Fluid Inclusion in Minerals: Principles, Methodology, Practice and Application
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Lecture - 34
Analysis of Fluid Inclusion (Contd.)

Welcome to today's session of the lecture series on Fluid Inclusions in Minerals. We shall continue our discussion on the techniques of in situ non destructive analysis of fluid inclusions micro analysis of fluid inclusions. And, we were at the middle of our discussion on the one of the techniques which is very widely used by many fluid inclusion is across the world, and is relatively is a simpler technique, but a powerful one that is the Laser Raman Micro spectrometric analysis or LRM as we call it.

So, just to recapitulate what we are discussing that, where we subject an inclusion which you have to choose under the microscope at a suitable magnification and, then select the inclusion which will be at a particular focus from the surface of the vapor. This individual inclusion has to be focused whether the laser light is also focused on the inclusion cavity below the surface of the vapor. And, then we expect to get some peaks at corresponding Raman shift, and the those peaks would be characteristic or the fingerprint of the molecules gaseous species, sometimes the solid crystal daughter crystals or sometimes when the spectra the spectra is been taken at a very low temperature which will be discussing subsequently.

So, we get a multiple of peaks corresponding to various values of the Raman shift which is nothing, but the difference in the frequency of the emitted light with respect to the incident laser frequency, which we know that we are using a monochromatic laser light of a chosen wavelength.

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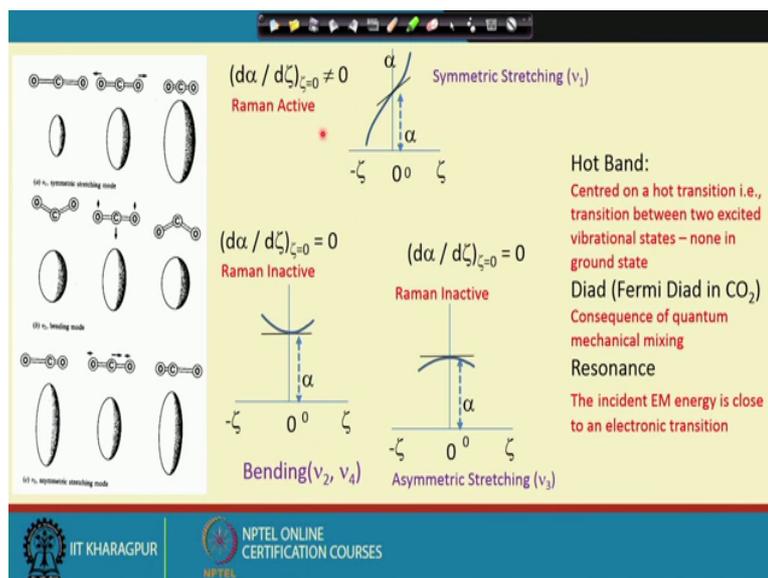
And so, let us have a look let us recapitulate that we discussed on this particular diagram with respect to a linear molecules which is carbon dioxide, where the number of vibration fundamental vibrational modes will be 3 and minus 5. And so there are 4 vibrational modes of 4 vibrational frequencies and corresponding to asymmetric stretching bending two modes of bending and asymmetric stretching. Just to put it in a more definitive way if it was not clear before, that this kind of diagram which is constructed from the classical mechanical for view point essentially we will give is giving a some guidelines and a that which of the fundamental vibrational modes will be Raman Active.

So, when we take this a diagram they take the value of alpha 0, where the derivative is the derivative of the polarizability alpha with respect of space. And, when this special displacement is 0 a value corresponding to alpha 0 and the derivative had displacement 0 will have some finite value and that would correspond to an active Raman band, Raman vibrational mode in which we would expect to have a peak on a spectra which will be Raman shift verses intensity.

As again that which is a Symmetric all the other cases of an Asymmetric Stretching or bending there the derivative at displacement 0 will be will have a value of 0 as shown on this two diagrams. And there the derivative at displacement 0 is equal to 0 and, there

these modes will correspond to Raman Inactive modes and in which we are we will not a getting any pay.

