Predicting the Properties of Conjugated Systems

C115 Quantum Mechanics of Molecules

Ayman El Amrani

1 Introduction

Lycopene is a naturally occurring, red carotenoid commonly found in tomatoes [9]. The molecule itself consists of a highly conjugated system and is the focus of this experiment. An electron in the molecular orbital of a conjugated system exhibits quantum behaviour and can as such be modelled, albeit crudely, as a particle in a one-dimensional box. Using this model and UV-Vis spectroscopy to identify the change in energy of the HOMO-LUMO electronic transition, one can make a prediction about the length of the box, and thus of the molecule itself. This experiment aims to extract lycopene from tomato paste, and to estimate its length using UV-Vis spectroscopy and the particle in a box quantum model.
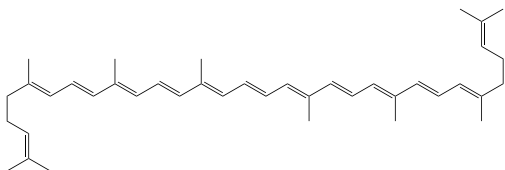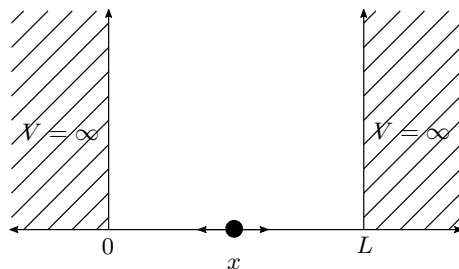

Figure 1: Structure of Lycopene. [5]

Figure 2: Particle in a one-dimensional box. [6]

2 Theory

2.1 MO Theory of Polyatomics

Molecular orbital theory provides a way of predicting the molecular orbitals in molecules, which in turn, describe the distribution of electrons. Its basis is the following assumption: the wave-function of an electron in a molecular orbital (MO) closely resembles the atomic orbital of the atom to which it is closest. As a result, the MOs in polyatomic molecules can be approximated by taking the weighted sum of the atomic orbitals involved in the bonding of a particular molecule. This approach is known as the linear combination of atomic orbitals (LCAO) [3, p 43].

Computing the MOs of conjugated systems using the LCAO approach simply becomes a question of taking the sum of the wave-functions of each contributing p_z orbital in the conjugated system. The number of resulting MOs is equal to the number of atomic orbitals involved, and each corresponds to a particular energy, in accordance with the laws of quantum mechanics. Half of the resulting MOs are known as are bonding orbitals (lower in energy than the non-bonded atoms), whilst the other half are known as anti-bonding orbitals (higher in energy than the non-bonded atoms).

The MOs in a conjugated system necessarily have π symmetry as they are a linear combination of p_z orbitals. The occupancy of each π MO is determined by doubly occupying each MO orbital, in order of increasing energy, until the number of electrons used is equal to the total number provided by each p_z orbital. [3, p 44]

Figure 3: MOs of buta-1,3-diene from left to right: 1π, 2π (HOMO), $3\pi^*$ (LUMO) and $4\pi^*$. [4, p 2]

2.2 UV-Vis Spectroscopy

UV-Vis spectroscopy concerns itself with electromagnetic waves of wavelengths in the ultraviolet and visible region, which, according to the Bohr frequency condition (1) [2, p 241], correspond to the particular amount of energy required to cause transitions in electronic energy levels. That is to say, an electron residing in a MO that absorbs a photon of wavelength in this region enters an excited state and transitions to a higher energy MO. In particular the electronic transition of interest concerns the excitation of an electron in the highest energy oc-

cupied molecular orbital (HOMO) to the lowest energy unoccupied molecular orbital (LUMO). [1, p 13]

$$\Delta E = h\nu \iff \Delta E = \frac{hc}{\lambda} \qquad (1)$$

One consequence of progressive conjugation in a molecule is that the HOMO-LUMO energy gaps decreases. Notice in Figure 4 how the HOMO-LUMO gap ethene is greater than that in butadiene. Therefore, the greater the degree of conjugation of a molecule; the smaller the resulting HOMO-LUMO energy gap, and the longer the wavelengths of the photons associated with the transition. In highly conjugated systems such as in lycopene, the HOMO-LUMO gaps is sufficiently small that the λ_{max} corresponding to the electronic transition is in the visible region of the electromagnetic spectrum and the substance appears to be 'coloured'.
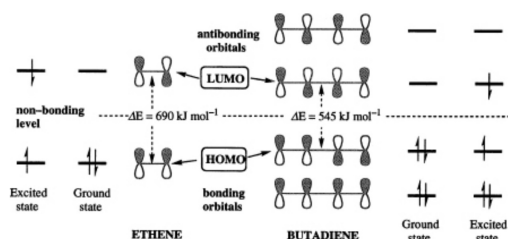

