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Lecture - 53 Raman Spectroscopy of Carbon Materials

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Hello everyone.in this lecture, we are going to discuss Raman Spectroscopy which is yet another very important tool for understanding carbon materials. Raman spectroscopy is often used as a supplementary technique or support technique with x-ray diffraction when it comes to large-scale carbon materials when we want to understand for example, how a carbon material is converting from disordered carbon to how it is gaining more order or graphitic content. But in the case of nano-scale carbon materials, it is sometimes even used as an independent characterization technique.

Why? because when we have single-layer graphene or bilayer graphene or multi-layer graphene, it's very difficult to separate them, to differentiate between them. Even the transmission electron microscope may not give you the information that is reliable.so there is a possibility of error in multiple techniques. But Raman spectroscopy is the only technique that can very nicely tell you the difference between single and bilayer

graphene. In fact, there is a significant difference between the peaks, the intensity of the peaks that you get in Raman spectroscopy; so in that case it is used extensively.

In this lecture, we might not go too much into the details of the Raman spectrum of graphene. I will tell you the fundamental things, but we may not go into too much detail because the materials that are more important in this particular course are the bulk carbon materials.

So, we will be focusing more on the Raman spectrum of graphite and of disordered carbons and the origin of some of the peaks. Let us see how much we can cover and how much we can understand. So, we start with the very fundamental aspect. What is the fundamental principle of Raman spectroscopy, which is known as the Raman effect.

What is Raman effect? Well, molecules are always vibrating. You probably know this, it is not that they are stationary, it is not that if you have six-membered during that is just always staying like that.no, it is always vibrating.

So, whenever we provide some energy using let us say a photon then we are actually interfering with the natural vibration. So, there will be some natural frequency of the vibration for every molecule which is the characteristic of that molecule of that material, which is dependent on not just the chemical structure, but also the geometry of the crystal and so on.

That is what actually gives you the information about the molecule. So, molecules are vibrating with a certain energy and we now provide some external energy using a photon. So, we are sort of interfering with the vibrational modes of the molecule. And because of that, some electrons get excited to a higher energy state and then they come back. When they come back they lose some radiation. That is what we measure, that is what we basically call Raman spectroscopy.

So, this is the fundamental principle. So, let us try to understand this with a simple diagram. So, I have drawn these three lines here. These are basically your states of the electrons. So, 0 is the ground state. There is energy; your electron is sitting at the ground state.

And there is this some virtual state, I will tell you what is the virtual state, but before that let's provide some energy to the electron. How do we provide energy? We take a laser that has some photons. And then this energy is provided to the electron, it takes some of it. And this interference with the vibration, we will also learn a little bit more about that.

Now, this electron goes to some state that we do not know and that is why we call it a virtual state. Basically, a virtual state is also not just one state, it can be multiple states. The idea is that we do not exactly know that what is this because it goes up a little bit. It can be little bit here, little bit there, but there is some sort of band of virtual state.so this is where our electron goes and now it comes back.

When it comes back without losing or gaining any energy then we call it Rayleigh scattering. So, you will also get Rayleigh scattering from the molecule, in fact, that is the more prominent one. So, this is known as Rayleigh scattering, but you can imagine your electron did not come back to its original ground state, but rather it gained some energy. So, it came back, but to a slightly higher energy state.

What also can happen is your electron actually gave some of its energy to the photon, so it lost some of its energy and it now came back to even lower than its ground energy state. So, both of these scattering pathways are also possible they are known as Stokes line or anti-Stokes line, also known as Stokes Raman anti-Stokes Raman because this is what you know.

The idea of Raman effect is that we can measure these Stokes and anti-Stokes lines and we also can measure this difference in the energy. So in fact, whatever is the addition, whatever is the gain of energy in the case of Stokes lines; pretty much the same is the loss in the energy in the case of anti-Stokes line.

And how do we measure this ΔE , this difference in energy? Well, we can measure one of the two lines and we know the energy of the ground state atom that we know. The energy of the Rayleigh scattering that we know how? Because that is same as the energy that you provided by the photon.

So, you see that there is no change in the state of the electron then basically whatever energy we provided is the energy of the Rayleigh scattering. So, this is the fundamental principle of Raman effect. So, well I told you all molecules vibrate. So, now, what are we exactly doing here? We provide some energy using the photons, but these photons would actually change the polarisability of the molecule.

