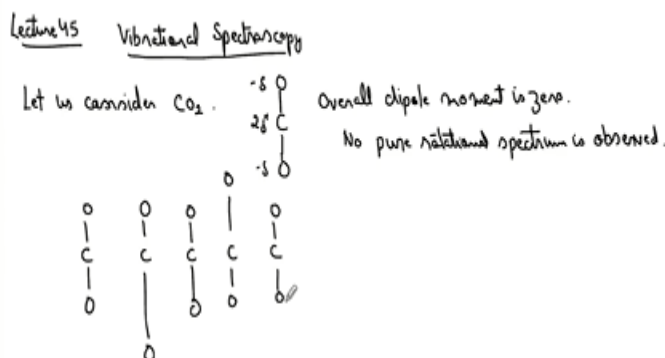


Symmetry and Group Theory
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Lecture -59
Vibrational Spectroscopy

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So, welcome back, let us continue our discussion of application of group theory to spectroscopy and in that topic we were discussing what is spectroscopy and we finished discussing rotational spectroscopy. So, let us now discuss vibrational spectroscopy. Again, this is not a comprehensive discussion on vibrational spectroscopy, this is just an overview. So we will not be deriving any questions I will just be giving you some information on what vibrational spectroscopy is.

So, that when we use the application of group theory, you know what it is. So, vibrational spectroscopy, as from the name it basically looks at the vibrating bonds, so let us consider for this spectroscopy let us consider a molecule CO_2 . So, CO_2 structure is, let me draw the structure like this, so I am not drawing the complete bonds and all so just, so, delta negative will be here delta negative will be here and two delta positive charge will be here.

So, if you look at the overall dipole moment of this molecule is 0. So, that means no pure rotational spectrum can be observed, we have discussed that, because there is no dipole moment

no electrical component of the EM wave cannot interact with the dipole moment component as the molecule is rotating, so no pure rotational spectrum is observed. Now, what do we do if we want to characterize the physical properties of the molecule, so even though the dipole moment is 0.

But, the change in dipole moment as the molecule vibrates, that is possible to observe, so what do I mean, so what I mean is let us say, this is the equilibrium position of the molecule now there can be a stretching which looks like this. See again, all these molecules can be described by ziggling and wiggling of atoms. So, no two atoms will be at constant position it is not a rod which is tying the two atoms together. They will be constantly moving and this will lead to vibrations.

So, again, it will go to its mean position and now the other carbon oxygen bond may stretch and again, it will go back to its mean position. So now, if I try to draw the component of this dipole.

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28 C
 O
 O
 O
 O
 O

Vibrations

Dipole Moment

Component of the dipole

No pure rotational spectrum is observed.

Frequency of light that interacts with this dipole component is in IR range.

Vibrational Spectroscopy can be understood by starting with a simple harmonic model.

A B
 m₁ m₂

O m m m m m O
 m₁ m₂

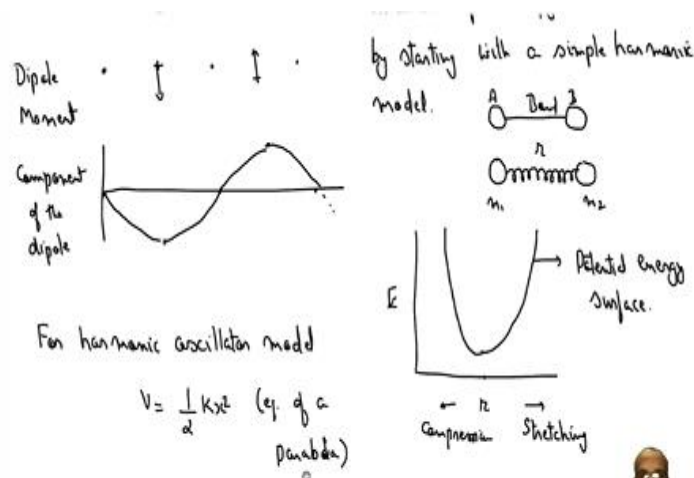
It will look like so the dipole is 0 over here, so these are vibrations and the dipole moment looks like this. So, dipole moment is zero here; I can say that the direction is downward here zero here again direction of the dipole is upwards, zero here again. So, again, it is following up periodic motion, if you look at the vertical component of the dipole moment. So, I can say the component of the dipole, so it will be 0 at this point, then negative at this point, zero again, positive, 0.

