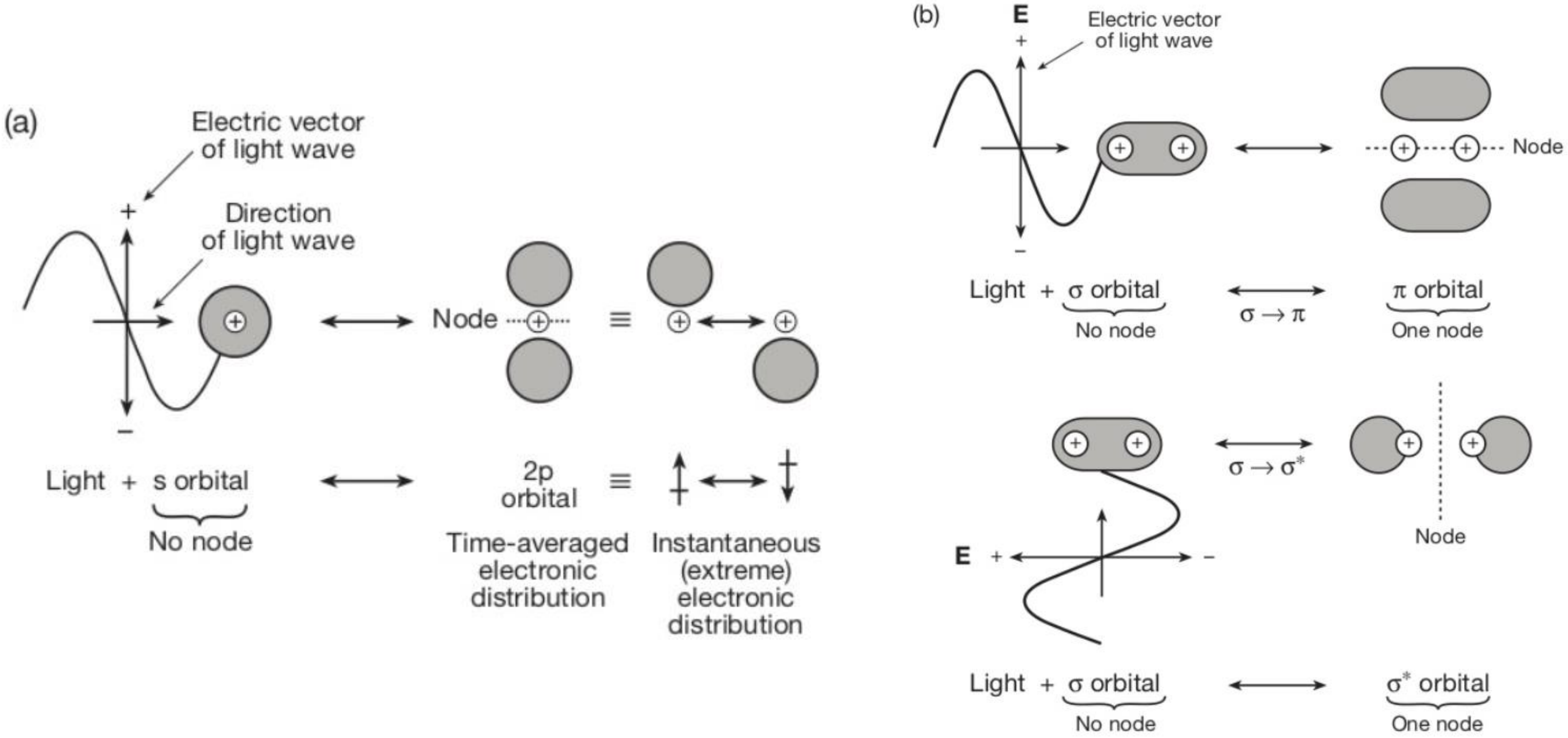
c_{light} = 3 x 10^{18} nm s^{-1}
$v_{electron}$ = 10^{15} – 10^{16} nm s^{-1}
v_{nuclei} = 10^{13} – 10^{14} nm s^{-1}
… so which term dominates the resonant response to light?