So, this is a providers some broad guide lines and some basic understanding about the use of Raman spectroscopy n characterization of the molecules that are present in a fluid inclusion, there will liquid state, or vapor state, that is does not matter and as long as they constitute of molecules in which there are covalent bonds. They will always be and some of those such Raman active modes will always be reflected has having peaks. But, then actually in reality what we get that sometimes we get lot many number of peaks.

Say for example, in case of carbon dioxide when there is only one mode which is supposed to be Raman active, but on a spectra of carbon dioxide we made see more than one such peaks many such many such peaks we will get as will see soon. Some of them maybe because of the hot band so this hot band is nothing, but it centered on a hot transition there is transition between two excited vibrational states, when lower region ground state.

So, these are some of the intricacies of these by interaction the spectroscopic intricacies of the spectroscopy based on very fundamental physical principles which we will not be discussing here in details, but they will be only of practical utility to us. You will get sometimes in a carbon molecule like carbon dioxide in side of one we get a Diad which basically is called a Fermi Diad. It is a consequence of quantum mechanical mixing, and sometimes on a Raman spectra for example, we take a silicon and try to take a spectra.

In addition to the very prominent peak corresponding to a Raman active vibrational mode we sometimes also get peaks which called as the Resonance peaks. And there the incident electromagnetic energy is close to an electronic transition. So, these are some of the simple things which always we kept in mind while taking Raman spectra of any particular inclusion.

So, here such kind of microscopic arrangement when a micro in a laser Raman spectrometer is coupled with a with a microscope, like normal polarizing microscope which we use in routine petrography, geological applications with higher magnification sometimes 500 or 1000 time magnification. Because sometimes we need to have the laser beam focused on a very small diameter and also, when where trying to examine the characterized in inclusion which is very small and a to power would like to put the laser

beam on a particular part of the inclusion, there sometimes we take it an higher magnification higher magnification use of higher magnification also sometimes has for a for much better quality of spectra that we need to take some times.

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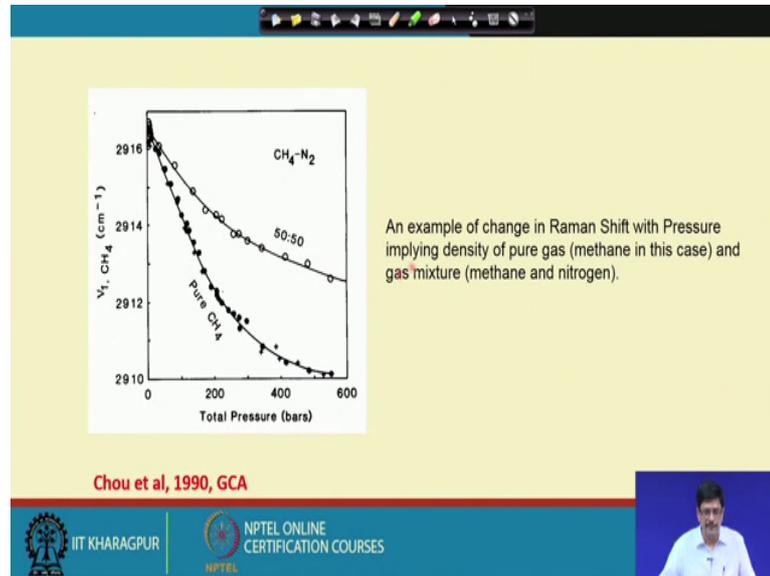
So, with this now let us try to look at that how the Raman spectroscopy is used in fluid inclusion research. As it is said in the context of Raman spectroscopy that Raman spectra of a particular molecule is it fingerprint means; we would possibly say that if there is a molecule like methane, and then it is Raman shift or you would expect or it is as it is documented in it in books certain standard literature that we should get peak around 2914 centimeter inverse.

But then this Raman this Raman shift, or this the Raman activity of this particular covalent bond which is there in this methane. We will always be function of the atomic environment in which it is present, and also the density of the particular gas, or the particular gas the molecule is in a liquid state. The density also is a function we also decides the precise position of this particular peak on a Raman spectra even though it will not very in very great ranges.

