Fundamentals of Spectroscopy

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Lecture-26

Vibrational Spectroscopy: Effects of Anharmonicity

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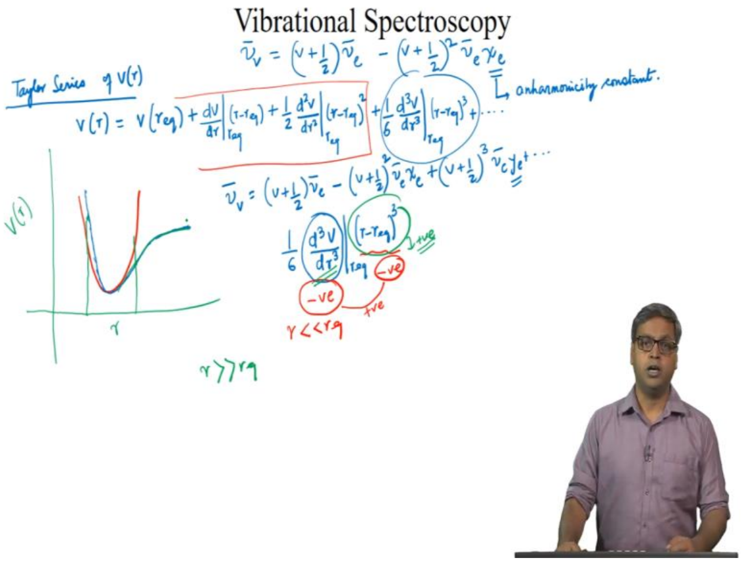

Vibrational Spectroscopy

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

↳ anharmonicity constant.

Taylor Series of V(r)

$V(r) = V(r_{eq}) + \left.\frac{dV}{dr}\right|_{r_{eq}}(r-r_{eq}) + \frac{1}{2}\left.\frac{d^2V}{dr^2}\right|_{r_{eq}}(r-r_{eq})^2 + \frac{1}{6}\left.\frac{d^3V}{dr^3}\right|_{r_{eq}}(r-r_{eq})^3 + \cdots$

$\bar{\nu}_v = \left(v+\frac{1}{2}\right)\bar{\nu}_e - \left(v+\frac{1}{2}\right)^2\bar{\nu}_e\chi_e + \left(v+\frac{1}{2}\right)^3\bar{\nu}_e y_e + \cdots$

$\frac{1}{6}\left.\frac{d^3V}{dr^3}\right|_{r_{eq}}(r-r_{eq})^3$

Hello everyone, in the last lecture, we discussed anharmonicity and how does anharmonicity affect vibrational energy levels the energy of an anharmonic vibrator associated to the vibrational quantum number v is given by nu bar v = v plus half nu bar e - v plus half, whole square nu bar e chi e here this chi e is the anharmonicity constant as anharmonicity is a part of vision to the harmonic system, let us revisit the Taylor series expansion of the potential V of r.

So we will revisit the Taylor series of V of r, so we can write the Taylor series expansion as V of r = v at equilibrium bond length, plus dv / dr at r equilibrium r - r equilibrium + 1 / 2 d 2 v dr 2 at r equilibrium, r - r equilibrium square + 1 / 6 d 3 v dr 3 at r equilibrium r - r equilibrium cubed and the other higher terms. So for the harmonic oscillator solution, we considered up to the second order term.

That means we have only considered up to this much. However, we know that anharmonicity affects the shape of the potential at distances away from the equilibrium bond length. Now, let us look into the differences in the shapes in the anharmonic and the harmonic potential again. So let us say this is our harmonic potential and here is our anharmonic potential. So the anharmonic potential is steeper at r less than r equilibrium and shallower at r greater than r equilibrium.

So although the Morse oscillator is quite useful in practice, a more general expression is nu bar v = v plus half nu bar e - v plus half nu bar e chi e this is square term v plus half cubed nu bar e y e + dot dot. So, here this y e like chi e is also an empirical dimensionless constant characteristic of the molecule these constants are used to fit the experimental data and to find the dissociation energy of the molecules. So, we can think of the perturbation to the harmonic potential as considering one mole higher order that is third order term in the Taylor series expansion.

So, if you look into this third order term that is 1 / 6 d 3 v dr 3 at r equilibrium r - r equilibrium cubed, we can see that if this third derivative is negative then V of r will be steeper for r less than r equilibrium, this is because if this third derivative is negative and we have r less than, less than r equilibrium, then this cube term is also negative. So that means if you take this product, this product becomes positive. What does this means that for some value of r we are plotting that V of r in the y axis.

