Activity #6

Standing waves, matter waves, and energy levels of polyenes

Name__________

Date___________

Goal: to relate the pattern of electron energy levels probed by UV-visible spectroscopy to the structure of the molecule.

You have probably seen the famous equation of deBroglie which gives the wavelength of matter waves: $\lambda = \frac{h}{p}$.

Here λ is the wavelength of the wave (in meters),

h is Planck's constant (6.63×10^{-34} J•s),

and p is the momentum of the particle ($p = m\text{v}$) . We'll be taking m to be the mass of an electron in what follows, $m=m_e=9.11\times10^{-31}$ kg.

The kinetic energy of an electron can be written: $E_{kin} = \frac{h^2}{2m\lambda^2}$

(this follows from the defining equation $K.E. = \frac{1}{2}m\text{v}^2$)

a. Calculate the kinetic energy of electrons whose wavelengths are given below and compare with the benchmark for electronic energy, the Rydberg constant $R_H=2.18\times10^{-18}$ J.

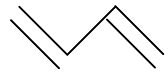
λ =1 Å = 1×10^{-10} m

λ = 10 Å

λ= 25 Å

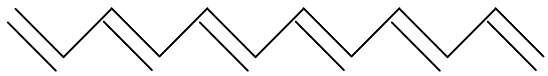
b. Let's us now use two cables (one longer than the other) to create standing wave patterns with a partner. Try making a standing wave with 0 nodes, 1 node, 2 nodes, 3 nodes. Can you relate the effort (energy) it takes to the number of nodes?

We will now consider the electron energy equation of part a) along with the patterns of standing waves of part b) to come up with a model of the pi-electron energy levels for conjugated polyenes like:

1,3-butadiene: $H_2C{=}CH{-}CH{=}CH_2$ or 

1,3,5,7,9,11-dodecahexaene: is

$H_2C{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH_2$

or 

We can think of a pi electron—one that contributes to the double bond character in these molecules as being delocalized across the whole length of the molecule and its wave properties require it to be in a standing wave that fits perfectly in this length. We shall use the rule of thumb that the length of a conjugated polyene is n x 1.4 Å where n is the number of C atoms. It is also the number of pi electrons.

c. Each group should take one molecule, C_6H_8 or $C_{12}H_{14}$ and figure out the wavelength of the longest standing wave that will fit into that length. Then figure out the wavelengths of the standing waves with 1, 2, …n nodes. What is the energy of each of these waves according to the energy formula of part a)?

d. Make an energy diagram in which the energy levels are drawn roughly to scale lowest to highest.

e. Use the Pauli principle to fill up these levels with the n pi electrons.

f. Identify the HOMO and the LUMO and calculate the transition energy. To what frequency and wavelength of light does this energy correspond? Compare your result with those of the other group. What statement can you make about the relationship of the UV-visible spectrum and the number of double bonds in the conjugated chain?