But here there is a diagram which you can see here there is a total pressures in bars versus this V 1 of methane this is the Raman active mode of methane with generally should be expected around 2914; can vary from to as a higher or 2916 291 to a 2910 depending on what is a pressure. So, as pressure is increased when density is higher we

would expect the Raman peak, the Raman shift to be occurring is lesser and lesser difference in the frequency, or in a spectra towards the lower value of Raman shift. And, this is show when as CO 2 and CH 4 and N 2 mixture whereas, 50-50 N 2 mixture you could see that a when it is present in a mixture in a different atomic environment, when it is not pure there also there is some shifting of the peak positions on a roman spectra.

They have been used or they can be theoretical they cannot be it can be utilized to talk about or to estimate the density of the liquid of the methane, which is present sometimes in mixture it carbon dioxide. It should be possible, so it is an so it is just to show that even though we take it for granted that Raman peak position should be a fingerprint of a molecule. But we may we should not expect any particular molecular species to be all the time abiding strictly by that principal and get to expect peak to occur exactly at a very fixed position well.

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This is coming to one of the may one of the important utility of Raman spectra which is being (Refer Time: 10:17) in the by many laboratories by many workers. So, the question that is it possible to have some kind of a semi quantitative idea about the composition of the material of the liquid or the gaseous or the gas in a in a vapor bubble in a inclusion or the liquid part in an inclusion, taken for granted the suppose it is a carbon dioxide and methane mixture.

So, if it is a carbon dioxide and methane mixture if there is no other species present. Is it possible to determine the proportion of carbon dioxide and methane because as we know saw before, they when the carbonic inclusion which is there in a sample is not pure as indicated by it is depression in the triple point from minus 56.6 we suspect there is methane. And from the melting temperature of the solid carbon dioxide and the parcel a homogenization of the carbonic phase by intersection of the curves which you saw before; we can have a rough idea about the mole percentage or in terms of mole fraction of methane in a carbonic nuclear, this is also possible if we have the Raman spectra.

So, for example, here A and B is the peak position of two species let us say A is methane and B is carbon dioxide. So, is it possible to have some kind of an idea about the proportion in which represent some very simple all though this kind of here we see there are three four parameters here. The A stand for the peak area of A and B. So, C is essential the concentration of A and concentration of B. So, that would that would be related to parameters which is shown as here is a sigma A and sigma B which is known as the Raman scattering cross section.

This is a fundamental parameter of particular a species they are wave length dependent, we have in standard literature the tabulator values of the Raman scattering cross section at different wave length if laser say for example, 5 1 4 or 526 785 or there are many wave length lasers which are use starting from the u v to y o rangers. And those values are tabulated in standard literature which you can get, suppose we want to determine the proportion of methane and carbon dioxide here. We can calculate the area of the peak my standard method of peak integration or which if you are using a software, there are today there a very very popular and accessible softwares which will be doing the integration for the peak from the graph

So, if we calculate the peak area. So, that peak area is going to be proportional to this ratio and here the other parameter a sigma A and sigma B is sorry xi A and xi B is basically is something called the instrumental efficiency of or instrumental sensitivity or instrumental efficiency. As you whatever you can put for those for that particular species. So, when we are getting the peaks of a methane and a carbon dioxide this peak that we are getting in the machine that we are using this parameter has to be determined.

So, what is exactly done is that if we have some standard material with variable concentrations of methane and carbon dioxide. So, some such synthetic fluid inclusions or natural fluid inclusions where the concentration has been measured by many different libraries and a value which known value is agreed upon that this particular inclusion or a series of such synthetic inclusions. Or even the gas mixture even if it could be done in a pressurized gas chamber, where we can take different proportion of the two gases and take the Raman spectra. Then it is possible to have such kind of standards and for any instrument that an individual is using this instrumental efficiency parameter for this gaseous species of for that matter many gaseous species could be known before hand

So, therefore, it is possible to calculate the concentration ratio of these two species that is; present in a inclusion fluid. Sometimes it so happens that suppose we are measuring or we were interested in determining the composition in terms of the concentration ratio of two gaseous species like methane and carbon dioxide. And as well as we just discuss and we will also see in the subsequent slide, that carbon dioxide will have more than one peak corresponding to the Fermi Diad one at 1285 and the other one is 1388.