So, polarisability is a property I hope you understand. I will also provide some references later on, but what we are doing is we are actually changing, we are playing with this polarisability. When we change the polarisability what happens? This induces a dipole moment so this is an induced dipole moment.

In some other spectroscopic techniques, you just have a dipole moment, but here we are inducing it and because of this there are some radiations that is what we gain. Because of this process that is happening, the excitation of the electrons and coming back of the electrons because of this induced dipole moment.

We get some of these radiations which could be in both Rayleigh and Stokes and anti-Stokes region. So, this is what we get. Now we get a lot of scattered radiations. And what we can do is we can have a filter, so this is a basic schematic of a Raman spectrometer.

So, you can have a filter where you can now get rid of the Rayleigh light, anyway we know that this is the same energy as the excitation energy. So, that we can filter out very easily and then whatever we can plot Stokes and anti-Stokes.

In some cases, some molecules will give you more Stokes line some will give you more anti-Stokes line that again will depend on the characteristic of the material and then we detected and we plotted and that is how we get the Raman spectrum. You will also often hear that this is a form of inelastic scattering, Raman scattering itself is inelastic.

So, what do we call elastic and inelastic if you think in terms of collisions when two balls collide? If they do not lose any energy then we call them elastic and if they lose some energy then we call it inelastic. Here, there is no collision or anything, but in the case of Raman spectroscopy or Raman effect you either lose or gain some energy. So, this is known as the inelastic scattering.

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Raman Spectrum of Graphite

- Single-crystal graphite has D_{6h} symmetry with 6 vibrational modes: $2E_{2g}$, $2B_{2g}$, E_{1u} , A_{2u}
- E_{2g} modes are Raman active. The first E_{2g} mode gives a peak at low wavenumbers (42 cm⁻¹). Second
 E_{2g} mode is responsible for the G band at 1581 cm⁻¹.
- G' band at ~2724 cm⁻¹ resulting from a higher order two-photon process.
- The electron gets excited but stays in a real state within the π -band. When it recombines, there is Stoke/ Anti-Stokes type scattering.
- G' band is also considered a second order (overtone) of the D band, hence sometimes called the 2D overtone. In principle, there are minor differences in G' and 2D peaks.
- Although G band has a strong presence in graphite, it is present in all sp² sites (e.g. chain-like molecules, polymers etc.).
- Raman spectra of carbon materials generally dominated by the *sp*² sites, because the excitation wavelengths used in Raman spectroscopy resonate with the π-states. (Exception: UV)



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Now let us move on to the Raman spectrum of graphite. We will first talk about 3D graphite as we always do and because all of our materials are related to it. So, all of you probably know that graphite single crystal has a D_{6h} type symmetry. What you may not know is that it has different vibrational modes so there are 6 vibrational modes there are $2E_{2g}$ modes.

So, I will not go into the details of the explanation of these modes. But you can probably from chemistry courses or from chemical spectroscopy courses you can definitely learn more about the symmetry in molecules. So, we have $2E_{2g}$ modes.

And this I have written with the bold letters because these are the modes that are Raman active. Basically, your molecule will have different types of vibrations, but not all of them will actually give you the Stokes and anti-Stokes type of scattering.

Some of the modes are known as Raman active and these are the modes that are allowed in Raman spectroscopy. So, these are the 6; so, $2E_{2g}$ modes, $2B_{2g}$ modes, E_{1u} and A_{2u} . You can read it from here. So, these are the vibrational modes. Now, we come to how our spectrum looks.

So, these E_{2g} modes are Raman active so that basically means they will give you some Stokes or anti-Stokes line. The first E_{2g} mode also gives you some spectrum, but that is at very low wavenumbers. What is the wavenumber? That is an inverse of your wavelength and typically we write it in the units of cm⁻¹.



you can also use any length unit. You can call it nm^{-1} , but the convection is that we write it in cm⁻¹. So, now the first E_{2g} mode also gives you some spectrum, but that is at very low wavenumbers; 42 or something, this is very low.

And we typically do not see it in a Raman spectrum. What we do see and that is what is known as the signature peak for graphitic carbons in Raman spectroscopy, is the another the second E_{2g} modes. The intensity that is the result of the second E_{2g} vibrational mode gives you what is known as the G band; at approximately 1581 cm⁻¹.

This is called the G band because of the fact that it is a characteristic graphite peak. So, for G people often use the term graphite band. So, this is the G band which you will pretty much always see long as your material is even slightly graphitic.

