# Fundamentals of Spectroscopy

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## Lecture-37
## Introduction to Raman Spectroscopy

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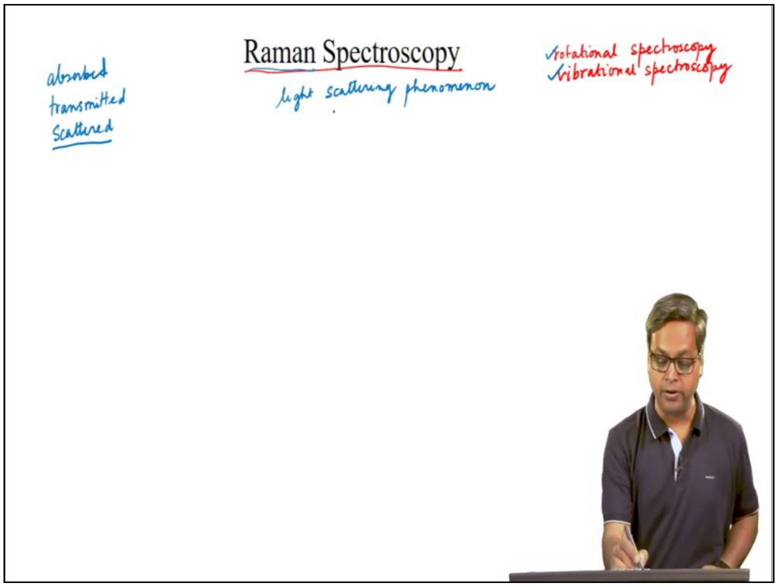

Raman Spectroscopy

light scattering phenomenon

absorbed
transmitted
scattered

✓rotational spectroscopy
✓vibrational spectroscopy

Hello everyone, welcome to the lecture. So, far we have discussed two different forms of spectroscopy one is rotational spectroscopy and the other is vibrational spectroscopy. So, today we will start a new module on Raman spectroscopy. The first thing we should know about the Raman effect is that Raman effect is a light scattering phenomena. So, what is the fate of the electromagnetic radiation when it falls and matter.

In general when light falls on matter it may be absorbed if the energy of the radiation corresponds to the separation of the two energy levels of the matter that is the atoms or the molecules is absorption does not take place. The electromagnetic radiation is either transmitted or scattered. Raman spectroscopy is related to this scattering of light. In this respect this spectroscopy is somewhat different in origin from the other spectroscopic techniques like rotational spectroscopy and vibrational spectroscopy that we have already studied.

Or it is also different from electronic spectroscopy which we will study in a later module. These spectroscopy's the rotational, the vibrational and the electronic spectroscopy's involved absorption and emission of light but Raman spectroscopy involves scattering of light.

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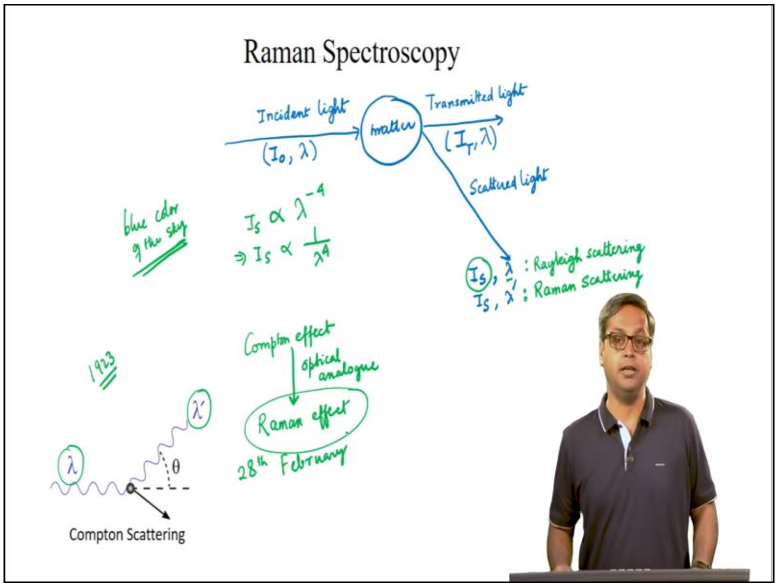

Raman Spectroscopy

So, the Raman effect can be illustrated as let us say we have a matter and the light or the electromagnetic radiation is incident on the matter. So here we have incident light. So, let us say the intensity of the incident light is I 0 and the wavelength of the light is lambda. So, if the light is transmitted so here we have transmitted light, so for the transmitted light the wavelength will not change, so it is still lambda. And as we have seen before during our discussion or Beer-Lambert law the intensity is represented by I T that is the transmitted light intensity.

