



# Lecture #9 of 12

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... wow, those were some neat examples of photochemistry...

(REVIEW/UPDATED) 209

... I wish I could learn more about all of them!

... Lucky you! ... Lucky us!

- Synchronous e-presentation: **11 min max + 2 min** for Q&A, as 6 – 8 slides *emailed to me the day before the presentation*
- One seminal and/or review publication (~70% of the time); include background and the nitty gritty of how it works; **your main goal should be to bridge information presented in the course to your topic, and to teach us something entirely new**
- One recent publication (within the last 5 years) (~30% of the time); include what the paper did, the major discovery, and a critical photochemical assessment of their data interpretation, **including at least one graph or plot of useful data!**

... this, plus discussion participation, equal 50% of your course grade, so take them seriously, but HAVE FUN!

- silver-halide photography
- photolithography
- vision
- vitamin D synthesis
- ultraviolet-light-driven DNA dimerization
- natural photosynthetic ion pump
- natural photosynthetic light-harvesting complex and coherent energy transfer
- natural photosynthetic Z-scheme electron-transport chain
- nanoparticle solar fuels photocatalysis
- dye-sensitized solar cells
- excitonic solar cells with trap states
- dye lasers
- medical applications
- fluorescence microscopy pH sensing
- fluorescence microscopy electric field sensing
- long-lived phosphorescence by organic molecules
- persistent luminescence by lanthanide-doped phosphors
- chemiluminescence
- photoredox catalysis in organic synthesis
- photolabile organic radicals
- atmospheric chemistry in the ozone layer with refrigerants
- photolabile inorganic coordination compounds
- light-induced excited spin-state trapping (LIESST) spin-crossover effect
- molecular solar thermal energy storage (MOST)
- triplet-triplet annihilation upconversion
- hot/ballistic excited-state electron transfer

... **or propose your own to me...** but I really do prefer topics from this list

You will get one of your top 5 choices... **so please email them to me ASAP!**



# Photophysical Processes

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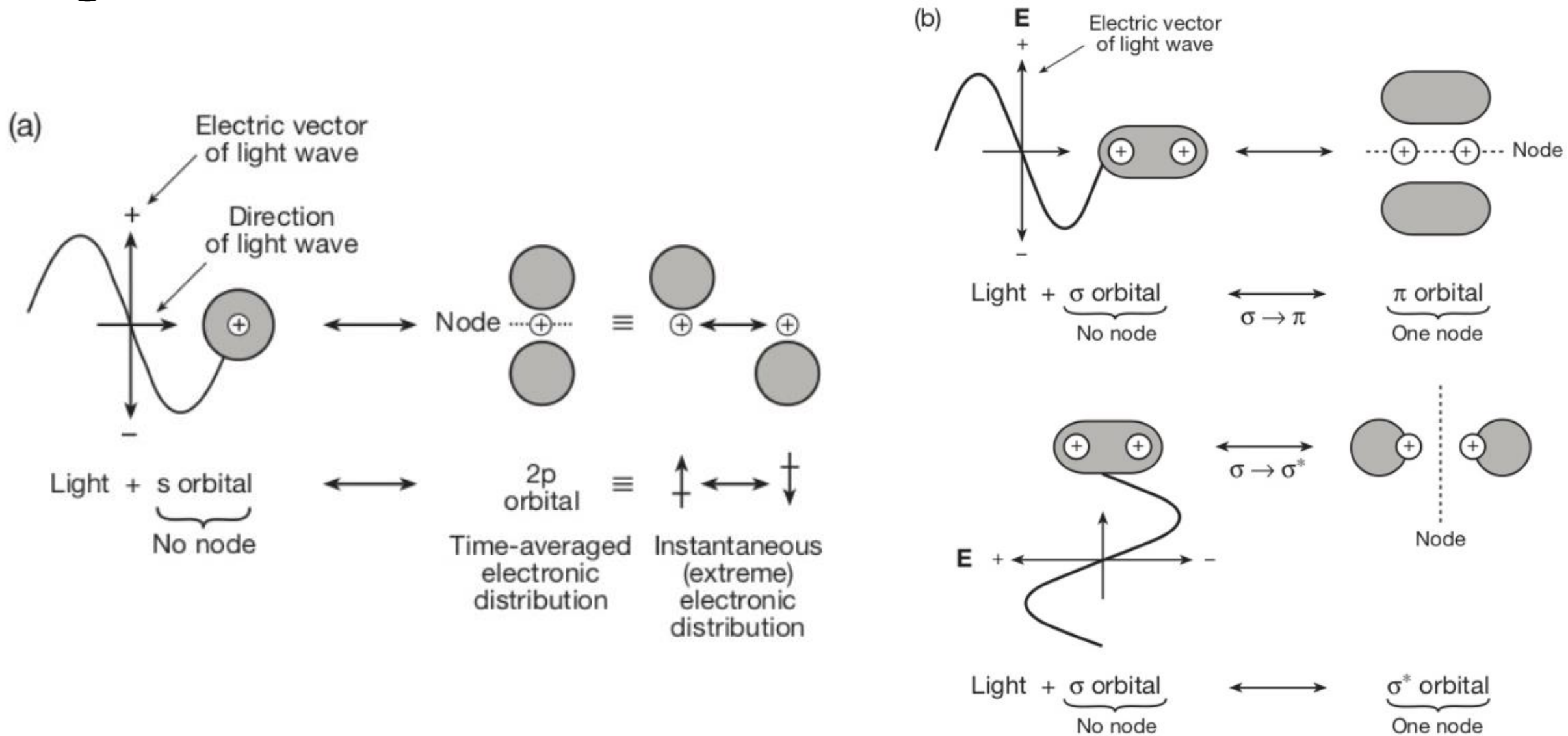
# Today's Critical Guiding Question

*What continuity/conservation laws are most important for photophysical processes like absorption and emission of photons... for real this time, again: Part 3?*

