Group Theory Methods in Physics
Prof. P. Ramadevi
Department of Physics
Indian Institute of Technology, Bombay

Lecture – 33
Infrared spectra and Raman Spectra

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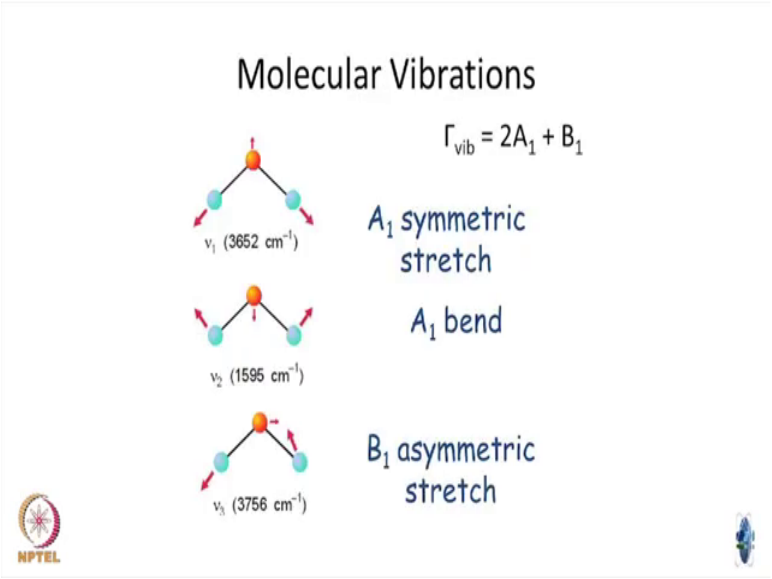

Molecular Vibrations

$\Gamma_{vib} = 2A_1 + B_1$

A_1 symmetric stretch

A_1 bend

B_1 asymmetric stretch

So, just to show you that experimental is have seen these frequencies which are non-degenerative symmetric A 1 bending, then B 1 asymmetric stretch.

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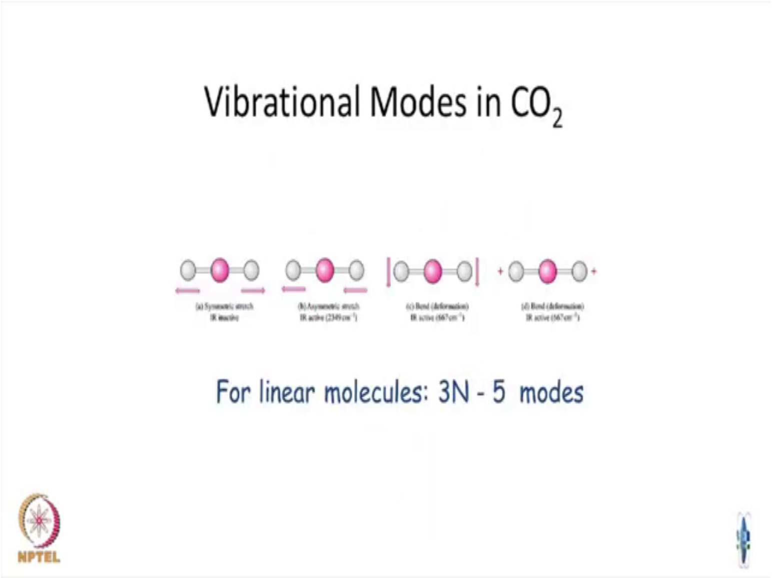

Vibrational Modes in CO_2

For linear molecules: 3N - 5 modes

And then there are these linear molecules which have 3N minus 5 degrees of freedom, vibrational degrees of freedom.

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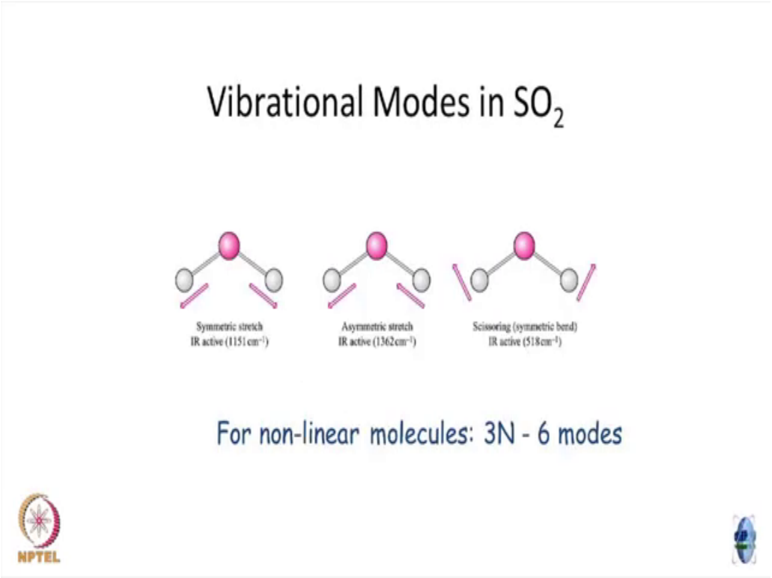

