UV-Vis Absorption Spectroscopy of Electronic Transition

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Abstract

In this experiment Analytical Ultraviolet-Visible Absorption Spectroscopy (UV/Vis)[1] was used to determine the various effects of chromophores, auxochromes, conjugation, absorptivity (ϵ), and solvents on a UV/Vis spectrum running from 200 to 400nm in wavelength, λ. The study of these effects was accomplished by running 11 samples containing various solute—solvent combinations and deducing logically the effects of each factor on the resultant spectra. It was

[1]Beckman DU® 7400 Spectrophotometer

found that solvent polarity affects both intensity and λ of an electronic transition according to which transitions are available, which itself depends on which chromophores are present, while the number of chromophores on a given molecule were found to only affect absorption intensity. Auxochromes similarly affected both intensity and λ. Sample solutions were prepared in 10mL volumetric flasks using minute solute volumes of known concentration. These prepared solutions were loaded into the instrument one at a time via cuvette and analyzed using the attached computer detection system and included UV/Vis analysis software. From here absorption and λ data were harvested for use in determining ϵ values and comparing λ shifts among samples under similar conditions, and subsequently determining the causes of the given dissimilarities.

0.1 Theory

It is known that both organic and inorganic molecules absorb visible and UV light which causes valence electrons to get excited and promoted to the lowest unoccupied orbital, which is generally an anti-bonding orbital. In Absorption Spectroscopy these absorptions are measured using a UV/Vis

spectrophotometer. From these measurements one can find the concentration of solute in a solution, which wavelengths within the specified region a given solute absorbs photons, and what effect the chosen solvent causes on the absorbance, and therefore the energy of the excitation. Given the chosen spectral range of 200-400nm these spectra showed three specific types of excitations: $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$, and $\pi \rightarrow \pi^*$. Other excitations such as $\sigma \rightarrow \sigma^*$ were therefore outside of range and ignored. In this procedure photons were passed through a 1cm cuvette which contained the sample as solute in a solution of known concentration. With that in mind, the point of this lab was not to determine concentrations as it was in the last UV/Vis lab[2]. Of special interest here was the effects of solvent on excitation wavelength, types of excitations, and comparison of spectra produced by similar solutes. The different types of excitations depended on which chromopore(s) each solute species contained, which was determined beforehand and is listed in table 3. In the event of multiple absorption peaks one was differentiated from the other by taking into consideration the electronic transitions possible, the relative energy of each transition, and the fact[3] that $\lambda \propto \frac{1}{E}$. Roughly, the three electronic transitions under scrutiny have relative energy values as

[2]http://science.herograw.net/chem333l/UV_Vis.pdf

[3]$E = h\nu = \frac{h \times c}{\lambda}$ where $h = 6.62607 \times 10^{-34} J \cdot s$

follows: $\pi \rightarrow \pi^* > n \rightarrow \sigma^* > n \rightarrow \pi^*$. When comparing spectra produced by similar solutes it was important to keep in mind that absorbance values were not necessarily directly comparable, as solute concentrations differed between solutions. For this reason absorptivity (ϵ) values were compared instead. This works according to Beer's law, which states $A = \epsilon \cdot b \cdot c$ where A is absorbance, b is path length of the cuvette (1cm as mentioned earlier), and c is concentration. By this equation, which professes a direct, linear relationship between ϵ and A, one would expect that at equal concentrations and using an identical cuvette across trials, ϵ works as an indicator of absorbance. Therefore, having calculated the ϵ values from given concentrations, path lengths, and absorbances, one could compare the relative intensity of similar substances. Most of the starting information is listed in table 2 and therefore will not be listed here or elsewhere. As is generally the case, the same cuvette was used in every experiment. This choice provides precision, as even cuvettes of the same purported path length cannot be guaranteed to possess the same structural makeup at the molecular level and would therefore be expected to scatter light differently.

