Lecture #14 of 14

(3: TThF, 5: MT*W*ThF, 4: MT*W*Th, 2: T**W**)

{Last one!... tear, again}

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Photochemistry

Straight into Groups!

Quiz Time!

Prof. Shane Ardo
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Photochemistry

- **Blackbody radiation, Carnot efficiency limits, Light–Matter interactions, Photon properties, Conservation laws**
- **Jablonski diagram, Internal conversion, Intersystem crossing, Kasha–Vavilov rule, Thexi state, Stokes shift, Luminescence processes**
- **Harmonic oscillator model, Born–Oppenheimer approximation, Franck–Condon principle, 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

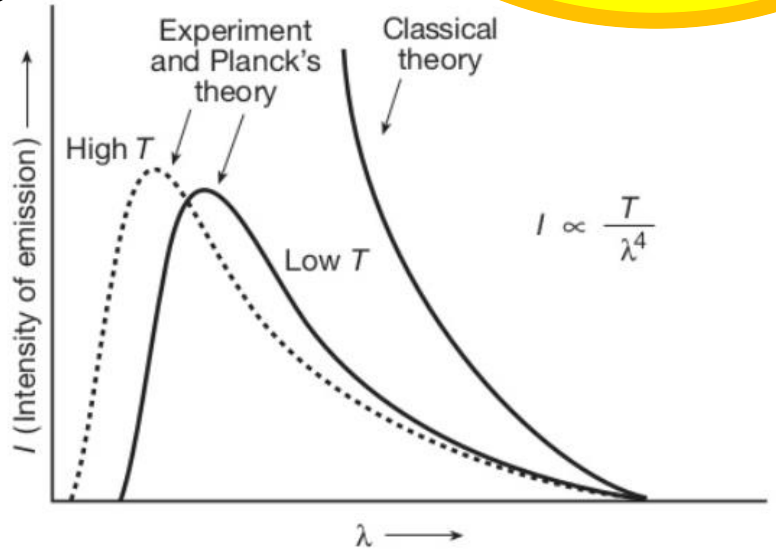
Blackbody Radiation

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

($T \approx 5790$ K)
SUN

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

EARTH
($T \approx 290$ K)



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

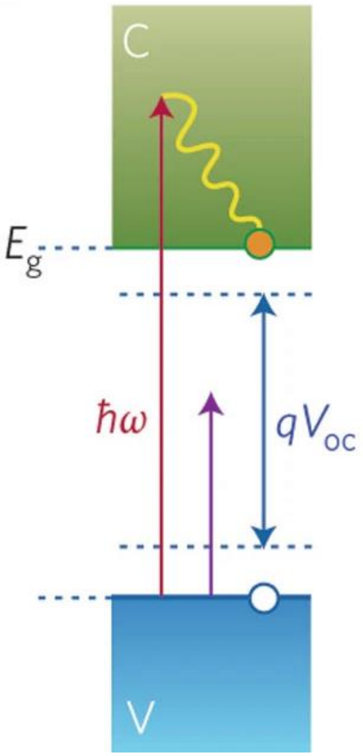
Carnot Efficiency Limits

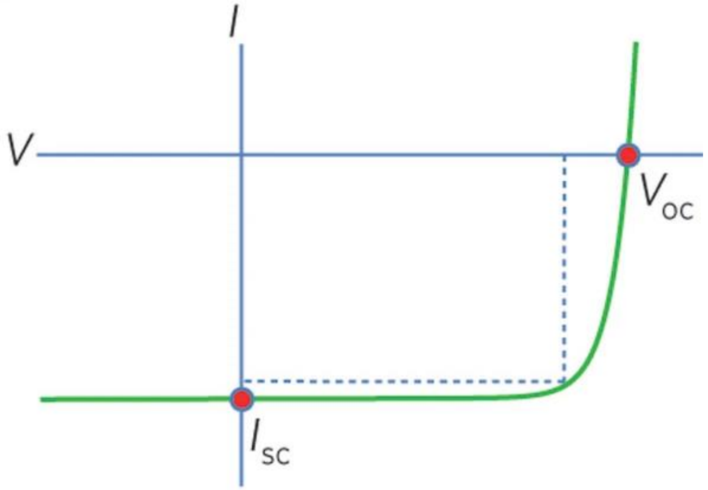
… thank you Shockley, Queisser, Ross, Hsiao, Henry, De Vos, Pauwels, Würfel, et al.!

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

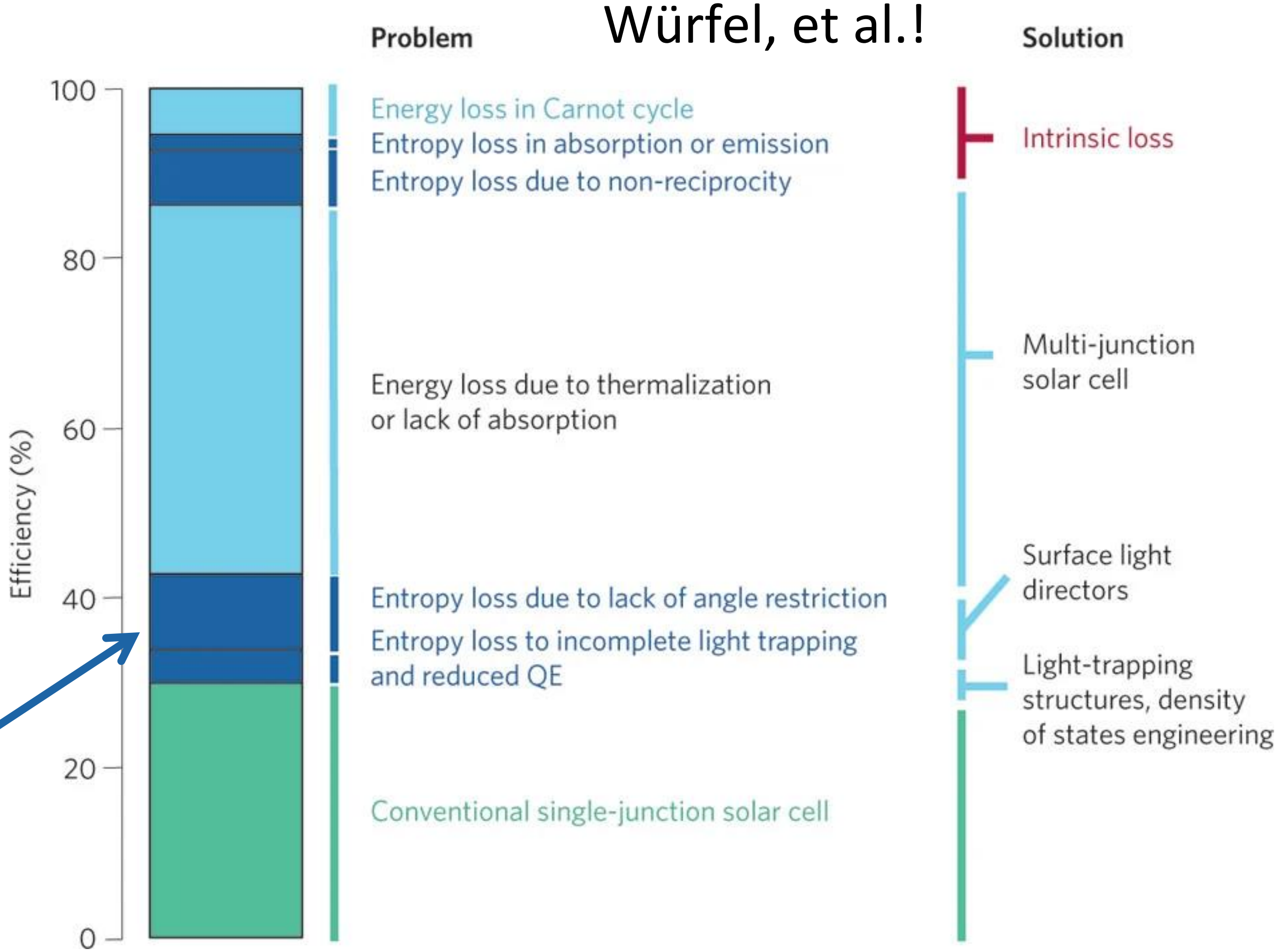
… $j = j_{\mathrm{o}}\left(1 - e^{qV/kT}\right) + j_{\mathrm{ph}}$…

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





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

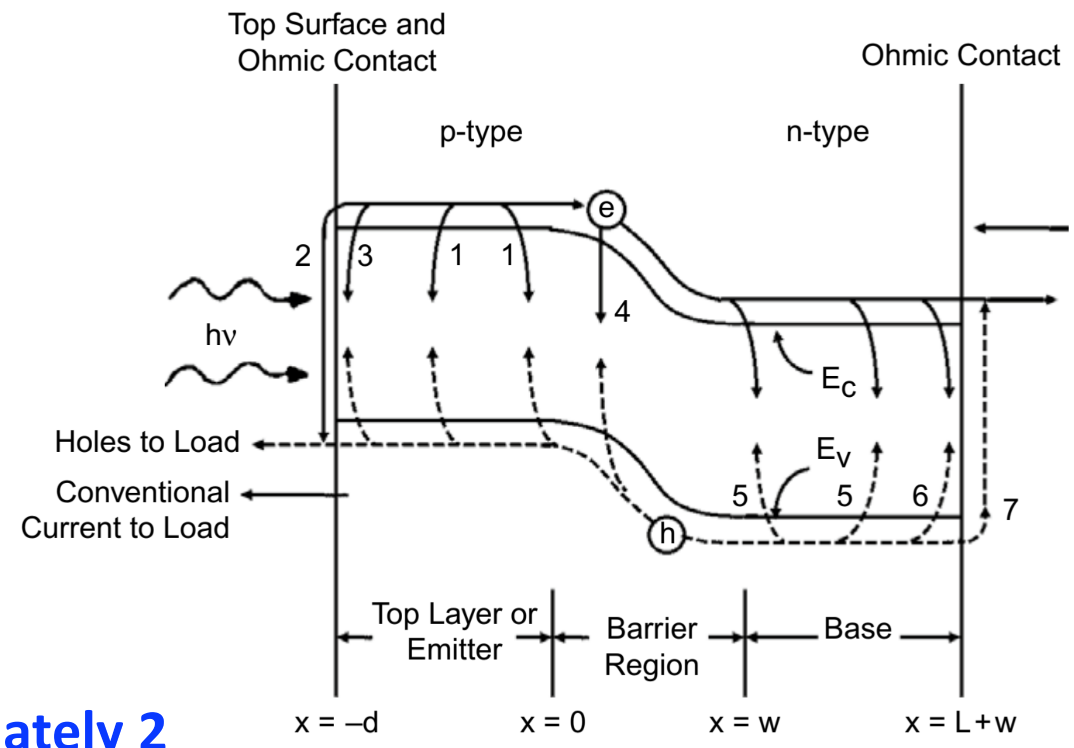


… a large V_{oc} ($\Delta\bar{\mu}_i$)… results in a large I_{sc} … and thus a large power conversion efficiency

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

Light–Matter Interactions

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



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! $\mathrm{A} + h\nu_{\mathrm{BB}} \rightleftarrows \mathrm{A}^*$

… at a microscopically reversible **equilibrium**, rate is equal to "**%A(*v*)** x PhotonFlux(*v*), integrated over *v*"

… $\bar{\boldsymbol{\mu}}_{\mathbf{A}} = \bar{\boldsymbol{\mu}}_{\boldsymbol{A}^*}$… with additional (sun)light absorption, $\bar{\mu}_{\mathrm{A}} < \bar{\mu}_{\mathrm{A,eq}}$ and $\bar{\mu}_{\mathrm{A}^*} > \bar{\mu}_{\mathrm{A}^*,\mathrm{eq}}$ = <u>useful work</u>!

Photon Properties & Conservation Laws

Where does light come from?

