

Skript zum Versuch

A50

Absorption Spectra of Cyanine Dyes

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1 Objective

The absorption spectra of four different cyanine dyes have to be measured in the wavelength range between 400 – 800 nm. The absorption bands have to be characterized with respect to the wave length of the maximum, the maximum absorption and the full width at halve maximum. Employing the quantum mechanical model of the particle in the box the absorption maximum and the molar absorption coefficient has to be calculated and compared to the experimental results.

2 What you should know

Concerns students (basic studies) in Chemie BA, Chem. Biologie, Lebensmittelchemie, Lehramt, Chemieingenieurwesen, Physik):

- Basics of quantum mechanics, model of the particle in the box (in one dimension).
- Working principle of an UV-VIS-NIR-spectrometer.
- For what purpose spectroscopy is employed in science. What can be learnt from the spectra?

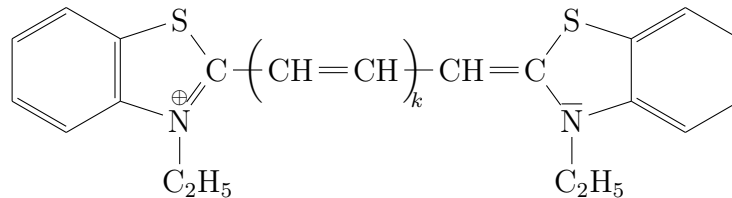
What advanced studies students should know:

- Theory behind equations (6) to (8).

3 Basics

3.1 Particle in the box as a model for cyanine dyes

In this experiment, the absorption behaviour of cyanine dyes is to be investigated. These dyes are a homologous series of conjugated double bond cations having the following structure:



with $k = 0, 1, 2$ und 3 . Iodide works as counter ion. The number j of the conjugated double bonds is then $k + 2$. The free electron pair at the nitrogen atom has to be included. Responsible for the light absorption are the π -electrons which move almost freely along the carbon chain, thus forming a delocalized electron cloud. The molecule forms a sort of „linear box“ with a length determined by the distance of the two nitrogen atoms.

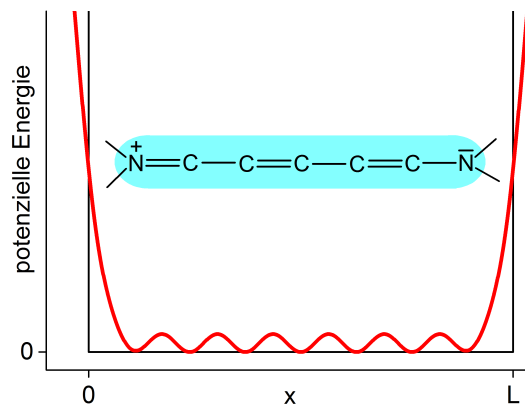


Fig. 1: Realistic potential curve for the movement of π -electrons (red) and potential curve according the particle in the box model (black). The blue area along the molecular chain represents the delocalized electron cloud.

The solution of the Schrödinger equation for free electrons in a one-dimensional potential well of length L gives the following normalized wave functions along the x -coordinate:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right); \quad \text{mit } n = 1, 2, 3 \dots \quad (1)$$

For the energy eigenstates one finds:

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

$m = 9,109 \cdot 10^{-31}$ kg is the electron mass, $h = 6,626 \cdot 10^{-34}$ Js is Planck's constant.

Since electrons are fermions the energy states are occupied according to Pauli's principle. Electrons do not obey the classical Boltzmann statistics. One begins with the energy state $n = 1$ and fills two electrons in each orbital up to the HOMO which has the quantum number n_H (**H**ighest **O**ccupied **M**olecular **O**rbital). The absorption band with the highest wavelength (lowest frequency/wave number/energy) results from the excitation of an electron from the HOMO (energy E_H) to the LUMO (energy E_L) (**L**owest **U**noccupied **M**olecular **O**rbital). One expects the absorption band at a transition energy:

$$\Delta E = E_L - E_H = \frac{h^2}{8mL^2} (n_L^2 - n_H^2) \quad (\text{in Joule.}) \quad (3)$$

Or in alternate units:

$$\underbrace{\lambda_{max} = \frac{hc}{\Delta E}}_{\text{wave length in m}}; \quad \underbrace{\nu = \frac{\Delta E}{h}}_{\text{frequency in s}^{-1}}; \quad \underbrace{\tilde{\nu} = \frac{\Delta E}{hc}}_{\text{wave number in cm}^{-1}} \quad (4)$$

with the speed of light in the vacuum: $c = 2,998 \cdot 10^8$ ms⁻¹.

