Fundamentals of Spectroscopy

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Lecture 44
Polarization Effects and Numerical

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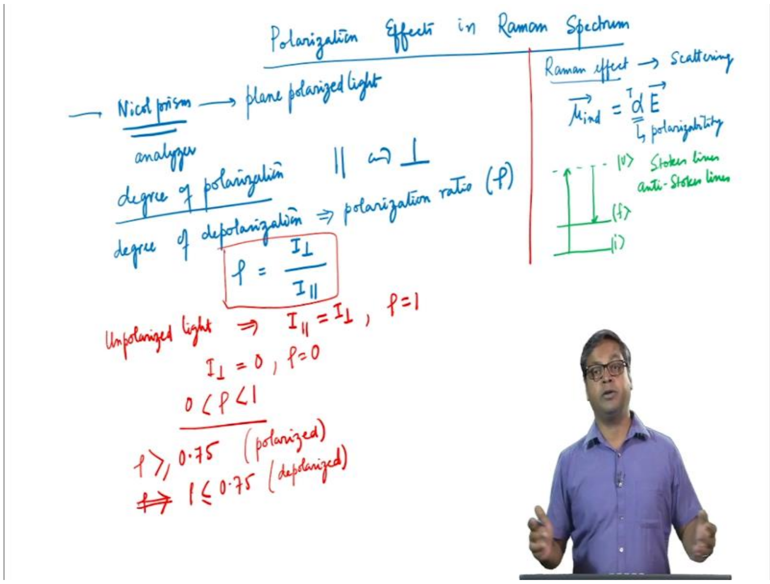

Polarization Effects in Raman Spectrum

→ Nicol prism → plane polarized light

analyzer

degree of polarization ∥ and ⊥

degree of depolarization ⇒ polarization ratio (ρ)

$$\boxed{\rho = \frac{I_\perp}{I_\parallel}}$$

Unpolarized light ⇒ $I_\parallel = I_\perp$, $\rho = 1$

$I_\perp = 0$, $\rho = 0$

$0 < \rho < 1$

$\rho \geq 0.75$ (polarized)

$\not\Rightarrow$ $\rho \leq 0.75$ (depolarized)

Raman effect → Scattering

$\vec{\mu}_{ind} = \overset{T}{\underline{\underline{\alpha}}}\vec{E}$

↳ polarizability

Stokes lines

anti-Stokes lines

Hello all welcome to the lecture. In today's lecture we will look into the polarization effects in Raman spectrum. So, when a beam of light is passed through a let us say, Nicole prism, the only light passing has its electric or magnetic field vector confined to a particular plane. So, the light that comes out of this nickel prism is known as plane polarized light. So, this light although is superficially indistinguishable, from unpolarized light, but when passed through another polarizing device, or a second polarizing device which is known as the analyzer.

The plane polarized light will pass with undiminished intensity, only if the polarizing axis of the two prisms the initial nickel prism and the analyzer, so if the polarizing axis of these two prisms are parallel to one another. At any other orientation of this axis the intensity of the light will be diminished. So, when the axes are perpendicular no light will pass through the analyzer. Thus the analyzer can serve both to detect the polarized light and determine if plane of polarization.

If the light incident on the analyzer is only partially polarized, that is, if the majority but not all of the Rays have their electric vectors parallel to a given plane, then, the light will not be completely extinguished at any orientation of the analyzer. So, we could then measure the degree of polarization in terms of the intensity of light transmitted in the parallel and perpendicular to the plane of maximum polarization. So, it is more convenient instead of measuring the degree of polarization to measure the degree of depolarization.

This is also known as the polarization ratio and is denoted by Rho. So, this Rho written as intensity of this perpendicular divided by the intensity of parallel, where the parallel or I parallel is the maximum and I perpendicular is the minimum intensity passed by the analyzer. So, if the scattered light is unpolarized I parallel will be equal to I perpendicular. So, for unpolarized light then I parallel would be equal to I perpendicular.

So, we can write Rho equals 1 if the scattered light retains this initial polarization. Then I perpendicular will be 0. So, if I perpendicular is 0 then Rho, which is given by I perpendicular divided by I parallel will also be 0. For intermediate degrees of polarization Rho will lie between 0 and 1. So, the relevance of this to Raman spectroscopy is that lines in some Raman spectra are found to be polarized to different extents even if the exciting radiation is completely unpolarized.

So, the Raman lines are classified as polarized if Rho is greater than equals 3 by 4 or 0.75. So, this is polarized and is classified as depolarized, if Rho is less than equals 0.75. So, this is depolarized only symmetric vibrations give rise to polarized line. So, by measuring the depolarization ratio we can distinguish between symmetric vibrational modes or the other modes for example, the bending modes or the asymmetric vibrational modes.

