Physics of Functional Materials and Devices
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Lecture – 47, Week 12
Fourier Transform Infrared Spectroscopy

Welcome to the first lecture of the final week. I hope you have by now got a feel of the topic of functional materials and in the last lecture of the previous week, I had started discussing the characterization tools which are routinely used to determine the properties of these functional materials. we started our discussions from a very common, but important characterization technique that is X-ray diffraction. Let us continue our discussion on characterization tools useful for us for the kind of materials that are being explained in this course in today's lecture. In today's lecture, I will introduce to you another important technique that is Fourier transform of infrared spectroscopy. For that we will start our discussions from IR spectroscopy.

What is IR spectroscopy? You will see that to obtain this spectrum using an IR source. You use Michelson's interferometer and that gives you certain interference patterns which have significant information about the material being investigated. What is the mechanism behind the FTIR spectroscopy? Why do you need to take the Fourier transform? and you must also know how does an FTIR instrument looks like, how do you prepare the samples which have to be investigated using the instrument and what is the typical way you get the data. In the end you will also see the applications of the data which is analyzed using various protocols and how it becomes important.

We started our discussion in the previous lecture with the introduction to some of the important characterization techniques that are used for materials. In the previous lecture, I had focused on X-ray diffraction. If you want to have the magnetic structure or you want to determine the displacements of lighter atoms even in presence of heavier atoms, then we tend to go to neutron diffraction. And if you have the need to determine the structure even at much smaller dimensions, then you go for electron diffraction. In today's lecture, let us discuss on one of the important spectroscopic techniques that is FTIR and may be in the third lecture of this week, I will then discuss with you the SEM and TEM.

If you look into the spectrum, then what do you have? You see you are mostly concerned about the ultraviolet radiations, the visible radiations or the infrared radiations. and these are the typical wavelengths which are associated with these radiations. Now, if you have the radiation we had seen that if a radiation is incident on a sample you can have emission or the radiation can get absorbed or you can have emission of additional radiation from

the sample and each of these parameters will give you information about the material. So, one of the major use of FTIR comes to determine the nature of vibrations which are stabilizing in the lattice made up of atoms what are the possible functional groups which are there in a given sample and what is happening to the nature of bonding if you change the structure of the material or you change the temperature or you change the water content or if any of the parameters which are expected to change the property of materials, if those are changed what happens to the vibration of atoms and how that is analyzed. If you have the infrared light what will happen? You have a photon with is incident on the sample.

Now, if you have this then you will find that this energy is going to be impinged on the sample. If that is the case then there are various types of motion which are there in the atomic arrangement. You can have symmetric stretching. So, both the atoms are moving away from the atom which is kept at origin or you can have anti symmetric stretching or you have the bending of bonds. Each of these things mean what? If you look into the lattice, it is basically the atomic displacements which you are familiar with.

And the nature of these stretching or bending modes will give you an indication regarding the nature of displacement in a given lattice. And that will give you what is happening to the material if it is being modified as a function of doping, as a function of pressure, as a function of temperature or any other parameters like stress. or you have electric field or magnetic field applied to it. Hence, you can use the IR source which is incident on the sample and then collect the transmitted light using a detector and you will get the information about the sample. you have two types of IR spectroscopy, you have the dispersive and the FTIR spectroscopy.

In them to carry out these measurements basically you are using an optical system, it must have a source the sample compartment where will you will install the sample which needs to be analyzed. then you will have a detector which will collect the signal which is being generated by the sample. And finally, you should have a processing unit which will collect the signal which was being generated by the detector and then process the data and give you meaningful information. FTIR as we said we have a Michelson's interferometer which records the spectrum as you are using Michelson's interferometer. So, you have improved signal to noise ratio.

