Fluid Inclusion in Minerals: Principles, Methodology, Practice and Application

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Lecture - 33
Analysis of Fluid Inclusion (Contd.)

Welcome, to today's lecture. So, we continue our discussion on the, on a bit of a Fundamentals Principles of Raman Scattering and then the way, the as much of principle that we must, have some idea. So, that we understand the think better and so, that we utilize the data or we know when we are generating the data what exactly we are doing.

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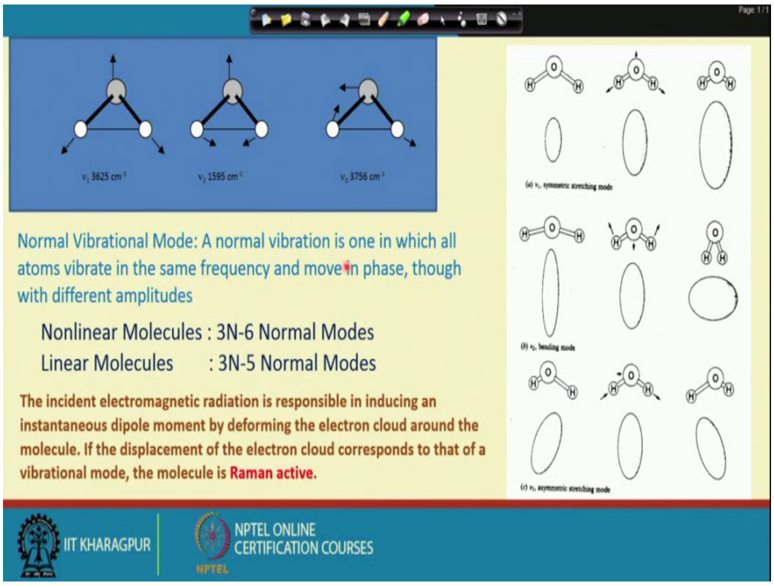

Normal Vibrational Mode: A normal vibration is one in which all atoms vibrate in the same frequency and move in phase, though with different amplitudes

Nonlinear Molecules : 3N-6 Normal Modes
Linear Molecules : 3N-5 Normal Modes

The incident electromagnetic radiation is responsible in inducing an instantaneous dipole moment by deforming the electron cloud around the molecule. If the displacement of the electron cloud corresponds to that of a vibrational mode, the molecule is **Raman active**.

So, coming back or continue with the last discussion, that we have considering simple molecules, like water which is a non-linear molecule, there we can have 3, 3N minus 6 normal modes or if we go to molecules which are non-linear which will see later it will be 3N minus 5, means number suppose for example, it is a carbon dioxide, there are 3 atoms. So, carbon dioxide will have 4, normal modes or the fundamental vibrational modes.

And so, incident electromagnetic radiation is responsible in inducing and instantaneous dipole moment which is; so, as represented by nu and by deforming the electron cloud around the molecule. So, if the displacement of the electron cloud corresponds to that of a vibrational mode then the mode will be Raman active. So, just to have this, corresponding diagram here which is taken from the fundamental textbook so, which I mentioned before, These water molecules three different vibrational states can be explained with this diagram. This is our normal molecule of water, then when we are, and the corresponding to nu 1 that is symmetric stretching. So, this stretching could be either in a positive direction or negative direction, means this ellipse is either contracting or expanding here, but they would correspond to the same and this same molecular water is actually undergoing symmetric stretching, either compression or extension.

Now, in contrast to that situation corresponding to nu 2 the original molecule here is actually getting distorted to either a polater and oblate depending on the stretching or the asymmetrical stretching of these two, of this bonds. Similarly, the third case is bending mode this is a bending mode and, this here we see, that this ellipse is distorted and, this also in two different situations possible. So, these give us a graphical idea about what exactly happening during the symmetric or asymmetric stretching and bending of the molecules.

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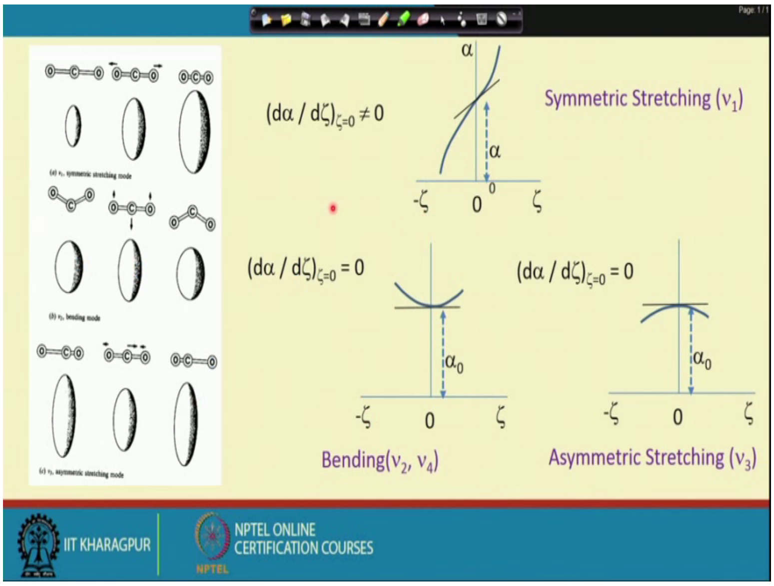