So, you can see that there is a sine wave which is being formed something like this. So, now again the frequency of light that interacts with this dipole component is in infrared range. So, you can also visually think or intuitively think that if the rotation is happening, the rotation would take lesser energy as compared to vibration of a bond. So, vibration is trying to overcome the two attractive forces here and it is trying to pull away the two atoms so this requires more energy.

So, that is how it goes from microwave to IR range when you go from rotational to vibrational spectrum. So, vibrational spectroscopy can be understood when you, again let us consider a diatomic molecule. So, we can say vibrational spectroscopy can be understood by starting with a simple harmonic model. So, what is a simple harmonic model? So, what you have is see in case of rotation we considered to atoms connected with a bond where the vibration was not considered, it was a rigid bond like a rod.

But, here we are considering two atoms with a bond which is where the vibration is possible, so what do I mean by vibration. It is like if two masses m_1 , so these are atoms and this is my bond but if I am considering that there are two masses m_1 , m_2 and they are connected with the spring something like that. So, now you can compress the spring, you can stretch the spring, and then you can allow it to freely come back to its mean position all that can happen.

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Now all of this will change the energy of this system, so how do I describe this change in energy? I can always say that if I plot energy here, and let us call the mean distance as r , r here. So, at the equilibrium distance, the energy will be minimum. Now, as I start to stretch the bond length will increase, so this is my bond length and the energy will increase so it will go like this. Now, as I start to compress again the energy will increase, it will go like this.

So, this is called as a simple harmonic model so either way you go, the energy will increase you so this side is compression of the spring or the bond and this side is stretching. Stretching of the bond or the spring, and this particular plot is called as potential energy surface. So, this is compression, stretching, and potential energy surface and now if you want to actually look at the equation, so for, we can say, for harmonic oscillator model to represent diatomic molecule.

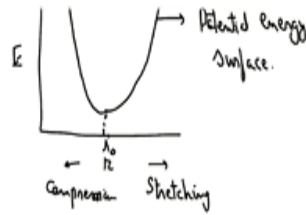
You can say the potential is equal to half it is a equation of a parabola, the potential is in the form of parabola, so I can say this is half kx^2 , this is equation of a parabola. You should all be aware of what is a parabola.

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vibr

For harmonic oscillation model

$$V = \frac{1}{2} kx^2 \quad (\text{eq. of a parabola})$$



k is bond force constant.

$x = r - r_0$ r is internuclear distance at a given time
 r_0 is " " " " equilibrium

For quantum systems, not all energies are possible. The possible vibrational states are given by vibrational quantum no. v .

$$E_v = \left(v + \frac{1}{2}\right) h\nu \quad \nu \rightarrow \text{fundamental frequency.}$$

So, what is k here? So, k is bond force constant very similar to spring constant, which you must have read in physics, maybe class 12th. So, Hooks law is considers the spring constant when you look at the young's modulus and all. So, x here is $r - r_0$, so which is, so r is internuclear distance and at a given time, and r_0 is the internuclear distance at equilibrium. So, that means x is the difference from the mean position, if this is my mean position I would call this as r_0 .

So, any deviation from r_0 will be called as x because r is the absolute value at a given point. So, now for quantum systems for quantum systems not all energies, all vibrational energies are not possible not all we will say energies are possible and the only possible vibrational states are given by vibrational quantum number v , so this is v and then energy of a particular vibrational state will be given by E_v is equal to $v + \text{half}$ into $h\nu$.

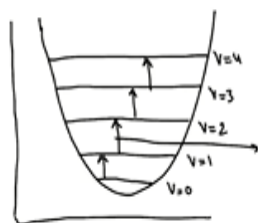
Now do not get confused between v and ν , so v is the vibrational quantum number and ν is the fundamental frequency. So, we try ν as the fundamental frequency.