Figure 4: MOs of ethene and butadiene. [1, p 15]

In standard UV-Vis spectroscopy, a dilute solution of the sample is made up using a carefully chosen solvent and the absorption at a range of wavelengths is measured using a UV-Vis spectrometer. The resulting absorption versus wavelength spectrum produced shows peaks corresponding to these electronic transitions. According to quantum theory [2], each MO has a particular energy, which implies that each electronic transition should correspond to a definite peak in the UV-Vis spectrum. However, this is rarely seen. This is because the HOMO-LUMO energy gap is also dependent on the rotational and vibrational energies of the MOs involved. The rotational and vibrational energy levels, however, are much smaller and constantly changing. By association with such simultaneous rotational and vibrational transitions, the HOMO-LUMO electronic transition occurs over a range of energies, and thus wavelengths, giving a broad peak.

One important consideration when obtaining UV-Vis spectra is the type of solvent used. Many of the commonly used solvents in UV-Vis spectroscopy have what is is referred to as a cut off point; a value given in nanometres that corresponds to the lower wavelength limit before the solvent itself produces a peak on the UV-Vis spectrum [1, p 15]. Choosing a solvent with a cut off point below that of your sample is essential when performing UV-Vis spectroscopy in order to be able to easily distinguish between peaks produced by the sample and peaks produced by the solvent. The same is true for the material of the cuvette, in particular, samples with small values of λ_{max} are usually run in quartz cuvettes (cut off of 190nm) [1].

2.3 Particle in a Box

Quantum theory is the theory that describes the behaviour of particles on the subatomic scale. The basis of quantum mechanics is to determine the wave-functions of such particles (a mathematical function containing all of the dynamical information about a quantum system) and to extract information from it using mathematical operators to determine properties about the system. The time-independent wave-function of one-dimensional particle can be found using the time-independent Schrödinger equation (2), determining the function for potential energy, $V_{(x)}$ and applying the relevant boundary conditions.

$$-\frac{\hbar^2}{2m}\frac{d\psi_{(x)}}{dx} + V_{(x)}\psi_{(x)} = E_{(x)}\psi \qquad (2)$$

Consider a particle of mass, m in a one dimensional box of length, L 2. The walls of the box are located at $x = 0$ and $x = L$, and are impenetrable by the particle. That is to say that the potential energy of the particle when $x < 0$ and $x > L$, rises abruptly to infinity. It is assumed that the potential energy of the particle inside the box is uniformly zero everywhere (see Figure 2 for diagram). The Schrödinger equation for this particle therefore reduces to,

$$-\frac{\hbar^2}{2m}\frac{d\psi_{(x)}}{dx} = E_{(x)}\psi$$

Given that the Schrödinger equation is a second order differential, its solutions must have a continuous slope, and therefore be continuous themselves. Using this restraint and the boundary conditions, $\psi_{(0)} = 0$ and $\psi_{(L)} = 0$, allow the Schrödinger equation to be solved for a particle in a one-dimensional box and normalised to give the following general solution:

$$\psi_{(x)} = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

Note that on solving the Schrödinger equation the quantum number, n is introduced. The number n can take the value of any positive integer, meaning that there are infinitely many, discrete solutions for the wave-function of a particle in a one-dimensional box.
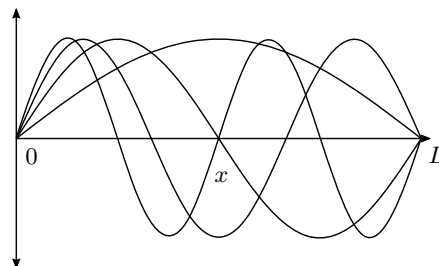