Improved signal to noise ratio means that you have low noise and as you are looking into the phenomena of interference you can have very high intensity spectrum with clear peaks which can be analyzed. And then if you take the Fourier transform the features become even more clear and you have better resolution and the capability to infer from the data which was collected. How does a Michelson's interferometer basically looks like? You have a sample, you have the source, then you have the fixed mirror and the movable mirror. So, that you have the movable mirror. So, that you can compensate the path difference.

So, you are not using a compensator in the reflected rays, but you are just having the movable mirror. So, you have the rays which are then reflected from two sides the fixed mirror and the movable mirror and from there what you do these from the. reflected beams which fall on the sample they generate a signal which is collected by the detector and that is fed into the computer. So, typical Michelson's interferometer. You have the various sources which can be used which generate the IR signal.

Then you have the arrangement for Michelson's interferometer, then you have the detector and before that you have the sample which is used. What will happen? If you have the detector which is detecting the transmitted wave, it will give you an interferometer. The Fourier transform of the time domain will be for a signal which is a function of time is given as:

$$G(f) = -\int_{\infty}^{\infty} g(t)e^{(-2\pi if)t}\,dt$$

Now, the resulting signal at the detector will appear as a spectrum and you can scan up to various wave numbers. So, let us say from 4000 to 400 centimeter inverse. All the signals which you will obtain will be representing a molecular finger print of the sample.

What is the driving force here? You are seeing interference of two virtually coherent source which you were obtaining using the Michelson's interferometer arrangement. If you have two virtually coherent source that means, either you can have constructive or destructive interference patterns and this can change depending upon the path length and that will be impacted by the arrangement of the atoms and the way the atoms come in the path of the rays which are passing through it. So, if you have constructive interference you know that the path difference would be either 0 or integral multiples of lambda. Destructive interference you will have the path difference as lambda by 2 or in you will have 3 lambda by 2, 5 lambda by 2 or (2 n +1) lambda by 2 and the rays will cancel each other and you will have minima. So, if you perform these FTR spectroscopy or for example, of ethanoic acid, you can clearly see that you have various peak which you see and they are appearing at different wave numbers.

By understanding the functional groups which are there in ethanoic acid, you can clearly correlate that for example, single bond CH would be giving signal between 2850 to 3300 centimeter inverse. Similarly, you can have the double bonded CO or you have the alcohol groups OH or the acid groups which have a very broad peak between 2500 to 3300. So, just by having this spectrum and knowing the bond structure you can clearly find out what would be the typical wave numbers around which the spectrum would originate. And if you see what are we doing? Let us say we have C and H, you consider two masses mA and mB. Now, they are effectively connected by a spring this is what you have the phonons.

Hence, the factors which would affect the peak intensity would be the mass, the bond strength, the dipole moment, the electronegativity. Wave number is what is equal to $\frac{1}{2\pi c} \times \frac{f(m_A m_B)}{(m_A + m_B)}$. This is effectively the reduced mass. Wave number will also depend on the bond strength f which is basically the force constant that is coming in from the phonons and the wave number is calculated according to the Hooke's law. So, this is what you simulate and if you have these atoms which are far away then obviously, the bond strength would be different if they are very near then the bond strength would be different if you have different arrangements of atoms which are connected through different springs, then the bond strands would be different and that is why you can clearly see that the nature of the spectrum would get changed.

You must realize that you can have either the stretching or the compressing nature of the bonds. And you will have certain bond structures which will be IR inactive. You need to have dipoles to have the IR signal and if you have that then you will have the IR active molecules. If you have the samples now what do we do? How do we find out what is happening to a given material which is unknown to us or we try to find out the nature of stretching and bending bonds in them. This is the typical FTIR instrument.

You have the compartment in which the sample has to be placed. Then you have the source and you have the detector. This is your typical sample holder. you cannot just put a powder there. So, for that you have the die set which will make the sample.

You use KBr as the matrix in which you will disperse your sample. So, that you have a transparent pellet through which the signal can be sent and collected at the detector. to make the pellets you have the hydraulic press. Let us see what happen, if you have this these are the process by which you will make the sample to be placed in the sample holder of an FTIR instrument.