In fact, sometimes even if it is very highly disordered and very little graphitic content is present still you will see this is a very dominant peak, so you will see it. So, how do you get this peak? So, we were talking about the vibrations of the molecule, so this is how they will.

So, this is one 6 membered ring and you see these red arrows; this is sort of a translational motion and this is how your molecule vibrates. What is very interesting about this peak is that, even though it is called graphitic peak and it is a signature of graphite. This is actually present in all sp^2 carbons. It is actually a characteristic peak and this kind of vibrational mode is characteristic of sp^2 type carbons, sp^2 sites. When we say sp^2 sites; that means, there as some sp^2 hybridized carbon atoms connected to each other.

Basically, any sp^2 site, even in polymer will give you this kind of vibrational mode. So, you do call it graphitic, but it is not necessarily, just because you would see this band that does not mean you have graphite in your material. So, turbostatic carbons definitely will give you some graphitic, some G band.

Even anything that contains these chain like structures which have sp^2 sites, sp^2 hybridized atoms will actually give you this G band. Now, there is another band which is rather found in graphite and graphene-like carbon. This is more in the purer the materials that are closer to graphite.

You will also see them in disordered carbon, but not in highly disordered carbon, you do not see this peak. So, this is at around 2720 cm⁻¹. This is what sometimes called that the higher-order peak or the higher order D band, I will tell you what it is. This is the peak which is very interesting.

We call it G prime. We also sometimes call it 2D overtone and overtone basically means second order in the context of Raman spectroscopy. So, this is also sometimes known as the second-order because of the fact that it is a 2 photon process, unlike the other processes. So, this is a 2 photon process and this is also something that you observed in your graphite Raman spectrum.

So, this is how it kind of looks. This is a hand-drawn spectrum so do not expect accuracy here. But, just to let you know that at 1581 you have the G band and that is often in the case of graphite; definitely it is very sharp. And often it has a very high intensity compared to most of the other bands and then 2720 or 2724, you will get this relatively shorter.

But still sharp enough peak in the case of graphene and graphite, so when you have less disorder in the material fine. So, basically what is happening here? Especially, why we can also get some very interesting results for graphene-like materials and also graphene is again because of pi band.

So, our pi band and the unhybridized p orbital and the electron in that p orbital and the fact that it is delocalized and it forms an electron cloud that is I told you therefore for most of the interesting properties of graphitic carbons that is the band or those pi electrons are actually responsible.

So, definitely also in this case of Raman spectroscopy, it becomes even more important because Raman spectroscopy really deals with excitation of electrons, the movement of electrons, the vibration of the overall molecule. So, there the fact that we have this sort of delocalized pi band present that can influence the virtual states of the molecule of your electron.

In fact, in some cases when we are talking about this G prime band; the electron does not even go into a virtual state, it remains in the real states. So, whatever energy, the electron gains rather than going very high up in the virtual state what it does? It gets lost in the cloud, it goes to the real state of let us say a neighboring atom or within the pi band.it stay there and then it comes back.

So, it is staying in the real state not going into the virtual state at all and that is why we call it G prime band and that is also when people want to differentiate between G prime and 2D overtone. Then the primary difference is that if you call second-order process, but you still are thinking that the atom or the electron is going into the virtual state.

But that is not the case, it is not going into the virtual state. It just goes into another real state and comes back and that is why it is more accurate to call it G prime. There are minor differences between these two bands G prime and 2D. But these are the things that are still being investigated.

So, yeah here is what happens. The electron gets excited but stays in the pi band. So, this is something specifically I am talking about G prime band, not all other peaks, this is particularly about this 2 photon process. And now what we get from here? So, when this the electron, which went into some other real states, but it did come back and when it came back then we had some Stokes or anti-Stokes lines.

And that is what we could measure and that is the reason we get this second peak. Now, this is something I already told you that G band does not really mean that you have graphite in your material and you will see it from all the sp² type sites, sp² type of carbon materials.