Figure 5: First four normalised wave-functions for a particle in a one-dimensional box. [6]

The operator that corresponds to the total energy (total kinetic energy in this case, since $V_{(x)} = 0$) is known as the Hamiltonian. By applying the Hamiltonian to the wave-function calculated, one can determine the energy of the particle for any value of n using the equation below.

$$E_n = \frac{n^2h^2}{8mL^2} \qquad n = 1, 2, 3\ldots$$

2.4 Modelling Lycopene

By making several assumptions, it is possible to model an electron residing in the MO of a conjugated system as a particle in a one dimensional box. It is important to note that, the particle in a box model described above is a very crude approximation for the true nature of an electron in a conjugated system.

The model makes the assumption that the potential energy, $V_{(x)}$ inside the box is zero everywhere. This is clearly not the case in a conjugated system, as the particle will vary in potential energy depending on its position within the box due to electrostatic interactions with the carbon nuclei and other molecular and atomic orbitals.

Furthermore, the model assumes that the potential energy rises abruptly to infinity at the walls of the box. In reality, the potential energy at the walls can be equated to what is known as the work function: the energy required to sufficiently excite an electron such that it can escape the molecule [2, p 244]. However, the work function is finite-valued, and therefore allows for the quantum-mechanical phenomenon known as tunnelling to take place. Quantum tunnelling predicts that the probability of finding the electron beyond a potential barrier of finite height is non-zero [2, p 268], and therefore the length of the box predicted using this model may not be accurate.

Another considerable source of inaccuracy is that the model assumes that the particle is confined to a single dimension, whereas in reality, it is free to explore all three dimensions, and therefore its energy is afforded two more degrees of freedom.

By disregarding these assumptions and accepting the particle in a box as a suitable model for an electron in a MO of a conjugated system, it becomes possible to predict the length of the system given the energy of an electronic transition within the system. By equating the principle quantum number, n to the particular π MO occupied, the energy of the any electronic transition is given by,

$$\Delta E = \frac{h^2(n_f^2 - n_i^2)}{8mL^2} \qquad (3)$$

The principle quantum number of the HOMO can be taken to be n and that of the LUMO to be $n + 1$. The mass of the particle is taken to be the resting mass of an electron, m_e. UV-Vis spectroscopy provides the value, λ_{max} (written simply as λ for clarity) which corresponds the energy of the HOMO-LUMO electronic transition according to the Bohr frequency condition (1). Thus, taking the principle quantum number of the HOMO to be equal to exactly half of the number of atomic orbitals combined, and rearranging the equation above for L gives,

$$L = \left(\frac{\lambda h(2n + 1)}{8m_e c}\right)^{1/2} \qquad (4)$$

3 Experimental

The first part of the experimental procedure consisted of obtaining the UV-Vis spectra for, hex-1-ene and two other known conjugated molecules, and determining their corresponding λ_{max} values. Using the particle in a box model, the expected λ_{max} value for each molecule was calculated. The expected values were then plotted against the experimental values and regression analysis was used to determine the function of a calibration curve.
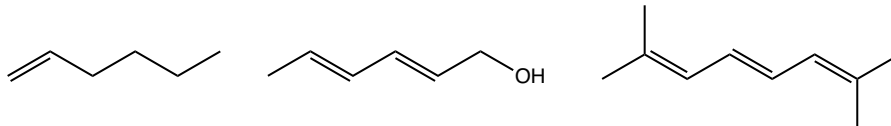

Figure 6: From left to right: hex-1-ene, (2E,4E)-hexa-2,4-dien-1-ol and 2,6-dimethyl-2,4,6-octatriene [6]

The second part of the experimental procedure consisted of isolating the chemical compound of interest, lycopene, from tomato paste. Both procedures are described below in detail.

3.1 Producing Calibration Curve

The following compounds were used to produce the calibration curve: hex-1-ene, (2E,4E)-hexa-2,4-dien-1-ol and 2,6-dimethyl-2,4,6-octatriene. Given that the type of solvent can affect the position of the peak produced, all three samples were dissolved in the same solvent. Cyclohexane, a non-polar, organic solvent was used due to its ability to solvate alkenes whilst also having a relatively low UV-Vis cut off point of 210 nm [8]. Once a dilute solution of each sample

was obtained, a small amount of each was transferred to a quartz cuvette (cut-off point of 190 nm), and a UV-Vis spectrum for each sample was obtained at a medium scan speed, and resolution of 2 nm.

