Fundamentals of Spectroscopy

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Lecture-22
Ro – Vibrational Spectrum - I

Hello everyone, welcome to the lecture. In the last lecture, we learned about the effects of anharmonicity. We discussed about the fundamental transitions, the overtones and the hot bands. Let us once more see where all these bands will appear in a spectrum.

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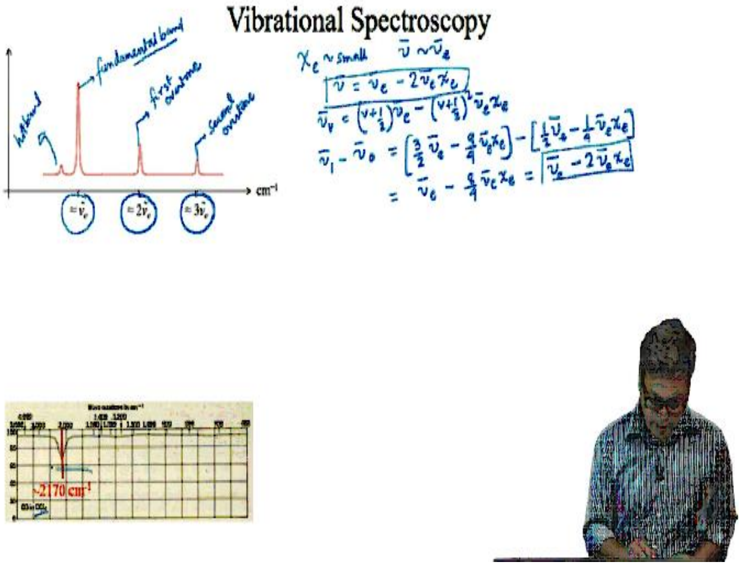

Vibrational Spectroscopy

$x_e \sim$ small $\quad \bar{\nu} \sim \bar{\nu}_e$

$$\boxed{\bar{\nu} = \bar{\nu}_e - 2\bar{\nu}_e x_e}$$

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

$$\bar{\nu}_1 - \bar{\nu}_0 = \left[\tfrac{3}{2}\bar{\nu}_e - \tfrac{9}{4}\bar{\nu}_e x_e\right] - \left[\tfrac{1}{2}\bar{\nu}_e - \tfrac{1}{4}\bar{\nu}_e x_e\right]$$

$$= \bar{\nu}_e - \tfrac{8}{4}\bar{\nu}_e x_e = \boxed{\bar{\nu}_e - 2\bar{\nu}_e x_e}$$

So, this figure shows 4 bands of different intensities at different frequencies, the leftmost band is the hot band, this band is at a frequency smaller than the fundamental band. So, this is our fundamental band. So, the hot band is at a frequency smaller than the fundamental band, because the gap between v = 1 and v = 2 is smaller than the gap between v = 0 and v = 1. This fundamental band approximately occurs at nu bar e the first overtone. So, here we have the first overtone.

So, this first overtone will occur at a frequency which is approximately twice that of the fundamental or approximately 2 nu bar e and the second overtone. So here we have the second overtone. So, the second overtone will occur at a frequency that is approximately 3 times that of the fundamental or 3 nu bar e, in reality the first and the second overtones are slightly less than twice and thrice the fundamental is the anharmonicity at constant that is chi e. If the chi e is small, then the fundamental frequency that is nu bar is approximately equal to nu bar e.

But if the anharmonicity constant is not small or if we just want to be accurate then The fundamental frequency, which is rigorously defined as the energy of v = 1 and v = 0 state, there is a difference between these 2 energies states is given by nu bar = nu bar e - 2 nu bar e chi e. So, let us see how we get this equation. So, we know that nu bar for any vibrational level v is given by v + half nu bar e - v + half square nu bar e, chi e. So, the fundamental frequency is the energy difference between v = 1 and v = 0 level.