Photon Particle Type: Boson

Mass: 0

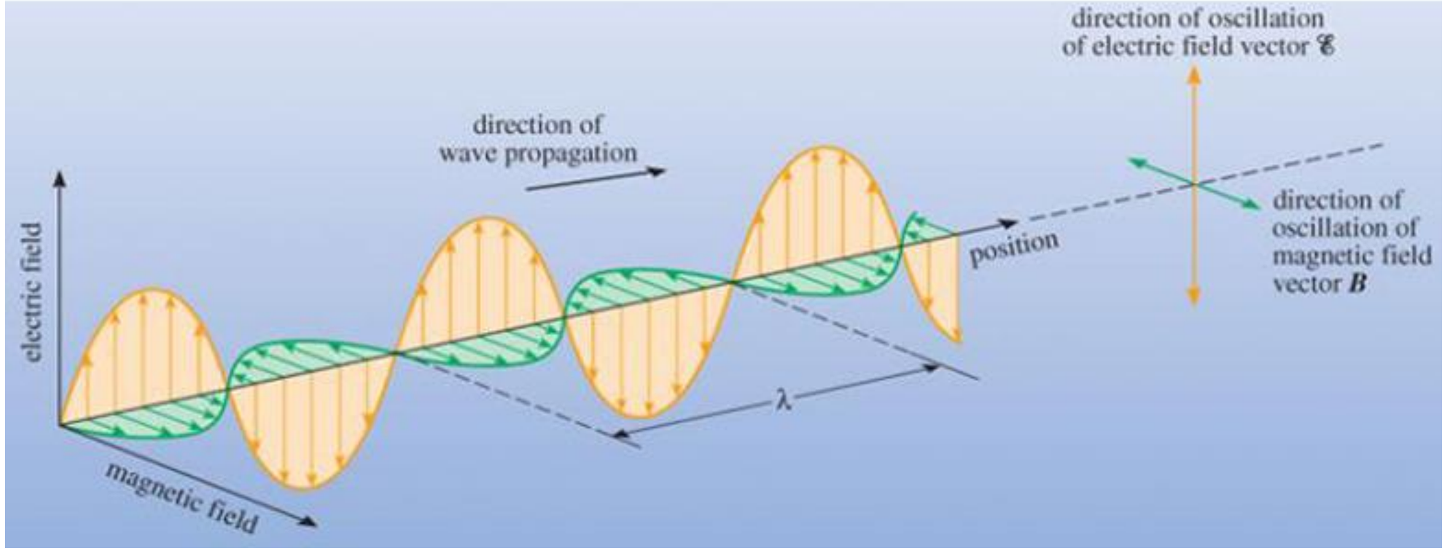
Charge: 0

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: $\pm\hbar = \pm\frac{h}{2\pi}$

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

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 x 10^{18} nm/s

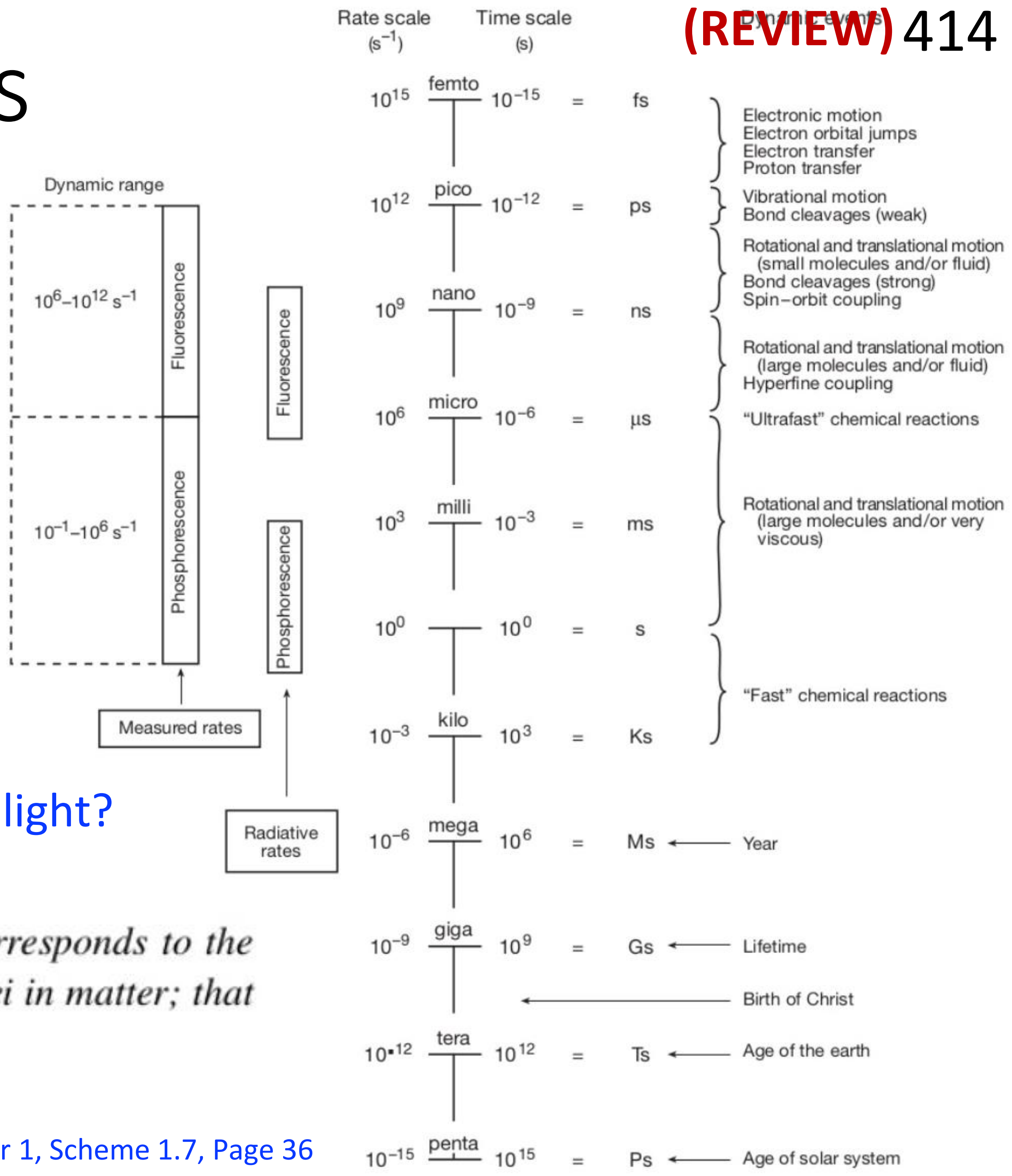
$v_{electron}$ = 10^{15} – 10^{16} nm/s

v_{nuclei} = 10^{13} – 10^{14} nm/s

… so which term dominates the resonant response to light?

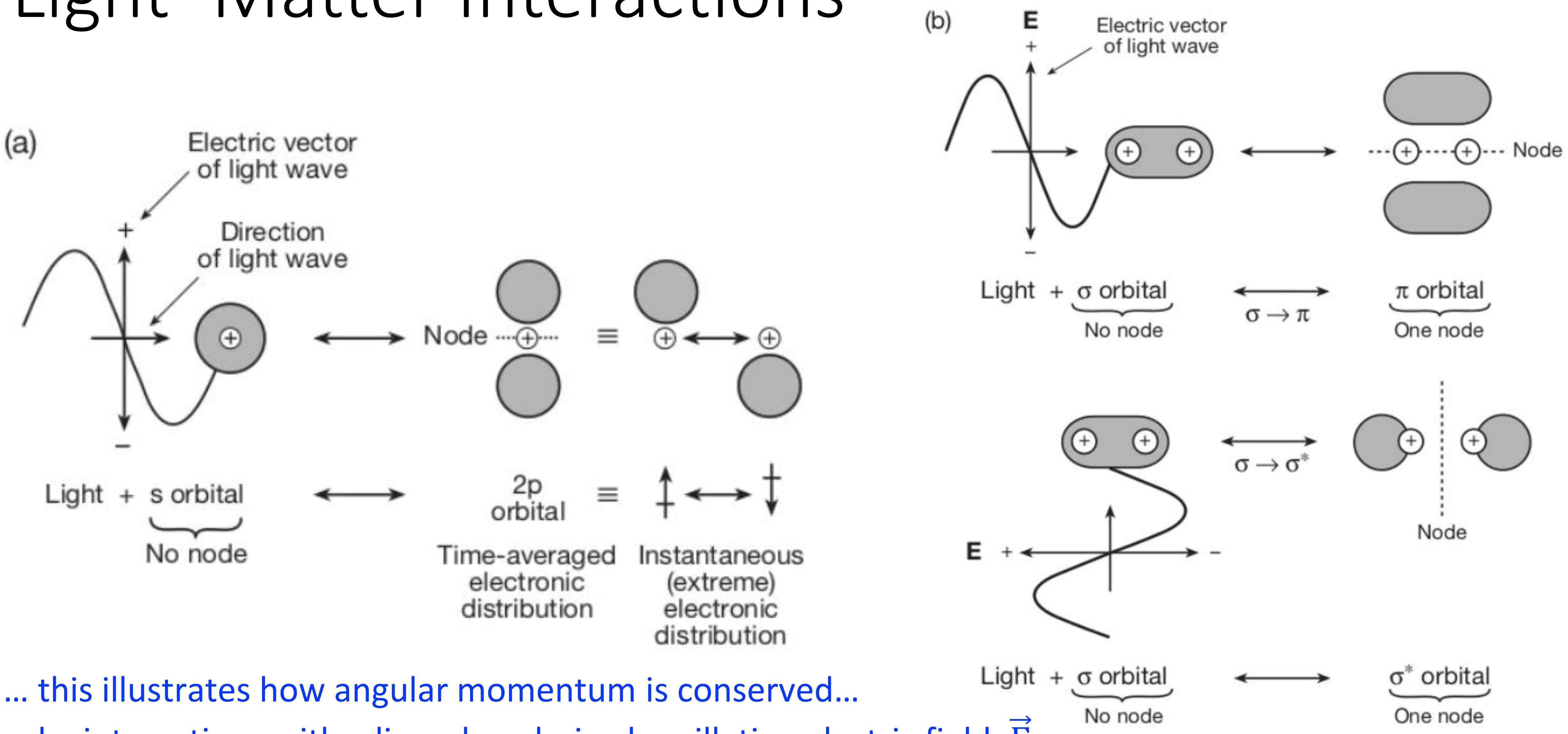
In more concrete chemical terms, the oscillation of the dipoles corresponds to the movements of electrons in bonds relative to positively charged nuclei in matter; that is, electrons oscillate about the nuclear framework of molecules.

Why do these timescales differ by so much?