To calculate the expected values of λ_{max} for each of the three molecules using the particle in a box model, the lengths of their respective π systems were first calculated. Whilst the alternating single double bond depiction of conjugated systems does not reflect the reality of their bond-

ing, it serves as a useful approximation for calculating their size. Typical carbon-carbon single bonds have a length of 154 pm whilst carbon-carbon double bonds have a length of 134 pm [4, p 3]. However, these bonds only represent the distance between the carbon nuclei. In reality, the MOs in the conjugated system extend beyond the terminal carbons, so an additional half-single bond length was added for either side of the molecule to account for this. The length of the conjugated system was then calculated by summing the lengths of each type of bond present and adding an additional full single bond length.

Since the HOMO represents the bonding orbital of highest energy, its principle quantum number, n is equal to exactly half of the number of contributing p-orbitals. Given the length of the conjugated system, L and the principle quantum number of the HOMO, n, the equation below, derived from the Bohr frequency condition (1) and the equation for the energy of an electronic transition for a particle in a box (3), can be used to predict the value of λ_{max}.

$$\lambda = \frac{8cm_eL^2}{h(2n+1)} \qquad (5)$$

Once the expected values of λ_{max} were calculated for all three molecules, they were plotted against the experimentally obtained values and a linear regression was performed on the data in order to obtain a calibration curve.

3.2 Isolation of Lycopene

Approximately 10 g tomato paste were added to a round bottomed flask along with 25 mL methanol, 50 mL dichloromethane and a stirring bar. The mixture was heated under reflux for five minutes with vigorous stirring, then allowed to cool. The mixture was then passed through a sintered glass funnel to remove any solid residue. The filtrate was transferred to a 250 mL separatory funnel, where the organic layer was extracted three times, each time being washed with 150 mL brine. The organic layer was then dried over magnesium sulphate and filtered under gravity. The remaining solution was then put onto a rotary evaporator until completely dry to obtain the crude product.

A column was prepared using a slurry consisting of 40 mL silica gel and 40 mL 60-80 petroleum ether. The crude product was then dissolved in 5 mL 60-80 petroleum ether and transferred to the column using a Pasteur pipette. The compound was eluted using a 5:1 volume-for-volume mixture of 60-80 petroleum ether and toluene. The eluate was collected in 50 mL portions and a TLC analysis was performed periodically to check for the presence of lycopene. All fractions of the eluate containing lycopene were identified and combined, then evaporated till dryness on a rotary evaporator to obtain the pure product.

Using cyclohexane (it is important to use the same solvent as the one used to produce the calibration curve, see Theory, UV-Vis above), a dilute solution of the product was made up and its UV-Vis spectrum recorded.

4 Results and Observations

4.1 TLC Plates

Despite running several TLC plates for each fraction of eluate during the isolation of lycopene, no spots were visible.

4.2 UV-Vis Spectra

The following UV-Vis spectra were obtained. The first, shows multiple spectra for the conjugated systems used to produce the calibration curve. Unfortunately, not all spectra were retained, however, the corresponding values for λ_{max} are all tabulated below. The second, is the UV-Vis spectrum for lycopene.

4.3 Collated Results

The following table contains the experimentally obtained values of λ_{max} as well as those calculated using the particle in a box model. The value obtained for hex-1-ene is likely anomalous given that literature values state that the peak should be located at around 170 nm [7], however, it was still included in the table below for completeness.

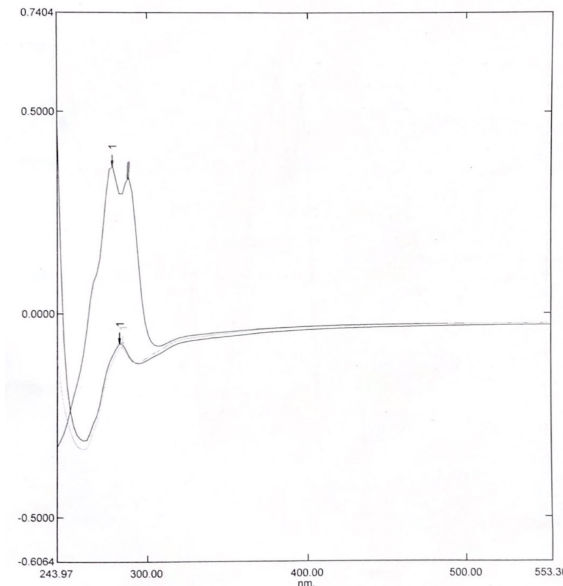| Compound	Experimental (λ_{max})	Expected (λ_{max})
hex-1-ene	232.2*	91.2
(2E,4E)-hexa-2,4-dien-1-ol	277.8	219
2,6-dimethyl-2,4,6-octatriene	288.9	352