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$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{where } k \text{ is bond force constant}$$

μ is reduced mass

Selection Rule is $\Delta v = \pm 1$ $\Delta E_{v \rightarrow v+1} = (v+1 + \frac{1}{2}) h\nu - (v + \frac{1}{2}) h\nu$



$$= h\nu$$

$$\frac{\Delta E}{hc} = \bar{\nu} \quad (\text{wave number}) \cdot \text{cm}^{-1}$$

all allowed transitions

$$I = \int \psi_v \hat{\mu} \psi_{v+1}^* d\tau$$

$\psi I \neq 0$, transition is allowed.

So, we can also write an expression for ν , ν is given by 1 over 2π square root k by μ and we have already seen what is k ? k is bond force constant and μ is reduced mass; reduced mass also we have discussed already in rotational spectra. So, selection rule for vibrational spectroscopy is selection rule is Δv should be plus minus 1 , so you can only carry out transition between v equal to 0 , v equal to 1 or v equal to 1 to equal to 2 and so on.

So, what we can say is we can say $\Delta E_{v \rightarrow v+1}$ can be written as $v+1 + \frac{1}{2} h\nu - v + \frac{1}{2} h\nu$. So, this comes out to be $h\nu$, v plus half and v plus half will get cancelled, so one $h\nu$ or we can say ΔE divided by hc and you can call it in $\bar{\nu}$, so this is wave number and the units are centimetre inverse. Typically in spectroscopy, sometimes wave numbers are used sometimes λ is used but typically in vibrational spectroscopy wave members are used.

So, that is why we have done it like wave number, now the kind of transitions which are possible let us try to draw. So, in case of harmonic oscillator model, if you notice that ΔE is equal to $h\nu$ or $\bar{\nu}$, so that means from it can be v equal to 0 or equal to 1 starting from v equal to any given thing; so this is v equal to 0 , v equal to 1 , v equal to 2 , v equal to 3 and so on. Now, the transitions which are possible are v equal to 0 to 1 , 1 to 2 , 2 to 3 , 3 to 4 , these are all allowed to transitions.

So, I will write down here, all allowed transitions, and how do you know what transitions are

allowed or not, so we have already seen that by looking at the this integral where we say that the wave function of a particular vibrational level and then the operator and wave function of $v + 1$ level and star in d tau. So, if I is not equal to 0, transition is allowed. So, this part you can actually look at the character table and find out what are the irreducible representations we have already done that, so, let us not go into those details.

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$\Delta E = h\nu$
 $\frac{\Delta E}{hc} = \bar{\nu}$ (wave number) $\cdot cm^{-1}$
 all allowed transitions
 $I = \int \psi_v \hat{\mu} \psi_{v+1}^* d\tau$
 If $I \neq 0$, transition is allowed.

Problems with Simple Harmonic Model.
 energy levels are equally spaced.
 equilibrium bond length is constant for all energy level.

So, this is basically called as simple harmonic model but there are problems with simple harmonic models, so what are the problems? Let us discuss that problem with simple harmonic model. So, first of all, it defines that all energy levels; all energy levels are equally spaced. That means all the spectral lines will come at exact same position in frequency but you do not see that you do see multiple lines.

Of course, it will all depend on the population distribution that which line will be more intense where the population difference will be maximum and so on, so forth. But they do appear at different frequencies so the simple harmonic model does not explain the multiple lines in the vibrational spectrum because it predicts that all the lines should have equal energy and hence all of them would come at same energy level or same frequency number.

So, all energy levels are equally spaced that is a problem, second problem is equilibrium bond length is constant for all energy levels. So, what do I mean here by saying equilibrium bond

length. So, if I look at the equilibrium values were here, it is something like this. So, at v equal to 0 or at a particular stretched state of a bond my r_0 is here. If I extend my bond again, my equilibrium bond length is still the same which does not describe the actually the vibration.

