Practical Exercises in Physical Chemistry

Advanced Level

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16: Anisotropy of light absorption

1 Basic Principles:

The absorption of visible and UV light occurs when molecules are excited from an initial state to an electronically excited state. The light absorption of a dye is essentially based on the excitation of π-electrons in the molecule. The dye in this experiment is one of the symmetric cyanines. In this class of substances all atoms of the mesomeric systems are connected via trigonal-planar bonds. Therefore each of them forms a planar zig-zag chain. Above and below of this plane are the charge clouds of the π-electrons (Figure 1). In the hatched area, the π-electrons can move more or less independently, but not totally freely, since close to the positively charged atomic residue there are stronger attraction forces than in the space between the atoms.
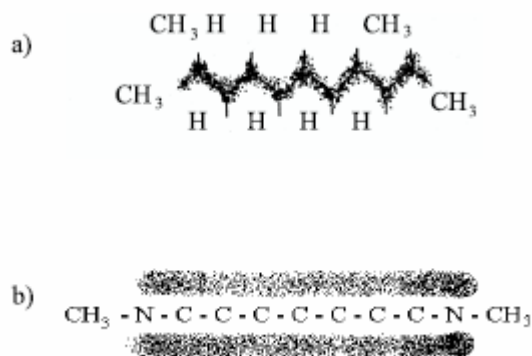

Figure 1: π-electron charge clouds of a dye: a) top view b) side view

In order to remove a π-electron from the hatched area in Figure 1, a tremendous amount of energy is needed, because of the charge separation into a negative electron and a positive molecule ion. Figure 2 schematically shows the potential energy of π-electrons along the molecular chain (*x*-axis).

To a first approximation, the potential energy function can be replaced by a rectangular box (Figure 3). In the region of the molecular residues V is assumed to be constant, and at the ends of the molecules V grows indefinitely.

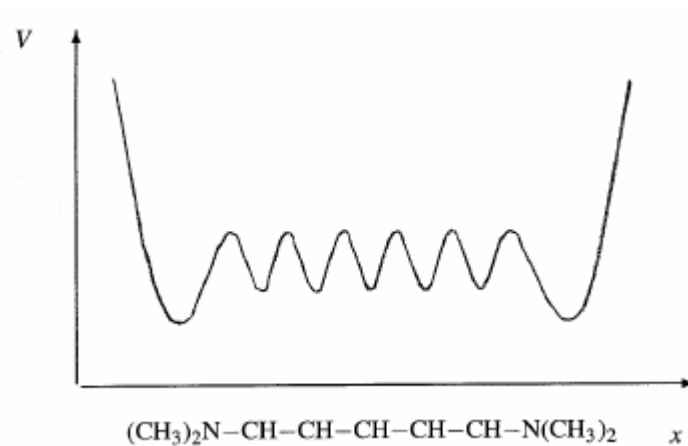$$(CH_3)_2N-CH-CH-CH-CH-CH-N(CH_3)_2 \qquad x$$

Figure 2: Potential energy of electrons in the field of the atomic residue.

Figure 3: Schemate of the box potential energy V (L = longitudinal extension of the π electron system in Figure 1).

In this approximation the π-electrons are assumed to be able to move freely (in a range from $x = 0$ to $x = L$). The de Broglie waves of the electrons are reflected at the ends of the potential well. Due to the interference of waves running in the opposite directions, standing electron waves are formed. The deflection of these waves ψ with respect to the x-axis is given by

$$\Psi = A \sin \frac{n\pi}{L} x; \qquad n = 1, 2, 3, ... \qquad (1)$$

The amplitude factor A is arbitrary, with the normalization condition

$$\int_0^L \Psi^2 dx = 1 \qquad (2)$$

This yields for ψ:

$$\Psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \qquad (3)$$

For the wavelength Λ of the standing wave we have

$$\Lambda = \frac{2L}{n}; \quad n = 1, 2, 3, \ldots \qquad (4)$$

Between Λ and the velocity u of an electron the following equation holds after de Broglie

$$\Lambda = \frac{h}{mu} \qquad (5)$$

(h: Planck's quantum of action, m: electron mass).

