Physikalische Chemie III für Lehramt

Übungsblatt 3

(05.05.2023)

Besprechung 11.05.2023

The Google Colab notebook that we created in our last meeting is here:
https://colab.research.google.com/drive/1Fm56SVv1-cLJ_Qe67IQbLfIXji02_C_l?usp=sharing
Complete your work on the second question from Ubungsblatt 2.

1 Effective bond length from the 1D box problem

The following expression for the frequency of the photon needed to excite a HOMO → LUMO transition in the 1D box problem was obtained in the lecture:

$$\nu_{\text{em}} = \frac{h}{8m_e}\frac{N+1}{L^2}. \tag{1}$$

Here h is the Planck constant, m_e is the mass of the electron, N is the number of π electrons in the molecule, and L is the length of the molecule along which the π electrons are allowed to move freely.

Let d_0 be the effective length of one C−C bond in the conjugated system, such that

$$L = Nd_0. \tag{2}$$

Substituting in (1), the excitation frequency can be written in terms of d_0 as follows:

$$\nu_{\text{em}} = \frac{h}{8m_e}\frac{N+1}{N^2}\frac{1}{d_0^2}. \tag{3}$$

The wavelength of this electromagnetic excitation is then

$$\lambda_{\text{em}} = \frac{c}{\nu_{\text{em}}} = \frac{8m_e c}{h} d_0^2 \frac{N^2}{N+1}. \tag{4}$$

In this question you will determine the d_0 which agrees best with the experimental values given in the lecture, and reproduced in Table 1. In terms of the variable x which is defined in the last column of the table, the above expression for the wavelength becomes

$$\lambda_{\text{em}} = \left(\frac{8m_e c}{h} d_0^2\right) x. \tag{5}$$

(a) Make a plot with the values of x along the horizontal axis and the corresponding wavelengths along the

Table 1: Experimental absorption wavelengths of organic dyes with different numbers of π electrons.

N	λ_{em} [nm]	$x = \frac{N^2}{N+1}$
6	332	5.14
8	459	7.11
10	587	9.09
12	716	11.08
14	844	13.07
16	973	15.06

vertical axis. On top of these experimental points, plot the line

$$\lambda = ax, \tag{6}$$

and manually change the slope a until the line approximates all experimental points.

(b) Once you obtain the numerical value of the slope a that best matches the experimental data, calculate the value of the effective bond length from

$$d_0 = \sqrt{a \frac{h}{8 m_e c}}. \tag{7}$$

Pay attention to the units! Compare your result with the known lengths of single and double C−C bonds.