Fundamentals of Spectroscopy
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Lecture 43
Vibrational Raman Spectroscopy

Hello all welcome to the 7th lecture on Raman spectroscopy. In the last lecture, we discussed two important aspects of Vibrational Raman spectroscopy.

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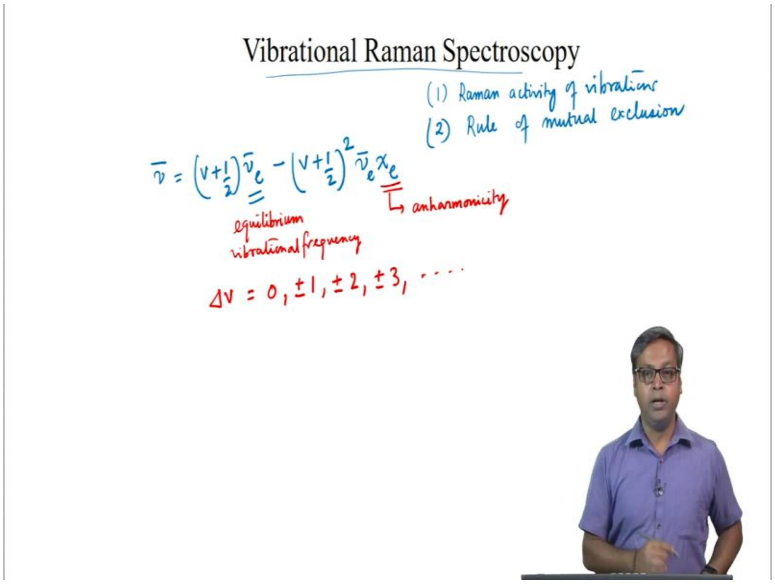

Vibrational Raman Spectroscopy

(1) Raman activity of vibrations
(2) Rule of mutual exclusion

$$\bar{\nu} = \left(v+\frac{1}{2}\right)\underline{\bar{\nu}_e} - \left(v+\frac{1}{2}\right)^2 \bar{\nu}_e \underline{x_e}$$

equilibrium vibrational frequency

↳ anharmonicity

$\Delta v = 0, \pm 1, \pm 2, \pm 3, \ldots$

And these two aspects are one is Raman activity of vibrations and the second aspect is rule of mutual exclusion. So, in today's lecture we will look into the details of Vibrational Raman spectrum. For every vibrational mode we can write the energy expression in the form of nu bar equals V + 1/2 nu bar e - V + 1/2 whole squared nu bar e chi e. So, here the nu bar e is the equilibrium vibrational frequency. And this chi e is the anharmonicity.

So, this is a general expression independent of the shape of the molecule or the nature of the vibration. And the selection rule is Delta V equals 0 + - 1, + - 2, + - 3, dot dot dot, so, the selection rule is the same for Raman as for infrared spectroscopy and the probability of this + - 2, or + - 3, decreases rapidly. So, if the selection rule is applied to the energy expression to obtain the transition energies what we get is let us say, if the transition is from V equals 0 to V equals 1.

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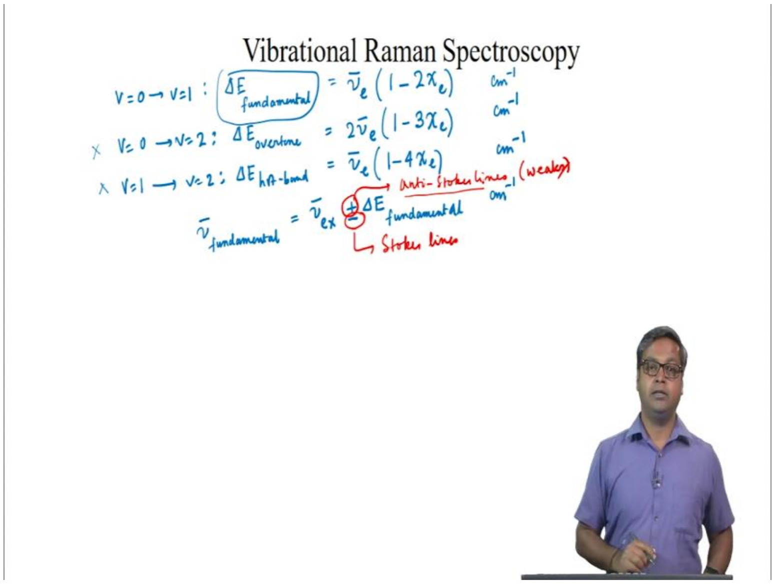