0.2 Procedure

The instrument was warmed up already so the initial step in this procedure involved preparing solutions for analysis. Solute and solvent volumes are provided in table 2 below. These solutions were prepared using a micropipet to draw the miniscule solute volumes (2.5-25.0μL) and purge them into a 10mL volumetric flask, one flask for each of the 11 solutions. It must be noted here that the flasks were pre-filled with solvent up to the 10mL mark and it should be expected that there will be some error due to this, which will be discussed later. The phenol and sodium phenolate solutions were prepared already, as well. When preparing the first two solutions, it was noticed that the micropipet's effective range would not allow it to go below 3μL, while the expected volume of solute was 2.5μL. This problem was worked around by putting 5.0μL of solute into the 10mL volumetric flask, gently shaking the mixture to allow for solute to spread throughout the solution, drawing out half of the solution with a 5mL pipet, and filling the flask back up to 10mL. This had the effect of diminishing the concentration by half and giving the expected 2.5μL of solute. Samples seven and eight were prepared by drawing out 25.0μL of samples five and six, respectively, and adding it to new 10mL volumetric flasks. The samples were run out of

order so that all samples with a given solvent could be run at once. The order of solvents was as follows: water, methanol, and hexanes. This made it possible for only three backgrounds (one for each solvent) to be run instead of eight. After running the appropriate background the cuvette was washed, dried, cleaned, and filled with sample solution. This sample solution was placed into the instrument and analyzed, using a computer interface. This computer interface also allowed for determining wavelength and absorption readings on a given printout, which was fully taken advantage of (see printouts, attached). These printouts were then analyzed.

0.3 Results

Molecule	Molecular Weight ($\frac{g}{mol}$)	Density, ρ ($\frac{g}{mL}$)
iodoethane	155.97	1.95
acetone	58.08	0.788
2,5-hexanedione	114.14	0.973
methyl vinyl ketone	70.09	0.842
benzene	78.11	0.870
phenol	94.11	2.72×10^{-5}
sodium phenolate	170.14	5.80×10^{-5}

Table 1: Literature Data

	← Solute	Solvent →	
Type	Amount	Type	Amount
iodoethane	$2.5\mu L$	hexane	10mL
iodoethane	$2.5\mu L$	methanol	10mL
acetone	$10.0\mu L$	water	10mL
2,5-hexanedione	$10.0\mu L$	water	10mL
methyl vinyl ketone	$25.0\mu L$	hexane	10mL
methyl vinyl ketone	$25.0\mu L$	water	10mL
diluted methyl vinyl ketone	$25.0\mu L$	hexane	10mL
diluted methyl vinyl ketone	$25.0\mu L$	water	10mL
benzene	$5.0\mu L$	methanol	10mL
phenol	0.0068g	methanol	250mL
sodium phenolate trihydrate	0.0145g	methanol	250mL

Table 2: Solution Preparation

Table 3 lists most of the data collected or calculated throughout the experiment. Note that in table 1 that sodium phenolate is actually sodium phenolate trihydrate, as in solution it is expected that this complex will form, and has therefore been taken into account for the calculations. Concentration values in table 3 were calculated using the following equation: $c = \frac{V_s \cdot \rho}{M \cdot V_{tot}}$ where V_s is the solute volume. The acetone calculation, using data from tables 1 and 2, will be shown here:

$$c = \frac{(10 \times 10^{-3} mL)(0.788 \frac{g}{mL})}{(58.08 \frac{g}{mol})(10 \times 10^{-3} L)} = 1.36 \times 10^{-2} \frac{mols}{L}$$

