Fundamentals of Spectroscopy

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Lecture-38
Quantum theory of Raman Effect

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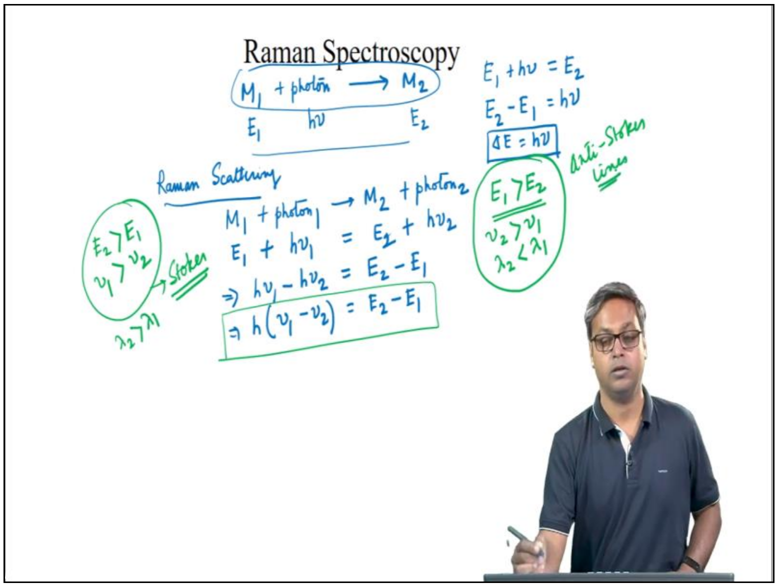

Raman Spectroscopy

$M_1 + \text{photon} \longrightarrow M_2$

$E_1 \quad h\nu \quad E_2$

$E_1 + h\nu = E_2$

$E_2 - E_1 = h\nu$

$\boxed{\Delta E = h\nu}$

Raman Scattering

$M_1 + \text{photon}_1 \rightarrow M_2 + \text{photon}_2$

$E_1 + h\nu_1 = E_2 + h\nu_2$

$\Rightarrow h\nu_1 - h\nu_2 = E_2 - E_1$

$\boxed{\Rightarrow h(\nu_1 - \nu_2) = E_2 - E_1}$

$E_2 > E_1$, $\nu_1 > \nu_2$ → Stokes

$\lambda_2 > \lambda_1$

$E_1 > E_2$, $\nu_2 > \nu_1$, $\lambda_2 < \lambda_1$

Anti-Stokes lines

Hello everyone welcome to the second lecture on Raman spectroscopy. In the first lecture we have discussed how Raman spectroscopy has a different origin from other forms of spectroscopy like we have rotational spectroscopy or vibrational spectroscopy. The Raman effect happens due to the scattering of the incident light by matter. So, this is exactly the reason why this Raman effect happens. So, in the last lecture we saw that if the wavelength of the scattered light is the same as the wavelength of the incident light it is known as Rayleigh scattering.

However in Raman scattering the wavelength of the scattered light is either longer or shorter than that of the incident light. So, we have also talked about the Stokes scattering where the wavelength is longer and the anti Stokes scattering where the wavelength is shorter. So, in the last lecture we have looked into the Raman effect using a classical model. In today's lecture we will try to understand the quantum theory of Raman effect.

So here we will think of light as made of photons instead of light as wave. So, because light is made of photons they have quantized energies when a photon of any frequency let us say the frequency of the photon is nu 0 impinges on a molecule the electrons are forced to oscillate at a frequency of the incident radiation and a radiation is emitted. If the frequency of the emitted radiation is the same as that of the incident radiation such elastic scattering between photons and molecules result in change of direction of the photons.

But there is no change in the energy in other words if we draw this is the incident light with intensity I 0 and frequency lambda. It interacts with the molecule or the matter and in this particular case of elastic scattering there is a change of direction but no change of energy. So, for the scattered light we can write I s as the intensity and lambda as the wavelength. The change of direction of photons he is known as scattering of the radiation Raman showed that change scattered frequencies are also present.

So, in other words Raman showed that I s that is the intensity of the scattered light can also have wavelengths other than that of the incident light and this is known as Raman scattering. So, we have discussed before when we are discussing the spectroscopic transitions or processes that we can represent a spectroscopic transition or a process using the equation like M 1 plus a photon gives M 2. So, the energy let us say of M 1 is E 1 and that of M 2 is E 2 and the energy of the photon is h nu.