Turro, Chapter 1, Scheme 1.7, Page 36

Light–Matter Interactions

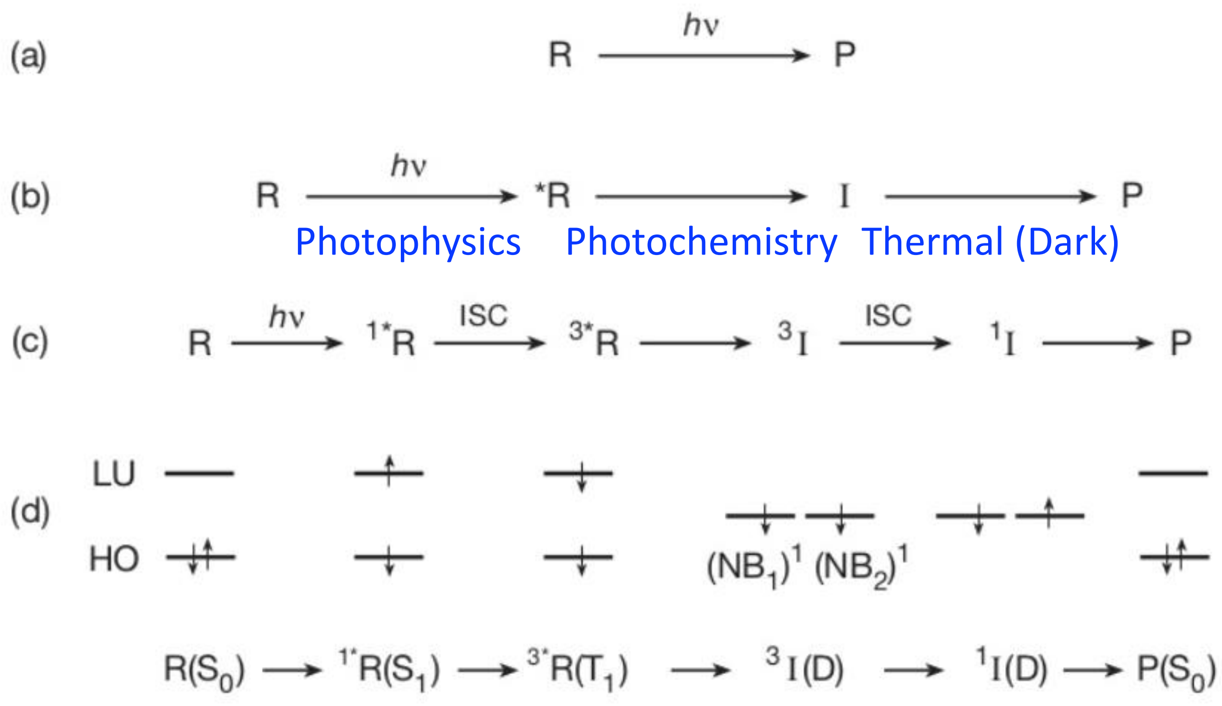


… this illustrates how angular momentum is conserved…

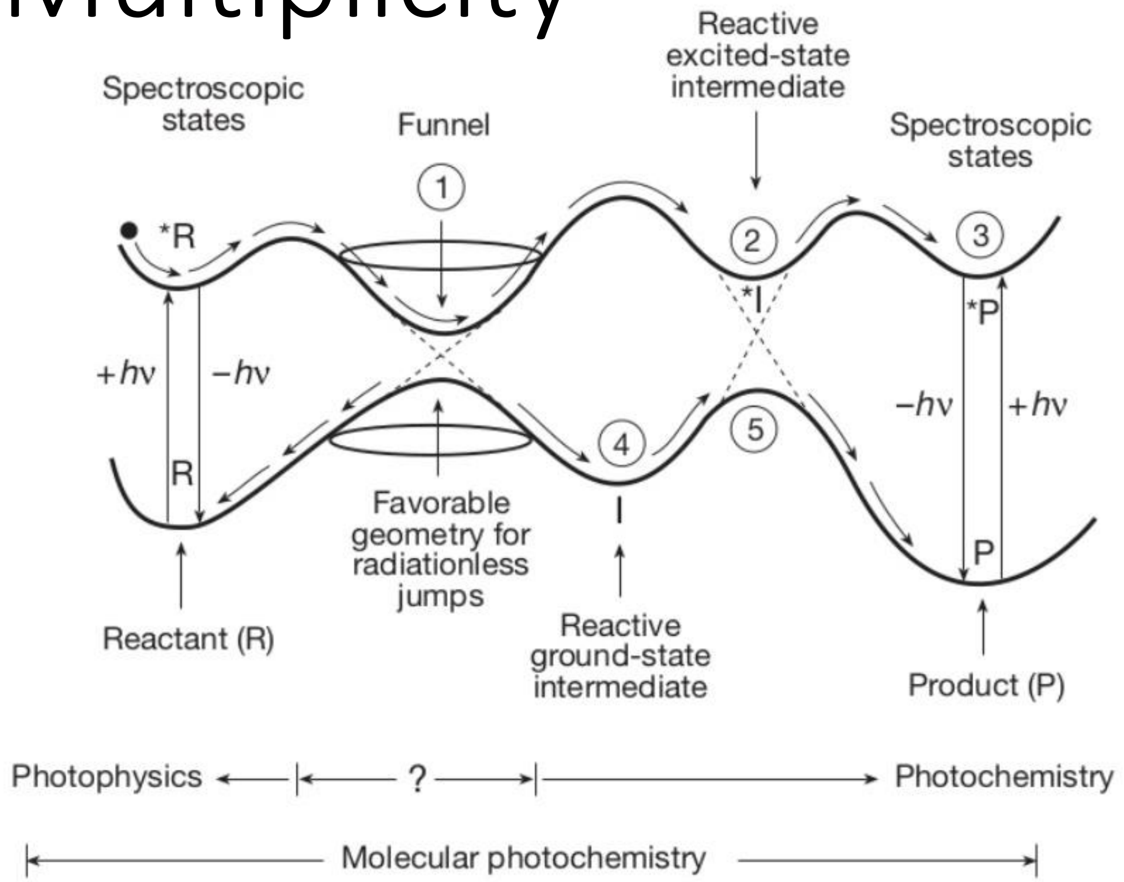
… by interactions with a linearly polarized oscillating electric field, $\vec{E}$

Turro, Chapter 4, Figure 4.6, Page 189

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

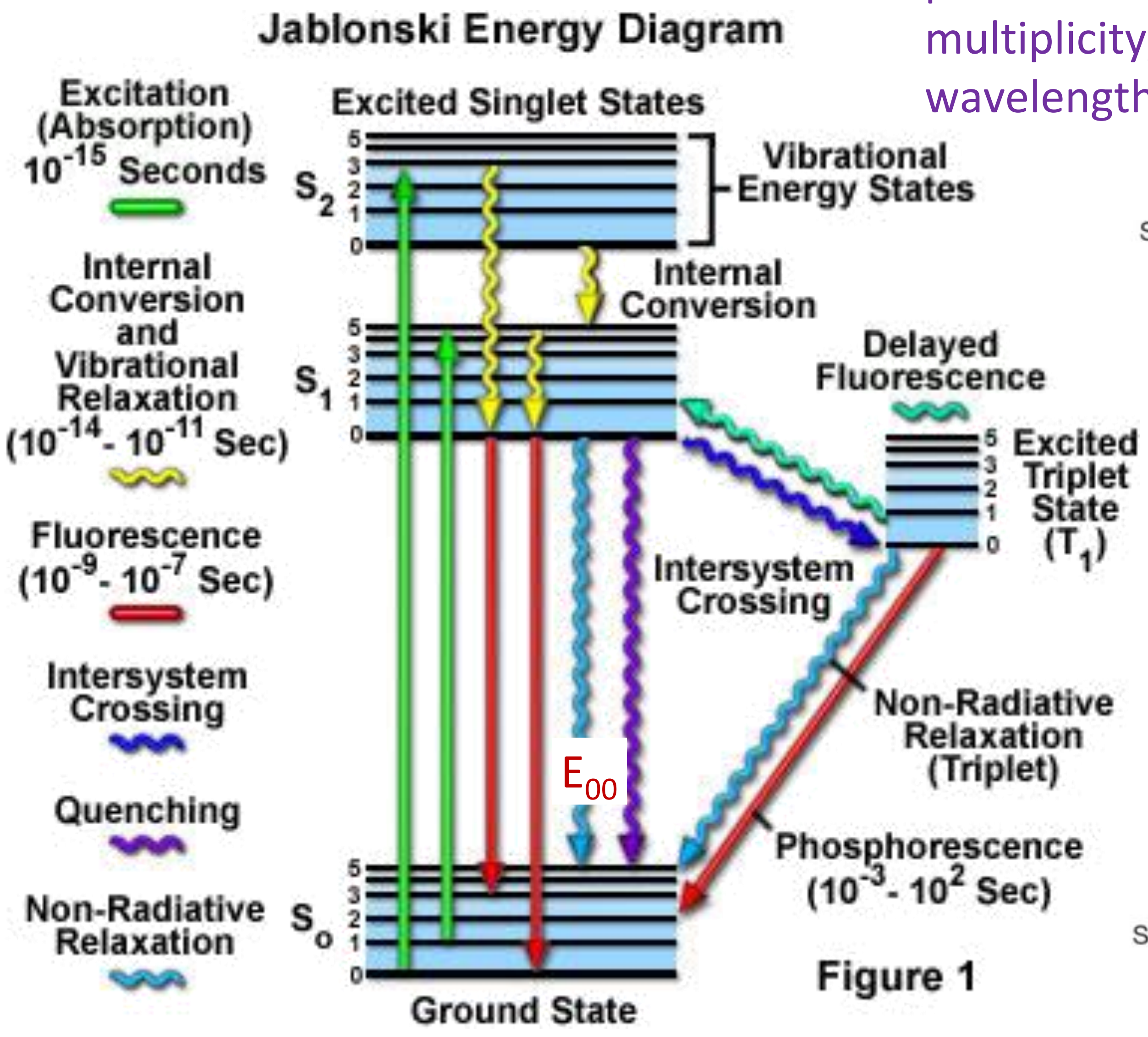
… **Angular Momentum Degeneracy**, g_J: $2J+1$

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

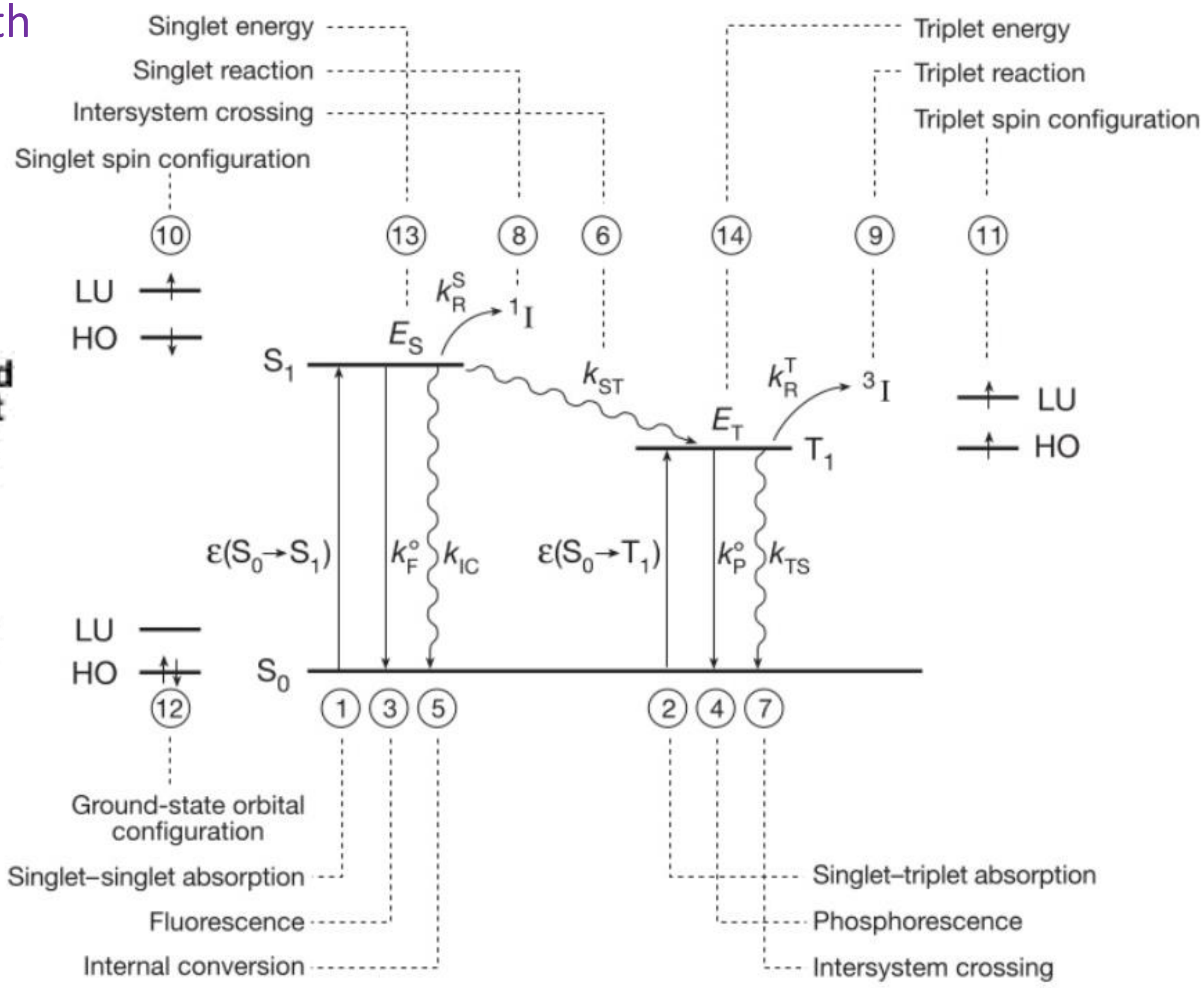
… when $J=1$, $g_J=3$… sounds like a "Triplet (T or ^{3}X)"