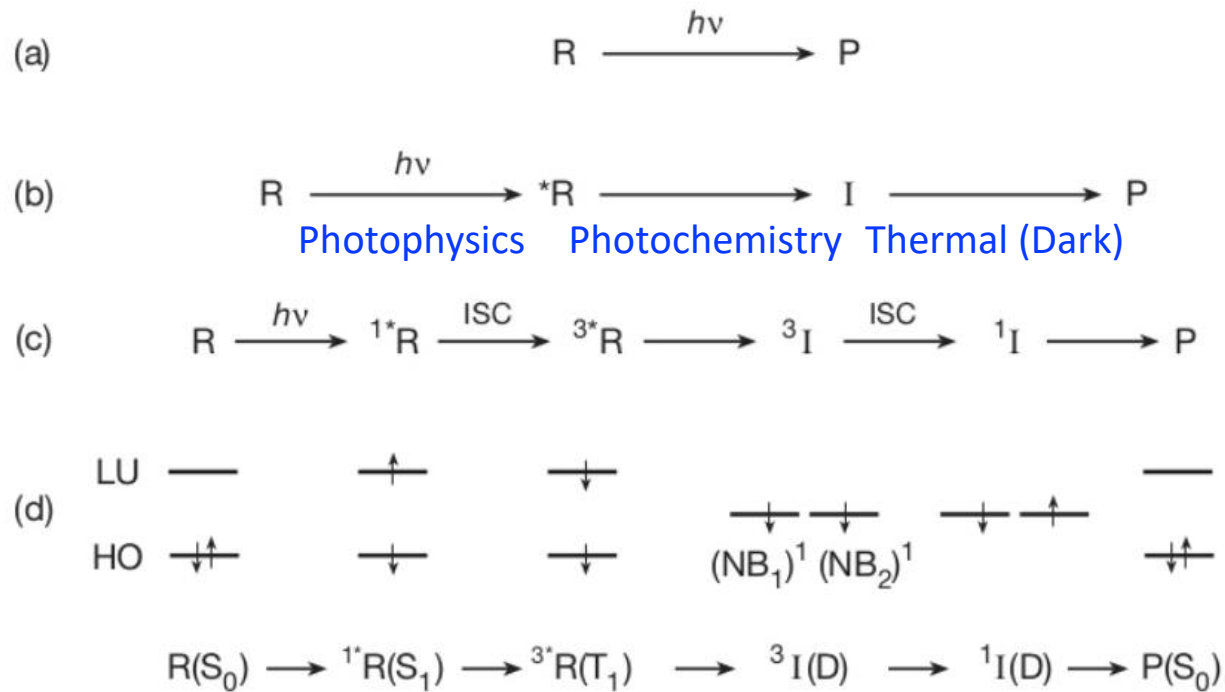
# Photophysical Processes

- 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

# Light-Matter Interactions



# Jablonski Diagram & Spin Multiplicity



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

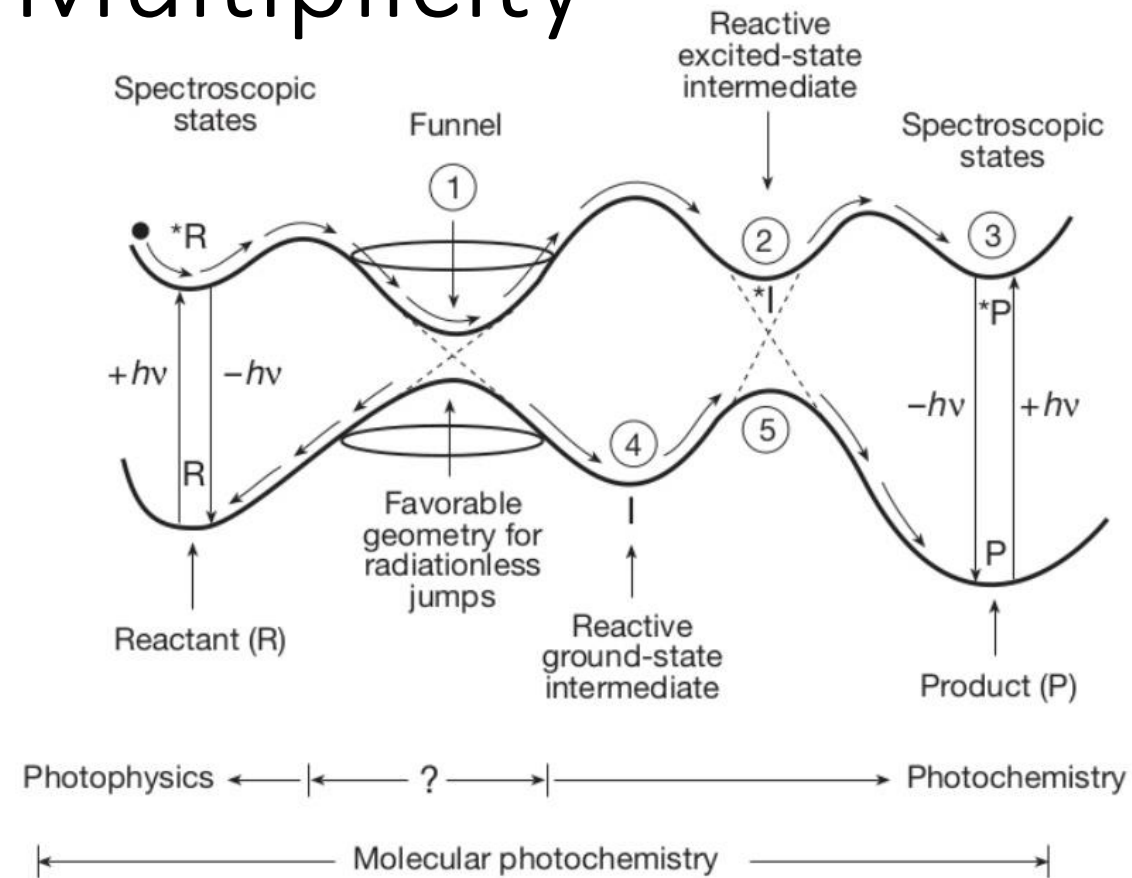
Turro, Chapter 1, Scheme 1.3, Page 13

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 <sup>1</sup>X)"

... when  $J = 1$ ,  $g_J = 3$ ... sounds like a "Triplet (T or <sup>3</sup>X)"



Turro, Chapter 1, Scheme 1.5, Page 21



# 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)

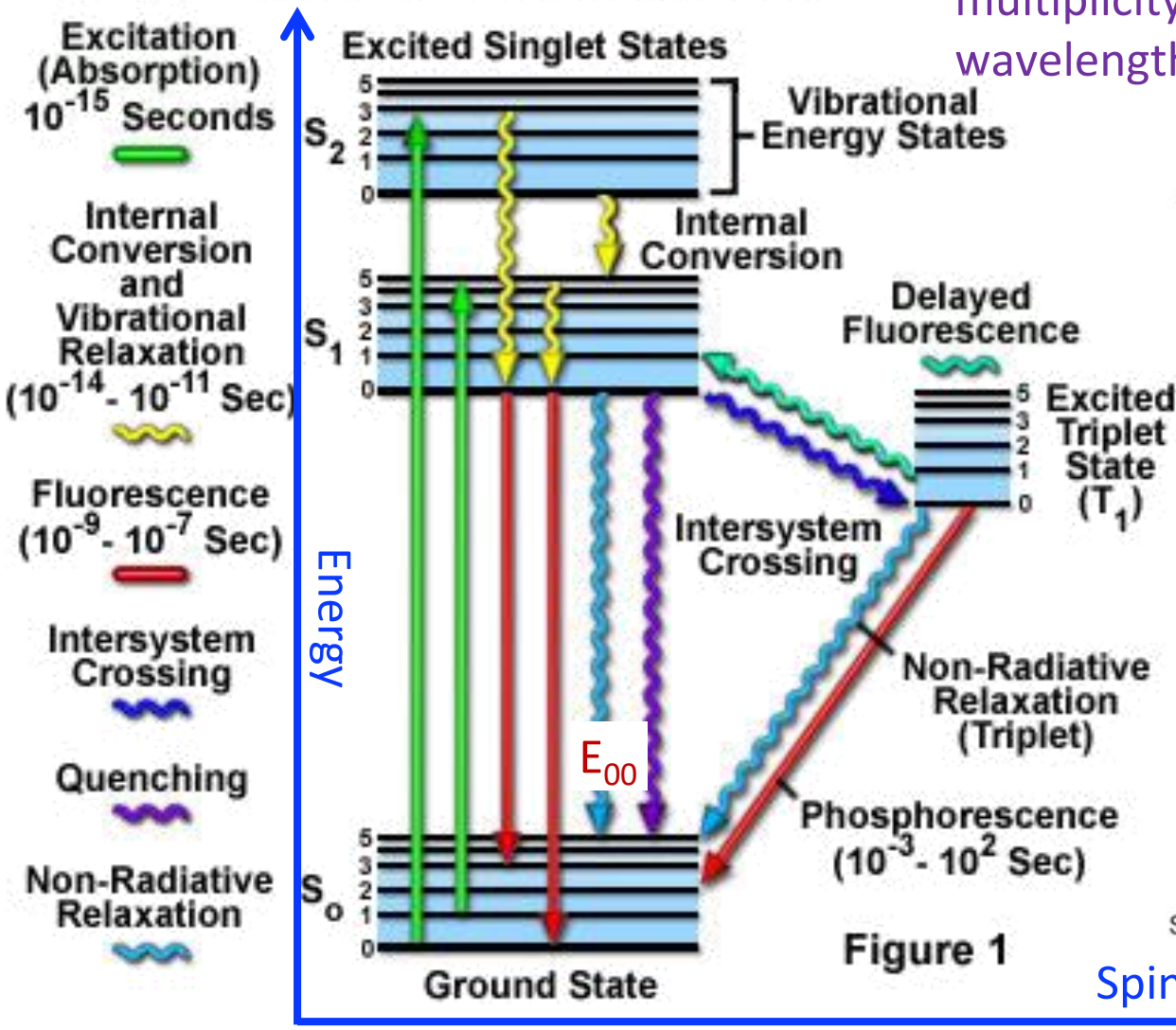
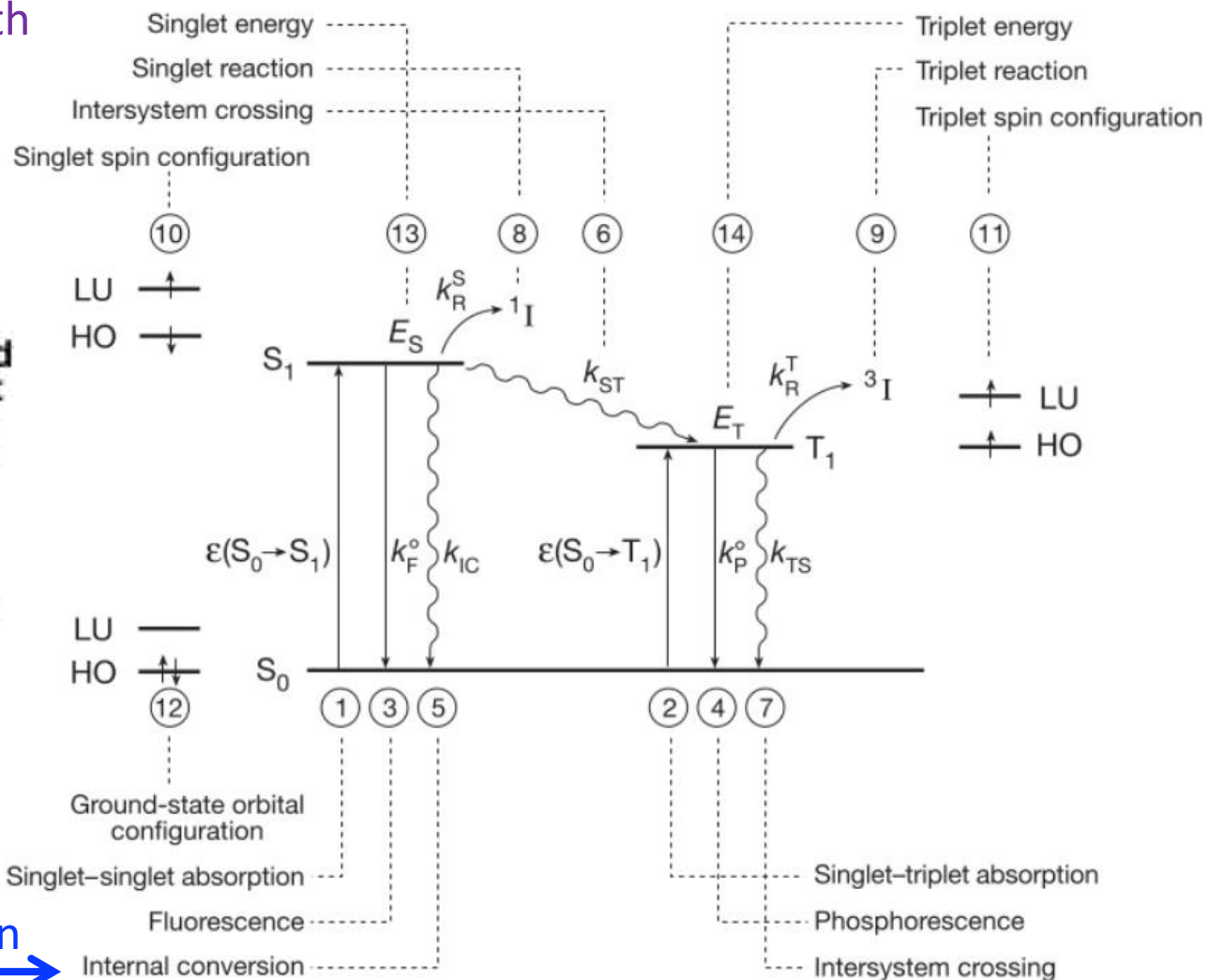
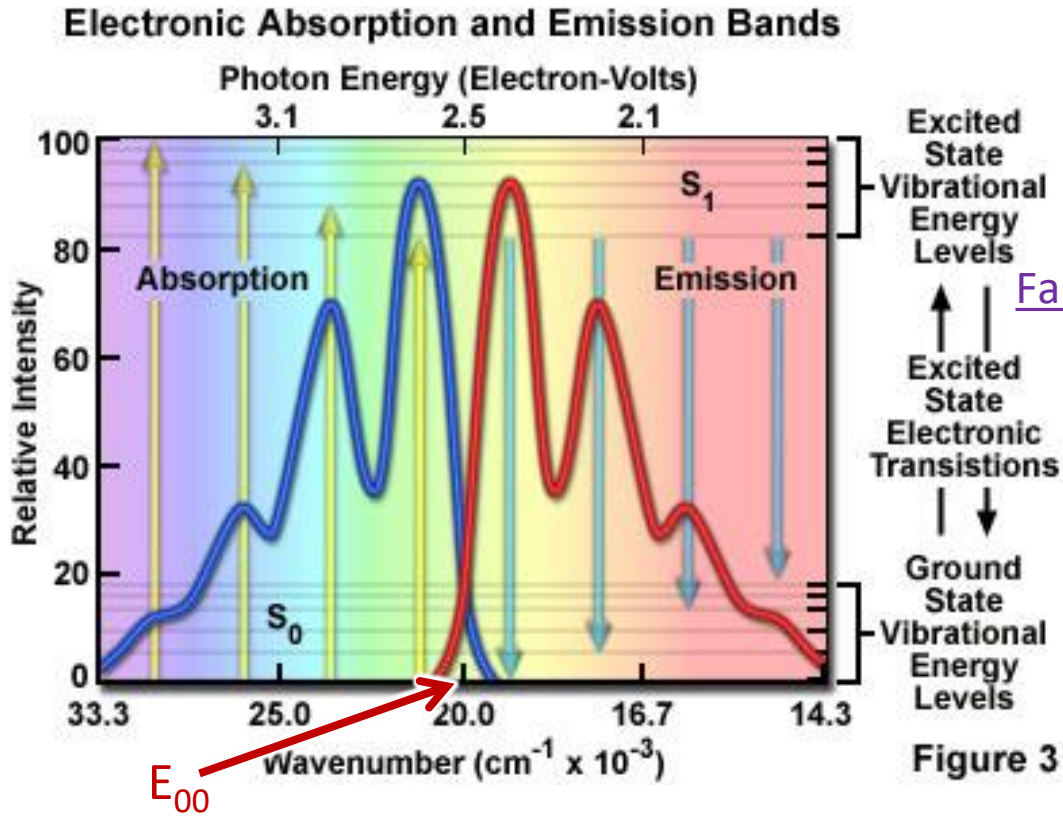


