UCI CHEM267 – Photochemistry, Spring 2023 208

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!

e-Presentation… topics… include… **(REVIEW)** 210

- 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!**

 211

Photophysical Processes

Prof. Shane Ardo
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Today's Critical Guiding Question

212

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

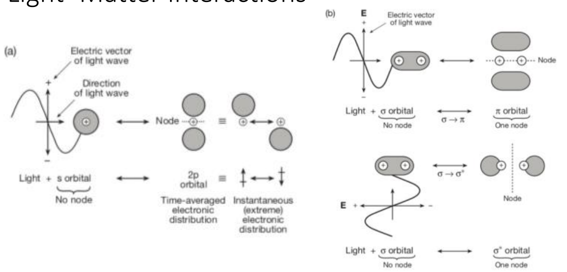
Photophysical Processes

(UPDATED) 213

- **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

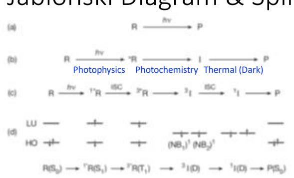
(REVIEW) 214



Turro, Chapter 4, Figure 4.6, Page 189

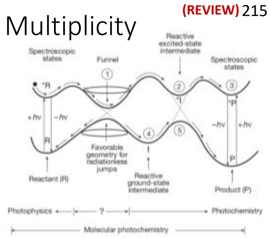
Jablonski Diagram & Spin Multiplicity

(REVIEW) 215



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: $2J+1$

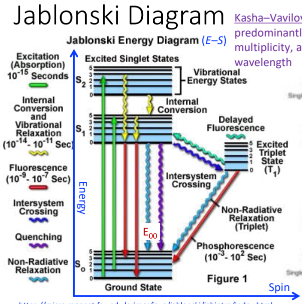
… when $J=0$, $g_J=1$… sounds like a "Singlet (S or ^{1}X)"

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

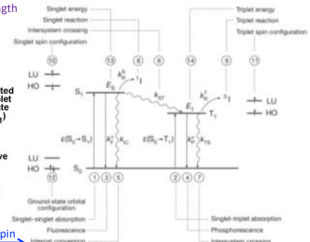
Jablonski Diagram

(REVIEW) 216

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



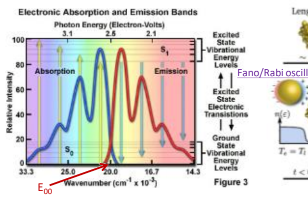
https://micro.magnet.fsu.edu/primer/java/jablonski/jabintro/index.html



Turro, Chapter 1, Scheme 1.4, Page 17

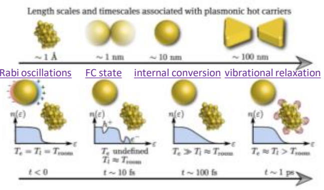
217

Thermally Equilibrated Excited (Thexi) State



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?!?!?!

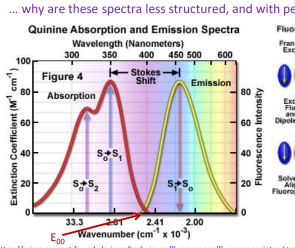
P. Narang, R. Sundararaman & H. A. Atwater, *Nanophoton.*, **2016**, *5*, 96–111

218

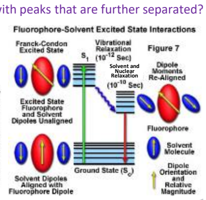
Stokes Shift

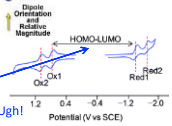
… why are these spectra less structured, and with peaks that are further separated?

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



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





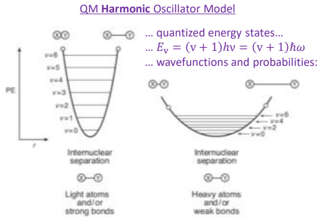
… solvent reorganization in the excited-state!… so is this correct?… No! Ugh!