So, it will all become a matter of choice that which particular peak has to be considered or whether both the peaks can be considered with some kind of an a averaging. The practice has always been to in case of carbon dioxide to choose the two nu to peak, that is at the 1388 centimeter inverse. And, then take the peak area and then ratio of the peak area to a methane peak at then calculate this particular ratio. Sometimes it also we might ask self is it possible that the Raman spectra can be used for analysis of the inclusion in bulk, it means; the thing is that inclusion in bulk means you can think of the situation where the inclusion is homogenous.

So, suppose for example, I have a aqueous carbonic inclusion where this is the Aqueous liquid and this is the carbonic liquid and the carbonic is parcel homogenization has taken place, and this particular inclusion is now homogenized to one liquid. Let us say it is homogenized aqueous liquid. So, now, this essentially is a homogenous fluid here and it does not matter where the ledgers spot is put here or here or here. So, it will give the same composition for this particular inclusion, but then this particular homogenous state is only attainable at a particular temperature. So, there are some workers who have use this and measure taken the Raman spectra. So, here also when we if this is a whom this is aqueous carbonic fluid inclusion which is homogenous. So, it has H2O and CO2 in it.

So, if we take the Raman spectra of this we were supposed to get the peaks of H2O and CO2, and we can use the same the workers who proposed that fit and empirical equation to the ratio of the peaks peak area of these two species H2O and CO2, but it will always be applicable to the measurement could only be or the whatever equation is proposed will be applicable only to that particular temperature. So, such situation as and when it is so, theoretically it is possible to estimate the bulk composition of a particular inclusion in terms of the proportion of this species, at least a very simple case when it is aqueous carbonic inclusion and water and carbon dioxide. And, if it is taken at higher temperature only these two molecular species could be identified, there we will not have much idea about the effect of the salinity of the particular aqueous component.

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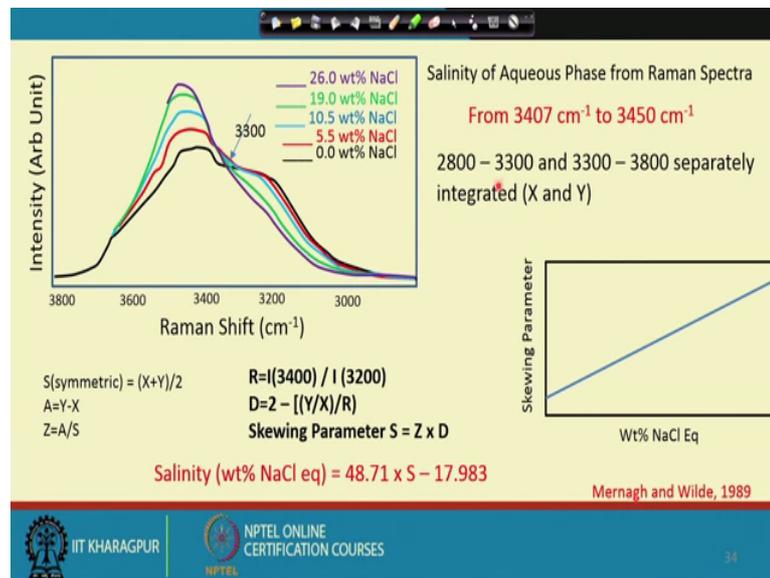
So, this is even though not very frequently used in literature, but some such possibilities also exist and it is just for the sake of the completeness of the information that, and also it is an interesting situation where there were some more one particular piece of research it attempted to estimate the salinity of the aqueous phase by taking the Raman spectra of that of the aqueous liquid at it could be just at normal temperature. We will now that and that the water will have it is peak because of the O H stitching the molecular vibration in the O and H. And the diagram here it shows the first black line corresponding to pure water which is 0 weight percent NaCl the red, blue, green and the purple curves correspondingly a representative of the aqueous liquid at 5.5, 10.5, 19 and 26 weight percent successively. And as we could see here that the peak centre part centre position

of the peaks seem to be shifting towards higher wave number with increasing weight percent of salinity