Figure 1

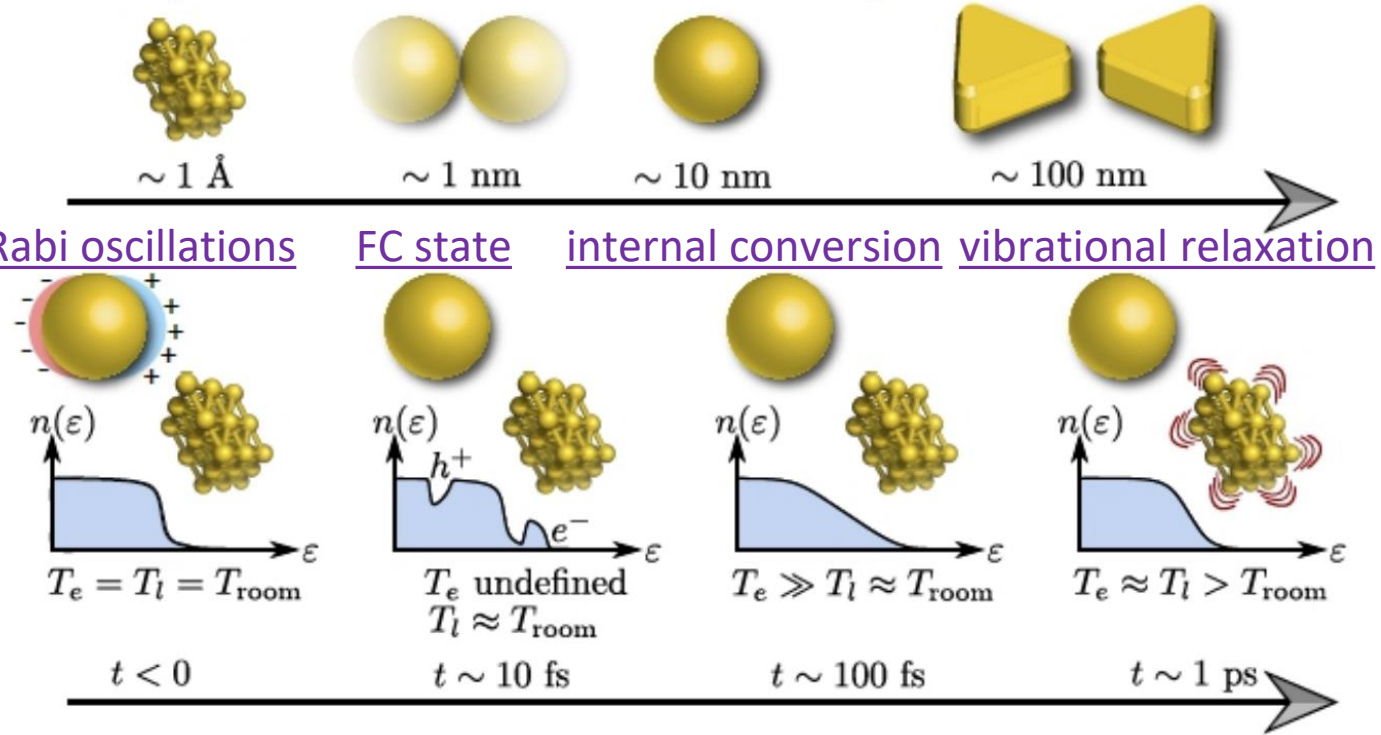
Spin



# Thermally Equilibrated Excited (Thexi) State



Length scales and timescales associated with plasmonic hot carriers



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

... and why are these spectra plotted as a function of wavenumber... and not wavelength?

... so that you can see the mirror-image "rule"