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

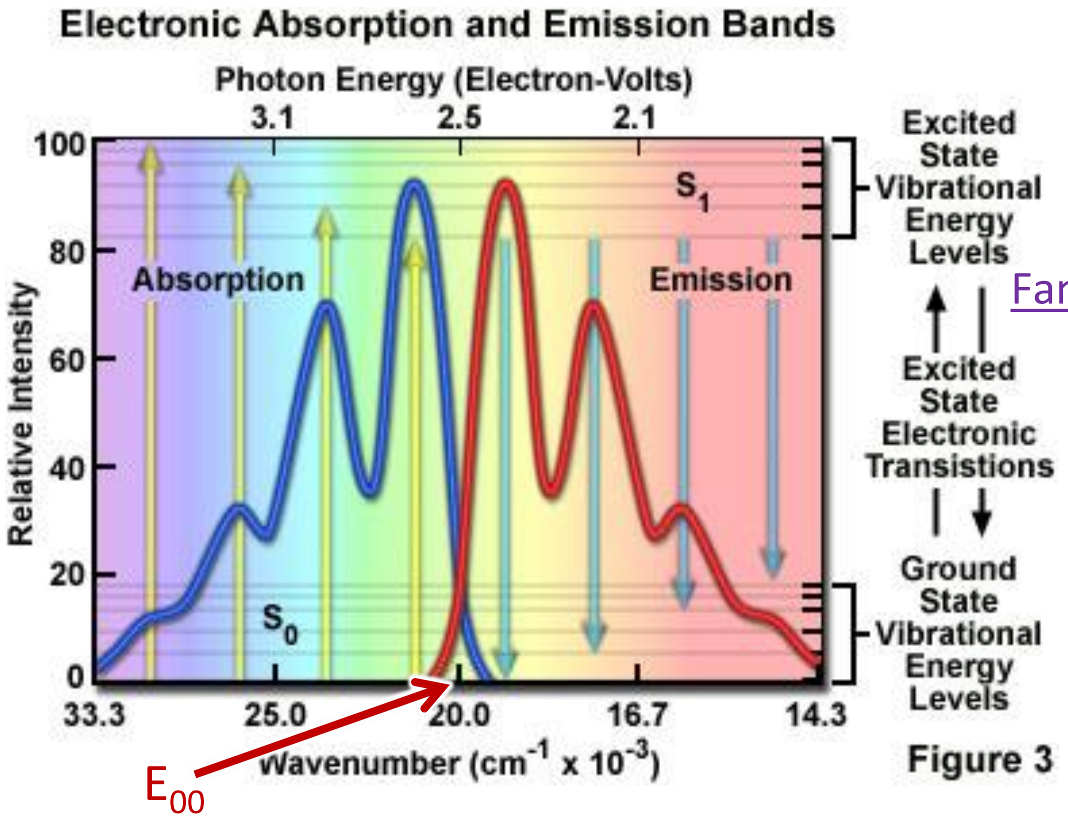


https://micro.magnet.fsu.edu/primer/java/jablonski/jabintro/index.html

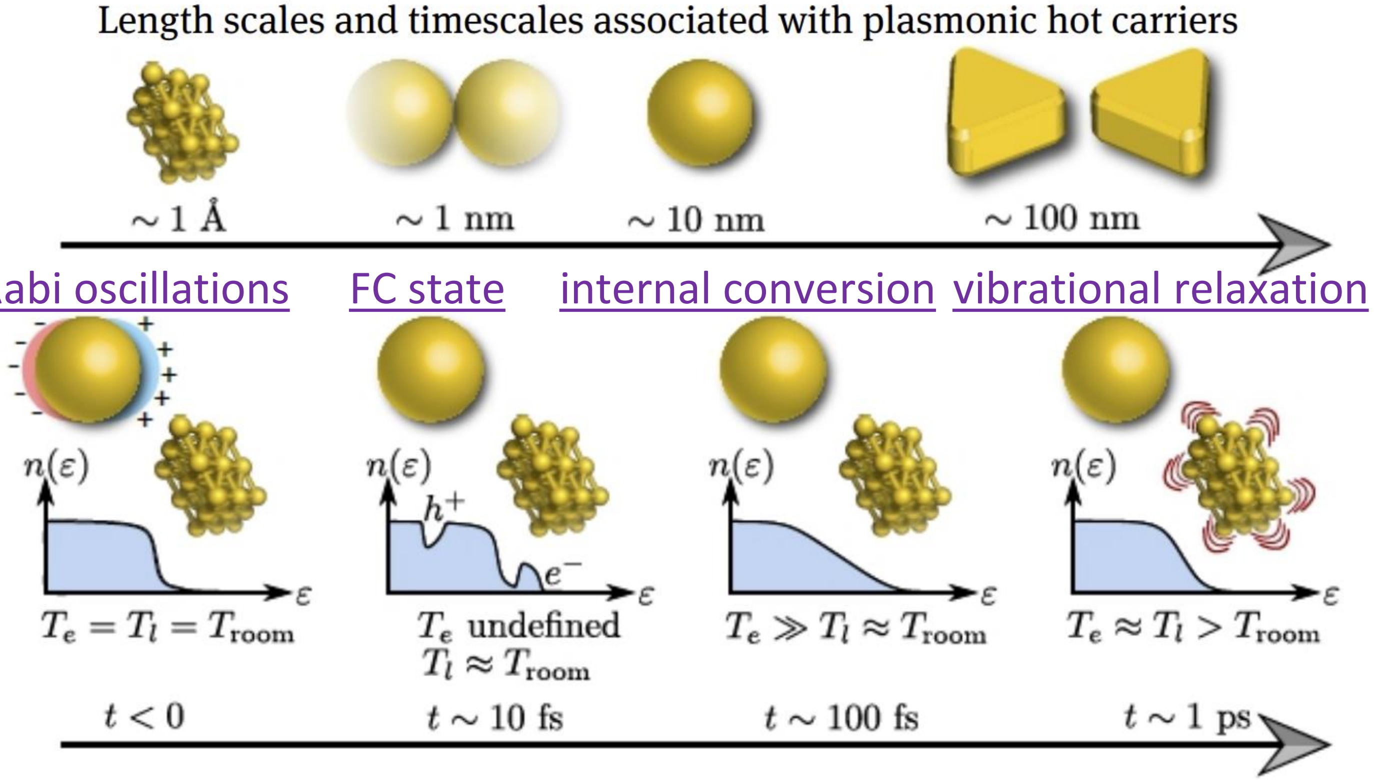


Turro, Chapter 1, Scheme 1.4, Page 17

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?

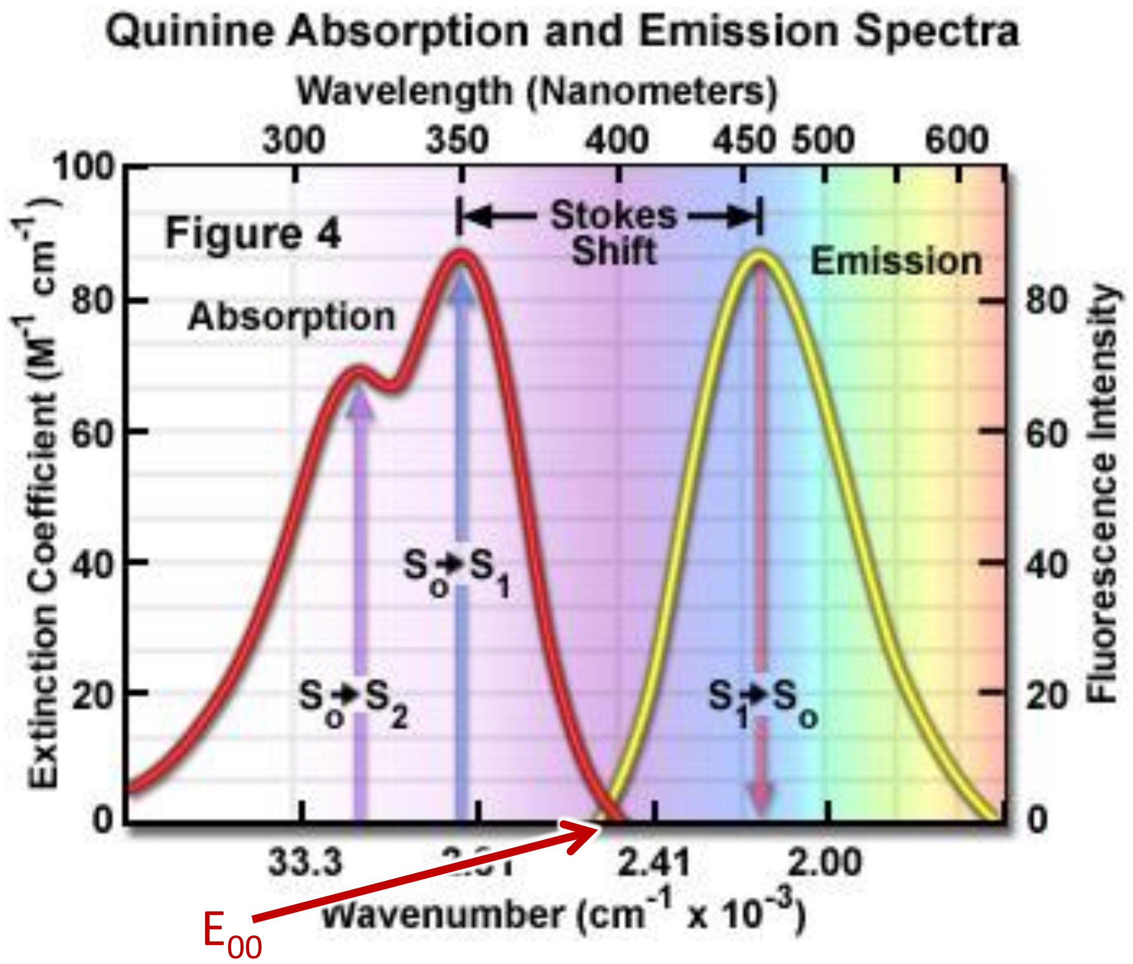
… so that you can see the mirror-image "rule"

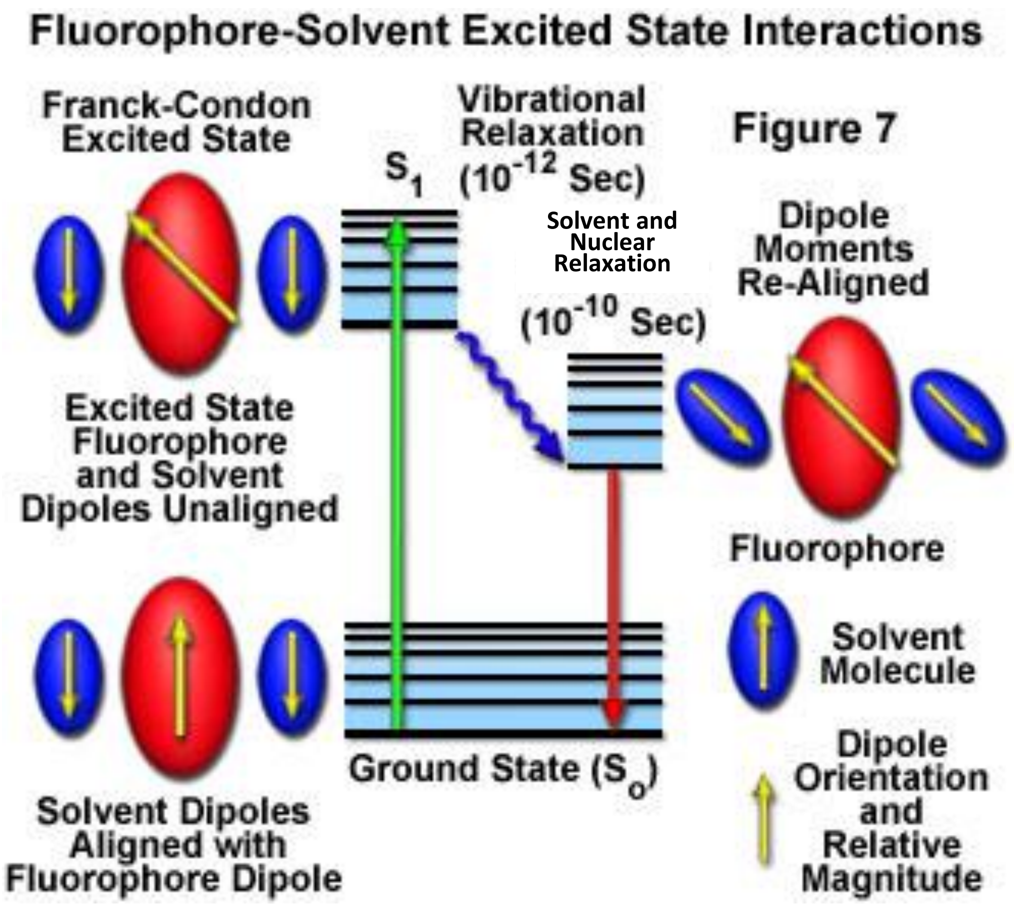
… wait, do molecules and materials undergo the same physical processes and follow the same laws of the Universe?… shocking, isn't it?!?!?!

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

Stokes Shift

… why are these spectra less structured and with further separated peaks?… polar and warmer

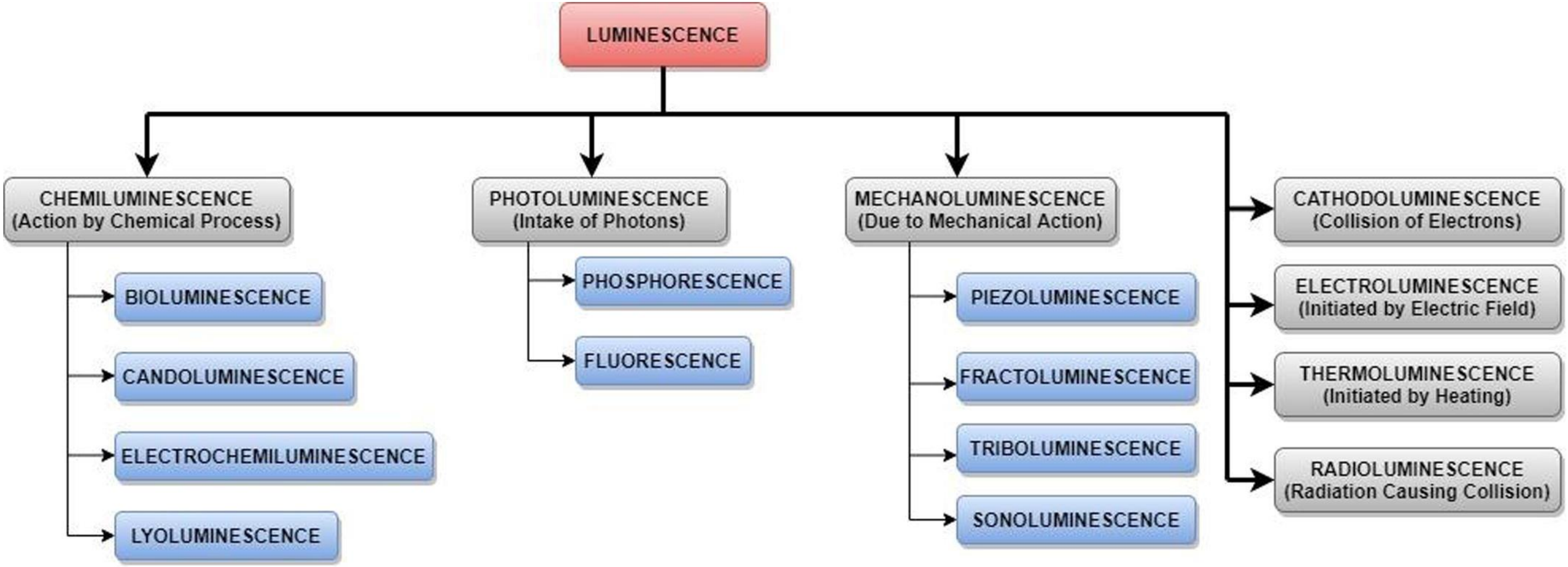




https://micro.magnet.fsu.edu/primer/techniques/fluorescence/fluorescenceintro.html

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...