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

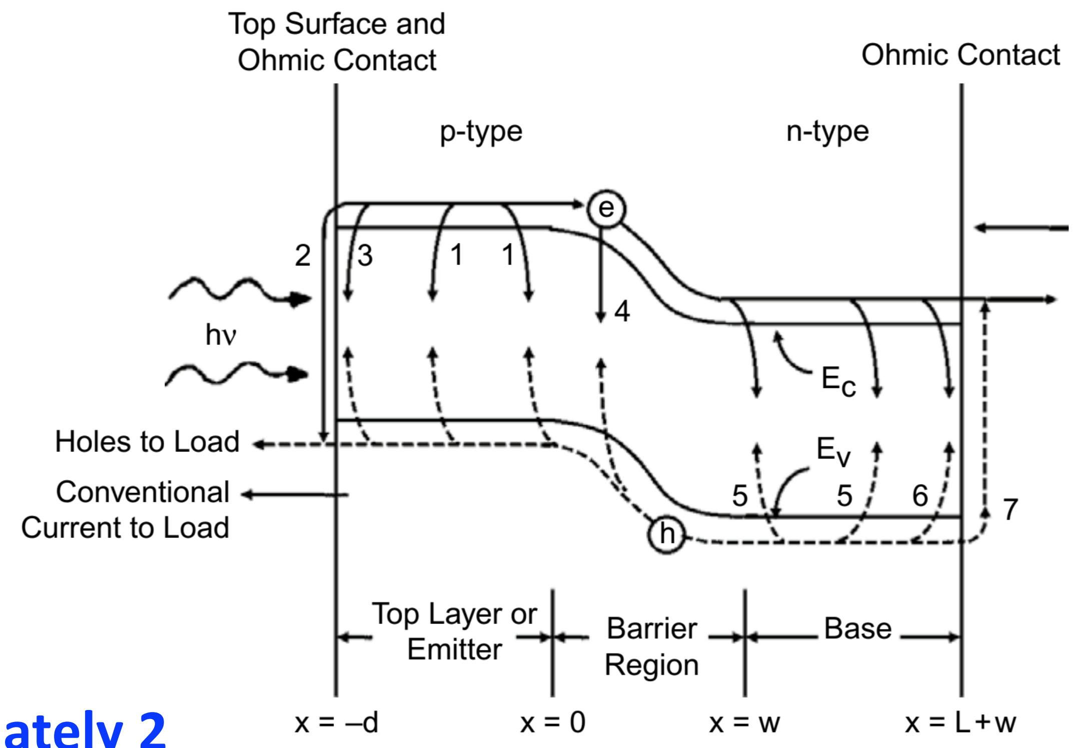
Light–Matter Interactions



Turro, Chapter 4, Figure 4.6, Page 189

Light–Matter Interactions

$$\frac{\partial c_{\mathrm{A},z_\mathrm{o}}}{\partial t} = \sum_j R_{\mathrm{A},j} - \frac{\partial \mathbf{N}_\mathrm{A}}{\partial z}$$