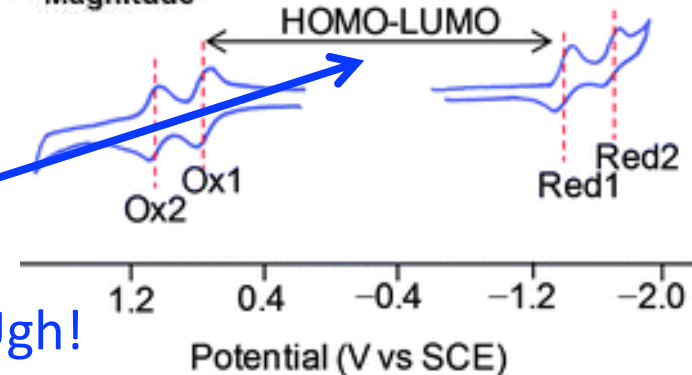
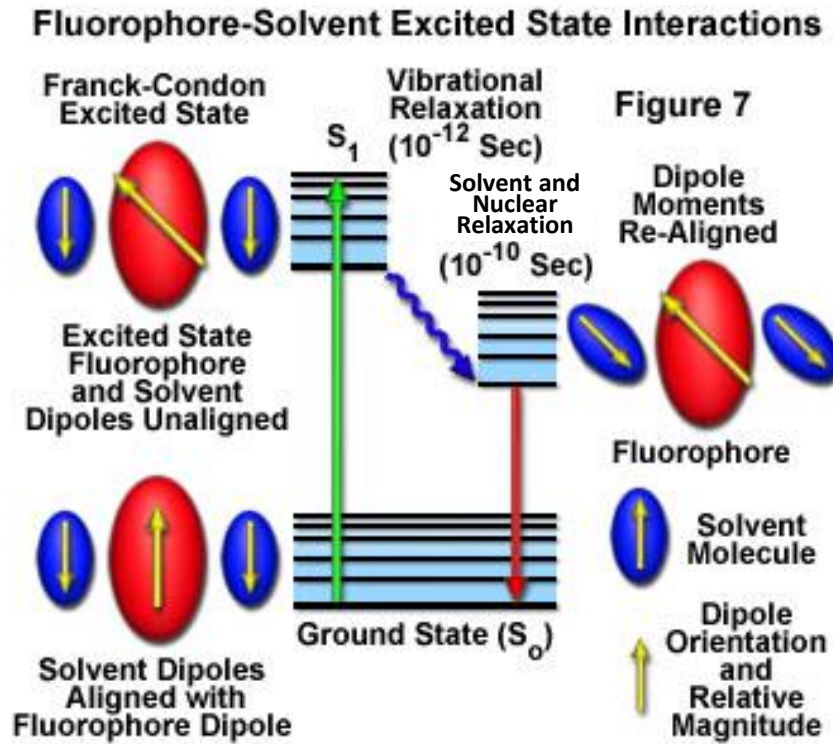
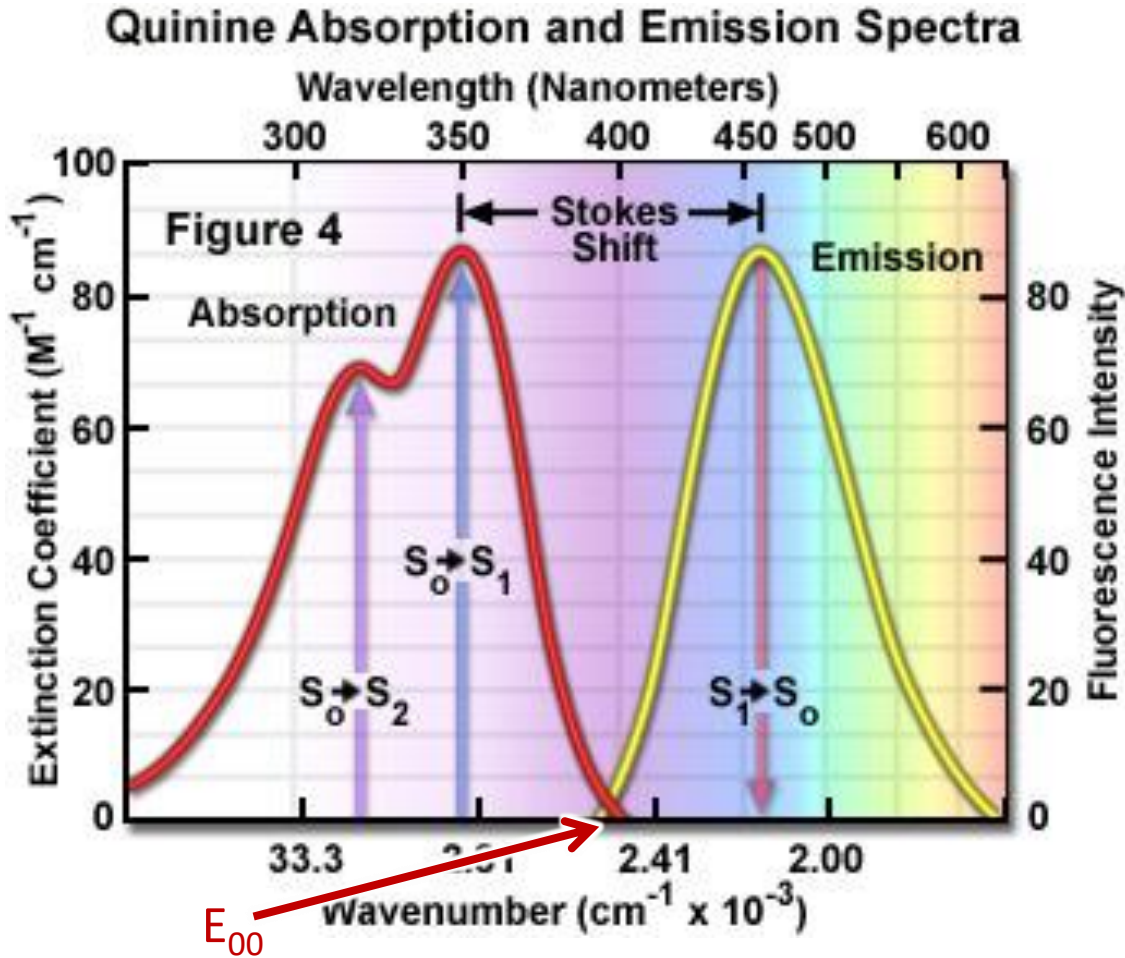
... wait, do molecules and materials undergo the same physical processes and follow the same laws of the universe?... shocking, isn't it?!?!?



# Stokes Shift

... why are these spectra less structured, and with peaks that are further separated?

- higher T
- multiple electronic states close in energy
- multiple strongly coupled vibronic modes
- polar and in solution



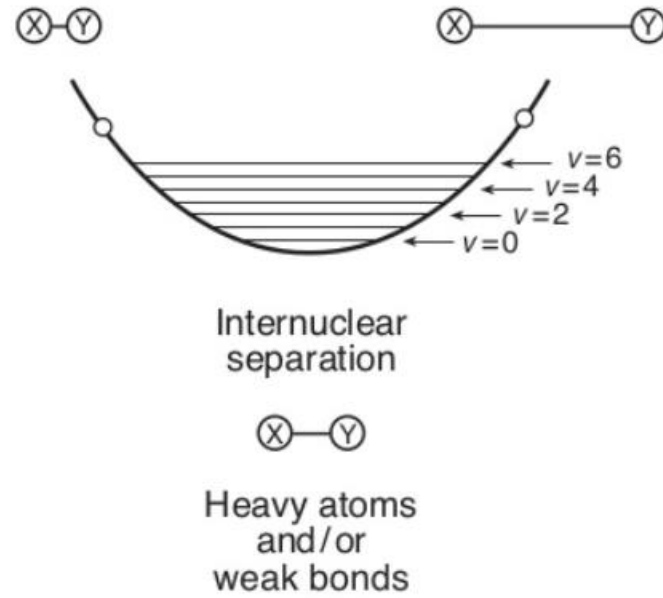
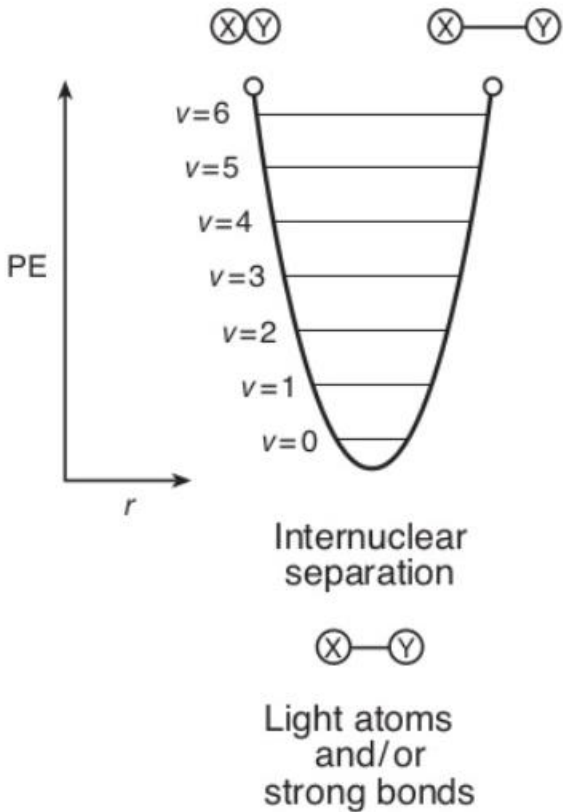
... solvent reorganization in the excited-state!... so is this correct?... No! Ugh!