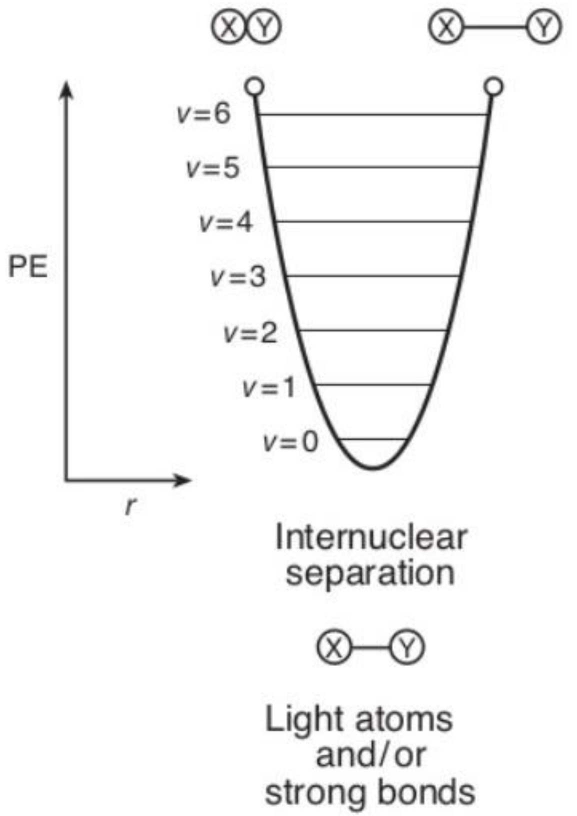
Jablonski Diagram

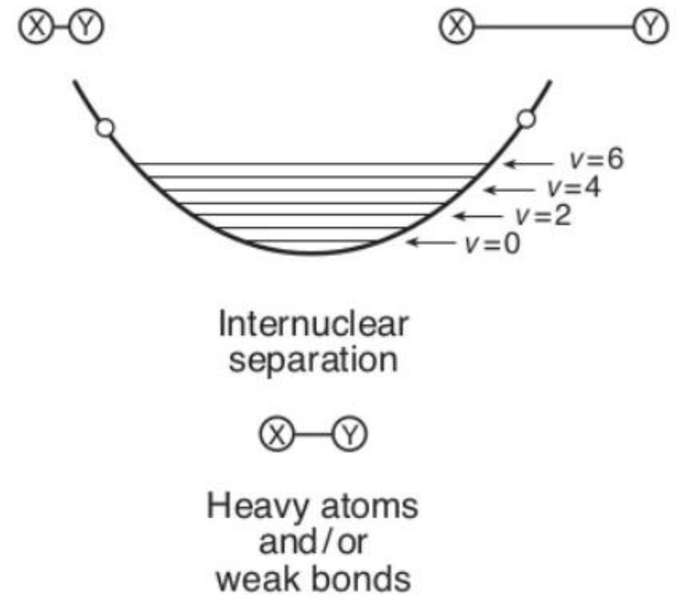
QM **Harmonic** Oscillator Model

… quantized energy states…

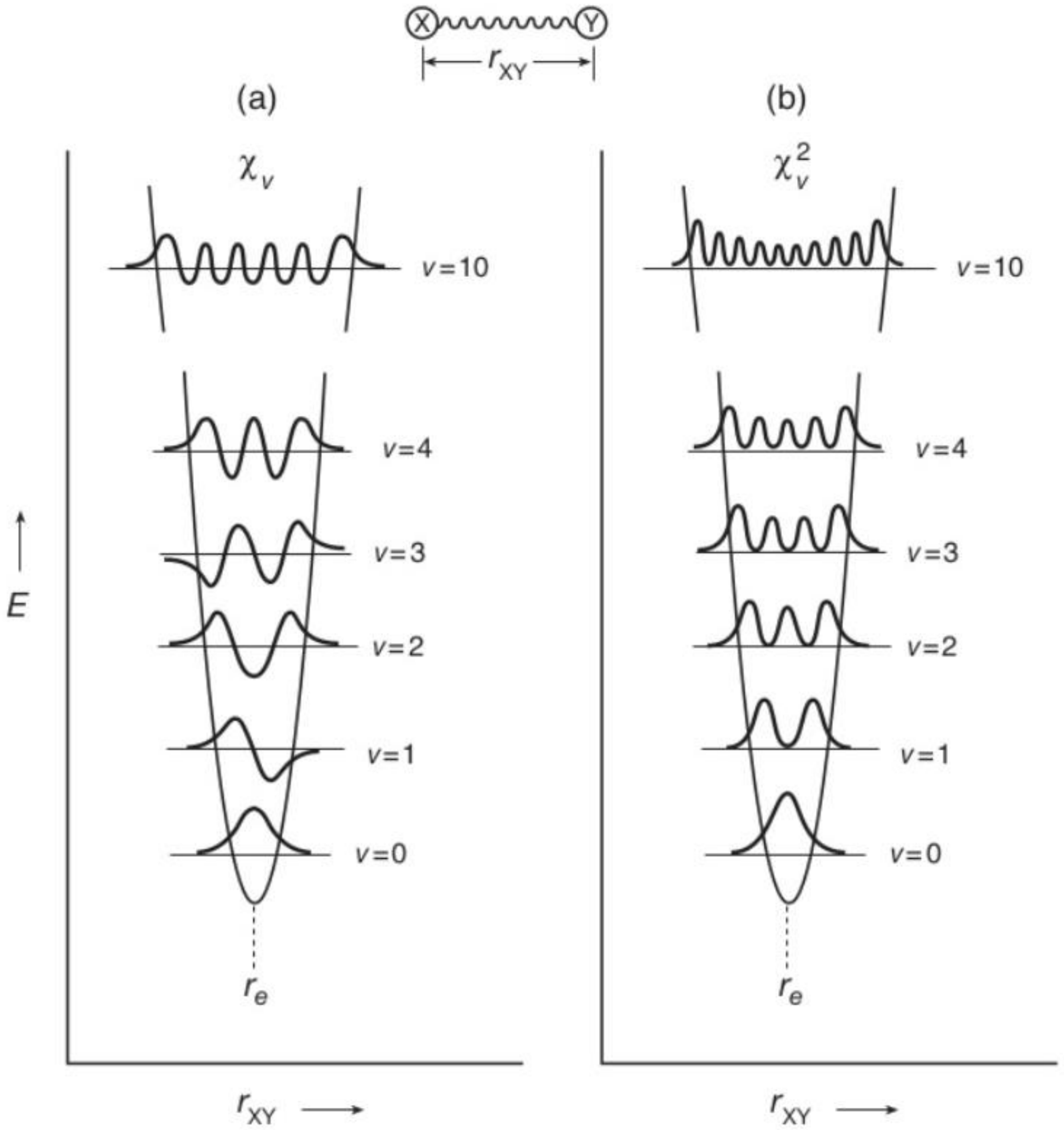
… $E_v = \left(v + \frac{1}{2}\right) h\nu = \left(v + \frac{1}{2}\right) \hbar\omega$

… wavefunctions and probabilities:





