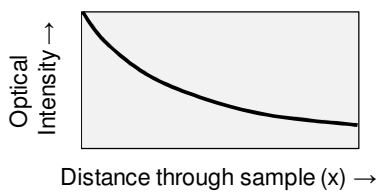
Theoretical Calculation of the Oscillator Strength of an Electronic Transition and Comparison with Experiment

There are multiple ways to express the strength of an optical transition in a spectroscopy experiment. The Beer-Lambert law is an empirical relationship that describes what is seen at the lab scale, while other approaches such as the transition moment and oscillator strength have strong theoretical foundations. This experiment is intended to explore the various methods of reporting the strength of optical transitions.

Beer-Lambert Law

The optical absorption relationship that is best known by students is the Beer-Lambert law (a.k.a. Beer's law). This approach is based on the concept that optical intensity drops off exponentially as it penetrates through an absorbing solution – the further the light penetrates, the more it gets absorbed and the weaker the remaining intensity.



$$I = I_o e^{-kx}$$

This can be rearranged into the familiar Beer-Lambert relationship:

$$A(\lambda) = -\log_{10}\left(\frac{I}{I_o}\right) = \varepsilon(\lambda)\cdot b\cdot c \qquad (1)$$

where $A(\lambda)$ = the absorbance at wavelength λ, $\varepsilon(\lambda)$ = the molar absorptivity at that wavelength, b = path length through the sample, and c = concentration of absorbing species in solution in units of molarity.

An important note to consider when applying the Beer-Lambert law is that the derivation makes the <u>assumption that the absorbing molecules along the optical path in the solution are exposed to an average diminishing intensity</u>. In highly absorbing solutions, however, samples near the far edge of the sample holder can be <u>physically shadowed</u> by other molecules that were earlier along the optical path. This is different than an analogous chemical kinetic experiment where concentrations may decrease with time, but the concentration gradient is constant across the sample. The result is that the relationship between $A(\lambda)$ and *concentration* is only linear for samples where the total absorbance through the sample is less than 1.

Limiting condition for Beer-Lambert Law: $A(\lambda) < 1.0$

The other note of importance is that the Beer-Lambert law is based on empirical observation. The molar absorptivity, $\varepsilon(\lambda)$, is a constant that describes the level to which light is absorbed at the lab scale for a given molecule and at a given optical wavelength, but it provides no information by itself with respect to underlying microscopic phenomena.

Transition Moment Integral, μ_{12}

If we consider the Beer-Lambert lab-scale empirical relationship as being at one end of a continuum, the transition moment integral, μ_{12}, can be considered to be at the other end of that continuum. μ_{12}, describes the strength of the quantum-mechanical interaction of light with the sample at the atomic or molecular level.

We use ψ_1 and ψ_2 to describe the stationary (time independent) wavefunctions for the initial and final quantum states of the transition. The transition itself, however, requires using the non-stationary (time dependent) version of the Schrödinger equation. This transition depends on the interaction between the electrons and the applied optical radiation field. The Hamiltonian, $\hat{H}'$, for the perturbation of an electron and an oscillating light field is:

$$\hat{H}' = -ezE_o \cos(2\pi\nu t) \tag{2}$$

where e is the charge on the electron, z is the coordinate of the electron in the direction of the light E-field polarization, E_o is the amplitude of the electric field vector of the radiation, ν is the frequency of the radiation, and t is the time. This oscillating field interacts with the molecular dipole moment of the quantum mechanical transition states.

It can be shown that the resultant strength of the optical transition depends on the transition moment integral:

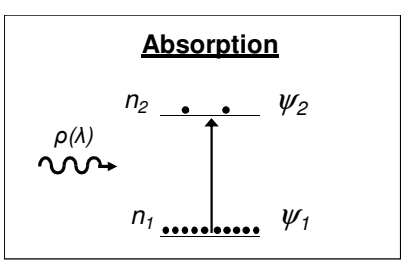
$$\mu_{12} = \int \psi_2 * \mu \psi_1 \, d\tau \tag{3}$$

where μ is the dipole moment of the molecule.

Einstein Coefficients

In 1917 Einstein formulated a kinetic model to explain and extend the Beer-Lambert law. Einstein's treatment predated quantum mechanics, but his approach has subsequently been adapted to serve as a bridge between the macroscopic Beer-Lambert relationship and the quantum mechanical microscopic transition moment. In other words, it connects what electrons experience at the molecular scale with what we see at the laboratory scale.