Table 1: (units in nanometres)

4

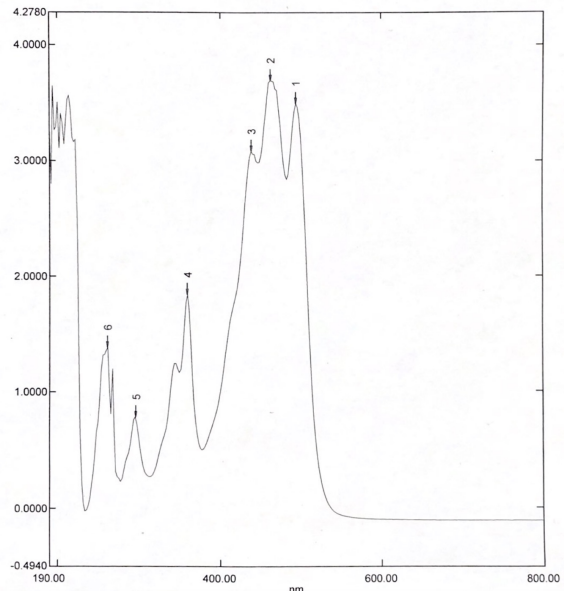Figure 7: UV-Vis Spectra for conjugated systems

Figure 8: UV-Vis Spectrum for lycopene

The following table contains the values for the wavelengths of the peaks that most likely correspond to lycopene (see lycopene spectrum [Figure 8] for labels). The second peak, $\lambda_2 = 462$ nm, is regarded as the major peak.

Peak	Wavelength (nm)
λ_1	493
λ_2	462
λ_3	438

Table 2

5 Analysis

5.1 UV-Vis Spectra

Despite the fact that no usable TLC plates were obtained, it was still possible to identify the fractions of eluate containing lycopene simply by their appearance (given lycopene's distinctly orange-red colour). However, this method was incapable of identifying other compounds present in the fractions, and therefore, likely introduced impurities into the final product. This would account for the presence of several peaks on the UV-Vis spectrum for lycopene.

Owing to the stability of conjugated systems and their correspondingly small HOMO-LUMO energy gap, the wavelength of light required to excite an electron and make this transition is therefore relatively large. It is thus possible to easily identify peaks corresponding to conjugated systems, such as lycopene, as they will lie to the right of the other peaks. However tomato paste also contains β-carotene and so this method should only be used as a rough guide.

5.2 Regression Analysis

The purpose of identifying the values for λ_{max} of hex-1-ene, (2E,4E)-hexa-2,4-dien-1-ol and 2,6-dimethyl-2,4,6- octatriene was to produce a calibration curve that could be used to convert the experimental value for lycopene. The UV-Vis cut off for cyclohexane is 210 nm, therefore, anything below this cannot confidently be associated with any compound. Literature values state that the peak for hex-1-ene should be located at around 170 nm. The value obtained for λ_{max} of hex-1-ene is therefore likely incorrect and was disregarded.

