

UV/Vis Spectra Simulations and Analysis: The Effect of the
Atomistic/Electronic Structure on the Optical Properties of a Material

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Abstract

The purpose of the lab was to validate that computational tools can predict the effects of atomic structure on the optical properties of materials and the corresponding energy by calculating the wavelengths of light absorbed by different atomic structures or molecules. Using the UV/Vis Spectra Simulator at the nanohub housed at Purdue University, the calculated spectra of phenolphthalein low and high pH structures were analyzed to determine the corresponding molecular structure for each one. The second part of the experiment was performed to explore how absorption of light changes as a function of the length of the molecular chain by analyzing the calculated the absorption spectra for alkene molecules having 8, 16, 24, 32, and 40 carbon chains. The absorption lead peak was identified to be at 503.5 nm and 212.72 nm for Phenolphthalein-1 and Phenolphthalein-2, respectively. The low pH structure has a greater separation in energy between allowed states since the absorption lead peak was at smaller wavelength. For the alkene molecules, the absorption lead peak was identified to be at 312.5, 405.08, 448.44, 471.88 and 485.35 nm with 8, 16, 24, 32, and 40 carbon chains, respectively. A more conjugated system has a lower energy gap between its allowed energy states with a longer wavelength. It was concluded that computational tools are reliable in predicting the macroscopic properties by asserting that changes in the atomistic/electronic structure change the macroscopic properties. In some cases, computational tools are the only possible approach for finding solutions that are extremely difficult to be found analytically.

Introduction

Color is an optical property of materials derived from the absorption of a certain wavelength of light in the region that ranges from about 400 nm to 800 nm. This region is commonly referred to as the ultraviolet-visible spectral region (UV/Vis), where absorption spectroscopy or reflectance spectroscopy occurs.¹ The sum of all wavelengths in this region produces the white light. When a material absorbs light in the visible region, a specific wavelength is removed; as a result, the material yields a complimentary color. In order to determine the color of a material, the complementary color wheel shown in Figure 1 is used. The method is to select the color placed in the opposite side of the circle once the absorption peak of a material is determined.

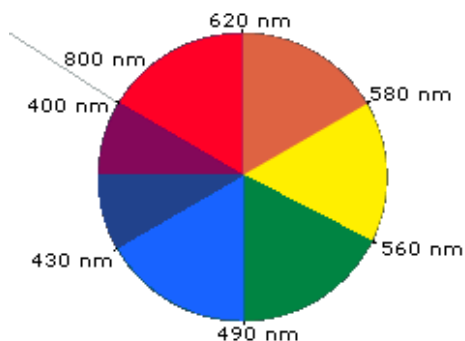


Figure 1. The complementary color wheel.²

Light as an electro-magnetic radiation has an incessant dissemination of energy that can be used to excite electrons in atoms, solids, or molecules.^{1,2} Electrons, in the early 20th century, were discovered to exist both as particles and as wave. Electrons behaviors depends on the change in the potential. When electrons are in the ground state, they will occupy the lowest allowed states. Each allowed state in atom has a quantized energy, the difference between which plays a critical role in defining which wavelengths can be absorbed. Once the electrons are excited, they will occupy

higher energy orbitals. In other words, the absorbed wavelengths in the UV/Vis range depends on the relative energies between allowed states, as demonstrated in Equation 1. These energy states are determined by electron interactions with atoms of different types, spacing, and arrangements.

$$E = h\nu = \frac{hc}{\lambda} \quad (1)$$

where E is the energy in joules, h is Planck constant, which equals to 6.63×10^{-34} J-s, c is the speed of light in vacuum, which equals to 3.0×10^8 m/s and λ is wavelength of light in meters.²

Absorption of wavelengths occurs only when the energy of the incoming photon exactly equals the difference in energy levels.^{2,3} As a result, electrons will transit from their ground state to an excited state. If no differences in energies between allowed states equals energies for light in the UV/Vis region, no absorption will occur.² Therefore, the material may appear clear or transparent. Based on this principle, calculation tools can be used to simulate the likely absorption spectrum for a configuration of atoms.

