Advanced Thermodynamics

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1. **Conjugated polymers: why the absorption wavelength increases with chain length**

   (a) The governing equation for the electron in the box is

   $$\frac{d^2\Psi}{dx^2} + G^2\Psi = 0$$

   where $G^2 = \sqrt{\frac{8\pi^2 mE_n}{h^2}}$. Solving the above equation we get:

   $$\Psi = C_1\cos(Gx) + C_2 sin(Gx)$$

   Given the boundary conditions

   $$\Psi|_{x=0} = 0, \Psi|_{x=l} = 0$$

   we can derive

   $$C_1 = 0, Gl = G(2N+1)d = \sqrt{\frac{8\pi^2 mE_n}{h^2}}(2N+1)d = n\pi$$

   We can further get the equation for calculating E_n:

   $$E_n = \frac{n^2h^2}{8md^2(2N+1)^2}$$

   Substituting n with N and $N+1$, we can get

   $$E_N = \frac{N^2h^2}{8md^2(2N+1)^2}, E_N + 1 = \frac{(N+1)^2h^2}{8md^2(2N+1)^2}$$

   So the absorption energy ΔE is

   $$\Delta E = E_N + 1 - E_N = \frac{h^2}{8md^2(2N+1)}$$

   (b) The wavelength of absorbed photon is

   $$\lambda = \frac{hc}{\Delta E} = \frac{8md^2c(2N+1)}{h}$$

   We can see that the wavelength increases with N, so the absorption wavelength increases with chain length.

2. **Why are conjugated bonds so stiff?**

   (a) Using the results from Q1, we have

   $$E_n \approx \frac{n^2h^2}{8md^2(2N)^2} = \frac{n^2h^2}{32md^2N^2}$$

   $$\begin{aligned}\sum_{i=1}^{N} E_i &= \frac{i^2h^2}{32md^2N^2} \\ &= \frac{h^2}{32md^2N^2}\frac{N(N+1)(2N+1)}{6} \\ &= \frac{h^2}{192md^2}\frac{(N+1)(2N+1)}{N}\end{aligned}$$

   Since N is usually sufficiently large, the above equation can be approximated as:

   $$\begin{aligned}\sum_{i=1}^{N} E_i &= \frac{h^2}{192md^2}\frac{(N+1)(2N+1)}{N} \\ &= \frac{h^2}{192md^2}(1+1/N)(2N+1) \\ &\approx \frac{Nh^2}{96md^2}\end{aligned}$$

The total energy of all electrons (2 in each energy level)

$$E_e = 2\sum_{i=1}^{N} E_i \approx \frac{Nh^2}{48md^2}$$

(b) The energy of an electron in energy layer n is now:

$$E_n = \frac{n^2h^2}{8md^2N^2}$$

$$\begin{aligned}\sum_{i=1}^{N} E_i &= \frac{h^2}{8md^2N^2}\frac{(N+1)(2N+1)N}{6} \\ &\approx \frac{Nh^2}{24md^2} \\ E_e = 2\sum_{i=1}^{N/2} E_i &= \frac{Nh^2}{12md^2}\end{aligned}$$

(c) The energy of the straight chain is only $\frac{1}{4}$ that of the bent chain, hence the straight chain has lower energy.