So when we looked into the conservation of energy what we saw that we can write this expression for energy conservation as E1 + h nu equals E 2 or in other words I can rearrange this and write E 2 - E 1 equals h nu or Delta E equals h nu. So, we discussed about this important equation or expression in spectroscopy where the left hand side gives us the property of the matter and the right hand side gives us the property of the light.

So, one can think of Raman scattering in a similar way so we can write for Raman scattering we can write M 1 + photon 1 gives M 2 + photon 2. So, again let us say we have energy is E 1 and E 2 for M 1 and M 2 and for the photon 1 we have energy h nu 1 and 4 photon 2 we have energy h nu 2. So, this is a case of inelastic scattering when energy or the frequency of photon 1 changes due to collision with M 1. So, again considering the energy conservation we can write E 1 + h nu 1 equals E 2 + h nu 2 or in other words I can write h nu 1 - h nu 2 equals E2 - E1 or if I take h common nu 1 - nu 2 equals E2 - E1.

So, now if the matter goes to a higher energy level during the process in other words if E 2 is greater than E 1 hence in this case from this equation we can say that nu 1 is greater than nu 2 that means the frequency of the scattered radiation will be less or in other words the wavelength of the scattered radiation will be longer than that of the incident radiation. So, this case we get the Stokes lines but when we have the opposite case that is E1 is greater than E 2 the frequency of the scattered radiation will be greater than that of the incident radiation. So, because E 1 is greater than E 2 that means nu 2 will be greater than nu 1.

So we can write lambda 2 is less than lambda 1 in the first case we had lambda 2 is greater than lambda 1. So, in this particular case where e1 is greater than e2 we can see the wavelength of the scattered light is lower than the wavelength of the incident light. And thus we get anti-stokes lines.

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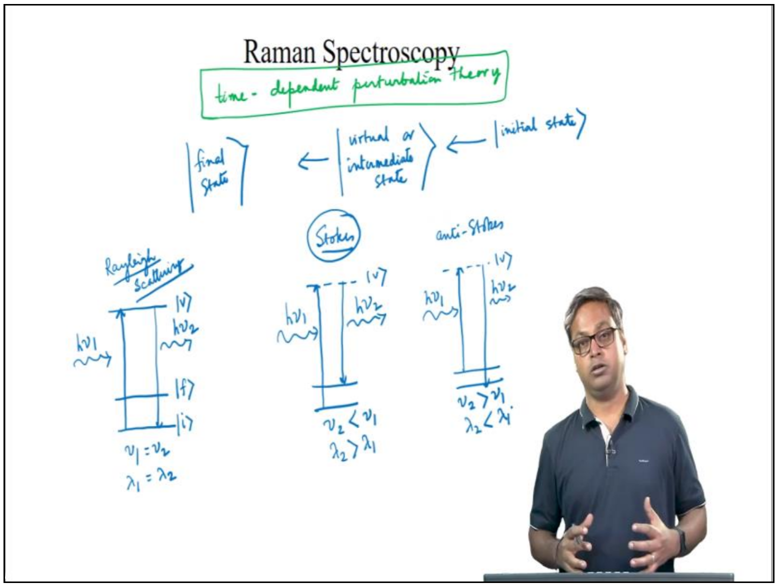
Raman Spectroscopy

The Raman effect can also be described by the time-dependent perturbation theory. So, my co-instructor Anirban Hazra has already talked about time-dependent perturbation theory in one of the lectures during the first module. So, in Raman effect we have to consider up to the second-order perturbation and physically the situation is as follows. So, we have an initial state from the initial state it goes to a virtual or intermediate state.

And from this virtual or intermediate state it goes to the final state while the initial and final states are necessary the transition to the final stationary state occurs by a virtual state which is non stationary. So, we can illustrate this pictorially, so let us say we have these two states. So, I have the initial state here and the final state here and I have a virtual state here and let us say light is incident with energy h nu1. So, from this initial state it goes to the virtual state however let us say it does not come back to the final state but it comes back directly to the initial state.