For the total energy of a π-electron follows thus

$$E = V + \frac{m}{2}u^2 = V + \frac{h^2}{2m\Lambda^2} = V + \frac{h^2}{8mL^2}n^2; \quad n = 1, 2, 3, \ldots \qquad (6)$$

The possible energy states are occupied following the Pauli principle. The absorption band with the longest wavelength of the dye corresponds to a transition of an electron of the highest occupied state (energy E_A, quantum number n_A) to the lowest unoccupied state (energy E_B, quantumv number n_B). For the excitation energy of this transition follows

$$\Delta E = E_B - E_A = \frac{h^2}{8mL^2}(n_B^2 - n_A^2) \qquad (7)$$

In this experiment we want to investigate which share of the entering light is absorbed by the dye molecules. This share depends on the structure of the dye molecule, on the nature of the examined electron transition and on the orientation of the molecule with respect to the electric field strength vector in the electromagnetic field of the light wave. The greater the share of the absorbed light by one single molecule, the greater the molar extinction coefficient ε of the solution.

$$\varepsilon = \frac{E}{Cd} \qquad (8)$$

(E: Extinction; d: layer thickness; C: concentration)

Molecules in solution often give rather broad absorption bands. This is due to the dye molecules being surrounded by solution molecules. Furthermore the immediate neighbourhood of the individual dye molecules is different because of the thermal motion. The energy of the excited state of the single molecules is differently influenced by solvation. Thus different molecules absorb at different wavelengths, and therefore a relatively broad absorption band results for the whole ensemble of solvated molecules.
The oscillator strength f is defined as

$$f = \frac{4m_e c^2 \varepsilon_0}{N_A e^2} \ln 10 \int_{band} \varepsilon_d \left(\frac{1}{\lambda} \right) \tag{9}$$

(*c*: velocity of light; N_A: Avogadro's constant, *e* : electrical elementary charge; λ: wavelength of the absorbed light)

and is a measure for the share of absorbed light in the range of the absorption band from the dye molecules. The integral in equation (9) is be obtained by plotting ε against $1/\lambda$ and by measuring the area below the curve. The oscillator strength of an absorption band can be calculated from the wave functions of the dye molecules. If the molecules are distributed randomly, it follows from quantum mechanical considerations that

$$f = \frac{8\pi m}{3h^2} \Delta E (X^2 + Y^2 + Z^2) \tag{10}$$

with the components *X, Y, Z* of the transition moment in *x, y, z* directions:

$$X = \int \Psi_A x \Psi_B d\tau$$
$$Y = \int \Psi_A y \Psi_B d\tau \tag{11}$$
$$Z = \int \Psi_A z \Psi_B d\tau$$

(ψ_A and ψ_B: wave functions of the highest occupied and lowest unoccupied states, respectively; $d\tau = dx\, dy\, dz$: volume element)

considering the long-chain cyanine dye in the *xy*-plane (Figure 1). We assume the molecule not to be zig-zag but prolate. Then $Y = 0$ and $Z = 0$ and from
equation (10) follows

$$f = \frac{8\pi^2 m}{3h^2} \Delta E X^2 \tag{12}$$

To calculate the transition moment *X* we set

$$\Psi_A = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L} n_A \quad \text{and} \quad \Psi_B = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L} n_B \tag{13}$$

This yields

$$X = \frac{2}{L} \int_0^L \left(\sin \frac{\pi x}{L} n_A \right) x \left(\sin \frac{\pi x}{L} n_B \right) \tag{14}$$

Integration yields for n_A even, n_B odd or vice versa,

$$X = \frac{-2L}{\pi^2}\left[\frac{1}{(n_A - n_B)^2} - \frac{1}{(n_A + n_B)^2}\right] \tag{15}$$