$(d\alpha / d\zeta)_{\zeta=0} \neq 0$

Symmetric Stretching (ν_1)

$(d\alpha / d\zeta)_{\zeta=0} = 0$

$(d\alpha / d\zeta)_{\zeta=0} = 0$

Bending(ν_2, ν_4)

Asymmetric Stretching (ν_3)

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So, now we have to understand that why in, some of the fundamental modes, vibrational modes are some are active and some are not. So, with respect to that same water molecule, here for what we sorry this is been this is in, relation to a carbon dioxide molecule. Here it is N is 3 and, it is be 3 and minus 5, that is four fundamental modes of vibration. So, here there is a carbon dioxide molecule, it is now it is a linear molecule, it is now also undergoing symmetric stretching. So, here what we observe in a symmetric stretching, can be represented by this displacement, which is represented by xi here either in a positive sign this compression or is extension and the what happens to the polarizability, that is alpha has this stretching is taking place which is represented by this coordinate.

So, what happens is that when the value of alpha, when this displacement is 0 exactly. So, at that point of time the slope of d alpha by d xi is not equal to 0 as you can see from this tangent which is drawn here. So, it is a symmetric stretching situation and then in the rest of the other cases, where it is a case of bending it could be bent in either of the ways, that shown by this ellipse here. So, in the bending case the when the displacement is 0 there we find that is d alpha by d xi is 0, in both the cases that is corresponding to sigma nu 2 and nu 4 and this representing nu 3.

So, these kind of idea or this kind of little bit of a fundamental without getting into any (Refer Time: 04:45) details of the physics of it. We now know, that considering simple molecules like water carbon dioxide or methane, when we are going to take their Raman's, their Raman spectra, so, they can that is at the back of on mind that we know that how many fundamental modes of vibration are going to be Raman active and can expect, the Raman peaks on those kind of situations and although it is not proper.

In this i r spectra are also they also work in this particular, wavelength region and there is a convention, that those bands which are essentially i r inactive. There may be Raman inactive, there may be i r active and they can be studied in an i r, infrared spectrometry, which we might may be discuss a little bit, in brief. So, Raman Spectroscope and the laser on the micro spectrometry and the infrared spectrometry which is essentially down with a Fourier transform infrared that is F T i r. They basically these methods are employed as non-destructive in situ analysis of the gaseous species in a molecular species rather I would say, in inclusion fluid and, they work in the same principle.

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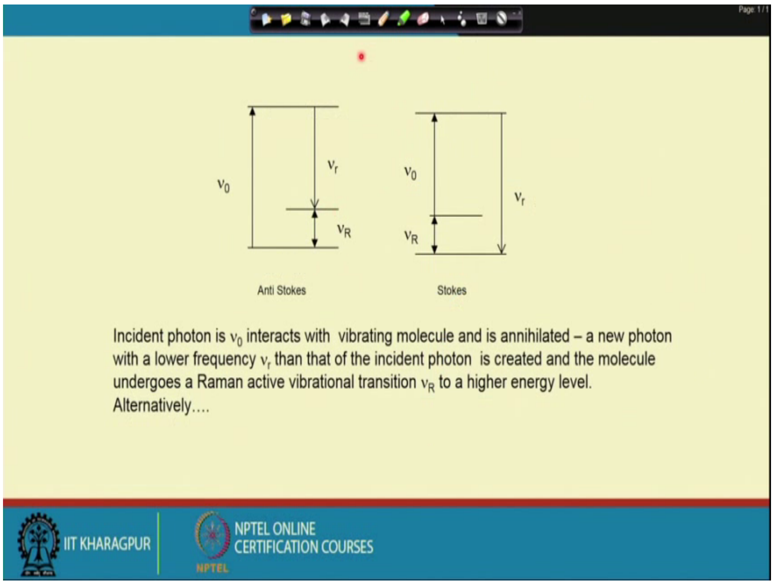

Incident photon is ν_0 interacts with vibrating molecule and is annihilated – a new photon with a lower frequency ν_r than that of the incident photon is created and the molecule undergoes a Raman active vibrational transition ν_R to a higher energy level.
Alternatively….

So, now, let us try to look at little bit simplistically is to what will happen. So, from the standard relations, it we know that if there is any scattering, there would be a major part of the light will be elastically scattered and a really negligible part of it will be in elastically scattered either with loss or gain in the energy of the emitted light. So, here in this case we represent the incident photon with nu 0 and that interacts with the vibrating molecule.