#	λ (nm)	Absorbance	[Solution] ($\frac{mols}{L}$)	ϵ ($cm^{-1}L^{-1}$)	Transition
1	261.0	1.61120	3.13×10^{-3}	515.49	$n \rightarrow \sigma^*$
2	257.0	1.34894	3.13×10^{-3}	431.58	$n \rightarrow \sigma^*$
3	266.0	0.39621	1.36×10^{-2}	29.203	$n \rightarrow \pi^*$
4	266.0	0.34776	8.52×10^{-3}	40.795	$n \rightarrow \pi^*$
5	332.0	0.54407	3.00×10^{-2}	18.116	$n \rightarrow \pi^*$
6	299.0	0.90663	3.00×10^{-2}	30.188	$n \rightarrow \pi^*$
7	205.0	0.15191	7.51×10^{-5}	2023.3	$\pi \rightarrow \pi^*$
8	212.0	0.76022	7.51×10^{-5}	10125	$\pi \rightarrow \pi^*$
9	256.0	0.82572	5.57×10^{-3}	148.27	$\pi \rightarrow \pi^*$
10	274.0	0.94548	2.89×10^{-4}	3271.3	$\pi \rightarrow \pi^*$
11	273.0	0.48139	3.41×10^{-4}	1412.1	$\pi \rightarrow \pi^*$

Table 3: Found and Calculated Data

The molar absorptivity, μ, was determined using Beer's Law, which takes the form $A = \epsilon \cdot b \cdot c$. Once again using acetone, the calculation would go as follows:

$$\epsilon = \frac{A}{b \cdot c} = \frac{0.39621}{(1cm^{-1})(1.36 \times 10^{-2}\frac{mols}{L})} = 29.203cm^{-1}L^{-1}$$

0.4 Discussion

The samples were prepared in 10mL volumetric flasks, as mentioned before. It was noted earlier that the actual solution volume ended up being

more than 10mL because the flask was already filled to its mark with solvent before the solute was added. Therefore, the actual volume would be $10mL + V_s$ which, for example in the acetone trial, would come out as 10.01mL. this change in volume is less than 1% in all cases, though, so the addition is negligible. More importantly, adding the solute first in an attempt to attain the correct volume of 10mL exactly would actually result in error, possibly of a greater magnitude. This is due to the fact that the solute volume is small and all of the given solvents tend to vaporize at room temperature. Because of this, a significant amount of solute would be lost to the atmosphere if it were added first, due to the time it takes to fill up the flask with solvent. Looking at the two iodoethane spectrums one could see the effects on absorption by choice of solvent. Taking the first printout (iodoethane in hexane) as the reference, there was a small hypsochromic shift when methanol was used as a solvent in place of water. It is known that solvent affects the magnitude of the energy system. It is also known that $n \rightarrow \sigma^*$ transitions are blue shifted in the presence of a hydrogen bonding solvent. This is exactly what's happening here. The second solvent is methanol, which can hydrogen bond. Because of this, the excitation wavelength shifts left, causing more energy to be required for

the given transition. Similarly, it is shown that the intensity (as judged by absorbance) decreases with $\Delta A = -0.26226$. This is called a hypochromic (intensity decreasing) shift and is known to occur in polar solvents, such as methanol. Note that stabilization generally doesn't only affect one state. Rather, it affects one more than another, thus giving a net reduction or increase. Acetone and 2,5-hexanedione (samples 3 and 4) reveal another important point. The molecules are very similar; 2,5-hexanedione is essentially two acetone molecules attached at one of the methyl groups on each molecule, thus providing two carbonyl groups. As is shown in the printouts and with the help of absorptivity values from table 3, both solutions provided an absorption peak at 266.0nm, but the intensities differed. This can be deduced by calculated ϵ values, where the absorptivity for 2,5-hexanedione was ≈ 1.397 times that of acetone. It can be seen then that more of the same chromophore does equate to a greater intensity, given two solutes with all other factors (concentration, solvent, path length) equal, but the increase is not twofold. Unlike the previously addressed samples, methyl vinyl ketone gives two absorption peaks. This is due to its structure. First its $n \rightarrow \pi^*$ peak will be addressed, which resides at a longer wavelength. Once again these two samples differ only in what solvent they are in.

