Visible Spectra of Conjugated Dyes: Integrating Quantum Chemical Concepts with Experimental Data

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The measurement and interpretation of electronic spectra of molecules is an interesting and important topic in physical chemistry. The nature of the excited state and the processes of absorption and emission are central ideas in modern spectroscopy. Additionally, the discussion of these concepts uses principles from quantum mechanics, thermodynamics, and kinetics (*1–4*), and thus encompasses a broad range of physical chemistry.

Electronic spectra are interpreted by simple models, semiempirical models, or advanced theoretical principles. Some simple models and all semiempirical models are based on parameterization. It is useful for students to learn that parameters are chosen to fit a given set of experimental data. An experiment that integrates both experimental and theoretical aspects of electronic spectra benefits students by developing connections between experiment and theory. For the past few years, students at La Salle University have been performing an experiment of this nature on a series of conjugated dyes.

The Basic Model

A rigorous approach to explain spectral data may use ab initio methods including configuration interaction. Such methods are usually beyond the scope of a first course in physical chemistry. A rudimentary technique using the particle-in-a-box model that is presented in all physical chemistry texts can be used to rationalize the wavelengths of maximum absorption in conjugated molecules. The model, modified by Kuhn (*5*), is unrealistic and deals only with the π electrons, but predicts trends reasonably well when applied to a series of similar conjugated cyanine dyes (*6, 7*).
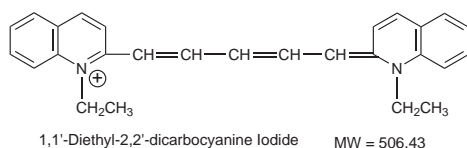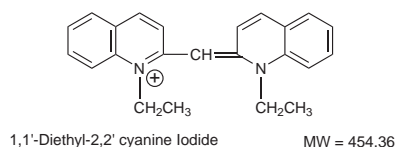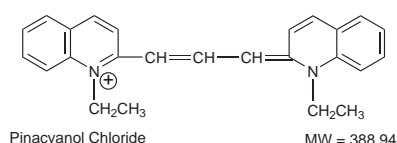

Figure 1. Structures of the conjugated dyes (anions omitted for clarity).

Students can readily understand the model, and it can be used to illustrate the process of parameterization of models to yield improved agreement with experimental data.

Each conjugated dye (Fig. 1) is approximated as a one-dimensional box of length L. The energy levels of this system are given by $E_n = h^2 n^2 / 8mL^2$ where n is the quantum number, m is the electron mass, and h is Planck's constant. Each dye will have, of course, a different value for the length. Since the Pauli principle limits the occupation of a nondegenerate energy level to two electrons, a molecule with N electrons has the $N/2$ lowest levels filled. The longest wavelength transition is, therefore, from level $n_l = N/2$ to level $n_u = (N/2) + 1$. The energy change for this transition is

$$\Delta E = \frac{h^2 \left(n_u^2 - n_l^2 \right)}{8\,m\,L^2} = \frac{h^2 (N+1)}{8\,m\,L^2}$$

The wavelength of the transition is

$$\lambda = \frac{8\,m\,c\,L^2}{h(N+1)}$$

where c is the speed of light.

The nitrogen atoms are assumed to be the walls of the box. The number of π electrons and the length of the polymethine chain in each dye (Fig. 1) are related to the number of double bonds between the nitrogen atoms; thus, the wavelength depends on this quantity. For example, pinacyanol has three double bonds between the two nitrogen atoms and has eight π electrons (six from the double bonds and two from the neutral nitrogen). Kuhn allowed the box to extend one bond length past each nitrogen to indicate that the electrons do not stop abruptly at these atoms. With this approximation, the length of the box is $(2k + 2)b$, where k is the number of double bonds along the polymethine chain and b is 139 pm, the carbon–carbon bond length in benzene. The wavelength of absorption for each dye is then easily calculated.

Students compare their experimental wavelengths to the calculated wavelengths and find that the experimental values are larger (Table 1). Since the number of π electrons is known, the length of the polymethine chain must be greater than the length determined by simply adding the carbon–carbon bond distances in the chain. Using data from one of the dyes, students parameterize the model to obtain improved agreement for the other dyes. This parameter is chosen so that the theory agrees with the wavelength for

Table 1. Wavelength of Maximum Absorption of the Dyes

Dye	λ_{max} (nm)		
	Theoretical	Experimental	Mod. Theory
Dicarbocyanine	580	706	—[a]
Pinacyanol	453	605	578
Cyanine	328	523	452

[a]This dye was used as a reference for the modified theory.

the largest dye, dicarbocyanine. They then discuss implications of this parameter and why the chain length should be greater than they originally thought. In some cases, students have also proposed new models to account for their observations.

