Interpretative Spectroscopy

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Lecture 21

Introduction to UV Spectroscopy

Hello everyone, I once again welcome you all to MSB lecture series on Interpretative Spectroscopy. In my previous lectures I had elaborated on NMR spectroscopy. What you should remember about NMR is: all nuclei with non-zero nuclear spin value would behave like tiny bar magnets and they will be randomly oriented in the absence of magnetic field. When you apply magnetic field, majority of them are aligned with the magnetic field and some of them will be opposing the magnetic field. And then, since they are charged species, what they do is with respect to the magnetic field they start precessing without aligning with the axis of rotation, precision with exact alignment with the applied magnetic field is not permitted according to quantum mechanical rules. As a result, what happens they will be precessing with an angle with respect to the applied magnetic field, the frequency with which they precess is called Larmor frequency omega, and if you consider that one to precision frequency since, it is angular we call it as $2\pi\nu$, that means omega (ω) Larmor frequency equal to $2\pi\nu$, and this is proportional to the gyromagnetic ratio of that nucleus and applied magnetic field that means $2\pi\nu$ equal to gamma B naught (γB_o). And if you consider the energy difference then $2\pi\nu h$ equal to $h\gamma B_o$ and then if you simplify what we get is nu (ν) equal to $\gamma B_o/2\pi$.

So this equation one should remember. Once you remember the equation, this gives you very nice correlation of the frequency of operation with respect to the applied field and gyromagnetic ratio. So here we use the term chemical shift. What happens when the nucleus is precessing with a frequency called Larmor frequency, this is aligned at an angle. So in order to flip that one, we have to apply another frequency in a direction perpendicular to the applied magnetic field, that influences or pulls down the nuclei away

from the axis of rotation with respect to the magnetic field and once when it completely comes off, it flips, so this is called transition or flipping. So in order to flip the nuclear spin to see transition we have to apply another frequency at right angle to the applied magnetic field which should match the Larmor frequency, then we call it as resonance; then we will see spectrum. So, in that case what is chemical shift? when nuclei are placed in the magnetic field, they are always surrounded by electron. We are not talking about naked nucleus. We are talking about the nucleus surrounded by electrons. So these electrons also charged particles; under the influence of magnetic field they also produce magnetic field which can either align with the magnetic field or it can oppose the magnetic field.

When it will be aligned with the magnetic field and when it is going to oppose the magnetic field, we should look into the symmetry of the electron density. If the symmetry of electron density or the circulation of electron density is symmetrical then there will be unhindered circulation we can observe under the influence of magnetic field. When there is unhindered circulation of electron density because of the symmetric distribution of the electrons, then what happens, the magnetic field generated because of circulation of electron density would always oppose the applied magnetic field. As a result, the net magnetic field experienced by the nucleus decreases and this we call it as diamagnetic shielding. In this case, what happens, since the net magnetic field experienced by the nucleus decreases, its Larmor frequency also decreases. Then we need to give a low frequency pulse to see resonance. That is the reason it is also called low frequency shift, diamagnetic shielding, low field shift and also low frequency shift. On the other hand if the electrons density surrounding the nucleus is unsymmetrical there will be hindrance for the circulation of electron density. So, when there is a hindrance for the circulation of electron density under the influence of magnetic field, what would happen is the magnetic field generated would be aligned with the magnetic field. As a result, the net magnetic field experienced by the nucleus would increase and hence its Larmor frequency also increases. As a result, another frequency we are applying to cause resonance would also be high frequency. That is the reason we call it as high frequency shift or down field shift. So in this case it is also called high frequency shift and this unhindered circulation of electron density happens when we have the nucleus surrounded

by uneven number of electrons. For example, if we have *p* electrons, s^2p^6 is not a problem, if we have other electronic configuration, in that case, since *p* orbitals are not spherically symmetrical. Unlike *s* orbitals no matter how many electrons are there, p-electrons always generate some hindrance for the circulation. As a result, what happens, the magnetic field generated would always align with the magnetic field and then this is called paramagnetic deshielding. When paramagnetic deshielding is there, we observe high frequency shift or more deshielded, whereas in case of diamagnetic shielding signals are more shielded.