The Einstein model for "induced absorption" describes the kinetic change in populations, n_1 and n_2, as being dependent on a rate constant, B_{12} (Einstein absorption coefficient), the number concentration of ground state molecules, n_1, and the "concentration of light" (actually the radiation density of photons at frequency ν, $\rho(\nu)$).



$$+\frac{\partial n_2}{\partial t} = -\frac{\partial n_1}{\partial t} = B_{12}\, \rho(\nu)\, n_1 \tag{4}$$

It can be shown that the Einstein coefficient for absorption, B_{12}, can be related to the quantum mechanical transition moment through the following equation:

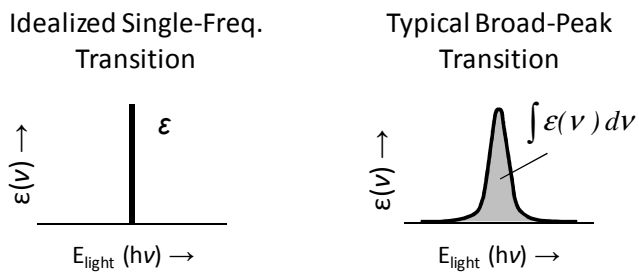
$$B_{12} = \frac{\mu_{12}^2}{6\varepsilon_o \hbar^2} \tag{5}$$

Similarly, B_{12} can also be shown to be related to the Beer-Lambert molar absorptivity (ε) and optical frequency (ν) through the next two equations:

$$B_{12} = \frac{c \cdot 2.303}{h\nu\, N_A} \cdot \varepsilon(\nu) \qquad \text{(for single-frequency transition)}$$

$$B_{12} = \frac{c \cdot 2.303}{h\nu_{peak}\, N_A} \cdot \int \varepsilon(\nu)\, d\nu \qquad \text{(for broad-peak transition)} \tag{6}$$

Ideally a transition would occur at a single frequency or wavelength. In practice, however the Heisenberg Uncertainty Principle demands there to be an uncertainty in the energy of the transition. Even more significant is the variability in environmental conditions and the concurrent vibrational and rotational interactions that lead to broad transitions that span across multiple frequencies.



The important thing to note with regards to earlier discussions in this document is that B_{12} can be related to both the macroscopic molar absorptivity and the microscopic transition moment integral and as such offers a bridge between the empirical and the fundamental.

Oscillator Strength

A final method of describing the strength of optical/molecular interactions is to calculate the oscillator strength, f. This parameter is often found in the spectroscopy literature.

The oscillator strength compares a quantum mechanical transition to that expected by a fully-allowed set of classical electromagnetic oscillators. It is a dimensionless quantity. A value of ~1 represents a strong transition while a quantum-mechanically forbidden transition might have f ~ 0.001. f is related to the transition moment and the Einstein coefficient by the following expressions:

$$f = \frac{4 m_e \pi\, \nu}{3 e^2 \hbar} \cdot \mu_{12}^2 \quad \text{or} \quad f = \frac{4\, \varepsilon_o\, m_e\, h\nu}{e^2} \cdot B_{12} \tag{7}$$

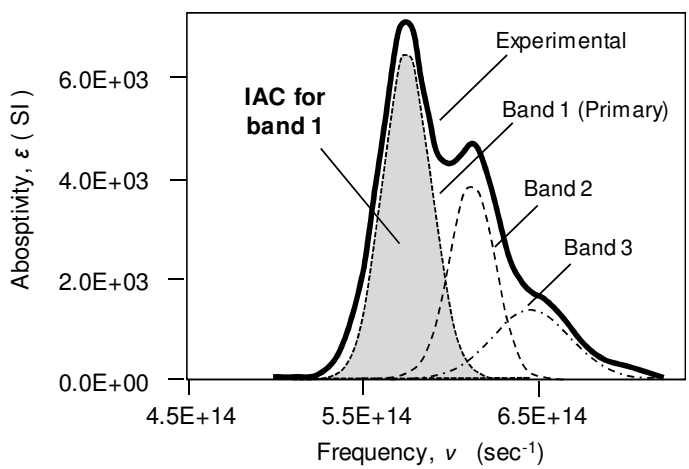
where ν is the optical frequency at the maximum absorption, m_e and e are the mass and electrical charge of an electron, and ε_o is the vacuum permittivity, all in SI units.

EXPERIMENTAL CALCULATIONS

In a previous experiment you measured the absorption spectra for a series of conjugated dyes. Import the spectral data for the dyes into Excel.

- Using your experimental concentrations and the Beer-Lambert law (eq 1), convert the absorbances for each dye into absorptivity $\varepsilon(\nu)$ values and convert the wavelengths into frequency, ν. The $\varepsilon(\nu)$ values will need to be in SI units, ε_{SI}, so you will need to convert path length to meters and molarity to moles/m^3. Plot your values of $\varepsilon_{SI}(\nu)$ vs. ν. Include these graphs in your report.