Another interesting thing about the Raman spectrum of all sp^2 type materials is that, even if your material has a reasonably high degree of disorder or let us say you are trying to do Raman spectroscopy of some diamond-like carbon film. So, in the case of diamondlike carbon we have both diamond and graphite type of sites. So, you have sp^3 and sp^2 sites. In fact, Raman spectroscopy is often used for differentiating between sp^2 and sp^3 sites. Even in those cases when you have a significant amount of non sp^2 sites; this spectrum is often dominated by the peaks that are generated due to the sp^2 sites. So, this is something very important and this is something very interesting, that is why a lot of studies are going on to understand that sometimes even when we have very little disorder. So, we should not see any peak for disorder still we see it. Similarly, at the same time when we have very little graphitic content in the material which is a highly disordered material still, we do see a peak for the G band with intensity that does not linearly decrease. So, these are actually very interesting things about the Raman spectroscopy or Raman behavior of graphite.

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On this slide, now you can see the different vibrational modes of graphite and also those of graphene, you can also call these phonon modes. The red arrows show actually what are the directions in which the atoms moved and that is why you have this overall vibration.

So, I have drawn this image from this review article from Andrea Ferrari which you should definitely read. I will also provide towards the end some other reading material because you see we cannot cover all the aspects, especially the aspects related to graphene and the physics behind it. We cannot cover all of them in this particular lecture.

So, the interesting part is how the vibrational modes of graphene and graphite are related. Because we initially started learning about graphite and then we moved on to graphitic or disordered carbons. So, we have not yet talked about the disorder. So, we moved on from graphite to disordered carbons to carbon nano materials and that is because all the vibrational modes of these graphene layers are connected.

Because you see on the left-hand side how the graphene vibrational modes give rise to a large scale vibration in your ABABA crystalline. Probably from these images you can

also understand there are certain modes that are only in plane. So that are only related to your basal planes while there are some other planes which have also 2 layers connected.

So, A and B layers connected, somehow there is a influence. So, which ones will you observe in non-graphitising carbons or turbostratic carbons and which one you should observe only when you have perfect graphite present. So, these are the different vibrational modes now; not all of them are active in Raman spectroscopy.

So, some of them are also active in IR; infrared spectroscopy. So, what is by the way, what happens in infrared? We have not discussed that. Sometimes you will perform infrared spectroscopy to understand the surface functional groups on let us say activated carbons.

So, what happens in the case of IR is that you remember this from the previous slide you remember that we have this energy level 0 and we have energy level 1 and -1 and so on. So, if the molecule just absorbs the energy of the photon and goes to level 1 from 0 and then nothing happens nothing; no radiation, nothing comes back.

Why because the molecule has actually absorbed the radiation. It has just gained that energy. So, that is what happens in the case of IR spectroscopy and that is why also it is sometimes called IR absorption because the molecule actually or the electron actually absorbs the energy of the photon.

So, what is also interesting is that in the case of a symmetric molecule or when you have the centre of symmetry present in the case of such molecules, not just graphene or graphite, but any other molecule; as long as you have the axis of symmetry present, the modes that are active in Raman spectroscopy are not active in IR and also the other way around.

So, in the case of graphene you see that you may have both IR and Raman activity, but when you have graphite then some modes are IR active, some modes are Raman active and some modes are also active in both, but in that case, you do not have the axis of symmetry present.

Now, you can see these different modes. We also already discussed that only E2g modes are allowed in Raman. So, you I have shown it with the circle, so these are the two

modes that are allowed in Raman spectroscopy. So, this is something we already discussed that you can use Raman spectroscopy to understand graphene.

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Raman Spectrum of Disordered Carbons

- The Raman spectra of disordered carbons show an additional peak: the D band at ~1350 cm⁻¹.
- This is assigned to the zone center phonons of E_{2g} symmetry and K-point phonons of A_{1g} symmetry (breathing mode).
- The position of this band changes with the excitation wavelength, i.e., it is dispersive.
- This mode is activated by six membered rings.
- The term D is often connected to disordered or defect band. Originally this was considered diamond (hence the D).
- D peak can arise from various types of non sp² sites including sp³ sites.
- The ratio of the intensities of the D and G peak can typically indicate the change in graphitic content of a carbon.
- Raman spectrum can also be used for La calculations but the methods are crystallite size dependent.
- Peak integration is challenging and is influenced by the fit parameters.



Now, we come to the disordered carbons. Disordered carbons are interesting to us. We do not always have graphite when we are doing manufacturing. It is rare to have perfect graphite. So, we understand again the effect of heat treatments using Raman spectroscopy. This is very common, how do we do that?

Now, we need to have some additional band which shows that your material is disordered. It turns out that we do have some other additional peak which is a result of the disorderness in the material. We call it the D peak and it comes at around 1350 cm⁻¹, may not always be at 1350.