That means for the same value of r, the V of r will have a larger value. This means that at r less than r equilibrium, the potential will be steeper. On the other hand, for r greater than, greater than r equilibrium, then this r - r equilibrium term will be positive. So the product will now be negative because we have a negative term that is the third derivative and we are multiplying with a positive term. So the product is negative. So this means for the same value of r now this V of r will have a smaller value that means this potential will be shallower at r greater than r equilibrium. So, let us now look into the effect of unharmonious city on the selection rules.

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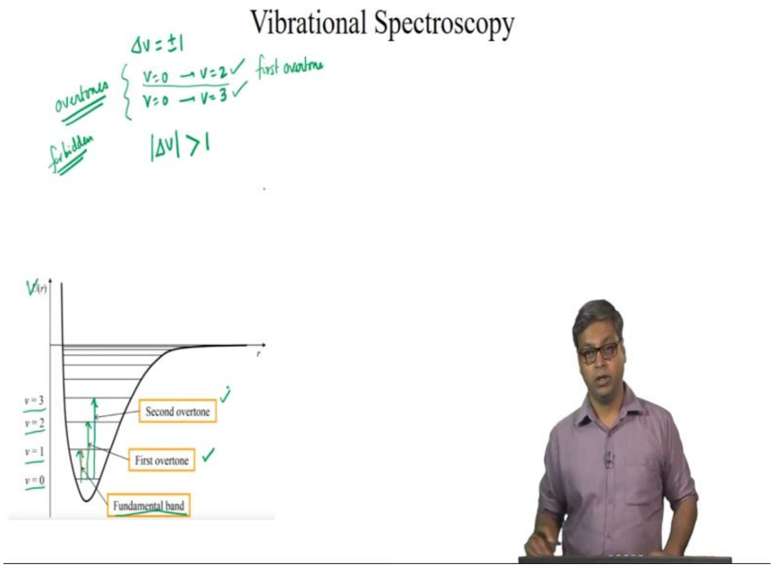

Vibrational Spectroscopy

$\Delta v = \pm 1$

overtones $\left\{ \begin{array}{l} v=0 \rightarrow v=2 ✓ \text{ first overtone} \\ v=0 \rightarrow v=3 ✓ \end{array} \right.$

forbidden

$|\Delta v| > 1$

So, because the energy levels are getting closer and closer together, the specific selection rule, which is given by delta v = + - 1 breaks down. This means we can have transitions from v = 0 to v = 2 or we can have transitions from v = 0 to v = 3. In other words, these transitions become allowed. However, the transitions were delta v is greater than + - 1 are very much weaker than the fundamental transition the bands in the IR spectrum arising from delta v, that is greater than + - 1 are known as overtones.

So all these bands are known as overtones, the way to think about is that anharmonicity is a small perturbation to the harmonic problem. The harmonic problem has a selection rule that delta v = + - 1, the selection rule gets broken down because of the small perturbation, but because this is a small perturbation, this means that the intensities of anything that breaks the harmonic rule are much weaker. We refer to transitions that break the selection rules as normally as for bidden transitions.

So you can ask if they are forbidden. Why do they occur? This is because that the assumptions about these transitions do not really hold in the real world. The harmonic oscillator approximation does not really hold in the real world because the molecules are anharmonic. We call them forbidden, because they break the ideal model. But whenever there is a forbidden transition, the intensities associated with the forbidden transitions are very much week.

The anharmonicity, as discussed in the last lecture, also shifts the energy levels. The energy levels get closer and closer as the dissociative limit is approached. For anharmonic oscillator, this delta v modulus is greater than 1, what the intensities of these transitions where delta v is greater than 1 is very much smaller, as we have just mentioned and can be obtained by solving the transition moment integral.

In other words, we will get transitions, we will get more transitions than a single peak, for example, from v = 0 to v = 2 from v = 0 to v = 3 other than from v = 0 to v = 1, the frequency of the first overtone that is, v = 0 to v = 2. So, this is the first overtone. So, this frequency will be approximately twice the fundamental frequency that is the energy gap between v = 0 to v = 1. However, it is not exactly twice the frequency as the energy levels come closer with increase the value of v in anharmonic oscillator.

