Symmetry and Group Theory
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Lecture - 40
Infrared and Raman Spectroscopy

Today we are going to wrap up that discussion and we are also going to talk about IR and Raman activity of normal modes of vibration.

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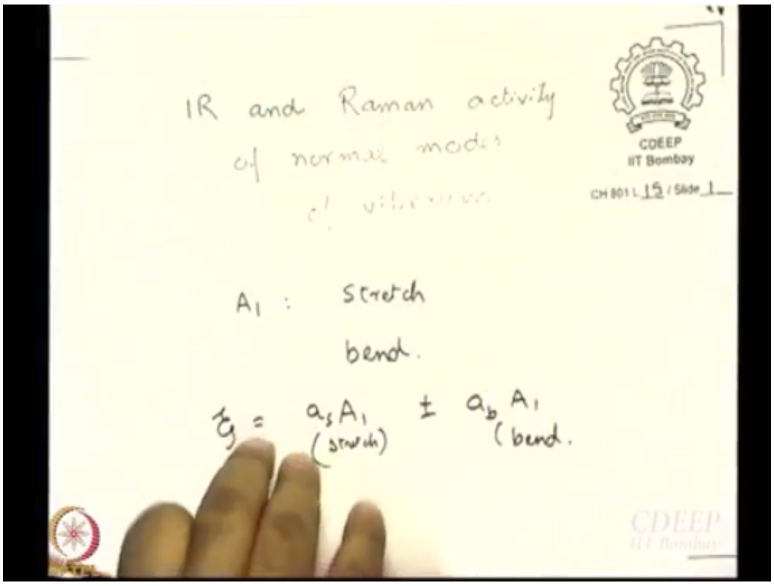

IR and Raman activity
of normal modes
of vibration

A_1 : stretch
bend.

$\xi = \underset{(\text{stretch})}{a_s A_1} \pm \underset{(\text{bend.}}{a_b A_1}$

Okay, that is what we are going to talk about today, but before that I asked you to do something at home. How many of us have worked it out? okay, good boy. Fine. So what we do today is we discuss those examples which you must have worked out last night. What you have done is we have worked out the symmetries of normal modes of vibration and hopefully you have worked out what is the contribution of internal coordinates to these modes, right.

So maybe I will just clarify something that seem to leave a doubt in your minds yesterday. What we said is that you have AG, was it AG or A1? A1. You have a stretch as well as bend right. So we had said that it has to be A1 stretch +/- A1 bend. Maybe I should clarify this a little bit. This is a liner combination right. So what we are saying is Xi = may be a stretch A1 stretch + a bend A1 bend, okay.

Now one of these coefficients can be 0. We are not saying that it can never be 0, but the general solution is that it is a linear combination of both. That is why we said that we expect the normal mode to be opening up while stretching that is 1 and the other is closing down while stretching. Now how much contribution of stretch and how much contribution of bend will be there, that depends on these coefficients right.

So special case would be one of the coefficients is 1, the other is 0, then it will be a pure stretch or a pure bend, but this is a general solution and the magnitude of the coefficients depends on things like the force constant and atomic weight that is something that we will not be able to cover in this course. For that you have to actually workout the Wilson's FG matrix and move over to what are called the symmetry coordinates.

We will not be able to do that in this course unfortunately, but that is what I thought I will make a point so that there is no confusion, okay, this is a general solution, okay. So today we want to talk about IR activity and Raman activity of normal modes, of course whoever has studied CH442 or an equivalent molecular spectroscopy course would already know this it would be revision for them.

"Professor - student conversation starts" yeah, there is no use, they are redundant, you throw them away. See why they arise. They arise because we are taking a coordinate that is not there okay. **"Professor - student conversation ends"** We are considering the 3 angles and we are getting the redundant coordinate that we always get is totally symmetric and it is impossible that all the angles will increase at the same time. If it is like BF3 in a plane.

If you have worked out the example of the tetrahedron CH4, there also you would have encountered a similar totally symmetric bending vibration which is redundant. For things like ammonia the problem is not there because it can expand there is no issue. All angles can increase at the same time, but if there is a fourth bond, like the CH4, if this increase takes place then automatically these angles become smaller. It is not possible for these angles to increase also.

So that is why you get a redundant coordinate in a system which is say tetrahedral or a system that is D3h for C3v there is no problem, alright. So redundant system arises out of taking one coordinate to many, but then as you saw your study if you do not take that one coordinate too many, it is very difficult to formulate the problem, that is why we take it and then we eliminate it at an appropriate time. Okay let us think of let us take a character table, any character table., which character table do you like, the one that is showing up.