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

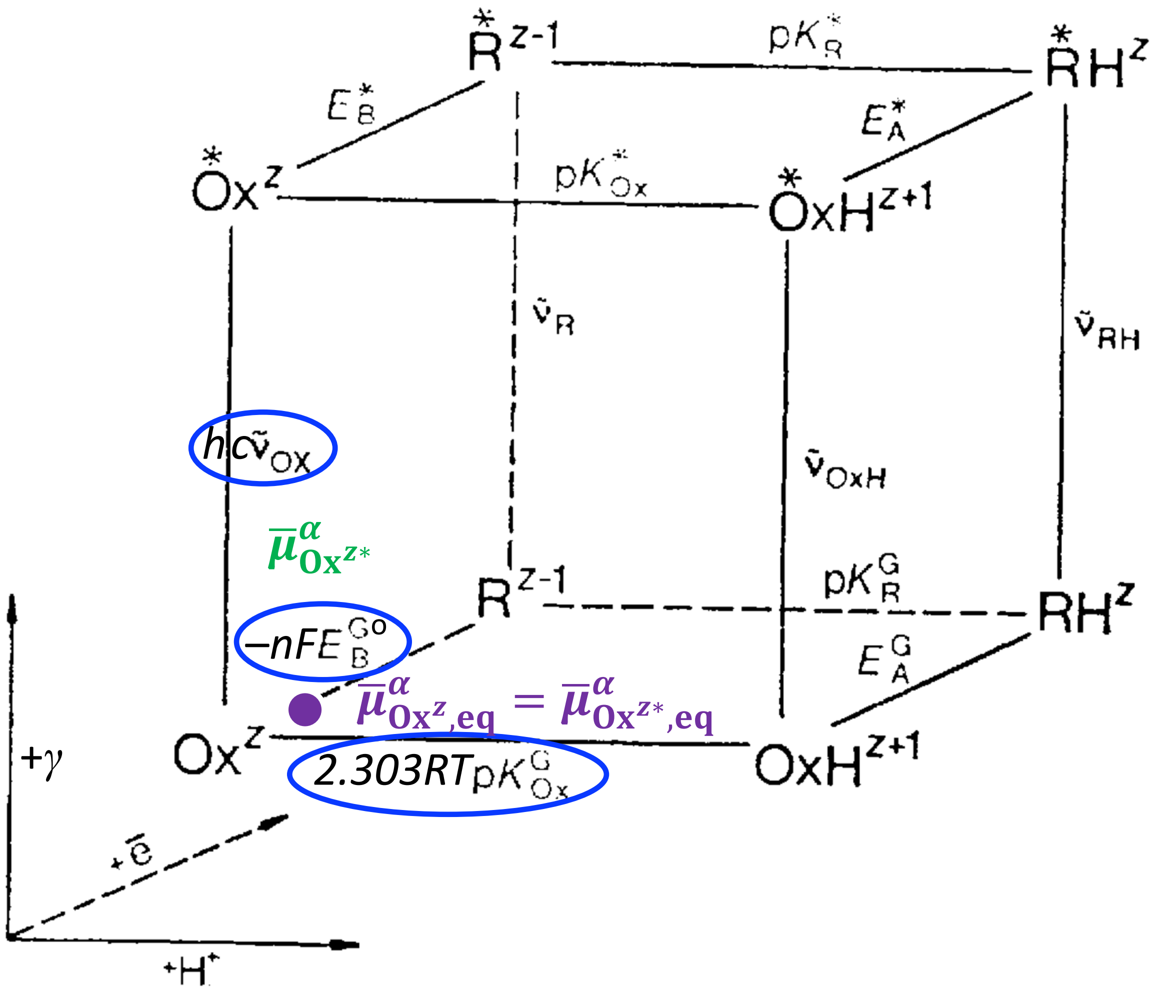
Given a box at temperature, *T*, by what processes can heat be transferred to something inside it?
Okay, now what if inside the box was a vacuum?

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

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

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

Förster Cube and Square Schemes



... all of these free energy terms 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?**

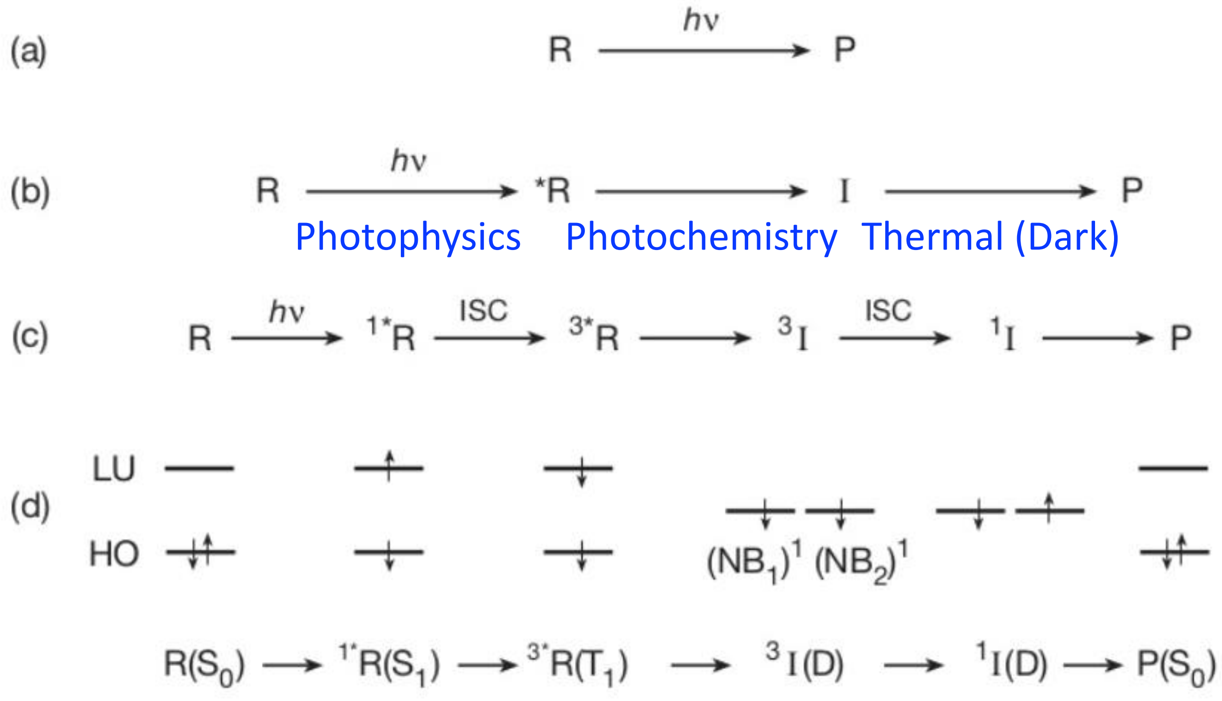
... now, how can one **push/pull** this system out of equilibrium?