So, the question is even though we definitely have an prior idea about the salinity in terms of weight present equivalent from the freezing study, but we know that it is a giving a cumulative effect and if you want to calculate the again in the to corporate it or to exactly to have a better idea we can use this. So, this particular peak of water the Raman spectra of this water unlike what we see in some species like carbon dioxide graphite or methane which we have seen earlier does not occur at very sharp peak. But, it occurs as a broad hump almost like from 2800 centimeter inverse to 3800 centimeter inverse. And what is generally observed here is in this particular the weight has been applied the write about 3300 centimeter inverse all this peaks have a common intersection kind of a point. And as you could see here the higher NaCl weight percent liquid has a broader hump corresponding to fluid with lower corresponding to water which is lower NaCl equivalent weight percent.

So, the several parameters have been derived here like if say; the area with the peak which is integrated from 2800 to 3300 that will be represent as X and 3300 to 3800 if it is dependent separately as Y. Then we get symmetric parameters which is X plus Y by 2, and then I get a parameter with asymmetric is Y minus X and then the ratio A by S gives us a parameter Z. And here from a literature it is one the parameter; that means, the intensity the peak intensity as 3400 and intensity of 3200 the ratio is taken to be a parameter which is important for a aqueous phase a line aqueous fluid and then this parameter which is a function of this Y by X and R.

And finally, in this particular hump what we can a parameter which you can think of is a skewing parameter, that is skewing parameter is dependent on this all these parameters that you have considered as the a ratio of the symmetric and the asymmetric the difference as well as the ratio of the intensity at 3400 and 3200 and a parameter D. So, if the diagram on the right hand side it just keeps that although I have not plotted the exact value at the exact species of the electro light here. But, all these electro light sodium chloride, potassium chloride, magnesium chloride, iron chloride they will all follow a situation chloride a skewing parameter is directly proportional to weight percent equivalent in the of the aqueous component. And when we calculate the Skewing

Parameter from this fundamental parameters then the salinity is a direct function as a linear function of this skewing parameter.

So, it is possible that the weight percent equivalent of the aqueous component can be estimated from Raman spectra, to collaborate the data that is obtained from the freezing experiment in the fluid inclusions. These just since we are considering the micro analytical non destructive technique we could see that all this possibilities are what people have attempted, so far. So, that it gives us an idea that in which of these methodologies it could still be improved to get better results and also making this technique a more useful one and already this Raman spectrometric technique is widely used.

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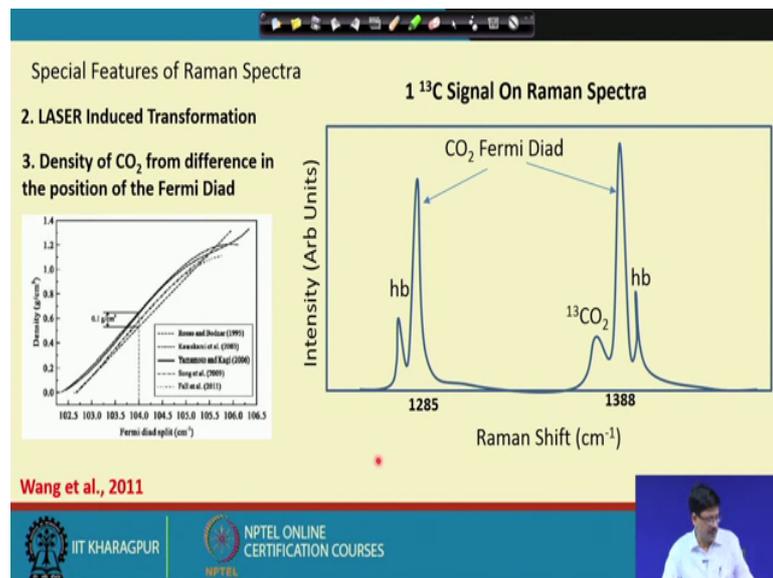
Some other kind of special features there it could see with Raman spectra, is here we just (Refer Time: 20:20) spark or up to say that actually they will be indicating the isotopic ratio and the carbon dioxide there is present.