So, in this module we saw that the Raman Effect is related to the scattering of light. So, Raman Effect is related to the scattering of light. So, this is somewhat different in origin from other spectroscopic techniques like rotational spectroscopy or vibrational spectroscopy. So, in this module we discuss the classical and quantum theory of Raman scattering. We have seen that the electric field which is denoted by E of the electromagnetic wave induces a dipole moment which is denoted by mu indene.

And this can be written as mu indene equals alpha times e. So, here alpha is the polarizability and we have seen that mu indene is a vector electric field is also a vector and the alpha is a tensor. So, we discussed that a virtual state is involved in the Raman process. So, if we want to draw the Raman process, we have the initial state and we have the final state but we also need a virtual or intermediate state.

So, from the initial state it goes to the virtual state and from the virtual state it comes back to the initial state. So, if the frequency of the scattered light is less than that of the incident light, we get what we call as Stokes lines. And if the frequent see of the scattered light is larger than the incident light, we get what is known as anti-stokes lines. So, we have further discussed rotational Raman spectroscopy and the effect of nuclear spin on rotational Raman spectra.

We looked into the polarizability tensor and discussed about the polarizability ellipsoids and finally we discussed the Raman activity of vibrations and vibrational Raman spectroscopy. So, we will end this lecture by solving a few problems.

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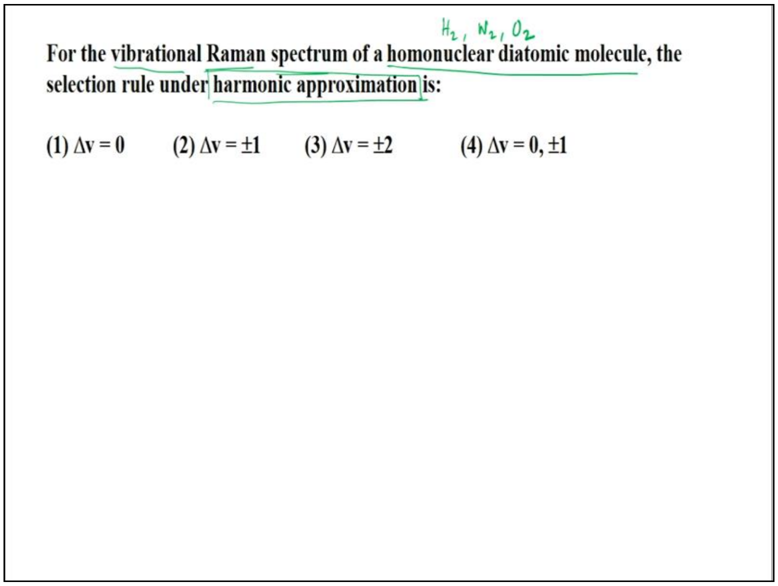


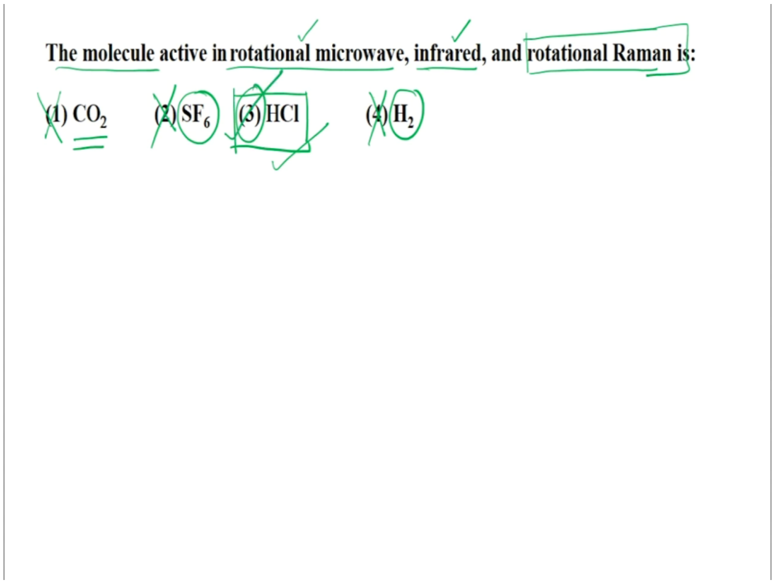
H_2, N_2, O_2

For the vibrational Raman spectrum of a homonuclear diatomic molecule, the selection rule under harmonic approximation is:

(1) $\Delta v = 0$ (2) $\Delta v = \pm 1$ (3) $\Delta v = \pm 2$ (4) $\Delta v = 0, \pm 1$

So, the first problem we have is it is a multiple-choice question. The question is for a vibrational Raman spectrum of a homonuclear diatomic molecule, so it can be like hydrogen, nitrogen, oxygen et cetera. The selection rule under harmonic approximation is, so, as we had discussed in the last lecture, the selection rule is the same for IR and Raman for vibrational transitions. And because we are talking about harmonic approximation, we know the selection rule is Delta V equals + - 1. So, the other three options 1 2 and 4 are not correct. The correct option is Delta V equals + - 1.

(Refer Slide Time: 11:00)



The molecule active in rotational microwave, infrared, and rotational Raman is:

(1) CO_2 (2) SF_6 [✓ (3) HCl] (4) H_2

So, the next question is it is given that the molecule is active in rotational microwave infinite and rotational Raman. So, we have four choices. We have to choose the molecule which is active in all these three cases, so the options we have is co2. So, we know it does not have a permanent dipole moment, so the rotational microwave is not possible. So, this is not the case SF6, is a symmetric molecule again this is not the case.

And hydrogen because it has zero dipole moment we will not have the rotational microwave. The only case is hydrochloric acid or HCl because HCl is a heteronuclear diatomic molecule. So, it has a permanent dipole moment so it is a microwave active. The HCL stretch gives rise to infrared spectrum and as I have already discussed the rotational Raman spectrum is also there for each here. So, the answer is 3 that is HCl. Now, we have a problem.

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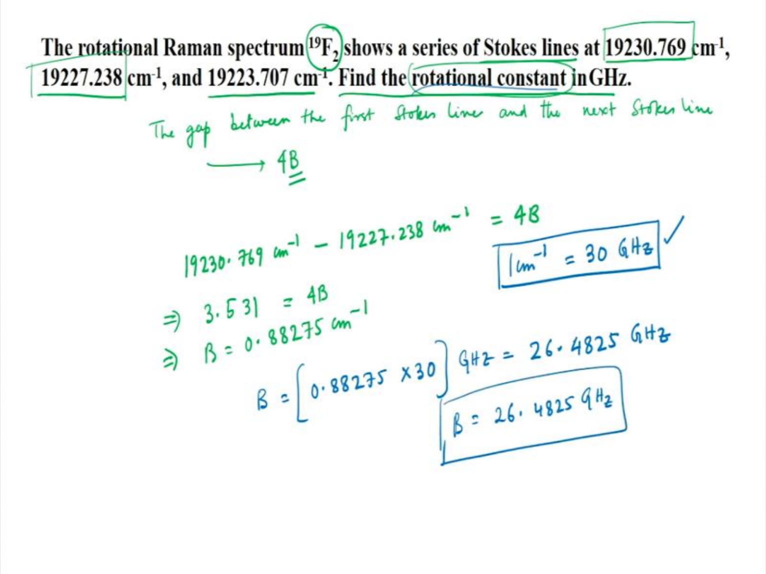

The rotational Raman spectrum $^{19}F_2$ shows a series of Stokes lines at 19230.769 cm^{-1}, 19227.238 cm^{-1}, and 19223.707 cm^{-1}. Find the rotational constant in GHz.

The gap between the first Stokes line and the next Stokes line $\longrightarrow \underline{\underline{4B}}$

$$19230.769\ cm^{-1} - 19227.238\ cm^{-1} = 4B$$

$$\boxed{1\ cm^{-1} = 30\ GHz}\ ✓$$

$$\Rightarrow 3.531 = 4B$$

$$\Rightarrow B = 0.88275\ cm^{-1}$$

$$B = [0.88275 \times 30]\ GHz = 26.4825\ GHz$$

$$\boxed{B = 26.4825\ GHz}$$

The problem states the rotational Raman spectrum of 19F that is fluorine shows a series of Stokes lines. And we have the Stokes lines at 19230.769 wave numbers then 19227.238 wave numbers and 19223.707 wave numbers. So, these are the series of the Stokes lines. So, the question is, find the rotational constant in gigahertz. So, we know the gap between the first Stokes line and the next Stokes line is 4 B, where B is the rotational constant that we have to find in this question.

So, we can write we have these two lines, this first line and the next line. So, we can write 19230.769 wave numbers – 19227.238 wave numbers equals 4B. So, this gives 3.531 equals 4B. So, we get B equals 0.88275 wave numbers. But we know that one wave number it was 30 gigahertz. So, you should check this relation yourself. So, for the time being we take this relation so we can write B equals 0.88275 times 30 gigahertz so that is 26.4825 gigahertz.