Vibrational Modes in SO_2

Symmetric stretch
IR active (1151 cm^{-1})

Asymmetric stretch
IR active (1362 cm^{-1})

Scissoring (symmetric bend)
IR active (518 cm^{-1})

For non-linear molecules: 3N - 6 modes

And then you also have similar to your water molecule, there are other molecules and methane, of course, I just briefly mentioned the td symmetry and you will have these 3N minus 6 molecule. I have written some things here or it is already there. It is not that thing is some of these modes all these frequencies for example if you saw these numbers, they are all in the infrared regime, centimeters.

So, they are all whatever you going to measure associated with the vibration mode of a molecule has opened up a new field called infrared spectroscopy, where they do these infrared spectroscopy to find the spectra of the molecules and so on so ok. So, in that sense what we are trying to only say is using the group symmetry, these are the kind of things have to be measured.

We do not know those frequency values. If you want to find these frequency values, you have to go through that long method, find the basis vectors and then find the frequencies by solving those basis vectors which I am not done here, ok. You can do it, but it is a little more work to be done, but experimentalists can give you that these frequencies are seen in the Infrared spectrum, these are seen in the Raman spectrum and so on ok.

Suppose I say a irrep is allowed for both Infrared and Raman, I will just explain what they are as far as the a group theory person is concerned and if they see the same frequency in both, we are actually validating it ok. So, let me give you some flavor of what exactly is happening, ok.

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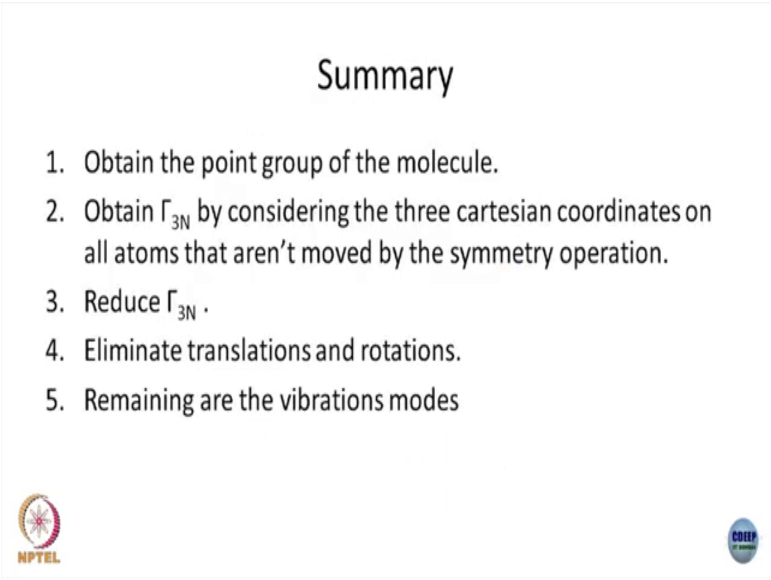

Summary

1. Obtain the point group of the molecule.
2. Obtain Γ_{3N} by considering the three cartesian coordinates on all atoms that aren't moved by the symmetry operation.
3. Reduce Γ_{3N} .
4. Eliminate translations and rotations.
5. Remaining are the vibrations modes

So, whatever we did so far is first you need to know the point group of the molecule and then, you obtain either you can obtain a complete motion of the molecule which has 3N degrees of freedom or you can subtract out the translation and rotation and write the vibrational representations also. Those are things which we can do.

But essentially you have to remember that the way we write those characters are which of the atoms are in moved by the symmetry operation that is encoded in the NC. NC is the number of atoms which is not moved by the operation and then reduce it by the conventional decomposition eliminate translation rotation. If you started with 3N degrees of freedom and the remaining what you get are the vibrational modes, ok.

