Physics of Functional Materials and Devices
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Lecture – 48, Week 11
UV- Vis Spectroscopy

Hello. In the previous lecture, I talked to you about the FTIR technique for characterizing materials. There is another technique which is very commonly used and that is the UV visible spectroscopy. In today's lecture, let us start our discussion on this very interesting and versatile spectroscopic technique. Similar to previous lecture method, we will give you a brief introduction about this UV visible spectroscopy. How do you handle sample? How do you take care of the instrumentation and what are the applications and advantages of these UV visible spectrum which you get for samples.

So, let us start our discussion on another spectroscopic technique that is the UV visible that is ultraviolet visible spectroscopy most commonly known as UV vis. If you look into the definition of spectroscopy, it tells us that you are looking into the measurement and interpretation of the interactions between an incident electromagnetic waves and matter which is characterized by nuclear, molecular or electronic changes or configurations. In NMR what do we do? We use the radio frequency to have information regarding the interaction which is coming in from the magnetic field of the EM wave, EM means electromagnetic waves. So, you take the magnetic component of this EM wave and how they are interacting with the magnetic dipoles of the given atom or particle which are made up of atoms and then you get information about the NMR spectrum.

In UV visible spectroscopy what do you do? During the excitation of the valence electron. So, you know that we have talked to you about the free electron model or nearly free electron model, we have also discussed about the origin of band gap. So, if you have the excitation of valence electrons, the movement of the electronic charges in the molecules will take place. This would mean that there is going to be change in the electric dipole moment. In UV visible spectroscopy, you get a spectrum which is generated by the interaction of these electric dipoles with the electric field of the electromagnetic waves.

So, NMR magnetic dipoles interacting with the magnetic field of the EM wave in UV vis the electric dipoles interacting with the electric field of the EM waves. So, you have spectroscopy here which is classified under two broad headings. Atomic spectroscopy here you get the changes in energy which takes place at atomic level. For example, you get atomic absorption spectroscopy. AS, but you can also have molecular spectroscopy.

What would that be? You can clearly see in molecular spectroscopy the changes in the energy would be taking place at the molecular level. and you use the molecular spectroscopy concepts to have the UV visible spectroscopy or IR spectroscopy measurement technique. UV visible spectroscopy is based on the Beer Lambert's law. This states that the amount of light absorbed by a solution is proportional to the concentration of the absorbing substance and to the path length of the absorbing material. Mathematically you can write the Beer Lambert's law as:

$$A = \log\left(\frac{I_0}{I_t}\right) = \varepsilon C l.$$

Where A is absorbance, ε is the molar absorptivity coefficient, l is the path length of the sample, I_0 and I_t are the intensity of the incident light and emitted light that is transmitted out of the sample respectively. and C is the concentration of the compound. According to this law if ε and l are constant then what you will get A would be proportional to concentration. This is basically showing you a linear relationship. Depending on this relationship you will get what? You will get quantitative data or information about the sample and you can use this information for example, to determine the concentration of unknown sample in a given solution.

This law is successful in describing the absorption behavior in dilute solutions only, because if the concentrations increase what will happen? The absorption coefficient and the refractive index of the sample changes and that leads to the drop in the intensity of the transmitted light. This law is not applicable in the case of suspensions. As scattering of light due to impurities may occur and you may get multiple signals which cannot be deciphered or you cannot have the pinpointed information regarding the scattering centers or the place from which the signals are originating. fluorescence or phosphorescence processes can occur as they can take place in the same wavelength range as UV visible. Hence, you should have strict adherence of an absorbing system to this law only when radiation used is monochromatic.

So, what you would be using? You would be using a monochromatic source. Let us take an example to explain what we have been saying. So, you have an unknown sample. What you do? First you take 4-5 standards of the unknown concentration analyte and measure their absorbance at specified wavelength. Prepare a calibration curve.

So, you plot absorbance as a function of concentration. You will get certain data points. You are expected to see a linear relation as we see here from the Beer Lambert's law. Epsilon can be obtained from the slope of the calibration curve given for a given wavelength and what will that give you will have the concentration of the analyte in the sample can then be easily obtained from the calibration curve using the Beer Lambert's law. So, very simple you can easily find out the calibration curve and then from there you can get the information about the concentration.

As mentioned earlier you should have very dilute solutions to carry out the meaningful experiments. In addition, the sample which is dissolved in some suitable solvent should not by itself start absorbing radiation in the region under investigation. Hence, you must choose the solvent carefully. Commonly used solvents are cyclohexane or 1,4-dioxane, water or 95 percent ethanol. In addition, suppose you take a solvent which is reacting with the sample, then the property of the sample will change.