Turro, Chapter 2, Figure 2.5, Page 76

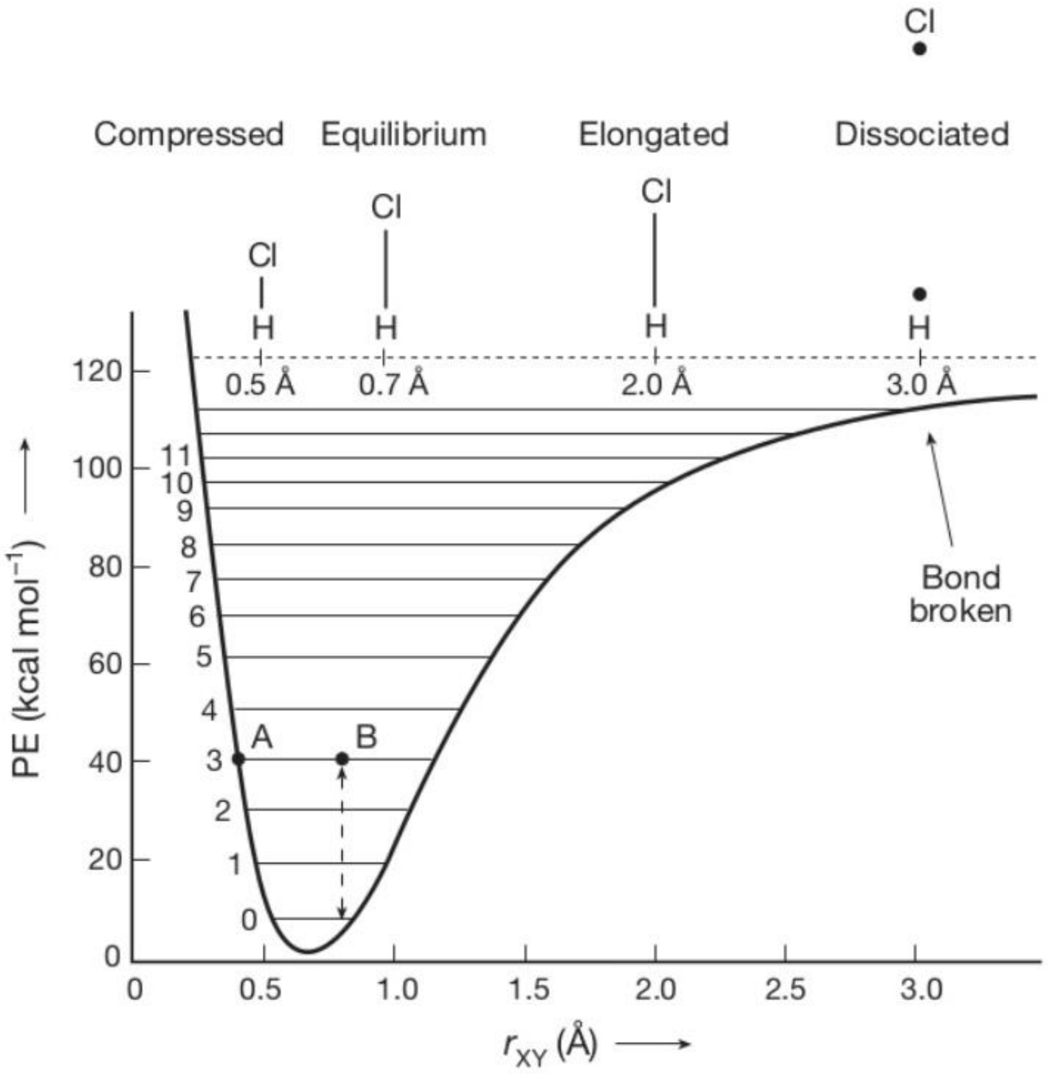


Probability Density$(x) = |\chi_v(x)|^2 = \chi_v^*(x)\chi_v(x)$

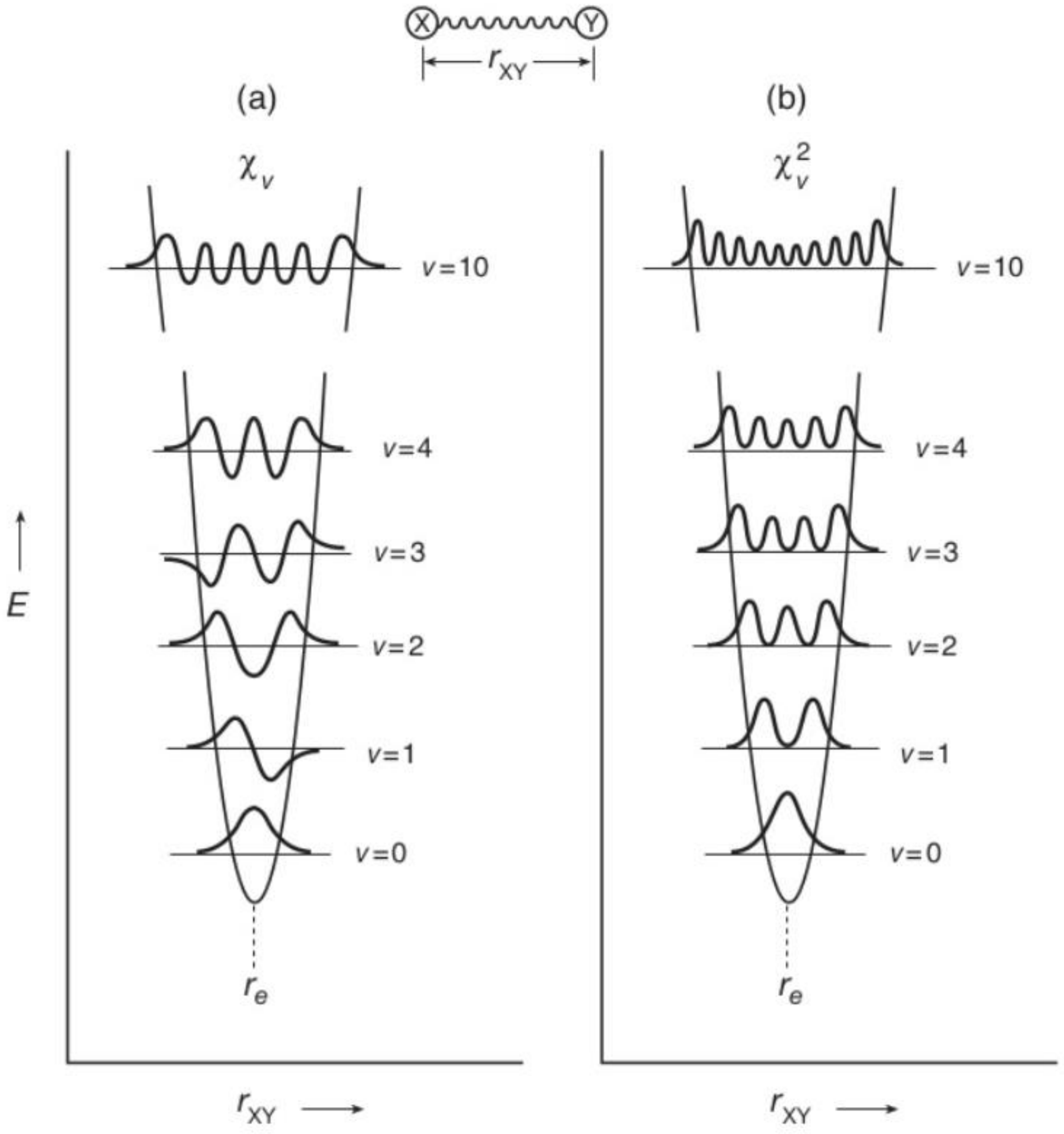
Turro, Chapter 2, Figure 2.6, Page 76

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

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

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

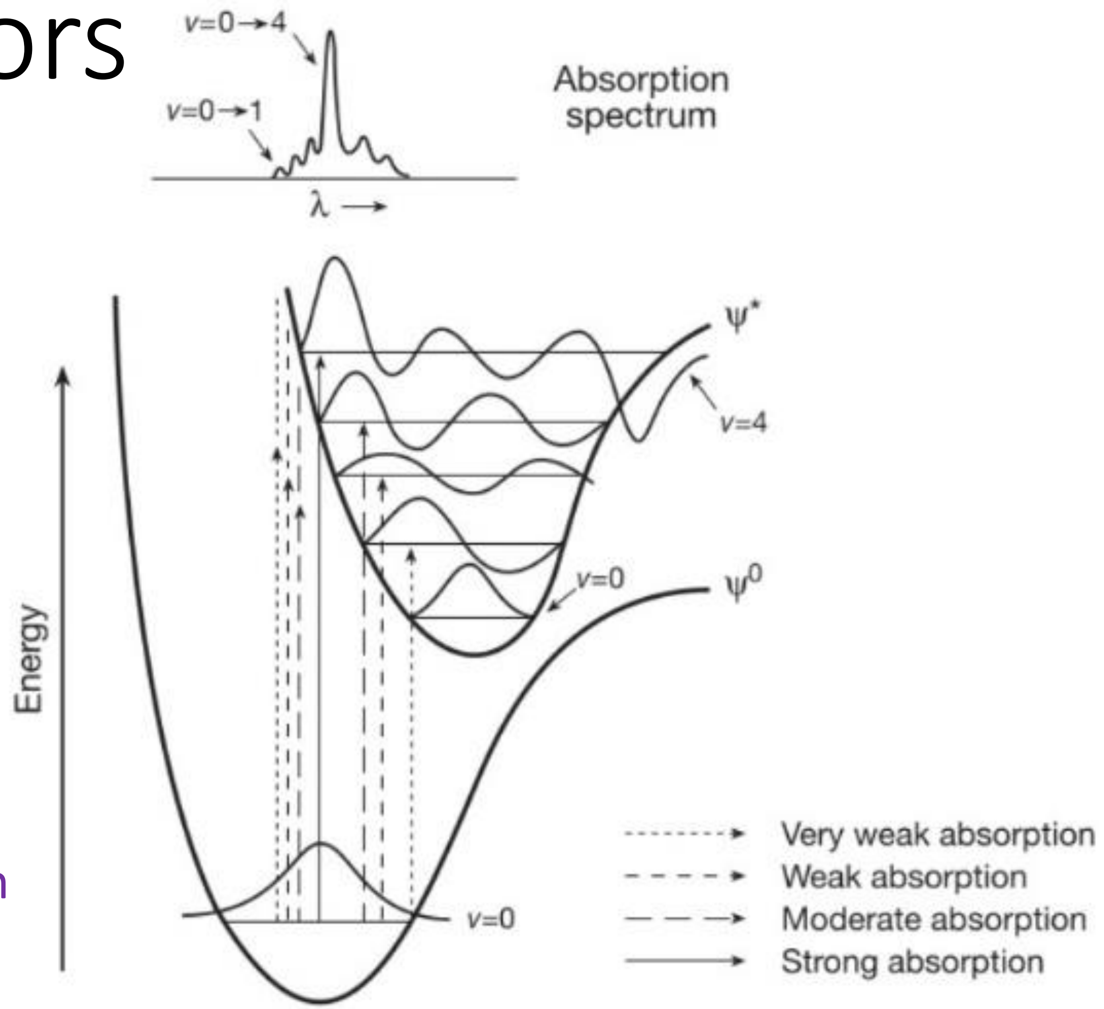
$\underbrace{\Psi}$	$\sim$	$\underbrace{\Psi_0 \chi S}$
"True" molecular wave function Exact solution to Eq. 2.1		(orbitals)(nuclei)(spin) Approximate solution to Eq. 2.1

… 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?

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

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

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

- Franck–Condon (F–C) principle: Nuclei are fixed during electron-transfer between orbital *(think Libby)*

- Transition dipole moment (TDM) operator, $\boldsymbol{\mu}$:

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

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

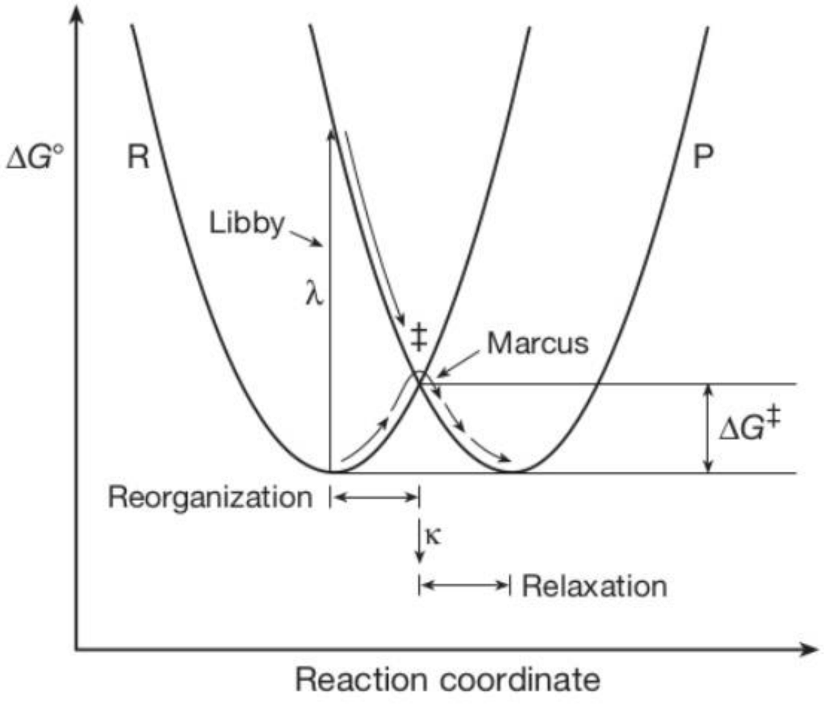
$$P = \langle \psi' | \boldsymbol{\mu} | \psi \rangle = \int \psi'^* \boldsymbol{\mu} \psi \, d\tau, \qquad \psi = \psi_e \psi_v \psi_s$$

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

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

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

... this factor is 0 when light changes ψ_e



Turro, Chapter 7, Figure 7.12, Page 429

Selection Rules

$$\underbrace{\int \psi_v'^* \psi_v \, d\tau_n}_{\text{Franck–Condon factor}} \; \underbrace{\int \psi_e'^* \boldsymbol{\mu}_e \psi_e \, d\tau_e}_{\text{orbital selection rule}} \; \underbrace{\int \psi_s'^* \psi_s \, d\tau_s}_{\text{spin selection rule}}$$

Angular Momentum Quantum Numbers

Photon… *which came from matter*: $s = 1, m_s = \pm 1$

Electron (Orbital): $l, m_l = [-l, l]$ in steps of 1

Electron (Spin): $s = \frac{1}{2}, m_s = \left[-\frac{1}{2}, \frac{1}{2}\right]$

… well these are just overlaps… and so the more overlap, the more favorable a transition…

… the F–C (nuclear vibrational) factor makes sense *based on pictures on the previous slides*

… but what does $\boldsymbol{\mu}_e$ do to a wavefunction?… it uses $\vec{\mathrm{E}}$ to make it coincide with an unoccupied orbital… and even if we didn't know, it better *change the angular momentum during photon annihilation*

… and what are spin wavefunctions?… just symbols!… spin does not fall out of $\boldsymbol{\mu}$… it's just math… so, the spin wavefunctions only overlap when they are identical… meaning *spin does not change*

(Angular Momentum) Atomic Selection "rules"

Orbital angular momentum (Laporte "rule"): $\boldsymbol{\Delta l = \pm 1}$… as $l_f = l_i \pm s_{\text{photon}}$

Spin angular momentum (Wigner "rule"): $\boldsymbol{\Delta m_s = 0}$… $\boldsymbol{\mu}_e$ does not act on spin

Orbital *z*-direction angular momentum: $\boldsymbol{\Delta m_l = 0, \pm 1}$… as $m_{l,f} = m_{l,i} \pm m_{s,\text{photon}}$

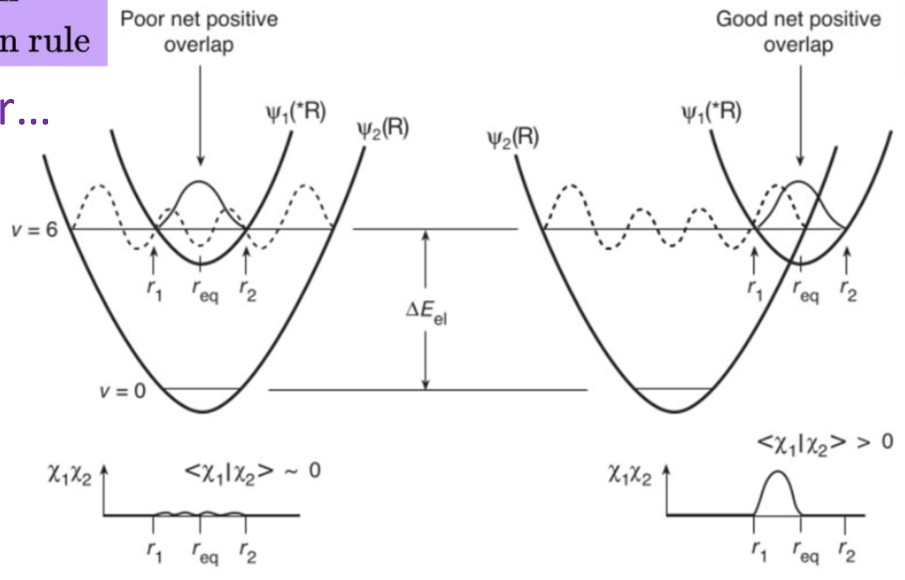
… the allowed 0 option can be envisioned as two vectors that are opposite in one direction

Selection Rules

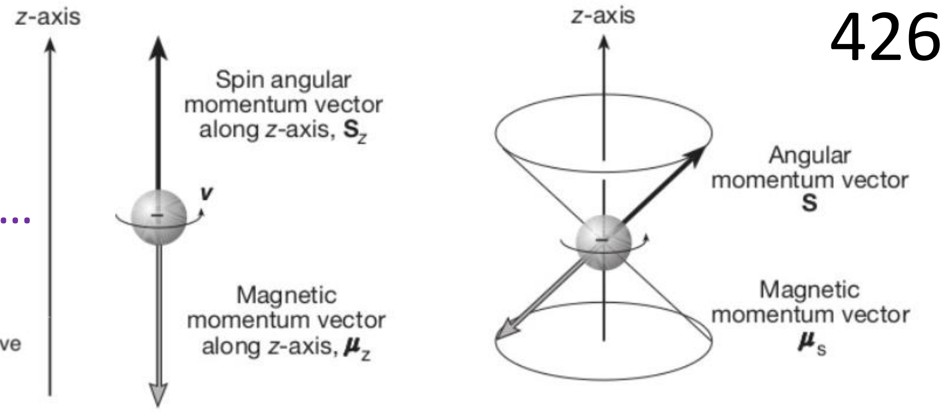
$$\underbrace{\int \psi_v'^{*} \psi_v \, d\tau_n}_{\text{Franck–Condon factor}} \quad \underbrace{\int \psi_e'^{*} \boldsymbol{\mu}_e \psi_e \, d\tau_e}_{\text{orbital selection rule}} \quad \underbrace{\int \psi_s'^{*} \psi_s \, d\tau_s}_{\text{spin selection rule}}$$

… related to spin–orbital coupling…

… related to the F–C factor…



Turro, Chapter 3, Figure 3.5, Page 133



Turro, Chapter 2, Figure 2.13, Page 99

State	State Symbol	M_s	Magnetic Energy (E_z)	Spin Function	Vector Representation
Doublet	D_+	$+1/2$	$+(1/2)g\mu_e\mathbf{H}_z$	α	
Doublet	D_-	$-1/2$	$-(1/2)g\mu_e\mathbf{H}_z$	β	
Singlet	S	0	0	$\alpha\beta - \beta\alpha$	
Triplet	T_+	$+1$	$+(1)g\mu_e\mathbf{H}_z$	$\alpha\alpha$	
Triplet	T_0	0	0	$\alpha\beta + \beta\alpha$	
Triplet	T_-	-1	$-(1)g\mu_e\mathbf{H}_z$	$\beta\beta$	

a. The mathematical normalizing factor is not shown for the spin function.