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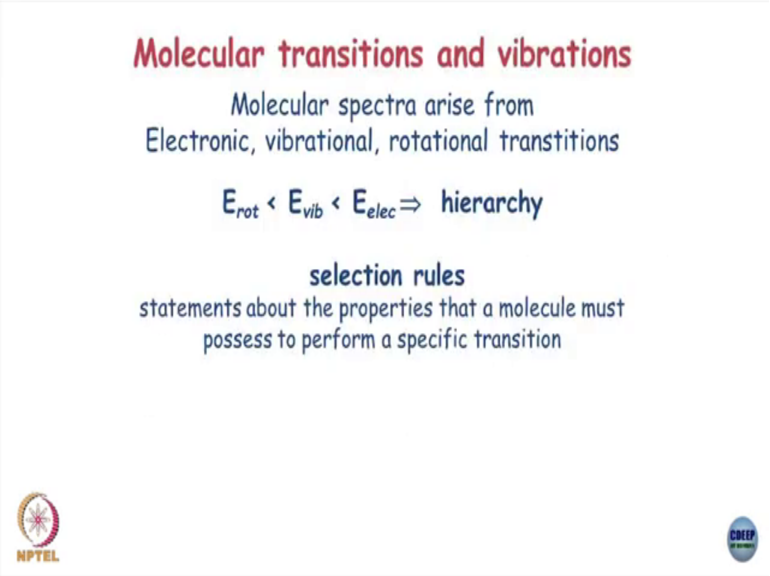

Molecular transitions and vibrations

Molecular spectra arise from
Electronic, vibrational, rotational transtitions

$E_{rot} < E_{vib} < E_{elec} \Rightarrow$ hierarchy

selection rules
statements about the properties that a molecule must possess to perform a specific transition

So, just to give you a flavor of what this experimental is, look at the molecular spectra is spectroscopy. So, you do have various vibrational rotational transitions and also you can have electronic transitions. Let me not get into too much of a detail here. Selection rules we have already seen for you to have a transition from one energy to another energy, such a transition which is triggered by an interaction is possible.

If they satisfy the rule that you know the tensor product of that interaction operator, the irreducible representations of the states if everything adds up to give you a unit representations multiplied tensor product, then you know that such a transition is allowed that we have seen in the two lectures before this, ok.

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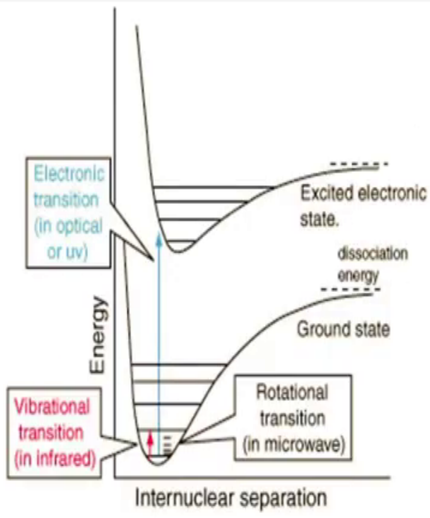

So, what I am trying to say is that here experimental is have tried to look at these vibrational transitions and they as I said the energy or frequencies are in the infrared rotations of course are in the microwave which I am not going to get into it.

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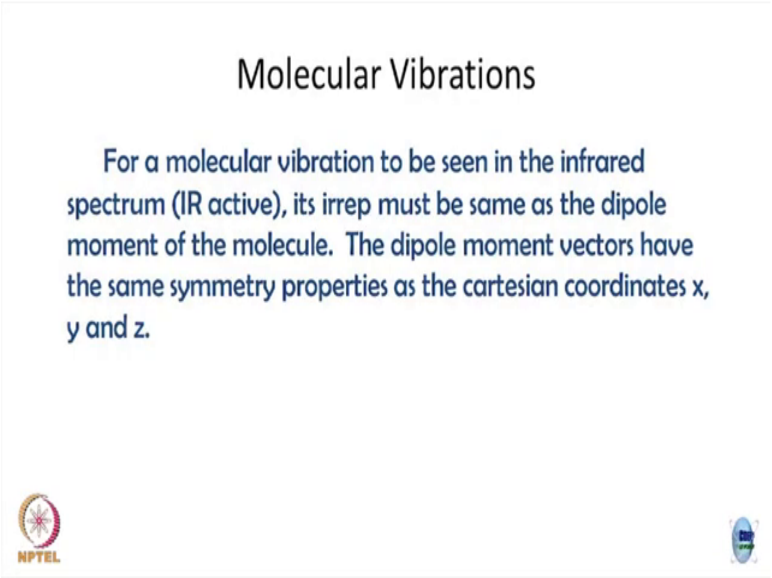

Molecular Vibrations

For a molecular vibration to be seen in the infrared spectrum (IR active), its irrep must be same as the dipole moment of the molecule. The dipole moment vectors have the same symmetry properties as the cartesian coordinates x, y and z.