Vibrational Raman Spectroscopy

$V=0 \rightarrow V=1 : \boxed{\Delta E_{\text{fundamental}}} = \bar{\nu}_e(1-2\chi_e) \quad cm^{-1}$

$\times \; V=0 \rightarrow V=2 : \Delta E_{\text{overtone}} = 2\bar{\nu}_e(1-3\chi_e) \quad cm^{-1}$

$\times \; V=1 \rightarrow V=2 : \Delta E_{\text{ht-band}} = \bar{\nu}_e(1-4\chi_e) \quad cm^{-1}$

$\bar{\nu}_{\text{fundamental}} = \bar{\nu}_{ex} \pm \Delta E_{\text{fundamental}} \quad cm^{-1}$

Anti-Stokes lines (weaker)

Stokes lines

Then, this transition energy we can write as, Delta E fundamental because this is the fundamental transition and this will be nu bar e times 1 - 2 chi e and the unit is in wave numbers. Now, instead of the fundamental transition if we think about the overtone, so, we have V equals 0 to V equals 2. So, in this case we will write Delta E, overtone that we can write as, 2 nu bar e times 1 - 3 chi e. Again the unit is in wave numbers and the other transition that we can get is a hot band in that case it starts from an excited vibrational level that is V equals 1 to V equals 2.

So in this case, we will write it Delta E hot band. This will be nu bar e times 1 - 4 chi e and the unit is in wave numbers. So, since the Raman scattered light is in any case of low intensity we can ignore the weaker effects such as the overtones or the hot bands. So, we would restrict our discussion today on the fundamental transitions. The Raman lines would appear at distances from the exciting line corresponding to each fundamental vibration.

In other words, we can write nu bar of fundamental will be equal to nu bar excitation plus Delta E fundamental. So, Delta E fundamental is the one which we wrote here and again the unit is in wave numbers. So, this is plus minus. So, the minus sign which we have here represents the stokes lines and the plus sign represents the anti-stokes lines. So, for the Stokes lines the molecule has gained energy at the expense of the radiation.

And that is the reason why the frequency or the wave number for the Stokes lines is less than that of the new body excitation. The anti-stokes lines are often too weak to be observed as very few molecules exist in the weak was one state at room temperature. The Vibrational Raman spectrum of a molecule shows a series of reasonably intense lines to the low-frequency side of the exciting line with a much weaker mirror image series on the high frequency side.

And the separation of each line from the center of the exciting line provides the Raman active vibrational frequencies of the molecule.

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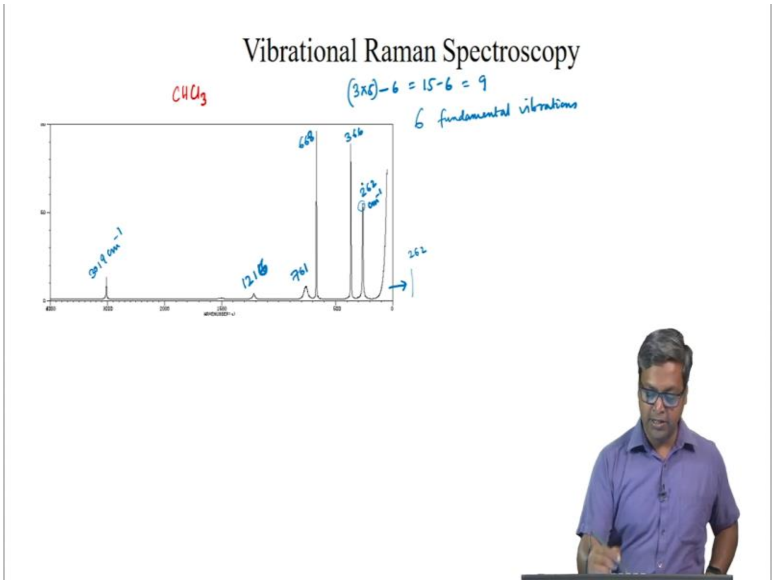

Vibrational Raman Spectroscopy

$CHCl_3$

$(3\times5)-6 = 15-6 = 9$

6 fundamental vibrations

So, this figure shows the Raman spectrum of chloroform or CHCL3. So, the Raman lines appear at 6 different places. So, we have lines at 262 wave numbers. We have another line at 366, then, another line at 668, then, we have another line at 761, and this 1216 wave numbers and we have one at 3019 line wave numbers. So, these are the lines on the low frequency side or the Stoke side of the exciting line.

