Lecture 12: **Chapter 18** **Electronic Transitions**

Homework #4 Due Tuesday Feb. 28th, 5:00 PM - Chapter 18: 1, 3, 5, 9, 10, 14, 18, 19 – Since answers listed in back of book, grading is based on work shown describing how you obtained answers.

I. UV-Vis spectroscopy: Electronic Transition

II. Beer-Lambert Law

I. UV-Vis spectroscopy: Electronic Transition

Stick →continuum

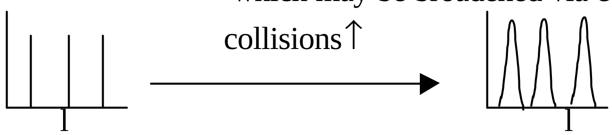
atom
↓
small molecule
↓
large molecule
↓
condensed phase

A. Intro:

Visible ~ 400 – 700 nm, UV 200-400 nm, VUV < 200 nm.

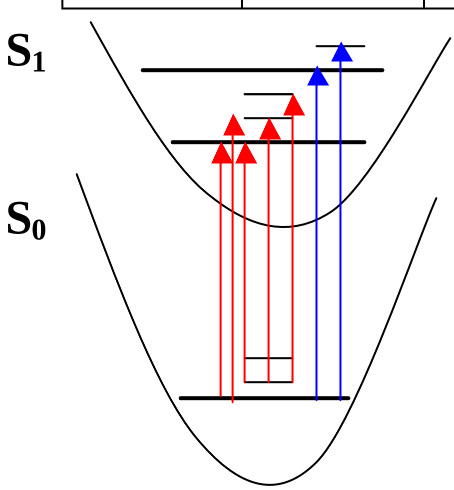
What explains structure in uv-visible absorption spectra of molecules?

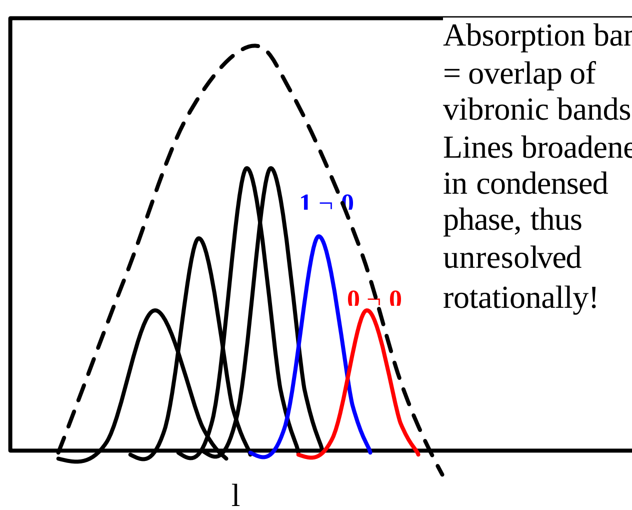
Atoms – Only lines (electronic transitions), which may be broadened via collisions



Molecules - Many lines (very dense) electronic, vibrational, and rotational transitions. A set of rovibronic lines belonging to the same vibronic transition comprise a band. For example the lines associated with $\upsilon''=0$ of S_0 to $\upsilon'=0$ of S_1 includes the following transitions:

S_0	S_1	u²	u¢	J²	J¢
BAND 0 ¬ 0		0	0	0	0
		0	0	0	1
		0	0	1	0
		0	0	1	1
		0	0	1	2
		⋮			
BAND 1 ¬ 0		0	1	0	0
		0	1	0	1
		⋮			

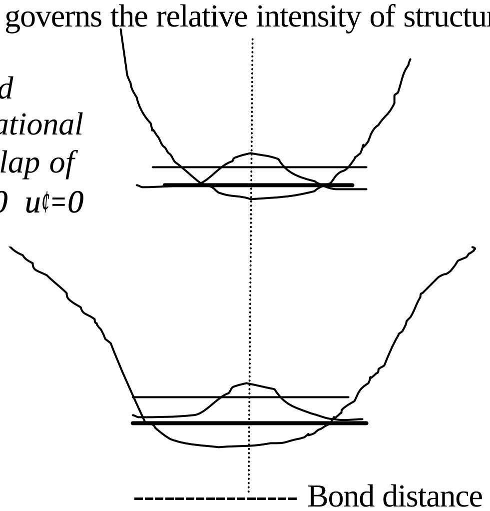




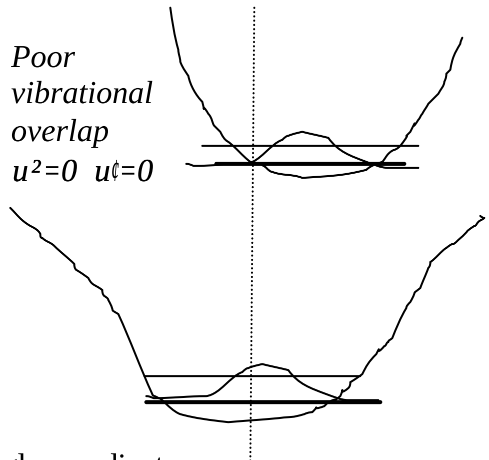
B. Franck-Condon Principle

Vertical Excitations – Electronic-vibrational (Vibronic) transitions occur at fixed nuclear geometries since the nuclei remain virtually fixed as electrons populate new orbitals (electronic transitio n). The probability is governed by several factors, one of which is the Franck-Condon Factor: $[\int \chi_1^* \chi_2 \; d\tau]^2$ = square of the vibrational overlap integral. This governs the relative intensity of structure found within an electronic transition.

Good vibrational overlap of u²=0 u¢=0



Poor vibrational overlap u²=0 u¢=0



--------------- Bond distance or Bond angle coordinate --------------------

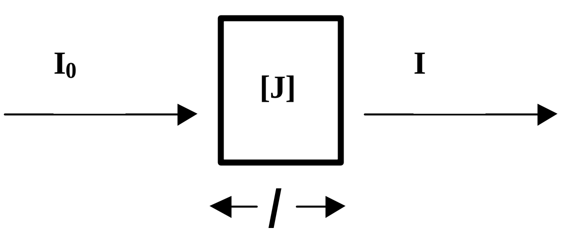
Understand how the intensity of the u¢=0 ¬ u²=0 transition instensity changes with the shift of the geometry of the excited state relative to that of the ground state.

II. Beer-Lambert Law

The change in light intensity dI is proportional to the light intensity (I), concentration [J], and pathlength dx: $dI = -\kappa [J] I dx$ where κ is a proportionality constant. Integrating this equation and switching from the natural bgarithms (ln) to base 10 logarithms (log) yields the Beer-Lambert Law.

$$\log\frac{I}{I_0} = \log T = -e[J]\ell \qquad \log\frac{I_0}{I} = Ae[J]\ell$$

where [J] is concentration of species J, *l* = pathlength, e is molar absorption coefficient or extinction coefficient usu. in units L mol^{-1} cm^{-1} , which is T dependent. **T = transmittance**, A = **Absorbance (optical density**), Fraction of absorbing = 1 - T , thus %absorption = (1-T)×100%



Also note alternative (base e) forms of Beer's Law keeping in mind ln x = ln10 log x

$$I = I_0 e^{-sn\ell}$$

s = absorption cross section (cm^2 $molecule^{-1}$)

n = number density = molecules cm^{-3}, and *l* = pathlength in cm.

Example 1:

PM-546 has $\varepsilon_{493} = 7.9\times10^4$ liter mol^{-1} cm^{-1} at 493 nm (it's absorption max). If you wanted to absorb 45% of the 493 nm light for a 1 cm pathlength, what concentration would you need to prepare?

(1-T)100% = 45% $\rightarrow$ (1-T) = 0.45 $\rightarrow$ T = 0.55=I/I$_0$

$A = \varepsilon[J]\ell$ $\rightarrow$ $A=\log(I_0/I)= -\log(I/I_0) = -\log T=\varepsilon[J]\ell$ $\rightarrow$ $[J]= -\log T/(\varepsilon\,\ell)$

$[J]= -\log(0.55)/(7.9\times10^4$ liter mol^{-1} cm$^{-1}\times 1$ cm$) = 3.29\times10^{-6}$ M.