On top of this we can have scattered light. So, let us say the intensity of the scattered light is I s and the wavelength of the scattered light can either with the same as that of the incident light or it can be different from that of the incident light. So, in one case I wrote lambda in the other case I wrote lambda prime. So, scattering of light with unchanged wavelength that is this case is known as Rayleigh scattering.

In 1871 Lord Rayleigh showed that the intensity or I s of the scattered light is related to the wavelength of the light by the relation I s is proportional to lambda to the power -4. So, this means I s is proportional to 1 by lambda to the power 4. In other words as lambda decreases the intensity of the scattered light increases. So, this scattering can explain the blue color of the sky because the blue radiation from the Sun which is of lower wavelength is scattered preferentially by the particles in the atmosphere and this results in a blue color for our cloudless sky.

On the other hand when there is a change in the wavelength of light we have Raman scattering. Historically soon after the discovery of Compton scattering in 1923 where x-ray is scattered by electrons and the wavelength of the x-ray is changed Raman thought that there must be an optical analog of Compton effect. So, we have Compton effect and the optical analog is what we will see in Raman effect. So, ultimately in 1928 CV Raman was able to discover the effect the official date of discovery of this Raman effect was 28th of February and it is interesting to note that this 28th of February is observed as the national science day in India.

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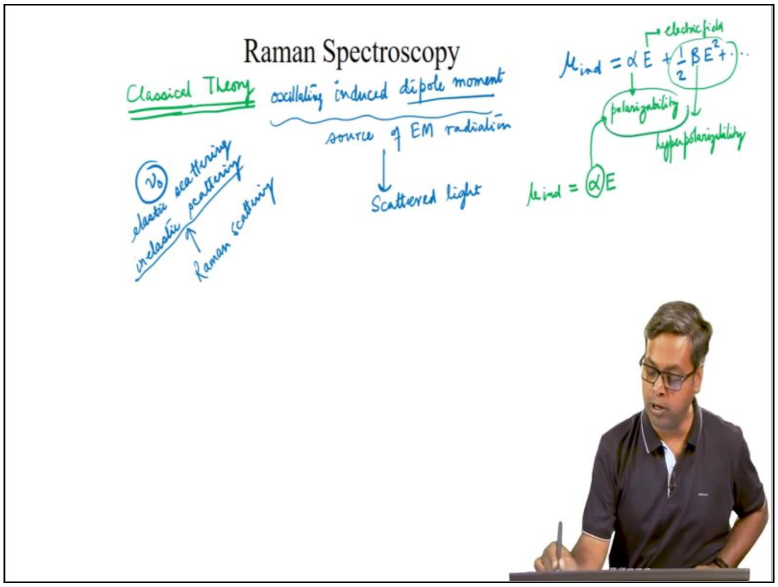

Raman Spectroscopy

So, now before going into the details of the Raman effect let us look into Raman's experimental set up. So, the first experiment that Raman did was done in a darkroom and sunlight was used as the light source. Because we know the sunlight is composed of various frequencies or various wavelengths that is sunlight is polychromatic. So, the sunlight is passed through a monochromator. So, this monochromator changes the polychromatic light into a monochromatic light of wavelength lambda.

So the light with wavelength lambda then falls on the sample the transmitted light that is let us the I T is blocked and the scattered light, so this is the scattered light. So, this light was passed through a filter to cutoff lambda which is the incident wave length of light and so the scattered light at any other wavelength other than the incident wave length was detected by the detector. And initially when Raman did the first experiment the detector that was being used is the naked eye of CV Raman.