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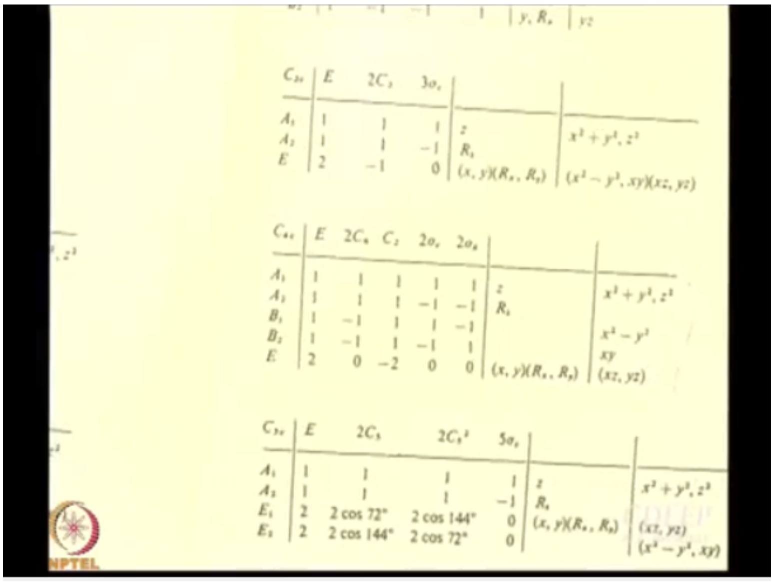

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		x^2-y^2
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$		
A_1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	−1	R_z	
E_1	2	2 cos 72°	2 cos 144°	0	$(x, y)(R_x, R_y)$	(xz, yz)
E_2	2	2 cos 144°	2 cos 72°	0		(x^2-y^2, xy)

Which character table do you like, it would not matter, it would not matter really. So let us say C4v. Now suppose I use xyz as basis does it describe everything? It only gives you an idea of E and A1 symmetry species. So you want to study IR activity and Raman activity. Now what is the meaning of IR activity, what is the meaning of Raman activity? I think many of you have at least some kind of molecular spectroscopy course has been studied by everybody, so you tell me.

We are talking about vibrations right. In what kind of spectroscopy do we see vibrations? Infrared spectroscopy right. What are the kind of spectroscopy can we use to see vibration? We can use what is called Raman spectroscopy, has everybody here know about Raman spectroscopy, if not do not be shy to say that. Today we do not have to finish at 6:30, okay. We will just give a very brief idea of Raman spectroscopy; it is like this.

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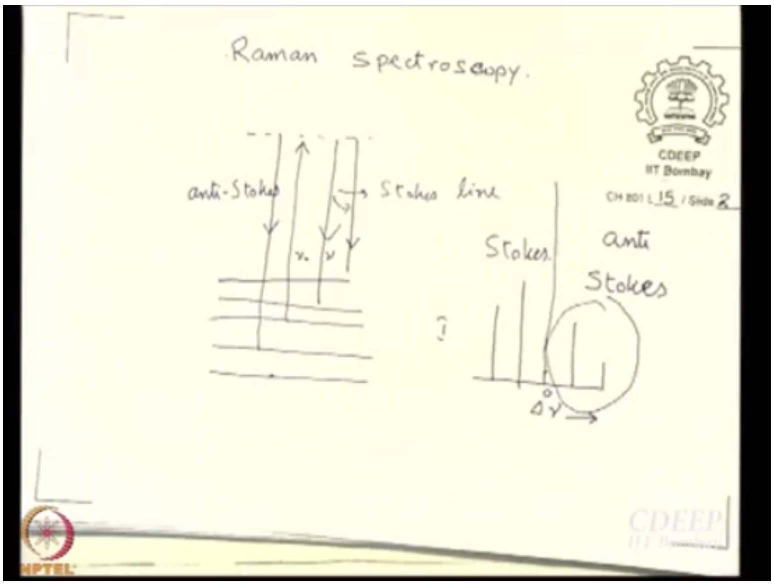

Let us say these are vibrational levels of a molecule in the ground electronic state, okay. Let us say you now hit the molecule with the laser of some particular wavelength new, alright. Then what will happen, the molecule will want to get excited. Let us say you start from here of course if this is a vibrational level it is not very easy to start from here at room temperature but just so that we perform a complete discussion.

Let us say that this is the many fold of states and I initiate an upward transition from here, okay, but let us say, you know about stationary states, what are stationary states? (()) (08:29) density is invariant with time, very good, any other way of defining stationary state? Energy does not change with time right, that was actually Bohr’s definition, that these are states in which the energy does not change with time.

So stationary not with respect to space, but with respect to energy, constant energy states. So these are say stationary states. What are non-stationary states? States whose energy changes with time right. So if the energy changes with time the issue is that you cannot have your molecule stay in those states for too long, okay. So let us say this is the manifold and the next higher manifold is there at 20,000 cm inverse, right.

However, I have hit this with a laser whose energy is 15,000 cm inverse, what will happen? The molecule will not reach the next stationary state, but it will try right. It will try because molecule has not studied quantum mechanics. So it does not know that is not supposed to absorb this photon of putting in very, very simple terms of course right. So what it will do is, it will try but then it would not reach a stationary state but there are many, many, many non-stationary virtual states in between.

So it is going to reach a virtual state, okay, without getting into any math we can perhaps develop some very qualitative idea about virtual states if you think of a game of basketball, okay. You have the basket is there, the ball is in your hand. If you hold it and stand that is the ground state, okay, unless you tire the ball is going to be in your hand forever, so lifetime is infinite, okay.