Example 2: If the absorbance of 3.24×10^{14} molecules cm^{-3} is 0.436, and $s = 7.53\times10^{-18}$ cm^2 molecule^{-1}, what is the pathlength? Use this form of Beer's Law:

$$I = I_0 e^{-sn\ell}$$

$$\ln\frac{I_0}{I} = sn\ell \quad\Rightarrow\quad \ell = \frac{1}{sn}\ln\frac{I_0}{I} = \frac{1}{sn}\ln 10\times\log\frac{I_0}{I}$$

$$\ell = \frac{1}{7.53\times10^{-18}\,cm^2\,molecule^{-1}\ \times\ 3.24\times10^{14}\,molecules\ cm^{-3}}\,2.303\times0.436$$

$$\ell = 411\,cm$$

We may use Beer's law to determine the conentration of 2 species A & B in a solution , usu. need 2 diff wavelengths: $A_{total\,\lambda} = A_{A\lambda} + A_{B\lambda}$

i.e. $\mathbf{A_{\lambda 1} = \varepsilon_{A\lambda 1}[A]\ell + \varepsilon_{B\lambda 1}[B]\ell}$ **and** $\mathbf{A_{\lambda 2} = \varepsilon_{A\lambda 2}[A]\ell + \varepsilon_{B\lambda 2}[B]\ell}$

This is a system of 2 equations and 2 variables, thus substitute to eliminate one variable.

Example 3: For the following 2 solute species **F** and **G** information about the absorbance was obtained for a 1 cm pathlength cuvette. Determine the concentration in terms of molarity for species **F** and **G**.

	450 nm	600 nm
ε **(F)** M^{-1} cm^{-1}	2.15×10^4	5.25×10^4
ε **(G)** M^{-1} cm^{-1}	4.87×10^4	7.23×10^3
Absorbance	0.148	0.207

Answer: 0.148 = $\varepsilon_{F\lambda 1}$ **[F]**ℓ + $\varepsilon_{G\lambda 1}$ **[G]**ℓ **and 0.207 =** $\varepsilon_{F\lambda 2}$ **[F]**ℓ + $\varepsilon_{G\lambda 2}$ **[G]**ℓ **ℓ =1cm**

0.148 = 2.15×10^4 **[F]**ℓ + 4.87×10^4 **[G]**ℓ **(1)** **0.207 =** 5.25×10^4 **[F]**ℓ + 7.23×10^3 **[G]**ℓ **(2)**

Let's make the coefficients of the species [F] the same by converting 2.15×10^4 into 5.25×10^4 by multiplying by the first equation by $5.25\times10^4 \div 2.15\times10^4 = 2.144186$

Equation #1: $0.3614 = 5.25\times10^4$**[F]**ℓ + 1.189×10^5 **[G]**ℓ

-

Equation #2: $0.207 = 5.25\times10^4$ **[F]**ℓ + 7.23×10^3 **[G]**ℓ

(2) - (1) : $0.1544 = 1.1167\times10^5$ **[G]**ℓ ® $0.1544 = 1.1167\times10^5$ l mol^{-1} cm^{-1} [G] 1 cm

[G] = 1.383×10^{-6} mol l^{-1} = $\mathbf{1.38\times10^{-6}}$ **M** $\rightarrow$ Substituting [G] into Eq. 1

[F] = $\{0.148 - 4.87\times10^4\ [G]\ell\} \div 2.15\times10^4$

$=\{0.148 - 4.87\times10^4 \times 1.38\times10^{-6}\} \div 2.15\times10^4 = \mathbf{3.76\times10^{-6}}$ **M**

Of course you should verify that these work by substituting for both equations 1 & 2.

isobestic wavelength = λ at which ε of both A & B components are equal: $A_\lambda = \varepsilon$ ([A]+[B])*l*

If A and B are in equilibrium A↔B, then regardless of the shift of equilibrium [A] + [B] remains constant, **isobestic point** (absorbance point that's invariant with equilibrium). The absorbance at the isobestic wave length is useful to measure the total concentration of two species in equilibrium, i.e. isomerization, association reactions (hemoglobin with O_2). Thus you may prove *only two solutes are in equilibrium* by observing equilibrium independent (i.e. change pH) isobestic points.