

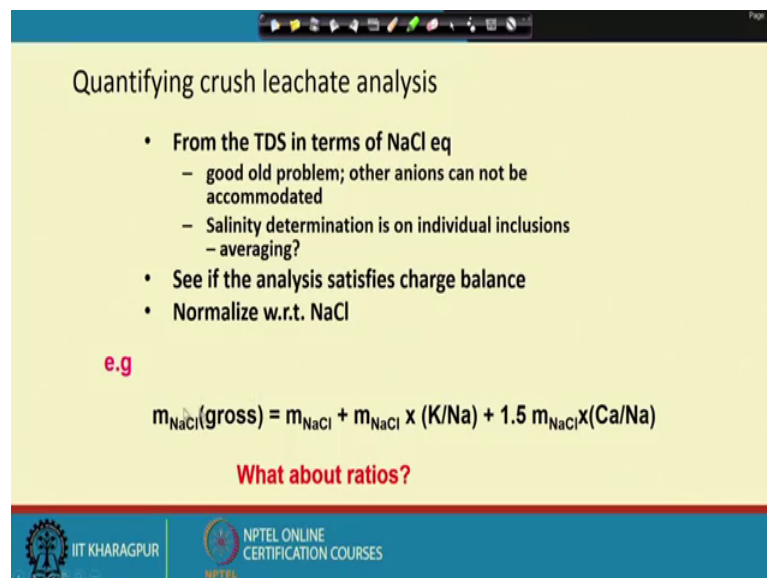
Fluid Inclusion in Minerals: Principles, Methodology, Practice and Application
Prof. M K Panigrahi
Department of Geology and Geophysics
Indian Institute of Technology, Kharagpur

Lecture – 32
Analysis of Fluid Inclusion (Contd.)

Welcome to today's lecture. We will continue our discussion on the Analysis of Fluid Inclusions and the data that we get from them and how we could advent the data that is generated by Fluid Inclusion Micro Thermometry, with the data that is generated by instrumental analysis through our destructive and nondestructive methods. To continue what we are discussing in the last class about the results of ion chromatography in which we the result that we obtained by ion chromatography is the analysis of different ionic and cationic species in concentration units of PPM or PPB. And then, knowing the leachate volume and also having a good idea about the volume of the inclusion fluid that we that could have been liberated in the process of crush leaching. We convert the concentrations from leachate to the concentration in the inclusion fluid.

And here is one more little bit of an example that this kind of these inclusions are understandably have been studied by micro thermometric methods in depression of freezing points and we have the weight percent NaCl equivalent and we have a measure the concentration of this species as potassium sodium calcium.

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Quantifying crush leachate analysis

- From the TDS in terms of NaCl eq
 - good old problem; other anions can not be accommodated
 - Salinity determination is on individual inclusions – averaging?
- See if the analysis satisfies charge balance
- Normalize w.r.t. NaCl

e.g

$$m_{\text{NaCl}}(\text{gross}) = m_{\text{NaCl}} + m_{\text{NaCl}} \times (\text{K/Na}) + 1.5 m_{\text{NaCl}} \times (\text{Ca/Na})$$

What about ratios?

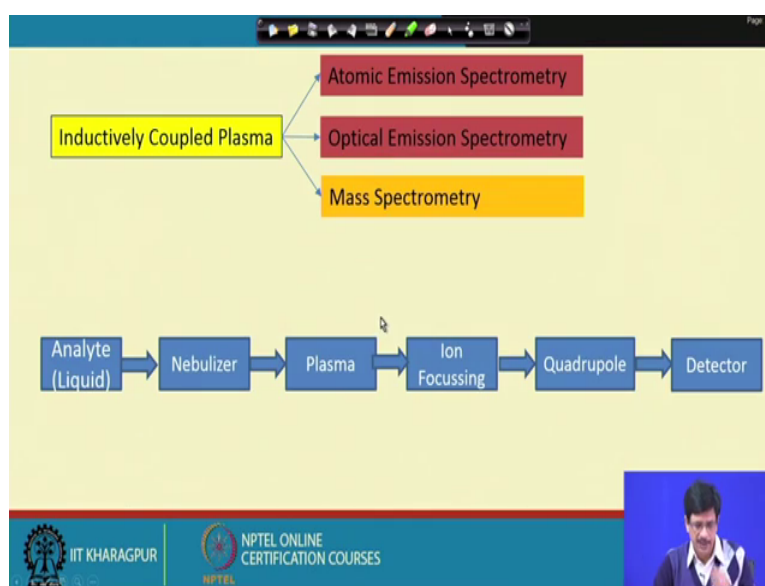
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And we could have such kind of formula that the total NaCl that we are that we got. So, from the total dissolved solids in terms of NaCl equivalent this that we suspect the there are other cat ionic species.