So, the fundamental frequency is given by nu bar 1 - nu bar 0. So we can write this as so nu bar 1 becomes 3 / 2 nu bar e - 9 / 4 nu bar e chi e and then we have to subtract the nu bar 0, that is half nu bar e - 1 / 4 nu bar e chi e. So if we put all the tones with nu bar together, what we have is nu bar e and if we collect all the tones with nu bar e chi e together, what we have is minus 8 / 4 nu bar e chi e. So, this becomes nu bar e - 2 nu bar e chi e.

So, this is the same expression that we have written before. So, this is the equation that enables me to convert nu bar to nu bar e or vice versa. So, let us now look at the higher spectrum of carbon monoxide dissolved in CCL 4 the fundamental band appears at 2170 wave numbers.

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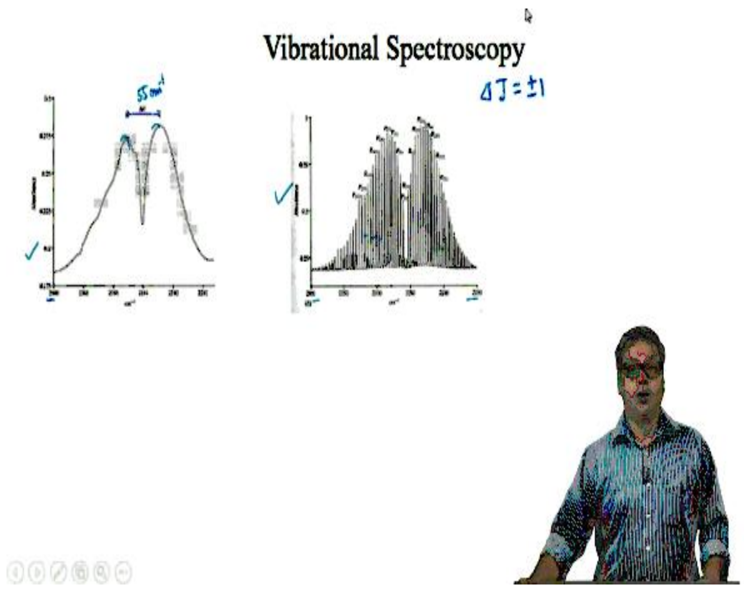

Vibrational Spectroscopy

$\Delta J = \pm 1$

However, if we look at the carbon monoxide spectrum in the gas phase, we see this kind of spectrum, the left spectrum, this one is obtained from measurement at low resolution, it looks like there are 2 peaks separated by some gap, which is roughly 55 wave numbers. At high resolution, we have these 2 bands of lines appearing and these lines are almost equally spaced. So, we need to explain these features and the reason why we get these additional structures that means is additional lines.

The spacing between the lines in the high resolution measurement that means, in this spectrum is of the same order as the carbon monoxide rotational structure; we can guess that this structure is due to the rotational structure of the molecule. So we can think that the molecules are not only vibrating, but they are rotating as well. So the molecules do have rotational energy, in addition to the vibrational energy. When we excite a vibration, we need to change the rotational energy of the molecule.

In other words, the rotational selection rule given by delta j = +- 1 still needs to be adhered too. We have to conserve the angular momentum during a transition and we cannot conserve angular momentum with pure vibrational transition. That is a transition that does not change it is rotational state.

