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Kanpur

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on
Technology Enhance Learning

Course Title
Advanced Characterization Techniques

Lecture-07

by…
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In this class today we are going to discuss about a very important spectroscopic techniques called Raman spectroscopy.

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Advanced Spectroscopic Techniques

Raman Spectroscopy

And as you know Raman was an Indian and lot of in Curtin aspects are involved in relating this spectroscopic technique so I will be able to do a little bit of justice to this in one-hour time but I do not think it is possible to talk about the details of the spectroscopy in just a short span of time because a lot of aided theories are needed to be covered in such a class but I am going to give you some basic idea of the spectroscopic technique how it can be related to applications and obviously some amount of instrumentations will be dealt with.

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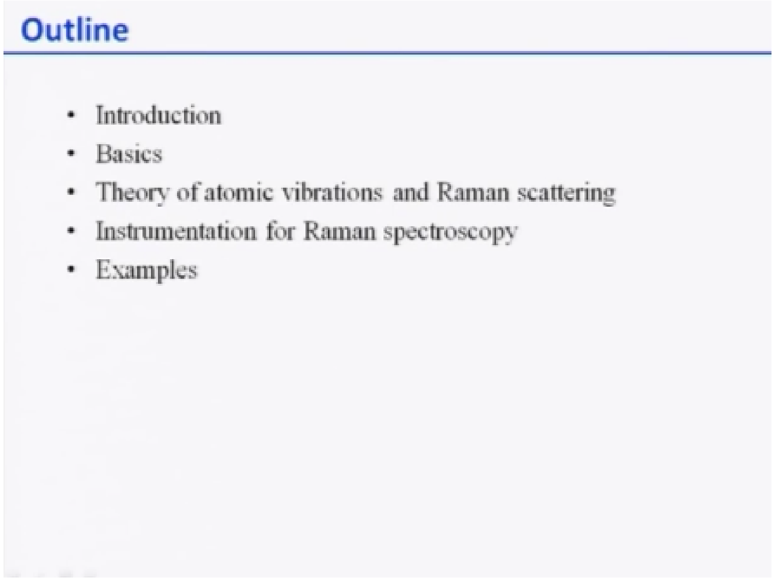

Outline

- Introduction
- Basics
- Theory of atomic vibrations and Raman scattering
- Instrumentation for Raman spectroscopy
- Examples

As you know the outline is like this obviously there will be some aspect of introduction going back to history and some basic features and then I will talk about some basics of the Raman spectroscopy where I will talk about theories and then some amount of scattering and vibrations and finally some instrumentation for Raman spectroscopy and obviously you know during the course of the lecture I am going to talk about some examples from the literature from some of our own work.

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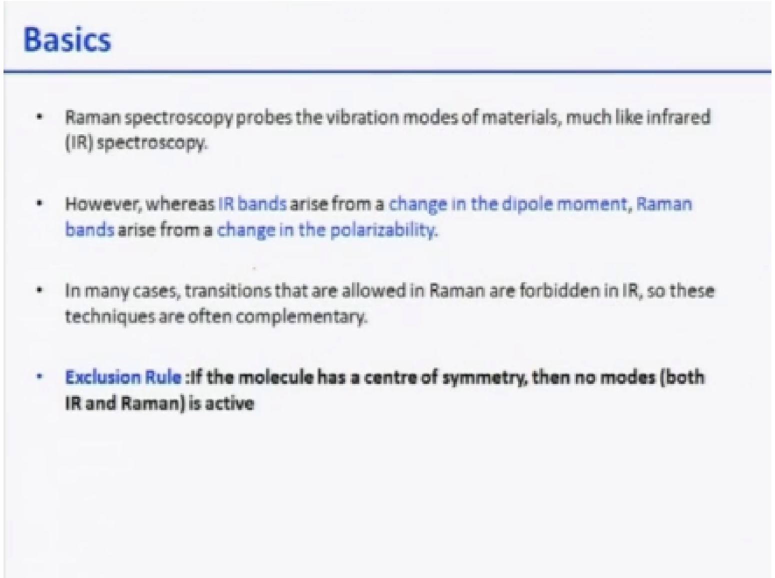

Basics

- Raman spectroscopy probes the vibration modes of materials, much like infrared (IR) spectroscopy.
- However, whereas IR bands arise from a change in the dipole moment, Raman bands arise from a change in the polarizability.
- In many cases, transitions that are allowed in Raman are forbidden in IR, so these techniques are often complementary.
- **Exclusion Rule :If the molecule has a centre of symmetry, then no modes (both IR and Raman) is active**

As far as the basics are concerned I am Raman spectroscopy square basically probes to the vibration modes of material it is more like an infrared spectroscopy I have already discussed when for inspectors could be in a few classes back and there I showed you by you know theoretical presentations that how this IR spectroscopy related to the vibration modes of the molecules.

But there is a distinct difference between IR and the Raman spectroscopy in fact IR spectroscopy the band's arises from the change in the dipole more and other molecule but Raman’s bands arise from a change of the polarizability not the change in the dipole moment remember so it is the porosity price the ability change that makes the Raman’s so interesting so therefore the symmetric molecule it will not work that is the most important problem in Raman spectroscopy.

In many cases transitions that are allowed amounts are forbidden in IR so there are techniques these two techniques are basically complimentary to each other so you will see that we also a comparable spectra from the Raman and from the IR to show you how this the techniques can be used for Complementary so therefore as I said at the very basic aspect of the Raman spans arising during measurements is the change in polarizability of the molecule that basically sets an exclusion rule.

What is the exclusion rule it says if the molecule has a center of symmetry then no modes are is active whatever is a IR and Raman so as you can look into his this slide you will it will be clear to you for a molecule.

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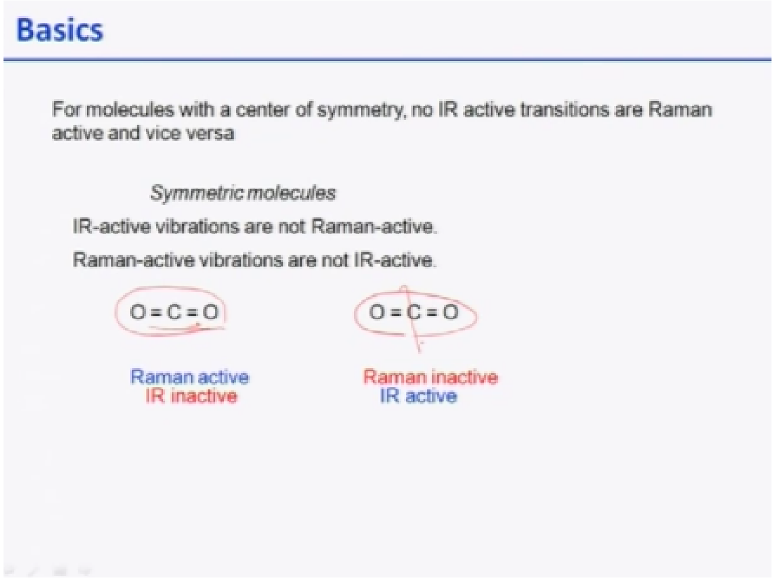

Basics

For molecules with a center of symmetry, no IR active transitions are Raman active and vice versa

Symmetric molecules

IR-active vibrations are not Raman-active.

Raman-active vibrations are not IR-active.

With a center of symmetry as I said no IR active tensions are Raman active or vice versa what is it let us suppose this molecule which is Coo that is co 2 and you know it is Raman active but IR active but on the other hand if the molecule has changed that means if this molecule is little bit of you know center of symmetry chain little bit this side right side then it becomes Raman active on the other hand if the molecule become fully central symmetric then no bands no none of these techniques can apply.

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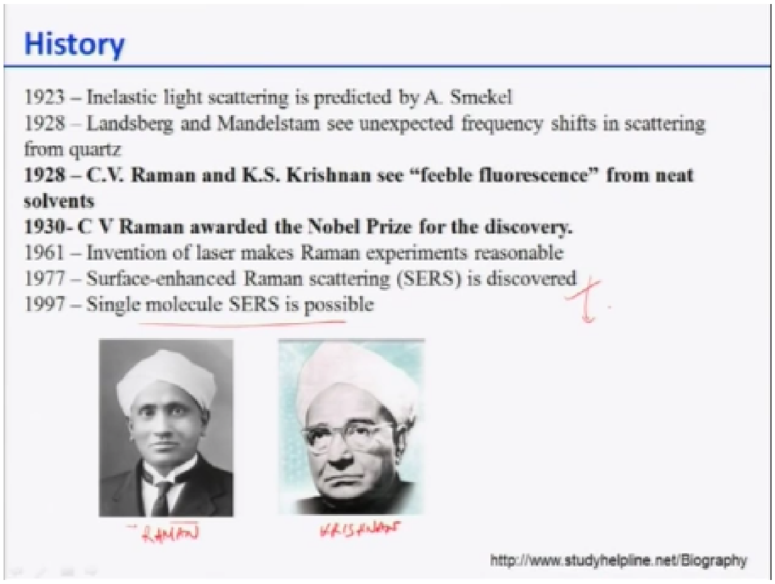

History

1923 – Inelastic light scattering is predicted by A. Smekel
1928 – Landsberg and Mandelstam see unexpected frequency shifts in scattering from quartz
1928 – C.V. Raman and K.S. Krishnan see "feeble fluorescence" from neat solvents
1930- C V Raman awarded the Nobel Prize for the discovery.
1961 – Invention of laser makes Raman experiments reasonable
1977 – Surface-enhanced Raman scattering (SERS) is discovered
1997 – Single molecule SERS is possible

RAMAN
KRISHNAN

http://www.studyhelpline.net/Biography

As far the history is concerned that needs to be told because human was the first normal laureate in science obviously his first noble noise from his countries was for literature in 1923 in 13 but 1930 CV Raman got Nobel Prize in Physics because of the discovery if I want to trace back the how this spectroscopic technique or the Raman effect came into picture first thing we need to understand is the Raman is basically to inelastic scattering so first time inelastic scattering light scattering as predicted by Smekel in 1923 and then after five years 1928 Landsberg and Mandlestam see the first unexpected frequency change in a scattering from a quartz.

That is what this Inelastic scattering means actually because Inelastic scattering was known or even long back from Raleigh law dry less time but Inelastic scattering was not fully understood so it was in the early part of the last century 20th century these things have started in 1928 CV Raman and one of his students very last is a student's K.S. Krishna first time while working on different solvents saw feeble fluorescence and it was reported.

And after within two years it was we have come so no intense our activity Raman was awarded Nobel Prize to tell you that K.S. Krishnan this is the picture both of them are taken form studyhelpline.net where you can get bio-data this is Raman's picture and this is Krishnan just to impress you up on that in those days when India was under British rule still there are scientists were working on path-breaking research.