And the so, now if you see that this analysis satisfies the charge balance and then, we in invariably it will not, but then it has to be within the a permissible limit. And we can also get some idea about what could be the total NaCl that could be present which would be as a total coming out from the morality of the NaCl and the morality of the NaCl into potassium by sodium because this is exactly because they are monovalent 1 is to 1 electrolyte.

And if we have calcium chloride magnesium chloride and that is actually contribute into 1.5 m NaCl. So, the total NaCl that we would have got, so now, from this, we can always; so, this we have got from the freezing point depression and this become the ratio as we know this potassium by sodium and the calcium by sodium or magnesium by sodium or for that matter even if we have analyzed some iron. And then, can calculate what is the actual NaCl that is present and also the other species that is present and to do any kind of analysis or any other kind of exercise that you want to do this characters of the fluid, to understand alteration characteristics and to understand their special variability and so on. So, this is all about the crush leach method and the analysis by ion chromatography and just about it verified this to how use them.

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So, this crush leach the leachate that we obtain in the crush leach method can also be analyzed by an Inductively Coupled Plasma; either it could be an Atomic Emission Spectrometry or the Optical Emission Spectrometry or a Mass Spectrometry.

We will not be discussing about this, they have they simply work on the principle of the concentration versus the intensity of the emission or the optical in the optical range when the ions are emitting wavelength the characteristic wavelength after they are excited.

So, the analysis this inductively coupled plasma mass spectrometry analysis is the improved technique in which we can analyze too much lower concentration in going to even parts, sometimes even a few parts per billion are going to even part spectrilium sometimes; if we have a well characterized well calibrated the instrument.

It also works on the as a quantitative method. It also works on reference standards; well calibrated the reference standard with concentration ranges. And here the Analyte, it is our a leachate is injected into a nebulizer where it is converted into an aerosol.

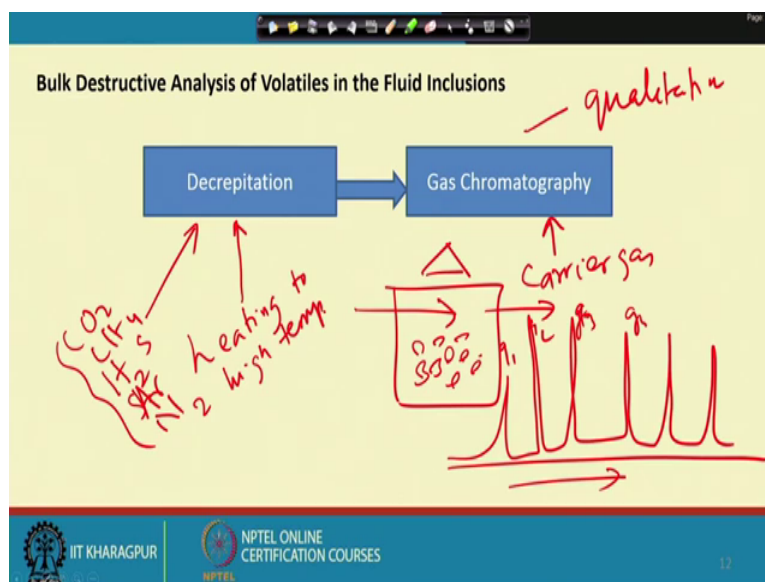
And now, it is introduced into a plasma which is created by in a gas in a environmental argon by raising the temperature to almost 7000 to 10000 Kelvin and by combination of the proper radio frequency that is that you can generating instrument and the whole idea is that the analytes are converted into their ionic state. And mostly single positive charge ions and even that particular temperature for the degree of ionization is quite substantial. We can expect that a large part of the analyte would be in a atomic and in an ionic state.

Now, once they are converted into in ionic state, they could be guided through some ion focusing by appropriate application of the current which essentially called the Ion lenses. But only just a combination of the current that is applied so that the ions are focused and are guided through a Quadrupole, where there are 4 rods which are having oppositely charge, oppositely we provided with detector in voltage and reduce frequency voltage and they are taken to the Detector, where the detector could be a device in which the ions hitting the detector and the signal that will be generated is proportional to the concentration of the ion.

So, this particular method is definitely it is a far more involved or complicated than normal ion chromatograph. But here also we get concentration range in terms of PPB PPT as we expect; very low concentrations in the inclusion fluids that we discussed. So,

stress concentrations of the lighter elements or even elements rubidium cesium or these base metals like upper lead zinc gold and iron etcetera could be analyzed with such kind of methods.