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

... hopefully this made a little more sense this time around... and if not, let's keep on trying!

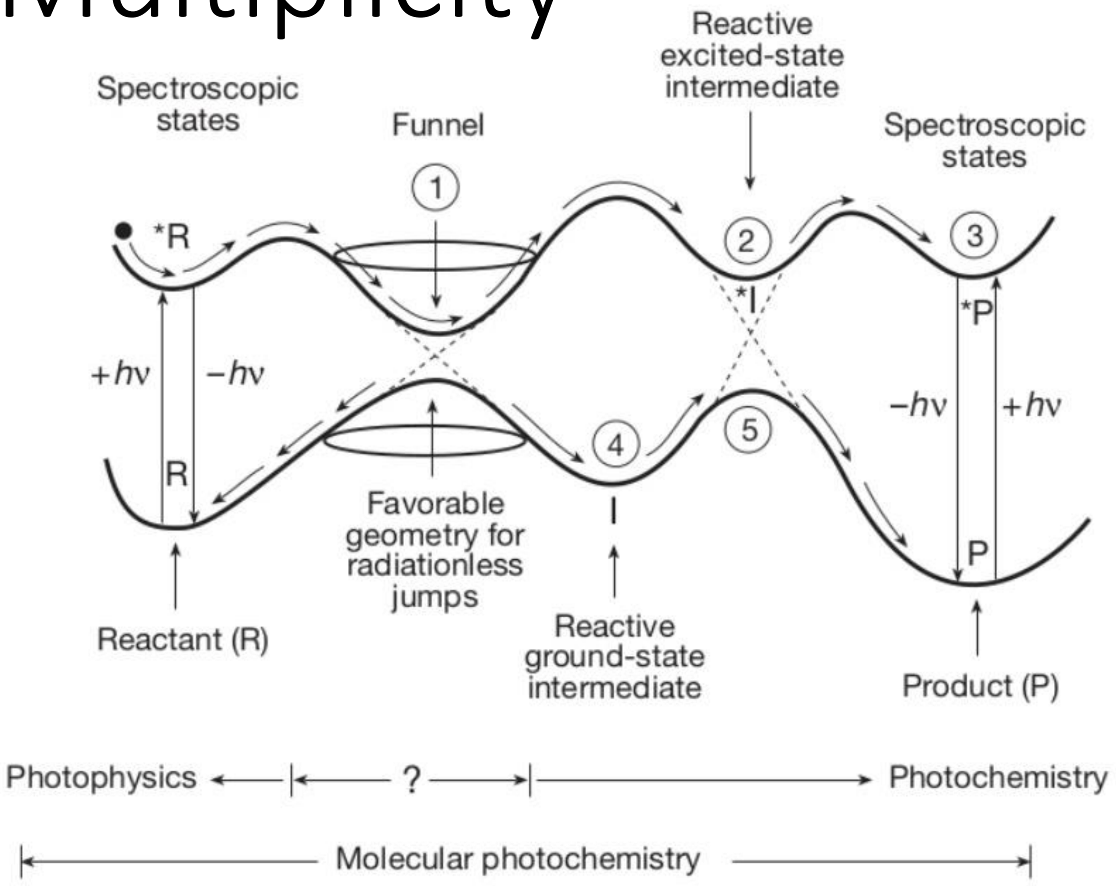
Z. R. Grabowski & W. Rubaszewska, *J. Chem. Soc. Faraday Trans. 1*, **1977**, *73*, 11–28

Jablonski Diagram & Spin Multiplicity



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

What is the origin of the names "singlet" and "triplet"?