The Transition Moment Integral, Transition Rates, and Spectral Intensity

Spectral data are based on quantum mechanical selection rules that are used to determine if a transition between energy states is allowed. Selection rules are useful in interpreting the peak positions and intensities. The most basic rules are derived from time-dependent perturbation theory (8) assuming the interaction of the radiation field occurs only through the molecular electronic dipole moment. From the theoretical perspective, the "allowedness" of a transition, within this electric dipole approximation, depends on the transition moment integral $D = \int \Psi_u \mu \Psi_l \, d\tau$, where Ψ_u and Ψ_l represent the wave functions for the upper and lower states of the transition, and μ is the dipole moment operator of the system. This integral is related to the intensity of the spectral peak. Within the Born–Oppenheimer approximation and assuming definite spin states, (i.e., singlets [S] and triplets [T]), it is often easy to determine if the integral is zero. Such arguments lead to the commonly used spin selection rule (S↔S, T↔T) and the Laporte selection rule (g↔u) where g and u represent states of even and odd symmetry with respect to the inversion operator.

One of the goals of this laboratory exercise is to demonstrate the connection between theory and experiment—a connection made through the selection rules. There are many experimental measures of the intensity of a transition, and hence its allowedness. The most common is the molar absorptivity, ε, defined through the Beer–Lambert law, $A = \varepsilon bc$, where b is the path length and c is the molar concentration. The dyes used in this experiment have molar absorptivities ~100,000 L/mol-cm, which indicate a strong transition. A better measure of intensity is the integrated absorption coefficient, IAC, which is the area of a spectral peak. One common definition of IAC is $\int \varepsilon \, d\nu$, where ν is the frequency of the transition. Integration is taken over the entire spectral band. The molar absorptivity has been used as a measure of intensity in the past because precisely measuring areas to calculate the IAC was tedious. The advent of computerized spectrometers, digitizing pads, and computers has made the calculation of such areas trivial (9, 10), and students should be encouraged to use the more precise IAC. Students also gain practical experience in the

numerical computation of the area under a curve (Fig. 2) and its relation to the integral. Typical IAC values for these dyes are 10^{18} L mol^{-1} cm^{-1} s^{-1} (10^{17} m^2 mol^{-1} s^{-1} in SI units).

The Einstein coefficients are related to the transition rates. Consider two states (lower state l and upper state u) in a radiation field. The rate of absorption is given by $N_l B_{lu} \rho(\nu)$, where N_l is the number of molecules in the state, B_{lu} is the Einstein coefficient of induced absorption, and $\rho(\nu)$ is the radiant spectral density at ν. The B_{lu} is therefore a measure of the probability of producing a transition in a radiation field. The rate of emission is composed of two terms, spontaneous and stimulated. The Einstein coefficient for spontaneous emission is A_{ul}; the coefficient for stimulated emission is B_{ul}. The coefficient of spontaneous emission is related to the fluorescence lifetime of the molecule. The rate of emission is $N_u[A_{ul} + B_{ul}\rho(\nu)]$. Einstein showed that $B_{lu} = B_{ul}$. The Einstein coefficients are dependent on the transition moment integral by

$$B_{ul} = \frac{D^2}{6\varepsilon_o \hbar^2}$$

where ε_o is the vacuum permittivity. Thus, all experimental measures of spectral intensity are ultimately derived from the transition moment integral, and they are all related. Relations between the various spectral quantities have been presented in this *Journal* (11, 12).

In the experiment, students study the visible spectra of three dyes: cyanine, pinacyanol, dicarbocyanine (Fig. 1). Solutions of the dyes in methanol are prepared at approximately 10^{-6} M and spectra are obtained from 400 to 800 nm (Fig. 2). Using the one-dimensional box model, the wavelength of maximum absorbance for each dye is calculated and compared with the experimental result (Table 1). Agreement is poor for a number of reasons: electrons in molecules are not independent particles; the molecule is not a one-dimensional box; and the molecule does not have a vertical potential energy wall. The model is modified by introducing a parameter, d, which allows for the electrons to penetrate past the nitrogen atoms. The data from dicarbocyanine are used to fix this parameter, and the improvement between experimental and theoretical results for the other dyes is apparent (Table 1).

The connection between experimental intensity data and theoretical models is developed in the second part of the experiment. Students digitize their absorbance–wavelength spectra, and these data are imported into a spreadsheet where the remaining calculations are completed. The absorbance–wavelength data are converted into molar absorptivity–frequency data. The integrated absorption coefficient could be computed by Simpson's rule, which students can program into their spreadsheets, or by deconvolution of the spectral data. My students use the software package ORIGIN (10) to deconvolute the data (dotted lines in Figure 2). The molar absorptivity–frequency data are converted to SI units and pasted from the spreadsheet into ORIGIN. After graphing the data, students begin the deconvolution by locating each peak maximum. ORIGIN uses these data as initial estimates for the fit. The software also estimates the width of the peak without user intervention. The Levenberg–Marquardt algorithm is used to fit the data. In addition to displaying the fitted curve and individual peaks, the program also supplies full statistical data on the fit.