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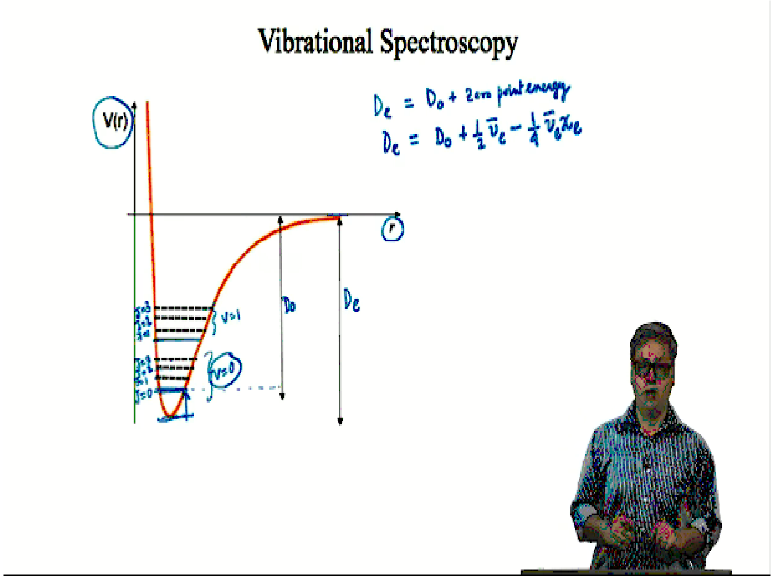

Vibrational Spectroscopy

$D_e = D_0 +$ zero point energy

$D_e = D_0 + \frac{1}{2}\bar{\nu}_e - \frac{1}{4}\bar{\nu}_e x_e$

So, before we discuss in detail about the fine structure associated with the diatomic vibrating rotor, let us look into a typical potential energy diagram or potential energy surface of a diatomic molecule. The potential energy that is v of r is plotted as a function of bond length that is r the potential energy surface is the surface upon which the nuclei are able to move. The 2 motions where interested in are rotation and vibration. So, they rotate and vibrate within this potential energy surface.

So, the difference in energy between the bottom of this potential well and the dissociation limit, that is, this energy level is the dissociation energy given by D e. This is also known as the equilibrium dissociation energy. So, the solid lines are the vibrational levels. So, the solid lines at the high vibrational levels and D 0. So, D 0 is the dissociation energy from the v = 0 level. So, this is the dissociation energy that can be spectroscopically measured.

Due to this, this is also known as the spectroscopy dissociation energy. The dashed lines shown in this figure these dashed lines have the same amount of vibrational energy. They are all defined by the vibrational quantum number v = 0, but they have different rotation and energies. That means they have different values of J. So the molecules at the energy level shown by this solid line associated with v = 0 also have the rotational energy, J = 0.

Molecules at the energy levels, shown by these other dashed lines also have vibrational energy associated with v = 0, but they have rotational energy associated with J = 1, J = 2, J equal 3 and so on. So similarly, these are the dashed lines shown here have energy associated with v = 1. But here we have J = 1, J = 2, J = 3. More importantly, we can define these levels on a given electronic state, either given by the solid lines, or the dashed lines, by 2 quantum numbers is vibrational quantum number V, and is rotational quantum number J.

In other words, we know how much rotational energy and vibrational energy the molecule has. The total energy is just the sum of the vibrational and the rotational energies. And that is the basis of spectroscopy. Once the energies of the different levels are known, and the selection rules are known, we know how J can change and how v can change. And thus we know what transitions are allowed in the system. And we can predict the spectrum. The 0 point energy is the energy difference between the bottom of the energy well, and v = 0. So this is the 0 point energy.

So we can write this D e = D 0 + zero point energy. And if we put the energy expression for anharmonic oscillator, we can write D e = D 0 + half nu bar e - 1 / 4 nu bar e chi e. So, when we excite a molecule from one vibrational state to another, we can predict there will also be a change in the rotational state, the molecule will either be rotational excited, or de-excited during the row vibrational transition. So this row vibration stands for rotation plus vibration. So, if we focus now.

