Lecture-38
Features of Vibrational and Electronic Spectroscopy

Welcome to the lecture number 38 of the course quantum mechanics and molecular spectroscopy. In the last class we solved couple of problems based on the rotational spectroscopy. In this class I will look at a problem on the vibrational spectroscopy and some aspects of the electronic transitions.

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In a vibrational spectrum ok one uses harmonic oscillator as a so we have talked about when we use this harmonic oscillate because at the bottom of the potential one can always have the harmonic oscillator and the wave function look like this ok, I told you that you know the potent k is given by D square v by d r square or d r square evaluated R 0. So, if the R 0 is your equilibrium distance ok.

So, this is nothing but the second derivative of the potential evaluated at the equilibrium geometry ok and the bottom of the well I can always consider as a harmonic potential. Now when you have a harmonic potential the frequency V 0 is given by the way harmonic oscillator has only one fundamental frequency V 0 that is given by 1 over 2 pi square root of k by mu ok.

Now if I can measure V 0 ok I will be able to get the force constant. Now force constant is nothing but it is the stiffness of the bond ok, what is stiffness of the? It is like a stiffness of a spring whether the spring is strong or whether spring is weak ok? So, force constant tells you whether the bond is strong bond or a weak bond. Now let us apply this concept to HCl again 1 and 35 and DCL 2 and 35 ok.

When I measure the IR spectrum of this what I get is a fundamental frequency which is given by for this value this is nu 0 bar because I am measuring in the centimeter inwards that is 2885.1 centimeter inverse and for this it will be 2091.1 centimeter inverse. So, I know the value of mu and I also know nothing but your nu or V 0 nu 0. So, let me call this as a nu, let me call this as neutral frequency.

So, nu 0 is nothing but equal to nu 0 bar into C, that is just the transformation between the velocity and but you see since we are measuring in centimeter this must be measured in centimetres per second. So, that is nothing but 2.997 into 10 power 10 centimetres per second, this is per second. So, this will be centimetres. So, that will be nothing but second inverse.

So, you have that, now if I now want to calculate this so nu 0, so what I have given is nu 0 1 over 2 pi square root of k by mu. So, I can slightly rewrite this equation. So, this will be nothing but nu 0 is nothing but nu bar into C. So, nu bar into C = 1 over 2 pi square root of k by mu. So, this I can always write as square root of k by mu = 2 pi nu 0 into C. Now I can take a square that implies k = 2 pi nu bar C into mu square.

So, I need to get that ok. Now I already know nu bar ok. So, for nu bar or nu 0 bar for Cl 35 is 2885.1 centimeter inverse and nu 0 bar for DCL is 2091.1 centimeter inverse , I think I made a mistake, this should not be like this, this should be square of this okay because I am taking a square ok, yeah sorry for that mistake.

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$$k = (2\pi c \bar{\nu}_0)^2 \cdot \mu$$
$$= 4\pi^2 c^2 \bar{\nu}_0^2 \mu$$
$$= 4\pi^2 (2.997 \times 10^{10})^2 (2885.1)^2 \times \frac{35}{36} \times 1.66 \times 10^{-27} \quad {}^1\text{H} - {}^{35}\text{Cl}$$
$$= \underline{476.4} \; \text{Nm}^{-1}$$

$$k = (2\pi c \bar{\nu}_0)^2 \cdot \mu \quad {}^2\text{H} - {}^{35}\text{Cl}$$
$$= 4\pi^2 (2.997 \times 10^{10})^2 (2091.1)^2 \times \frac{70}{37} \times 1.66 \times 10^{-27}$$
$$= \underline{486.4} \; \text{Nm}^{-1}$$

So, now k will be nothing but 2 pi C nu 0 bar whole square into mu. Now this will be nothing but 2 pi square is nothing but 4 pi square C square nu 0 bar square into mu. So, this will be nothing but 4 pi square okay C square is nothing but 2.997 into 10 power 10, I told you, you have to take centimetres per second as a speed of light whole square into nu bar square is 2885.1 square into mu ok.