So the energy released is h nu2 if we think so then we can write nu 1 equals nu 2 or in other words lambda 1 equals lambda 2 and this is the case for Rayleigh scattering because the incident light wavelength is equal to the scattered light wavelength however if we want to draw for the Stokes lines. So, let us say we want to draw for the Stokes lines let us say we have these two states here which are stationary States and when we have a non stationary virtual state.

So, let us say the molecule goes from here to the virtual state but comes back to the upper state. In this particular case we can see the initial energy is h nu 1 and the emitted energy is h nu 2 so nu 2 is less than nu 1 or we can write lambda 2 is greater than lambda 1. So, we can see that the wavelength of the scattered light is longer compared to the wavelength of the initial or incident light and that is how we get the Stokes lines.

If you want to draw the anti-stokes lines, so we have the virtual state here and we have these two stationary states. Now the initial transition has to happen from the upper state and that is equals to h nu1 that is the energy difference and the final transition happens from the virtual state to the lower energy state and that is if we write h nu2 so we have nu 2 is greater than nu 1 or lambda 2 is less than lambda 1. So, this is the anti-stokes case where we can see the wavelength of the scattered light is shorter than the wavelength of the incident light.

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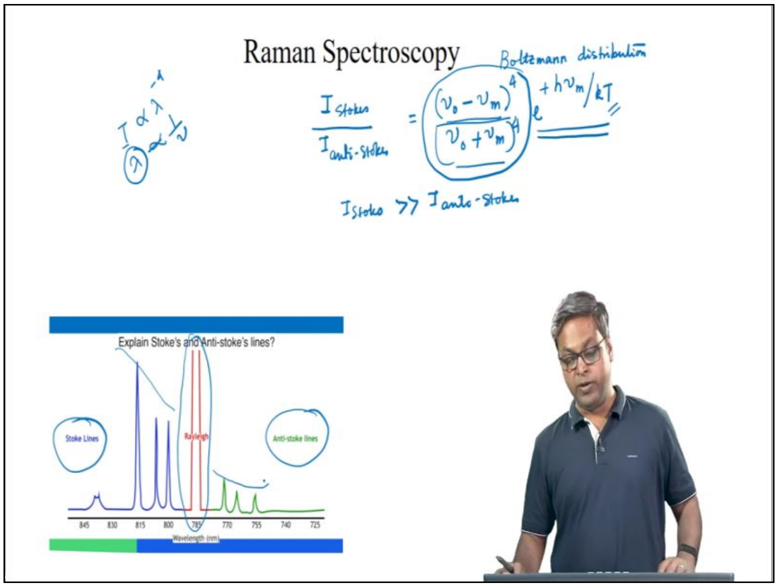

Raman Spectroscopy

Boltzmann distribution

$I \propto \lambda^{-4}$

$$\frac{I_{Stokes}}{I_{anti\text{-}Stokes}} = \frac{(\nu_0 - \nu_m)^4}{(\nu_0 + \nu_m)^4} e^{+h\nu_m/kT}$$

$I_{Stokes} >> I_{anti\text{-}Stokes}$

Explain Stoke's and Anti-stoke's lines?

So in the quantum mechanical model the intensity depends on the population of the initial state and this is determined by the Boltzmann distribution. Thus the intensity ratio for a non degenerate vibration can be written as I can write intensity of the Stokes divided by the intensity of the anti-stokes. So, this will be equal to nu 0 minus let us say nu M to the power 4 divided by nu 0 + nu M to the power 4 and then we have e to the power plus h nu M divided by kT.

So the first term comes because we know we have already talked about in the last lecture that the intensity is proportional to lambda to the power -4 and because lambda is inversely proportional to the frequency what we have here we have this is a Stokes frequency nu 0 - nu m and this is the anti Stokes frequency. So, other than this we have this exponential term which comes from the Boltzmann distribution. So, the ratio depends on temperature and for vibrational Raman spectrum which we will discuss in a later lecture.

The gap between the levels that the two vibrational levels is large and hence the population is much larger in the ground vibrational level compared to the excited vibrational level hence in this case we will have the intensity of Stokes will be much, much greater than the intensity of the anti-stokes line. So, the Stokes lines are nearly 100 times more intense than the anti Stokes lines as shown in this figure. So, we can see here we have the Rayleigh scattering and at wavelength larger compared to the Rayleigh scattering we have the Stokes lines.

