



UCI PHYSICS/CHEM207 – Applied Physical Chemistry, Summer 2022

435

Lecture #15 of 14

(3: TThF, 5: MTWThF, 4: MTWTh, 2: TWTh)

{Okay... let's wrap this up}

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UCI PHYSICS/CHEM207 – Applied Physical Chemistry, Summer 2022

436

Photochemistry

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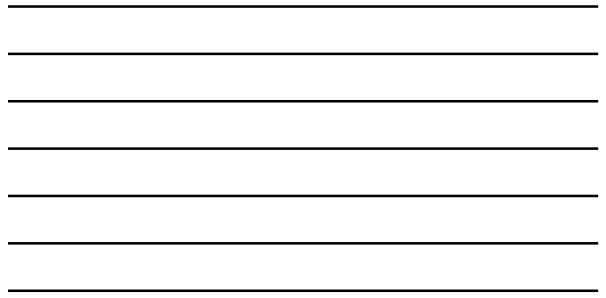
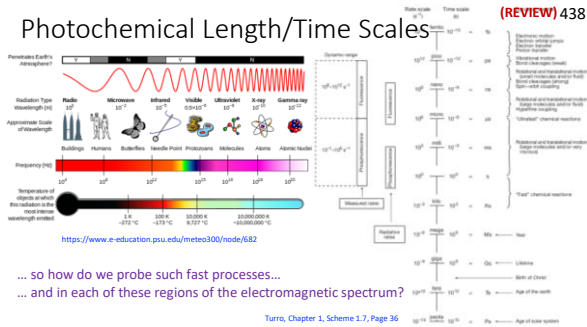
Photochemistry

437

- 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, Absorbance, $E-k$ diagrams

Photochemical Length/Time Scales

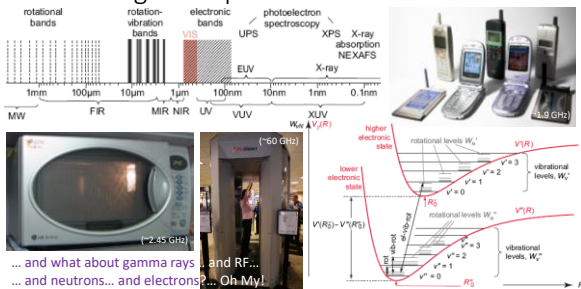
(REVIEW) 438



Electromagnetic spectrum

(REVIEW) 439

... what can one do with microwaves?



Nuclear Terms & F-C Factors

(REVIEW) 440

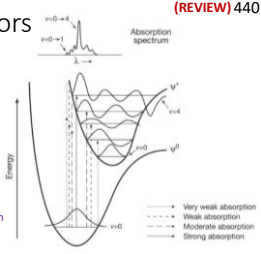
$k_{obs} \sim \rho | \langle \Psi_1 | P_{1-2} | \Psi_2 \rangle |^2$ Fermi's golden rule

Observed Rate Constant = Zero-point Motion-Limited Rate Constant = "Fully Allowed Rate"

$k_{obs} = k_{obs}^{vib} \times f_{FC} \times f_{ZP}$

... separable due to the Born-Oppenheimer approximation

Overlap integral, $S_{12} = \int_{-\infty}^{\infty} \chi_1^*(x) \chi_2(x) dx = \langle \chi_1 | \chi_2 \rangle$
 Franck-Condon factor, $(\langle \chi_1 | \chi_2 \rangle)^2$



B-O Approximation, F-C Principle, TDM Operator (REVIEW) 441

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

$$\Psi \sim \Psi_{el} \Psi_N$$

"The" molecular wave function Exact solution to Eq. 2.1

(electronic wavefunction) 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, μ :**

$$\mu = \mu_e + \mu_N = -e \sum_i r_i + e \sum_j Z_j R_j$$

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

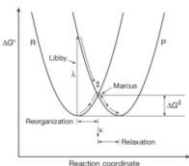
$$P = \langle \psi' | \mu | \psi \rangle = \int \psi'^* \mu \psi d\tau$$

$$P = \langle \psi'_e \psi'_N | \mu | \psi_e \psi_N \rangle = \int \psi'_e \psi'_N \langle \mu_e + \mu_N \rangle \psi_e \psi_N d\tau$$

$$= \int \psi'_e \psi'_N \langle \mu_e \rangle \psi_e \psi_N d\tau + \int \psi'_e \psi'_N \langle \mu_N \rangle \psi_e \psi_N d\tau$$

