

XIV

Spectroscopy

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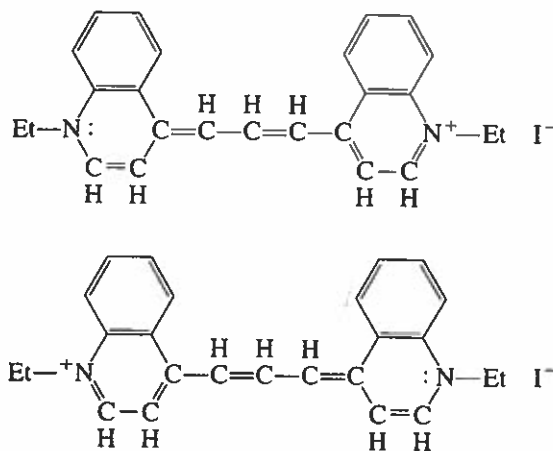
Absorption Spectrum of a Conjugated Dye

Absorption bands in the visible region of the spectrum correspond to transitions from the ground state of a molecule to an excited electronic state that is 170 to 300 kJ mol^{-1} above the ground state. In many substances the lowest excited electronic state is more than 300 kJ mol^{-1} above the ground state and no visible spectrum is observed. Those compounds that are colored (i.e., absorb in the visible) generally have some weakly bound or delocalized electrons such as the odd electron in a free radical or the π electrons in a conjugated organic molecule. In this experiment we are concerned with the determination of the visible absorption spectrum of several symmetric polymethine dyes and with the interpretation of these spectra using the “free-electron” model.

THEORY

The visible bands for polymethine dyes arise from electronic transitions involving the π electrons along the polymethine chain. The wavelength of these bands depends on the spacing of the electronic energy levels. Bond-orbital and molecular-orbital calculations have been made for these dyes, but the predicted wavelengths are in poor agreement with those observed. We shall present here the simple free-electron model first proposed by Kuhn;^{1,2} this model contains some drastic assumptions but has proven reasonably successful for molecules like conjugated dyes.

As an example, consider a dilute solution of 1,1'-diethyl-4,4'-carbocyanine iodide (cryptocyanine):



The cation can “resonate” between the two limiting structures above, which really means that the wavefunction for the ion has equal contributions from both states. Thus all the bonds along this chain can be considered equivalent, with bond order 1.5 (similar to the C—C bonds in benzene). Each carbon atom in the chain and each nitrogen at the end is involved in bonding with three atoms by three localized bonds (the so-called σ bonds). The extra valence electrons on the carbon atoms in the chain and the three remaining electrons on the two nitrogens form a mobile cloud of π electrons along the chain (above and below the plane of the chain). We shall assume that the potential energy is constant along the chain and that it rises sharply to infinity at the ends; i.e., the π electron system is replaced by free electrons moving in a one-dimensional box of length L . The quantum mechanical solution for the energy levels of this model³ is

$$E_n = \frac{h^2 n^2}{8mL^2} \quad n = 1, 2, 3, \dots \quad (1)$$

where m is the mass of an electron and h is the Planck constant.

Since the Pauli exclusion principle limits the number of electrons in any given energy level to two (these two have opposite spins: $+\frac{1}{2}$, $-\frac{1}{2}$), the ground state of a molecule with N π electrons will have the $N/2$ lowest levels filled (if N is even) and all higher levels empty. When the molecule (or ion in this case) absorbs light, this is associated with a one-electron jump from the highest filled level ($n_1 = N/2$) to the lowest empty level ($n_2 = N/2 + 1$). The energy change for this transition is

$$\Delta E = \frac{h^2}{8mL^2} (n_2^2 - n_1^2) = \frac{h^2}{8mL^2} (N + 1) \quad (2)$$

Since $\Delta E = h\nu = hc/\lambda$, where c is the speed of light and λ is the wavelength,

$$\lambda = \frac{8mc}{h} \frac{L^2}{N+1} \quad (3)$$

Let us denote the number of carbon atoms in a polymethine chain by p ; then $N = p + 3$. Kuhn assumed that L was the length of the chain between nitrogen atoms plus one bond distance on each side; thus $L = (p + 3)l$, where l is the bond length between atoms along the chain. Therefore

$$\lambda = \frac{8mcl^2}{h} \frac{(p+3)^2}{p+4} \quad (4)$$

Putting $l = 1.39 \text{ \AA} = 0.139 \text{ nm}$ (the bond length in benzene, a molecule with similar bonding) and expressing λ in nanometers, we find

$$\lambda \text{ (in nm)} = 63.7 \frac{(p+3)^2}{p+4} \quad (5)$$

If there are easily polarizable groups at the ends of the chain (such as benzene rings), the potential energy of the π electrons in the chain does not rise so sharply at the ends. In effect this lengthens the path L , and we can write

$$\lambda \text{ (in nm)} = 63.7 \frac{(p+3+\alpha)^2}{p+4} \quad (6)$$

where α should be a constant for a series of dyes of a given type. If such a series is studied experimentally, this empirical parameter α may be adjusted to achieve the best fit to the data; in any event, α should lie between 0 and 1.¹

In order to compare the results of the free-electron model with calculations based on simple bond-orbital or molecular-orbital schemes, let us use Eq. (5), which assumes that $\alpha = 0$, to calculate the wavelength λ for cryptocyanine (in which $p = 9$) and compare that value with those obtained from orbital calculations:

Free electron	$\lambda = 707 \text{ nm}$
Bond orbital (case 1) ⁴	$\lambda = 3900 \text{ nm}$
Bond orbital (case 2) ⁴	$\lambda = 2900 \text{ nm}$
Molecular orbital ⁴	$\lambda = 2700 \text{ nm}$
Hückel model ⁵	$\lambda = 475 \text{ nm}$

Note that only the free-electron and Hückel models predict an absorption band in the visible in agreement with observation. While the orbital calculations in Ref. 4 are poor for polymethine dyes, they are in principle a superior approach and have given excellent results for saturated hydrocarbons. Indeed unsaturated molecules like the polymethines can be very well modeled by the semiempirical configuration interaction (CIS) method.