And at wavelength smaller compared to the Rayleigh scattering we have the anti Stokes lines and also the intensity of these Stokes lines are much, much larger or more intense compared to those of anti-stokes lines.

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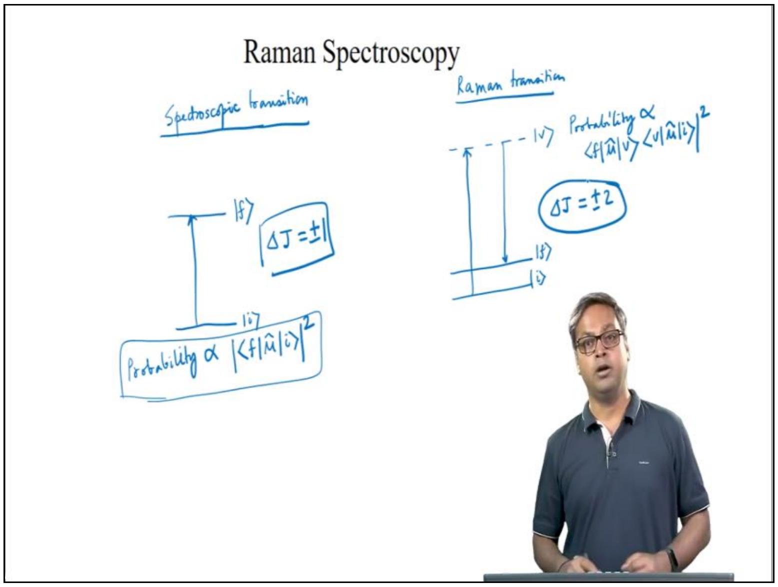

Raman Spectroscopy

Thus the mechanism of Raman transition is different from that of a spectroscopic transition. So, let us say we have a spectroscopy transition. So, we can depict this transition by saying we have an initial state. And we have a final state and so we have a transition from the initial to the final state and the probability of this transition is proportional to the we can write the final state we have the dipole moment operator. We have the initial state and the entire thing modulus is squared.

And we know this because this is the transition dipole moment. But for a Raman transition so now let us try to draw it for a Raman transition. So, for a Raman transition we know we have let us say we have an initial state, we have a final state. And we also need a virtual state, so initially it goes from the initial to the virtual state and then it comes back to the final state. So, in this case we can write the probability is proportional to the product of these two transitions or the product of the probabilities of these two transitions.

So the first transition we can write the virtual state the dipole operator initial state and for the second transition we can write the final state dipole operator and the virtual state the entirety modulus squared that gives me the probability. So, the transition probabilities are different for a spectroscopy transition where we are talking on absorption process and Raman transition. And we know that the expression of probability determines the selection rules.

Thus the selection rules for Raman transition will be different from the corresponding absorption transition. So, thus when the initial and the final states are rotational States we know the selection rule for microwave or rotational spectroscopy is Delta J equals + - 1, but in the case of rotational Raman spectroscopy the selection rule will be Delta J equals + - 2. So, we will discuss more on this in the next lecture and we will end this lecture by solving a problem related to Raman spectroscopy what we have discussed so far.

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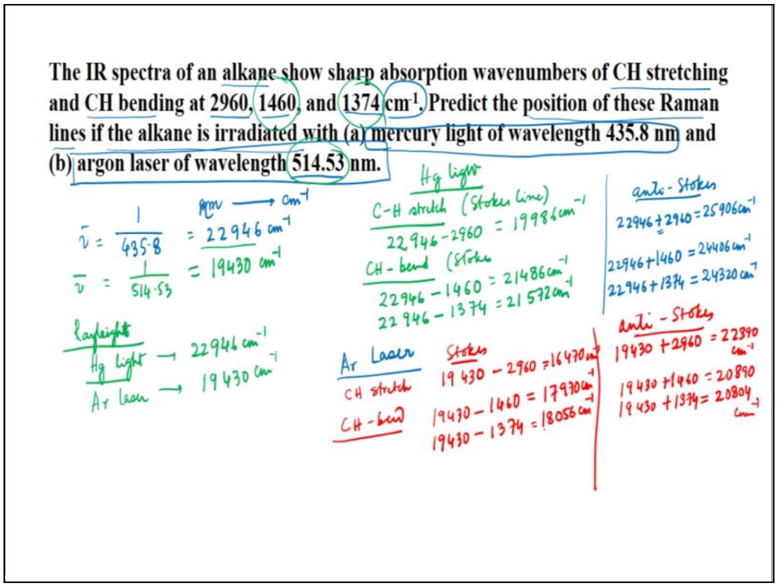