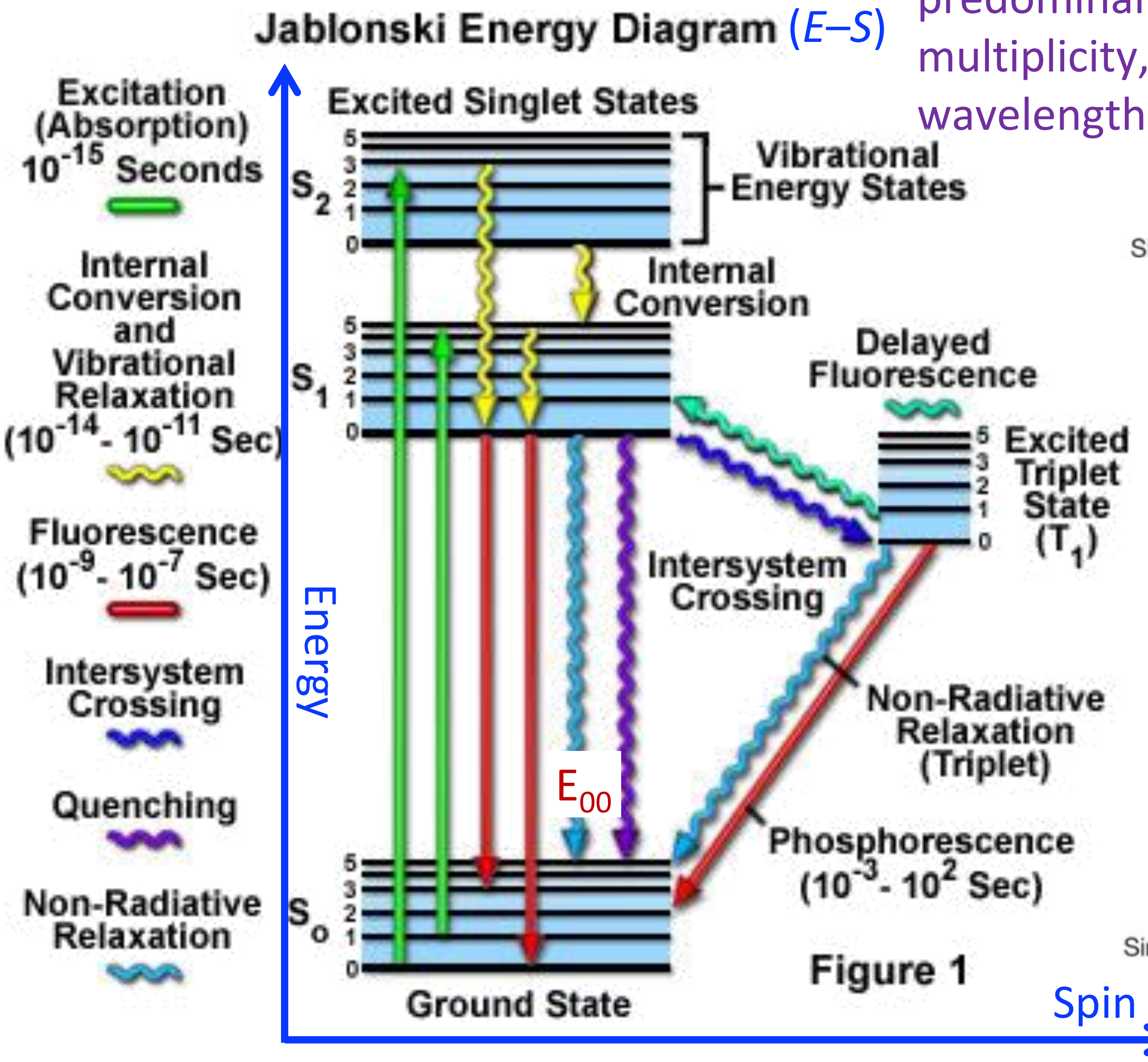
… Angular Momentum Energy Degeneracy, g_J: $2J + 1$