So, for a molecular vibration to be seen in the infrared spectrum, they call it IR active. You should have in the vibrational modes. The irrep of these vibrational modes should be same as the irrep which are you associated with a dipole moment, ok. So, this is what is the approach of looking at basically the molecules which has a net dipole moment, they are supposed to be infrared active, ok.

So, what happens in the water molecule is that you do have A 1 irreps. Irepps is like the z component basis right and they are like the dipole moment z component. So, in that sense you can say the two frequencies associated with the two. So, for the water molecule we found that the vibration is two times A 1 plus B 1 A 1 irrep the basis was z basis equivalently I can write the electric dipole moment which is the z basis.

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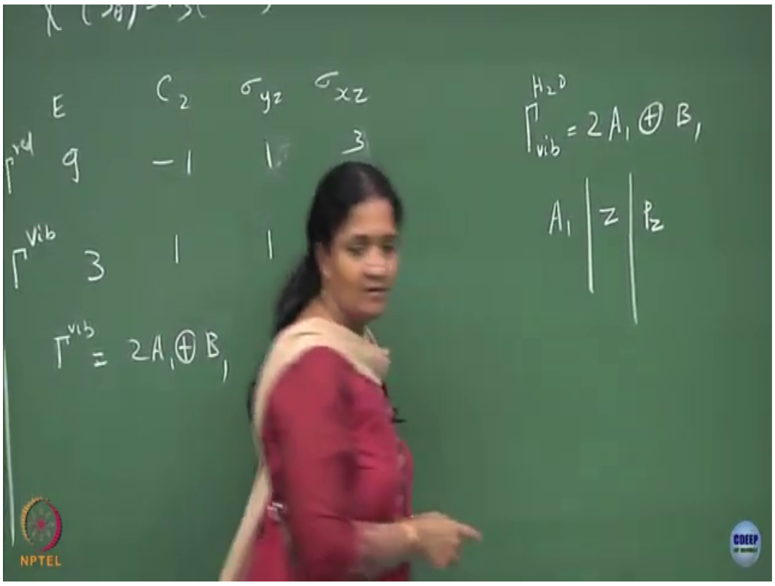

So, since A 1 is transforming like the z component of the electric dipole moment, I can say that the vibration mode associated with the irrep A 1 which is seen in the water molecule should be IR active, ok. So, the A 1 the two A 1s must be IR active.

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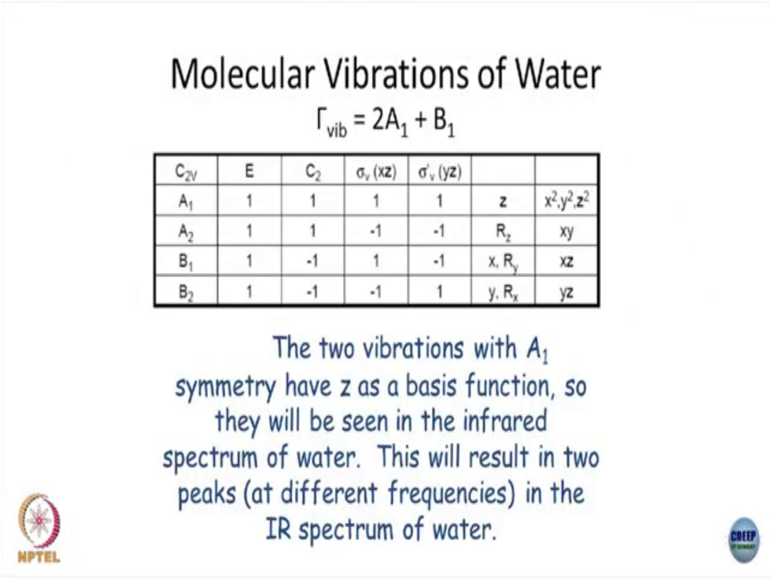

Molecular Vibrations of Water

$\Gamma_{vib} = 2A_1 + B_1$

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The two vibrations with A_1 symmetry have z as a basis function, so they will be seen in the infrared spectrum of water. This will result in two peaks (at different frequencies) in the IR spectrum of water.

