Problem 2 - How Long (Has This Been Going On)

Based on spectroscopic data obtained from Kuhn Cyanines, we provide an estimation for the length of a Carbon-Carbon bond in a chain of alternating simple and double bonds.
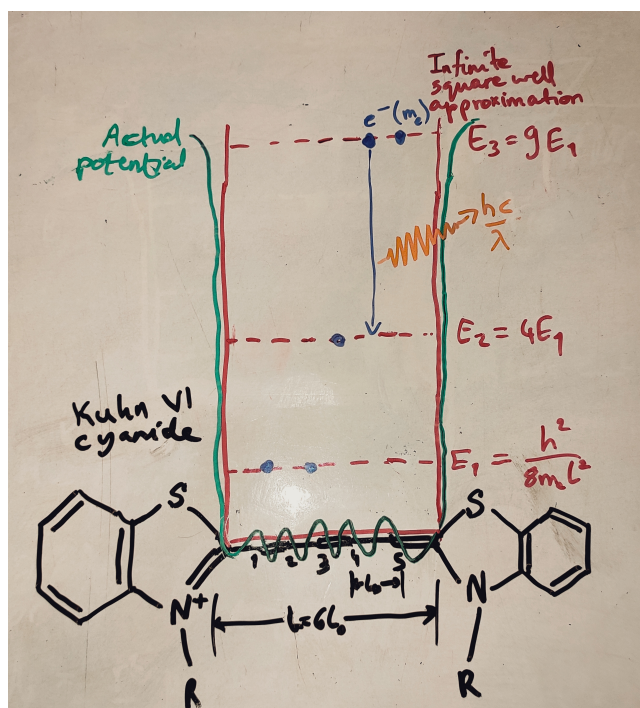
Physical Model

Figure 1: Diagram of cyanine with 5-carbon chain. Since the electrons are restricted to the chain, we straighten the chain out in the diagram to show it against the width of the potential well L.

Since the free electrons are confined along the carbon chain, we can model it as an infinite potential well where the infinite potential represents the impossibility to exit the chain. Moreover, we assume that the contributions of the carbon atoms to the potential are negligible, ie. that the "bottom" of the potential well is "flat" (the potential is a finite constant inside the well and infinite outside). The difference between the "actual" potential (green curve) and "model" potential (red solid lines) can be seen in figure 1.

In our model we will now only consider the free electrons, i.e those involved in a double bond. We consider that every carbon atom contributes one free electron to the system. Thus there are N free electrons in the potential well. Moreover, from Pauli's exclusion principle, as electrons have spin 1/2, there can be at most 2 electrons per energy level.

We will model the absorption and emission processes using a semi-quantum model. Within this model, an absorption/emission of a "photon" leads to the transition of one electron between two energy levels, whose difference is equal to the photon's energy. Lastly, what we are interested in are the electrons that have the highest energy as they are the only ones who have a higher energy level which is free, due to Pauli exclusion principle. Thus they can excited and then deexcite down by spontaneous emission which will result in a photon being released. Since the amount of free electrons is odd, there are 2 electrons that can be excited: the one at the $\frac{N+1}{2}$ energy level as well as one on the $\frac{N-1}{2}$ energy level. However the probability of going from level $\frac{N-1}{2}$ to level $\frac{N+1}{2}$ is greater as going from level $\frac{N+1}{2}$ to level $\frac{N+3}{2}$, as the associated energy is smaller. Hence, we will only consider the energy transition between levels $\frac{N-1}{2}$ and $\frac{N+1}{2}$.

Relevant Quantities

- Constants

  - Planck's constant $h = 6.62 \cdot 10^{-34}\,Js$
  - Electron mass $m_e = 9.11 \cdot 10^{-31}\,kg$
  - Speed of light in vacuum $c = 2.99 \cdot 10^8\,ms^{-1}$

- Given (for each of the Kuhn cyanines we discuss)

  - Number of carbon atoms in the chain N (odd for all given cyanines)
  - Wavelength corresponding to observed transition λ

- Unknowns

  - Length of the carbon chain L (for each of the cyanines)
  - Length of a carbon-carbon bond L_0 💬