Because like, if the vibration is happening there is a stretching which has happened, so the equilibrium bond length should change.

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Problems with Simple Harmonic Model.

- 1) All energy levels are equally spaced.
- 2) Equilibrium bond length is constant for all energy levels.
- 3) Does not account for the possibility of bond dissociation.
- 4) Extra repulsive force at very small bond lengths (the reason nuclear fusion reaction occurs at very high temperature).



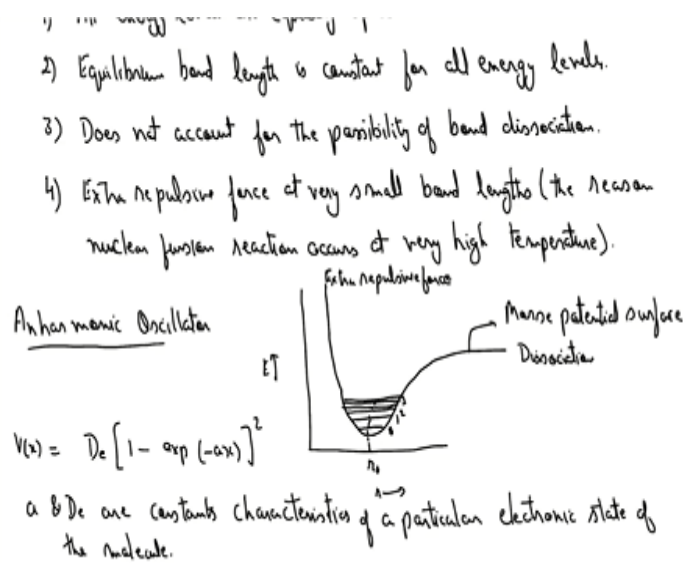
Now, the simple harmonic model does not explain that. So, it also does not account for possibility of bond dissociation. So, that means no matter how high a vibration is happening, it will never break, which is not true, if you vibrate a bond at very high frequency, it will eventually break down. So, this particular model does not explain that. So, that means we have to do some adjustment to this model.

So, another factor which the model does not explain is the extra repulsive force at very small bond lengths. That means if I am going down in the bond length, I have not written, what is what here? So, this is r and this is E . So, if I go down in the bond length it does not explain basically that the nuclear fusion reactions for example, should occur at very high temperatures. So, here like if I keep continuing this it will not go to infinity.

The energy will not go to infinity whereas nuclear fusion reactions require, very, very high

energy as compared to vibrations of a bond or dissociation of a bond. So, this is not explained, so the extra repulsive force which comes when you bring two atoms very close by in space, that is not explained by simple harmonic model. So, we will say the reason, nuclear fusion reaction occurs at very high temperature.

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So, now the modification of this model is called as anharmonic oscillator. So, which takes into account all these problems which are described above, so it is called as anharmonic oscillator, how does it look? So, this goes like vertical and then come down and then you go here, so here is the extra repulsive force because the energy is too high. So, it does describe that now here it is this particular state is dissociation of a bond when the bond is no longer there.

Also the difference is that at v equal to 0, v equal to 1, v equal to 2, the distance between the two consecutive vibrational levels 0, 1, 2, 3 keeps on decreasing. So, now the frequencies the differences between v equal to 0 to v equal to 1 and v equal to 1 to v equal to 2 will be at different the energy differences will be different here and also the equilibrium bond length will keep on changing this is now my r_0 and this surface is called as Morse potential surface.

This is after the scientist who made these changes to the harmonic model, his name was Morse. So, Morse potential surface describes all these problems which are there in the harmonic oscillator or the simple harmonic oscillator model. So, r_0 is not constant, you can see extra

repulsive force, you can also see dissociation. Now what is the surface equation looks like, $v \times x$ equals to $D_e (1 - \exp(-ax))^2$, where a and D_e are constants characteristic of a particular electronic state of the molecule, so that is clear.