And it was only possible because of these two gentlemen who worked hard to put the things into the world's perspective as per scientific content is concerned so and but you know Nobel Prize was given to C.V. Raman, K.S. Krishnan obviously was a PhD student who work hard to prove that so his contributions were null nowhere less so that is why I already show you and then 1961 laser came and on the maser actually after the Second World War and 1977 first time using laser surface yeah enhance Raman scattering was discovered.

This is thanks to laser on a lead as possible to discover that and 1997 that is the big change happened in the Raman spectroscopy another big change when single molecule shows surface enhance among spectroscopy spectrum or scattering so therefore nowadays we can actually go all the way to the single molecule and get Raman scattering and then prove it using Raman spectroscopy technique.

So that is how it is actually possible as soon as you understand talking all this surface on Raman's spectroscopy and single molecules almost Raman's spectroscopy another spectroscopy is beyond the scope of this course so those of you who are really interested or maybe using this technique extensively they can look at different books which I will show you even some of the references while give me the lectures and then understand or try to understand maybe these are very advanced topics not even part of the discourse.

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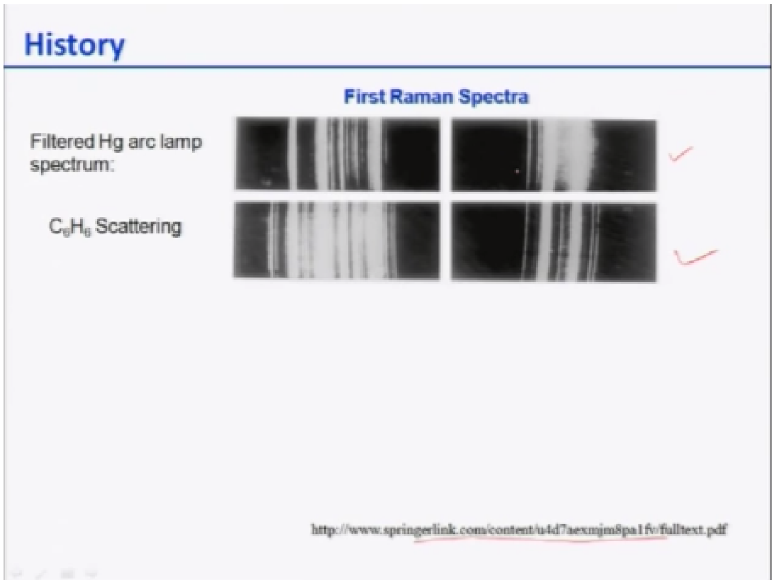

History

First Raman Spectra

Filtered Hg arc lamp spectrum:

C_6H_6 Scattering

http://www.springerlink.com/content/u4d7aexmjm8pa1fv/fulltext.pdf

Well to show you how the first Roman Spectra looked like this is taken from this paper which is published long back okay you can see this is the spectrum Raman’s flows and spectrum obtained from silk mercury arc lamp and this one is from benzene okay C6H6 so there are distinct bands you can see on it from the photographic plates and these bands actually are related to Inelastic scattering molecule.

Let us look into theory in detail that will tell you hi the Raman’s actually scattering happens and how it can be utilized.

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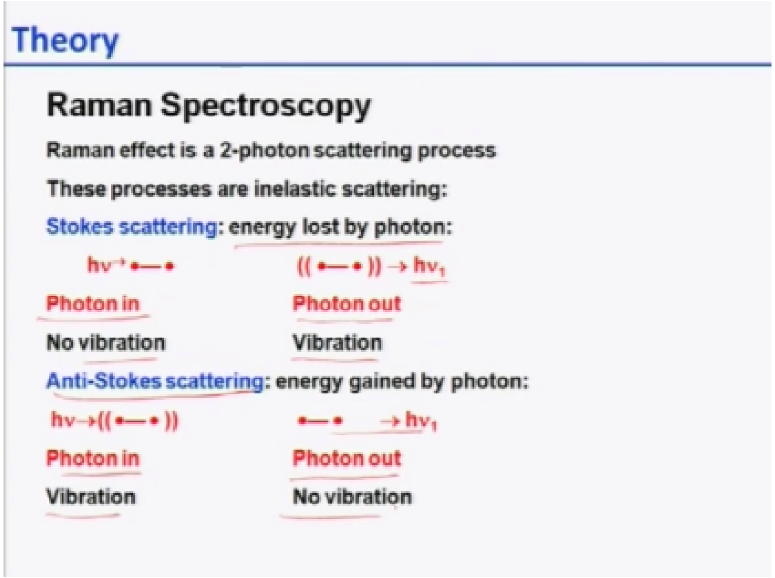

Theory

Raman Spectroscopy

Raman effect is a 2-photon scattering process

These processes are inelastic scattering:

Stokes scattering: energy lost by photon:

$h\nu \rightarrow$ •—•	((•—•)) $\rightarrow h\nu_1$
Photon in	Photon out
No vibration	Vibration

Anti-Stokes scattering: energy gained by photon:

$h\nu \rightarrow$ ((•—•))	•—• $\rightarrow h\nu_1$
Photon in	Photon out
Vibration	No vibration

If I have a tell you in one sentence and Raman’s effect is a two photon scattering process it is no longer a single photon scattering process and these processes are all Inelastic scattering type so first thing when you talk about this talk scattering and Stokes scattering is all this analysis because energy is lost by the photon now if I have put on in and obviously there is no vibration here and therefore this photon will be absorbed by the molecule there are so sufficient enough for it to you know get excited to the excited States.

And some amount of photon with less frequency obviously will come out because some I want to has been absorbed that is what is the nature of inelastic scattering you should know that and this will lead to vibrations under these vibrations can lead to fluorescence and this source scatterings and as is gained by the photon instead of loss so what happens you have a photon in and there is a vibration.

And then photon absorbs this molecule exclaims of a photon so some photon goes out but you know energy is gained by the photon in this way so there is no vibrations but there are two kinds of scattering as you see in which one is energy is lost by the photon or other energy is gained by the photon and both inelastic is scattering times they are called Stokes and Anti Stokes now there is obviously dominant scattering process which is inelastic scattering.

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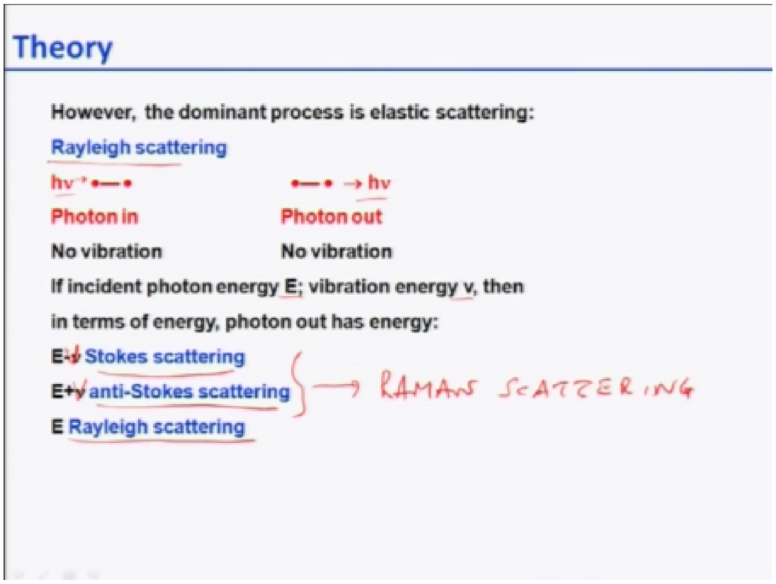

Theory

However, the dominant process is elastic scattering:

Rayleigh scattering

hv → •—• •—• → hv

Photon in Photon out

No vibration No vibration

If incident photon energy E; vibration energy v, then

in terms of energy, photon out has energy:

E-v Stokes scattering

E+v anti-Stokes scattering → RAMAN SCATTERING

E Rayleigh scattering

Inelastic scattering means there is no energy loss when the photon is absorbed photon is out and this is what is known by name of rod literally Rayleigh long back and this is simple energy absorbed energy goes out so in both the cases no vibrations so aggressive scattering is cannot give these Raman scattering if instead of photon energy and the vibration fake energy is P okay this is V so V then in terms of energy we can write E - V is a Stokes scattering a + P anti strokes scattering and E is a inelastic scattering and E is a inelastic and these two gives Raman scattering not the last one you should know that this has all been taught for the different set of particles.

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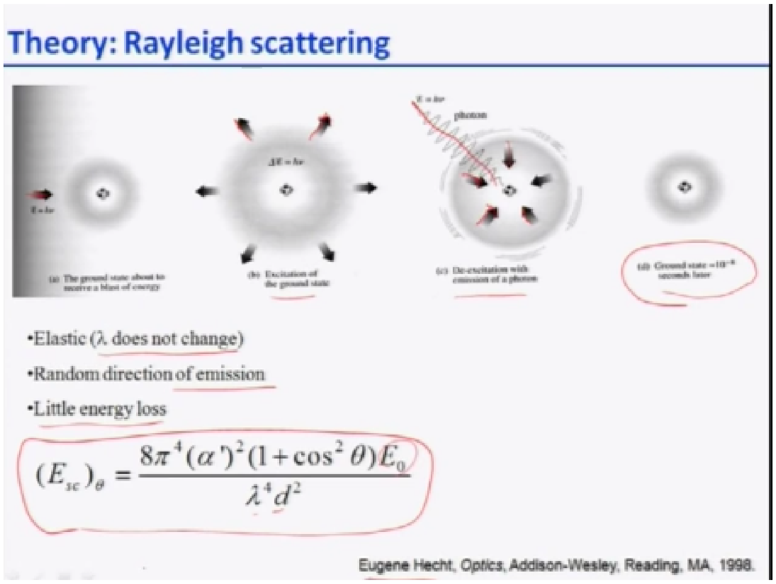

Theory: Rayleigh scattering

- Elastic (λ does not change)
- Random direction of emission
- Little energy loss

$$(E_{sc})_\theta = \frac{8\pi^4(\alpha')^2(1+\cos^2\theta)E_0}{\lambda^4 d^2}$$

Eugene Hecht, *Optics*, Addison-Wesley, Reading, MA, 1998.

Now to talk about more about less scattering this is again taken for huge in Hecht optics book so if I have a molecule you can see nucleus and electron cloud there and certain photon energy comes H nu and then it is get excited ground states to the higher on this state it goes I can see that and then the excitation can always happen that means the molecule can come back to the original ground state by emission of this photon this is fine and you know this can happen in the order of 10 to - 8 seconds.

So therefore inelastic scattering basically λ does not change the length of the vibration does not change it can have random direction of emissions does not lead to fluorescence and there were little energy loss so therefore it is not and this is what is the basically the scattering energy where these are the different parameters the λ disturb when these energies energy ground state θ is the energy at which it is scattering of angle.