This band we call it D band and often the term D is related to disorder. So, you can call it a disorder band. You will also read the term defect band, actually it originated from diamond, but it is the D band. Now, this band have been studied a lot, the origins of why we have the D band.

Because it does not shift its position, its intensity does not linearly increase with the increase in disorder. However, in certain region you can have relatively linear increase in

the intensity, but there are interesting things about the D band which we probably still do not know all of them.

This is known as the A1g breathing mode. So here I have shown this is the motion of your atoms in the hexagonal rings. So, this is what is your breathing mode and this gives rise to the D band. However, what is very interesting that this D band is activated by the presence of hexagonal rings which means that if your material is 100 percent disordered, which is a hypothetical situation, does not really happen to manufacturing material at least. But if your carbon were to be 100 percent disorder let us say it can also be diamond which does not have any 6 membered rings it is not disordered, but it does not have sp2 type or 6 membered ring structures.

In that case you will have no D band in principle and that is why it is also not correct to call it diamond band, but this is the history, this is how it started. The point is that this mode is due to the presence of non sp2 sites, but it is activated by the presence of sp2 sites and that is the reason also, it does not necessarily linearly increase all the time because there are two factors that are influencing it.

One is the presence of disorder and two is also the presence of graphitic regions or sp2 regions. This mode is known as dispersive or it is dispersive. What does it mean to have a dispersive mode in Raman spectroscopy? If you change the wavelength of the excitation laser then in that case the position of the D band changes that is what we call dispersive band.

The most common wavelengths that are used for excited excitation in the case of Raman spectroscopy or between 500; so, 515, 514.5 nm and 632 nm are the most common ones. So, if you move from 515 to 632 in that case the position and even the intensity of your D band can change; that does not happen to the G band. G band remains there, but this particular band is dispersive.

But there are exceptions, this does not happen so much in the case of UV excitation, so the entire process slightly differs when you have UV excitation. So, often you do not use UV, but if you want to understand your material or you want to also understand Raman spectroscopy itself then you might want to use the UV excitation, probably you can even go to higher energy excitations.

a typical spectrum of a disordered carbon would look something like this. 1350 and 1580, 1581 that is what you have basically these two prominent peaks, you will have in your material. So, D band and G band are often merged. So, this spectrum could be of a glass-like carbon, this could be also of an activated carbon or porous carbon or some type of even diamond-like carbon films can also give you this kind of spectrum.

So, the two peaks are quite merged together and it is difficult to separate them, but this is what you see as the signature peak. There is also the second order. So, I have shown this in the first order and second order peaks and that is why I have separated them. So, the second order will have your G prime or the 2D overtone peak around 2700. So, this is the overall spectrum.

I told you that initially because non sp^2 sites will give you the D band, it was call the diamond band, but now we call it the disordered band. You already know that anything that is non sp2 can give rise to the disordered band.

So, it could be sp^3 sites as well it could also be any non sp^2 sites. We know that in our carbon materials we have these sp^{2+n} type hybridization, also in that case also you can get this kind of peak.

Now, I told you that what is challenging here is the integration these 2 peaks because these 2 peaks are often merged. So, you need to use certain software and then you need to sort of fit these curves. And the fitting parameters can actually make a lot of difference.

Because in order to understand the increase in graphitization, the one important parameter that you use is the intensity difference between the D and the G band so that is known as ID/IG. Now, again the calculation of D and G, the intensities can be done just based on the height of the peaks or it can also be done based on the area of the peak in some cases.

So, in that case these little calculations can make actually a lot of difference to what you understand of your material. You could potentially calculate the crystallite size, but you can already see that in the case of graphite-like, graphitic carbons it is already difficult to have these to fit the parameters.

And in addition to that sometimes this has also been reported when the crystallite size too small then the calculations methods may not work.

So, typically for manufacturing materials you will not calculate La or Lc for that matter using Raman spectroscopy. For that purpose, you will use x ray diffraction. So, in general the peak integration is challenging. So, Raman spectrum looks very simple, but its interpretation is not very simple.

And especially understanding its origin because whenever we are trying to characterize something; we want to understand what is the origin of this kind of peak and in the case of Raman spectroscopy, we still do not completely understand the molecular behaviour.

