

Department of Chemistry
University of Massachusetts Amherst
Graduate Core Course I (891G): Physical/Organic Chemistry

Problem Set #1

Due Tuesday 13 September 2011

1. UV/Vis Spectroscopy of Conjugated Alkenes: Particle in a Box Model

Modeling the conjugated π electrons in molecules like β -carotene (Fig 1) can be achieved with very simple quantum models. In this problem, we will apply the simplest of all; we will assume the π electrons are non-interacting “particles in a box.” As discussed in class, this means we assume the electrons vibrate independently in a one-dimensional region of length L . Using this approach, we will interpret the UV/Vis spectra of such species.

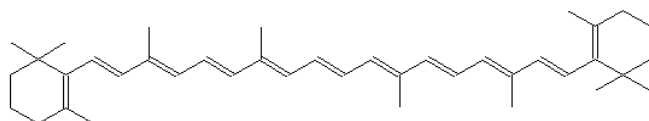


Fig 1. Structure of β -carotene.



Fig 2. Some carrots; color from β -carotene.

- (a) For the molecule 1,3,5-hexatriene, we assume that the 6 π -electrons are non-interacting electrons in a linear box of length L . Assuming a carbon-carbon bond length of 1.4 \AA (appropriate for conjugated systems), determine the box length L .
- (b) Using the fact that each carbon in the conjugated system contributes 1 π -electron, draw a schematic picture of the first 6 quantized energy levels, showing which levels are occupied by electrons and which are vacant. Label the HOMO (highest occupied molecular orbital) energy level, and the LUMO (lowest unoccupied molecular orbital) energy level.
- (c) Particle-in-a-box energies take the form (Fig 3):

$$E_n = \epsilon n^2 = (h^2/8m_e L^2)n^2,$$

where $h = 6.6 \times 10^{-34} \text{ J}\cdot\text{s}$, m_e = electron mass, and n = quantum number starting at $n = 1$ for the ground state of an isolated electron. Using this formula, estimate the HOMO \rightarrow LUMO transition energy ΔE in kcal/mol for 1,3,5-hexatriene.

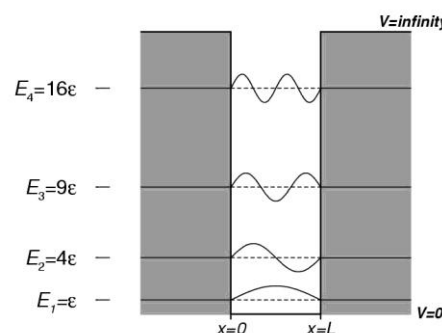


Fig 3. Particle-in-box energies.

Hint: You can do this in many different unit systems. Atomic units are particularly convenient; in these units, $h = 2\pi$ and $m_e = 1$. The atomic unit of length is the “Bohr radius” = 0.53 \AA . The resulting atomic unit of energy is the “Hartree” = 627 kcal/mol .

- (d) Using the fundamental formula of spectroscopy, $\Delta E = hc/\lambda$, where λ is the absorption wavelength and c = speed of light = 137 atomic units, determine the wavelength of light in nm that can excite the HOMO→LUMO transition in 1,3,5-hexatriene.

Compare your result to the experimental value of $\lambda = 268$ nm; what approximation(s) cause the most error?

- (e) *Extra Credit:* Consider a linear conjugated alkene with $2k$ carbons and hence k double bonds (1,3,5-hexatriene is the $k = 3$ case). Show that the absorption wavelength (nm) takes the form:

$$\lambda = (260 \text{ nm})k^2/(2k+1) \approx (130 \text{ nm}) k,$$

suggesting that each double bond added to the conjugated chain increases the wavelength by 130 nm. Experimentally it is found that each double bond adds approximately 30-50 nm to the wavelength. As such, although the particle-in-a-box is not quantitative, it does capture the qualitative fact that absorption wavelength varies roughly linearly with alkene chain length.

Explain the physical origin of this linear relationship between chain length and HOMO→LUMO absorption wavelength.