The purpose of the lab was to validate that computational tools can predict the effects of atomic structure on the optical properties of materials and the corresponding energy by calculating the wavelengths of light absorbed by different atomic structures or molecules. Using the UV/Vis Spectra Simulator at the nanohub housed at Purdue University, the calculated spectra of phenolphthalein low and high pH structures were analyzed to determine the corresponding molecular structure for each one. Phenolphthalein is widely used to visually determine the pH of a solution because it remains unchanged when added to low pH (0 to ~8) solutions whereas it turns the high pH (~8 – 12) solutions to pink/red.² The second part of the experiment was occupied to explore how absorption of light changes as a function of the length of the molecular

chain by calculating the absorption spectra for alkene molecules having 8, 16, 24, 32, and 40 carbon chains.

Experimental Procedure

The computational tool used in this lab was UV/Vis Spectra Simulator on nanohub.org, an open resource provided by Purdue University. With this tool, the jobs were created and submitted using the web browser. These jobs run on Purdue's super-computers, where the assignments were submitted sequentially.² The samples being examined in this experiment were provided in the course locker as Experiment8-Structures.xlsx. The files included two structures, one Phenolphthalein-1 and one Phenolphthalein-2 and five structures of alkene oligomers having 8, 16, 24, 32, and 40 carbon chains. In the web browser, UV/Vis Spectra Simulator was found under My Tool Search. The tool was launched, each data was uploaded taking into account the charge and multiplicity provided in the files. Then the spectra for the samples were obtained by choosing Absorption Spectrum under the result bar after running the simulations.

Results and Discussion

Using UV/Vis Spectra Simulator, the absorption spectrum calculated for Phenolphthalein-1 was found to have an absorption peak at 503.3 nm as shown in Figure 2, (a). Interestingly, the absorption peak for Phenolphthalein-2 was determined to be 212.7 nm as demonstrated in the calculated absorption spectrum in Figure 2, (b).