But for the sake of our understanding and this in information its very interesting to see; this is the spectra of carbon dioxide this is occurring a 1285 it is the nu 1 and this is it 2 nu 2 that is 1388 centimeter inverse these two comparably known as the carbon dioxide Fermi Diad. So, what we see here as we discuss as before that we see a lot many more of other different types of peaks with variable intensity, at different positions of Raman shift for example, if take carbon dioxide then in case of carbon dioxide in the new one peak

just before the new one peak we get one hot band as we know that there the transition between the two excited states of two vibrational, or to vibrations at a excited state and that is 1388 peak also to the right that is one hot band.

But interestingly to the left of this 1388 peak we get one small peak which is essentially due to the 13 carbon. In sometimes while taking Raman spectra we do observe and most of the cases we do not and is it look as it is been suggested that this particular the prominence presence of the prominence of this particular peak is depending on what is the concentration. Or what is the as we expect what is the del 13 C value sometime it is putted about 20 per mill or 27 per mill if it is less than that then this peak will do not appear as it look like it does offer some promise. That, it may be that if this technique could possibly be further enhance by taking the Raman spectra in some special conditions for example, integration a very long time and at using some technique.

If this kind of peak could possibly be retrieve then we also do get some idea about the isotopic ratio what is the proportion of 13 C that could be present in the inclusion fluid and we although that is very important parameter. And, sometimes that a laser induced transformation the laser spot when it falls one the at really it generates a lot of heat, and that that heat could be calculated because it depends on the laser wavelength and also depends on the laser diameter, and the this kind of exactly in terms of the heat generated can be calculated.

And we know that they this heat is very significant and sometimes they may cause laser induced transformation there lot of much uses for as fluid inclusion researches concerned. But, sometimes this kind of laser spot induced in a carbon dioxide in a methane mixture they do result in instantaneous formation of graphite which is reflected or which is expressed as a in the Raman spectra

But will be discussing exactly about the origin of graphite in a in a later section. Even and this as for as this diagram is concerned which is coming from Wang et al., 2011 we see here that the density of carbon dioxide wearing form almost like 0.2 3. 2 almost 1.4. And when if you see this difference between Fermi Diad Diad in terms of the value what we get is wearing from 102.5 to 106.5 and this difference in the Fermi Diad is also an expression of the density of the carbonic phase.

So, Raman spectra in a way gives us lot more of information and it could still be further work up on to get any more of such information from Raman spectra. The density of the carbon dioxide also can be obtained if we have use a and such kind of diagrams. And, then finally, we look for an equation which you would relate us the density to the difference in the Raman shift between the two Fermi Diad in carbon dioxide. Let us just quickly you were although cannot be we know that it cannot be exhaustive

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But let us quickly look at some of the points, because knowingly I am giving a bit of emphasis on this particular micro beam technique, because it is the instrumentation is very simple. And, any fluid inclusion is to a bit of interest in instruments handling of the instruments and easily use or can easily have handle an equipment run the equipment to get Raman data or Raman spectral spectroscopic data. And can so, here some of the frequently asked questions that which laser wavelength to use we know that shorter is the wavelength it is definitely high energy of the laser.

But sometimes high energy also is a little bit of disadvantage because of the material is highly fluorescence, then it is always advisable to take a longer wavelength laser where the fluorescence is minimized. So, depending on that is the reason why sometimes during the sample preparation also we have to take some extra care that we the kind a mounting media that were using a should not be a fluorescing or even if we are using that mounting

media is always advisable to take the vapor out of the slide on which it is mounted in before we go for taking the Raman spectra.

So, wave length selection is depending on that and definitely will they signal will be always better. Therefore, a short shorter wavelength and a higher energy for example, if we compare it in a 514 nanometer being laser or a 785 i r or laser then it is always the shorter wavelength laser will always give better signals. So, the other what are the other problems generally we encountered while taking a Raman spectra, sometimes the fluorescence is I said it always gives us a very noisy baseline.