Turro, Chapter 2, Table 2.4, Page 102

Summary of Atomic Selection "rules"

$\boldsymbol{\Delta l = \pm 1}$, since $l_f = l_i \pm s_{\text{photon}}$… $\boldsymbol{\Delta m_s = 0}$… $\boldsymbol{\Delta m_l = 0, \pm 1}$, since $m_{l,f} = m_{l,i} \pm m_{s,\text{photon}}$

Heavy Molecule (Russell–Saunders L–S Coupling) Selection "rules"… for linear oscillating photon $\vec{\mathrm{E}}$

Total angular momentum: $\boldsymbol{\Delta J = 0, \pm 1}$ … and $\boldsymbol{\Delta S = 0}$… and $\boldsymbol{\Delta L = 0, \pm 1}$

Total z-direction angular momentum: $\boldsymbol{\Delta m_J = 0, \pm 1}$… and $\mathbf{0}$'s are there for the reason before

Spin–Orbit Coupling & C–T Transitions

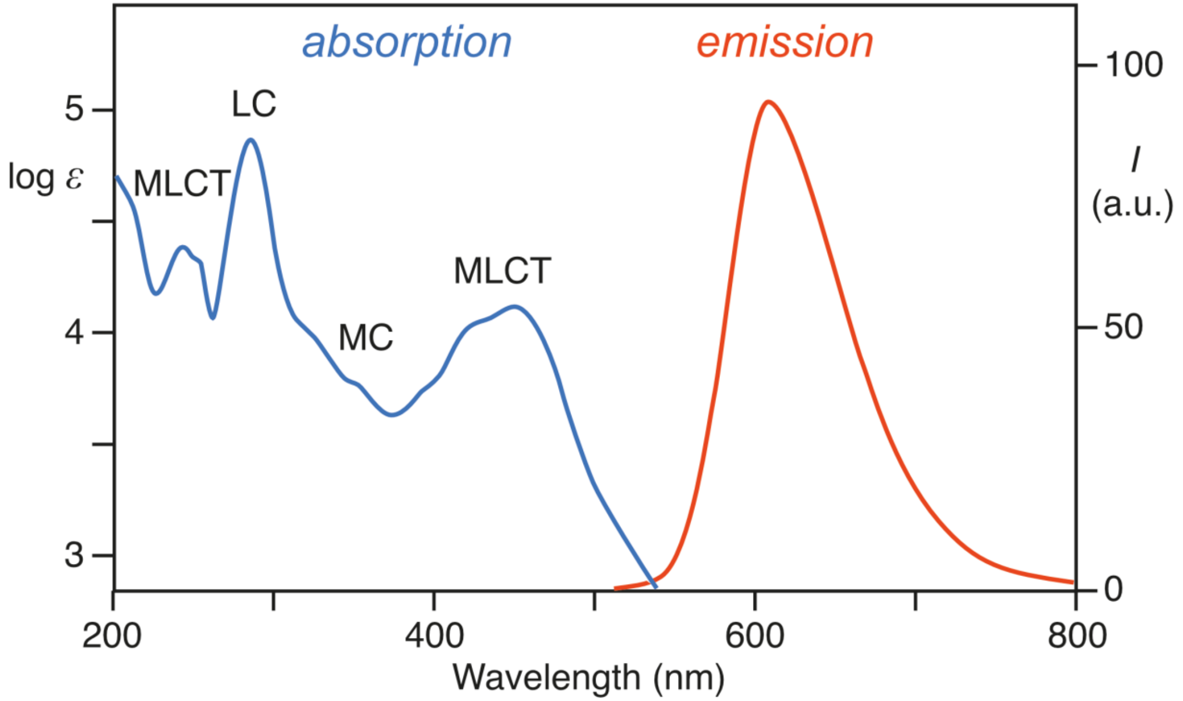
The Hamiltonian for spin–orbit (S–O) coupling results in the heavy-atom effect…

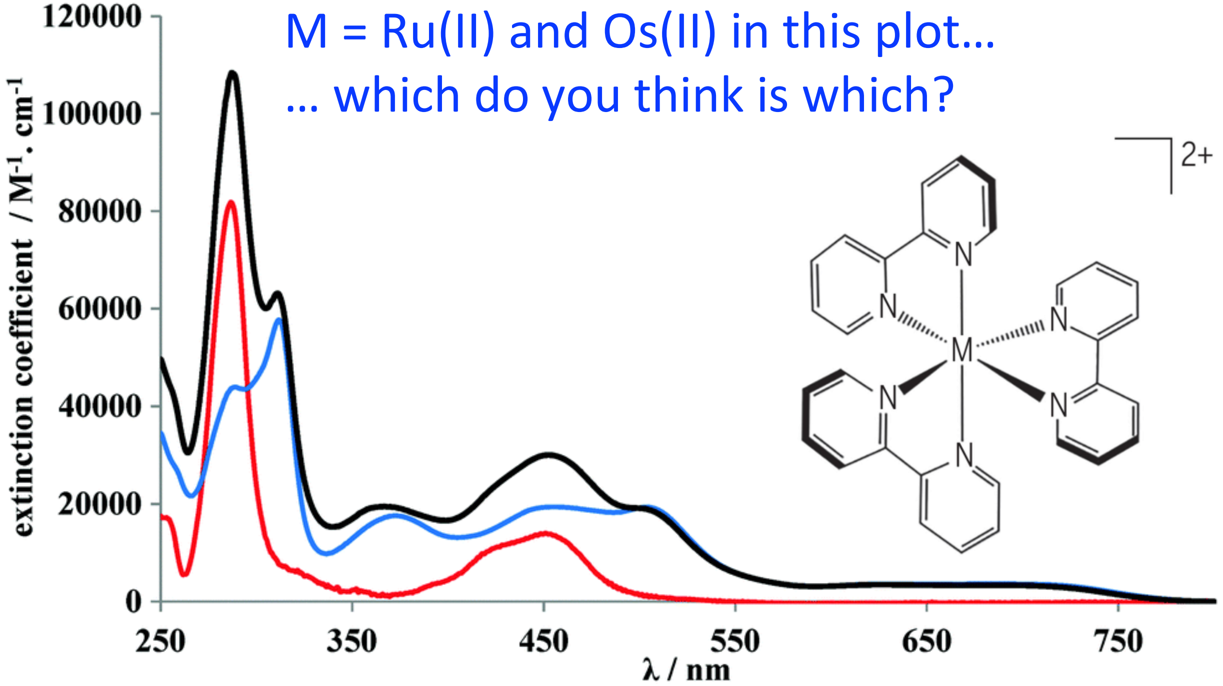
… and it also results in variation in the selection rules…

Total angular momentum: $\boldsymbol{\Delta J = 0, \pm 1}$

Total *z*-direction angular momentum: $\boldsymbol{\Delta m_J = 0, \pm 1}$

$$E_{SO} = \boldsymbol{Z^4}\alpha^2 hcR_H \left\{ \frac{j(j+1) - l(l+1) - s(s+1)}{2n^3 l\left(l+\frac{1}{2}\right)(l+1)} \right\}$$



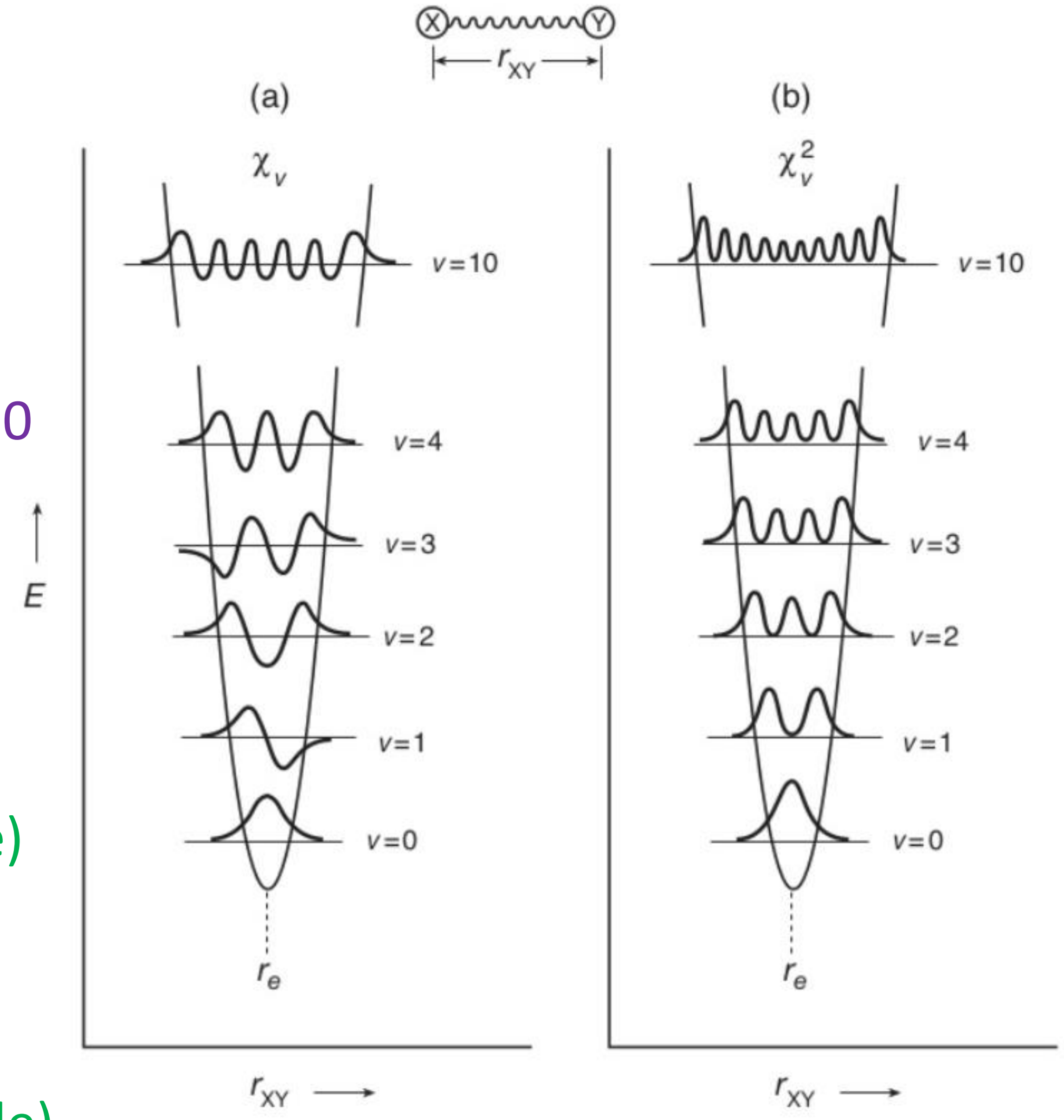


… oh, now I see it in those spectra… and how the black spectrum is just a linear combination

Selection Rules

$$\underbrace{\int \psi_e'^* \psi_e \, d\tau_e}_{\neq 0} \int \psi_v'^* \boldsymbol{\mu}_N \psi_v \, d\tau_v \int \psi_s'^* \psi_s \, d\tau_s$$

When light does not change ψ_e…
… this factor is non-zero… and the other factor is 0
This means that the photon absorption event…
… is nuclear… and is not electronic