Mu is nothing but for HCl H 1 35 C l, mu will be nothing but 35 divided by 36 into 1.66 into 10 power -27 kg. So, if I solve this I will get value of 476.4 Newton per meter okay. Similarly if I take k = 2 pi C nu 0 bar square into mu, but now it is 2 H Cl 35, if I plug it in 4 pi square C square will be same 2.997 into 10 power 10 square. Now this will be 2885 in the case of HCl, but this will be 2091.1 square.
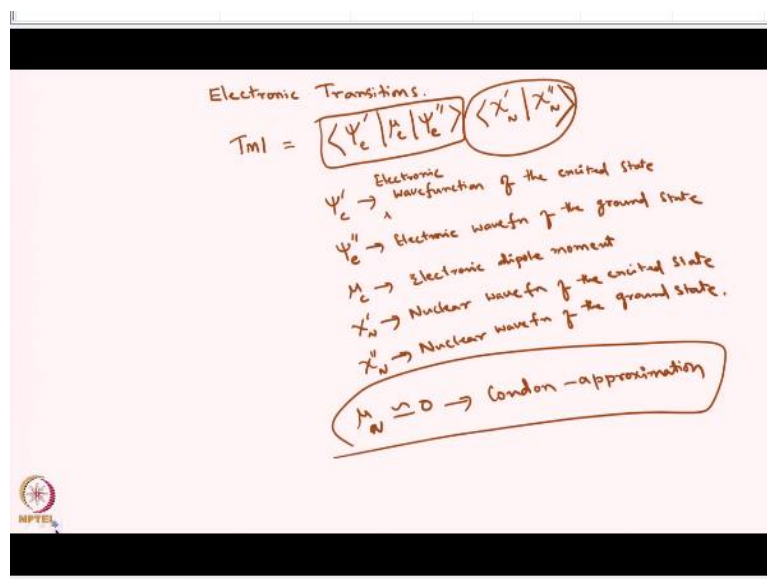
Because the frequency has changed into even the reduced mass has changed. So, this will be 70 divided by 37 into 1.66 into 10 power -27. Now when I do this I will get 486.4 Newton per meter ok. Now you see the force constant of HCl and DCl is actually not exactly equal, even though one would expect that the force constant should be equal. Now of course there is an assumption that the everything else are fundamental constants, nothing has changed except this frequencies are one which are measured experimentally ok.

So, if these if one assumes that the frequencies that you measure are accurate then I will see that the force current of HCl is marginally different than force current of a DCl, it is about by 10 Newton per meter ok. The stiffness of bonds is when you do isotopic substitution may not be exactly the same as exactly the same ok. So, when you measure the vibration frequency

the moral of the story that I am going to tell you is that when you measure the vibrational frequencies you can convert the vibrational frequencies into the stiffness of the bond ok.

One can say the bond is stronger or bond is weaker or you know something like the stiffness of the bond ok, by this token you can tell that the DCl bond is more stronger or more stiffer than the HCl bond. So, the vibration of spectroscopy tells you about the stiffness of the bond or the strength of the bond. But the bond distances are measured by the rotational spectroscopy which I talked about in the last lecture. There is one more factor that I want to teach you is something called related to electronic transitions ok.

(Refer Slide Time: 10:00)

Electronic Transitions.

$$Tml = \langle \psi_e' | \mu_e | \psi_e'' \rangle \langle \chi_N' | \chi_N'' \rangle$$

$\psi_e' \rightarrow$ Electronic Wavefunction of the excited State

$\psi_e'' \rightarrow$ Electronic wavefn of the ground State

$\mu_e \rightarrow$ Electronic dipole moment

$\chi_N' \rightarrow$ Nuclear wavefn of the excited State

$\chi_N'' \rightarrow$ Nuclear wavefn of the ground state.

$\mu_N \simeq 0 \rightarrow$ Condon - approximation

Now if I go back few lectures you will see the electronic transitions TMI is given by psi electronic excited state mu e psi electronic ground state multiplied by Xi nuclear excited state multiplied by Xi nuclear ground state. So, let me define what it is? Psi prime e is wave function of the excited state ok. Of course this has to be electronic wave function, psi e double prime is electronic wave function of the ground state.