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So, this is also that was a destructive method in which we are analyzing the aqueous liquid for its concentration of different aqueous species. So, the other type of species that we have in the fluid inclusions are the volatiles. They are the carbon dioxide methane the sulphurous vapor and so on; H₂S or SO₂. So, how we generally could analyze them?

So, for that we definitely have to release the volatile species the gaseous species is from the inclusion cavities and that we can achieve by heating to a high to high temperature. This could be this could be achieved by designing some kind of a chamber in which the kind of a furnace, where the temperature could be raised to very high values; 1000 degrees are even more than that in which we could ensure that most of the inclusions which had this volatile species like a carbon dioxide, methane or the other species like H₂S and organ or nitrogen and so on could be released from the sample.

And now, if we if this is a chamber in which we have heated, we have produced; we have supplied heat to this particular chamber. And here, the sample the sample which we had with the containing inclusions which you have done the petrography and have reduced them to workable size so that the decrepitation will be more efficiently achieve there.

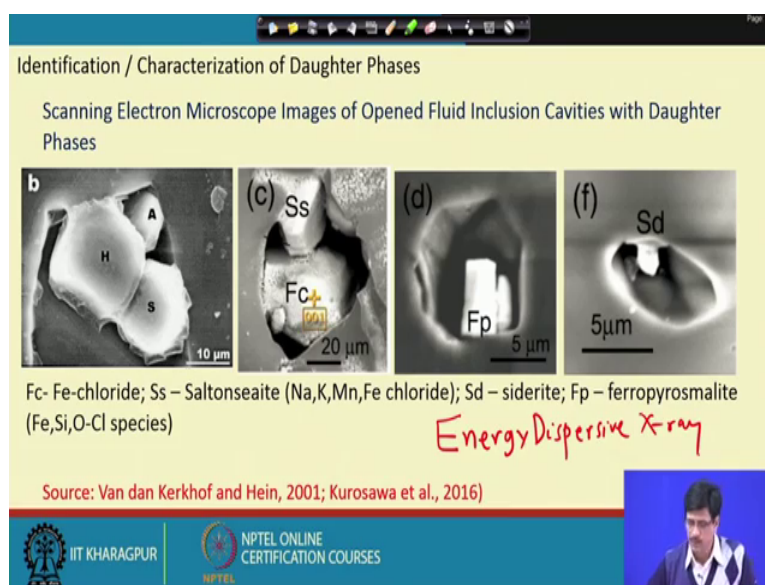
And if you can carry this whatever volatile is released within this particular chamber, can be carried with a carrier gas and this carrier gas along with the gases which is liberated from this particular a decrepitation process can be taken to a gas chromatography to analyze the different gases and such kind an analysis are also based also standard base.

If we have some standard materials in which the concentration of the gases are in known quantity, then we can always get a quantitative estimate or just by getting the, if we do not you can also do it by a qualitative analysis. So, that the principle of the gas chromatography is more or less similar to the ion chromatography that we discussed before. It also has a mobile phase to with the gases get attached occluded edge of them some mechanism.

And then, the gas which is shown through and it also acts as something like simulated mechanism to the element there and different gases are released different times from the stationary phase and they could be seen on a chromatogram, where the peaks will be there for different gases.

So, gas 1, gas 2 and gases species 1 2 and 2 and so on and the positions of this kind of or the or the sequence in which in a mixture of this gases which gases are sequentially released is known and then from that the at least we could make a qualitative estimate about the gases that are present in this inclusions.

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The other aspect or the third components of the fluid inclusions are the Daughter crystals. Daughter crystals are usually in many of the cases are identifiable; it is a major important, one of the important objective is to actually identify the daughter crystal which is inside in inclusion cavity.

Sometimes, a daughter crystal like halite is possibly could be easily identified and, but the sometimes that are daughter crystals which also remain identified. In some situations, where there are multiple daughter crystals which occur in situations like (Refer Time: 12:00) depositor many such even sometimes there are many different types of a daughter phases which observed in inclusion cavity.

So, one of the ways to identify and also to have kind of semi quantitative information about the daughter crystal is to study them and the scanning electron microscope. So, as we know that scanning electron microscope is essentially is a method which gives the characteristic on the surface, surface features, surface characteristic just to may be just about a few nanometer deep.

So, it is always that inclusions are the samples which contain the daughter crystals can be when they are polished for a prepare external normal wafer or the doubly polished thin plate in which we study this fluid inclusions. It is also quite probable that the inclusion cavities would have been opened and the inclusion cavities when they are opened, the daughter crystals generally remain in them adhere to the wall of the inclusion; the cavity inclusion cavity. And when we see them in a scanning electron microscope in a very high magnification, we can we see very very conspicuous and very clear picture; 3-dimensional image of the daughter crystals. Because the liquid part of the inclusion has been bring out, has been opened and leaked out and so, this is the solid part which are remaining. So, these images haven taken from standard literature which available to just give you an idea about how they look like and there are several such many such illustrations in literature which are available one can find them out.