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at $x = \infty$, $V(x) = D_e$

$$\frac{E_v}{hc} = e_v = \left(v + \frac{1}{2}\right) \bar{\nu} - \left(v + \frac{1}{2}\right)^2 \bar{\nu} \chi_e + \text{higher order terms (omitted)}$$

\hookrightarrow anharmonicity constant.

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

\hookrightarrow vib. quantum no. of lower energy state
from where the transition is originating

$$\frac{N_{v=1}}{N_{v=0}} = e^{-\frac{\Delta E_{v=1} - E_{v=0}}{kT}} \approx 0.008 \text{ at } T = 300\text{K}$$

$v=0$ to $v=1$ transition is called as fundamental transition and is very intense.



Now let us see what happens at x equal to infinity, so if I put x equal to infinity I will have $v \times x$ equal to D_e , because now the rest of the term will go to 1. Now I can calculate my energy here E_v divided by $h c$, so it will be e_v . So, $v + \frac{1}{2} \bar{\nu} - (v + \frac{1}{2})^2 \bar{\nu} \chi_e$ and plus higher order terms which are generally omitted because those will be very small. So, rest of the terms you already know.

So, χ_e is the only new term which was not there in simple harmonic model and this is called as anharmonicity constant. So, this will depend on multiple things, now if I calculate from here from v equal to 0 to v equal to 1, if I calculate ΔE it will be $\bar{\nu} - 2\chi_e \bar{\nu} (v+1)$, where v is the vibrational quantum number of lower energy state from where the transition is originating, lower energy state.

So, now you have ΔE , you can also calculate the population difference between v equal to 0 and v equal to 1, so you can calculate $N_{v=1}$, $N_{v=0}$, this can be now given by $e^{-\frac{\Delta E_{v=1} - E_{v=0}}{kT}}$. Now, if you put in all the values here, you will get that this is approximately equal to 0.008 this is the ratio, so it tells you the

population difference this will be equal to this 0.008 at room temperature 300 K.

So, we call v equal to 0 to v equal to 1 transition. So, similarly you can estimate what will be the population difference between v equal to 1 to v equal to 2 that will be very, very small. So, that means if the population difference is very, very small the intensity of the vibrational line will also be very, very weak. So, v equal to 0 to v equal to 1 transition is called as fundamental transitions and is very intense.

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At $v=0$, all molecules have a min. of the zero point energy. This is a consequence of the uncertainty principle.

Often one observes combined vibrational-rotational spectrum.

$$E_{Rv} = B J(J+1) + (v + \frac{1}{2}) \bar{\nu} - X_e (v + \frac{1}{2})^2 \bar{\nu} \quad \text{cm}^{-1}$$

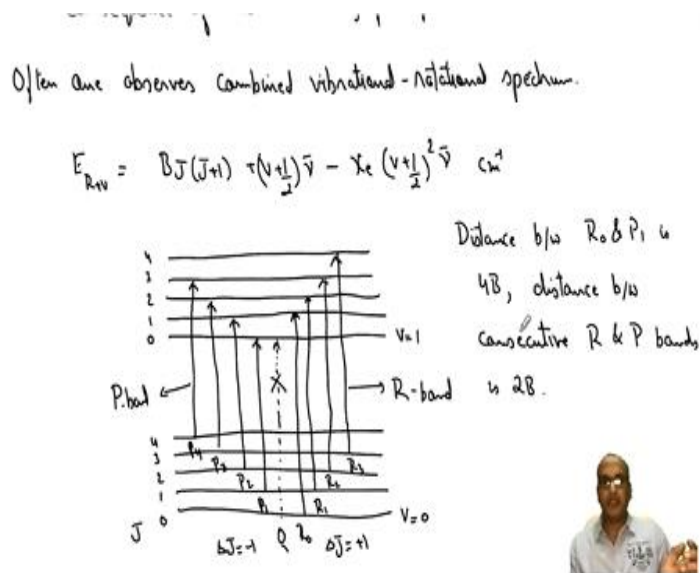


Also, if you notice that even at v equal to 0 molecule will have certain energy, so at v equal to 0 even though we are saying that the vibrational quantum number is 0. All molecules have a minimum of the 0 point energy and this is a consequence of the uncertainty principle. Again, we are not going to go into details of this, but it is just to mention that at v equal to 0 the graph is not touching the value 0, there is some energy, which is there.