And mu e is the electronic dipole moment and Xi N prime is the nuclear wave function of the excited state and Xi double prime is the nuclear wave function of the ground state ok. There is one more thing that I have to tell you is that to get to this TMI we assumed that mu 0 is nuclear is approximately equal to 0 ok. This is Condon approximation which says that the nuclear dipole moment is does not change related to the electronic coordinates or changes very little with respect to the nuclear electronic coordinates/.

So, this is the Condon approximation, so to get this TMI we have used the Condon approximation. Now this will tell you whether the transition is going to be allowed or not? But one of the important factors is this ok, is the overlap.
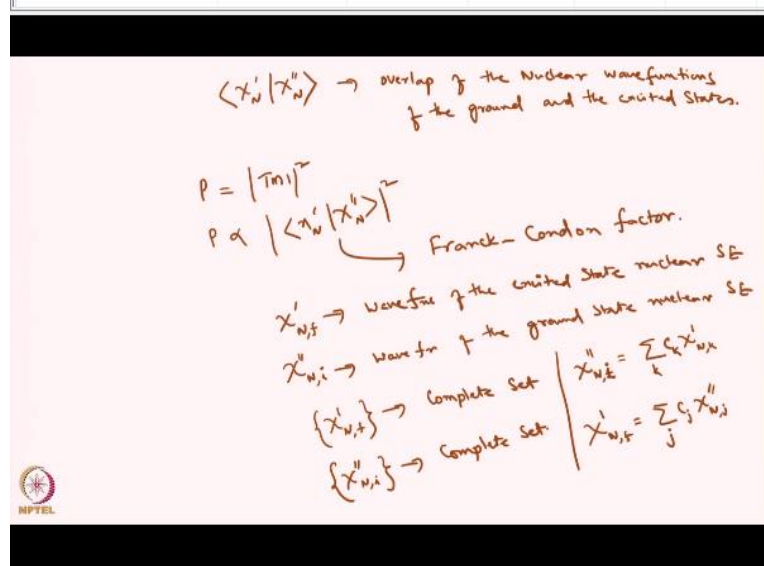
So, Xi N prime Xi N double prime, this is nothing but overlap of the nuclear wave functions of the ground and the excited states ok. But probability of transition p is equal to modulus of TMI square. So, when I use that the probability must be proportional to modulus of Xi N prime Xi N double prime square and this value is called Franck Condon factor ok. Franck Condon factor is nothing but the overlap of the nuclear wave functions of the ground and the excited states square of it okay.

Now there is one small theorem that I want to prove is that, now let us suppose Xi N prime is a wave functions ok, let me call it some quantum, let me give some quantum number f because final you know excited state ok. So, wave functions of the excited state nuclear Schrodinger equation and Xi double prime N and Xi i is given by or given by wave functions of the ground state nuclear Schrodinger equation ok.

Now because these are the solutions of Schrodinger equation, they should form complete set. So, you have a complete set Xi prime N with contour number f and forms complete set. Similarly f Xi double prime N i also forms a complete set. Now there is something that you must always remember, is that whenever I have a complete set okay. Any other wave function can always be written as a linear combination of this completed wave functions.

So, which means I can always write Xi double prime N f should be equal to sigma over let us say k C k Xi N k and I can always write sorry, this is i f is equal to sigma over k let us say j C j Xi N j double prime. So, one can always express the nuclear wave function of the excited states as a linear combination of the ground state wave functions. And one can always express the nuclear wave function of the ground state as a linear combination of the excited state wave functions okay. Now if I have any.

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If I take Xi ground state nuclear wave function i, this wave function to be equal to sum over j Xi C j N j. Now if I assume that all functions are orthonormal, all functions are normal then it turns out that C j square modulus of j should be equal to 1, because total coefficients should add up to 1 ok. So, this is the let us look at Xi prime N, let us say some function f integral Xi double prime N.

So, I want to look at this. So, this I can always write that sum over Xi N f, but this wave function I can always write it as this. So, this is equal to sum over j ok Xi prime N j C j ok. Now whenever this j will become equal to f whenever, so this value of the integral will be equal to C j delta f j. So, whenever f and j are not equal then this overlap integral will go to 0, otherwise it will survive and become C j ok.

Now this is only for one wave function. Now if I want to take over all the final wave function if I f Xi prime N comma f sigma over j i prime N j C j, this will be nothing but sigma over f ok each of the time will get j ok, but j = f okay. So, if I get f, only survive when f is equal to

say what will get is C f ok. Now I do not want this, what I want is the modulus of Xi N f Xi double prime N i square sigma over f.