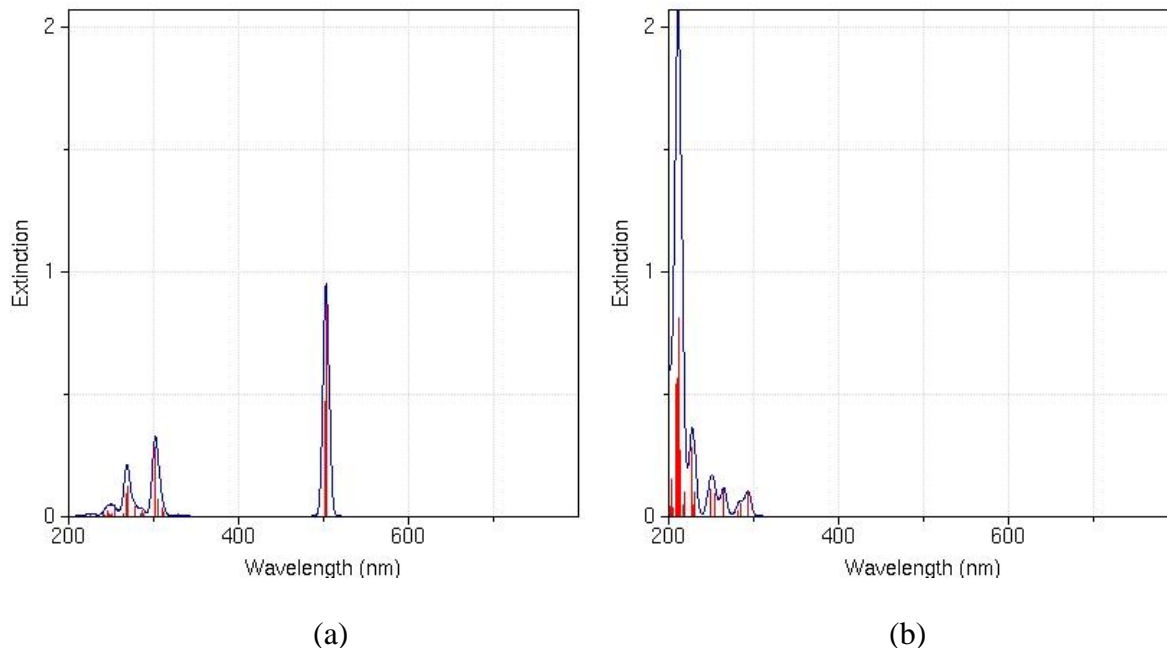


Figure 2. The calculated absorption spectra for (a) Phenolphthalein-1 and (b) Phenolphthalein-2 using UV/Vis Spectra Simulator.

Based on the results, Phenolphthalein-2 was determined to be the one corresponding to the low pH structure. The identified peak of Phenolphthalein-2 was found to be out of the visible range, indicating that it is colorless. In contrary, Phenolphthalein-1 was determined to correspond to the high pH structure. The identified peak of Phenolphthalein-1 was found to be within the visible range, indicating that it appears colored. Using the complementary color wheel, the 503.3 nm wavelength links to red, which confirms the findings. This difference in optical properties occurred due to the differences in their atomic structures. The main variance in the structure is that the low pH structure is bonded to two hydrogens atoms whereas the high pH structure is not, as shown in Figure 3. The difference explains why the net charge in the low pH structure is zero whereas the net charge in the high pH is -2. In terms of the electronic states and wavelength, the high pH structure was found to be red because the electrons were excited by the photons that had a wavelength of 503.3 nm, which derived the electrons to jump from a lower energy orbital to a higher one, leaving the structure

with a -2 charge.² The low pH structure was found to be clear because no absorption accrued, which means that the electrons were not excited because no match between the wavelengths in the visible region and the difference in the allowed states energy found.^{1,2}

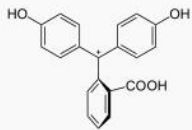
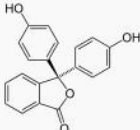
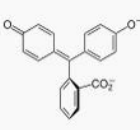
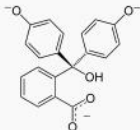
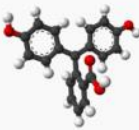

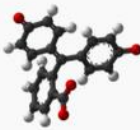



Species	H_3In^+	H_2In	In^{2-}	$In(OH)^{3-}$
Structure				
Model				
pH	<0	0-8.2	8.2-12.0	>13.0
Conditions	strongly acidic	acidic or near-neutral	basic	strongly basic
Color	orange	colorless	pink to fuchsia	colorless
Image				

Figure 3. The structural or chemical differences of Phenolphthalein when added to solution of high and low pH.²

In order to determine how the differences in energy of the allowed electronic states change as a function of structure, the results were rationally interpreted with the given relationship between the energy and the wavelength as stated in Equation 1. It can be drawn that the high pH structure has a smaller difference in energy between the occupied and the unoccupied states than the pH structure. In other words, a greater separation in energy between allowed states can be concluded for the low pH since it observed smaller wavelength.³ Furthermore, it can be concluded from the calculated absorption spectra in Figure 2 that the absorbed wavelength is

directly proportional to the pH of a material; that is as the pH increases, the absorbed wavelength increases, the energy gap between the allowed states decreases. The results agreed with the literature.^{1,3}

Figure 4, (a) shows an absorption peak of 312.5 nm for the alkene molecules having 8 carbon chains whereas Figure 4, (b) shows an absorption peak of 405.1 nm for the alkene molecules having 16 carbon chains.