So, here in this case, there is one halite, there is sodium chloride, sylvite and anhydride. These 3 solid crystal phases within an inclusion cavity just one here in quartz; this shows a inclusion cavity there is iron chloride F c and something like saltonseaitie items named under the geothermal system; saltonseaitie which is sodium, potassium, magnesium, iron, chloride.

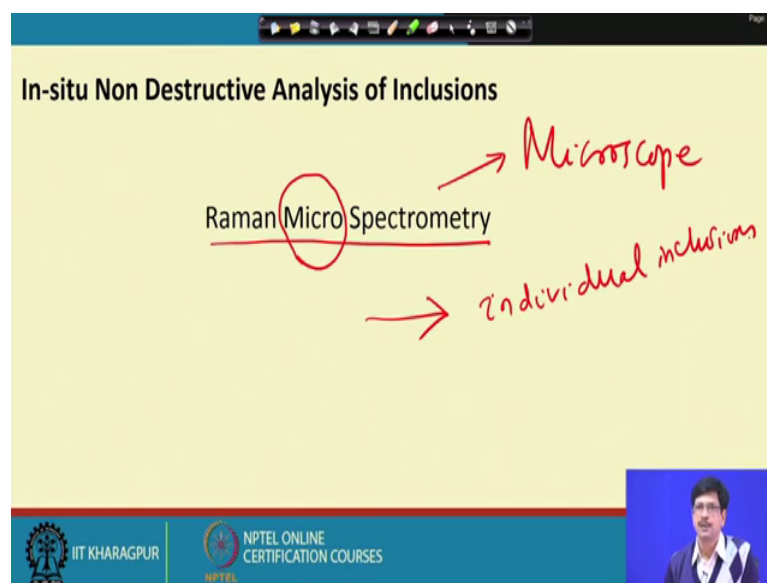
And this is a inclusion which is ferropyrrosmalite which is iron, silicon, oxygen, chloride, species and this is siderite and sometimes there are many phases which we can identify local label them as unidentified phase. So, other than just getting and these also help us because you can see the crystal morphology very clearly. For example, we see a cubic crystal, we can identify that is a halite or we see a prismatic crystal like this which can be suspected to be a sulfide like and an hydride or a gypsum.

Now, they can still further be forward the procedure can still be improved. Even if you can if we have an Energy Dispersive analysis attachment which is basically know as the EDX. So, that gives qualitative picture, qualitative idea about the composition of the solid phase that becomes even further easier to identify or exactly know toward the meshed. That could be in terms of the elemental like sodium, potassium, calcium or iron or chlorine. So, this peaks will be obtained when we use an energy dispersive X-ray in a scanning electron microscope.

Sometimes it is also there is also report the such kind of samples could also be and made able to some extra diffractometries kind of study in which if the daughter crystals present in this in this in the inclusions, can also have can be also be identified from their peaks on the X-ray die photogram. So, this is just a little bit of ideas to what we can do to these inclusions.

So, this is also a destructive, this can also be called as a destructive in a way destructive method because we are not able to utilize this particular inclusions again. But the wafer in which we are studying could possibly be again studied; but as far as the inclusions are concerned, we have opened them up. So, they could also be coming under the destructive method.

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Well, so, this much of brief idea about the Destructive methods of Analysis of Fluid Inclusions. We will now move on to our discussion on the In-situ Non Destructive Analysis of Inclusions.

So, here it is In-situ means we know that the wafer, the fully fluid inclusions section that we have used for doing routine petrography and also have taken the chips for micro thermometry such kind of chip can be used in this analysis without actually destroying the inclusions. And one such very popularly used instrumental methods is Raman Micro Spectrometry, in which we use the of course, very proudly use this concept of Raman Scattering which is essentially a manifestation of the molecular species depending because of the covalent bonds that the atoms are combined with.

And the vibration ranges or the molecular the within the infrared range of vibration for this molecules that is that principle is utilized. Utilizing the principles of interaction of electromagnetic radiation with the bonds in the compounds, this phenomena is very effectively utilized in studying the or characterizing substances and there also could be very widely used for characterizing contents of inclusion fluids, from all types of environments representing all the spectrum of processes that you have discussed. We have also at time set referred to this particular technique before for analysis of or a detecting the presence of methane and so on.