3.2 Quantitative analysis of absorption spectra

Absorption spectra can be employed for the identification of unknown substances and for the determination of their concentration. A quantitative description is given by Lambert-Beer's law which relates the intensity impinging on the cuvette ($I_0(\nu)$) to the transmitted intensity ($I(\nu)$):

$$OD(\nu) = \log_{10} \frac{I_0(\nu)}{I(\nu)} = \varepsilon(\nu) c_J D \quad (5)$$

with the length of the cuvette D and the concentration c_J of substance J . The extinction coefficient $\varepsilon(\nu)$ depends on the frequency ν of the light. When c_J is measured in $\frac{\text{mol}}{\text{L}}$ then $\varepsilon(\nu)$ is called the molar extinction coefficient. $OD(\nu)$ is the *optical density* or *absorbance*, in earlier times named *extinction*. The plot of OD or ε versus frequency, the wave number or the wavelength is called the absorption spectrum of the investigated molecule.

In the graduate course for molecular spectroscopy it will be shown that the transition probability to excite an electron from an initial state i (initial) to a final state f (final) can be calculated by the transition dipole moment:

$$\mu_{fi} = e \int_{-\infty}^{\infty} \psi_f^* x \psi_i dx \quad (6)$$

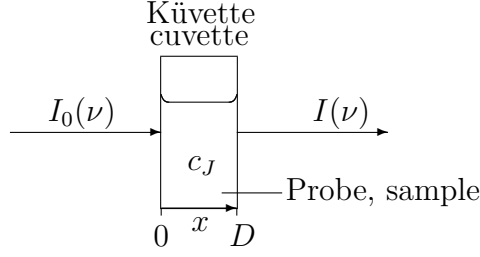


Fig. 2: Lambert-Beer's law: the incoming intensity $I_0(\nu)$ is reduced to $I(\nu)$ as the light beam travels through the cuvette.

In the present case ψ_f is the wave function of the LUMO, and ψ_i is the wave function of the HOMO. The integral of the absorption band depends on μ_{fi} as follows:¹

$$\underbrace{\varepsilon_{max}}_{\text{in } \frac{\text{m}^2}{\text{mol} \cdot \text{s}}} \cdot \underbrace{\text{HWB}}_{\text{in } \text{s}^{-1}} \approx \int_{\nu_1}^{\nu_2} \varepsilon(\nu) d\nu = \underbrace{\frac{N_A}{6 \cdot \ln 10 \cdot c \cdot \varepsilon_0 \cdot \hbar^2}}_{=1,477 \cdot 10^{93} (\text{mol A}^2 \text{m}^2 \text{kg s})^{-1}} \underbrace{\Delta E}_{\text{in J}} \underbrace{|\mu_{fi}|^2}_{\text{in } (\text{A m s})^2} \quad (7)$$

The integral of an absorption band can be approximated by the product of band height (ε_{max}) and full width at half maximum (HWB). These quantities can be easily read out of the spectra. Now, this integral is proportional to ΔE from equation (3) and the square of the transition dipole μ_{fi} . The proportionality constant is a combination of natural constants.

For the connection of the molecular properties (μ_{fi}) and the measured quantities (band integral) one has to solve the integral in equation (6) employing the wave functions from equation (1).

$$\begin{aligned} \mu_{fi} &= e \int_0^L \sin\left(\frac{(n+1)\pi x}{L}\right) x \sin\left(\frac{n\pi x}{L}\right) dx \\ &= -e \left(\frac{2}{L}\right) \frac{(2n+1)^2 - 1}{(2n+1)^2} \left(\frac{L}{\pi}\right)^2 \approx -\frac{2eL}{\pi^2} \end{aligned} \quad (8)$$

μ_{fi} is measured in units of a dipole moment: Coulomb $\times$ Meter. This is the reason for the name *transition dipole moment*. It can be calculated from the box length L in a surprisingly simple way.

Figure 3 shows how one extracts the data needed for the left side of equation (7). Employing equation (8) the right side of equation (7) can be calculated.²

¹For the interrelation between transition dipole, oscillatory strength and band intensity see e.g.: P. W. Atkins und R. Friedman, *Molecular Quantum Mechanics*, Oxford (5th edition) 2011, see p. 432.

²Hinweis: die Gleichungen (6) bis (8) sind in der Modulabschlussprüfung des Grundmoduls **nicht** prüfungsrelevant. Equations (6) to (8) are not relevant for the examination in the final module examination of the basic module.