So some important points about this Raman's experimental setup so as I already mentioned the Sun was used as a light source and the position of Sun changed during the time of the experiment this is because a long exposure is needed in the experiment to have a detectable effect. So, the alignment of this monochromator was changed as the position of the Sun changed during the experiment. The scattered light was gathered perpendicular or at a 90-degree geometry so as to minimize the crosstalk between the incident light and the scattered light.

In the original experiment as I mentioned I was used as the detector afterwards light was allowed to fall on a photographic plate. So, now let us look into the Raman effect using a classical description. So, let us look into the classical theory of Raman effect. The scattering of light may be thought of as the redirection of light that takes place when an electromagnetic wave that is an incident light ray encounters an obstacle or inhomogeneity.

So in this case the scattering material is the obstacle which can be solid liquid or gas. A molecule as we know is made up of positively charged nuclei embedded in negatively charged electron cloud. So, when an electric field is incident on a molecule the electrons and nuclei respond by moving in opposite directions in accordance to Coulomb's law. As the electromagnetic wave interacts with the matter the electron orbits within the Constituent molecules are perturbed periodically with the same frequency as that of the electric field of the incident wave.

The oscillation or perturbation of the electron cloud results in a periodic separation of charge within the molecules and this is called the induced dipole moment. In other words the electric field induces a dipole moment in the molecule. So, the oscillating induced dipole moment so this oscillating induced dipole moment is manifested as a source of electromagnetic radiation and thereby resulting in scattered light.

The majority of the light is scattered in the identical frequency let us say nu 0 of the incident light and this process is referred to as elastic scattering. However as we will see later in Raman effect additional light is scattered at different frequencies. A process referred to as in elastic scattering. So, Raman scattering is one such example of inelastic scattering. An incident electromagnetic wave induces a dipole moment during the light matter interaction.

And the strength of this induced dipole moment so we can write induced dipole moment as mu induced and the strength of this induced dipole moment is given by mu induced equals alpha E + half beta E squared plus we can also have some higher order terms of E. So, here alpha is the polarizability constant and beta is the hyper polarizability constant. And E is a strength of the electric field of the incident wave.

As long as the electric field of the electromagnetic radiation or the incident light is not too strong the induced dipole moment is directly proportional to the applied electric field. And so we can neglect the second term and we can write mu induced equals alpha times E here again this alpha is the polarizability. The polarizability is a characteristic of the molecule that depends on the molecular structure and the nature of the bonds.

As the electric field oscillates with sufficiently large frequencies only the electron cloud of a relatively small inertia will be able to follow and the molecule gets distorted. This distortion of the molecule is called polarizability.

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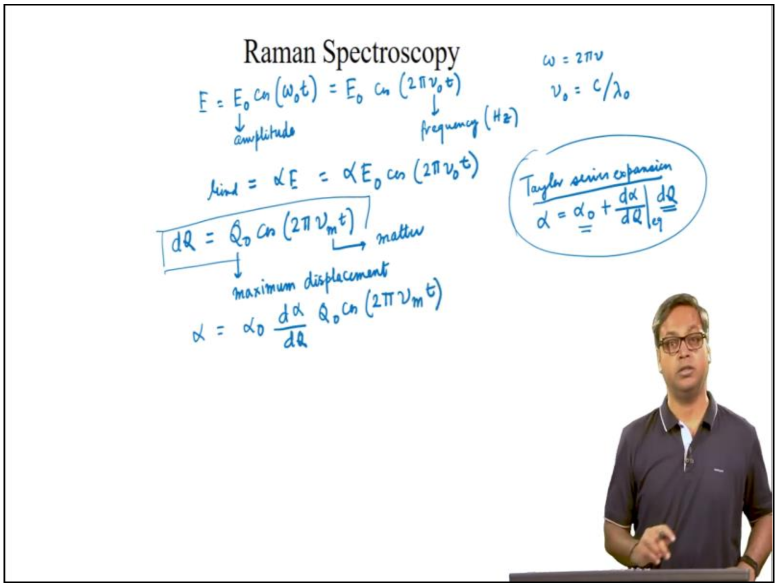
Raman Spectroscopy