- If the data consist of a single peak it is fairly straightforward to find the area underneath the peak. However it is more likely that the data will be a composite of multiple overlapping peaks. You will therefore need to separate the data to obtain the area of the single peak of interest. You can do this by using Solver within Excel to deconvolute your experimental spectrum into individual peaks. See Addendum at end of this document for directions on how to do this. The program assumes a Gaussian shape for each underlying peak.



You will need to find the **Integrated Absorption Coefficient, *IAC***, for the primary peak.

$$IAC = \int \varepsilon(\nu)\, d\nu \qquad (8)$$

One method of finding IAC is to use calculus or Mathematica to determine the integral of the equation for the Gaussian curve that was generated in the deconvolution program.

$$\varepsilon(\nu) = \varepsilon_{max} \cdot e^{-(\nu-\nu_{max})^2/2\sigma^2} \qquad (9)$$

where ε_{max} is the height of the primary peak, ν_{max} is the frequency location of the peak, and σ is the peak bandwidth – all of these parameters being reported by the deconvolution program.

An alternative method is to do a summation of the calculated data for the primary peak.

$$IAC \cong \sum_{i=data\ pts} \left[\varepsilon_i \cdot \Delta\nu_{i\to(i+1)} \right] \qquad (10)$$

- Once IAC is known you can then calculate the Einstein coefficient, B_{12} , of the primary peak for each of your spectra using eq. 6.

- After calculating B_{12} you can calculate the transition moment integral, μ_{12}, and the oscillator strength, f, for each of your spectra using eq's 5 and 7. Express the transition moment integral in both SI units and in Debye units. A Debye (D) is the traditional non-SI unit of dipole moment. The conversion between D and SI units is

  $1.0\ D = 3.336 \times 10^{-30}$ coulomb-meter.

REPORT

- Prepare a table that lists the following data for each dye: number of double bonds in chain, λ_{max} , ε_{max} , IAC, B_{12}, μ_{12}, and f (in SI units and Debyes).

QUESTIONS

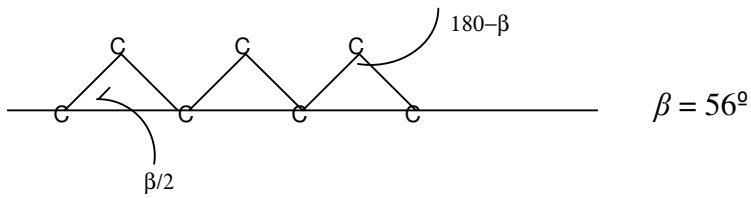
1. How do the values in the data table vary as a function of the chain length in the conjugated dyes? Comment on any trends that you see.

2. We previously used these dyes and their spectra to explore the use of the particle-in-a-box model to describe the transition energies for systems of conjugated double bonds. We were able to show that the energy for a given electronic state in a particle in a box is:

$$E_n = \frac{h^2 n^2}{8ma^2} \qquad \text{with } a = \text{total "length" of box}$$

The data agreed reasonably well with this theoretical model if we added a "fudge factor" to correct the length due to the fact that we do not have hard walls with $V=\infty$ at the ends of a conjugated molecule.

An additional discrepancy with an ideal particle in a box is that a conjugated system is not linear but actually zigzags. The path of the electrons follows this zigzag path.



$\beta = 56^{\circ}$

We "leave it to the reader to show…" that after applying this geometric correction to the particle-in-a-box model, the theoretical oscillator strength the model is:

$$f_{p.in\,box} = \frac{4N^2(N+2)^2\cos^2(\beta/2)}{3\pi^2(N+1)^3} \qquad (11)$$

where N is the number of pi electrons in the conjugated system. Use eq. 11 to calculate the theoretical oscillator strength for each dye. (Remember that one of the nitrogens at the end of each chain contributes a lone pair set of electrons to the conjugated system.) Compare the theoretical values to your experimental results and comment on the agreement. What might account for discrepancies between your data and the theoretical predictions?

3. The oscillator strength is a measure of the "allowedness" of a transition. An oscillator strength ~1 implies that a transition is completely allowed (an ideal oscillator). Comment on the "allowedness" of your transitions.

Typical Order-of-Magnitude Results (your data should be in these ranges)

Absorptivity, ε	~	$10^{+3} - 10^{+4}$	$(\text{mol/m}^3)^{-1}\ \text{m}^{-1}$
Frequency, ν	~	$10^{+14} - 10^{+15}$	s^{-1}
IAC	~	$10^{+17} - 10^{+18}$	$(\text{mol/m}^3)^{-1}\ \text{m}^{-1}\ \text{s}^{-1}$
B_{12}	~	$10^{+21} - 10^{+22}$	$\text{J}^{-1}\ \text{M}^3\ \text{s}^{-2}$
μ_{12} (SI units)	~	$10^{-29} - 10^{-28}$	coulomb·m
μ_{12} (Debyes)	~	1 – 20	D
f	~	0.1 – 10	–