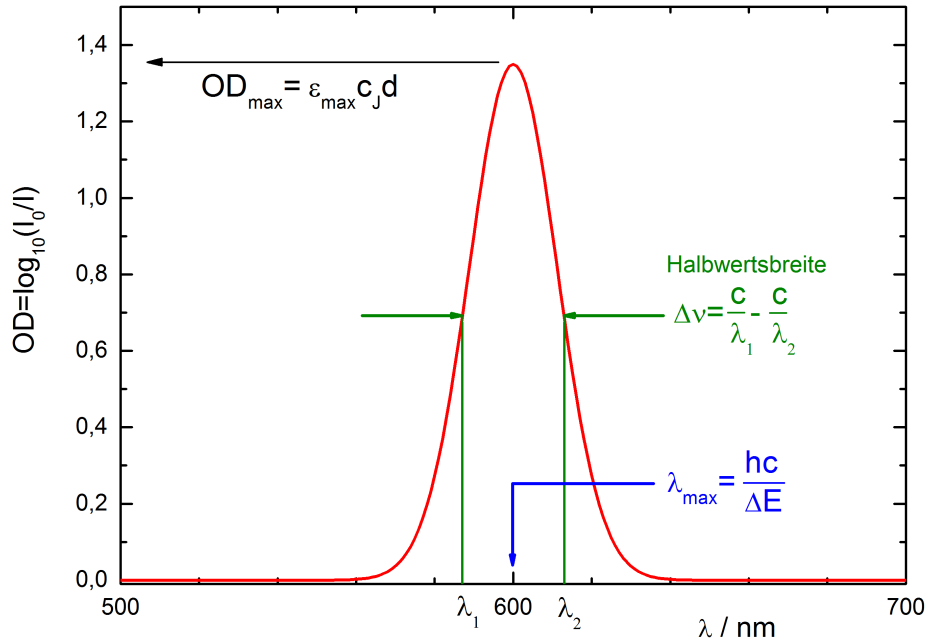


Fig. 3: Schematic representation of the absorption band

4 Experimental Procedure

The absorption spectra of the cyanine dyes with $k = 0, 1, 2$ und 3 are to be measured in the wavelength range from 400 bis 800 nm.

Instructions for use of the spectrometer

- Start the PC
- Create a directory with your group number under
C:\Praktikum
\"Praktikumsbezeichnung(z. B. : A-Praktikum-WS-17-18)
\"Gruppenname(z. B. Gruppe A13)“
- Switch on the spectrometer.
- Open the program **Lambda-SPX** from the desktop and choose **Scan**, or wait briefly until the start window (Fig. 4) opens: After the calibration procedure of the spectrometer in the top right corner of the window should appear the value 652,2 nm (or another weird wave length). If it does not, call for assistance. In this case the calibration routine with the D-lamp didn't work properly (defect D-lamp or blocked beam path).
- First of all, record a base line. During this run the spectrometer will shut off the UV-lamp, thus, the production of ozone is minimized.
- Set under **options** the previously created directory as the default storage location of your data.