This will be nothing but sigma over f okay C f square actually not like this because you have to individually square them not the sum of the square so square of this. So, this is nothing but sum over f C f square. So, we know that when they are orthogonal and f or j or anything they are all dummy indices should be equal to 1 ok. So, the moral of the story is when you have electronic transient some of the Franck Condon factors must be equal to 1.

(Refer Slide Time: 20:57)

Which simply means that when I have a probability p that is equal to and then I have probability p for an electronic transition going from a ground state to excited state. This must be equal to square of the tangent moment integral square. So, this will be nothing but psi e excited state mu e psi e ground state square multiplied by Xi prime nuclear double prime square but this is only for one wave function.

So, if you have to look at all the nuclear wave function, so then it should be sum over all the nuclear wave functions f, then but this some or all nuclear wave function is equal to 1. So, that is nothing but psi e mu e psi square because this is equal to 1. So, if you take the electronic transitions over various nuclear states vibrations and rotations and if you add all of them it should be equal to get equal to 1.

So, the contribution of the nuclear wave function is only partial, every nuclear wave function is only partial, it can go from 1 to 0**,** if it is 1 then there are others do not contribute, if it is 0

that would not contribute everything else will contribute. So, the sum of all the nuclear wave functions overlap must be equal to 1okay. So, that is the factor. So, what is the sum of Franck Condon factors for an electronic transition should be equal to 1.

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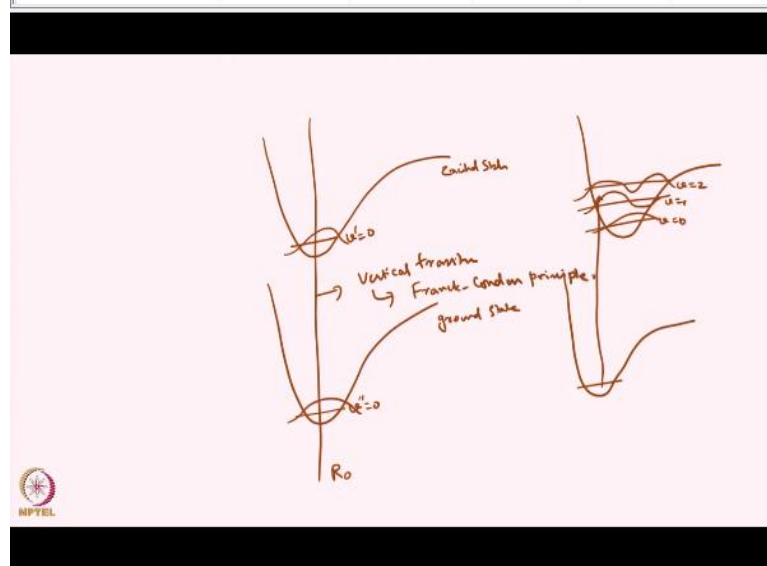
Now see the equilibrium distance R 0 in the ground, this is ground state, this is excited state. They are equal. So, what happens the transition from V = 0 V prime = 0, this is going to be most overlapping, but instead of that if you have something like that where R 0 is the same. So, if you make a vertical transition then, so we the lowest energy transition will not have the overlap.

Overlap will be the next vibration level, not the V = 0 but V = 1 and sorry not V = 1 sorry 0 but V =1 and V = 2. So, the transient will shift, so based on whether the transient will be shifted or not shifted one can tell whether the geometry has changed or not? The geometry changes is larger than the more and more the geometry changes the more and more the shift in the transition will happen ok.

So, by the way this is called a vertical transition and the principle that governs is called Franck Condon principle ok. We will stop it here and this brings to the end of my lecture series in this course, we have covered in this course how the transient moment integral comes by and use the transition integral to get to various spectroscopic techniques rotational, vibrational and the electronic transitions.

You can always give me a feedback about this course and I am always reachable on my email address that are even when you this course is not running you can always write to me on nareshchem.iitb.hc.in, my email address at the department of chemistry IIT Bombay to reach out on any questions that are related to this course, thank you very much.