*** ADDENDUM ***

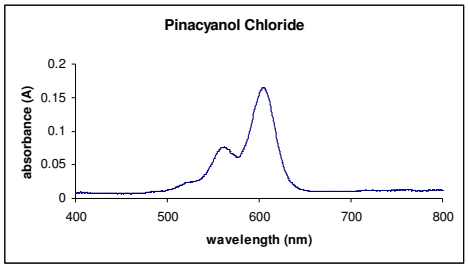
Deconvolution of Optical Spectra

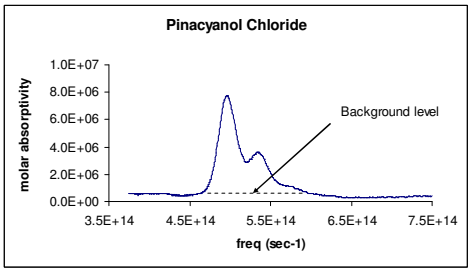
UV/Vis absorption spectra often consists of multiple overlapping peaks. This is due to the energy gap between successive optical transitions being smaller than the line broadening that occurs for molecules in solution. Excel can be used to "deconvolute" (separate) the experimental signal into individual bands. The program assumes that the individual transitions follow a Gaussian line shape.

An Excel template has been prepared to perform this deconvolution. It uses the Solver Add-in package that can be installed with Excel. (Part of the MS installation disk.)

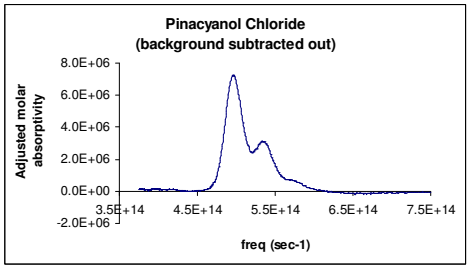
Specific steps can be found in the lab write-up and in the instruction sheet on the Excel spreadsheet. But there are several general steps that must be taken.

1) Convert wavelengths to frequencies and convert absorbances to absorptivities (SI units).

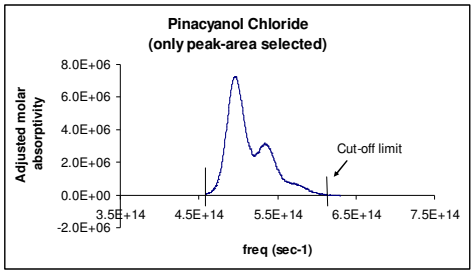




2) Subtract out a constant residual background level if there is one.

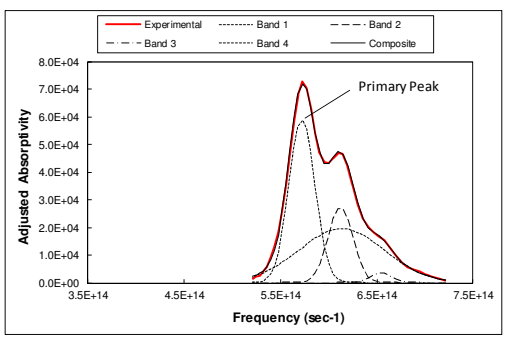


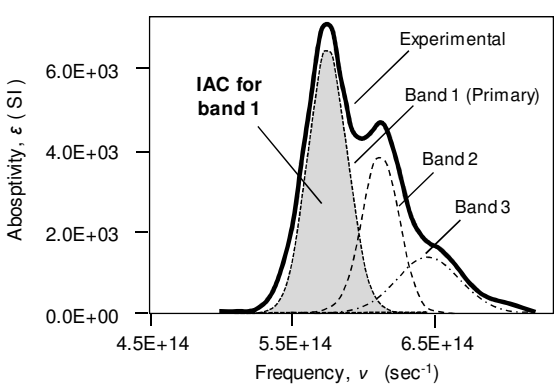
3) Copy just the spectral region of interest to the deconvolution spreadsheet. (Do not want to analyze the flat part of the spectrum since that will unnecessarily distort the deconvolution calculation.)



4) Enter approximate best guesses as to band peaks and frequencies. This is necessary to avoid having the program sub-optimize around incorrect peak assignents.

5) Run Data/Solver (after entering initial best guesses) to separate out the peaks.
(Requires enabling Solver by going to File/Options/Add-ins)
(Mac users will need to Google® to find a solver package for the Mac version of Excel)



5) Find the area under the curve of the primary peak by finding the sum of
(the intensities across the primary weak width times the step change in frequency).
This is the Integrated Absorption Coefficient (IAC)

$$IAC = \int \varepsilon(\nu)\, d\nu \cong \sum_{i=data\ pts} \left[\varepsilon_i \cdot \Delta\nu_{i \to (i+1)} \right]$$