The Einstein coefficient for stimulated absorption, B_{ul}, is computed from the IAC by
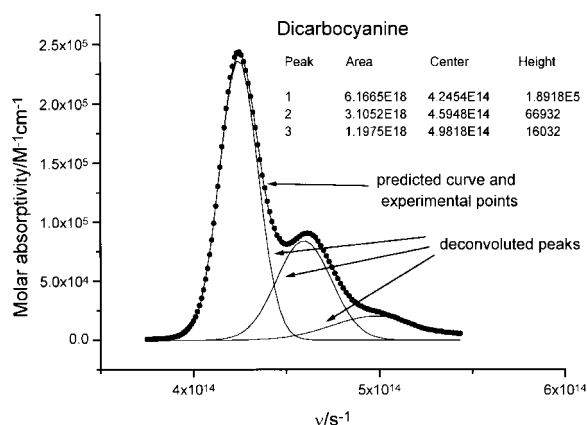
Figure 2. Spectrum of dicarbocyanine.

$$B_{ul} = \frac{c \ln 10}{h\nu N_A} \int \varepsilon \, d\nu$$

Table 2. Experimental Properties of the Dyes

Dye	λ (nm)	ν (s^{-1})	ε (L mol^{-1} cm^{-1})	IAC (L mol^{-1} cm^{-1} s^{-1})	IAC (m^2 mol^{-1} s^{-1})
Dicarbocyanine	706	4.25×10^{14}	1.9×10^5	6.2×10^{18}	6.2×10^{17}
Pinacyanol	605	4.96×10^{14}	1.2×10^5	3.9×10^{18}	3.9×10^{17}
Cyanine	523	5.73×10^{14}	5.8×10^4	2.7×10^{18}	2.7×10^{17}

Table 3. Calculated Properties of the Dyes

Dye	B_{ul} (J^{-1} m^3 s^{-2})	d (cm)	D (debye)	f	A_{ul} (s^{-1})	τ (ns)
Dicarbocyanine	2.5×10^{21}	3.9×10^{-29}	12	0.89	1.2×10^8	8
Pinacyanol	1.4×10^{21}	2.8×10^{-29}	9	0.56	1.0×10^8	10
Cyanine	8.2×10^{20}	2.2×10^{-29}	7	0.39	9.6×10^7	10

Table 4. Theoretical Properties of the Dyes

Dye	ν (s^{-1})	B_{ul} (J^{-1} m^3 s^{-2})	d (cm)	D (debye)	f	A_{ul} (s^{-1})	τ (ns)
Dicarbocyanine	5.2×10^{14}	2.6×10^{21}	4.0×10^{-29}	12	1.14	2.3×10^8	4
Pinacyanol	6.6×10^{14}	1.7×10^{21}	3.1×10^{-29}	9	0.93	3.0×10^8	3
Cyanine	9.1×10^{14}	9.3×10^{20}	2.3×10^{-29}	7	0.71	4.4×10^8	2

Not only is B_{ul} a rate constant for absorption, but it is directly related to the transition moment integral, which can then be calculated:

$$D^2 = 6\varepsilon_o \hbar^2 B_{ul}$$

The Einstein coefficient for spontaneous emission is also related to B_{ul}:

$$A_{ul} = \frac{8\pi h\nu^3}{c^3} B_{ul}$$

The reciprocal of A_{ul} is often called the intrinsic lifetime of the excited state. This is the lifetime the state would have in the absence of all other deactivating processes such as vibrational relaxation, quenching, and intersystem crossing. As such, it gives an estimate of the lower limit of the lifetime of the excited state.

Another spectral quantity that can be obtained is the oscillator strength, f. The oscillator strength represents, in principle, the number of electrons undergoing a transition. Oscillator strengths of ~1 signify intense transitions, while oscillator strengths of ~0.001 denote weak (nonallowed) transitions. Since the values for f typically lie between zero and one, students find f most convenient for discussing transition intensity. The oscillator strength can be calculated from any of the aforementioned quantities; one form is

$$f = \frac{4\varepsilon_o c m_e \ln 10}{e^2 N_A} \int \varepsilon \, d\nu$$

where e and m_e are the charge and mass of an electron. All quantities in these equations are in SI units. Typical student data are presented in Tables 2 and 3.

After the experimental data are used to calculate spectral parameters, students use equations developed from the simple one-dimensional box to predict the spectral quantities. These theoretical values (Table 4) are within an order of magnitude of the experimental data—good agreement considering the rudimentary approach used.

In summary, this project accomplishes the following:

- enhances student knowledge of spectral quantities;

- demonstrates that basic theoretical models describe experimental data;

- shows that rudimentary models can be parameterized to agree better with observations;

- demonstrates the interrelationships between molar absorptivities, integrated absorption coefficients, and Einstein coefficients; and

- shows that approximate fluorescence lifetimes are obtainable from absorption data.

Acknowledgment

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