So, in this case the incident photon nu 0 is annihilated and a new photon with a lower frequency of nu r is, then incident photon is created. So, it is a less in its energy than the incident photon and the molecule under goes a Raman active vibrational transition that is nu r to a higher energy level. Alternatively in this diagram when there is a gain then the electromagnetic energy gains the energy and is emitted with a higher frequency.

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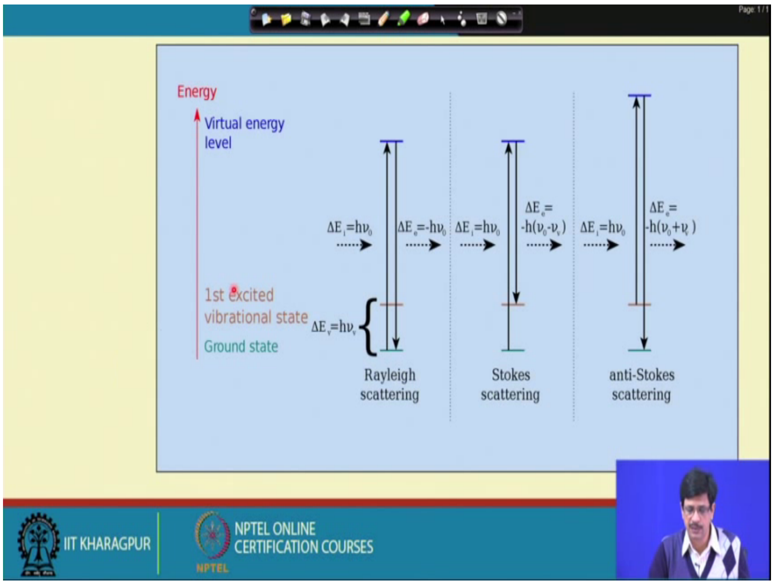

So, that we say in this case which Stokes and the other reverse case we case; I will say anti-Stokes which is also shown by this energy level diagram. And so, this is a Rayleigh scattering where we see, that there is no change that is del E i is h nu 0 del E, that is incident and emitted that is also h nu 0. This is also h nu 0 and there is no, loss or gain in energy and this is the Rayleigh scattering and in this case del E i is h nu 0 where del E, E that is your, that is emitted the change in the energy of emitted is minus h into nu 0 minus nu v that is the stoke scattering and here it is nu 0 plus nu v. This is how we can understand the process of the inelastic scattering resulting in either a Stokes scattering or an anti-Stokes scattering.

In the Stokes scattering, the emitted, electromagnetic wave has higher, lower frequency and lower energy corresponding to the incident wave. And. so, here the energy the excess energy is given off to the vibrating molecule which now vibrates with a higher frequency. And the reverse is true where the where bond is already vibrating at an excited state and it gives off the energy to the incident electromagnetic energy and which is emitted with a higher frequency and higher energy possibly this, is the way very simplistic way of understanding it.

Now, then when we are considering any particular molecule, which is a say for example, at a particular state at room temperature. So, how many of such, the how about the, the scattering that is taking place for to do the percentage of heat which will be scattered by Stokes scattering or the one which will be scattered by anti-Stokes will be depending on they, basically statistics, the statistically speaking, how many bonds will be actually vibrating in their normal ground state or how many bonds will be vibrating in their excited state, keeping many things many other parameters not considering them at least.

We can expect, that if the temperature is higher than the possible the probability of more bonds vibrating with their, with an excited state will be more compared to what we get in a lower temperature. So, in a typically in a Raman Spectroscopy, we should be seeing at both the Stokes and anti-Stokes scattering, but for most of our practical purpose, when you do fluid inclusion analysis and very interested in knowing the detecting the presence of various molecular species only the Stokes part, which is essentially statistically much more significant suffices our factors.

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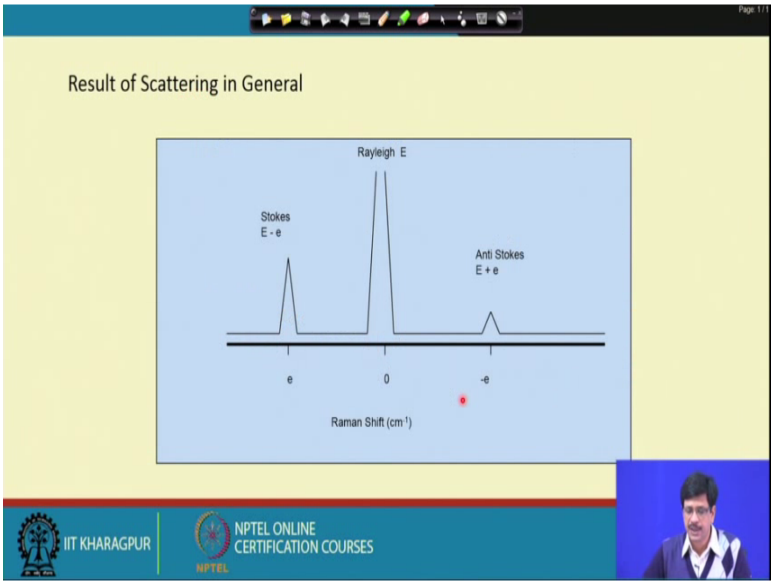