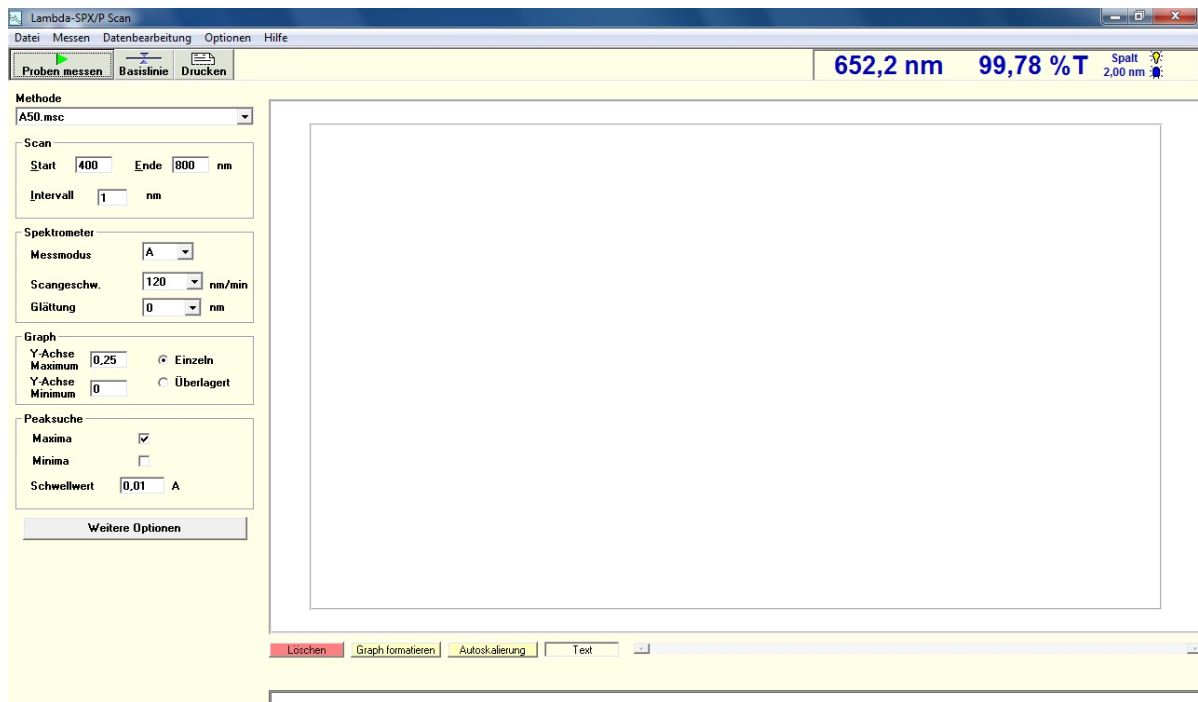


Fig. 4: Start screen of the spectrometer

- Choose the method A50.msc
- In the main window most of the relevant recording parameters can be set:

Start/Ende	Sets the start and end wavelength of the spectrum; never go to a wavelength of 0 nm, since the monochromator works in this position in zero order, which might overload the detector.
Intervall	Sets the steps of the data points. Choose a small number if you expect narrow spectral features.
Messmodus	Choose setting A. The spectra are then represented in units of $\log_{10} \left(\frac{I_0}{I} \right)$ (absorbance, optical density)
Scan Geschwindigkeit	Small for high resolution.
Glättung	Sets a smoothing filter, removes noise in the spectra. Avoid overdamping.
Y-Achse Max./Min.	Sets the lower and upper end of the absorbance axis. Choose „Einzeln“.
Peaksuche Maxima	If activated a peak pick function.
Schwellenwert	Keep at 0,01 A.
Weitere Optionen	Other options are not needed

- If you change the wavelength range or other recording settings a new baseline must be measured.
- Put a sample in the beam path and start a measurement by choosing „Probe

Messen“. Note the cuvette length. In the dialog box set your group number as „Bearbeiter“. Under „Probe“ choose a name for your sample that unambiguously identifies it. This will also be the name of the data file. Set the scan speed under „Beschreibung“.

Hinweis: The data will be stored in the CSV-format, that can be read using various spreadsheet programs. Copy your files to your personal USB-memory stick.

After finishing the measurements: Close the program, shut off the spectrometer. Make sure, that you have copied your data and shut off the PC.

5 Data evaluation

1. Extract the following data from your spectra and represent and tabulate them as function of the numbers k and j : λ_{max} and ΔE , the half width $\Delta\nu$ in s^{-1} , the absorbance (optical density) at the maximum of the band OD_{max} .
2. Using equations (3) and (4) the energy difference ΔE and wavelength λ of this transition must be calculated. The quantum numbers n_H and n_L have to be determined. The box length L must be estimated. These data are included in the above table. It is clear that (why?):

$$n_H = j + 1 \quad \text{und} \quad n_L = j + 2 \quad (9)$$

With n_H : quantum number of the HOMO and n_L : quantum number of the LUMO. In addition, we assume that the π -electron system extends about one bond length over the conjugated chain. Thus, L might be calculated in the following way:

$$L = (2j + 2)d, \quad (10)$$

The average bond length in the conjugated system can be assumed as $d = 144 \text{ pm}$. With these information eqs. 4 and 8 can be calculated.

3. Compare the calculated maximum wavelengths with those of the experimental spectra. Discuss the results (consider e.g. the following aspects: how good does the simple model describe the real molecules? Do you expect a better description for the shorter or the longer dyes?).
4. Calculate for the dyes with the square and the cross the quantity $\varepsilon_{max} \cdot \Delta\nu$ employing equation 7. Assume a concentration of $6 \cdot 10^{-6} \frac{\text{mol}}{L}$. Estimate the real concentration in the respective samples.

Hints for the risk assessment: Think of the toxicity of the dyes:

N,N'-diethyl-2,2'-thiacyanine iodide (DTI),

N,N'-diethyl-2,2'-dithiacarbocyanine iodide (DTCI),

N,N'-diethyl-2,2'-dithiadibenzocarbocyanine iodide (DTDCI),

N,N'-diethyl-2,2'-dithiaditricarbocyanine iodide (DTTCl)

and of the solvents (Methanol),

consider the brittleness of the cuvette, and the O₃ production of the UV-lamp,

think of electrical and IT safety.