Hence, the chosen solvent should also be inert to the sample. So, you do not want any modifications in the nature of the bonding or the dipoles which are being analyzed by the spectroscopic techniques. What would be the typical instrumentation? You will have a light source, then you will have a monochromator and what other thing you must have a reference cuvette because a cuvette where you would be putting the solution. So, you will have a reference cuvette and a sample cuvette. So, that you can take out the contribution of the cuvette if there is any from the final spectrum which you are collecting.

For visible light, cuvettes made up of PMMA, polystyrene or normal glass is quite ok. For UV light, you have cuvettes made up of quartz glass or special types of plastics. What would be the fourth ring? You will have detectors. These would receive the signal which is coming out of the sample and the detectors mostly having the photo multiplied tube based functioning. If you look into the block diagram of the UV visible spectrometer, this is the typical block diagram of the UV visible spectrometer.

So, you have the reference cuvette and the sample cuvette and then the signals which are coming out are being received by the two detectors and you can just remove the signal which is originating from the reference cuvette. and the remaining signal would be from the sample in the sample cuvette. This is a typical UV visible spectrophotometer and you have the sample stage inside the cavity which is enclosed by the shutter. If you open the shutter it looks something like this. Let us see how you have the signal being analyzed.

So, you can see you will have the light coming out and then hitting the sample. So, now, if this is your sample solution then you insert it. in the sample stage, then you close it and you switch on the UV source, it will generate UV waves which will hit the sample and then that would be received by the detectors and you can analyze the spectrum. So, this is what is basically happening. As I mentioned in the previous lecture also, here also you should keep the instrument switched on for at least 15 minutes or more so that the deuterium lamps and the tungsten halogen lamp are warmed up and when you switch on you have the desired intensity and wavelength.

After you define the parameters, the wavelength which needs to be scanned, then you have the scan range, what should be a steps at which the data should be collected, then you just need to give the details about the sample, the name and after the parameters have been defined, what you need to do? We need to start the nature of scan which is to be initiated.

Once you define the way you want to see the screen you just press the start button and you will see that you will get the spectrum. So, you have the absorbance versus wavelength curve. So, you can clearly see the wavelengths at which the sample is absorbing. Once you have completed the data you can then analyze it.

One of the most common examples of the UV-Vis spectra is to determine the band gap using the tauc relation. What you do? Here you assume that the energy dependent absorption coefficient which is alpha can be expressed by the following equation. That is:

$$\alpha h\nu^{\frac{1}{2}} = \beta(h\nu - E_g)$$

Where E_g is the band gap, h is the Planck's constant, ν is the photon frequency and β is a constant. The factor n depends on the nature of the electron transition. n is considered to be equal to half for direct band gap and n is equal to 2 for indirect band gap.

So, what do you do? You collect the usable spectrum in a given range and then you plot for direct band gap materials a plot between $\alpha h\nu$ square versus energy and a fit a linear line. the intercept will give you the band gap. For indirect band gap plot $\alpha h\nu$ raised to the power of half versus h nu and perform the fitting the intercept will give you the band gap. Let us see what you have to do. So, this is a typical graphitic carbon nitride gC_3N_4.

You have the energy that is $h\nu$ that is equal to $\frac{hc}{\lambda}$ energy in eV is equal to $\frac{1240}{\lambda}$. You need to plot alpha αhν square as a function of energy. So, what you do get? You get a curve for the same figure this is the corresponding graph which you will get you get this linear region, extend the linear region to the x axis, the point it intersects is going to give you the value of band gap. So, now, you can clearly see that determining the band gap of semiconductor materials is an extremely easy process. If you have materials which are having different band gaps, what you will do? You will just collect different UV-Vis spectrums because each will correspond to one material.

Plot these curves and you will be easily able to carry out the linear fitting and that will give you the value of band gap. So, determining the band gap is an extremely easy method. You can extend the application of UV visible spectroscopy. to understand the presence or absence of saturation, unsaturation or other functional groups or even hetero atoms in various organic compounds. In the field of nanotechnology this technique is used to determine the color absorption properties of metallic nanoparticles or you can also use them as a detector in HPLC that is high performance liquid chromatography. Now, if the system is continuously changing its nature, then by monitoring the UV vis signal you can analyze the chemical kinetics. which is commonly used while you determine the catalytic properties of materials or you can use these techniques to estimate the concentration of let us say any proteins in DNA or you have nucleic acids in various biologic samples you can determine those concentrations using the UV Vis spectroscopic data. Hence, this technique

has become one of the most fundamental technique for carrying out qualitative as well as quantitative analysis of samples. One of the most common use of this technique is to determine the band gap in semiconductors.

To have more understanding about this topic you can see and go through these references and I thank you for attending lecture number 2 of the final week of this course. Thank you very much.