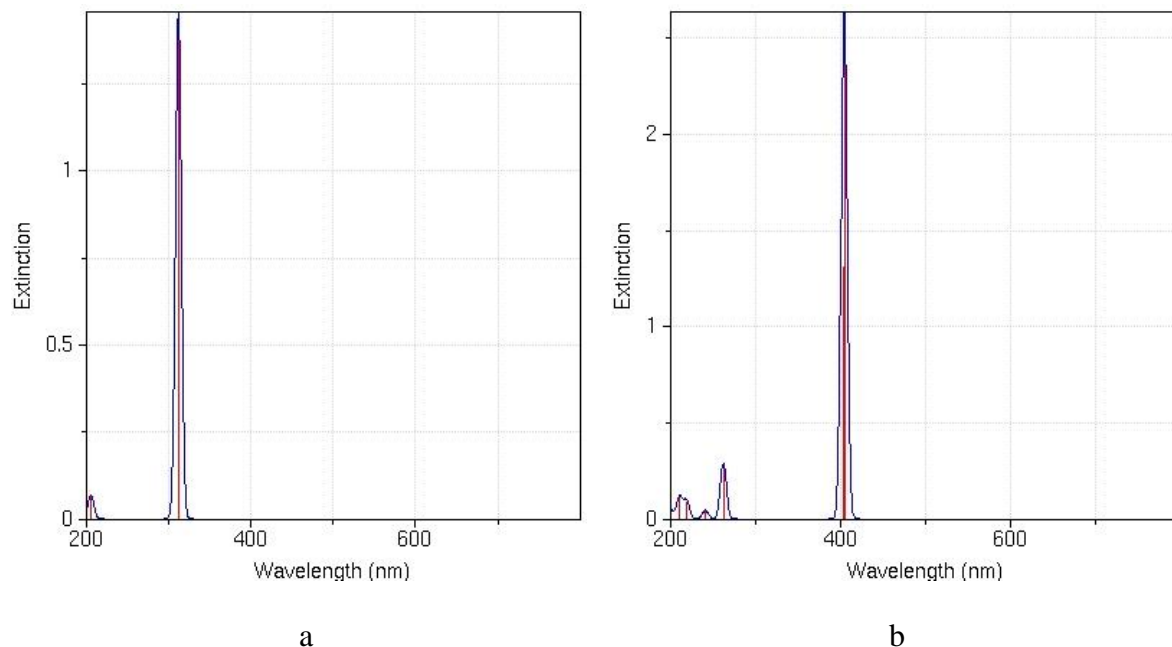


Figure 4. The calculated absorption spectra for (a) alkene molecules having 8 carbon chains and (b) alkene molecules having 16 carbon chains using UV/Vis Spectra Simulator.

Figure 5, (a) shows an absorption lead peak of 448.44 nm for the alkene molecules having 24 carbon chains. Figure 5, (b) shows an absorption lead peak of 471.88 nm for the alkene molecules having 32 carbon chains. Figure 5, (c) shows an absorption lead peak of 585.35 nm for the alkene molecules having 40 carbon chains. It was found that changing the conjugation length alters the wavelength of the lead peak. It was observed that as the conjugation length increased, the wavelength at which the lead peak was identified increased.