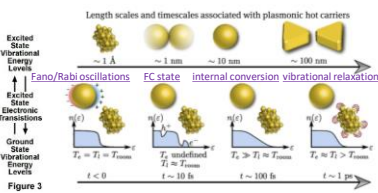
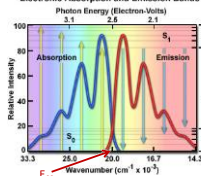
$$= \int \psi'_e \psi_e d\tau \int \psi'_N \mu_N \psi_N d\tau + \int \psi'_e \psi'_N d\tau \int \psi_e \mu_e \psi_e d\tau$$

... this factor is 0 when light changes ψ_e Turro, Chapter 7, Figure 7.12, Page 429



Thermally Equilibrated Excited (Thexi) State (REVIEW) 442

Electronic Absorption and Emission Bands



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

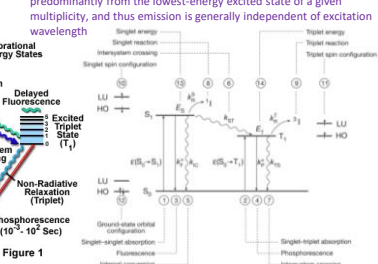
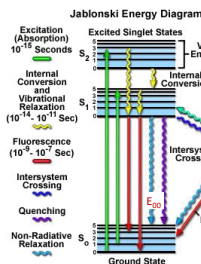
... and why are these spectra plotted as a function of wavenumber... and not wavelength?
 ... so that you can see the "mirror-image" rule"

... 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. Sundaraman & H. A. Atwater, *Nanophoton.*, 2016, 5, 96-111

Jablonski Diagram (REVIEW) 443

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

Selection Rules

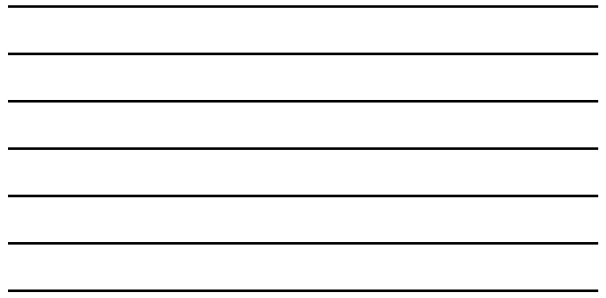
Angular Momentum Quantum Numbers (REVIEW) 444
 Photon... which came from matter: $s = 1, m_s = \pm 1$
 Electron (Orbital): $l, m_l = [-l, l]$ in steps of 1
 Electron (Spin): $s = \frac{1}{2}, m_s = [-\frac{1}{2}, \frac{1}{2}]$

$$\int \psi_f^* \psi_i d\tau \int \psi_f^* \mu_x \psi_i d\tau \int \psi_f^* \psi_i d\tau$$

Frank-Condon factor orbital selection rule spin selection rule

... 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 μ_e do to a wavefunction?... it uses \vec{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 μ_e ... it's just math...
 so, the spin wavefunctions only overlap when they are identical... meaning spin does not change

... simplified systems... **(Angular Momentum) Atomic Selection "rules"**
 Orbital angular momentum (**Laporte "rule"**): $\Delta l = \pm 1$... as $l_f = l_i \pm s_{\text{photon}}$
 Spin angular momentum (**Wigner "rule"**): $\Delta m_s = 0$... μ_e does not act on spin
 Orbital z-direction angular momentum: $\Delta m_l = 0, \pm 1$... 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