The remaining two data points provide insufficient data to produce a calibration curve of statistical significance. Therefore, note that the calibration curve below, on performing the linear regression, should *not* be used.
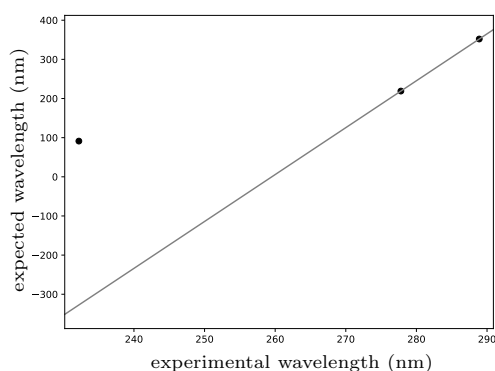
Figure 9: Calibration curve [6]. Statistically insignificant

5.3 Predicting Lycopene's Length

The major peak in the lycopene spectrum has a value of 462 nm. The MOs in lycopene's conjugated system are formed by the linear combination of 22 adjacent p orbitals. The principle quantum number, n for the HOMO in lycopene is therefore equal to 11. Using the equation (4) previously derived for a particle in a box, the length of lycopene was estimated to be 1795 pm. Taking single carbon-carbon bond lengths to be 154 pm, and double carbon-carbon bond lengths to be 134 pm, the actual length of lycopene's conjugated system is found to be 3104 pm.

One possible reason for this discrepancy is that the calibration curve calculated using regression analysis was deemed to be insufficiently statistically significant, due to a lack of data points, and was therefore not used. Perhaps, if a suitable calibration curve had been produced, the value for the length of the conjugated system calculated would have been closer to the true value.

However, a more likely explanation for the discrepancy is that, the particle in a box model is simply a very poor model for conjugated systems. The model incorrectly assumes that the potential energy of the electron is zero everywhere inside the molecule, whereas in reality, the electron varies in electrostatic potential energy depending on its position within the box due to electrostatic interactions with positively charged nuclei and other MOs.

The assumption that the particle's potential barriers are infinitely high also means that the quantum tunnelling effect of the electron cannot be considered, since the greater the height of the barrier, the smaller the degree of tunnelling. Therefore, as the height of the barrier approaches infinity, the degree of tunnelling approaches zero. In reality, the potential barriers are finite and can be equated to lycopene's work function. There must, therefore, be a finite amount of tunnelling outside of the molecule, which in turn likely affects the position of the peak in the UV-Vis spectrum.

Another source of inaccuracy stems from the fact that the model assumes that the particle is confined to a single dimension, whereas in reality, it is free to explore all three dimensions. It is therefore fair to say that the particle in a box model is an extremely crude approximation for an electron in a conjugated system and that any value produced from it has little significance.

6 Conclusion

The main objective of this experiment was to predict the length of the conjugated system in lycocpene by modelling an electron in its HOMO as a particle in a one-dimensional box. The final value calculated was out by a factor of approximately two, however, there it was determined that the particle in a box model was far too crude for this result to have any significance.

A future experiment of a similar nature, may use a greater number of conjugated systems, and a different approach than linear regression, to produce a statistically significant calibration curve in order to successfully convert values calculated from the quantum model to real values.

Perhaps of more importance, would be the use of a more advanced quantum model that takes into consideration the electrostatic potential energy of the particle, the finite height of a conjugated molecule's potential barriers, and the electron's freedom to explore all three dimensions. However, one must appreciate the difficulty (if it is at all even possible) of solving the Schrödinger equation for such a model, and furthermore, the benefits of the relative simplicity of the particle in a box model.

References

(1)   Harwood, L. M.; Claridge, T. D. W., *Introduction to Organic Spectroscopy*; Oxford University Press: 1997.

(2)   Atkins, P.; de Paula, J.; Keeler, J., *Atkins' Physical Chemistry 11th Edition*; Oxford University Press: 2017.

(3)   Weller, M.; Overton, T.; Rourke, J.; Armstrong, F., *Inorganic Chemistry 7th Edition*; Oxford University Press: 2018.

(4)   Manual, *C115 - Quantum Mechanics of Molecules.pdf*, 2019.

(5) Amrani, A. E., *Drawn in ChemDraw*, 2020.

(6) Amrani, A. E., *Drawn in Inkscape*, 2020.

(7) NIST 1-Hexene. `https://webbook.nist.gov/cgi/cbook.cgi?ID=C592416&Mask=400#UV-Vis-Spec.`, (accessed: 20/05/2020).

(8) University of California, L. A. UV-Vis Solvent Cutoffs. `https://www.chem.ucla.edu/~bacher/General/30BL/tips/solvent.html`, (accessed: 20/05/2020).

(9) WebMD Lycopene. `https://www.webmd.com/vitamins/ai/ingredientmono-554/lycopene`, (accessed: 20/05/2020).