The overtone frequency will be slightly smaller than the double of the fundamental frequency. So, now, let us try to visualize these transitions. So, as you can see, we have this v = 0 v = 1 v = 2 v = 3. So, we are plotting V of r here and we see the transition from v = 0 to v = 1 is the fundamental band from v = 0 to v = 2 is the first overtone and from v = 0 to v = 3 is the second overtone.

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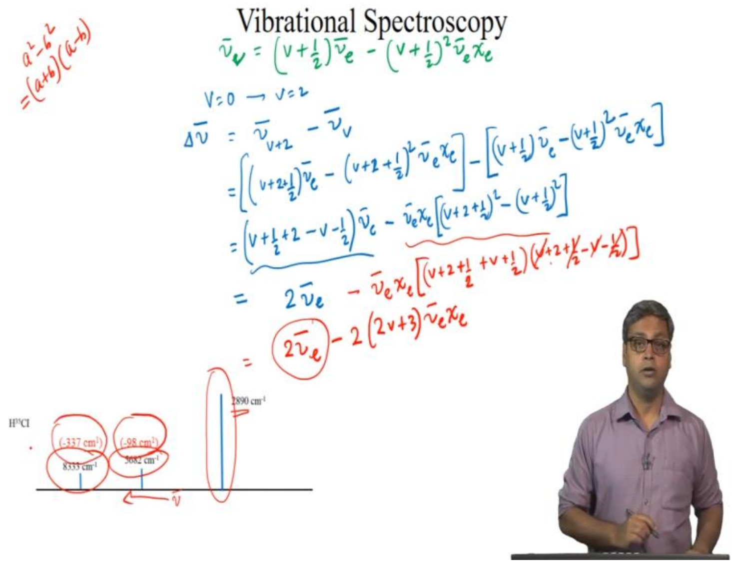

Vibrational Spectroscopy

$a^2-b^2 = (a+b)(a-b)$

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

$v=0 \rightarrow v=2$

$$\begin{aligned}\Delta\bar{\nu} &= \bar{\nu}_{v+2} - \bar{\nu}_v \\ &= \left[(v+2+\tfrac{1}{2})\bar{\nu}_e - (v+2+\tfrac{1}{2})^2\bar{\nu}_e x_e\right] - \left[(v+\tfrac{1}{2})\bar{\nu}_e - (v+\tfrac{1}{2})^2\bar{\nu}_e x_e\right] \\ &= \underbrace{(v+\tfrac{1}{2}+2-v-\tfrac{1}{2})\bar{\nu}_e} - \bar{\nu}_e x_e\left[(v+2+\tfrac{1}{2})^2-(v+\tfrac{1}{2})^2\right] \\ &\qquad \bar{\nu}_e x_e\left[(v+2+\tfrac{1}{2}+v+\tfrac{1}{2})(\cancel{v}+2+\cancel{\tfrac{1}{2}}-\cancel{v}-\cancel{\tfrac{1}{2}})\right] \\ &= 2\bar{\nu}_e - \bar{\nu}_e x_e\left[(v+2+\tfrac{1}{2}+v+\tfrac{1}{2})\right. \\ &= \boxed{2\bar{\nu}_e} - 2(2v+3)\bar{\nu}_e x_e\end{aligned}$$

So, if we now use the anharmonic energy expression that is nu bar e = v plus half nu bar, so, this is nu bar v, so nu bar e here - v plus half square nu bar e chi e the energy difference corresponding to the first overtone, we can find out. So, because the first overtone is from v = 0 to v = 2, so the energy difference that is the delta nu bar for the first over tone will be the nu bar for v + 2 and we have to subtract nu bar of v from nu bar of v + 2. So, now let us right so, nu bar of v + 2 we can write as v + 2 plus half nu bar e - v + 2 plus half square nu bar e chi e.

So this is one term, this is nu bar v + 2. And now we have to subtract of nu bar v, so that is v plus half nu bar e - v plus half square nu bar e chi e. So we can simplify this, we can put the similar terms together. So we have v plus half, + 2 - v - half nu bar e. And then if you take - nu bar e chi e common, what we have is v + 2 plus half square - v plus half square. So as we can see, the first term gives us 2 nu bar e. And for the second term, we know that a square - b square = a + b times a - b.