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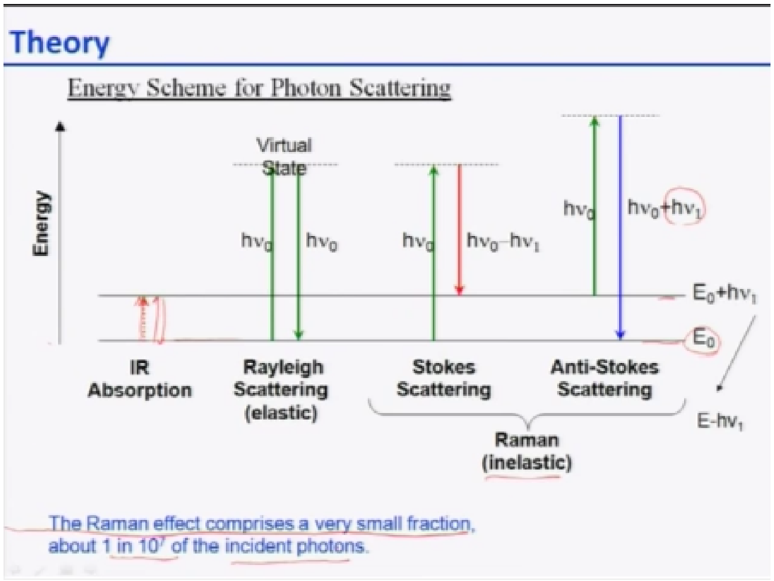

Theory

Energy Scheme for Photon Scattering

The Raman effect comprises a very small fraction, about 1 in 10^7 of the incident photons.

Now if I want to put it to ignoise scattering in two perspectives so I can actually make a schematic diagram and show you that so you know this is what is ground state energy level E0 you can see and then if I have some photon in the wavelength of IR radiations the molecule based excited to the higher energy level E0 + hν and when it come well this can be also explained using the photon scattering in a energy landscape.

So as we see I have seen that there are two kinds of scattering one is elastic other one is Stokes anti-stokes which are basically known as inelastic scattering and they are ready to Raman so if I consider E0 as my ground state for the molecule and this is the vertical axis the energy so whenever certain infrared radiation is imposed on this molecule it will absorb and go to the high energy band that is suppose the excited States and when it is comes backs it gave it the radiation and that would detect it and that is what is the principle of IR spectroscopy.

Now, one can always think the glace scattering or elastic scattering in this way we have a higher energy hν0 by which the molecule is goes to virtual excited States not the nearest excited state and when similar amount of energy is released by the molecule it comes back to the ground state that is what I have shown you in the last slide here exactly the same thing now in case of Stokes suppose molecule is excited to the higher in the state of virtual state by h ν energy level and there is some inelastic scattering happens some energy get lost.

So that it does not come back to the ground state at all that means it lost energy but the molecules can come back by losing this energy hν 0 - hν1 to then excited States and vibration States the above the ground state that is what is this one so if you see obviously you can see it confuse easily when it comes back to the ground state another situation can happen an anti stroke scatter what is that molecule can get excited to the hierarchy state previously virtual states okay.

And when it goes there it gets to these virtual states it gathered more energy maybe it can have h ν 1 external g okay so that total energy of the molecule increased because it absorb another photon other than hν0 and when it comes back to the ground States it just have external energy which is also coming out hν + h2o this can also lead to fluorescence.

So therefore both at stop scattering anti scattering can lead to Roman that is what I am saying but the catch is this the Raman's effect comprises a very small fraction about 100 of those 7 of the incident photon so that means we need to have very good probe to detect the small number of photons which are actually undergoing this.

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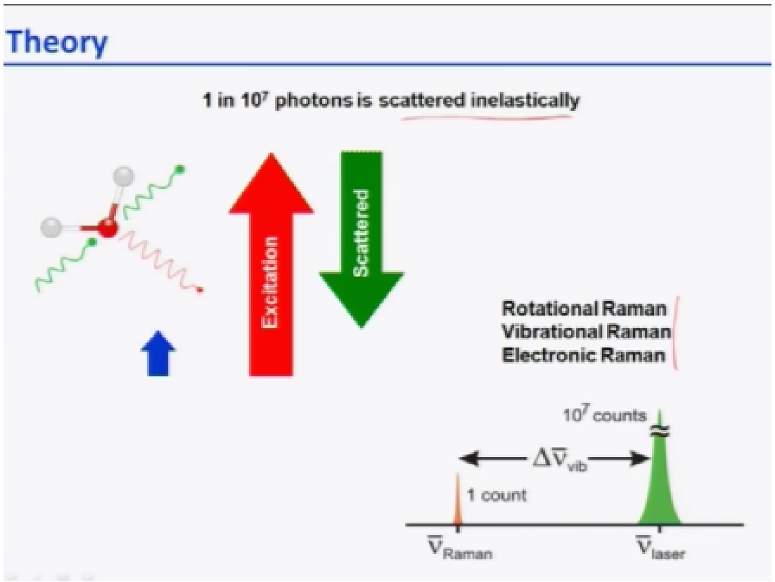

Theory

1 in 10^7 photons is scattered inelastically

Rotational Raman
Vibrational Raman
Electronic Raman

Because most of these and the events will be happening in the really scattering things now if I want to put it in perspectives in front of you if I have molecule energy goes out and energy comes go seen and as it comes out so that means get excited and it gets scattered so only you can see that Raman count is only one that it is actually the laser actually which is used for scattering is very high into the seven counts.

So that means one into verse seven photons is scattered in less physically so almost bulk of the photons get scattered by inelastic and they can have we can have different kinds of Raman spectroscopy depending on what kind of you know scattering is what kind of things are happening like rotational States or vibration States or electronic states energy level.

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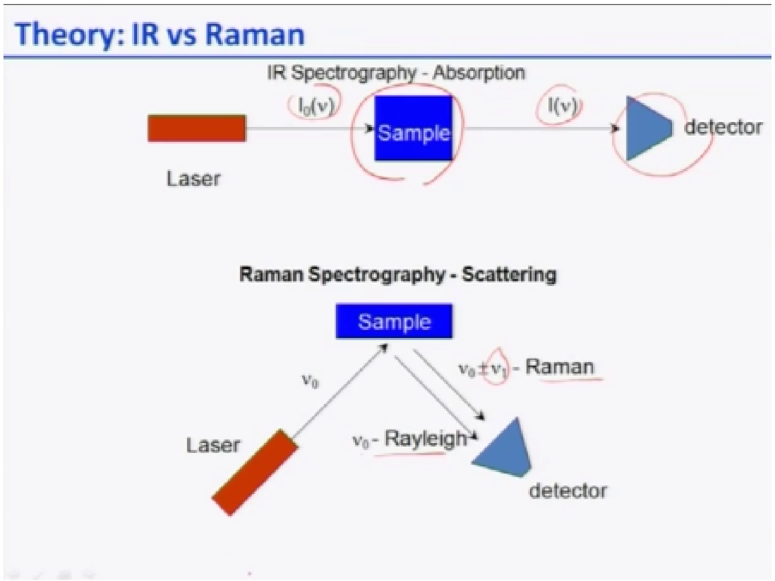

Theory: IR vs Raman

To put it in terms of IR and the Raman spectroscopy in IR we have a laser beam certain intensity of the energy of the driven frequencies in poor fall put on the sample this one it absorbs and the cosmetic downstate releases energy of different intensity and detector and we will get the IR spectrogram spectrum in Raman it is basically not the transmission or absorption it is the scatter so laser fall energy falls on a sample is get scatter because of this is you know Raman scattering and null scattering this is Raman which is has changed because of the externality or loss of energy and then that is what is detected so you have this is the major difference between these two techniques.

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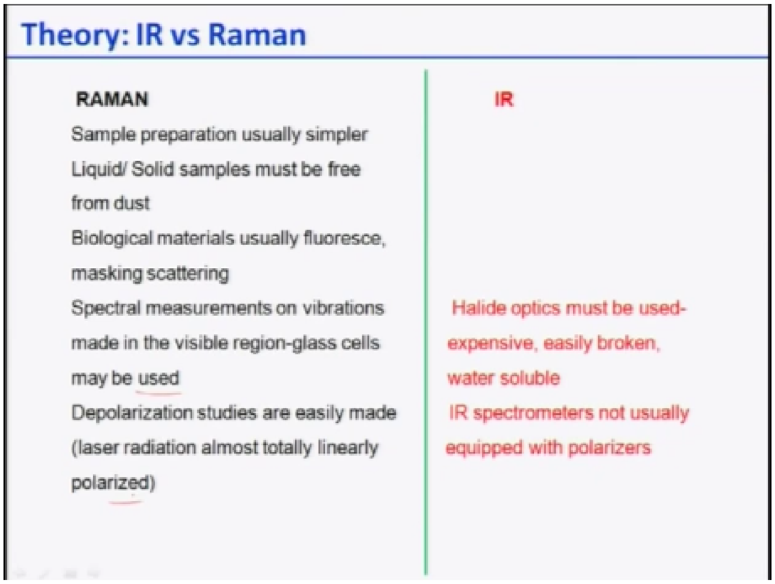

Theory: IR vs Raman

RAMAN	IR
Sample preparation usually simpler	
Liquid/ Solid samples must be free from dust	
Biological materials usually fluoresce, masking scattering	
Spectral measurements on vibrations made in the visible region-glass cells may be used	Halide optics must be used- expensive, easily broken, water soluble
Depolarization studies are easily made (laser radiation almost totally linearly polarized)	IR spectrometers not usually equipped with polarizers

If I want to put it in much better way Raman scattering sampled version is really simpler liquid solid samples must be free of dust IR you cannot do that biological material which usually flows masking scattering is also possible so which is are not possible in curves IR spectral measurements and vibration modes invisible regions glass cells can be used and depolarizing studies are easily made the laser radiation are almost certainly linearly polarized.

But in case of IR halide optics must be used as we have seen they are very expensive can be broken it can be water absorb also because they do not absorb the basically are then halides and IR radiation and it is not possible to get a good data IR spectrum emitters are not usually equipped with polar ideas on the other hand now inspectors meters are usually grouped with polarizer's.

How does the Raman spectra spectrum look like well this is what is shown you in dumps in the picture.

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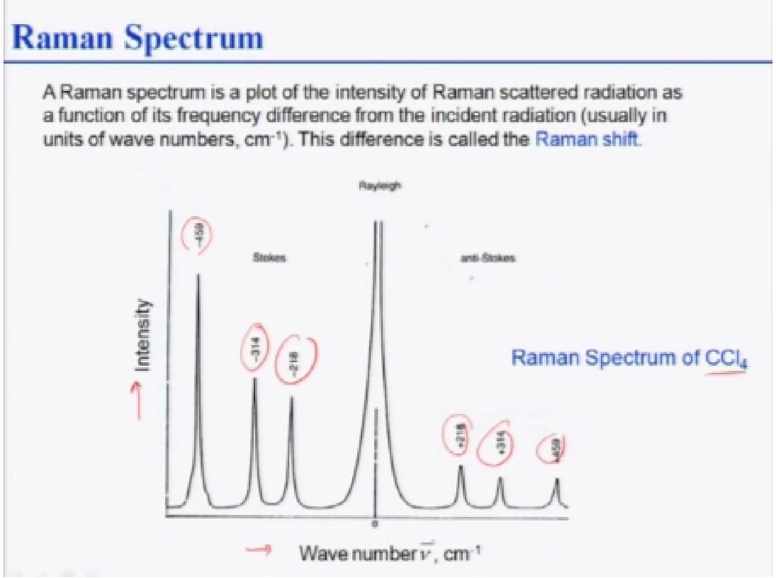

Raman Spectrum

A Raman spectrum is a plot of the intensity of Raman scattered radiation as a function of its frequency difference from the incident radiation (usually in units of wave numbers, cm^{-1}). This difference is called the Raman shift.