So, also when these vibrations are happening the molecule is still rotating, even though you will not observe a pure rotation spectrum for a molecule which does not have a dipole moment, but molecule is still rotating, it has some energy so it will keep on rotating, so you will never observe a vibrational spectrum a pure vibrational spectrum in itself, so but you will observe typically vibrations lines are always observed with rotational lines.

So, we write often one observes combined vibrational rotational spectrum. So, a combined set of energy levels so is given by rotational plus vibrational is given by $B J(J+1) + v + \frac{1}{2} h \nu$ which is in the same units. So, that means we will have h by c over here divided by h by c nu bar - $x e v + \frac{1}{2} \text{square nu bar}$. So, this is in centimeter inverse so we will have h by c over here or we will just write we will not write anything here because we had h by c within v , so the idea is to just have the centimeter inverse units.

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Now, we can always calculate now the ΔE between different levels between different J levels and different v levels. So, now let us look at a transition between v equal to 0 to v equal to 1, so for every vibrational level there are some rotational levels, because at each vibrational state a molecule is rotating, so those rotational levels will correspond to that particular v . So, let us say this v equal to 0 and v equal to 1, so at this we I will have different J levels like this.

Similarly, this v equal to 1, also I will have some J levels which are rotational levels. So, these are the J values 0, 1, 2, 3, 4 0, 1, 2, 3, 4; now my possible transitions are Δv equal to plus minus 1. So, I am going from 0 to 1, so all these transitions will be allowed and ΔJ has to be plus minus 1. So, let us see if I go from v equal to 0 to v equal to 1 from 0 to 0, so that transition is not allowed, so I will not draw this line 0 to 0 but I can draw the line from 0 to 1, so this line.

So, now this is the allowed transition. Similarly, if I go from 1, so I have to land up to 2, so

because my ΔJ also has to follow the rotational. Remember, the rotational spectrum had the selection rule as ΔJ plus minus 1, so 3 will be like this. So, now, it is also possible that I can go from 1 to 0 because ΔJ here, ΔJ is equal to + 1. So, similarly I can have ΔJ is equal to - 1 because + - both are allowed. Now, 1 to 0 is allowed, 2 to 1 will be allowed.

And 3 to 2 will be allowed and 4 to 3 will be allowed. So, all those fine structures will be present in the fundamental transition, which is v equal to 0 to v equal to 1. Now, this set of and the line which is not observable will be like this. So, this is not observable which is 0 to 0. Similarly, 1 to 1 is not observable 2 to 2 is not observable and so on. Now, typically these lines are called as R lines and these lines are called as P lines.

So, P band or R band and the q band is the 1 which is not observed. Now, if you see here this can be numbered as r 0, so basically 0 or the subscript is the vibrational quantum or the rotational quantum number from where the transition is starting. So, this line will be R1, R2, R3. Similarly, here, this will be P1. There cannot be any P0, because you cannot go from 0 to -1 there is no -1 rotational state, so P2, P3 and P4.

Now, why we are discussing this because if you notice or you can actually calculate the distance between the frequency distance I mean, distance between R0 and P1 is $4B$. So, if you know B again, you can go back and calculate the bond length because from B you can get the moment of inertia, from moment of inertia, you know the μ which is the reduced mass so you can calculate r and difference or distance we have used the word distance.

Distance between consecutive R and P bands is $2B$. So, R0 to R1, R1 to R2 and so on. So, P0 to P1, so these are $2B$ values and the central two lines will be $4B$. So, this can be very easily now so B can be very easily measured and you can calculate the bond length. So, even for the molecules which are not having dipole movement, so vibrational spectrum can get you the physical properties.

So, this is the introduction for vibrational spectroscopy and next class we will be discussing another spectroscopy, which is Raman spectroscopy and then we will go to atomic motions. So,

that is all for today see you on next class.