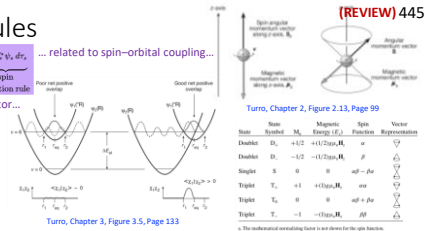


Selection Rules

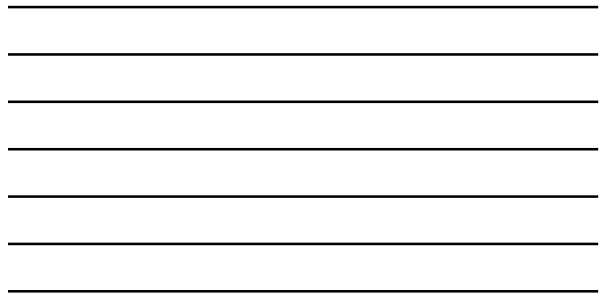
(REVIEW) 445
 ... related to spin-orbital coupling...
 ... related to the F-C factor...

$$\int \psi_f^* \psi_i d\tau \int \psi_f^* \mu_x \psi_i d\tau \int \psi_f^* \psi_i d\tau$$

Frank-Condon factor orbital selection rule spin selection rule



... simplified systems... **Summary of Atomic Selection "rules"** Turro, Chapter 2, Table 2.4, Page 102
 $\Delta l = \pm 1$, since $l_f = l_i \pm s_{\text{photon}}$... $\Delta m_s = 0$... $\Delta m_l = 0, \pm 1$, 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{E}
 Total angular momentum: $\Delta J = 0, \pm 1$... and $\Delta S = 0$... and $\Delta L = 0, \pm 1$
 Total z-direction angular momentum: $\Delta m_j = 0, \pm 1$... and 0's are there for the reason before



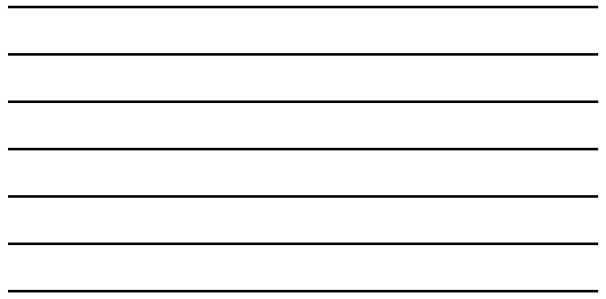
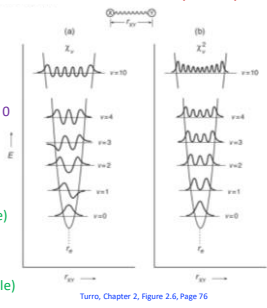
Selection Rules

(REVIEW) 446


$$\int \psi_f^* \psi_i d\tau \int \psi_f^* \mu_x \psi_i d\tau \int \psi_f^* \psi_i d\tau$$

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

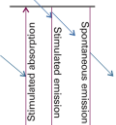
Summary of Nuclear Selection "rules"
 Vibrational (Harmonic Oscillator):
 $\Delta v = \pm 1$ (change in dipole)
 Vibrational (Harmonic Oscillator) Scattering:
 $\Delta v = \pm 1$ (polarizable)
 Rotational (Rigid Rotor Spherical Harmonics):
 $\Delta J = \pm 1$ (permanent dipole)



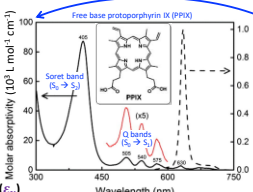
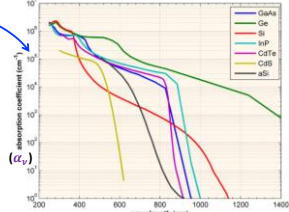
Absorption Coefficient & Beer–Lambert Law 447