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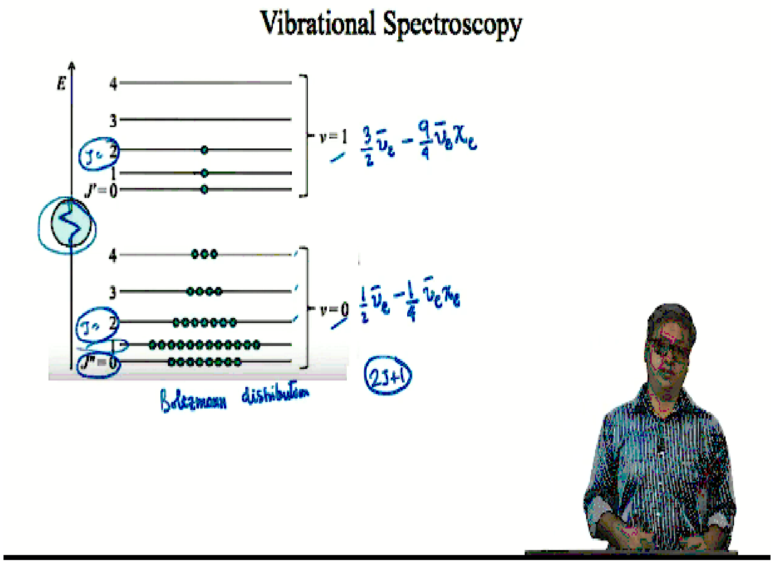
Vibrational Spectroscopy

On the v = 0, and the v = 1 levels and kind of expand them, we see there is a big gap between the v = 0 and v = 1 level. So that is why we have this zigzag line on the y axis. All the rotation levels with v = 0 quantum number has exactly the same amount of vibrational energy, which is given by half nu bar e - 1 / 4, nu bar e chi e. And all the levels identified with v = 1 quantum number have exactly the same vibrational energy given by 3 / 2 nu bar e - 9 / 4 nu bar e chi e. Now, if we think about the 2J = 2 levels, so we will think about this 2 levels of v = 0 v = 1, they have more or less the same rotational energy.

However, they do not have the exactly the same rotational energy. Because as we go from v = 0 to v = 1, the bond length slightly changes due to anharmonicity, the bond length changes means the rotational constant J changes, and thus, the rotational energy changes because the rotational constant J is proportional to the rotational energy. So if we know the value of v, and J, and although there is a little bit of coupling between these 2, we can determine exactly what the energies are for all these different energy levels.

If the molecule is excited from v = 0 to v = 1, it can increase it is rotational energy or decrease his rotational energy, because the selection rule for the rotational transition is delta J = +- 1. In other words, it is rotational excited, or de-excited when we have rotational excited molecule. The figure here also illustrates the Boltzmann distribution. The v = 1, J = 0 state that is, we are talking about this state has higher population than v = 0 J = 0 that is this state. And this is due to degeneracy as we already know the level of degeneracy increases as 2J + 1. So, in the next lecture, we will look into more details about this row vibrational transitions. We will end this lecture by solving a few problems.

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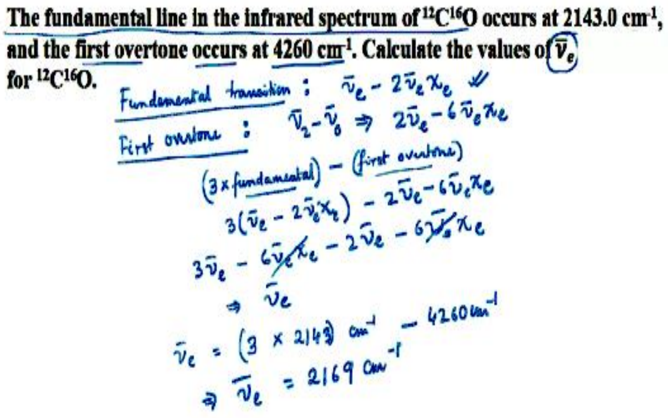

The fundamental line in the infrared spectrum of $^{12}C^{16}O$ occurs at 2143.0 cm^{-1}, and the first overtone occurs at 4260 cm^{-1}. Calculate the values of $\boxed{\bar{\nu}_e}$ for $^{12}C^{16}O$.