So For this term, we can write – nu bar e chi e then I have v + 2 plus half + v plus half, this is one time, the other term is v + 2 plus half - v - half. So, these cancel out. So, what we have is 2 nu bar e - 2 times 2v + 3 nu bar e chi e. So, this is the energy difference for the first overtone thus we can see that the first overtone will appear at a frequency slightly less than twice of the fundamental. So, now, let us see the experimental frequencies of HCL.

So, we have already seen this in the last lecture, but let us focus on the transition frequencies of the fundamentals and the overtones now. So, we have the fundamental band here and the frequency nu bar is increasing to the left hand side. So, we can see the first overtone is that 5682 wavenumbers, but the fundamental was that 2890 wavenumbers. So, there is a difference of 98 wavenumbers so, it is not twice of 2890 but it is twice of 2890 - 98 wavenumbers. Similarly, the second overtone is at 8333 wavenumbers and this is also off by 337 wave numbers.

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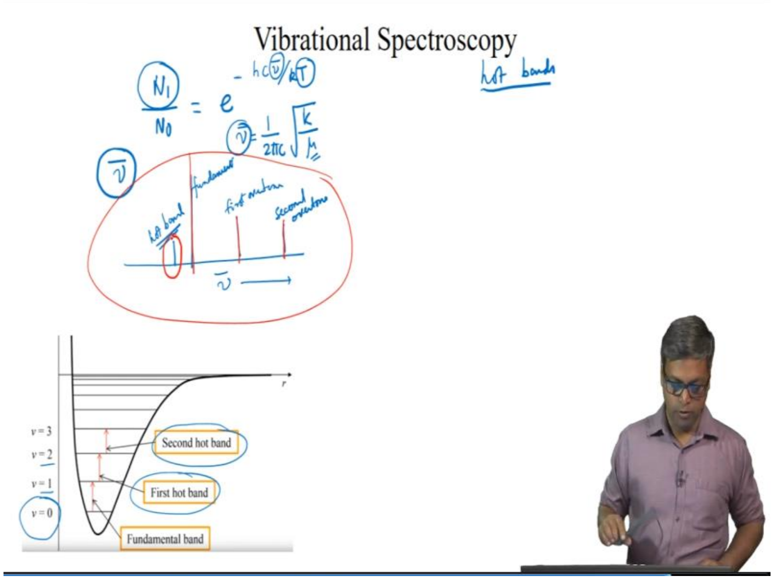

Vibrational Spectroscopy

$$\frac{N_1}{N_0} = e^{-hc\bar{\nu}/kT}$$

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

You can imagine, because we know the energies of the Morse potential from the Schrodinger solution, we can use this information about the frequencies of the fundamental and the first overtone to determine what an harmonious the constant is for the molecule, there is another kind of transition known as the hot bands. So, we have the hot bands. And these hot bands also have smaller intensity than the fundamental like we saw in case of overtones, but this smaller intensity is for an entirely different reason.

So, we can have a transition from v = 1 to v = 2. This is the first hot band. So the transition from v = 1 to v = 2 is the first hot band. We can also have transition from v = 2 to v = 3, which we call as the second hot band. The intensities of these hot bands are very much smaller than the fundamental band. The reason for this is that the population of v = 1 and v = 2, which are the initial states of the first and second hot bands respectively, are very much smaller than the population of v = 0 state, which is the initial state of the fundamental band.

So we can see hot bands at much higher temperature, where the population of the v = 1 level increases as calculated from the Maxwell Boltzmann distribution. So hot bands can also be seen for a much heavier molecule where the frequency is much small, like a heavier diatomic molecule. So this is because when we talk about the Maxwell Boltzmann distribution, let us say we have N 1 / N 0, we can write this as exponential or e to the power - h c nu bar / kT.

So, we can increase the population in the v = 1 state or we can increase the N 1, either by increasing the temperature or by decreasing the nu bar. So, now, if we have a heavier diatomic molecule, then we know that nu bar is given by 1 / 2 pi c root over k / mu. So the mu increases for the heavier diatomic molecule. And because the mu increases, the nu bar decreases. And as I already mentioned, the decrease of nu bar has a similar effect as the increase of temperatures.

But we should always remember that we only see these hot bands in the iron spectrum because of anharmonicity if everything was harmonic, then all the energy levels will be spaced out by the same frequency or the energy difference that is nu bar. However, because we have anharmonicity at the energy levels come closer and closer. That is why if let us say the wave number is increasing to the right and this is my fundamental band and this is my first overtone and this is my second overtone.