If n_A, n_B is even or odd, we obtain $X = 0$. From equation (12) we obtain for f from equation (7) and equation (15)

$$f = \frac{8\pi^2 m}{3h^2}\frac{h^2}{8mL^2}\left(n_B^2 - n_A^2\right)\frac{4L^2}{\pi^4}\left[\frac{1}{(n_A - n_B)^2} - \frac{1}{(n_A + n_B)^2}\right]^2$$

$$f = \frac{64}{3\pi^2}\frac{n_A^2 n_B^2}{(n_B^2 - n_A^2)^3} \tag{16}$$

In our case $n_A = z/2$ and $n_B = z/2+1$ if each occupied level possesses two electrons and z is the total number of electrons. Then we get

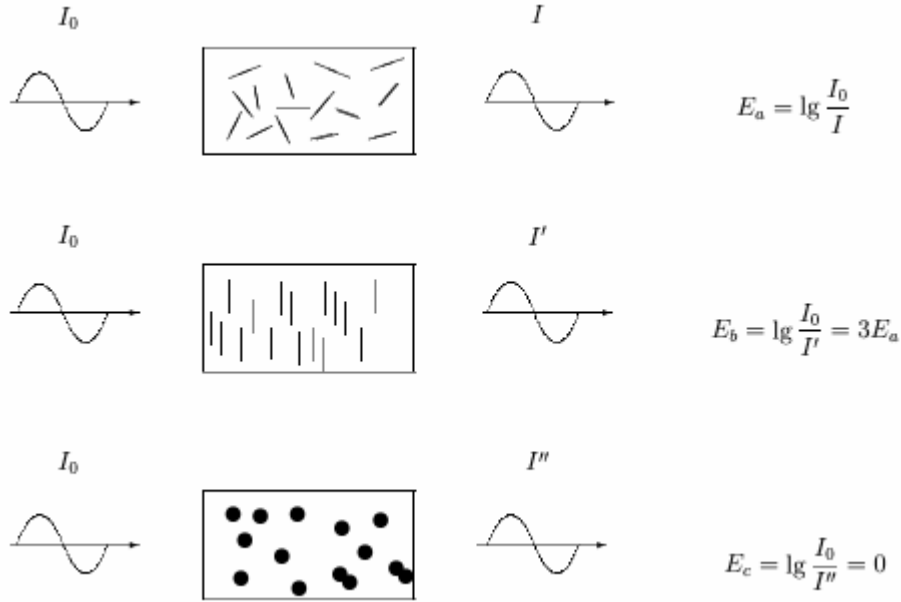$$f = \frac{4}{3\pi^2}\frac{z^2(z+2)^2}{(z+1)^3} \tag{17}$$

Figure 4: Light absorption of dye molecules a) statistically distributed molecules b) transition moments parallel to the vector of the electric field intensity c) transition moments perpendicular to the vector of the electric field.

Since the highest occupied state is occupied by two π-electrons and both electrons could be excited, the true oscillator strength is twice as high as that given in equation (17):

$$f_{true} = \frac{8}{3\pi^2}\frac{z^2(z+2)^2}{(z+1)^3} \tag{18}$$

The equations (16) and therefore (18) are based on statistically distributed dye molecules in solution. Since the extinction of the solution in this case is independent of whether polarized light is used or not, the experimentally measured oscillator strength also does not change if light with a distinct polarisation direction passes through the solution. If the dye molecules are not distributed statistically but oriented, the molecules absorb light only when the vector of the electrical field of the light wave has a component oscillating in the same direction as the transition moment of the observed band (Figure 4b). If the vector of the electric field oscillates perpendicularly to the vector of the electrical field (Figure 4c), no light is absorbed. The transition moment of the band of the cyanine dye with the longest wavelength ($X \neq 0$ and $Y = Z = 0$) is oriented in x-direction. In the case of Figure 4b, the extinction and therefore the oscillator strength is three times higher than in the case of Figure 4a (molecules distributed equally in all three directions); in the case of Figure 4c, it is zero.