You throw the ball in the right direction with right energy what happens is, it enters the basket, it is entangled in the net so stays there for a very small time and then it falls, so it has a finite lifetime there. So the basket is analogues to a stationary state, but an exited state. However, if you throw it with not enough energy then what will happen? The ball will reach some height depending on how hard you have thrown it and then it will go up and it will come down right.

So it is maximum height that it is reaching is analogues to a virtual state, 0 life time, alright and then you can reach the exited state only if you throw the ball with the particular energy in a particular direction. However, you can reach an infinite number of virtual states in between, right depending on how hard you throw the ball, so it is something like that of course not completely analogues and the other way you could think is that what happens when light is absorbed.

A transition takes place right electron goes from some molecular orbital to another molecular orbital right. So you can think that what happens essentially very qualitatively once again when a photon impinges on a molecule is that the electron cloud starts getting distorted right. Let us say this is the ground state demo, and let us say this is the exited state demo. The shape is going to change from here to here upon excitation.

So it starts getting distorted but if you have not given it enough energy what it does is. It gets distorted to the maximum (()) (12:10) possible and then it comes back, but it cannot go beyond. It cannot stay like this. It would have stayed like this if you had given enough energy because that is the stationary state. You have not given enough energy, so it starts getting distorted and then it comes back also immediately, okay, that is virtual state alright, so far so good.

So one thing that this last example brings out is the importance of polarisability, is not it. If the electron cloud is polarizable then you can do this very easily. If it is not so polarizable you cannot do it very easily. So polarisability has got to do with Raman spectroscopy and it comes out very elegantly if you perform a classical treatment of this Raman effect problem, but that let that be the story for the end of the day if at all, okay.

For now, I think you understand this diagram right. It goes to a virtual state and then it comes down. Now if I go back to the basketball analogy just thrown it, right, it has gone up there, comes down, right, I can reach out and catch the ball a little higher, right, or I could catch it lower, depending on whether I catch it higher or lower, what will happen is the energy that is lost by the ball will be more or less than the energy that had provided, right.

Same thing can happen here, suppose while it comes down it comes down to this state, then what will happen, energy of this state, energy that is emitted of the photon is going to be less than the energy of the photon that you had provided right. So what kind of shift do you get? You get a red shift, so this kind of a line is called a Strokes line. The name of the guy was Stokes, not stoke, so please do not write Stoke's poor chap will be (()) (14:09) in his grave, Stokes one word no apostrophe, Stokes shift, okay.

What is the length of this? 5 cm, what is the length of this say 4 cm. So if cm just a map of energy, then 4 cm is lower energy than 5 cm, and this is even lower, know, that is also Stroke shifted. Got it, Strokes shift, but it can be other way round as well, I can catch the ball a little lower, here also, the way I have drawn it you have levels that are lower in energy, so if the system comes down to a lower level then what will happen, the energy of the light will be greater than the energy of the light that you have provided.

You will get a blue shift and this will be called an anti-Strokes shift the was no such scientist named anti-Stokes, I am sure there are plenty of people who are anti this Stokes guy but this is just you know Stokes shift and anti-Stokes shift, understood. So now if I draw, what I can do is instead of drawing these absolute frequencies, I can draw delta nu, I can plot intensity versus delta nu. What is the meaning of delta nu?

Whatever is the frequency here minus this frequency nu – nu 0 alright. So let us say this is 0 line, will you get a line at delta nu = 0? Yes, the strongest line will be delta nu = 0, but that is not the Raman line, it is called the Rayleigh line. This is to something that is known. This was known before. See Raman was younger than Rayleigh actually. So Rayleigh came to this world earlier and he discovered the easy thing earlier, okay delta nu = 0 that is Rayleigh line, okay.

You put in 400 nanometer light, you get out 400 nanometer light is just scattered. Raman observed the more difficult thing. He observed lines like this. This side will be what Stokes or anti-Stokes? Delta nu is increasing this way. So negative here, positive here. This is Stokes or anti-Stokes. The good thing about writing Stokes first is that you can write anti over it, anti-Stokes and what about this.

This is of course Stokes line. Now so what do I get here. What do this delta nu stand for? Do not they stand for the gaps in between vibrational levels. So this is kind of vibrational spectrum of the molecule if these are vibrational levels. Of course, if this is vibrational levels then it is extremely difficult to observe this anti-Stokes lines because only the 0th level is populated.

So you can get Stokes shift but not anti-Stokes shift so easily if you are working on simple Raman spectroscopy, alright. Okay, question? Fourth year undergraduates question because you have not studied this year I think. Alright, okay, fine. Now not to say that anti-Stokes lines can never be observed for vibrational levels okay. It can be observed by special techniques.

There is something called (()) (18:06) cars where what you do is you amplify the anti-Stokes line, coherent anti-Stokes shift is observed there, but that is different. Stokes is very easy to observe. Now what is the difference between IR and Raman spectroscopy? Do you see the same lines in IR and Raman, no, not always, that is what we will slowly learn today why you do not? Now what is important for IR spectroscopy is dipole moment. What is important for Raman spectroscopy is polarisability.