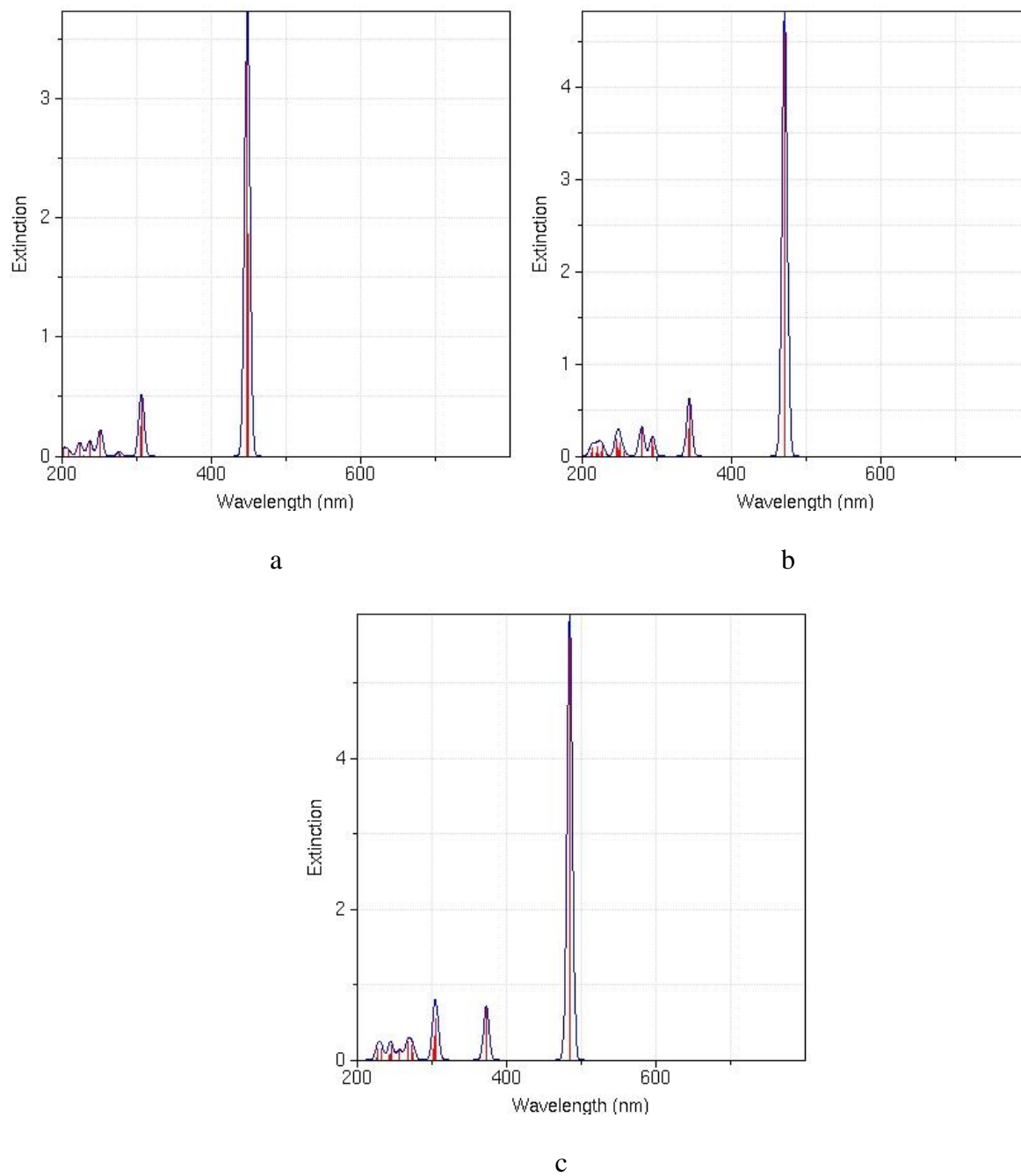


Figure 5. The calculated absorption spectra for (a) alkene molecules having 24 carbon chains, (b) alkene molecules having 32 carbon chains and (c) alkene molecules having 40 carbon chains using UV/Vis Spectra Simulator.

It was also observed that changing conjugation length alters the difference in energy of the allowed states. The increase of the number of carbon chain was found to increase the wavenumber absorbed, which indicates that the difference in energy of the allowed states decreases.^{1, 2} From the calculated absorption spectra in Figure 4 and Figure 5 and the complementary color wheel shown in Figure 1, the expected optical property for alkene molecules having 8 carbon chains is colorless since it absorbed a wavenumber outside of the visible range, whereas the other alkene molecules are colored. The expected color for the alkene molecules having 16 carbon chains is yellow. The expected color for the alkene molecules having 24, 32 and 40 carbon chains is orange ranging from orange/yellow to orange/red. Figure 6 shows the lead peak as a function of conjugation length of the calculated alkene molecules. It can be determined that the lead peak increases slowly as a function of conjugation length, which indicates that the rate change of the lead peak as a function of conjugation length is decreasing. A more conjugated system has a lower energy gap between its allowed energy states, therefore the absorption lead peak will be of a longer wavelength.³