Raman Spectrum of CCl_4

There is the intensity this is the wave number again centimeter to the universe and you know a spectrum is nothing but a plot of intensity of the Raman scattering radiation is a function of wave number or frequency depends from the irradiated radiations is really in units off of number so these difference is called Raman’s shift incident and the scatter radiation difference but this is for the carbon tetrachloride.

So you can see these are the frequency differences - and these are the frequency different + for the anti Stokes and this is a Ray lied so Rallied will be the highest peak because inelastic scattering on the left of the ray lay but less wave numbers will be the strokes on the right side will anti strokes by elastic scattering in inelastic scatterings where energy is lost energy is gained.

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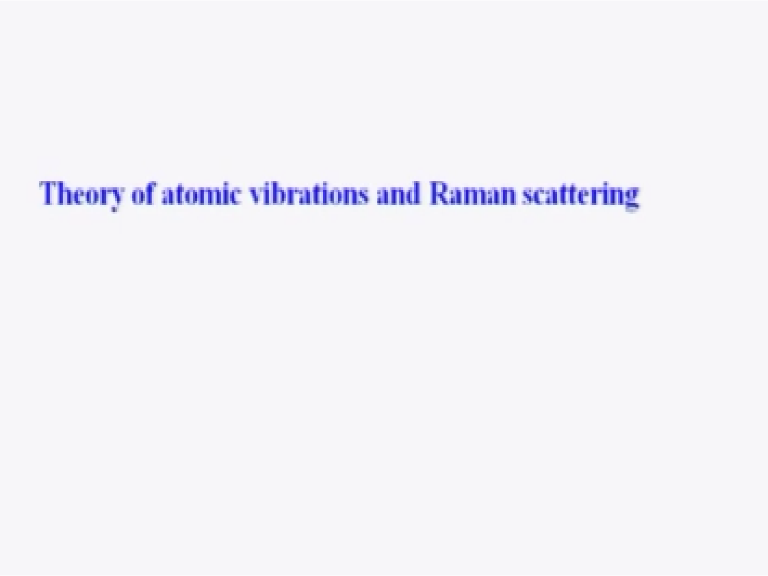

Theory of atomic vibrations and Raman scattering

So let us look into the detailed theory of atomic vibration and Raman scattering.

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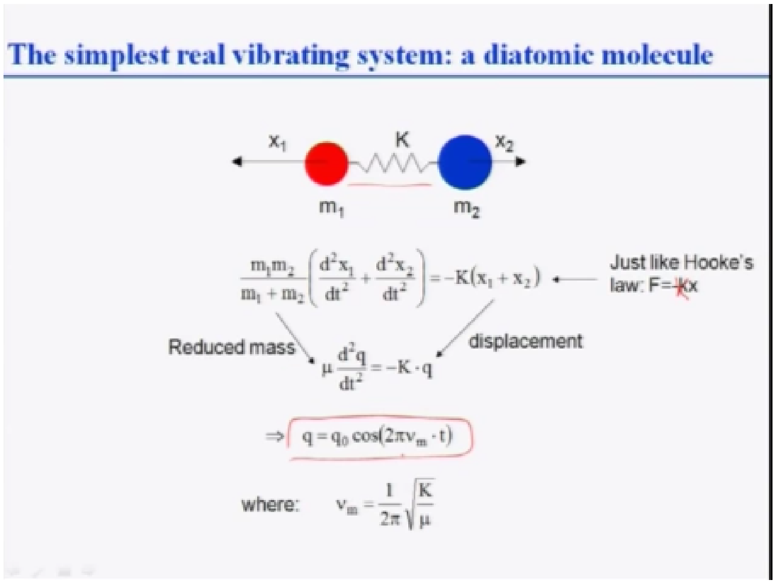

The simplest real vibrating system: a diatomic molecule

$$\frac{m_1 m_2}{m_1 + m_2}\left(\frac{d^2x_1}{dt^2} + \frac{d^2x_2}{dt^2}\right) = -K(x_1 + x_2) \longleftarrow$$

Just like Hooke's law: F=-Kx

Reduced mass

displacement

$$\mu\frac{d^2q}{dt^2} = -K \cdot q$$

$$\Rightarrow \boxed{q = q_0 \cos(2\pi v_m \cdot t)}$$

where: $v_m = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$

Which can be just helpful as to helpful for us to understand the simple formalisms well as you know we can always consider a diagonal molecule and with the spring attached to it one can be considered spring and they are all getting stretched the spring is getting stretched by mass m1 and m2 spring constant is K so if I stretch this molecule that is what is excitation basically by x1 amount this side extreme amount is on the right side of myself.

So I can always write down this is the Hookes law force law basically m1 m2 / m1 + m2 double derivative of space or the extension with respect to the time this is nothing but this + this sorry this nothing but acceleration or deceleration this the mass this basically reduced mass you can say and that will be related to be the K x1 + x2 so therefore I can write down this in terms of µ dq/ dq^2 q/ dt$^{2 =}$ K into q - this is q is extra displacement and this can be solved this where Vm µ m basically = 1 /π √K/µ.

This is nothing but the frequency of vibrations so that is what is the you know whenever a molecule is stretched or excited this is what will happen it will X private with this and this will be d basically displacement can be related to the vibration this way cubes will accuse you the cause of 2π through µm into T.
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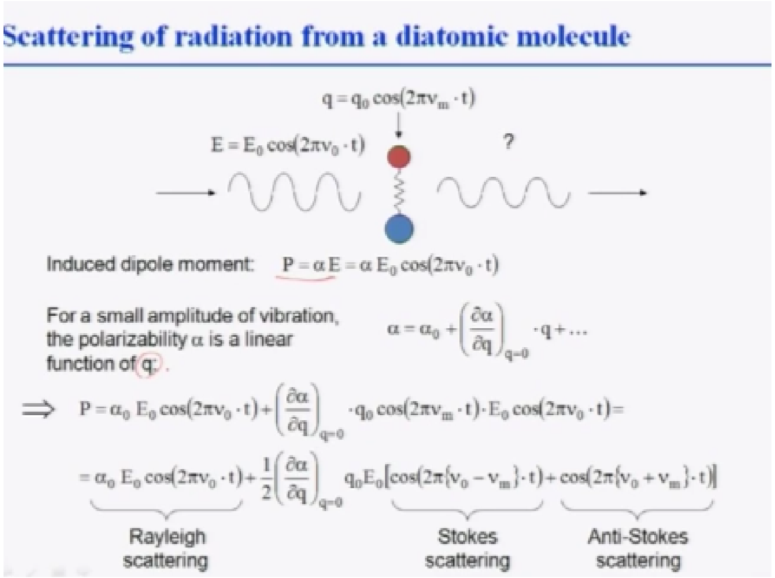

Scattering of radiation from a diatomic molecule

$q = q_0 \cos(2\pi v_m \cdot t)$

$E = E_0 \cos(2\pi v_0 \cdot t)$

?

Induced dipole moment: $P = \alpha E = \alpha E_0 \cos(2\pi v_0 \cdot t)$

For a small amplitude of vibration, the polarizability α is a linear function of q.

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial q}\right)_{q=0} \cdot q + \dots$$

$$\Rightarrow \quad P = \alpha_0 E_0 \cos(2\pi v_0 \cdot t) + \left(\frac{\partial \alpha}{\partial q}\right)_{q=0} \cdot q_0 \cos(2\pi v_m \cdot t) \cdot E_0 \cos(2\pi v_0 \cdot t) =$$

$$= \underbrace{\alpha_0 E_0 \cos(2\pi v_0 \cdot t)}_{\text{Rayleigh scattering}} + \frac{1}{2}\left(\frac{\partial \alpha}{\partial q}\right)_{q=0} q_0 E_0 [\underbrace{\cos(2\pi\{v_0 - v_m\} \cdot t)}_{\text{Stokes scattering}} + \underbrace{\cos(2\pi\{v_0 + v_m\} \cdot t)}_{\text{Anti-Stokes scattering}}]$$

Now if once you look at it you know in different perspectives suppose this is the molecule which is vibrating as you see last time and this is the probably change of distance vibration Q and we are putting in certain radiations which is given by this equal to E= E0 cos of 2 π µ0 T so therefore this will lead to an dipole moment induced dipole moment that committed to α into e α is the paralyzed and E is this E0cos of this so for small amplitude of vibration the polarizability α is linear function of q as you can see.

So therefore we can write down α = α 0 al dl α /dq into q and ignoring the high order terms so P can be related to this way α 0 a 0 you can see you can plug in this one and a big equation and as finally after solving all this equations which I have done here in the slide you can get inelastic scattering it given by this and unless the scattering is given by this in the inelastic scattering part you can always get µ 0 - µ Pm or µ 1 µ 0 + µ m so this is basically Stokes this is anti-stokes.

These two are the factors which are responsible for the Raman's scattering so by just putting is this is simple molecular structure and then one radiations we can always calculate the polarization or induce dipole moment and you can see dipole moment can calculation can lead to us this kind of mathematical theory so therefore if I want to give you some example let us suppose for carbon dioxide here you have CC.

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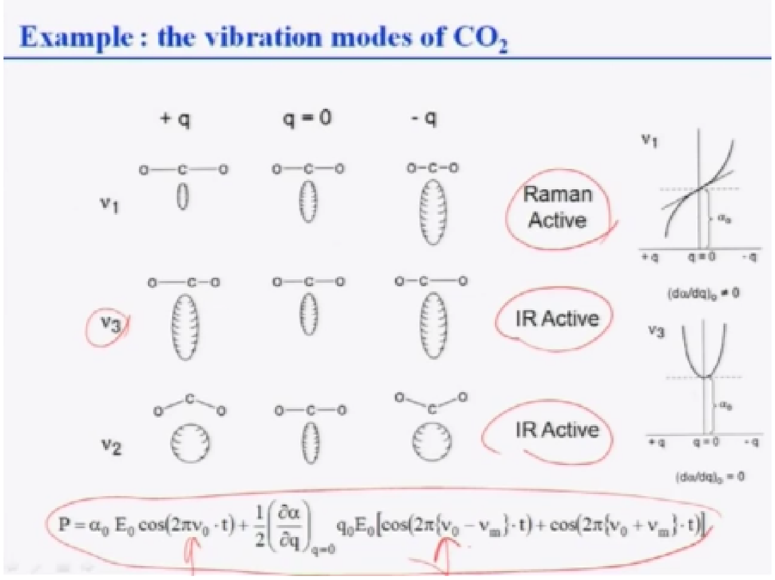

Example : the vibration modes of CO_2

$$P=\alpha_0 E_0\cos(2\pi\nu_0\cdot t)+\frac{1}{2}\left(\frac{\partial\alpha}{\partial q}\right)_{q=0} q_0E_0\left[\cos(2\pi\{\nu_0-\nu_m\}\cdot t)+\cos(2\pi\{\nu_0+\nu_m\}\cdot t)\right]$$

So Co O molecule q+ qo q okay so you can see that this is what is this no there is no displacement here as per displacement has a negative displacement here Q you remember so if I like mu 1 but this Q space that's what will give so that is this is the polarizability that there is a polarizer which is change this is where Raman active but on the other hand if there is no probability change this is the band in which it happens that this will be our activity will not one active if the molecule is stretch or change this configuration this way this also be directive this can also show you the change in the five frequency as function of cube.