Result of Scattering in General

So, this gives a rough idea is to got exactly the same. So, what happens is that, this is kind of a rough sketch of scattering in general now on a, you can say the x axis is corresponding to, the frequency the energy, which is now converted in terms of or which is essentially the relative a scale with respect to the frequency of the energy of the incident electromagnetic wave.

So, if we take the difference the centre will be 0 and then here on this side it is positive; that means, how much of energy is actually lost. So, where it is E minus e, that is how much of energy is lost by the, incident electromagnetic energy in undergoing the Stokes, scattering and here it is the anti-Stokes scattering and it is very symmetrical means, now here we are plotting this or we are getting the spectra plotting the spectra on a scale where we say that it is something called a Raman Shift.

So, shift will always be a relative, relative to the energy of the incident, electromagnetic wave. And so, as you see here the Stokes, side is shown by a peak which is, higher in its, amplitude. It is a more intensity corresponding to what we get in an anti-Stokes and that is what happens in most of the cases. So, if we were to study. So, if you take a molecule in that molecule there are say n number of Raman active modes.

So, if there are N number of Raman active modes this N number of Raman active modes will undergo Stokes scattering at corresponding to different value of the difference in their energy definition. Raman shift which will be represented as more than one number of peak on a on something which will call as a spectro as a spectra as a spectrum. How many of the just to, keep this idea, that whenever we are able to represent the result of the an interaction of the electromagnetic energy with the bonds and we able to represent them in terms of intensity versus, frequency in terms of the ray difference.

So, we will call it as a Spectrometry, because there is, enough of scope that we could also do some semi quantitative, method means analysis of the species and then in, in most of the cases, we buy our optical device, that we are using. It may be possible to only observe the stoke side of the spectrum, but most of the material science and most of the applications the both Stokes and anti-Stokes are studied, but for our purpose, the stoke side of the spectrum is, quite sufficient for us.

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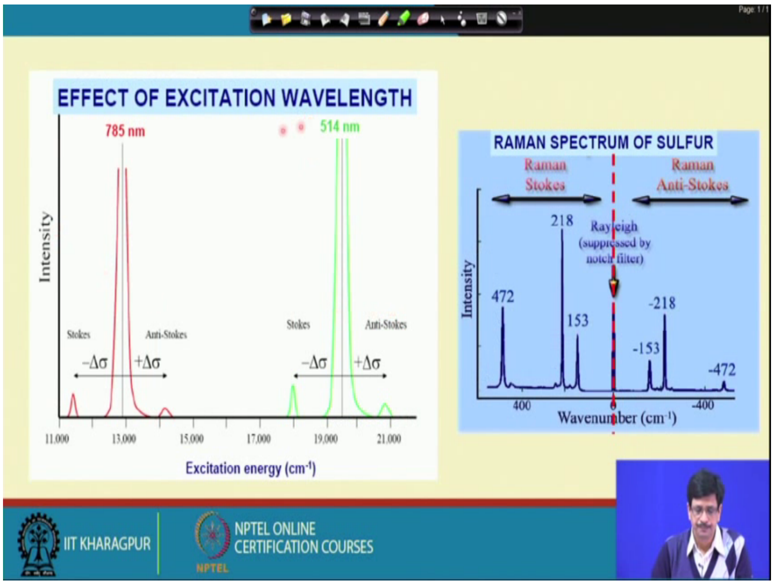

EFFECT OF EXCITATION WAVELENGTH

RAMAN SPECTRUM OF SULFUR

So, here, it is an example that it actually, ok. So, before, before we go to the this thing these discussions it is also essential to know, that when we are we are, attempting to understand this process the principles of Raman Scattering, by using an electromagnetic energy and its interaction with the vibrating molecular vibrating bonds in a molecule. It has to be a single wavelength, light.

So, we use, monochromatic light as we, discussed. We; if we use a (Refer Time: 14:24) and, laser generally which are available as, either a 520 nanometer within the visible, part of the spectrum. It can see them as green color or we can use, red a solid state laser which, where the laser light is emitted at a wavelength of 785 nanometer, we will discuss about which wavelength to choose later on, but this is an example, that normally the shorter wavelength, the higher frequency the shorter wave light, laser is of higher energy, excitation energy.