Turro, Chapter 2, Figure 2.6, Page 76

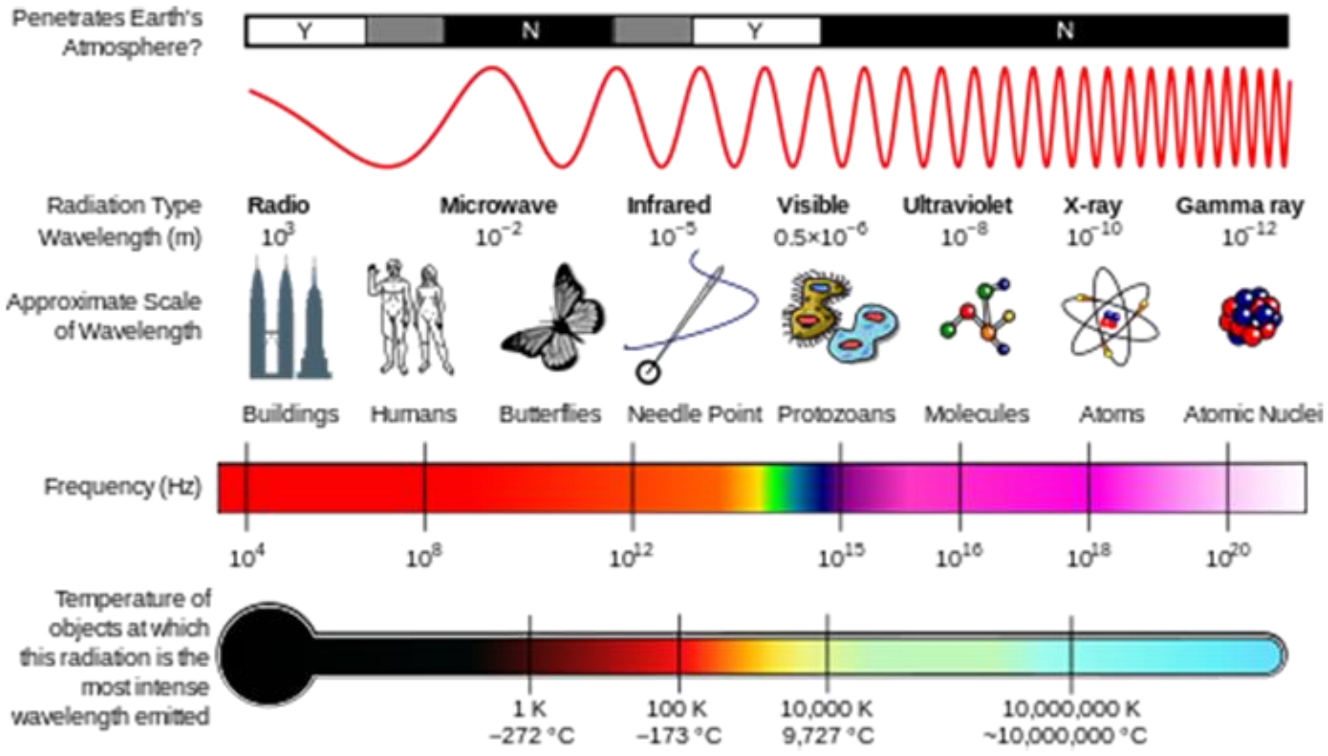
Summary of Nuclear Selection "rules"

Vibrational (Harmonic Oscillator):
$\mathbf{\Delta v = \pm 1}$ (change in dipole)

Vibrational (Harmonic Oscillator) Scattering:
$\mathbf{\Delta v = \pm 1}$ (polarizable)

Rotational (Rigid Rotor Spherical Harmonics):
$\boldsymbol{\Delta J = \pm 1}$ (permanent dipole)

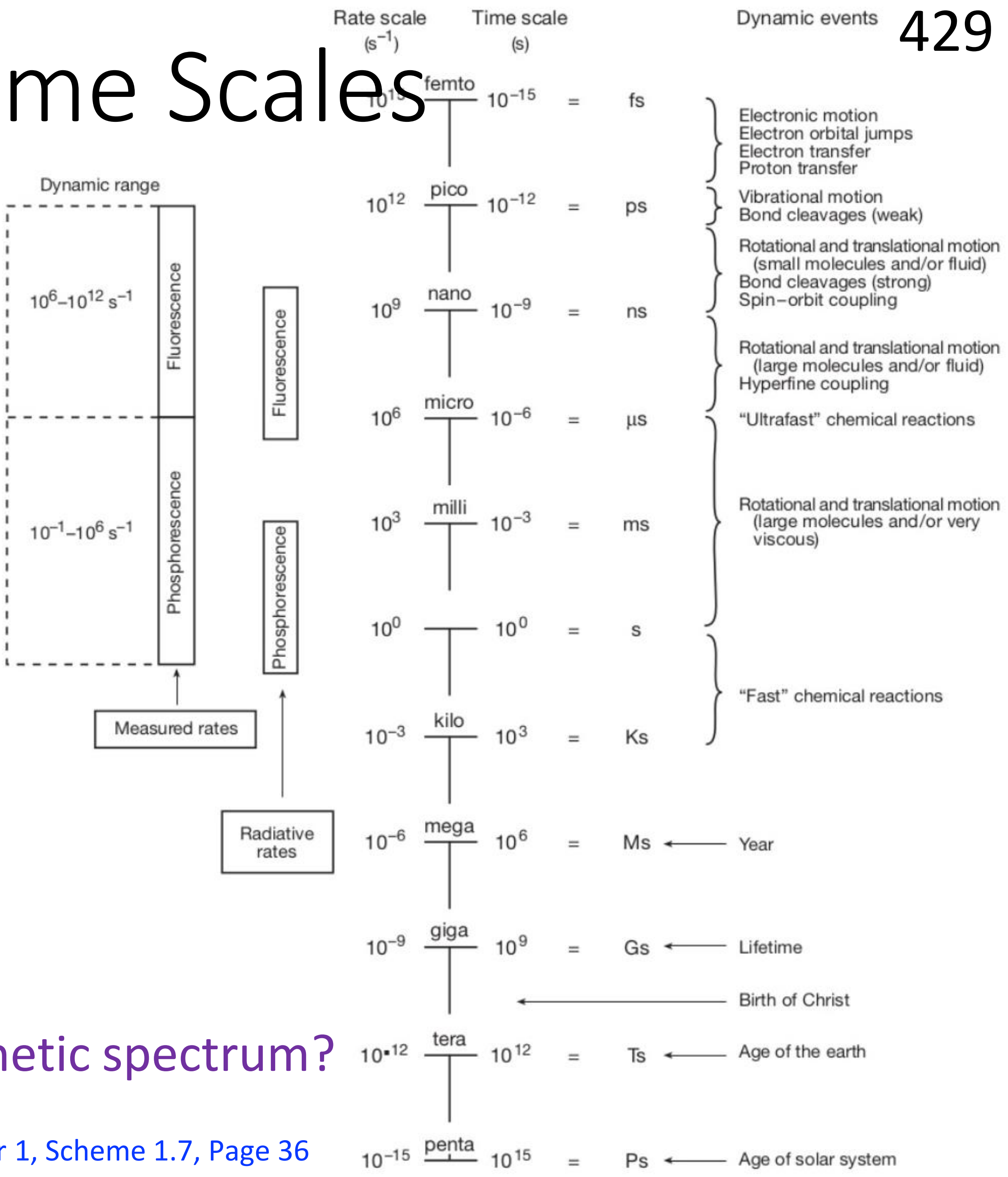
Photochemical Length/Time Scales



https://www.e-education.psu.edu/meteo300/node/682

... so how do we probe such fast processes...

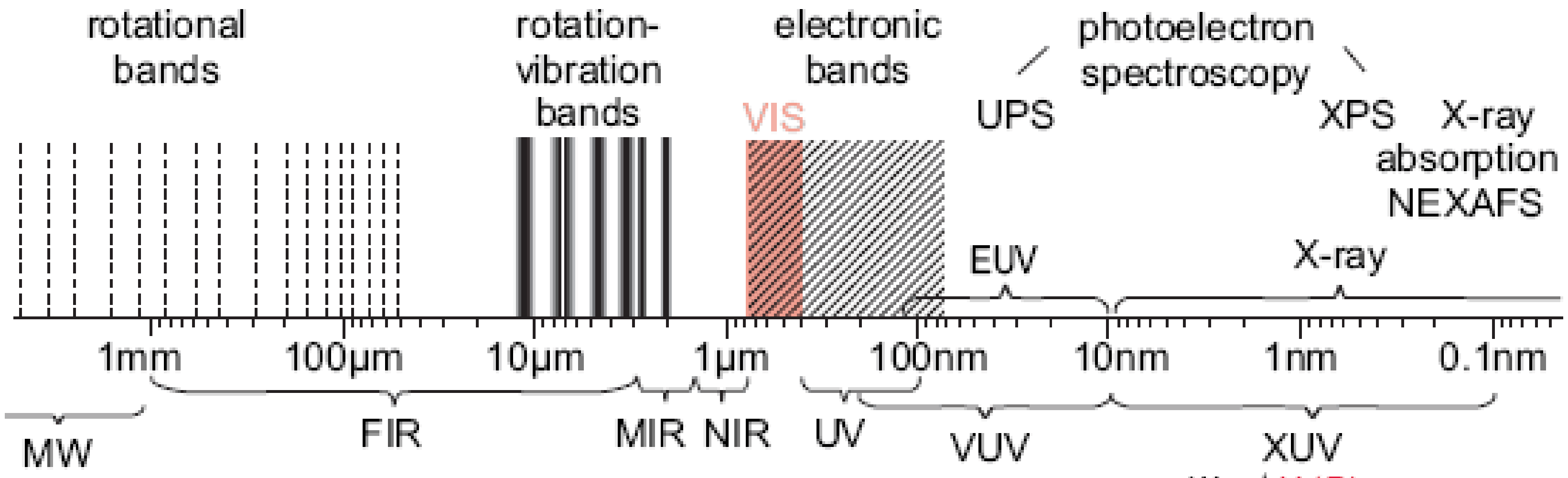
... and in each of these regions of the electromagnetic spectrum?

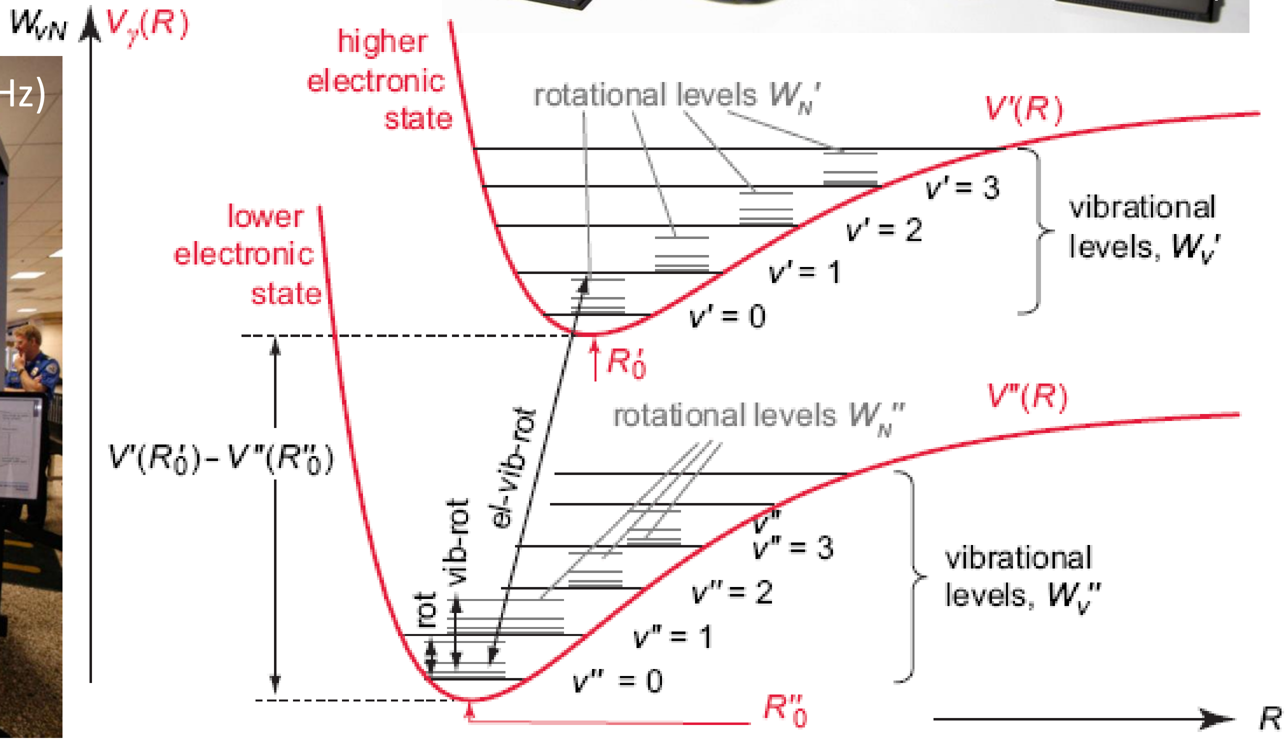


Turro, Chapter 1, Scheme 1.7, Page 36

Electromagnetic spectrum

... what can one do with microwaves?





... and what about gamma rays ... and RF...

... and neutrons... and electrons?... Oh My!

Photochemistry *(summary for today)*

- Blackbody radiation, Carnot efficiency limits, Light–Matter interactions, Photon properties, Conservation laws
- Jablonski diagram, Internal conversion, Intersystem crossing, Kasha–Vavilov rule, **Thexi state, Stokes shift, Luminescence processes**
- **Harmonic oscillator model, Born–Oppenheimer approximation, Franck–Condon principle, 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

Paper Time!