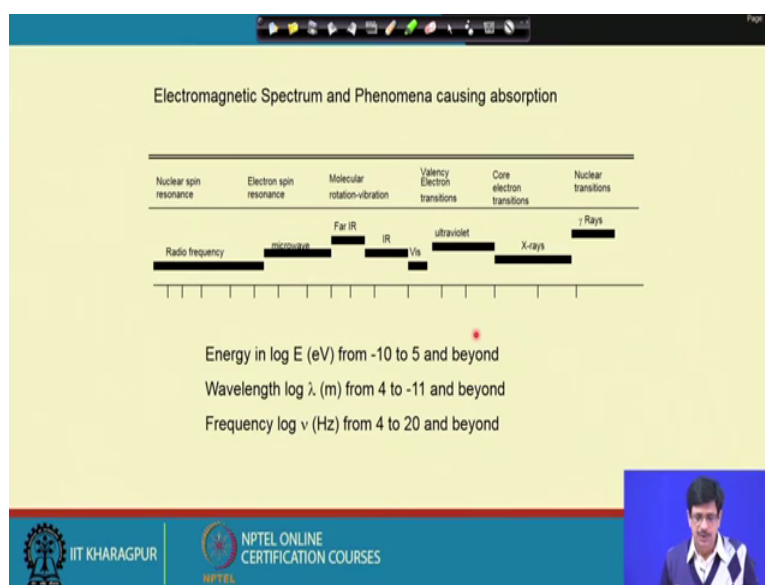
So, it is essentially a micro as for the micro technique. So, it has to be a device. So, which will be essentially the Raman Spectrometer; we need to for this is for a specialized for purpose of fluid inclusion analysis or for any other geological application, it has to be mounted on microscope and some such devices are quite available.

Now, in many establish laboratory is where routine Raman micro spectrometry is being done two characterize fluid inclusions and since, as I told that this is also be an instrumental method which will be within the within the you know jurisdiction or within the purview of a person who is doing the fluid inclusion work because it is it does not require a very very specialized a person to run the equipment.

A person or it is rather its more advisable that a fluid inclusion list also has the necessary idea about the working principles of the of the Raman spectrometry, Raman micro spectrometry because it is the material that is actually known to him only or her and the choice of inclusion or exactly because since these are done under the microscope.

So, the individual inclusions; so, it is actually is an analytical procedure which is taken on individual inclusions. So, one has to know very well, identify the particular inclusion under the microscope and the inclusion to be analyzed. So, it requires that that the person who does the fluid inclusion work is actually doing analysis of the inclusions that he studied studies in his own samples.

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So, I just quickly bonds through the underlying principles, the basic principles, governing principles of Raman spectrometry. So, we have said that we are essentially dealing with molecular vibrations; vibration of the bonds which make the molecules; our familiar molecules water, carbon dioxide, methane and many other molecules. And if you see the entire range of the electromagnetic spectrums starting from radio frequency which are applicable to our study in nuclear spin resonance to as small electromagnetic radiation in the wavelength is the gamma rays.

And the range of the wavelength in which the interaction this, these interaction processes scattering processes studied is this particular wavelength corresponding to IR because that is the wavelength which called the or the frequency which corresponds to the vibration of the bonds which binds the molecules and so, here, here is the range.

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What is Raman Scattering?

- It is inelastic
- It is weak

Quantum Theory

Interaction of a photon (of energy $h\nu$) with a vibrating molecule

Elastic – no change in frequency of the emitted photon

Inelastic

- 1) the incident photon loses energy ΔE and the emitted/scattered photon's frequency changes to $\nu - (\Delta E/h)$
- 2) the incident photon gains energy ΔE and the emitted/scattered photon's frequency changes to $\nu + (\Delta E/h)$

Which vibrating bond will have an inelastic scattering with the incident photon is dictated by Selection Rule – beyond the scope of discussion here

Handwritten red notes: $10^{-6} \rightarrow \text{LASER}$
Ar-ion laser
Solid state laser

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So, Raman Scattering is we all know that it is inelastic scattering means the interaction of the electromagnetic energy with the molecule to the bond of the molecules happens in such a way that the incoming or the incident electromagnetic energy either loses or gains in energy. In contrast to a perfectly elastic scattering in which the incident electromagnetic energy neither loses nor gains in its energy and emits in the same wavelength and frequency.

But the problem is that it is a weak scattering and we can only think of that if the quantum of electromagnetic energy which is undergoing inelastic scattering will be

something like 10^{-6} part of the intensity of the electromagnetic energy which actually undergoes inelastic scattering.

So, normally in that case, to study this inelastic scattering would be very difficult to do it with ordinary light, ordinary in the common light, the ordinary light that we are using. So, we need to have electromagnetic energy the light which will of very much higher power than the normal light which we generate by a normal device.