As you can see, the green is actually for the green (Refer Time: 15:01) and laser 514 nanometer and, this is the Stokes and anti-stokes, which is shown, which is with a minus, delta sigma apparatus sigma and here it is a the case of a, 785 nanometer, that laser whose energy is worthless. We will, discusses to which laser to choose for our application later on. This is an example of a Raman Spectrum of Sulphur, where you could see that both Stokes and anti-Stokes are shown and, characteristically could see that, they very symmetrically, placed at 218, minus 218, 153, minus 153, 472, minus 472 and 472 and here, what is basically presented here is the, Raman shift.

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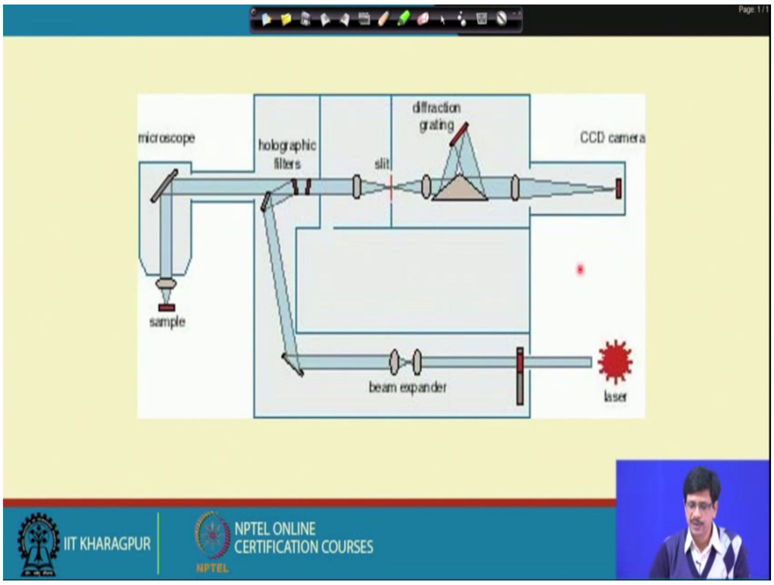

Means, the change of the difference and the frequency of the incident laser with the emitted, with the frequency of the emitted light and here intensity are could be in arbitrary unit. And, just to give you up, because these days the instrumentations are very much, being improved be modified at the, very periodically and in very short, frequencies of time. So, I am just giving you a very rough idea about how a, Raman Spectrometer is specifically the components are design. So, this is a laser source is a continuous, laser source it, because we are interested in studying the, interaction in a kind of a time span.

So, it has and also, I am just, I will just discuss it. So, this is the laser source the laser source is, getting guided through series of lenses and mirrors with the laser light is actually getting incident through the objective on the sample. So, here is basically the when we say it is laser micro, Raman Micro Spectrometry, we are using a microscope. So, the laser, the Raman Spectrometer is coupled to a microscope and sensibly we represent that, this through the microscope objective which we high power objective through which the laser spot is made to be incident or focused on the sample.

So, here our sample is a wafer in which inclusions are there and we need to focus the laser light which will be, of the size of the order of a 1 micron in its diameter and the diameter could possibly be varied, but not only when we try to study an inclusion which will be about a couple of tense of microns or been less than that in its maximum dimension. And sometimes will be needing to focus on a part of the inclusion to know the characteristic there, what is the gas there. So, this particular laser light has to be focused on the sample it is not only the sample since inclusion should be placed below the surface of the sample.

So, will have to we have to focus on deeper, on their own planes which are below the surface and once we focus them the device is so, design that, wherever we get the optical focus to look at the inclusion, the laser also will be focused there. Means say for example, we just want to focus the laser light about 5micron below the surface where an inclusion is placed, we can exactly focus the laser light exact on the inclusion itself.

If the laser is not been able to focus on the inclusion, then we are not we cannot expect a good signal or a good spectra to be obtained at the same time. Since, this inelastic scattering is also very weak scattering, we can also we also need to be, cautious about the depth at which we would like to get the information and inclusion which is below the depth about 550 microns are. So, from the surface, generally by the time the inelastically scattered Raman, Scattering is coming from the material. It is actually getting attenuated or absorbed by the through the thickness of the wafer, as coming and the experience says, that inclusions which are placed from surface to within at least about 50 micron depth, there Raman signal could be very effectively collected.

So, here the optics work like this, its 180 degree scattered the laser light laser is focused on the sample and this scattered Raman signal is also collected through the same objective and is, guided through to the detector. Now, what happens here is that the device is the spectrometer is soon designed as we know that the major part of the, scattered light is elastically scattered. So, with that elastically scattered part of the light corresponding to this particular which would be a much much more stronger in, in its intensity compared to the inelastically scattered part of the light. So, this spectrometer there should be some kind of filtering mechanism which should be there.

So, that the Rayleigh scattered wave, Rayleigh scattered light will has to be absorbed or cut off by this particular filter has been filtered out by the cutoff and only the inelastically scattered part of the light will be able to pass through and through a series of, optical devices like a slate and it. Again, which will be, made to be fall in the surface of a prism on the parallel light and. Then this, this light which is the Raman scattered or the inelastically scattering light which is coming through this will be coming through all its wavelengths ranges. And the only the ones will be having the, we want that the, the frequency of the Raman shift part of it of our interest.