Sometimes, rising baseline it is because of the fluorescence even the material which is present within inclusion cavity, or in the host mineral. There so, many interferences sometimes we get strong interference from cosmic ray, and it generally the software there are provisions to get rid of this kind of cosmic ray or even manually it could be removed and sometimes if the because of ignorance if we have lot of light the. So, that there is a reason why a Raman spectroscopy is carried out in a either in an enclosed space without any outside light or somewhere in a essentially in a dark room.

So, if you have extraneous light coming it will interfere and because the kind of detectors which are used here so sensitive that any amount of extra light will always saturate the detector and the signal will be lost. So, is it possible to analyze aqueous spices inclusions by Raman spectrometry? The answer is yes it would actually the Cryo Raman when it cool the freeze the inclusion to very low temperature almost like 180 very nearly to the liquid nitrogen temperature. Because, at that type of situation where we can get the stroke side of the spectrum more clearly and we also do have the provision that the same setup on which we are the spectrometry and the microscope are coupled we do also have the a hot the stage like a Linkam stage mounted on that.

So, we can take the Raman spectra when the temperature is very low. So, it is basically known as the Cryo Raman spectrometry. So, sometimes you may not get the Raman peak at the expected shift as mentioned the literature. First we have to see that whether you are properly focus the inclusion that we want to analyze the laser alignment is also another important factor. And, today's most of the present day recruitment do have alignment systems by the old one where the manual alignment is has to be done. So, their laser aligned is on problem and peak shifting is also one of the reasons in such kind of systems

we use standard material for checking the calibration or the peak positions. For example, the silicon crystal is used to check whether the Raman shift is coming exactly on the same position as expected.

And there are this at the instrumental parameter could be adjusted to get the unknown peak at the proper position and if that is so, then we would definitely get the desired signals at expected peak position as mentioned in the literature. Raman Mapping and imaging are essentially done for solids it is rarely for inclusion, but still could be done. So, Raman mapping is essentially by taking a lots of scans on lines take the Raman spectra as reconstruct the Raman spectra and three dimensional manner all the peaks, or imaging it is a essentially is you know in a kind of concentration map, that can be obtained and it is a could be still done for fluid inclusion.

But as you know that their simply homogeneous it the situation or the need does not arise commonly. So, the peak is shifted to higher or lower Raman shift as it can always be there because with instrumental, parameters or the reasons that we have shown for example, like methane peak are always shift depending on the density and as well as the carbon dioxide peak, and sometimes when while taking a Raman spectra we may say we may see that there is no peak coming only base line is showing.

So, it generally happens when the Raman insanity is so high, that the detectors get saturated and it does not show any peaks. So, those kind of situation many of the even this machines which are available in the present day in the market will always have provisions to have the laser intensity decreased either in a very continuous manner or discrete for example, a laser light could be reduced to 50 percent 25 percent 20 percent even up to 1 percent, depending on the material if the fluorescence is very high.

Then sometimes we do work at much lower intensity than the full intensity. For example, let 20 milli watt laser to the intensity we can reduce to almost even 1 percent of that and the peak positions does not match with any commonly known gas molecular solids. So, this is a situation which can happen if there is some material or some compound some gases species which is there in the inclusion fluid. But there are Raman library. So, generally this point I have mentioned keeping in mind that many of the many of us many people many of the inclusion is to work having a Raman system if they do not have

Raman library inbuilt. So, then this searching of the library to exactly to see which molecule within the this particular spectra is matching.

And sometimes the baseline is also very noisy and erotic which could happen because the extraneous light or could be fluorescence. And, there are they could be manually or using some software the baseline could be corrected. And as the last point the Raman peak may not always be very sharp. For example, the reassurance peaks are generally broad and sometimes as we see inherently water gives a very broad hump rather than a sharp peak. So, these are some of the frequently asked questions and I know that it cannot be an exhaustive view of questions. And, I still would be would like to answer any such questions with the come up in the forum later on.

So, we conclude our discussion on the Raman spectroscopic technique. We will continue in the next class.

Thank you.