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

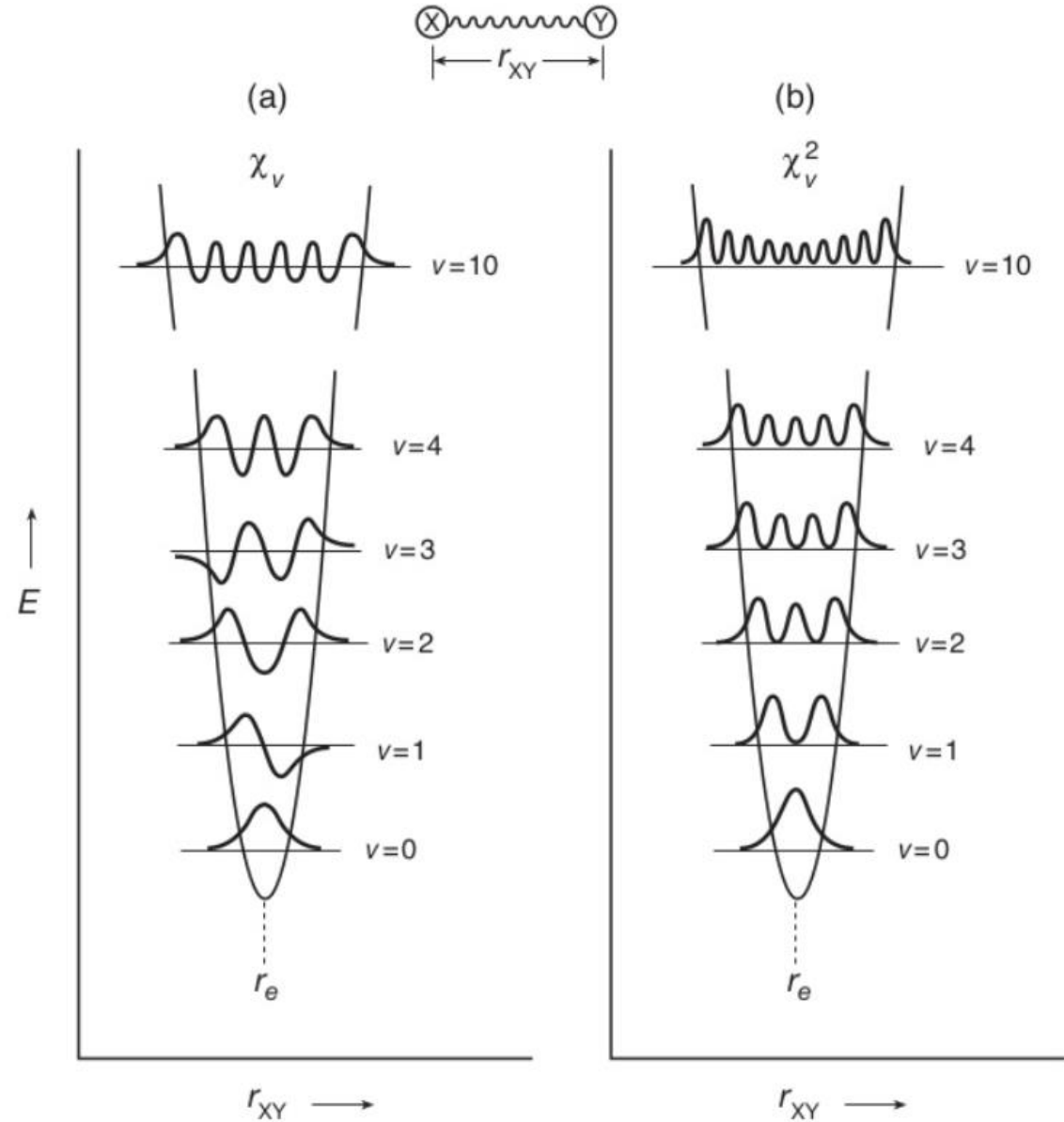
# Jablonski Diagram

## QM Harmonic Oscillator Model

... quantized energy states...  
 ...  $E_v = (v + 1)h\nu = (v + 1)\hbar\omega$   
 ... wavefunctions and probabilities:



Turro, Chapter 2, Figure 2.5, Page 76

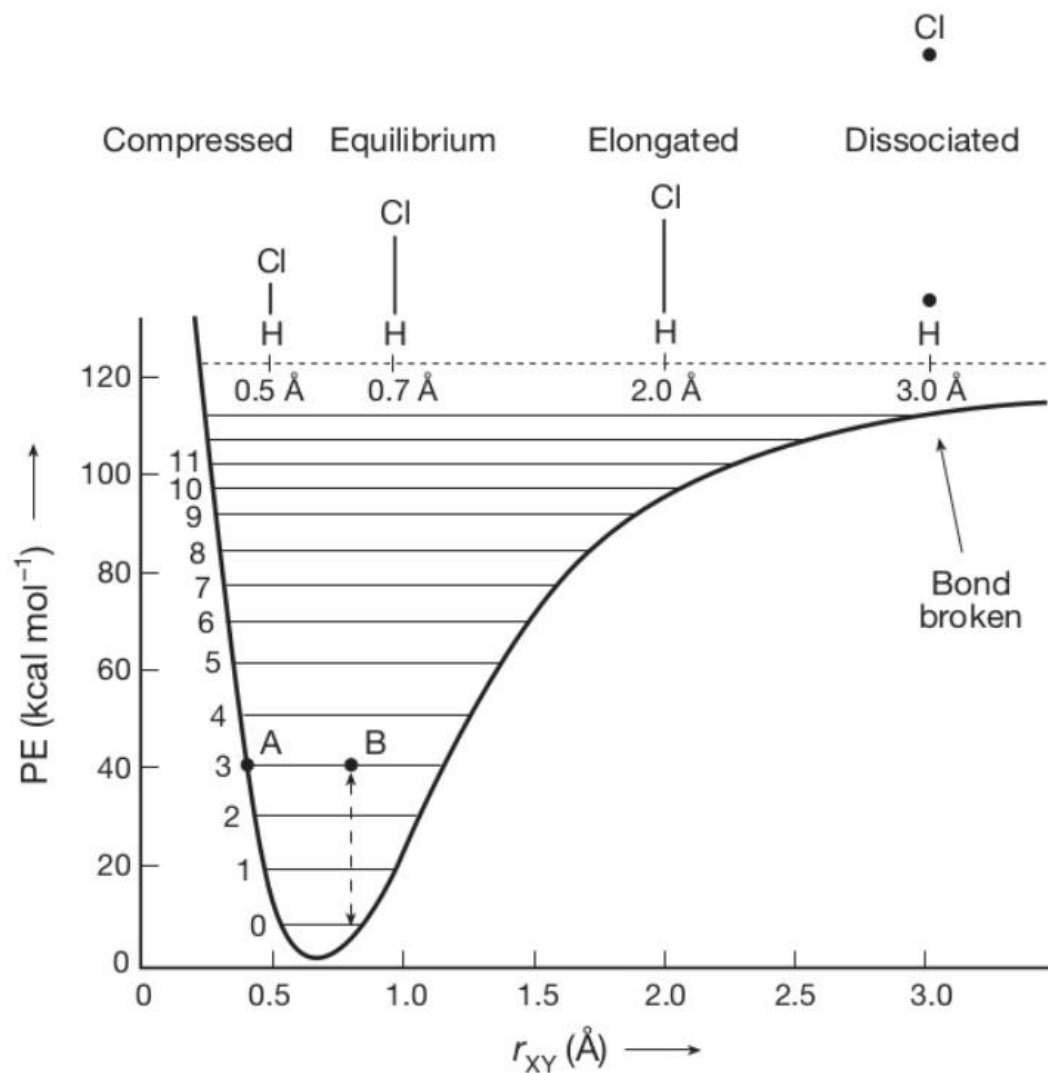


Turro, Chapter 2, Figure 2.6, Page 76

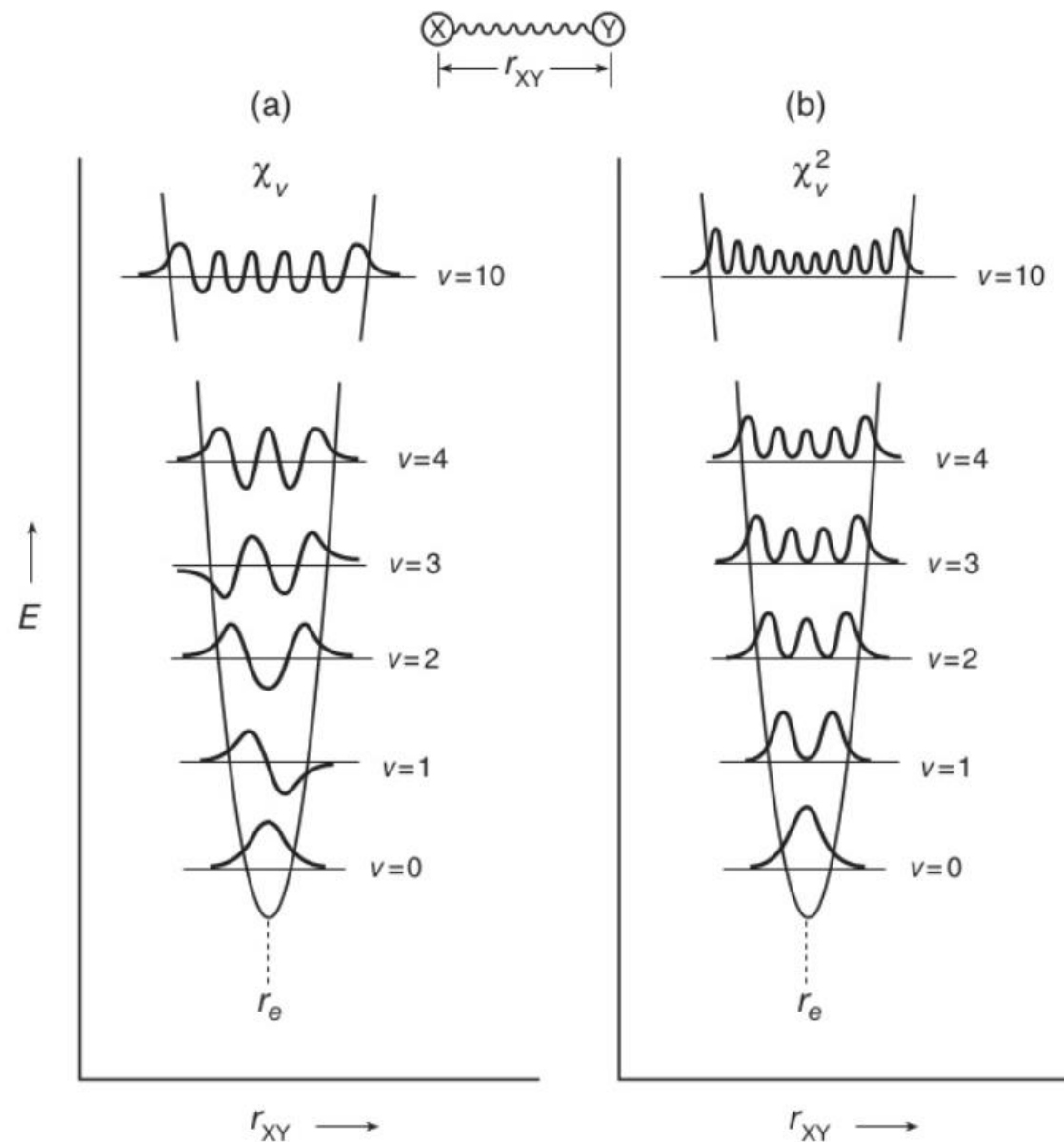
Probability Density(x) =  $|\chi_v(x)|^2 = \chi_v^*(x)\chi_v(x)$

# Jablonski Diagram

## QM Anharmonic Oscillator Model



Turro, Chapter 2, Figure 2.7, Page 81



Turro, Chapter 2, Figure 2.6, Page 76

# Nuclear Terms & F–C Factors

Turro, Chapters 2 and 3

$$k_{\text{obs}} \sim \rho [\langle \Psi_1 | P'_{1 \rightarrow 2} | \Psi_2 \rangle]^2 \quad \text{Fermi's golden rule}$$