An orientation of the dye molecules can be achieved by incorporating them into a high-polymeric foil and subsequent stretching in one direction. First, the molecules in the unstretched foil are statistically distributed though they cannot move freely like in a solution. By stretching the foil, the longitudinal axis of the molecules are oriented mainly in stretching direction.
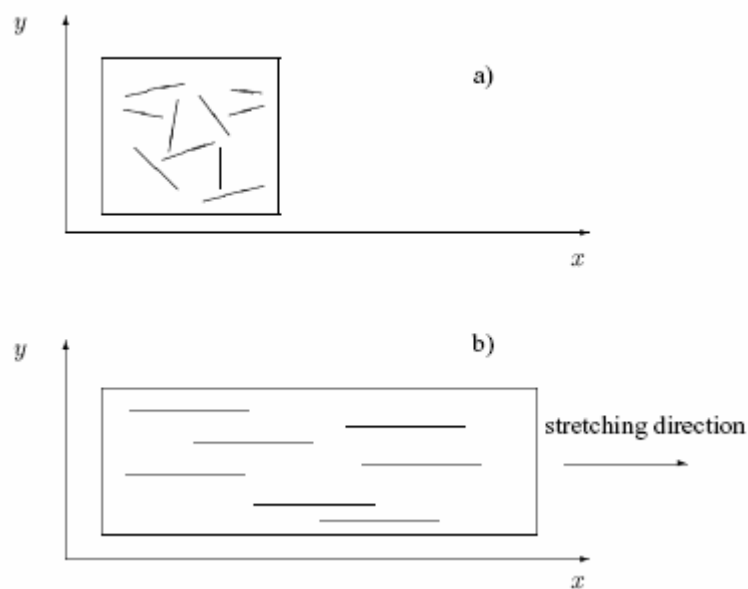

Figure 5: Statistical distribution of molecules (a) and orientation after stretching of the foil (b).

If the foil is now irradiated with light whose electric vector oscillates in the stretching direction the absorption should be stronger than for the unstretched foil. If the polarisation plane of the light is rotated by 90° the absorption should decrease enormously.

2. Exercises:

1. Derive equations 15 and 17! Why are the transition moments for the dye in Figure 1 in y and z direction for the electronic transition with the longest wavelength equal to zero?

2. Measure the absorption spectra of a solution of the dye
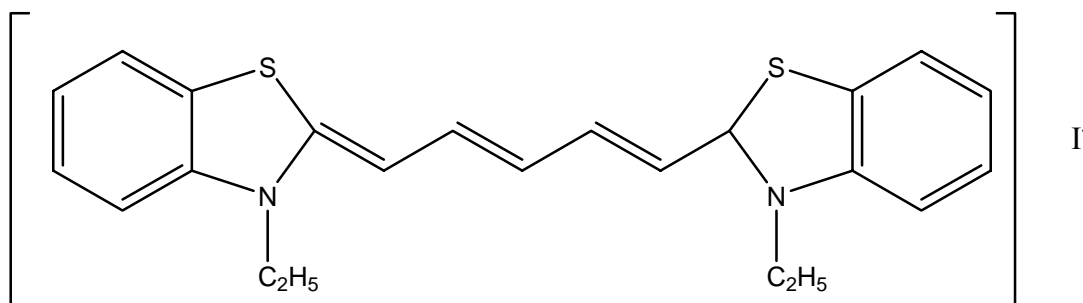
in methanol (concentration ca. 10^{-5} mol/l).

3. Stretch the polyvinyl alcohol foil (with dye molecules) to different degrees, thus achieving different degrees of orientation of the dye molecules. Use polarized light to measure the absorption spectra of the unstretched and stretched foil (vector of the electric field parallel and perpendicular to the stretching direction).

4. Calculate the oscillator strength from the spectra in exercise 2 and compare it to the expected values (sulphur bridges and benzene units are neglected).

5. Derive the degree of orientation of the foil from the spectra measured from exercise 3. Follow the orientation degree in dependence of the stretching ratio.

6. Consider why and in which direction a neglection of the sulphur bridges and the benzene units could yield inaccurate results.

3. References

[1] W. Kauzmann, "Quantum Chemistry", Academic Press, New York 1957.
[2] E. W. Thulstrup and J. Michl, "Elementary Polarisation Spectroscopy", VCH 1989.