Shielded means the electron density prevents the nucleus from experiencing the magnetic field. Then frequency decreases, Larmour frequency decreases, that is called diamagnetic shielding, and this is called paramagnetic deshielding. That is the reason wherever we come across nucleus having only s electrons in their valence shell, the spectral width is very small because whether you have one electron or two electrons because of the symmetric nature of s orbital, always the magnetic field generated by electrons would be very small and hence we will see either small diamagnetic shielding or small paramagnetic deshielding. As a result, spectral width would not go beyond 1 to 10 or sometime it is 1 to 15, but on the other hand, when we have *p*-electrons, the magnitude of paramagnetic deshielding is enormous. That is reason, in case of nuclei such as ^{19}F, ^{31}P or ^{13}C, we will see a wide chemical shift range. I also discussed several examples, and also many nuclei. Again I will come back at the end to discuss more about the problems.

With this, let me start discussion on UV visible spectroscopy. So here I have shown the electromagnetic spectrum and here lot of information is there. You can see the wavelength in meters is given here. The size of the wavelength is also given. What would happen to the size of wavelength from left to right and common name of wave also given. For example, radio waves, microwaves, infrared, visible, ultraviolet, soft x-rays, hard x-rays, and gamma rays and then the sources of the corresponding frequency are also shown here and frequency waves per second is also shown here and also the energy of one photon in electron volts also given here. it is a very useful slide. Just go through it. Our attention should be towards UV visible and region in the electromagnetic spectrum.

So, this is the range we are going to focus in our discussion on UV-visible spectroscopy. Before we go further, let us again look into the approximate time scale for structure determination with various techniques. As I had mentioned earlier, electron diffraction up to 10 raise to minus 20 (10^{-20}), X-ray up to 10 raise to minus 18 (10^{-18}), UV and visible will be coming in this range 10 raise to minus 15 (10^{-15}) to 10 raise to minus 14 (10^{-14}) and of course later when I take up IR it would be around 10 raise to minus 13 (10^{-}) and ESR is 10 raise to minus 4 (10^{-4}) to 10 raise to minus 8 (10^{-8}). We discussed NMR and also we saw some NMR dynamic process and all those things, fast kinetics would be 10 raise to minus 3 (10^{-3}) to 10 raise to 2 (10^{2}) and for physical separation of isomers, the time scale is greater than 100 seconds. We should be able to visually monitor and visually we should be able to look into the morphology and we should be able to separate, if the crystals have different morphology.

So let us look more in a simpler way to understand ultraviolet spectroscopy. Ultraviolet spectroscopy involves the measurement of absorption of light in the visible as well as ultraviolet region. So visible region, we are talking about is 400 to 800 nanometer, whereas UV region is around 200 to 400 nanometer (nm), so that means this essentially involves the absorption of light by the substance under investigation. Since the absorption of light involves the transition from one electronic level to another electronic level, UV spectroscopy is also known as electronic spectroscopy. What we should do to get a spectrum, that means for recording the UV spectrum, the given compound is dissolved in a suitable solvent and the solution is placed in a quartz cell of path one centimeter, we call it as path length. At the same time, solvent is taken separately in another quartz cell, that is known as reference cell. The sample solution and the solvent are simultaneously exposed to UV and visible radiation in a spectrophotometer. The spectrophotometer operates by comparing the amount of light in the beam that we supplied, transmitted through the sample as well as the reference and then whatever the light absorbed by cell as well as the reference will be subtracted from the light absorbed by the substance to get the actual absorbance by the sample so that determining the spectrum would be easy. So, this is how spectrometer measures the amount of light observed by the compound at each wavelength of the UV as well as visible region. The absorption gets recorded in a chart as