219

Jablonski Diagram

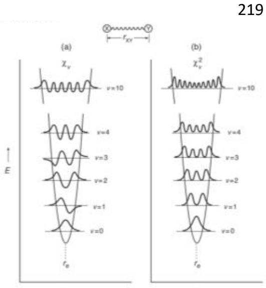
QM **Harmonic** Oscillator Model

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



Turro, Chapter 2, Figure 2.5, Page 76

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

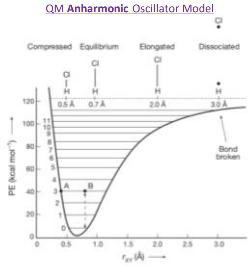


Turro, Chapter 2, Figure 2.6, Page 76

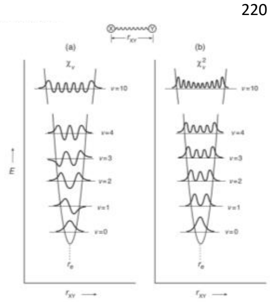
220

Jablonski Diagram

QM **Anharmonic** Oscillator Model



Turro, Chapter 2, Figure 2.7, Page 81



Turro, Chapter 2, Figure 2.6, Page 76

221

Nuclear Terms & F–C Factors

Turro, Chapters 2 and 3

$k_{obs} \sim \rho[<\Psi_1|P'_{1\to 2}|\Psi_2>]^2$ Fermi's golden rule

Observed Rate Constant		Zero-point Motion-Limited Rate Constant	"Fully Allowed Rate"
$\underbrace{k_{obs}}_{\text{Prohibition to maximal caused by "selection rules"}}$	=	k^0_{max}	$\underbrace{f_e \times f_v \times f_S}_{\text{Prohibition factors due to changes in electronic, nuclear, or spin configuration}}$

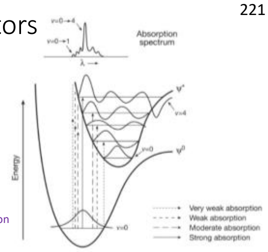
$$\underbrace{\Psi}_{\text{"True" molecular wave function, Exact solution to Eq. 2.1}} \sim \underbrace{\Psi_0 \chi \mathbf{S}}_{\text{(orbitals)(nuclei)(spin), Approximate solution to Eq. 2.1}}$$

… separable due to the Born–Oppenheimer approximation

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

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?

222

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

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

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

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

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

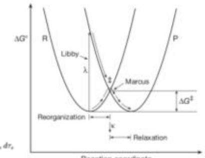
The probability amplitude P for the transition between these two states is given by

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

$$P = \langle\psi'_e\psi'_v\psi'_s|\boldsymbol{\mu}|\psi_e\psi_v\psi_s\rangle = \int \psi'^*_e\psi'^*_v\psi'^*_s(\boldsymbol{\mu}_e + \boldsymbol{\mu}_N)\psi_e\psi_v\psi_s\,d\tau$$

$$= \int \psi'^*_e\psi'^*_v\psi'^*_s\boldsymbol{\mu}_e\psi_e\psi_v\psi_s\,d\tau + \int \psi'^*_e\psi'^*_v\psi'^*_s\boldsymbol{\mu}_N\psi_e\psi_v\psi_s\,d\tau$$

$$= \underbrace{\int \psi'^*_v\psi_v\,d\tau_n}_{\text{Franck–Condon factor}} \underbrace{\int \psi'^*_e\boldsymbol{\mu}_e\psi_e\,d\tau_e}_{\text{orbital selection rule}} \underbrace{\int \psi'^*_s\psi_s\,d\tau_s}_{\text{spin selection rule}} + \underbrace{\int \psi'^*_e\psi_e\,d\tau_e}_{0} \int \psi'^*_v\boldsymbol{\mu}_N\psi_v\,d\tau_n \int \psi'^*_s\psi_s\,d\tau_s$$



Turro, Chapter 7, Figure 7.12, Page 429

223

Today's Critical Guiding Question

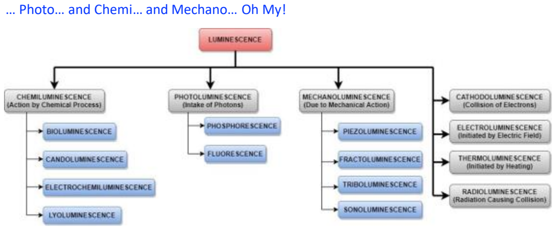
What continuity/conservation laws are most important for photophysical processes like absorption and emission of photons… <u>for real this time, again: Part 3</u>?