So, it has to be a LASER that is your Light Amplified by Stimulated Emission of Radiation and this kind of lasers are generated by many different devices, they could be and also the materials the kind of laser that we use for laser Raman micro spectrometric study are generally low power laser and they could be the gas laser like Ar-con Ar-con ion laser or maybe Solid State laser which will be having the power of 2200 mili what a range of power.

And since for geological applications, these kind of ranges are sufficient and that is why the methodology actually is very popularly known as the laser Raman micro spectrometry or LRM and so, the fundamental aspect is that it is inelastic scattering and it results out of the interaction of the electromagnetic energy with the bonds vibrating bonds in the molecules.

So, the if we can understand them by using quantum theory which will be bit difficult for us to understand and also it will be bit out of scope of this particular lecture series, but just to begin with that we know that the interaction of a photon, the photon will be having the energy of $h\nu$ with a vibrating molecule.

So, elastic is no change in frequency. Inelastic is the incident photon, loses it energy by a quantity ΔE and the emitted scattered photon frequency changes from ν minus ΔE by h . h means it will be emitted with the frequency which is less than the original incident frequency by a quantity which will be the difference and energy divided by the plus constant or it may happened that the incident photon gains some energy. So, it will only depending on the vibrational state that ground state or excited state between the bond of the molecule and the incident electromagnetic energy.

So, the thing is that the. So, the particular you will see in subsequent slide, these are molecules which are the atoms are bond with this bonds joined or connected to the

bonds; these bonds are actually vibrating and there will be many vibrating bonds and many such vibrations that are possible in a particular molecule.

But all the vibrations will not be resulting in inelastic scattering. So, that is actually governed by some principle which is known as the selection rule as per the Quantum theory. But we will rather take an easier route to understand it by the classical concept.

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The slide is titled "Classical Theory of Raman Spectroscopy". It features a diagram of a diatomic molecule on the left, consisting of two masses m_1 and m_2 connected by a spring with force constant k . Below this, it states: m - mass of atom, k - force constant (chemical bonding). To the right of the molecule diagram, the reduced mass is given as $m_r = \frac{m_1 \cdot m_2}{m_1 + m_2}$, and the vibrational frequency is $\nu_{\text{molecule}} \sim \sqrt{\frac{k}{m_r}}$. On the right side of the slide, there is a diagram illustrating Raman scattering. An incident wave (black) interacts with a vibrating molecule (blue spheres connected by a spring). This results in two outgoing waves: an "inelastic part" (red) with a lower frequency $\nu - (\Delta E/h)$ and an "elastic" part (green) with a higher frequency $\nu + (\Delta E/h)$. The slide also includes logos for IIT Kharagpur and NPTEL Online Certification Courses at the bottom, and a small video inset of a presenter in the bottom right corner.

So, here it is shown here that think of a molecule in which these atoms are the m_1 and m_2 and the bond representing the bond actually we join the 2 can be thought of as a spring which is having a spring constant.

And this frequency of the vibration of the molecule will be a simple formula, this force constant divided by the μ m_r which is basically m_1 into m_2 by m_1 plus m_2 . So, here, that means from this for many given any particular the bond this force constant value and the mass of the atoms, we can always calculate or if you know what are the different frequencies in whose the bonds will be vibrating. Here is a very crude and other schematic representation of what exactly happens?

So, this is the incident this represents our molecule in which the atoms joined or connected to this bond; the bond is like a spring which is having its own vibration as per the formula that we have given here. So, now, in this is an incident electromagnetic energy and it interacts with this bond, then what will actually happen?

So, this black line represents the incident electromagnetic the frequency and the wavelength represent in the incident electromagnetic energy and which is also have shown its a same black wave which is going, which is getting reflected a scattered, retaining its frequency and the wavelength exactly and as we said that this is the major part of it this. This part is the major part which is actually scattered.

Now, this green is representing the emitted electromagnetic energy with the frequency which is $\nu - \Delta E/h$ and this red in which we see that the frequency is increased is actually emitted has $\nu + \Delta E/h$.

So, actually it is actually they are travelling the same distance and same just only a representation just to distinguish them. So, this is the. So, this is the kind of a schematic representation of what happens to explain the process of this wave represented by green and the blue, they represent the inelastic arch and the one which is black is the elastic. So, the black is elastic and the green and the red an inelastic ok.