Observed Rate Constant      Zero-point Motion-Limited Rate Constant      “Fully Allowed Rate”

$$\underbrace{k_{\text{obs}}}_{\text{Prohibition to maximal caused by "selection rules"}} = k_{\text{max}}^0 \underbrace{f_e \times f_v \times f_s}_{\text{Prohibition factors due to changes in electronic, nuclear, or spin configuration}}$$

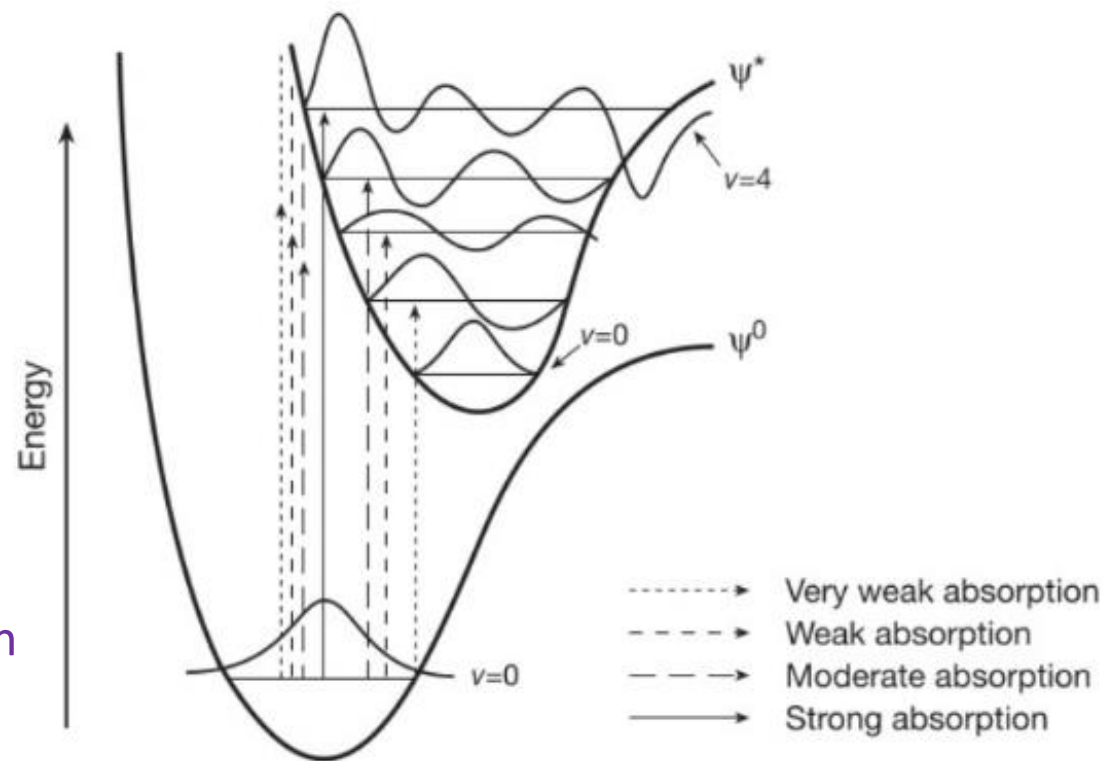
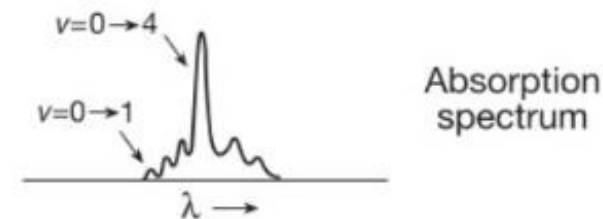
$$\underbrace{\Psi}_{\text{"True" molecular wave function Exact solution to Eq. 2.1}} \sim \underbrace{\Psi_0 \chi S}_{\substack{\text{(orbitals)(nuclei)(spin)} \\ \text{Approximate solution to Eq. 2.1}}}$$

... separable due to the Born–Oppenheimer approximation

$$k_{\text{obs}} = \underbrace{\left[ \frac{k_{\text{max}}^0 \langle \psi_1 | P_{\text{vib}} | \psi_2 \rangle^2}{\Delta E_{12}^2} \right]}_{\text{Vibrational coupling}} \times \underbrace{\left[ \frac{\langle \psi_1 | P_{\text{so}} | \psi_2 \rangle^2}{\Delta E_{12}^2} \right]}_{\text{Spin-orbital coupling}} \times \underbrace{\left[ \langle \chi_1 | \chi_2 \rangle^2 \right]}_{\substack{\text{Vibrational overlap} \\ \text{Franck-Condon factors}}}$$

Overlap integral,  $S_{12} = \int_{-\infty}^{\infty} \chi_1^*(x) \chi_2(x) dx = \langle \chi_1 | \chi_2 \rangle$

Franck–Condon factor,  $\langle \chi_1 | \chi_2 \rangle^2$



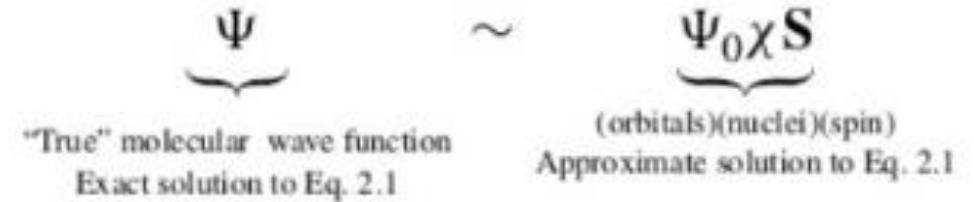
Turro, Chapter 3, Figure 3.3, Page 129

Transition to what vibronic state is most favorable/rapid by absorption?  
... and what about by emission?



# B–O Approximation, F–C Principle, TDM Operator

- Born–Oppenheimer (B–O) approximation: separability of electronic and nuclear terms in the wavefunction



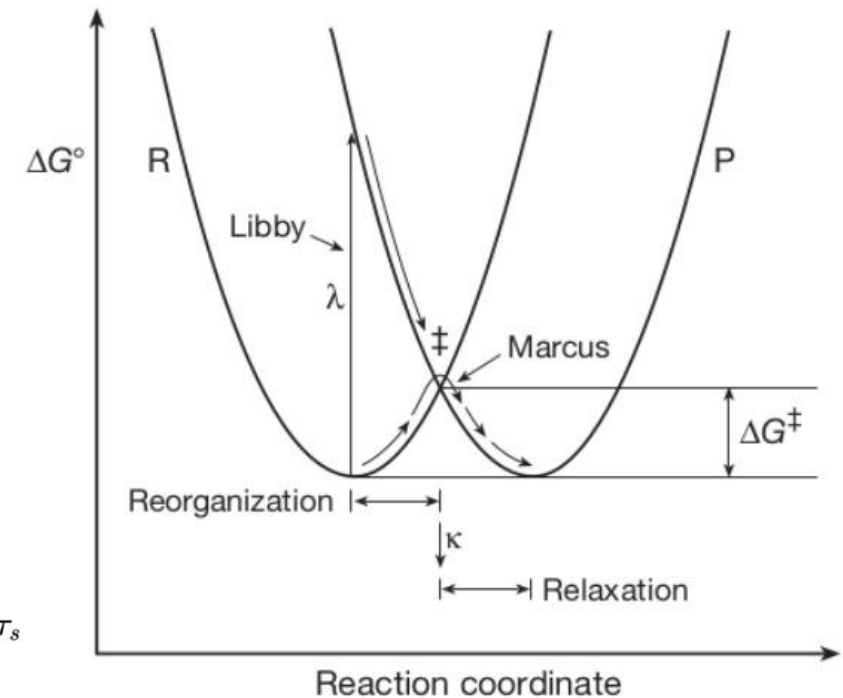
- Franck–Condon (F–C) principle: Nuclei are fixed during electron-transfer between orbital (*think Libby*)
- Transition dipole moment (TDM) operator,  $\mu$ :

$$\boldsymbol{\mu} = \boldsymbol{\mu}_e + \boldsymbol{\mu}_N = -e \sum_i \mathbf{r}_i + e \sum_j Z_j \mathbf{R}_j.$$

The probability amplitude  $P$  for the transition between these two states is given by

$$P = \langle \psi' | \boldsymbol{\mu} | \psi \rangle = \int \psi'^* \boldsymbol{\mu} \psi d\tau, \quad \psi = \psi_e \psi_v \psi_s.$$

$$\begin{aligned} P &= \langle \psi'_e \psi'_v \psi'_s | \boldsymbol{\mu} | \psi_e \psi_v \psi_s \rangle = \int \psi'_e{}^* \psi'_v{}^* \psi'_s{}^* (\boldsymbol{\mu}_e + \boldsymbol{\mu}_N) \psi_e \psi_v \psi_s d\tau \\ &= \int \psi'_e{}^* \psi'_v{}^* \psi'_s{}^* \boldsymbol{\mu}_e \psi_e \psi_v \psi_s d\tau + \int \psi'_e{}^* \psi'_v{}^* \psi'_s{}^* \boldsymbol{\mu}_N \psi_e \psi_v \psi_s d\tau \\ &= \underbrace{\int \psi'_v{}^* \psi_v d\tau}_{\text{Franck-Condon factor}} \underbrace{\int \psi'_e{}^* \boldsymbol{\mu}_e \psi_e d\tau_e}_{\text{orbital selection rule}} \underbrace{\int \psi'_s{}^* \psi_s d\tau_s}_{\text{spin selection rule}} + \underbrace{\int \psi'_e{}^* \psi_e d\tau_e}_0 \int \psi'_v{}^* \boldsymbol{\mu}_N \psi_v d\tau_v \int \psi'_s{}^* \psi_s d\tau_s \end{aligned}$$