And there will be lines in the anti stroke sites for example we will get another line around 262 but at higher frequency of the exciting line. But this intensity will be much lower than the 262 wave number line for the stoke side as we had discussed before. So, this chloroform we have 5 atoms so we have 3 times 5 - 6 that is 15 - 6 or 9 vibrations. So, we can expect 9 vibrations but out of these three vibrations are doubly degenerate.

So, we are left with 6 fundamental vibrations and the 6 fundamental vibrations we see here in this C in the 6 different Peaks.

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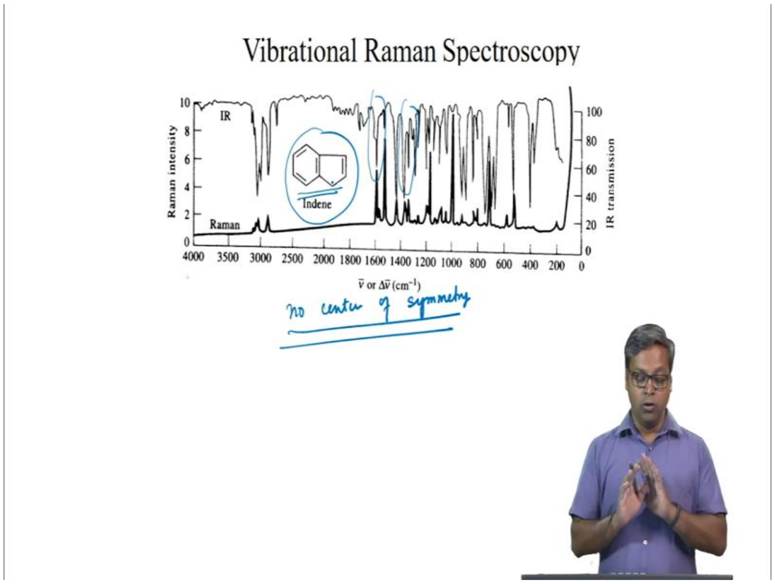

Vibrational Raman Spectroscopy

no center of symmetry

So, here we see another molecule that is Indene. So, we see the IR and the Raman spectra of Indian. So, we can see the different modes are active in both IR and Raman spectrum. So, the immediate conclusion is that the molecule has no center of symmetry. And this is also clear, if we look into the structure of the molecule ending and we can see it has no center of symmetry. So, now let us move on to the vibrational rotational Raman spectroscopy. The fine structure is rarely resolved except in the case of diatomic molecules.

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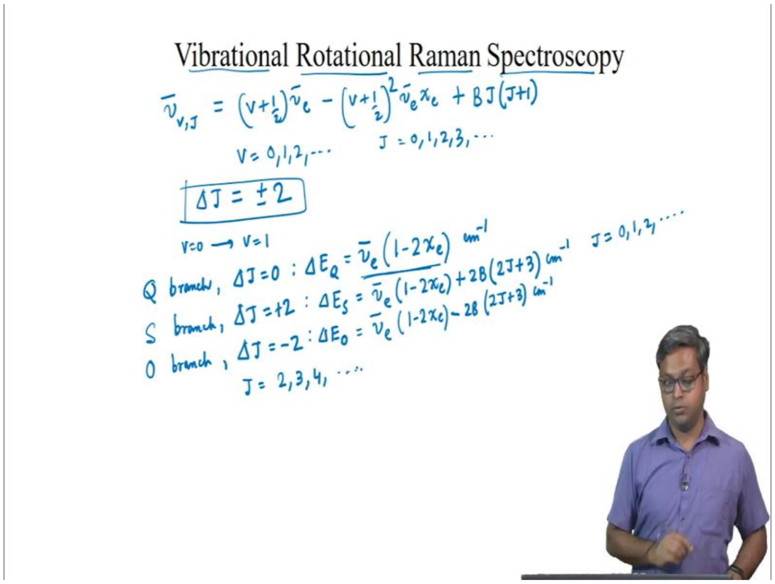