So finally again I put down this equations where the rally the Inelastic scattering and unless the scattering events are both are given.

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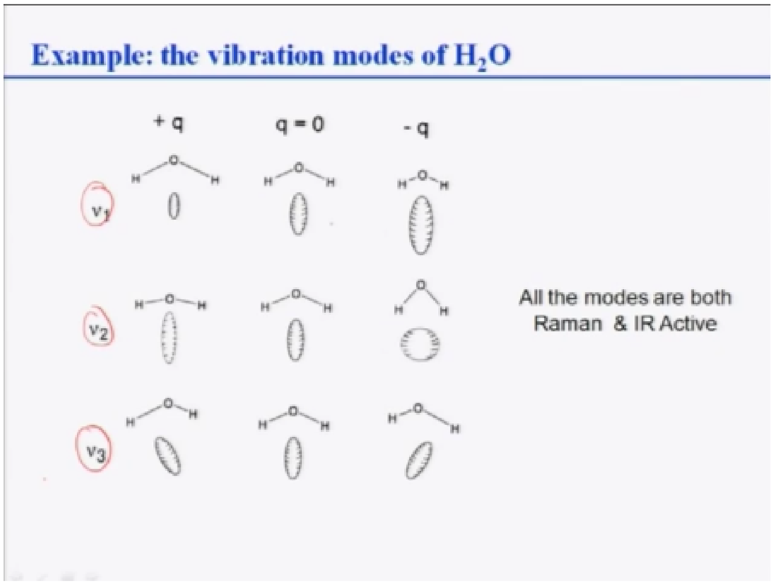

Example: the vibration modes of H_2O

All the modes are both Raman & IR Active

One can do it for our molecule side water you can see all the modes are in water actually ν 1 ν 2 ν 3 are active it Raman base because this leads to change in polarizability and changing and the polarization both.

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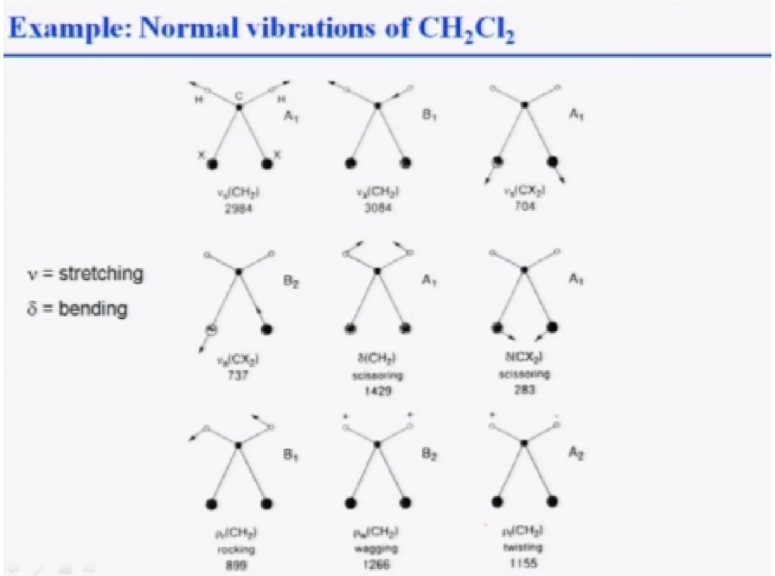

Example: Normal vibrations of CH_2Cl_2

ν = stretching

δ = bending

If we take CH2CL2 there are stretching and bending both possible here so if I consider vs this is this is the stretching bands for this our va ps here actually that 3 a1, b1 a1 so that you know change in the stretching can lead to scattering or you can have a bending actually you can see this is scissoring you can have see that these are all we discussing in the IR spectroscopy or you can have a rocking or wiping on twisting these vibrations can lead to Raman active spectrum.

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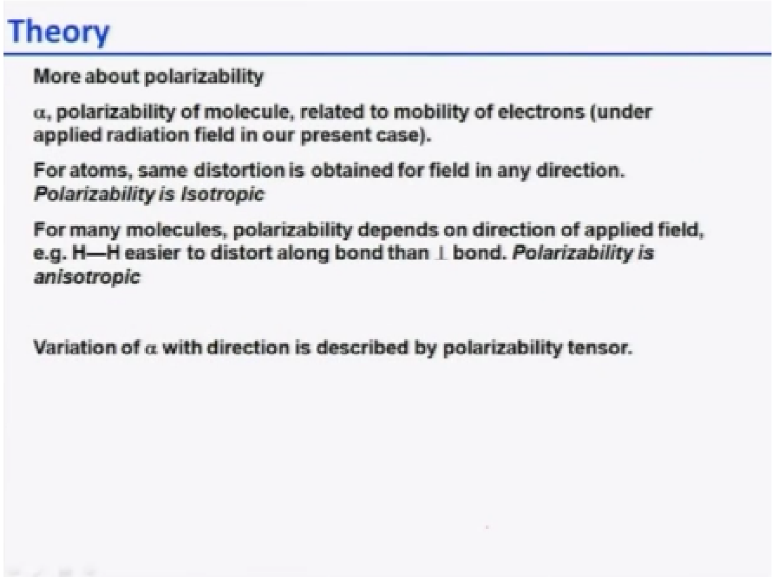

Theory

More about polarizability

α, polarizability of molecule, related to mobility of electrons (under applied radiation field in our present case).

For atoms, same distortion is obtained for field in any direction. *Polarizability is Isotropic*

For many molecules, polarizability depends on direction of applied field, e.g. H—H easier to distort along bond than ⊥ bond. *Polarizability is anisotropic*

Variation of α with direction is described by polarizability tensor.

So to give you little more aspects of the polarizability if you have not understood much so that you can go back and look at the slides polarizability molecular rate the mobility of the electrons when you apply a field basically you apply field how the electrons move they move symmetrically then there is no change of polarity they move and distortion happens in the field direction of the field okay and then in the isotropic but if suppose distortion is same this is isotropic.

So more molecules per many molecules probably difference in the direction of the applied fields tension of the applied fields like hh easier to distort along the bonds than partner to the bond so plausibility is anisotropic variation of the A with Direction is describe a possibility tensor a tensor is another vector which can be used to detect to basically show a variation of α with the direction now vibration is active it is if it has a changing probability any vibrations in the molecule if you put in an aunty will be active Raman active if there is a change in the polarizability α.

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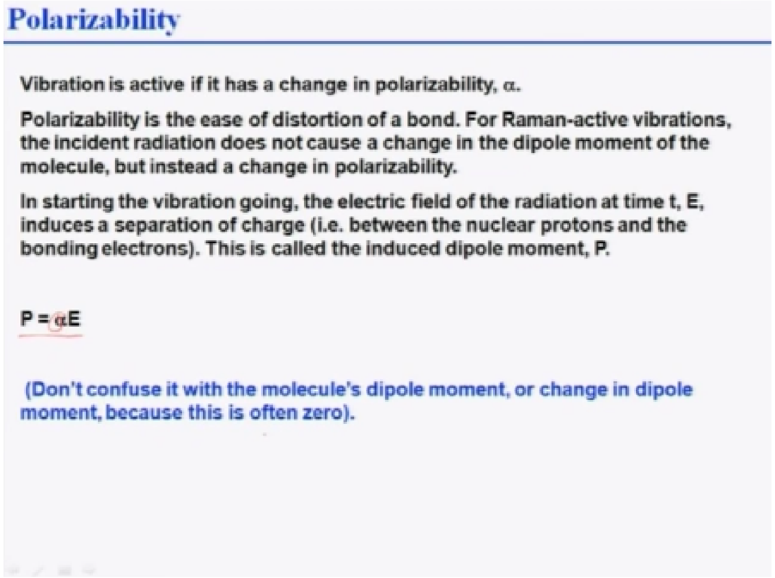

Polarizability

Vibration is active if it has a change in polarizability, α.

Polarizability is the ease of distortion of a bond. For Raman-active vibrations, the incident radiation does not cause a change in the dipole moment of the molecule, but instead a change in polarizability.

In starting the vibration going, the electric field of the radiation at time t, E, induces a separation of charge (i.e. between the nuclear protons and the bonding electrons). This is called the induced dipole moment, P.

$P = \alpha E$

(Don't confuse it with the molecule's dipole moment, or change in dipole moment, because this is often zero).

So basically I can tell this way polarizability is the ease of distortion of the bond so therefore for Raman active vibrations incident addition does not cause a change the dipole moment of the molecule but it changed the probability of the molecule that means change the electronic distortion of the molecule it does not really change the basically dipole moment that the molecule that the dipoles are not going apart the strengths are not changing but their polarizability means electronic the mobility of the electrons are getting distorted or changed.

So the starting vibration going the electric field of the radiation at time T is induced due to separation of charges as you at the beginning you put electric field it is separate some charges and then this is called singly dipole moment which can be related to this P into α and we remember α is basically the polarizability so we are talking about this change of α not change of P which is required for Raman change of P is required for the iron please do not get confused to the molecules dipole moment or the change in dipole moment because this is always case to be 0, these molecules again I come back to see a stood CL $_2$ okay, so sorry I come back to this wrong I come back to co_2.