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Classical Theory of Raman Spectroscopy

Banwell and McCash: Fundamentals of Molecular Spectroscopy

$\mu = \alpha E$

μ is the size of the induced dipole and E is the magnitude of the applied Electric Field

α is the polarizability

If sample of such a molecule is subjected to a beam of radiation of frequency ν the electric field experienced by each molecule varies according to

$E = E_0 \sin 2\pi\nu t$

$\alpha = \alpha_0 + \beta \sin 2\pi\nu_{\text{vib}} t$

$\mu = \alpha E = \alpha E_0 \sin 2\pi\nu t$

α_0 – equilibrium polarizability
and β is the rate of change of polarizability with vibration

$\mu = \alpha E = (\alpha_0 + \beta \sin 2\pi\nu_{\text{vib}} t) E_0 \sin 2\pi\nu t$

$= \alpha_0 E_0 \sin 2\pi\nu t + \frac{1}{2} \beta E_0 \{ \cos 2\pi(\nu - \nu_{\text{vib}})t - \cos 2\pi(\nu + \nu_{\text{vib}})t \}$

Rayleigh Stokes Anti Stokes

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Now, we take the little bit of an easier route to understand the situation here; what exactly happens in a elastic and non inelastic scattering. This have been taken from standard text books like the Introduction to Fundamentals of Molecular Spectroscopy by Banwell and McCash and any interested reader who will wants to know little more about it, have a better or more fundamental idea about this spectroscopy as it is applied.

So, both Infrared and Raman spectroscopy are covered as a part of molecular. They are the molecular spectroscopy; so, quickly browsing through the principles. So whenever there is an electrical, if the electromagnetic energy electromagnetic wave is interacting with a molecule. So, actually what happens it is a electric field of the electromagnetic energy which is responsible an inducing the dipole in the molecules.

So, molecules have got there inherent dipole moment. For example, water which is the higher dipole moment than carbon dioxide, but inherent dipole whatever it could be, but this incident electromagnetic energy the electrical field of that part induces that dipole. It actually induces a dipole and which is this μ is the size of the induced dipole which is proportional to the applied electric at the electric field of the electromagnetic radiation.

And the professionally constant is α is the polarizability of the molecule. So, this is a very important parameter in relation to Raman Spectroscopy. So, if a same sample is subjected to a beam of radiation of frequency ν , the electric field experienced by each molecule is actually given by. So, the electric field E is the $E_0 \cos 2\pi \nu t$. So, ν is the frequency and α is given by this formula that $\alpha_0 \cos 2\pi \nu t$ vibration into t .

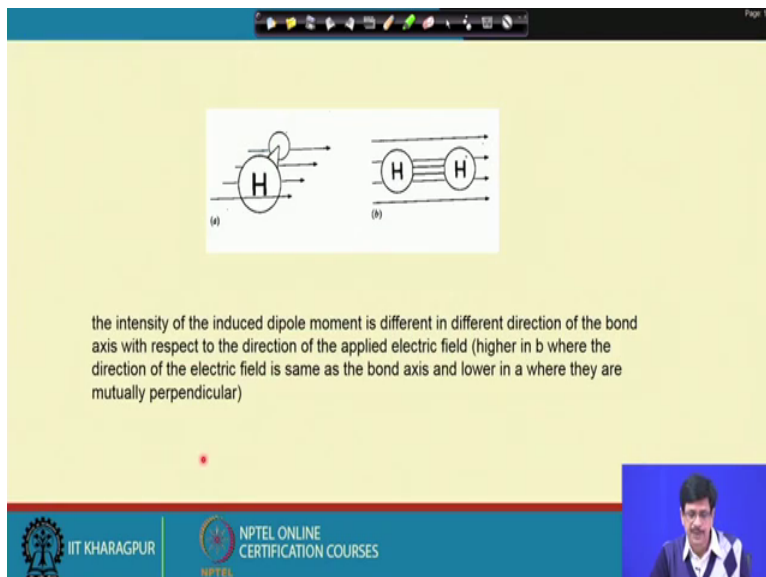
So, if I replace this α in the expression of the induced dipole that is μ , then we get an expression where it is $\alpha E_0 \cos 2\pi \nu t$ and if we expand it just by using our trigonometry relationship in case of this $\sin 2\theta$ kind of expression. Then, we get a component which is $\alpha_0 E_0 \cos 2\pi \nu t$ plus half of these terms which is coming into here is first term where it is you could see that $\nu - \nu_{\text{vibration}}$ into t and here it is $\nu + \nu_{\text{vibration}}$ into t .

So, here we see that the incident electromagnetic and so, this part is representing the scattering analysis scattering which actually is not involving any loss or gain of energy and the light the energy is emitted by the same frequency ν ; whereas, the other situations which is possible here is that here its actually going by a emitting by a reduced frequency and here itself added one.

So, this components one is that where it is actually deposits inelastic scattering is actually 2 different types of possibilities which can happen; one is a loss in the energy of the frequency and the other one is gain. So, the first one is basically known as the Stokes scattering and the other one is called as the Anti-stokes scattering. So, here α_0 is the

equilibrium polarizability and the beta is the rate of change of polarizability with the vibration.