Vibrational Rotational Raman Spectroscopy

$$\bar{\nu}_{v,J} = \left(v+\tfrac{1}{2}\right)\bar{\nu}_e - \left(v+\tfrac{1}{2}\right)^2\bar{\nu}_e x_e + BJ(J+1)$$

$v = 0, 1, 2, \ldots$ $J = 0, 1, 2, 3, \ldots$

$$\boxed{\Delta J = \pm 2}$$

$v=0 \longrightarrow v=1$

Q branch, $\Delta J = 0$: $\Delta E_Q = \underline{\bar{\nu}_e(1-2x_e)}$ cm^{-1}

S branch, $\Delta J = +2$: $\Delta E_S = \bar{\nu}_e(1-2x_e) + 2B(2J+3)$ cm^{-1} $J = 0, 1, 2, \ldots$

O branch, $\Delta J = -2$: $\Delta E_O = \bar{\nu}_e(1-2x_e) - 2B(2J+3)$ cm^{-1}

$J = 2, 3, 4, \ldots$

So, we can write the energy expression as nu bar as a function of the vibrational quantum number V and the rotational quantum number J and nu bar V J equals V + 1/2 nu bar e - V + 1/2 whole squared nu bar e chi e plus the rotational term that is B times J times J + 1. So, here we can take the values of 0, 1, 2 etcetera and J can take the values of 0, 1, 2, 3, et cetera. So, we know for diatomic molecules the rotational selection rule is Delta J equals + - 2 for Raman spectroscopy.

So now, if we combine this rotational selection rule with the transition, that is a fundamental transition that is v equals 0 to V equals 1, first of all, we get something known as the Q branch. So, for the Q branch Delta J equals 0. So, we can write Delta E for the Q branch is nu bar e times 1 - 2 chi e wave numbers. We also get something known as the S branch. So, for the S branch Delta J equals + 2. So, we can write Delta E of S branch equals nu bar e 1 - 2 chi e.

So, we are repeating what we wrote for Q branch but we have an extra term that is + 2 B times 2 J + 3 wave numbers. And in this case J equals 0, 1, 2 and so on. And we can have another branch that is the O Branch. So, for the O branch we have Delta J equals -2 so we can write Delta E for the O branch so we will write the first term as that of the Q branch nu bar e 1 - 2 chi e and then we have - 2 B 2 J + 3 wave numbers and for this case J equals 2, 3, 4, dot dot dot.

So, does the Stokes slides lying at the lower frequency or the lower wave number side of the exciting radiation will occur?

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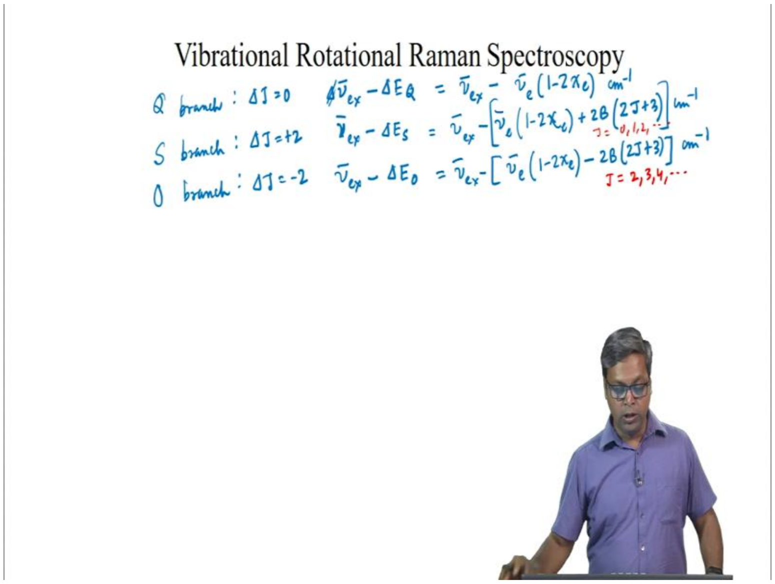