# Today's Critical Guiding Question

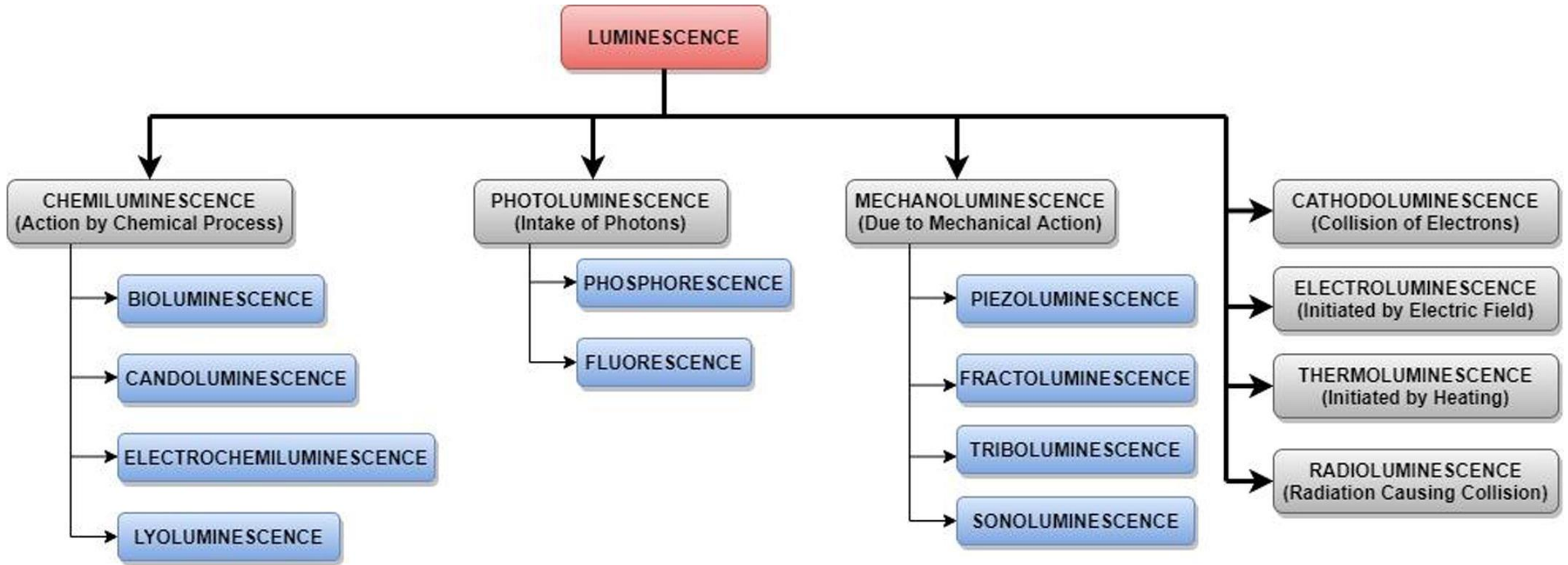
*What continuity/conservation laws are most important for photophysical processes like absorption and emission of photons... for real this time, again: Part 3?*



# DISCUSSION SESSION TOPICS

# Luminescence Processes

... Photo... and Chemi... and Mechano... Oh My!



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

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

# Energy Transfer Processes

Four mechanisms...

(1) Radiative (emission + reabsorption)

... as described by Fermi's Golden Rule... overlap matters a lot...

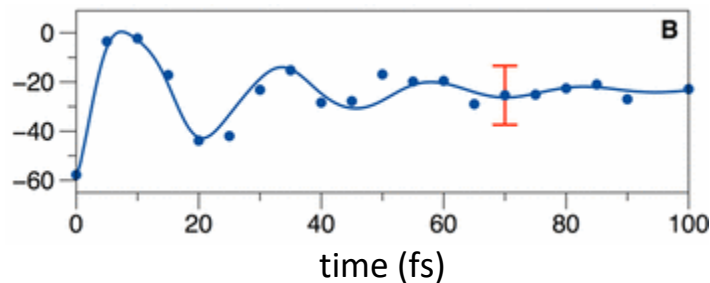
$$J(\lambda) = \int_0^{\infty} F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda = \frac{\int_0^{\infty} F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda}{\int_0^{\infty} F_D(\lambda) d\lambda}$$

...  $J$  is the (spectral) overlap integral

...  $F_D$  is the Donor fluorescence intensity

...  $\epsilon_A$  is the Acceptor absorption coefficient

(2) Coherent:



<https://pubs.acs.org/doi/10.1021/acs.jpcllett.7b01791>

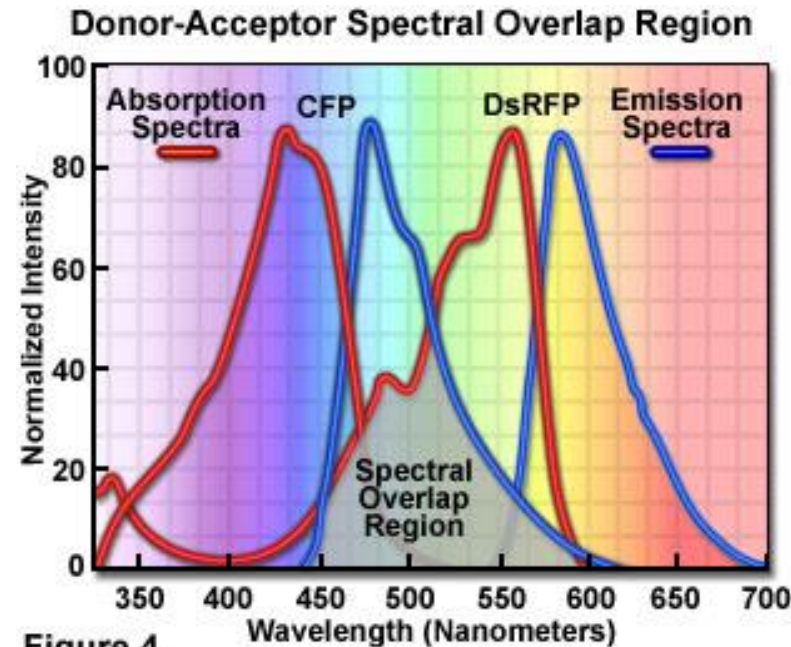
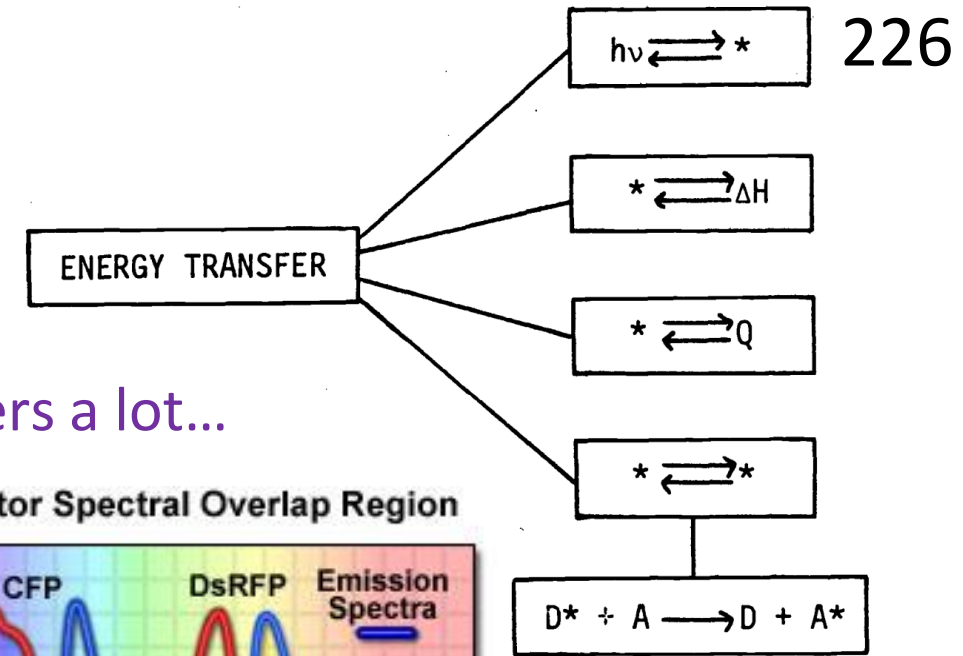


Figure 4

<https://www.olympus-lifescience.com/en/microscope-resource/primer/techniques/fluorescence/fret/fretintro/>

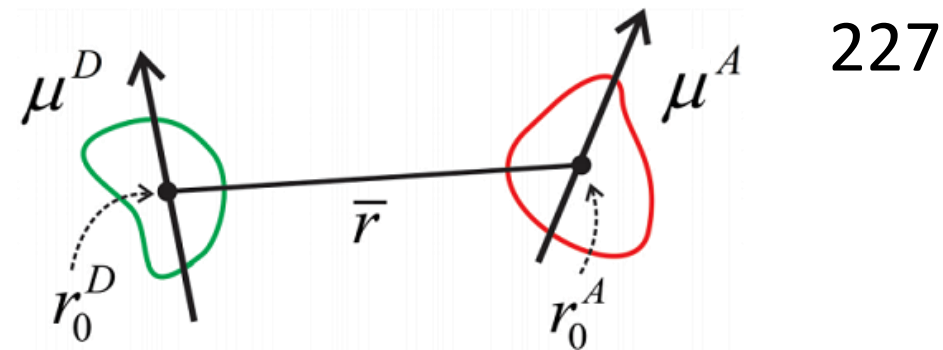
... and rather unrelated... when an excited state species ( $D^*$ ) reacts with a ground-state species ( $A$ )...