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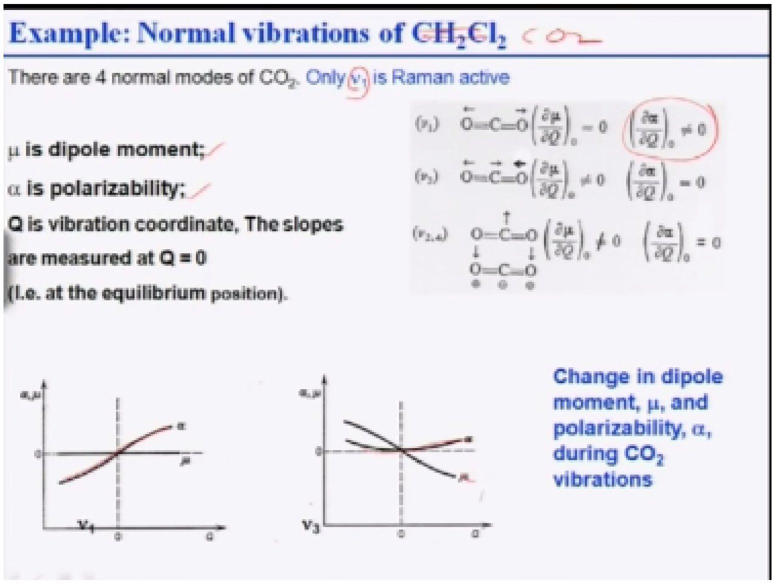

Example: Normal vibrations of ~~CH_2Cl_2~~ CO_2

There are 4 normal modes of CO_2. Only ν_1 is Raman active

μ is dipole moment;

α is polarizability;

Q is vibration coordinate, The slopes are measured at Q = 0 (i.e. at the equilibrium position).

(ν_1) O=C=O $\left(\frac{\partial \mu}{\partial Q}\right)_0 = 0$ $\left(\frac{\partial \alpha}{\partial Q}\right)_0 \neq 0$

(ν_3) O=C=O $\left(\frac{\partial \mu}{\partial Q}\right)_0 \neq 0$ $\left(\frac{\partial \alpha}{\partial Q}\right)_0 = 0$

$(\nu_{2,4})$ O=C=O $\left(\frac{\partial \mu}{\partial Q}\right)_0 \neq 0$ $\left(\frac{\partial \alpha}{\partial Q}\right)_0 = 0$

Change in dipole moment, μ, and polarizability, α, during CO_2 vibrations

There are four moles of co₂ and only four out of four all the new one is Raman active, so new one is this one CCO, so there is a change in you can see dipole moment is changes there is not 0 μ 3 and μ 4 basically tool for the IR active, so have me use the dipole moment μ which to the α probability Q is the vibration coordinate RS basically used is basically the displacement which we used that.

And this is what we can show this is a μ one so you can see Paula little is changing like this is μ 3 small not active but polarization dipole of moment is changing extensively, here dipole movement does not get changed.

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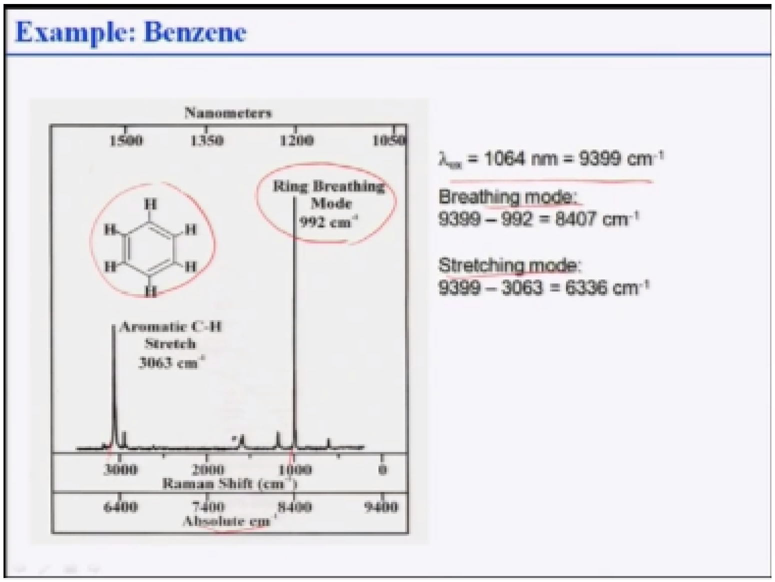

Example: Benzene

$\lambda_{ex} = 1064 \text{ nm} = 9399 \text{ cm}^{-1}$

Breathing mode:
$9399 - 992 = 8407 \text{ cm}^{-1}$

Stretching mode:
$9399 - 3063 = 6336 \text{ cm}^{-1}$

To give another example of benzene actually benzene as you know this is as aromatic CH ring and as a stage band at about close to three thousand actually and then you have a ring breathing mode which is about 992 and Raman this is these basically Raman ships you can see these are the Raman ships and this is the basically absolute CM, that one slipped is calculated in by difference between the insulation and the and the vibration is coming out. And this is what is the breathing mode and this is what a stretching mode can be calculated.

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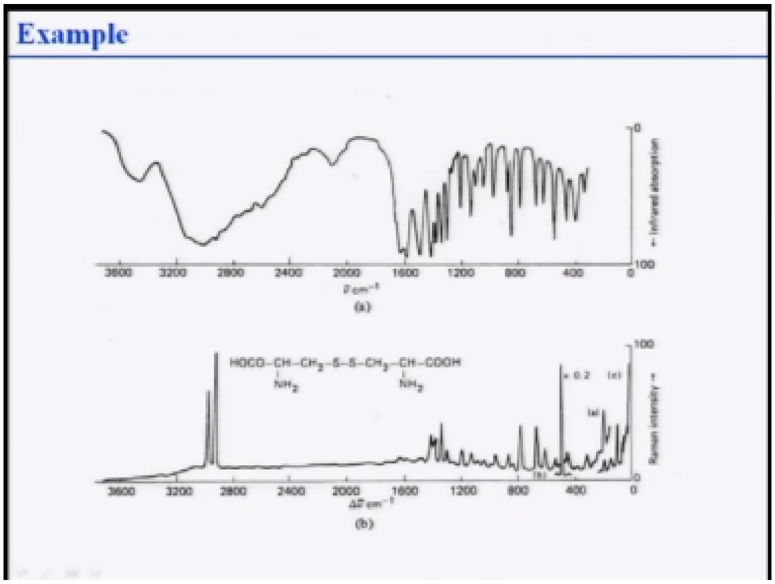

Example

Now to throw the difference between infrared and Raman I take this complex molecule with nh$_{-2}$ groups, so you can see that Raman ships gives you very nice spectra as compared to the IR and Raman ships comes out of higher Δ µ then a µ actually this frequency change in wave number this is a µ and this is fingerprint regions here in IR but the most important things comes in this higher changing the wave number regions.

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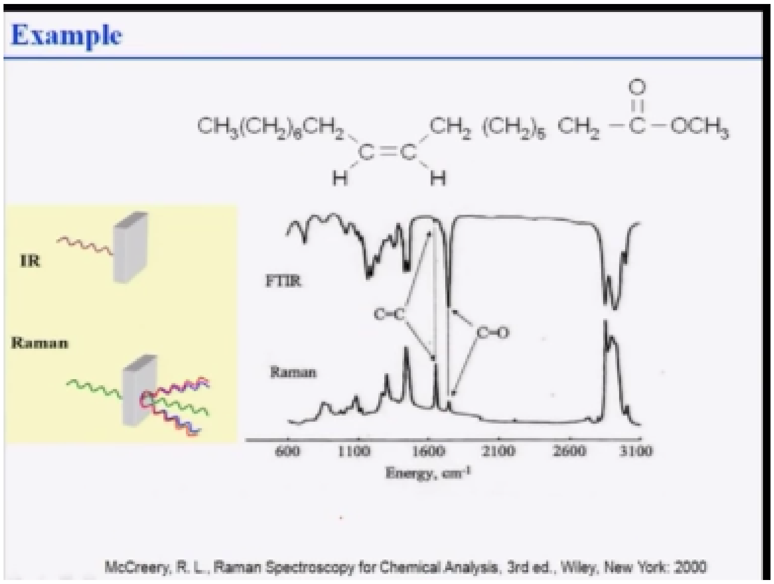

Example

$CH_3(CH_2)_6CH_2-CH=CH-CH_2(CH_2)_5CH_2-C(=O)-OCH_3$

McCreery, R. L., Raman Spectroscopy for Chemical Analysis, 3rd ed., Wiley, New York: 2000

So this is again shown here this is the 50th Raman I can see that Co, Co is same but cc this one is highly increased by Raman and we can get other Peaks also which is very similar in this case of molecule ii obtained from my crease book.

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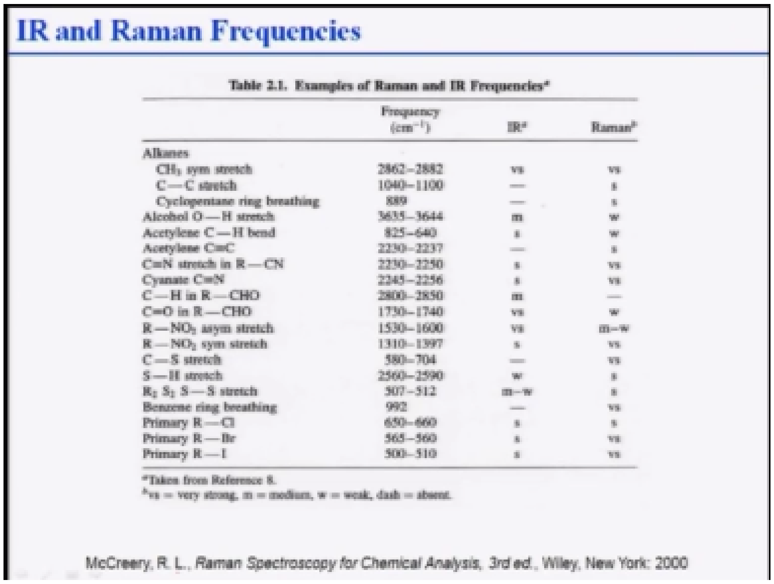

IR and Raman Frequencies

Table 2.1. Examples of Raman and IR Frequencies[a]

	Frequency (cm^{-1})	IR[a]	Raman[b]
Alkanes			
CH$_3$ sym stretch	2862–2882	vs	vs
C—C stretch	1040–1100	—	s
Cyclopentane ring breathing	889	—	s
Alcohol O—H stretch	3635–3644	m	w
Acetylene C—H bend	825–640	s	w
Acetylene C≡C	2230–2237	—	s
C≡N stretch in R—CN	2230–2250	s	vs
Cyanate C≡N	2245–2256	s	vs
C—H in R—CHO	2800–2850	m	—
C=O in R—CHO	1730–1740	vs	w
R—NO$_2$ asym stretch	1530–1600	vs	m–w
R—NO$_2$ sym stretch	1310–1397	s	vs
C—S stretch	580–704	—	vs
S—H stretch	2560–2590	w	s
R$_2$ S$_2$ S—S stretch	507–512	m–w	s
Benzene ring breathing	992	—	vs
Primary R—Cl	650–660	s	s
Primary R—Br	565–560	s	vs
Primary R—I	500–510	s	vs

[a] Taken from Reference 8.

[b] vs = very strong, m = medium, w = weak, dash = absent.