a plot of wavelength of the entire region on the horizontal axis versus the absorbance of light at each wavelength on the vertical axis. That is y-axis, so this is how the typical UV visible spectrum would look like. What is the principle involved in UV visible spectroscopy? Absorption of visible and ultraviolet light results in the excitation of electron from a lower to a higher energy level, that means, when we supply energy in the UV visible region depending upon the gap between the two levels where transition is supposed to occur. That means HOMO highest occupied molecular orbital and lowest unoccupied molecular orbital (LUMO), so each electronic level in a molecule is associated with a number of vibrational sub levels and also each vibrational energy level in turn is associated with a number of rotational sub levels. For example, if we consider an electronic level, say E_o, so it is made up of several vibration levels V_0, V_1 etc., and each vibration level is also made up of several rotational levels, R_0, R_1, R_2 etc., like that. That means when we are performing transition of an electron from one energy level to another energy level it is not guaranteed that the electron will be originating from E_0 V_0 and R_0. Instead, it can go from anywhere between those allowed vibrational levels and rotational levels. As a result, what happens? Same thing happens to the excited state also. Because of the presence of several vibrational levels and rotational levels in the electronic state, and also the energy required to promote electrons from different vibration level is very small, when we look into electronic transition and hence we observe several transitions starting from different vibrational and rotational levels to the excited state. As a result, net spectrum obtained will look much broader. As a result, absorption spectrum contains a large number of lines which are too close together to be distinguished are separated and are recorded in the form of broad bands in the spectrum. For the same reason, UV spectrum looks much broader unlike other spectra. This is how a typical instrument looks like. Here two sources are required to scan the entire UV visible band because we are scanning for both UV as well as visible. So deuterium lamp covers 200 to 300 nanometer (nm), this is for UV region and tungsten lamp covers 300 to 700 nm, this for visible region. The lamp illuminates the entire band of UV or visible light. The monochromator sends the radiation to the beam splitter. The beam splitter sends a separate band to a cell containing sample solution and a reference solution, you can see here. The detector measures the difference between the transmitted light through

the sample versus the incident light and sends this information to the recorder and then we get a plot in this fashion. This is how a spectrum can be obtained. The sampling handling is also very very important, in any measurement for that matter. So, UV spectra recorded in solution phase. Cells can be made of plastic, glass or quartz; preferably glass should be used because only quartz is transparent in the full 200 to 700 nanometer (nm) range. Plastic and glass are only suitable for visible spectra. Solvent should not have conjugated π system or carbonyl groups or any other groups with a pair of electrons. The commonly used solvents are acetonitrile, chloroform, cyclohexane, 1,4-dioxane, 95% ethanol, n-hexane, methanol, isooctane and water, depending upon the solubility of the sample. We can conveniently use one or the other solvents shown here. Then there should be certain rules we should follow while measuring the spectrum, so we have to put together two well-known laws that is called Lambert's law and Beer's law. What Lambert's law says is "absorbance A proportional to the path length of the absorbing medium," path length of the quartz cell we are using; it refers to that one, and then Beer's law says absorbance is proportional to the concentration of the sample. So when you combine together, we call it as Beer-Lambert's law, that says "absorbance is proportional to the concentration as well as the path length". That means for most spectrometers, the path length would remain constant, so standard cells are typically 1 centimeter in path length and concentration is typically varied depending on the strength of absorption observed or expected and epsilon (ε) is molar absorptivity, vary by order of magnitude. For example, if you look into the values in the range of 10 raise to 4 to 10 to minus 6 (10^4-10^6), they are termed as high intensity absorptions. If the value is in the range of 10 raise to 3 to 10 raised to 4 (10^3-10^4), they are termed as low intensity absorptions. On the other hand, if the value is much below like 0 to 10 raised to 3 (10^3), the absorptions are weak absorptions. Very weak absorptions are forbidden transitions. They are due to forbidden transitions. We will be knowing later what are the forbidden transitions and what are the allowed transition. What are selection rules? All those things in more detail, when we go to transition metal complexes. So, absorbance equal to log 10 into I_o over I, that is equal to epsilon (ε). Epsilon, molar absorptivity coefficient, and C is the concentration and l is the path length. This equation is very very important, so here a longer path length, l through the sample will cause more UV light to be observed so the