To describe attenuation of light intensity/power through matter due to absorption only... one writes $\frac{\partial I_v}{\partial z} = -\alpha_v I_v$... where α_v is the **linear Napierian absorption coefficient** (cm^{-1})
 Rearranging to $\frac{\partial I_v}{I_v} = -\alpha_v dz$, and integrating from $I_{v,\text{front}}$ to $I_{v,\text{back}}$ over ℓ leads to... 
 $\ln\left(\frac{I_{v,\text{back}}}{I_{v,\text{front}}}\right) = -\alpha_v \ell$... or $I_v = I_{v,0} e^{-\alpha_v \ell}$, where $I_v = I_{v,\text{back}}$ and $I_{v,0} = I_{v,\text{front}}$ (Labovitz, Chapter 2, Figure 2.52, Page 59)
 ... where $T_v = \frac{I_v}{I_{v,0}}$ (transmittance) and $A_v = -\log(T_v) = \log\left(\frac{I_{v,0}}{I_v}\right)$ (absorbance)
 ... but the **absorption coefficient** can take on many forms/units... sorry...
 $\log\left(\frac{I_v}{I_{v,0}}\right) = -a_v \ell$... where a_v is the **linear decadic absorption coefficient** (cm^{-1}) [not often used]
 $\ln\left(\frac{I_v}{I_{v,0}}\right) = -K_v c \ell$... where K_v is the **molar Napierian absorption coefficient** ($\text{M}^{-1} \text{cm}^{-1}$) [n. o. u.]
 ... since $\text{M}^{-1} \text{cm}^{-1} = \text{L mol}^{-1} \text{cm}^{-1} = \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$, $\sigma_v = \frac{1000 K_v}{N_A}$ is the **absorption cross-section** (cm^2)
 $\log\left(\frac{I_v}{I_{v,0}}\right) = -\epsilon_v c \ell$... where ϵ_v is the **molar decadic absorption coefficient** ($\text{M}^{-1} \text{cm}^{-1}$)... finally!...
 ... leading to the **Beer–Lambert law**... $A_v = \epsilon_v c \ell$... a succinct and well-known equation in the end
<https://goldbook.iupac.org/terms/view/R00037>

Einstein Coefficients & Oscillator Strength 448

Oscillator strength (f_{12}): integrated strength of an absorption band relative to a completely allowed transition
 ... is emission the microscopically reversible opposite of absorption? ... **Nope!** allowed transition
Absorption = -Stimulated Emission... but not Spontaneous Emission
 Spontaneous Emission $\frac{\partial n_1}{\partial t} = A_{21} n_2$ Positive Absorption = Stimulated Absorption $\frac{\partial n_1}{\partial t} = -B_{12} n_1 \rho(\nu)$
 Negative Absorption = Stimulated Emission $\frac{\partial n_1}{\partial t} = B_{21} n_2 \rho(\nu)$

 Consider all possible reactions to be at equilibrium...
 $\frac{\partial n_1}{\partial t} = -\frac{\partial n_2}{\partial t} = 0 = A_{21} n_2 + B_{21} n_2 \rho(\nu) - B_{12} n_1 \rho(\nu)$... $g_1 B_{12} = g_2 B_{21} = \frac{g_1 c^2 f_{12}}{4 \epsilon_0 m_e h \nu}$
 ... where $\rho(\nu)$ is an irradiance... in units of energy per volume per frequency, ν
 R. C. Hilborn, Am. J. Phys., 1982, 50, 982–986 ... $A_{21} = \frac{8 \pi h \nu^3}{c^3} B_{21} = \frac{16 \pi^3 \nu^3 \mu_{21}^2}{3 \epsilon_0 h c^3}$
 R. C. Hilborn, arXiv:physics/0202029

Absorption Coefficient 449

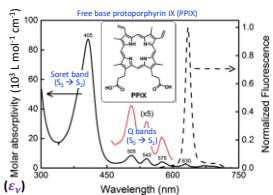
... what is the name of each absorption coefficient?... and how do we compare them?
 ... well, what is the concentration in a metal?... **Maybe 1 M-ish?**


<https://www.sciencedirect.com/science/article/pii/S0009261417301756>
<https://www.pveducation.org/pvcdrom/jpn-junctions/absorption-coefficient>

Absorption vs Absorbance vs Absorptance

450

... let's use each in a sentence, okay?