We need to only determine that, and whenever there is, and the component, the other part with which is coming out of, because of the Stokes or an a Stokes scattering at any different, corresponding to your different discrete, values of the Raman shift will be able to get them by using a grating which is actually is something which is being used for dispersing this, in elastically scattered light into its constituent, wavelength or frequency. So, by using that device we can again by a; so, it if this device a there is grating which, which made to be rotate through a angular value given up to when can maximum to rotate up to 180. So, depending on that the position of that particular grating will allow only that particular frequency, or electromagnetic wave to pass through and again fall on the detector.

So, the basic units of this Raman, Spectrometer, which a laser on a spectrometer is the source laser source which could be a (Refer Time: 21.03) and laser or a solid state laser or may be some, better developed things of the right, but this moment and has to be a guided through the optics the incident on the microscope. Through the microscope objective on the sample must have a device to filter out the Rayleigh and then have a device over here, because we are doing it only in the in a normal, frequency mode. So, here it has to be a grating which will disperse the, the emitted or the with a, inelastically scattered light and the that light will fall on the detector and the detector will sense based on the intensity of that particular light corresponding to that particular frequency.

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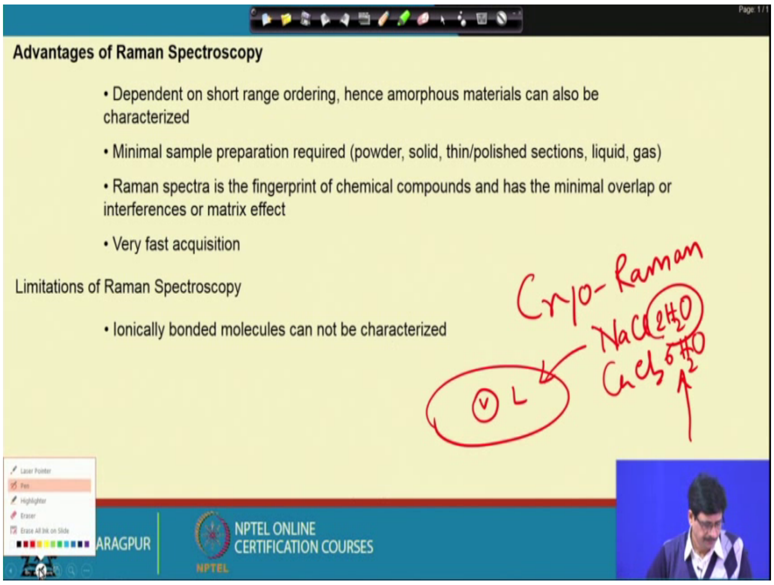

Advantages of Raman Spectroscopy

- Dependent on short range ordering, hence amorphous materials can also be characterized
- Minimal sample preparation required (powder, solid, thin/polished sections, liquid, gas)
- Raman spectra is the fingerprint of chemical compounds and has the minimal overlap or interferences or matrix effect
- Very fast acquisition

Limitations of Raman Spectroscopy

- Ionically bonded molecules can not be characterized

Cryo-Raman

$NaCl \cdot 2H_2O$

$CaCl_2 \cdot 6H_2O$

V L

So, the advantage of the Raman Spectroscopy, Raman Spectrometry other I will say, that it depends depended on short range ordering. So, amorphous materials can also be characterized this minimal minimum sample preparation required. Raman Spectroscopy does not require any elaborate. Sample preparation the same wafer, which you are using for a micro thermometer study, can be used for the, Raman Spectrometric study and when it at the material is something different. It could be powder, it could be solid or thin polish sections liquid chamber we can or a gas can be easily be used for studying Raman Spectroscopy.

So, one which is very important aspect of Raman spectrometry is that the Raman spectra. If we, see the fundamental, literature on Raman Spectrometry, it tells us that Raman spectra is the fingerprint of the chemical compounds and is the minimum overlap or interference or the matrix effect. So, if we if we have characterize many with that is why, we generally able to identify. If we get a peak at a particular position and we know that it is, because of that particular molecule.

So, it is basically if there is no scope of any confuser any overlap and for the occurrence of that of course, will be discussing a little bit where this could be violated and its very fast acquisition when the when we use such equipment, we can just take the spectra for a few seconds. And, the if the instrumental, parameters all are working fine then will we get a very, acceptable and very good quality spectra.

So, here the limitation as far as the fluid inclusion studies are concerned, that it is only; that the ionically bonded molecules can be characterized the sorry ionically bonded molecules cannot be characterized. This only, we are will be analyzing the ones which are the, molecules which are bonded by covalent bonds. The molecules which are of our interest water carbon dioxide, methane, nitrogen (Refer Time: 24:51) Now the thing is that so; that means, it essentially would rule out to analyze any of the dissolved across species in the liquid part of the fluid inclusion and then this, kind of things are also being now, worked upon and there are many improved methods of studying Raman Spectroscopy.