And we still we do understand a lot of things about it, but if you change minor things in your material and you expect sometimes the Raman spectrum to change, but it does not change and sometimes you do not expect it to change, but it does. So, these kinds of things are still there when it comes to Raman spectrum

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Raman Spectroscopy: Applications in Carbon Technology

- Raman spectroscopy can be used for characterizing surface defects in carbon fibers, doping/ intercalation in carbon.
- Raman spectroscopy is a good tool to understand the effect of heattreatment on all annealed carbons.
- Raman spectroscopy is based on a simple technique and the spectra also look simple. But there are still some unanswered questions related to origin of the D and G' peaks, relationship between G' and 2D peaks, nonlinearity of the D peak and the sp² dominance of the spectra.





Further reading:

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Now let us briefly talk about the other possible peaks in your Raman spectrum of carbon and also some of the applications. This is another hand-drawn spectrum and please do not scale it and I suggest that do not use it anywhere else as an example because this is just to show you the positions of the peaks. And in fact, in some cases I have just made the peaks bigger just to show you that they come at those positions, but some of these peaks are very small. So, often they are merged also with the other peaks and you may not see them. So, you see that around 1300-1350, you have the D band and then at 1580 you have the G band.

In this particular case, the D band is very strong, but you often get these two peaks merged and you do not get the D band so strong compared to with let us say if it is a highly disorder carbon or something. Then after that, you see this very small D prime band which is often merged with the D band or you would just see a slight shape change in your D band, that could be due to this D prime band and then you can see all other potential peaks.

The G prime or 2D band that I have shown here may not be as strong and sharp as it looks. Because you see the material is highly disordered, but these are just the positions of the possible peaks if you are analyzing a disorder carbon material. What are the application we know? I mean we use it for characterizing the material when we are performing the heat treatment.

So, this is definitely one application. Other than that it is also very interesting when you have intercalation compounds. Intercalation means you have these two layers of your graphite, if something goes inside and comes out. So, let us say there is some little ball which goes inside my hands; these are the two layers, so this is your intercalation. So, intercalation compounds basically cause some deformation or some curls and sometimes also defects in your material.

So, defects can be very nicely understood by Raman spectroscopy, but in that case your starting material should not have the defect. So, you cannot understand intercalation materials, but it will be very difficult to understand intercalation behavior in the case of disordered carbons.

Because you already have a lot of defects, because of the disordered carbons and then you will also induce some more defects because of intercalation. So, either you need to completely understand or defects that are induced should be completely different from the already present defects. In that case, maybe you can understand, otherwise it is difficult. But in the case of pure graphite definitely you can understand the intercalation compounds very well using Raman spectroscopy. What else can you do? It is heat treatment of annealed carbon is fine, but also for understanding the defects in carbon fibers.

It is difficult to understand surface defects or differentiate between surface defects and the defects that are under the surface or in the core of the carbon fibers using X ray diffraction or other techniques. But Raman spectroscopy only let us see one micrometer of your top surface, sometimes even less than one micrometer is what is analyzed using Raman spectroscopy.

So, that is also something you need to remember. So, in that case whatever are the surface defects, you can differentiate between surface and core defects of carbon fiber. So, that is why industrially it is used for this purpose as well. So, one interesting thing is that I have told you before that this Raman spectroscopy is very simple and we also can perform the experiments very easily. You do not need to worry about the substrate very much.

You can take a material inside a polythene bag and then you can just take the Raman spectrum at various places. Also, the setup compared to many other techniques is not terribly expensive you just need a laser source. In fact, if you think about the original work that was done by Raman; he just used sunlight as the source of photons.

So, this is a simple technique in principle also the spectrums spectra look very simple, but what is more complicated is the interpretation and understanding the origin of each peak. So, when you analyze the Raman spectrum, try to understand why do you get a certain peak and why do not see too much change in your material when you make minor changes when you make changes to your material; why do not they completely reflect in your Raman spectrum?

So, the origins of all of these Raman behavior of the molecule is what is very interesting and also reasonably complex and that is why it is a topic of research. You definitely should read at least some of these papers. The first one is a book, but the rest of them are publications. So, last one I have mentioned here is the original paper on Raman effect by C. V. Raman and Krishnan. So, all of these things you should definitely read and we can probably find out some new techniques related to Raman spectroscopy. In fact, many such techniques are already available, but perhaps this spectroscopy still has a lot of scope for improvement when it comes to characterizing carbon materials.