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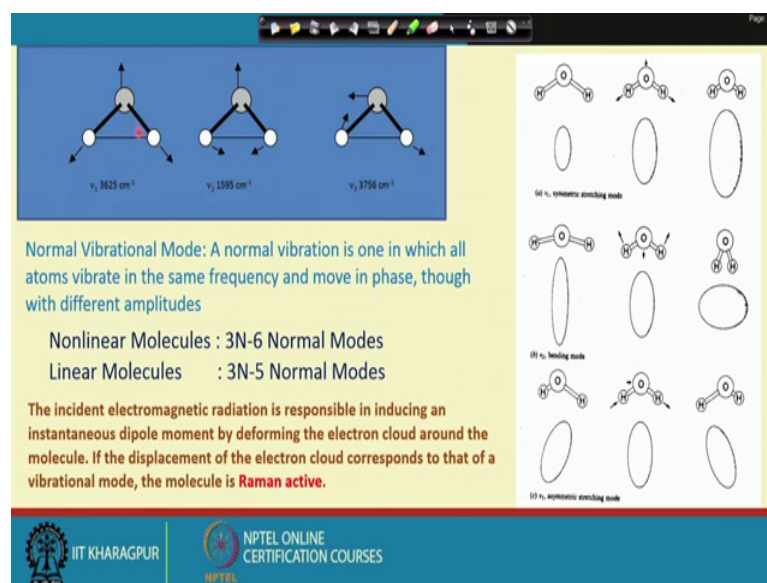
the intensity of the induced dipole moment is different in different direction of the bond axis with respect to the direction of the applied electric field (higher in b where the direction of the electric field is same as the bond axis and lower in a where they are mutually perpendicular)

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So, this is the pictorial presentation as to what happens. So, suppose we have a molecular hydrogen in which the bond direction is in this shown on the paper, perpendicular to the paper and the direction of the electric field is shown by the arrow. In one case and the other case, it is the direction which is shown parallel.

So, here the intensity of the induced dipole moment is different in different directions of the bond axis with respect to the direction of the applied electric field. In case of b, it is higher for the direction of the electric field is parallel to the direction of the bond axis and is lower in case of the case for its perpendicular.

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And now, we come to would because we deal with the normal our inclusions contain the gas molecules water carbon dioxide.

Let us see let us try to look through this procedure by very simple consideration and this is the water molecule. So, we have now the know the background that depending on the electric field and its interaction the polarizability is something which is coming out to be a very important parameter as far as the scattering is concerned. And now let us let us see this water molecule which can be visualized as a molecule which a non-linear and is bonded in this way with the 2 hydrogen atom and 1 oxygen.

The stronger O and H bond with the weaker H and H bond which is conventionally represented, you can see in any textbook. So, this molecule of water can have 3 such different states. For the arrows marked is essentially that there is force acting on it. So, that these bonds are actually stretched all the 3 bonds are in a state of stretch. This is this can be called as One mode which I will come to later and this is one possibility that this bond which is the H S bond is undergoing a bit of bending and the HOH bonds are stretched; in this case it is the OH bond its getting bent and the 2 other bonds are getting stretch.

So, these are the 3 possible states in which the molecule of water and the bonds hydrogen and O and H bonds would be in a state of vibration. So, when we look at any molecules like this, we think of or we know that what we can call a something as a Normal

Vibrational Mode. So, Normal Vibrational Mode is one in which all the atom all the atoms vibrate in the same frequency and move in phase even to their amplitudes could be different.

Other the simple thumb rule which is adopted here that if the molecule is non-linear. So, this will call is a normal mode there are vibrational mode fundamental modes and how and which we call this in particular is the normal modes which as essentially important for Raman Scattering to understand the Raman Scattering. And this is the thumb rule that the number of such normal mode normal vibrational modes will be $3N$ minus 6 in case of non-linear molecules. So, N stands for the number of atoms.

So, if we have a atom of water in which there are 3 atoms sorry a molecule of water is there are 3 atoms. So, 3 into 3 , 9 ; 9 minus 6 ; so, there are 3 fundamental or normal vibrational modes which are shown with this ν_1 3625 centimeter inverse; ν_2 as 1595 centimeter inverse and ν_3 as 3756 inverse.

And now we have we said that the Raman Scattering is actually the Raman scattering would be involving interaction or inelastic scattering of the incident electromagnetic energy with the bonds of the molecule. Now if there are 3 fundamental modes vibrational modes, then will the scattering Raman will the Raman Scattering take place in all the 3 modes or it will be observable in only one or more less than the total number of vibrational mode and if so, why?.

So, we will continue discussing on this in a next class.

Thank you.