McCreery, R. L., *Raman Spectroscopy for Chemical Analysis, 3rd ed.*, Wiley, New York: 2000

To give you a list of the Raman and higher frequency for different functional groups alkenes this is very strong in higher Raman is also very strong CC stage obviously is strong where IR is not at all available and then other others see triple bonds CN, you can see strong and very strong Raman scattering then you have strong a scattering for primary these points but weak Raman scattering and very strong Raman scattering also scam foresee a stress.

Because there is a lot of change of probability of the molecule they are all obtained from municipal.

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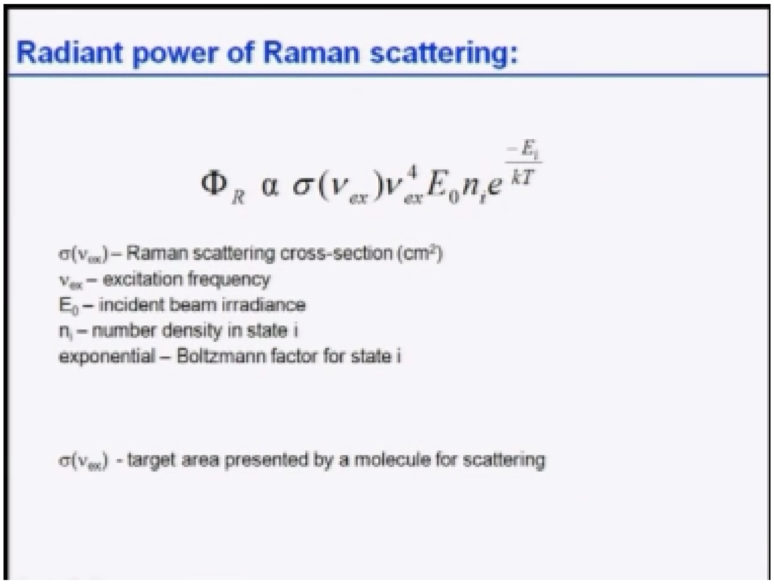

Radiant power of Raman scattering:

$$\Phi_R \;\alpha\; \sigma(\nu_{ex})\nu_{ex}^4 E_0 n_i e^{\frac{-E_i}{kT}}$$

$\sigma(\nu_{ex})$ – Raman scattering cross-section (cm^2)
ν_{ex} – excitation frequency
E_0 – incident beam irradiance
n_i – number density in state i
exponential – Boltzmann factor for state i

$\sigma(\nu_{ex})$ - target area presented by a molecule for scattering

Well there are other things which is no we should also know for Raman scattering is the radiation power or radiant power as you see this in power π R is proportional to σ V X V X to the per new extra σμ X μ X ^{4} EA by K T where σμX is basically Raman scattering cross-section which is in terms of centimeter Square and image the excitation frequency by which you are putting an energy plus the women Angie easier is the incident beam in radiance you nice in a mob density states in any state I.

And E is the energy of that states and they this is basically exponential term conflicts of Boltzmann's. So this σ Thomas target is represented by a molecule for scattering that is what is this scattering cross-section, how much is that area target area by molecule for scattering even occurs?

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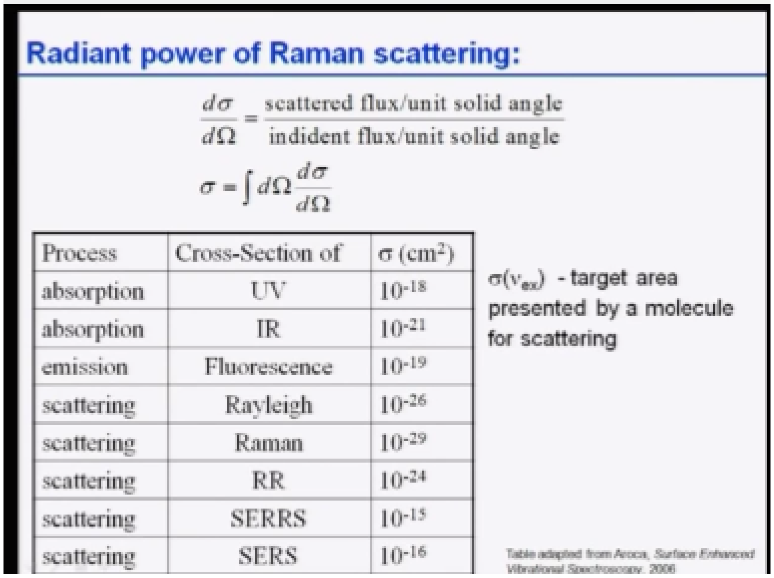

Radiant power of Raman scattering:

$$\frac{d\sigma}{d\Omega} = \frac{\text{scattered flux/unit solid angle}}{\text{incident flux/unit solid angle}}$$

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega}$$

Process	Cross-Section of	σ (cm^2)
absorption	UV	10^{-18}
absorption	IR	10^{-21}
emission	Fluorescence	10^{-19}
scattering	Rayleigh	10^{-26}
scattering	Raman	10^{-29}
scattering	RR	10^{-24}
scattering	SERRS	10^{-15}
scattering	SERS	10^{-16}

$\sigma(v_{ex})$ - target area presented by a molecule for scattering

Table adapted from Aroca, *Surface Enhanced Vibrational Spectroscopy*, 2006

So that can be also you know put it in it this way so as you see σ is basically this σ capital σ σ by D so disease is scattering cause integration of the whole scattering for the molecule and this σ by σ D σ means this is small σ this capital σ is nothing but scatter flux per unit solid angle divided by incident flux this is C, incident flux by unit solid angle, so scattering by incident and then you multiply the whole side angle which is coming out and you get that.

So if I have to compare this with other techniques like UV IR flow sensor Ally Raman and other surface enhanced Raman you can see the scattering cross section is very high very high means not very high 10 to the -18 is pretty low but still it is high in case of UV and IR relay and Raman is pretty low 10 to the - 26 - 29 that is the problem actually I want spectroscopy you need to have a very good detector to detect this scattering turrets.

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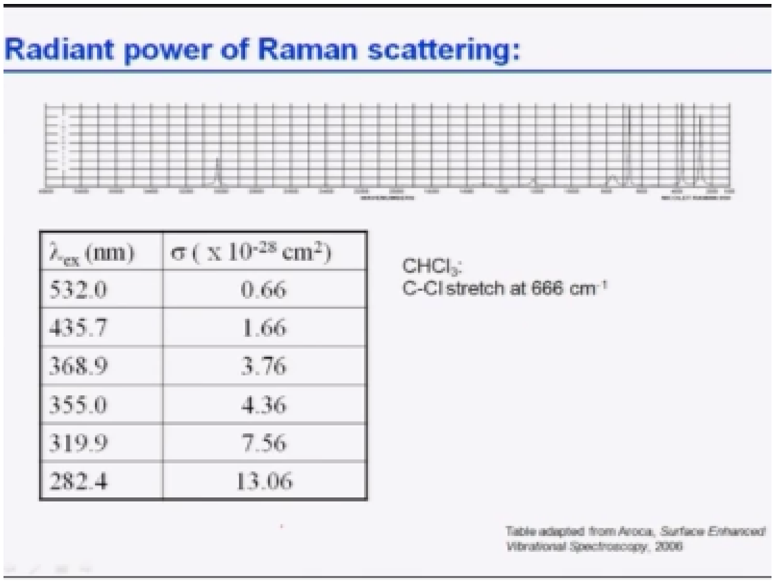

Radiant power of Raman scattering:

λ_{ex} (nm)	σ (x 10^{-28} cm^2)
532.0	0.66
435.7	1.66
368.9	3.76
355.0	4.36
319.9	7.56
282.4	13.06

$CHCl_3$:
C-Cl stretch at 666 cm^{-1}

Table adapted from Aroca, *Surface Enhanced Vibrational Spectroscopy*, 2006

Again for excitations I am giving you some values for CS TCL okay you can see that these are the you have lengths excitation table and these are the σ values all in the range of 10 to the- 20 centimeter square these are all adopted from accrues book of surplus and amps vibration spectroscopy.

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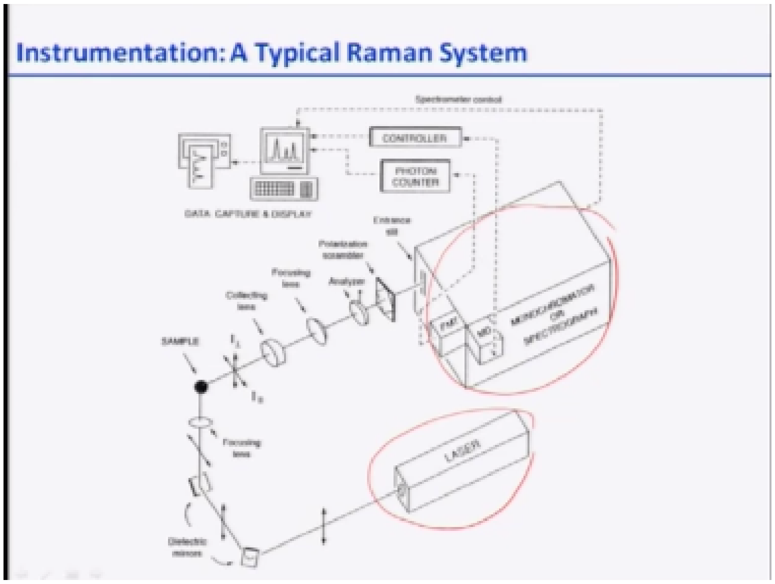

Instrumentation: A Typical Raman System

Now lastly which we are going to talk about is the typical element set up about things how it is done in the lab scale as you can see this is very complex first part of this most important part of this monochromatic spectrograph and then ever laser beam this source which is basically passes to dielectric mirrors and then put the sample, then it is radiation is collected or the scattering events are collected.

It is you can see that it is false and then does not grow like this but it comes back and I am scattering angle collected by colleague collecting lens focusing lens analyzer then polarizations gambler and then it goes to this in slits and then want to come across things in this part of this monochromatic you have several important aspects one is the controller, second one is the photon counter proton gain can be counted by PMT photo multiplier tube and then you have a controller which you plot this display this data and I never display.

So that is what is the basically I think I have already discussed with you was monochromatic in case of total emission spectroscopy, so the spectral gap is where the data are plotted.