greater the concentration of the sample, the more UV light will be absorbed. So UV visible spectrum consists of A absorption on y-axis and wavelength on horizontal axis. So now let us look into the different type of electronic transitions we come across in molecules. So electronic transition occurs from HOMO that is highest occupied molecular orbital to the lowest unoccupied molecular orbital, that means we call it as HOMO to LUMO transition. What are the different types of transition we can have: sigma sigma* transition (σ→σ*), highest in energy and then we have n non-bonding electrons to sigma* transition (n→σ*) and then we have pi-pi* transition (Π→Π*), and also we can come across n to pi* transitions (n→Π*). So, energy follows this order; energy required is very high and energy decreases means the gap is decreased. For example, you can see here sigma to sigma* (σ→σ*) the gap is more here. Energy required is very high and then between pi pi* (Π→Π*) is lower npi* (n→Π*). is even much lower. It follows this order which is the typical the energy you can expect for sigma pi and n electrons. This is unoccupied level and this is occupied level. In which compounds we come across this kind of transitions. For example, if you consider all cases we invariably see sigma to sigma* transitions (σ→σ*), and you can see the gap is more here, sigma to sigma* (σ→σ*) the high energy ones and then if you have carbonyl groups, then we can anticipate sigma to pi* transition (σ→Π*). In case of unsaturated compounds, where double bonds are there pi-pi* (Π→Π*) are quite common. On the other hand, if you have in the compound oxygen, nitrogen sulfur or halogens, we can anticipate n to sigma* transitions (n→σ*), and again carbonyls can also show n→ pi* transition (n→Π*). These are the few transitions, we come across in the electronic spectroscopy. You can see here, the energy gap or energy difference or energy required for different types of electronic excitations or transitions and of course the magnitude it gives and also what range energy required. Also, can be clearly seen by looking into the gap between the HOMO and LUMO levels. Among them n to pi* (n→Π*) is the lowest one and then it goes to pi to pi* (Π→Π*) and then n to sigma* (n→ σ*) and the highest energy one is sigma to sigma* (σ →σ*). Let us look into now different type of electronic transition. As I mentioned, sigma to sigma* transitions (σ →σ*) are shown by saturated hydrocarbons in which all valence electrons are involved in the formation of sigma bond, that means, we do not have any lone pairs in the system. These transitions require very

high energy and occur at lesser wavelengths. That means less than 200 nanometer and fall in vacuum UV region, and n to sigma* ($n \rightarrow \sigma^*$); compounds having non-bonding electrons on heteroatoms such as oxygen, nitrogen, sulfur or halogens can show such type of transitions. The energy required for these transitions decrease with the decrease in electro negativity of heteroatom and therefore the wavelength of absorption increases. For n to pi* ($n \rightarrow \Pi^*$), we come across, where we have double bonded heteroatoms like C=O, C=S and C=N double bond, which show these kinds of transitions. These transistors require only small amount of energy and take place within the range of ordinary ultraviolet spectrophotometer. However, the intensity of absorption is generally very low having epsilon values of less than 10 raise to 4 (10^4). Pi-pi* ($\Pi \rightarrow \Pi^*$), transitions occur in compounds having double bonds. The intensity of absorption is very high for these transitions. These transitions have epsilon value of 10 raise to 4 (10^4) or more, and they are called allowed transitions.

Let us look into more details in my next lecture, until then have an excellent time reading about spectroscopy.