... they form an excited complex (exciplex) or, when  $A = D$ , excited dimer (excimer) N. Turro, *Pure Appl. Chem.*, **1977**, *49*, 405–429

# Energy Transfer Processes

Four mechanisms...

## (3) Förster Resonance Dipole–Dipole Coupling (1948)



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$$V(r) = -\frac{2\vec{\mu}_1\vec{\mu}_2}{4\pi\epsilon_0 r^3} = -\frac{|\mu_{\parallel 1}\mu_{\parallel 2}|}{4\pi\epsilon_0 r_{12}^3} (\cos\theta_{12} - 3\cos\theta_1\cos\theta_2)$$

$$w_{ET} = \frac{1}{\hbar^2} \frac{\langle \kappa^2 \rangle}{r^6} |\mu_{DD^*}|^2 |\mu_{AA'}|^2 \int_{-\infty}^{+\infty} d\omega \sigma_{abs}^A(\omega) \sigma_{fluor}^D(\omega)$$

$$k_T(r) = \frac{Q_D \kappa^2}{\tau_D r^6} \left( \frac{9000(\ln 10)}{128\pi^5 N n^4} \right) \int_0^{\infty} F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda = \frac{1}{\tau_D} \left( \frac{R_0}{r} \right)^6$$

...  $F_D$  is the Donor area-normalized fluorescence intensity

...  $\epsilon_A$  is the Acceptor absorption coefficient

...  $Q_D$  is the Donor quantum yield for emission

...  $\tau_D$  is the Donor excited-state lifetime

...  $\kappa^2$  is the orientation factor

...  $R_0$  is the Förster distance (at  $r = R_0$ , energy transfer is 50% efficient)

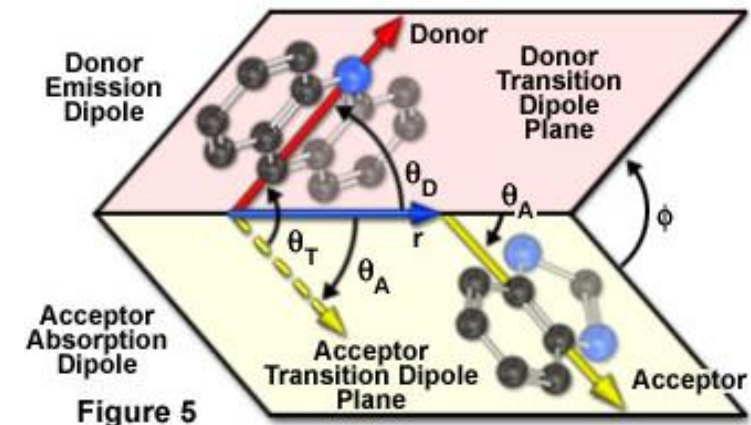
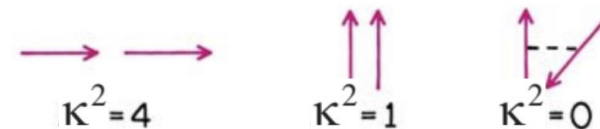


Figure 5



$$\kappa^2 = (\cos\theta_T - 3\cos\theta_D\cos\theta_A)^2$$

$$\kappa^2 = (\sin\theta_D\sin\theta_A\cos\phi - 2\cos\theta_D\cos\theta_A)^2$$

Figure 13.5. Dependence of the orientation factor  $\kappa^2$  on the direction of the emission dipole of the donor and the absorption dipole of the acceptor.

Should photon absorption selection rules apply?... You betcha!

# Energy Transfer Processes

Four mechanisms...

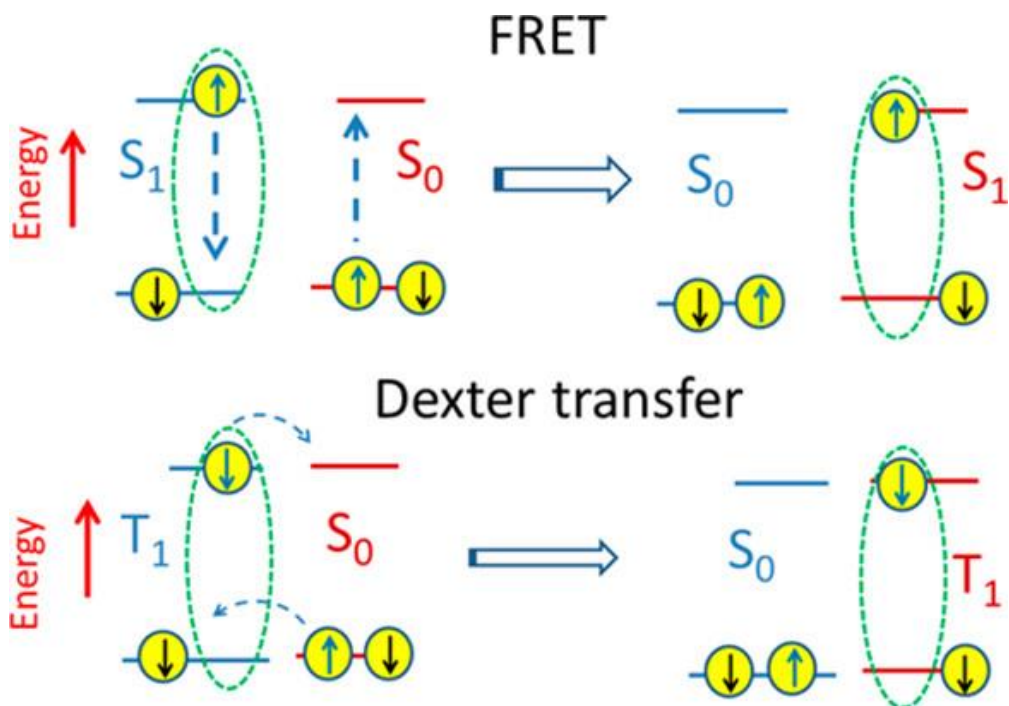
## (4) Dexter Electron Exchange Interaction (1953)

... electron spin is unchanged during pseudo-paired electron transfer

... rate constant depends on wavefunction overlap

$$\left\{ \underbrace{\frac{\hbar^2}{2m_e} \nabla_1^2}_{\text{Kinetic energy}} - \underbrace{\sum_{j=1}^N \frac{Z_j e^2}{4\pi\epsilon_0 r_{j1}}}_{\text{Electron-nucleus attraction}} + \underbrace{\int \frac{\rho(r_2) e^2}{4\pi\epsilon_0 r_{12}} dr_2}_{\text{Electron-electron repulsion}} + \underbrace{V_{XC}(r_1)}_{\text{Exchange-correlation}} \right\} \psi_i(r_1) = \epsilon_i \psi_i(r_1)$$

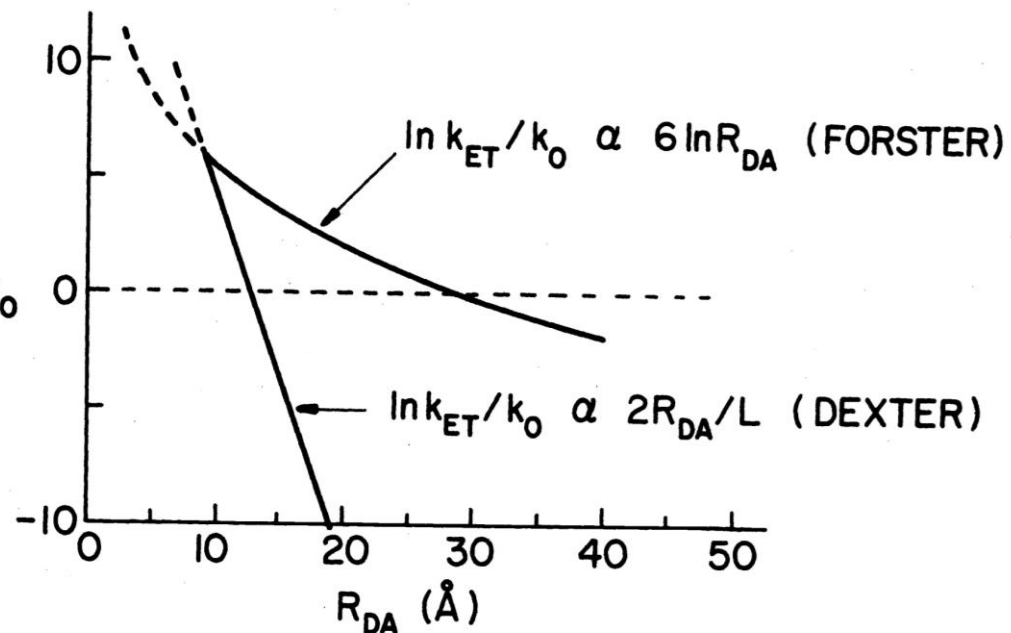
... quantum effect due to the Pauli principle



$$k_{ET} \text{ (electron exchange)} \propto \frac{\langle \psi_{D^*A} | \psi_{DA^*} \rangle^2}{\Delta E} J$$

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

$$k_{ET} \propto J \exp \left[ \frac{-2r}{L} \right]$$



... only Dexter energy transfer can result in fast T–T EnT