One of which basically is now is known as the CRIO Raman Spectroscopy or spectrometry in which if we have an inclusion and this inclusion. We know that, when it is frozen to conditions corresponding to its, turner eutectic or burn by of the depending on the fluid mixture it is. So, in a completely frozen state it is forming the solids like an ice or now say for example, we, but we cannot analyze normally I whispered this limitation is that how much of sodium how much of potassium or calcium is there in that aqueous part of the liquid, but then if some such these all species are going to form their hydrates say for example, N a C l 2 H 2 O, I say hydro halide or C a C l 2 6 H 2 O is an un (Refer Slide Time: 26:27) and there many such, mineral species whose many such require species who perform their respective hydrates.

These can be characterized by the, these have their corresponding, Raman, characteristics which can be identified on the, Raman peak where, because the moment, there is a water molecule coming to the attached to that solid. There will be OH bending field stretching characteristic and associated with that characteristic, vibration modes of the molecule. All this we are not, elaborating in detail, they can be pursued anybody was interested in this.

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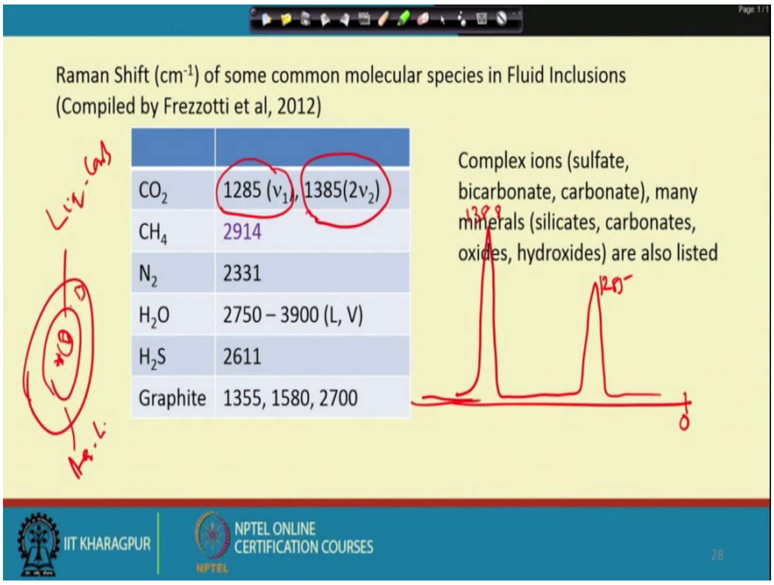

Raman Shift (cm^{-1}) of some common molecular species in Fluid Inclusions (Compiled by Frezzotti et al, 2012)

CO_2	1285 (ν_1), 1385($2\nu_2$)
CH_4	2914
N_2	2331
H_2O	2750 – 3900 (L, V)
H_2S	2611
Graphite	1355, 1580, 2700

Complex ions (sulfate, bicarbonate, carbonate), many minerals (silicates, carbonates, oxides, hydroxides) are also listed

And so, how we actually, then the in a we get the Raman spectra, when we have some molecules we put the laser beam on it and then acquire the, spectra correspond the inelastically scattered part of the light. So, how we use them? So, definitely we need to have some standard, will some will characterized material or some known value for their occurrence of this, peaks corresponding to the Raman shifts and will be essentially based on those, modes or those, fundamental vibration modes which are Raman active.

So, some such I have just listed here, from standard literature where you can see the whole list of such gases solids hydrates and. So, on and their corresponding Raman shift. These are actually corresponding to the Raman shift exactly the way we have put here putting 0 over here and since we know that we are not interested in the, anti-Stokes part of it. We can we say that ok, we basically could starts from start from somewhere as 0 and go to the higher Raman shift can go to anything 5000, 6000, 7000, centimeter inverse, in terms of the frequency difference with the incident, electromagnetic energy.

So, this is carbon dioxide, carbon dioxide is characterized by its nu 1 with, because we say that has the symmetric stretching nu 1 which is Raman active and, the other three are not Raman active. But, sometimes there are certain things which come up as, some other kind of phenomena that takes place which, are kind of over to one are some kind of, resonance things which take place which we are not discussing in details.

Here, say for example, carbon dioxide will be very well characterized by a peak occurring at, say this is for example, 0. So, a corresponding to 1285 and 1388 centimeter inverse; so, this is very; so, whenever we, we are putting the laser beam on the part say, we also must keep in mind, that whenever we are doing Raman spectroscopy. We are not taking the bulk inclusion characteristics, it is only focusing the laser beam on the part which were sometimes will be suppose, this is an inclusion and aqueous carbonic conclusion and this is the liquid carbonic part and this is the aqueous liquid and this is may or may not have a carbonic vapor.