The IR spectra of an alkane show sharp absorption wavenumbers of CH stretching and CH bending at 2960, 1460, and 1374 cm^{-1}. Predict the position of these Raman lines if the alkane is irradiated with (a) mercury light of wavelength 435.8 nm and (b) argon laser of wavelength 514.53 nm.

nm $\longrightarrow$ cm^{-1}

$\bar{\nu} = \frac{1}{435.8} = 22946$ cm^{-1}

$\bar{\nu} = \frac{1}{514.53} = 19430$ cm^{-1}

Rayleight

Hg light → 22946 cm^{-1}

Ar laser → 19430 cm^{-1}

Hg light

C-H stretch (Stokes line)

22946 - 2960 = 19986 cm^{-1}

CH - bend (Stokes

22946 - 1460 = 21486 cm^{-1}

22946 - 1374 = 21572 cm^{-1}

anti - Stokes

22946 + 2960 = 25906 cm^{-1}

22946 + 1460 = 24406 cm^{-1}

22946 + 1374 = 24320 cm^{-1}

Ar Laser

Stokes

CH stretch 19430 - 2960 = 16470 cm^{-1}

CH - bend 19430 - 1460 = 17970 cm^{-1}

19430 - 1374 = 18056 cm^{-1}

anti - Stokes

19430 + 2960 = 22390 cm^{-1}

19430 + 1460 = 20890

19430 + 1374 = 20804 cm^{-1}

So, we have the problem here so the question is the IR spectra of an alkane shows sharp absorption wave numbers of CH stretching and CH bending at 2960 1460 and 1374 wave numbers. So, we have to predict the position of these Raman lines if the alkane is irradiated first let us say we have a mercury light of wavelength 435.8 nanometer and second the argon laser is irradiating the sample and the wavelength of the argon laser is 541.53 nanometer.

So first of all we have to convert these wavelengths which are given in nanometer to wave numbers. So, if I want to convert 435.8 nanometer then in wave numbers it will be 1 by lambda that is 1 by 435.8 and that will be 22946 wave numbers. And for the other case where we have the wavelength as 514.53 the wave number will be 1 by 514.53 and if you do this you will get 19430 wave numbers. So, we can see that the Rayleigh line let us say we have the Rayleigh line and for the case of the mercury light it will be exactly at the same frequency.

So it will be 22946 wave numbers and for the argon laser it will be at 19430 wave numbers. Now the question is where will we have this Stokes and the anti-stokes lines. So, let us first try to find it out for this mercury light. So, for the mercury light the CH stretch for the Stokes line will appear at 22946 – 2960 and that is 19986 wave numbers. For the CH bends and we are still talking about the Stokes lines we will have two transitions one at 22946 - 1460 because this is one of the CH bent wave numbers so this is 21486 wave numbers and the other will be at 2294 6 - 1374 that we have here so that will be 21572 wave numbers.

Now if we think about the anti-stokes lines so for the CH stretch the anti-stokes lines, so now we are talking about the anti-stokes lines? So the CH stretch will be at 22946 + 2560 so the only difference is in the plus sign and we will have that is 25 9:06 wave numbers for the CH bends I will have lines at 22946 + 1460 and 22946 + 1374 so this will be 2406 wave numbers and the next one will be 24320 wave numbers.

So now let us go for the argon laser and let us say we are talking about the CH stretch and the CH stretch we are talking about the Stokes here and we will calculate the anti Stokes here. So, for the C stretch the Stokes line will appear at 19430 - 2960 that is 16470 wave numbers. And now you can already find out that the CH bend will appear at 19430 - 1416 and 194 0 - 1374 so this will be 17970 wave numbers and this will be 18056 wave numbers so for the anti-stokes lines what we have we have is for the CH stretch will have at 19430 + 2960.

So that is 20 - 390 wave numbers and for the CH band will have 2 lines 19430 + 1416 and 19413 + 1374, so we will have at 2890 and at 2804 wave numbers. So, these are the different lines will observe for the c stretch and the CH Bend when we irradiate the alkynes either with mercury light or with argon laser.