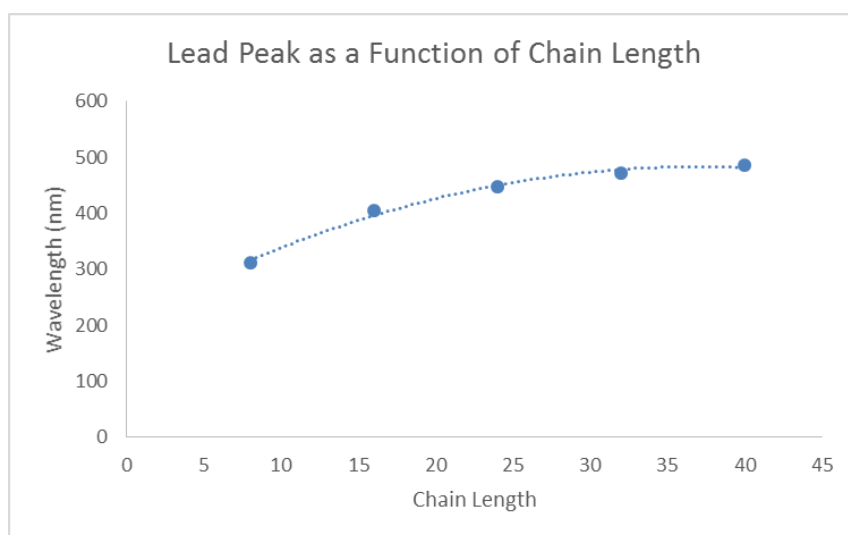


Figure 6. The lead peak as a function of conjugation length of alkene molecules having 8, 16, 24, 32, and 40 carbon chains from calculated absorption spectra using UV/Vis Spectra Simulator.

Conclusions

The purpose of the lab was to validate that computational tools can predict the effects of atomic structure on the optical properties of materials and the corresponding energy by calculating the wavelengths of light absorbed by different atomic structures or molecules. Using the UV/Vis Spectra Simulator at the nanohub housed at Purdue University, the calculated spectra of phenolphthalein low and high pH structures were analyzed to determine the corresponding molecular structure for each one. The second part of the experiment was performed to explore how absorption of light changes as a function of the length of the molecular chain by analyzing the calculated the absorption spectra for alkene molecules having 8, 16, 24, 32, and 40 carbon chains.

Overall, the experiment was successful; the findings agreed with expected results from the lecture. It succeeded in showing that computational tools are reliable in predicting the macroscopic properties although slight differences may occur when compared the experimental results. These variations can be ignored because they are very not significant. UV/Vis Spectra Simulator was effective in asserting that changes in the atomistic/electronic structure change the macroscopic properties. The absorption lead peak was identified to be at 503.5 nm and 212.72 nm for Phenolphthalein-1 and Phenolphthalein-2, respectively. It was determined that Phenolphthalein-2 was is the one corresponding to the low pH structure with a greater separation in energy between allowed states since the absorption lead peak was at smaller wavelength. For the alkene molecules, the absorption lead peak was identified to be at 312.5, 405.08, 448.44, 471.88 and 485.35 nm for 8, 16, 24, 32, and 40 carbon chains, respectively. A material with alkene molecules having 16 carbon chains was expected to appear clear. The expected color for the alkene molecules having 16 carbon chains was found to be yellow and alkene molecules

having 24, 32 and 40 carbon chains was orange ranging from orange/yellow to orange/red. It was concluded that a more conjugated system has a lower energy gap between its allowed energy states; as a result, the absorption lead peak is found to be of a longer wavelength.

It is worthwhile to note that in some cases, computational tools are the only possible approach for finding solutions that are extremely difficult or impossible to be found analytically. One example is solving for the Schrödinger equation (partial differential equation), which analytically describes the behavior of electrons.²

References

¹ W.D. Callister Jr., *Materials Science and Engineering: An Introduction, Seventh Edition* (Wiley, New York, 2007).

²D. Irving, *UV/Vis Spectra Simulations*, MSE 255 Course Locker, 2016.

³ J. Workman, *Handbook Of Organic Compounds. NIR, IR, Raman and UV-Vis Spectra Featuring Polymers and Surfactants: UV-Vis and NIR Spectra* (Academic, San Diego, CA, 2001).