So, will would be interested in characterizing only the carbonic part of it. So, we will put the laser spot on the carbonic part and the spectra that will get will correspond to that only that particular part on which we have focus the laser. So, it is does not take the whole inclusion content it does not give the idea about, what is the composition of the whole content of the whole inclusion or some time we will be interested in just getting it, getting the vapor bubble. And, see what is its composition or sometimes we were see, there is some solid in it and try to find out what is the, composition of that particular solid or it is which will happens to be a molecule, that can be characterized by Raman Spectroscopy, then we can put the beam on there.

So, now with that so, similarly there is these, there the peak position of methane, the nitrogen, water H2S graphite, these are all they definitely. So, these things have been studied with Raman Spectroscopy, in the laboratory and confirmed as almost like as if in say, in case of a reference material, that we study in our other analytical, methods. So, this Raman or the peak positions in a Raman, spectra are prior are known, before, beforehand and only thing is that whenever, we try to characterize something which is a mixture.

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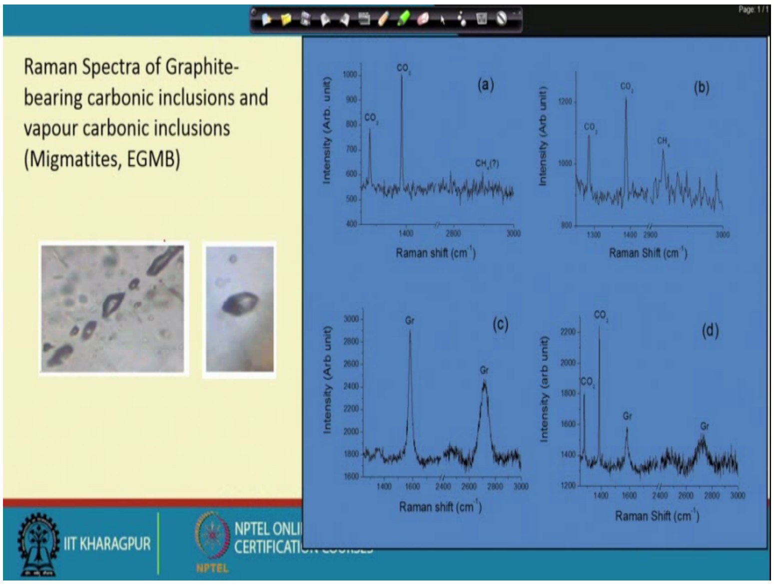

Raman Spectra of Graphite-bearing carbonic inclusions and vapour carbonic inclusions (Migmatites, EGMB)

So, here are some examples, you could see here, these are some of the vapor carbonic inclusions, occurring in the migmatites in histogram mobile belt and, the spectra light shown here in B, where you could see, that these are the carbon dioxide two peaks. So, here we are going from, 0 to 3000 in this, range and here this corresponds to 1285 peak and this corresponds to the 1388 peak of carbon dioxide.

So, when we get a specter spectrum like this; so, there is possibly know much of, suspicion on no doubts is to whether, what it could be. So, we know the peak is coming at 1388, we know it is, because of carbon dioxide and you could see a small peak of, methane somewhere, here and then this is an inclusion, where it is a graphite bearing inclusion and the laser being, being put on the liquid part of it is keeps carbon dioxide and little bit of methane. It is purely carbon dioxide and when the laser beam is put on this black part which is graphite you get a spectra like this. Sometimes, you can put somewhere, little bit in between or on the boundary of the fibers or graphite over here and the liquid you get the spectra for the two-carbon dioxide peak here and the graphite.

So, graphite is also well, known where the graphite peaks will come, one is coming at around 1350, another one is about 1580 and the other one is 2700s. So, this are so, one is to go through standard literature and the updated information about the Raman spectral characteristics of different types of gaseous species and their, and the different solid species. So, that any unknown sample, when we are taking our fluid inclusions we subjected to

Raman Spectroscopy, a study using a Laser Raman Micro Spectrometer we know what we got.

So, this is also another example from, the Auriferous Schist belt of Dharwar Craton, where you see a very clear-cut graphite, bearing inclusion if put the laser beam. So, these are this is 20 micron. So, then the graphite bearing part a 1 micron laser beam could be put here and you see the three graphite peaks put on the liquid part when you seeing carbon dioxide and methane. So, the as compared to the previous case, but we saw. So, this proportion of the my peak of the methane is, more. So, it exactly goes very qualitative with that way; that means, the material corresponding to this particular inclusion, that is being analyzed here definitely has a much more proportion of methane and whether it is exactly that or something also has to be considered; in addition to that, will discuss ok.

So, we will continue our discussion on the application of Raman Spectroscopy to fluid inclusions and how to utilize the data, what interpretations we can make in the next class.

Thank you.