$\underline{E} = E_0 \cos(\omega_0 t) = E_0 \cos(2\pi\nu_0 t)$

$E_0 \downarrow$ amplitude

$\nu_0 \downarrow$ frequency (Hz)

$\omega = 2\pi\nu$

$\nu_0 = c/\lambda_0$

$\mu_{ind} = \alpha \underline{E} = \alpha E_0 \cos(2\pi\nu_0 t)$

$\boxed{dQ = Q_0 \cos(2\pi\nu_m t)}$

$m \rightarrow$ matter

$Q_0 \downarrow$ maximum displacement

Taylor series expansion

$\alpha = \underline{\underline{\alpha_0}} + \left.\frac{d\alpha}{dQ}\right|_{eq} \underline{\underline{dQ}}$

$\alpha = \alpha_0 \frac{d\alpha}{dQ} Q_0 \cos(2\pi\nu_m t)$

So, for the incident electromagnetic wave the electric field may be expressed as E equals E 0 cos Omega 0 t so because we know Omega equals 2 PI nu we can write this as E 0 cos 2 pi nu 0 times t. so, E 0 here is the amplitude of the incident monochromatic light and nu 0 is the frequency of the light that is incident on the sample and the unit here for frequency is Hertz. So, if we want to convert this frequency into wavelength we can always do that by writing nu 0 equals C by lambda 0.

Thus we get the time dependence of the induced dipole moment because mu induced equals alpha times E which we can write now alpha times E 0 cos 2 pi nu 0 T because the ability to perturb the local electron cloud of a molecular structure depends on the relative location of the individual atoms. It follows that the polarizability is a function of the instantaneous position of the constituent atoms. The physical displacement let us say dQ of the atoms about their equilibrium position due to a periodic motion it can be either rotation or vibration.

So this physical displacement dQ can be expressed as Q 0 cosine of 2 pi nu m t. So, here m stands for matter because the matter is oscillating here. So, Q 0 is the maximum displacement about the equilibrium position. For a typical diatomic molecule for example nitrogen the maximum displacement is about 10% of the bond length. So, for such small displacements the polarizability may be approximated by Taylor series expansion.

So we can write alpha equals alpha 0 + d alpha dQ at the equilibrium position times dQ so here alpha 0 is the polarizability of the molecule at the equilibrium position. So, based on this expression for the displacement the polarizability may be given as so we can write alpha equals alpha 0 times d alpha dQ but instead of this dQ term here we'll put this expression so what we get is Q 0 cos 2 pi nu m times t.

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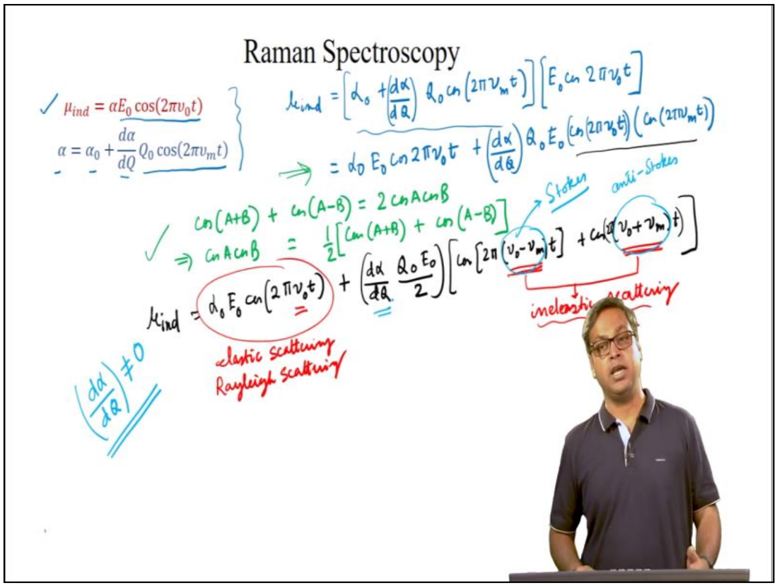