Laws at stake

- Energy of the n-th level of an electron of mass m_e, in an infinite square well of width L:

$$E_n = \frac{n^2 h^2}{8 m_e L^2} \tag{1}$$

- Energy of a photon emitted from an electronic transition between energy levels $m > n$:

$$E_\gamma = E_m - E_n \tag{2}$$

- Energy of a photon in terms of its wavelength λ:

$$E_\gamma = \frac{hc}{\lambda} \tag{3}$$

- According to the Pauli exclusion principle, for odd N, the two lowest levels between which a transition may take place are

$$n = \frac{N-1}{2} \text{ and } m = \frac{N+1}{2} \tag{4}$$

- The length L of the well associated with a chain of N carbon atoms:

$$L = (N+1)L_0 \tag{5}$$

Results and discussion

Equations 1 - 5 lead us to the following relation between the emission wavelength of a cyanine and the number of carbon atoms in its backbone

$$\lambda = \frac{8 m_e c}{h} L_0^2 \frac{(N+1)^2}{N} \tag{6}$$

Therefore, within our model, the dependence of λ on $\frac{(N+1)^2}{N}$ should resemble a straight line passing through the origin, with slope $\frac{8 m_e c}{h} L_0^2$. The value of the slope of this line, $\frac{8 m_e c}{h} L_0^2$, would give us access to the length of a carbon-carbon bond, L_0. 💬

The data confirms this dependence, as can be seen in figure 2. The data fits very well (correlation 0.98) on a straight line passing through the origin (blue line in figure 2). From the slope of this line, we extract the following value for a carbon-carbon bond length

$$L_0 = 1.45 \cdot 10^{-10} \text{ m} = 1.45 \text{ Å}$$

If we introduce another degree of freedom by allowing a nonzero intercept, we obtain an even better quality of fit, with a slope of similar value. However, a nonzero value of the intercept cannot be explained within the framework of our model, thus we choose not to draw any conclusion from this alternate fitting at the moment.
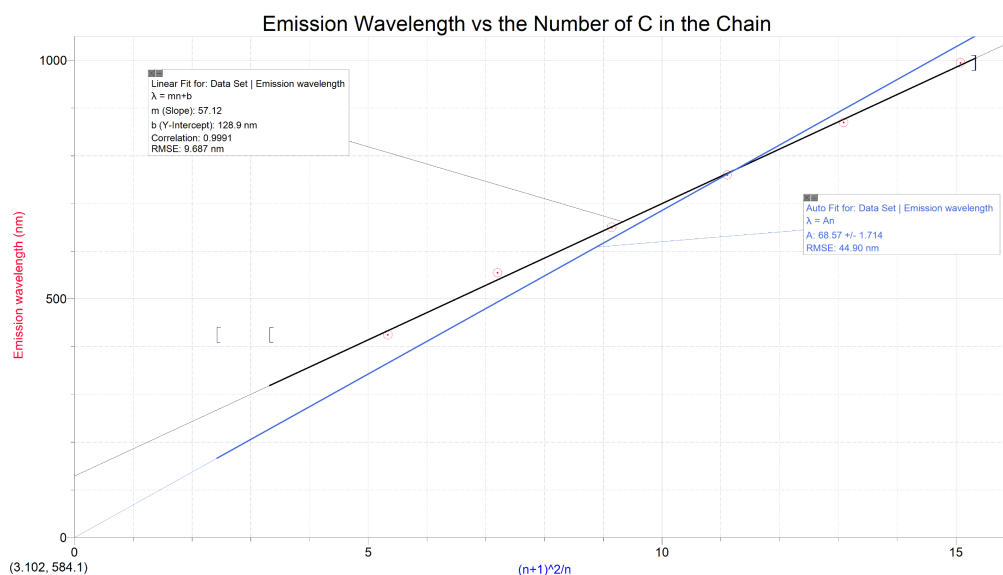
Figure 2: Linearized dependence of emission wavelength on the number of carbon atoms and its fit line with a nonzero intercept (black line) and a zero intercept (blue line).

However, we acknowledge that a more sophisticated model (for example, considering the "bumps" at the bottom of the well) might accurately explain this small deviation.

As a final point in our discussion, we note that the value of the bond length is on the order of typical atomic sizes, i.e. one Angstrom. Furthermore, the tabulated value for the carbon-carbon bond length in diamond[1] is $1.54\,\text{pm}$, obtained in crystallographic experiments. It is expected that the length of a single bond in organic molecules is the same and that single-double bond hybrids, as in our molecules, are slightly shorter. Therefore, our result is coherent with tabulated values obtained in experiments of different nature.

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[1] https://en.wikipedia.org/wiki/Bond_length