Vibrational Rotational Raman Spectroscopy

Q branch : $\Delta J = 0$ $\bar{\nu}_{ex} - \Delta E_Q = \bar{\nu}_{ex} - \bar{\nu}_e(1-2x_e)$ cm^{-1}

S branch : $\Delta J = +2$ $\bar{\nu}_{ex} - \Delta E_S = \bar{\nu}_{ex} - [\bar{\nu}_e(1-2x_e) + 2B(2J+3)]$ cm^{-1}

$J = 0, 1, 2, \cdots$

O branch : $\Delta J = -2$ $\bar{\nu}_{ex} - \Delta E_O = \bar{\nu}_{ex} - [\bar{\nu}_e(1-2x_e) - 2B(2J+3)]$ cm^{-1}

$J = 2, 3, 4, \cdots$

So, for the Q branch the Stokes line will occur at we can write, so we know for Q branch Delta J equals 0 so, it will occur at Delta Nu or rather nu bar excitation - Delta E Q. so, we know the expression for Delta E Q so we can write nu bar excitation - nu bar e 1 - 2 chi e and this unit here is wave numbers. Similarly, for the S branch where we have Delta J equals + 2 so it will occur at new bar excitation - Delta E S.

So, it will be nu bar excitation - nu bar e 1 - 2 chi e and then we have + 2B 2J + 3 wave numbers. And for the O Branch where delta j equals -2 the stokes lines will occur at nu bar excitation - delta E 0 or Delta E O, and which is nu bar excitation - nu bar e 1 - 2 chi e - 2 B times 2 J + 3 wave numbers. So, again we can see for this particular case J equals 0 1, 2, dot dot dot and for the O Branch is J equals 2, 3, 4, so on.

So, the nu excitation that we are writing in these expressions, this nu excitation is the frequency of the incident radiation.

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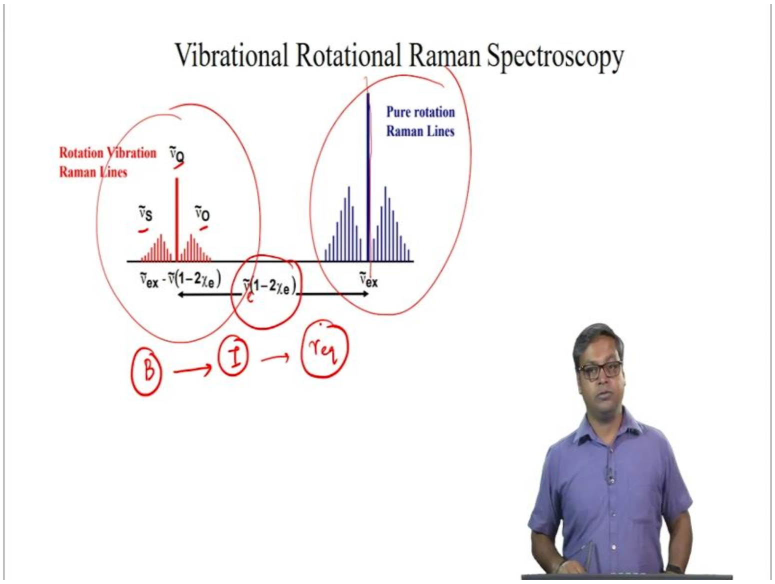

Vibrational Rotational Raman Spectroscopy

So, here you can see a spectrum the rotation vibration Raman lines are shown in the red. And the pure rotation lines are shown on the right in blue the O, Q and the S branches are shown and we can see the Rotational Vibrational Raman band is shifted from the excitation frequency by this nu bar e times 1 - 2. The presence of the strong Q branch in the Raman spectrum is to be noted and compared with the P and our branches only which occur for a diatomic molecule in the infrared.

The analysis of the O and R branches in the Raman spectrum can provide us the value of the rotational constant that is B. And once we know B, we can get the moment of inertia that is I and once we know the moment of inertia, we can get the equilibrium bond length or r equilibrium. So, if we think about larger molecules we can ignore since the fine rotational structures are not resolved for larger molecules.