... For example, "I do not understand the difference between A., A., and A.?" ... Hal j/k



... "This plot displays an **absorption spectrum**"
 ... "The ordinate is often **absorbance**, which is dimensionless... and definitely not "a.u.""
 ... "Absorbance, *A*, is directly related to concentration... and so its range is [0, ∞)"
 ... "Absorptance, *α*, is the fraction (or percentage) of light absorbed... it goes well with *T* (or %*T*)"
 ... "Photochemists must know **concentrations** (via *Abs*, *A*) and **amount of light absorbed** (as *Abt*, *α*)"

$$%R_v = \left(\frac{n_2 - n_1}{n_2 + n_1} \right)^2$$

$$%T_v = (100\% - \%R_{v,front})10^{-\alpha_v c l} - \%R_{v,back}$$

$$%T_v = (100\% - \%R_{v,front})e^{-\alpha_v c l} - \%R_{v,back}$$

... and based on the Fresnel equations, for light with normal incidence... %*A_v* + %*T_v* + %*R_{v,total}* = 100%



E-k Diagrams

451

Phonon

Particle Type: Boson

Mass: 0

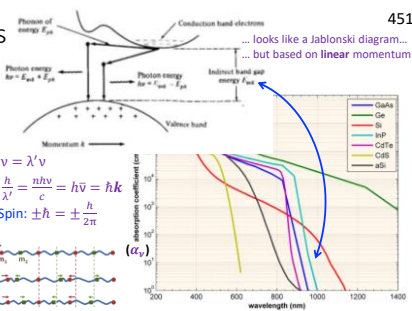
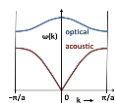
Charge: 0

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

Linear Velocity: $\frac{E}{\hbar} = \left(\frac{\hbar}{m\lambda}\right)v = \lambda'v$

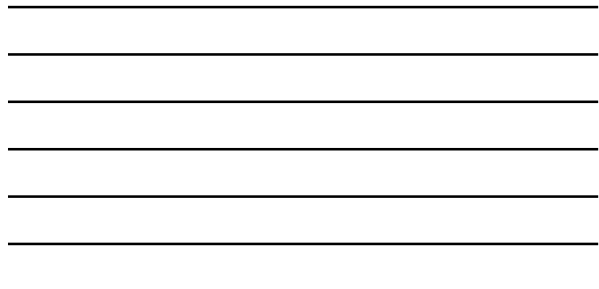
Linear Momentum: $p = \frac{h}{\lambda'} = \frac{\hbar v}{c} = \hbar\tilde{\nu} = \hbar k$

z Angular Momentum / Spin: $\pm\hbar = \pm \frac{h}{2\pi}$



<https://www.pveducation.org/pvcdrom/jpn-junctions/absorption-coefficient>

... looks like a Jablonski diagram...
 ... but based on **linear momentum**



Photochemistry (summary for today)

452

- 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!



Photochemistry (*let's review TWTh*)

453

- T: Blackbody radiation, Carnot efficiency limits, Light–Matter interactions, Photon properties, Conservation laws
- W: 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
- Th: Beer–Lambert law, Absorption coefficient, Einstein coefficients, Oscillator strength, Absorptance, E–k diagrams

454

ALL DONE!...

... THANKS SO MUCH FOR TAKING PART IN THIS
(RATHER) NEW COURSE!

Take-home messages:

- (1) Some chemists know a lot of physics;
- (2) Physicists (you!) now know a lot of Chemistry;
- (3) Who wants to switch to a Ph.D. in Chemistry?

Final Exam Time!