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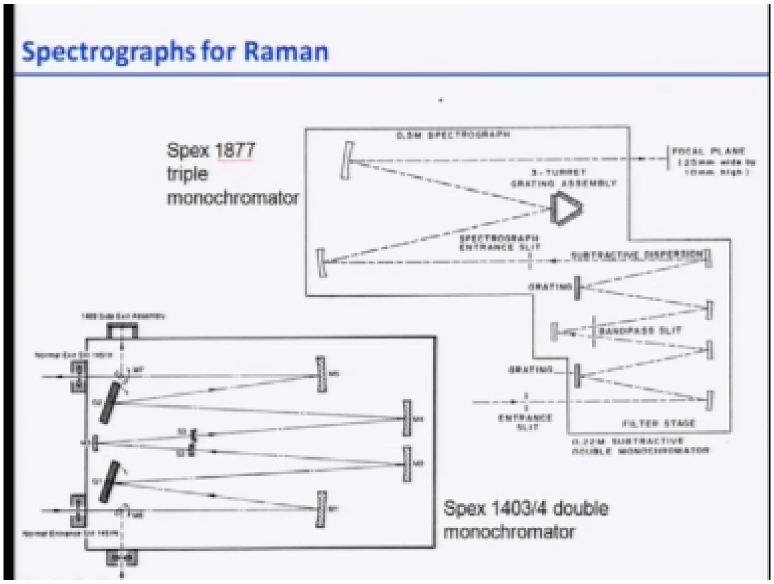

Spectrographs for Raman

So scattering can be done in both ways for the laser light can falls and scattering and happen at a 90 ^{0} this way 180 ^{0} coming and scattered and then fall scattering light falls on a lens and again this is focused and then they collected this. So I was shown here collecting lens focusing lens analyzer and this then it enters the monochromatic you can spectrograph pictographs can be for almonds actually this is for this a 187 7 tipple monochromatic the whole thing is basically monochromatic this is the specs 1 3 what 0 3 1 / 2 3 4 double monochromatic.

Let us look at first a double monochromatic, so you can clearly see that these are these splitters mirrors actually it falls comes and falls on a mirror I am sorry it falls on m1 then goes on to G 1 then again M 2 gets reflected finally it's comes out through this, so entrance and this from the entrance and the exit there are only 1 M 1 2 m 5 there are 5 minutes and there are this splitters G 1 G 2 and they are all actually an indeed by this way you can actually get these monochromatic radiations.

And otherwise you can do what you can do is this way you can have entrance then it passes to lot of bands passes finally it goes to the subtractive dispersal and it falls on a three turret getting assembly and then comes out well we will not discuss, so much detail but there are two types of spectral gaps used one is a double monochromatic type one is typical monochrome and depending on this has a better ability to collect data than this one.

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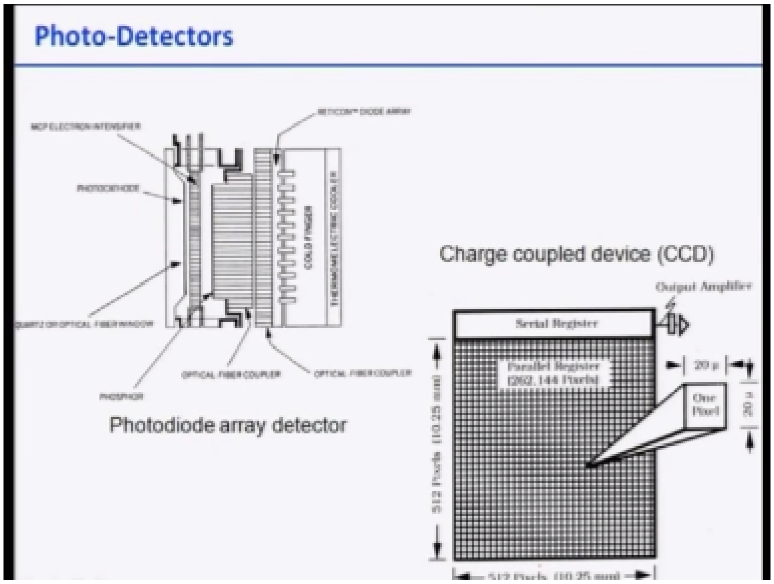
Photo-Detectors

Otherwise you can use photo detectors and actually nowadays people use photo detectors because this are easy to manipulate and easy to work with photo detector is nothing but basically you have you can see here you have photo cathode with a and then you have a within that you have electronic intensifier which will intensify and then these are actually cool cold finger which will be cooling it and your optical fiber capital R which will couple that.

And you can always use otherwise CCD cameras are charged coupled device where you can actually pixel types in which you can detect radiations coming on each pixel.

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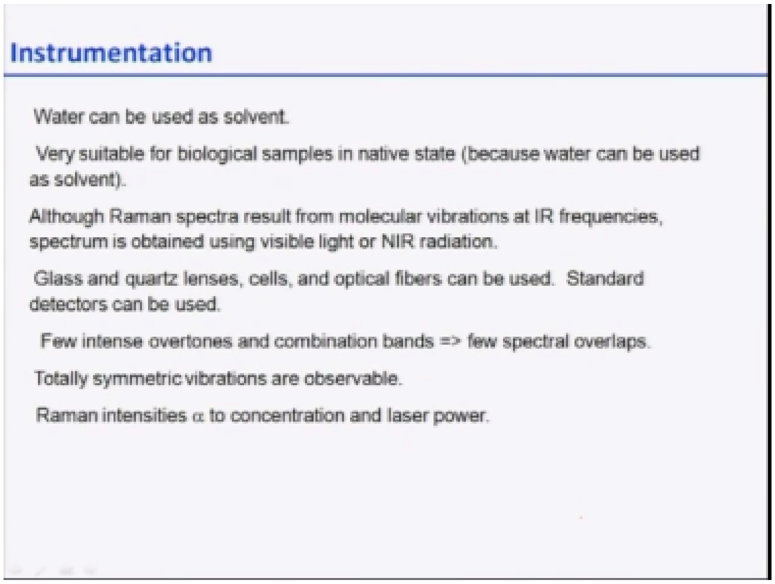

Instrumentation

Water can be used as solvent.

Very suitable for biological samples in native state (because water can be used as solvent).

Although Raman spectra result from molecular vibrations at IR frequencies, spectrum is obtained using visible light or NIR radiation.

Glass and quartz lenses, cells, and optical fibers can be used. Standard detectors can be used.

Few intense overtones and combination bands => few spectral overlaps.

Totally symmetric vibrations are observable.

Raman intensities α to concentration and laser power.

So and what about others in this case water can be used to the solvent and very suitable for biological samples we know in IR we cannot use water as a solvent it can absorb and then because, what I can use this is very easy validate service can be done Raman spectra results from a molecular vibration of Pi at fire frequencies victims are obtained using visible lights are you can near-ir radiations glass or quad lenses cells optical fibers can be used standard in Texas always used but nowadays no longer.

Few invents of atoms on combination bands like few spectral of elapsed can be done you can totally symmetric vibrations are observable Ramans in the cities are basically proposition the concentration and the laser power this is the proportionality constant not α. Well as you have seen that this is much simpler and cheaper than the spectroscopy it has experimentation is too medicine is much less but the lower detection limit is the problem in case of Raman so background flow sense can always propagate which you will see how to take care and more suitable for vibration with bonds in low like chlorine carbon fluorine bonds.

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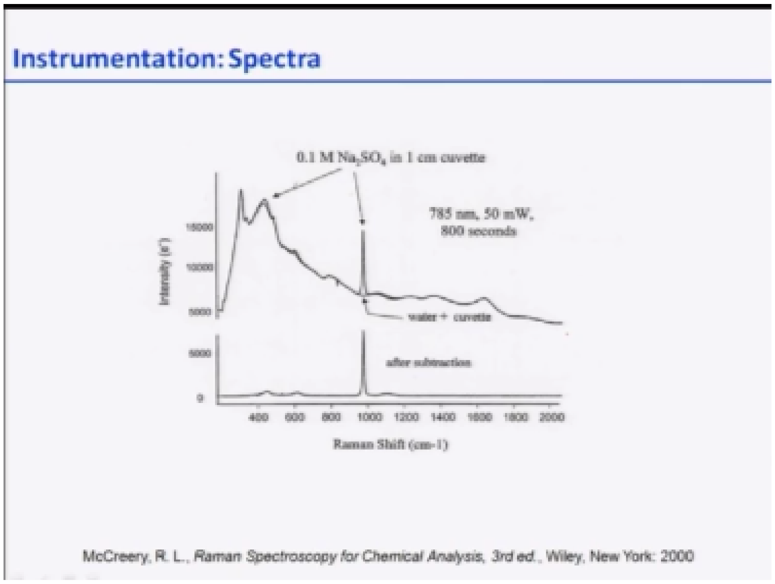

Instrumentation: Spectra

McCreery, R. L., *Raman Spectroscopy for Chemical Analysis, 3rd ed.*, Wiley, New York: 2000

So how to take care of this rate of background so if you suppose take with water and q8 this spectra and then supply Luke intake for water and q8 without sample for sample air is basically sodium sulphate and then you can basically subtract and get this the background removed that is what is can be done routinely nowadays for the computers.

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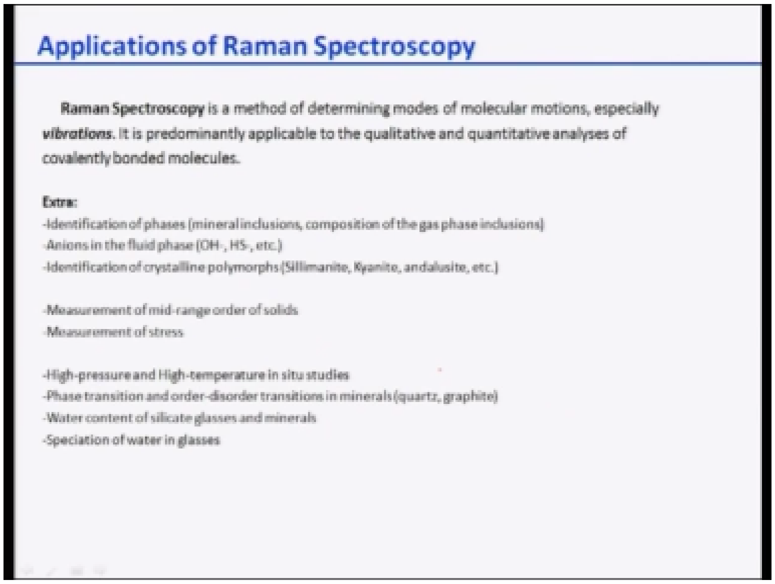

Applications of Raman Spectroscopy

Raman Spectroscopy is a method of determining modes of molecular motions, especially ***vibrations***. It is predominantly applicable to the qualitative and quantitative analyses of covalently bonded molecules.

Extra:
-Identification of phases (mineral inclusions, composition of the gas phase inclusions)
-Anions in the fluid phase (OH-, HS-, etc.)
-Identification of crystalline polymorphs (Sillimanite, Kyanite, andalusite, etc.)

-Measurement of mid-range order of solids
-Measurement of stress

-High-pressure and High-temperature in situ studies
-Phase transition and order-disorder transitions in minerals (quartz, graphite)
-Water content of silicate glasses and minerals
-Speciation of water in glasses

Applications Raman spectra can be used to many situations like molecular vibrations our quantity quality and this also it can be done for all kinds of elements salt maintenance all weights stress measurements high pressure and glasses also, there are large number of occasions so with this I close this chapter on Raman spectroscopy there are only thing which is left over is these STEM, EELS and the last spectroscopy which we will discuss in the next two classes.

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