Fundamental transition : $\bar{\nu}_e - 2\bar{\nu}_e x_e$ ✓

First overtone : $\bar{\nu}_2 - \bar{\nu}_0 \Rightarrow 2\bar{\nu}_e - 6\bar{\nu}_e x_e$

$(3 \times \text{fundamental}) - (\text{first overtone})$

$3(\bar{\nu}_e - 2\bar{\nu}_e x_e) - 2\bar{\nu}_e - 6\bar{\nu}_e x_e$

$3\bar{\nu}_e - \cancel{6\bar{\nu}_e x_e} - 2\bar{\nu}_e - \cancel{6\bar{\nu}_e x_e}$

$\Rightarrow \bar{\nu}_e$

$\bar{\nu}_e = (3 \times 2143)\ cm^{-1} - 4260\ cm^{-1}$

$\Rightarrow \bar{\nu}_e = 2169\ cm^{-1}$

So, the first question we have is the fundamental line in the infrared spectrum of carbon monoxide occurs at 2143.0 wave numbers and the first overtone occurs at 4260 wave numbers. So, we have to calculate the values of nu bar e and nu bar e chi e for carbon monoxide. So, we know the fundamental transition happens at the energy associated in wave numbers for the fundamental transition is nu bar e - 2 nu bar e chi e. So, we just showed this expression in this lecture. Now, let us look into the first overtone.

So, if you do the same math for the first overtone that is nu bar 2 - nu bar 0, what you will get is 2 nu bar e - 6 nu bar e chi e. So, if we take the fundamental and multiply it with 3 times, so, 3 times fundamental and then subtract of the first overtone expression, so, what we get, we get 3 times nu bar e - 2 nu bar e chi e - 2 nu bar e - 6 nu bar e chi e. So, this is 3 nu bar e - 6 nu bar e chi e - 2 nu bar e - 6 nu bar e chi e, this gets cancelled. So, this becomes nu bar e.

In other words, this fundamental transition frequency is given the first overtone frequency is given. So, we can write nu bar e = 3 times the fundamental that is 2143 centimeter inverse minus 4260 centimeter inverse. So, if you solve this we will get nu bar e = 2169 centimeter inverse.

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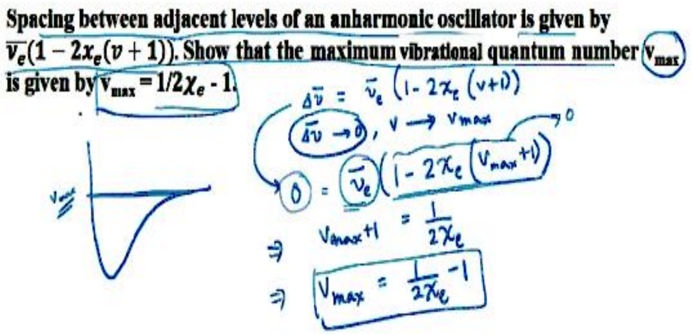

Spacing between adjacent levels of an anharmonic oscillator is given by $\overline{\nu_e}(1-2x_e(v+1))$. Show that the maximum vibrational quantum number v_{max} is given by $v_{max} = 1/2\chi_e - 1$.

$$\Delta\bar{\nu} = \bar{\nu}_e\left(1-2\chi_e(v+1)\right)$$

$$\Delta\bar{\nu} \to 0, \quad v \to v_{max}$$

$$0 = \bar{\nu}_e\left(1-2\chi_e(v_{max}+1)\right) \to 0$$

$$\Rightarrow v_{max}+1 = \frac{1}{2\chi_e}$$

$$\Rightarrow \boxed{v_{max} = \frac{1}{2\chi_e}-1}$$

So, now, let us look into the second problem, the spacing between adjacent levels of an anharmonic oscillator is given by this expression. Show that the maximum vibration well quantum number that is v max is given by v max = 1 / 2 chi e - 1. So, if we draw this an anharmonic potential, the maximum vibrational quantum number v that is v max appears. So, in other words, it has been given that delta nu bar = nu bar e 1 - 2 chi e v + 1. So, at the dissociation limit, this delta nu bar will approach 0 and that means v will approach v max.