All other aspects of the solution are the same. Knowing this, all differences in absorption spectra can rightly be attributed to solute-solvent interaction. In water the wavelength is shorter and the absorptivity is greater, both of which point to an increase in energy. This occurs because the hydrogen bonding in water stabilizes the bonds and decreases the energy in n electrons. This widens the gap between n and π^* so that more energy is required to excite the electrons, which results in a smaller wavelength. Note also that spectrum #5 is the only one that deviates from the 200-400nm spectral range. instead of 200nm it starts at 260nm. This is because the relative intensity of the $\pi \rightarrow \pi^*$ peak is such that, when scaled, it totally obscures the $n \rightarrow \pi^*$ peak. This is caused by the computer interface's formatting feature. Therefore, an increased lower spectral limit had to be picked that would leave the $\pi \rightarrow \pi^*$ peak out at least while analyzing the $n \rightarrow \pi^*$ peak. Converse to the $n \rightarrow \pi^*$ peaks just discussed, the $\pi \rightarrow \pi^*$ peak undergoes a bathochromic shift when in polar solvent as compared to a non-polar solvent. Note that this in itself can be used as an indicator of whether or not chromophores giving $\pi \rightarrow \pi^*$ transitions are in a solution at all, because this bathochromic shifting tendency in the presence of a polar solvent goes against what is seen for $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ shifts. This occurs

because in a polar solvent the dipole-dipole interactions tend to decrease the excited π^* state more than the unexcited π state, thus reducing the gap between energy levels which, as stated previously, equates to increased wavelength. Benzene, phenol, and sodium phenolate all have very similar chemical structures, so it isn't surprising that their spectra look similar. Because of its chemical makeup, benzene's sole transition within the given spectrum is $\pi \rightarrow \pi^*$. But as is generally the case, benzene shows an unusual pattern. According to literature sources[4] benzene gives three of these transitions, two of which occur within the active range, and the weakest of which is under scrutiny for the purposes of this lab. This weakest band (the so-called B band) appears as several choppy peaks, the apex of which occurs at $\lambda = 256.0nm$. The other two solutes and their accompanying spectra have been chosen to show the effects of auxochromes on chromophores. In both phenol and sodium phenolate the wavelengths are around 274nm, a bathochromic shift. This shift occurs because in both instances the Oxygen acts as an auxochrome and, with its nonbonding electrons, serves to stabilize the π^* state, thus lowering its energy and significantly closing the energy gap in the $\pi \rightarrow \pi^*$ transition, which causes the observed red shift. In

[4]Chapter 7 - Absorption Spectroscopy of Electronic Transitions

terms of intensity the two auxochrome-enhanced solutes absorbed far more than benzene, especially phenol. Lastly, comparing acetone and methyl vinyl ketone in water, as they are very similar molecules, shows the effects of conjugation as an auxochrome on both intensity and wavelength. What this shows about intensity is that it essentially has no effect, for the absorptivity values of these two solutes were closer than any other two solutes. However, conjugation did have quite an effect on wavelength. Methyl vinyl ketone gave a considerably bathochromic absorption peak, shifting a good +33nm. This shift implies that conjugation lowers the energy of excitation. This happens because with conjugation comes resonance, and with resonance comes stability, specifically stability in the π^* state. On the other hand, it doesn't do as much for non-bonding electrons as it does for π electrons so the net difference dictates that there will be a lower energy and thus a higher wavelength.

0.5 Conclusion

The intent behind this experiment was to describe certain quantitative tendencies involving electronic transition brought on by UV/Visible photons.

It was seen through comparison among the 11 samples that the net effect on $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions by polar solvents is a hypsochromic shift, while the opposite is true for $\pi \rightarrow \pi^*$ transitions. It was also determined that more than one of the same chromophore on a given molecule provides an increased absorption intensity over a similar molecule with only one chromophore. Additionally, we deduced that factors such as extra nonbonding electrons and conjugation served to reduce the required energy for absorption, thus increasing the absorption peak wavelength. This occurs, like in other cases, due to increased stability and a resultant diminishing disparity between the excited state and the ground state. With the knowledge of these tendencies and why they occur, it empowers one to analyze spectra with limited information and determine important features of a solute, such as π bonding, conjugation, overall transition types, and perhaps the identity of any present chromophores and auxochromes. This information serves as a useful supplement to the previously discovered Beer's Law relationships in making Absorption Spectroscopy of Electronic Transitions a valuable tool in the field of Chemistry.