Then I will see a hot band which is smaller in the intensity and also at a smaller frequency compared to the fundamental. So, this will be let us say the first hot band. So, however, there will be a change in the response of the hot bands as compared to the overtone as there is a change in temperature. With increasing temperature, the population of the excited vibrational state will increase at the detriment of the v = 0 state.

This means that the intensity hot bands will also increase and the intensity of the fundamental band will decrease as we increase the temperature, this behavior is not the same as the overtones with overtones, the initial state is always v = 0. So, the intensities of the overtones will also decrease with increasing temperature in the same way that the intensity of the fundamental band decreases with increasing temperature.

So, let us see what will all these transitions look like for diatomic molecule? Fairly large spectral region, so as I have already drawn it here, we are talking about a fairly large spectral region because we have the fundamental band here. The first overtone here the second overtone here and the hot band, which appears at a smaller wavenumber as compared to the fundamental transition. So, v = 1 to v = 2 is that a frequency smaller than the fundamental? This is because the gap between the v = 2 and v = 1 level is smaller than the gap between v = 1and v = 0 levels. So, now, we will solve one problem before we end this lecture.

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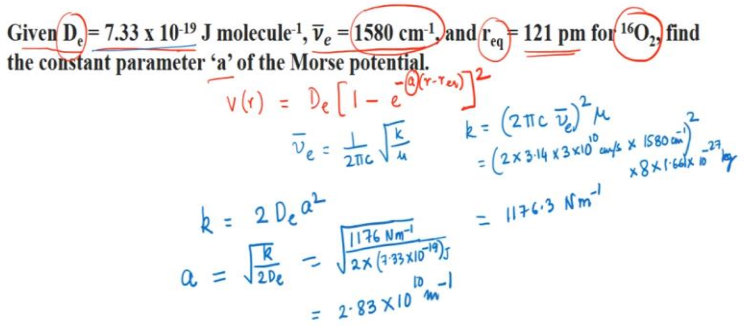

Given D_e = 7.33 x 10^{-19} J molecule^{-1}, $\overline{\nu}_e$ = 1580 cm^{-1}, and r_{eq} = 121 pm for $^{16}O_2$, find the constant parameter ‘a’ of the Morse potential.

$$V(r) = D_e\left[1 - e^{-a(r-r_{eq})}\right]^2$$

$$\overline{\nu}_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$k = (2\pi c\, \overline{\nu}_e)^2 \mu$$

$$= (2\times 3.14 \times 3\times 10^{10}\ \text{cm/s} \times 1580\ \text{cm}^{-1})^2 \times 8 \times 1.661 \times 10^{-27}\ \text{kg}$$

$$= 1176.3\ \text{Nm}^{-1}$$

$$k = 2D_e a^2$$

$$a = \sqrt{\frac{k}{2D_e}} = \sqrt{\frac{1176\ \text{Nm}^{-1}}{2\times(7.33\times10^{-19})\text{J}}}$$

$$= 2.83\times 10^{10}\ \text{m}^{-1}$$

So, the problem is given the dissociation energy that is D e 7.33 times 10 to the power - 19 joules per molecule and the nu bar e there is a fundamental frequency is 1580 wave numbers and the bond length that is r equilibrium is 121 pico meter for oxygen that is 16 oxygen, find the constant parameters a of the Morse potential. So, we know the Morse potential that is given by V of r = D e 1 - e to the power - a, r - r equilibrium, the whole scored.

So, we have to find the value of this a. So, we know nu bar e is given by 1 / 2 pi c root over k / mu. So, we can write k = 2 pi c nu bar square times mu. So, this is 2 times 3.14 times 3 times 10 to the power 10 centimeter per second and times nu bar that is nu bar e, which is given us 1580 centimeter inverse this square. And then we have mu and mu because oxygen is a homonuclear diatomic molecule, we can approximate this as 8.

And if you convert it into kgs, it will be 1.661 times 10 to the power - 27 kg. So you should do this calculation you will find the answer to be 1176.3 neutron meter inverse and we have discussed in the previous lecture that k is given by 2 D e times a square. So, if we want to find e or if you want to find a, then a equals root over k / 2D e. So, we can write this as k is 1176 neutron meter inverse divided by 2 times D e, which is given here. So, 2 times 7.33 times 10 to the power - 19 joules per molecule. So, this will be 2.83 times 10 to the power 10 meter inverse.