… when $J = 0$, $g_J = 1$… sounds like a "Singlet (S or ^{1}X)"

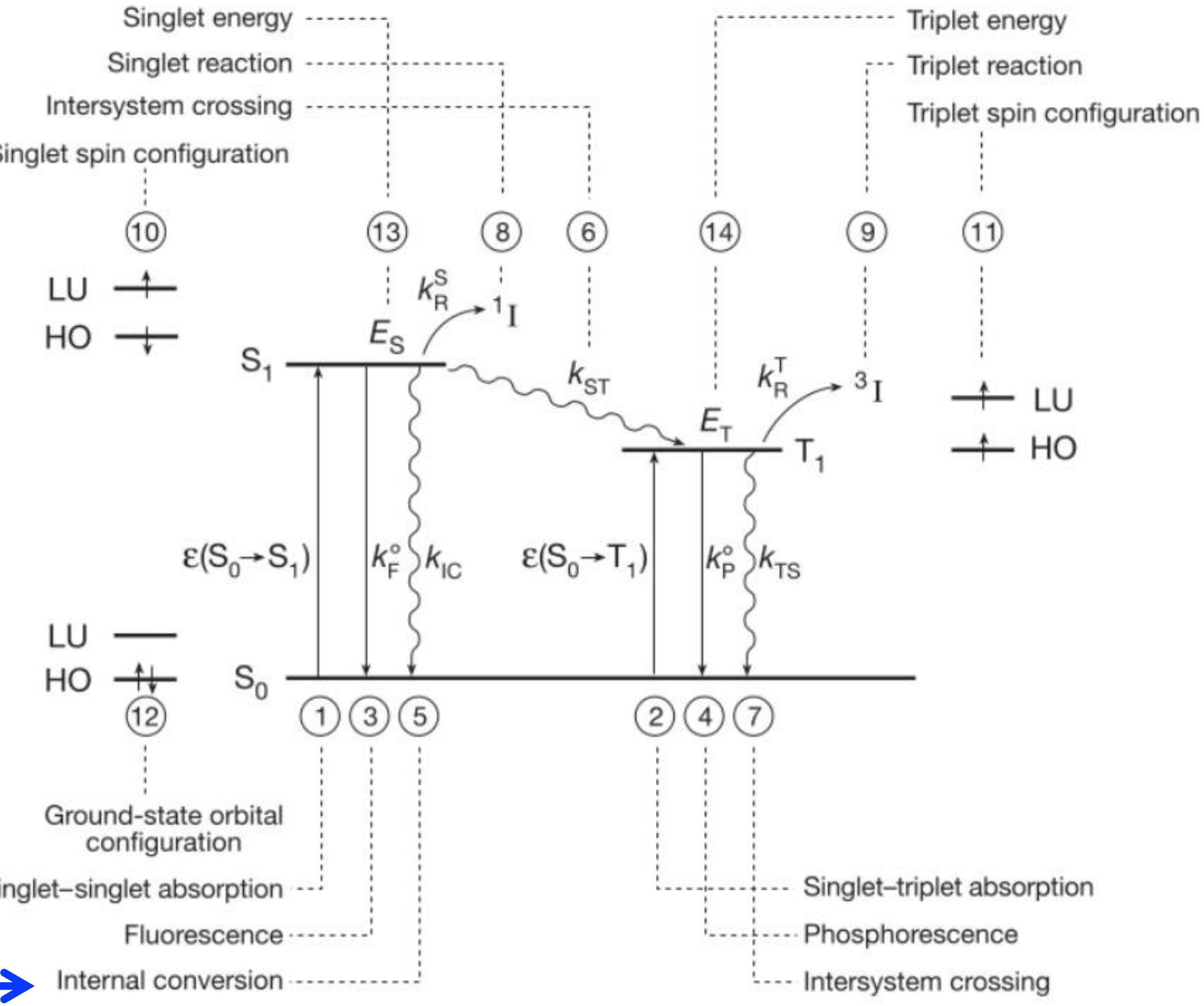
… when $J = 1$, $g_J = 3$… sounds like a "Triplet (T or ^{3}X)"

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

Today’s Critical Guiding Question

What continuity/conservation laws are most important for photophysical processes like absorption and emission of photons… for real this time: Part 2?