DISCUSSION SESSION TOPICS

225

Luminescence Processes

… Photo… and Chemi… and Mechano… Oh My!

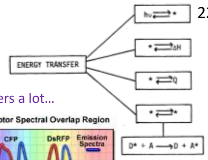


https://www.sciencedirect.com/science/article/pii/S2214785321017272

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

Energy Transfer Processes

226



Four mechanisms…
(1) Radiative (emission + reabsorption)

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

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

… J is the (spectral) overlap integral
… F_D is the Donor fluorescence intensity
… ε_A is the Acceptor absorption coefficient

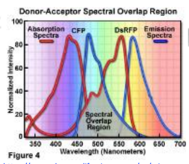
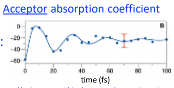


Figure 4

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

(2) Coherent:

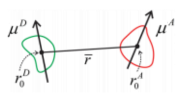


https://pubs.acs.org/doi/10.1021/acs.jpclett.7b01791

… 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

227



Four mechanisms…
(3) **Förster Resonance Dipole–Dipole Coupling** (1948)

$$V(r) = -\frac{2\vec{\mu}_1\vec{\mu}_2}{4\pi\epsilon_o r^3} = -\frac{|\mu_1||\mu_2|}{4\pi\epsilon_0 r_{12}^3}(\cos\theta_{12} - 3\cos\theta_1\cos\theta_2)$$

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

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

… F_D is the Donor *area-normalized* fluorescence intensity
… ε_A is the Acceptor absorption coefficient
… Q_D is the Donor quantum yield for emission
… τ_D is the Donor excited-state lifetime
… κ^2 is the orientation factor
… R_0 is the Förster distance (at $r = R_0$, energy transfer is 50% efficient)

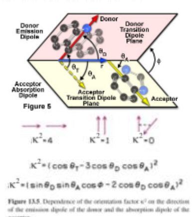


Figure 13.5. Dependence of the orientation factor κ² on the direction of the emission dipole of the donor and the absorption dipole of the acceptor.

Should photon absorption selection rules apply?… You betcha!

Lakowicz, Chapter 13, Figure 13.5, Page 449

Energy Transfer Processes

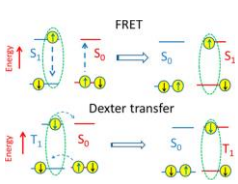
228

$$\left\{-\frac{\hbar^2}{2m_e}\nabla_1^2 - \sum_{j=1}^{N}\frac{Z_j e^2}{4\pi\varepsilon_0 r_{j1}} + \int\frac{\rho(r_2)e^2}{4\pi\varepsilon_0 r_{12}}dr_2 + V_{XC}(r_1)\right\}\psi_i(r_1) = \varepsilon_i\psi_i(r_1)$$

(Kinetic energy; Electron–nuclear attraction; Electron–electron repulsion; Exchange-correlation)

Four mechanisms…
(4) **Dexter Electron Exchange Interaction** (1953) … quantum effect due to the Pauli principle
… electron spin is unchanged during pseudo-paired electron transfer
… rate constant depends on wavefunction overlap

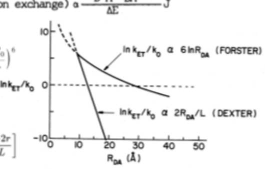
$$k_{ET}\ (\text{electron exchange}) \propto \frac{\langle\Psi_{D^*A}|\Psi_{DA^*}\rangle^2}{\Delta E} J$$



https://pubs.acs.org/doi/10.1021/acs.chemrev.6b00215

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

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



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

N. Turro, *Pure Appl. Chem.*, **1977**, *49*, 405–429