So, first you take the KBr. then in a mortar pestle then you take your material which needs to be analyzed. You have to drop minimal amount of sample in this KBr powder. So, that you do not disturb the transparent nature of the pellet which is required, but you have dispersed your sample which here you saw was black. So, it was opaque, but then also if they get dispersed in matrix which is made up of KBr. So, if you run a spectrum for KBr and then you have a spectrum with KBr and your sample in it, then you can just subtract the signal which is expected from a KBr, spell it and you will get a resultant that is coming out from your sample.

Then you crush it make it into a fine powder why do you need to make it into fine powder otherwise making pellets would be difficult and you will not get a stable pellet which can be placed in the sample holder. This is a typical die press machine setup. So, you have the die, then you take the base insert it put the powders in between and then you put in the plunger. So, now, you have the base then you have the powder and then you have a plunger

and that will go from the top and now just rotate it slightly. So, that you do not have the rough surface at the bottom.

Then you install the O-ring and then put this die in the load press. you have the piston which comes down from the hydraulic load press, you must ensure that the center of the piston is exactly coinciding with the plunger otherwise if you will have load which is not coming down directly and you may break the plunger and then you apply load. once you have applied the load. Leave the sample for certain time so that the shape is obtained and finally, what you will get is the pellet which can be installed in the sample holder. So, this is the way you install the sample in the sample holder of the IR machine.

It is now ready you can clearly see that it is transparent and now you just have to go and put this sample holder in the sample compartment. So, from one side there would be incident line and from the other you will get the transmitted beam. This is what we have done and you can clearly see the same thing in this figure. Please note that one of the trickier things this technique is how to make a sample, but once you practice you would be able to make the samples quite easily. You need to have transparent materials for cuvettes or you will have to use the systems in which these samples are being sandwiched and those need to be made up of transparent materials.

So, after you install the sample, then light will come in and the IR signal would be then received from the detector. Close the sample compartment and then you need to start the experiment define the experimental parameters. The system would then check the apparatus first at all the parameters have been defined, the light source is aligning with the detector and then only it will start the measurements. In most of these instruments you must remember that you must switch on these instruments at least half an hour to 45 minutes before you start taking the data. So, that the components are properly functioning and you do not have any component which is not working because of thermal effects.

So, the system has reached a thermal equilibrium and then only you start taking the data. You can define the range the nature of radiation and then you can just start the measurements and what you will get is a typical spectrum like this. Once you modify the background, you perform the background analysis you will get a much smoother curve. and that would be giving the signal that is correlated with your sample. So, then you will get the data which is to be analyzed.

This is a typical example of what you get for ethylene carbonate and dimethyl formides and you can clearly see that you have various peaks and those are correlated with different symmetric and asymmetric stretching or bending modes. Because of the flexibility of this technique, it is used in various places from functional group identification to drug cell interaction to determining the purity of a material or metal complex nanoparticle interactions. You can have structural determination in small molecules to determining the

effect of additives in polymer matrix and many more. The advantages are that it is simple, you have fast data acquisition and lot of applications are there. But the problem which are associated with FTIR is molecule must be active in the IR region, you must test the transparency of these materials in the spectral range of interest and you get minimal information about the elemental concentration of the sample.

Therefore, as you change the arrangement of atoms in the material you have different FTIR signals and then you can easily find out what is the nature of displacements or atomic arrangement in the given material and that will give you many more information about the stretching or bending modes that can give you information about the bond strengths and nature of bonding and from there you can then move on to calculate the lattice energies. Hence, FTR has become a very important experimental tool for materials characterization and the protocol to collect data and analyze the same are now well understood and you can use it quite easily. To have more information about this technique you can look into these references which will more understanding about the topic and the technique of FTIR. So, thank you very much for attending lecture number 1 of week 12.