Raman Spectroscopy

✓ $\mu_{ind} = \alpha E_0 \cos(2\pi \upsilon_0 t)$

$\alpha = \alpha_0 + \frac{d\alpha}{dQ} Q_0 \cos(2\pi \upsilon_m t)$

$\mu_{ind} = \left[\alpha_0 + \left(\frac{d\alpha}{dQ}\right) Q_0 \cos(2\pi \nu_m t)\right]\left[E_0 \cos 2\pi \nu_0 t\right]$

$\Rightarrow = \alpha_0 E_0 \cos 2\pi\nu_0 t + \left(\frac{d\alpha}{dQ}\right) Q_0 E_0 (\cos(2\pi\nu_0 t))(\cos(2\pi\nu_m t))$

✓ $\cos(A+B) + \cos(A-B) = 2 \cos A \cos B$

$\Rightarrow \cos A \cos B = \frac{1}{2}\left[\cos(A+B) + \cos(A-B)\right]$

$\mu_{ind} = \alpha_0 E_0 \cos(2\pi\nu_0 t) + \left(\frac{d\alpha}{dQ} \frac{Q_0 E_0}{2}\right)\left[\cos[2\pi(\nu_0 - \nu_m)t] + \cos(2\pi(\nu_0 + \nu_m)t)\right]$

Stokes

anti-Stokes

inelastic scattering

elastic scattering

Rayleigh scattering

$\left(\frac{d\alpha}{dQ}\right) \neq 0$

So, we have these two expressions one is mu induced equals alpha times E 0 cos 2 pi nu 0 t and alpha can be expanded as alpha 0 + d alpha dQ times Q 0 2 pi nu m t. So, if I combine these two expressions we can write mu induced equals alpha 0 + d alpha dQ times Q 0 cos 2 pi nu m t. So, this is my alpha part and we have to multiply this with E 0 cos 2 pi nu 0 t. So, we can write this as alpha 0 E 0 cos 2 pi nu 0 t + d alpha dQ times we have Q 0 we have a E 0 and then we have the two cosine terms.

We can write cos 2 pi nu 0 t times cos 2 pi nu m t. So, now we can use the trigonometric identity which says cos A + B + cos A - B equals 2 cos A cos B. If you want to rewrite this we can write cos A cos B equals 1 by 2 cos A + B + cos A – B. So, if we use this trigonometric identity we can recast this expression and write mu induced equals alpha 0 E 0 cos 2 pi nu 0 t and then we can write d alpha dQ times Q 0 E 0 divided by 2.

And then we have this cos Aa cos B form which we can now write as cos 2 pi nu 0 - nu m t + cos mu 0 + nu m t, so we have two pi here so this is the final expression that we can write. So, if we examine this final expression we can see that the induced dipole moments are created at three different frequencies one is nu 0 1 is nu 0 - nu M and the other is nu 0 + nu m so these frequencies result in the scattered radiation in the same 3 frequencies.

The first data frequency that is this term corresponds to the incident frequency hence this is elastic scattering elastic scattering or we can write this is Rayleigh scattering. While the later two frequencies that is nu 0 - mu m and nu 0 + nu m are shifted to either lower or higher frequencies. And therefore these are examples of in elastic scattering. The scattered light in these two cases is referred to as Raman scattering with the downshifted frequency that is the frequency with a longer wavelength is known as the Stokes scattering and upshifted frequency that is frequency with the shorter wavelength is referred to as the anti Stokes scattering.

Note however that the necessary condition for Raman scattering is that d alpha dQ must be equal to nonzero in other words d alpha dQ not equal to 0 because if we have d alpha dQ equals 0 then the entire term vanishes and we will not have the Raman scattering term. This condition can be physically interpreted to mean that the rotational or vibrational displacement of atoms corresponding to a particular vibrational mode results in a change in the polarizability.

Further the simple classical derivation that we just did here is very deceptive since it predicts that the Stokes and the anti Stokes scattering have the same intensity. Bbut this is usually not the case. So, we will discuss more about this and also about the quantum model to explain the Raman effect in the next lecture.