METHOD

Many commercial visible-UV spectrophotometers are suitable for this experiment. These instruments range from simple single-beam devices such as the Spectronic model 20 to high-performance double-beam scanning spectrophotometers such as various Varian-Cary models. The components and operational principles of these instruments are

discussed in Chapter XIX, and this material should be reviewed prior to undertaking the experiment.

It is necessary to define several terms commonly used in spectrophotometry. Absorption spectra are often characterized by the *transmittance* T at a given wavelength; this is defined by

$$T = \frac{I}{I_0} \quad (7)$$

where I is the intensity of light transmitted by the sample and I_0 is the intensity of light incident on the sample. When the sample is in solution and a cell must be used, I is taken to be the intensity of light transmitted by the cell when it contains solution, while I_0 is taken to be the intensity of light transmitted by the cell filled with pure solvent. Another way of describing spectra is in terms of the *absorbance* A , where

$$A = \log \frac{I_0}{I} \quad (8)$$

A completely transparent sample would have $T = 1$ or $A = 0$, while a completely opaque sample would have $T = 0$ or $A = \infty$.

The absorbance A is related to the path length d of the sample and the concentration c of absorbing molecules by the Beer-Lambert law,⁶

$$A = \epsilon cd \quad (9)$$

where ϵ is called the *molar absorption coefficient* when the concentration is expressed in moles per unit volume.[†] The quantity ϵ is an intrinsic property of the absorbing material that varies with wavelength in a characteristic manner; its value depends only slightly on the solvent used or on the temperature. The SI unit for ϵ is $\text{mol}^{-1} \text{m}^2$, but a more practical and commonly used unit is $\text{mol}^{-1} \text{L cm}^{-1}$, which corresponds to using the concentration c in mol L^{-1} and the path length d in cm.

For quantitative measurements it is important to calibrate the cells so that a correction can be made for any small difference in path length between the solution cell and the solvent cell. For analytical applications, one must check the validity of Beer's law, since slight deviations are often observed and a calibration curve of absorbance versus concentration is then required. Such corrections will not be necessary in the present work.

EXPERIMENTAL

For the present experiment, a manually scanned spectrophotometer with a resolution of 10 to 20 nm is adequate, although an autoscanning instrument is, of course, more convenient. Instructions for operating the spectrophotometer will be made available in the laboratory. Turn on the instrument as instructed, and allow it to warm up for a few minutes in order to achieve stable, drift-free performance.

Several polymethine dyes should be studied, preferably a series of dyes of a given type with varying chain length. In addition to the 1,1'-diethyl-4,4'-carbocyanine iodides mentioned previously, 1,1'-diethyl-2,2'-carbocyanine iodides and 3,3'-diethyl thiocarbocyanine iodides are suitable. Other possible compounds can be found in the literature.⁷

[†]The quantity ϵ was previously called the *extinction coefficient*, and this name is still frequently used in the scientific literature.

Choose any one of the available dyes, and prepare 10 mL of a solution using methyl alcohol as the solvent. The concentration should be approximately 10^{-3} M. (If the solutions are to be kept for a long time, they should be stored in dark-glass bottles to prevent slow decomposition by daylight.)

Follow the spectrophotometer operating instructions carefully, and obtain the spectrum of this initial solution. Take absorbance readings at widely spaced intervals throughout the spectrophotometer range until the absorption band is located. Then take readings at much closer intervals throughout the band. Dilute the initial solution and redetermine the spectrum. Repeat this procedure until a spectrum is obtained with an absorbance reading of about 1 at the peak (transmittance ~ 0.1). The band shape may change at high concentration, since many dyes dimerize. At the final concentration used in this experiment, no dimer contribution is expected.

Make up solutions (10 mL) of the other dyes at approximately the same molar concentration that gave the best results previously. Obtain their spectra in the same way.

CALCULATIONS

Present all the spectra obtained (plotting A versus λ if data were obtained manually); label each plot clearly with the name of the compound and the concentration used. Determine λ_{\max} , the wavelength at the peak, for each dye studied.

Using Eq. (6), calculate λ from the free-electron model for each compound. If a series of dyes of a single type has been studied, choose α to give the best fit for this series. Alternatively, one could fix α by fitting any one of the series and use this value for all others in the series.

Report in a table your experimental and theoretical values of λ_{\max} .

Theoretical Calculations. As a project exercise, the measured energy separations of the upper and ground electronic states of cryptocyanine might be compared with values calculated using quantum theory. Semiempirical methods using the *configuration interaction singles* (CIS) method can be done reasonably rapidly with the program HyperChem, which also gives intensities for the transitions. Hehre et al. describe a similar application using the program Spartan.⁸ Calculations of excited state energies using the ab initio program Gaussian at the CIS level are described by Foresman and Frisch⁹ and are more time intensive. In general, theoretical values for excited-state properties of molecules are less accurate than ground-state values.

SAFETY ISSUES

None.

APPARATUS

Spectrophotometer, such as a Bausch & Lomb Spectronic or Beckman DU series; four Pyrex or polystyrene sample cells; lens tissue; several 10-mL volumetric flasks; wash bottle.

Reagent-grade methyl alcohol (150 mL); several polymethine dyes, preferably a series such as 1,1'-diethyl-4,4'-cyanine iodide, -carbocyanine iodide, and -dicarbocyanine