So, in the question we are asked to find the rotational constant that is B in gigahertz. So, the answer is B equals 26.4825 gigahertz. So, now let us look into the last question.

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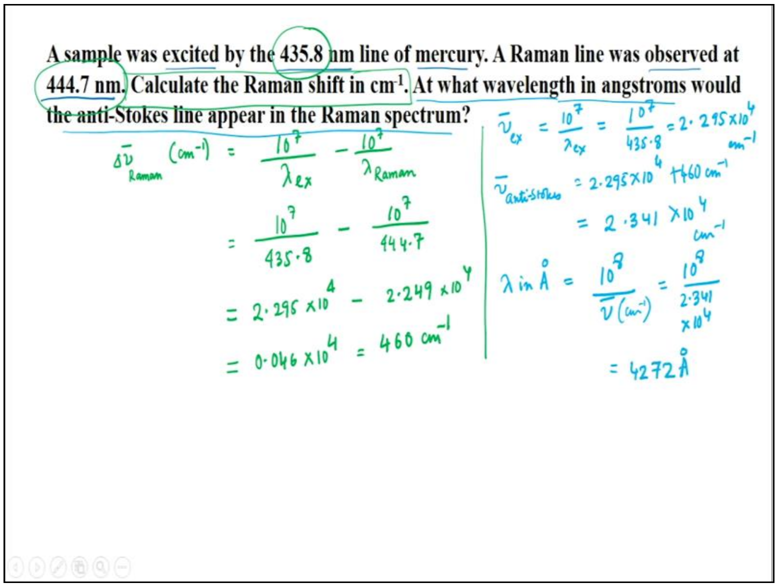

A sample was excited by the 435.8 nm line of mercury. A Raman line was observed at 444.7 nm. Calculate the Raman shift in cm^{-1}. At what wavelength in angstroms would the anti-Stokes line appear in the Raman spectrum?

$$\delta\bar{\nu}_{Raman}\,(cm^{-1}) = \frac{10^7}{\lambda_{ex}} - \frac{10^7}{\lambda_{Raman}}$$

$$= \frac{10^7}{435.8} - \frac{10^7}{444.7}$$

$$= 2.295\times10^4 - 2.249\times10^4$$

$$= 0.046\times10^4 = 460\ cm^{-1}$$

$$\bar{\nu}_{ex} = \frac{10^7}{\lambda_{ex}} = \frac{10^7}{435.8} = 2.295\times10^4\ cm^{-1}$$

$$\bar{\nu}_{anti\text{-}Stokes} = 2.295\times10^4 + 460\ cm^{-1}$$

$$= 2.341\times10^4\ cm^{-1}$$

$$\lambda \text{ in } \mathring{A} = \frac{10^8}{\bar{\nu}\,(cm^{-1})} = \frac{10^8}{2.341\times10^4}$$

$$= 4272\ \mathring{A}$$

A sample was excited by the 435.8 nanometer line of Mercury. A Raman line was observed at 444.7 nanometer the first question is we have to calculate the Raman shift in wave numbers. So, let us focus on this first question. First, so the Raman shift which is given by Delta a nu bar Raman and will calculate in wave numbers is 10 to the power 7 divided by lambda excitation - 10 to the power 7 divided by lambda Raman.

So, 10 to the power 7 divided by lambda excitation is this mercury line, so is 435.8 - 10 to the power 7 divided by lambda Raman. So, the Raman line is observed at 444.7 nanometers. So, if we do this calculation what we get is, the first term becomes 2.295 into 10 to the power 4 the second term becomes 2.249 x 10 to the power 4 so, this is 0.046 times 10 to the power 4 or we can write 460 wave numbers.

So that is the first part. Now, the second question that we have is at what wavelength in angstroms would the anti-stokes line appear in the normal spectrum? So, we know that the nu bar excitation is given by 10 to the power 7 divided by lambda excitation. So, this is 10 to the power 7 divided by 435.8. So, this is 2.295 into10 to the power 4 wave numbers. So, the anti-stokes lines that is nu anti-stokes will appear at 2.295 into 10 to the power 4 that is nu bar excitation plus 460 wave numbers.

Now what we get here is 2 .341 into 10 to the power 4 wave numbers. So, the lambda in angstrom equals 10 to the power 8 divided by this nu bar and a Stokes in wave numbers equals 10 to the power 8 divided by 2.341 into 10 to the power 4 that is 4272 angstroms.