So, when delta nu bar approaches 0, this expression we can write 0 = nu bar e, 1 - 2 chi e, then I can write v max here plus 1. In other words, I can write v max + 1 = 1 / 2 chi e, this is because the left hand side is 0. So either this or this has to be 0. So because this frequency is not 0, we are equating this part the entire part to be 0. So from this we get v max = 1 / 2 chi e - 1 and this is exactly what we needed to prove.

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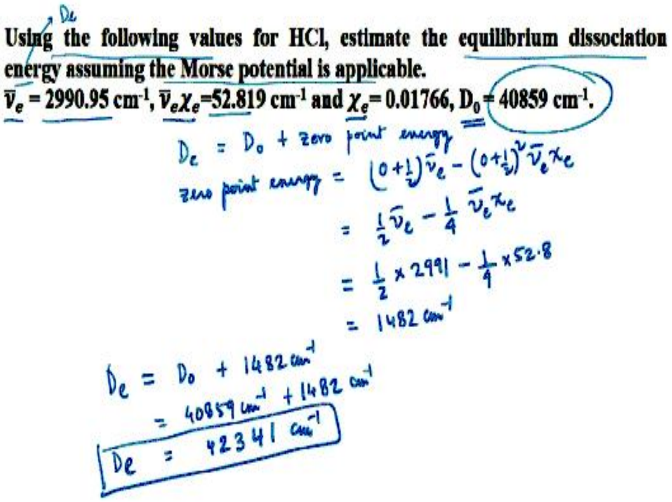

Using the following values for HCl, estimate the equilibrium dissociation energy assuming the Morse potential is applicable.

$\bar{\nu}_e = 2990.95\ \text{cm}^{-1}$, $\bar{\nu}_e\chi_e = 52.819\ \text{cm}^{-1}$ and $\chi_e = 0.01766$, $D_0 = 40859\ \text{cm}^{-1}$.

$D_e = D_0 + \text{zero point energy}$

$\text{zero point energy} = (0+\tfrac{1}{2})\bar{\nu}_e - (0+\tfrac{1}{2})^2\bar{\nu}_e x_e$

$= \tfrac{1}{2}\bar{\nu}_e - \tfrac{1}{4}\bar{\nu}_e x_e$

$= \tfrac{1}{2} \times 2991 - \tfrac{1}{4} \times 52.8$

$= 1482\ \text{cm}^{-1}$

$D_e = D_0 + 1482\ \text{cm}^{-1}$

$= 40859\ \text{cm}^{-1} + 1482\ \text{cm}^{-1}$

$\boxed{D_e = 42341\ \text{cm}^{-1}}$

So now let us look into the third problems. So there are few values given that is nu bar e nu bar e chi e and chi e and the spectroscopy dissociation energy that is D 0. So, using these following values of HCl, you have to estimate the equilibrium dissociation energy. That means this is D e assuming the Morse potential is applicable. So we know D e is given by D 0 + zero point energy. So, the zero point energy is at v = 0, so that is 0 + half nu bar e - 0 + half squared nu bar e chi e.

So this is half nu bar e - 1 / 4 nu bar e chi e. So if I put in the values approximately, what we get is 1 / 2 tends 2991 where approximating. So I am approximating this as 2991 and then I have minus 1 / 4 times 52.8 where is 52.8. Then what I get the zero point energy is 1482 wave numbers. So D e that we need to figure out in this question is given by D 0 + 1482 wave numbers, so the D 0 is given that is 40859 wave numbers + 1482 wave numbers. So D e = 42341 wave numbers