So, that is what I am trying to say here if you see the basis the two vibrations with A 1 symmetry as z as a basis function, they will be seen in the infrared spectrum of water. This will result in two peaks. You have to get two peaks at different frequencies. You should not see them to be very close, should not be degenerate because the C 2 v symmetries are ok.

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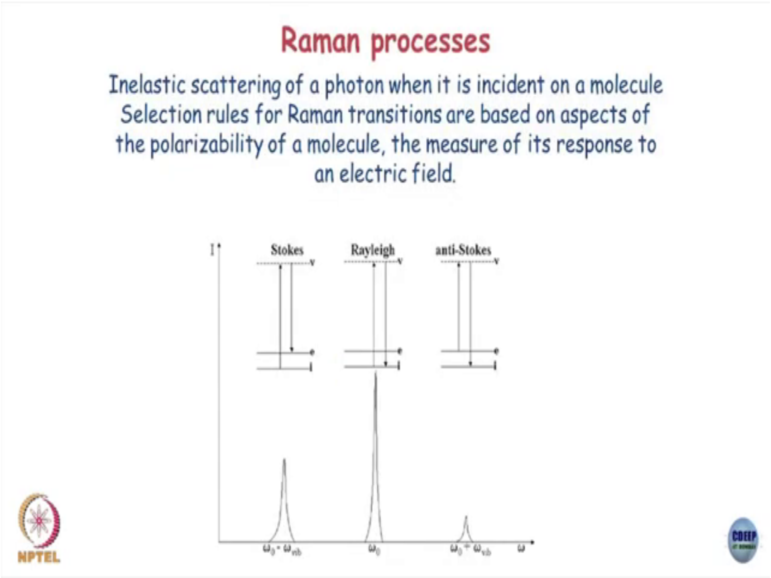

Raman processes

Inelastic scattering of a photon when it is incident on a molecule
Selection rules for Raman transitions are based on aspects of the polarizability of a molecule, the measure of its response to an electric field.

So, that is why it is the water molecule is sometimes called as a infrared active spectrum. The other Raman process have you all done? This Raman have you how many raise your hands ok. So, let me just give you what exactly I am trying to say. In this case it is just that you can send in you know you can have an initial level with some frequency omega it gets excited, but it gets de-excited with a lower energy, ok.

So, omega naught is the initial energy and then omega vibration is that it is final. So, this is the difference, ok. You start seeing a peak. These differences you can see that omega naught minus omega vibration is positive. So, these are called stokes lines. Usually when we have been doing all our exercises, if you excite an atom, take it to an excited state, it de-exits back and you see that energy is equal to the energy.

When it de-excites back, this is something which we always do which is the Rayleighs Rayleigh line, ok. The anti-stoke is the opposite of stokes. You get excited with lower energy, but it de-exits with the higher energy, ok. So, this is something which is not very normally seen in molecules, but it could be generated as what is the these are the three lines and they call this as Raman active if you find such frequencies in these vibrational modes of the molecule, ok.

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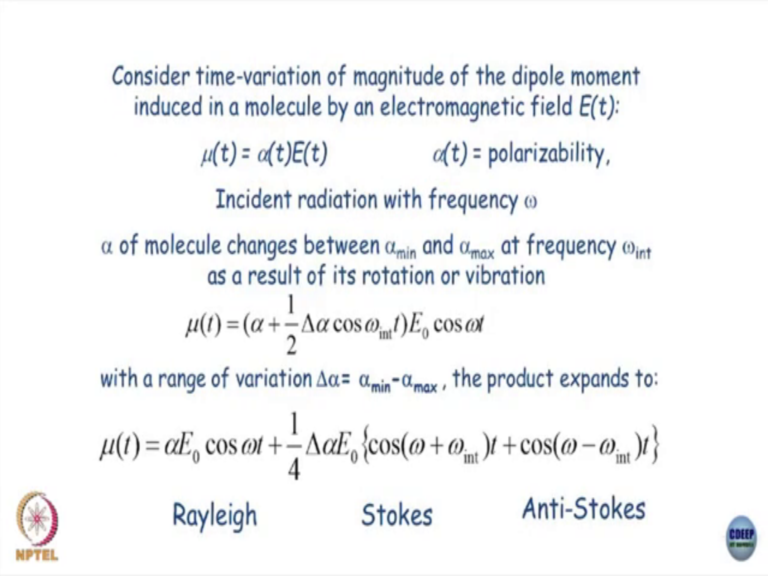

Consider time-variation of magnitude of the dipole moment induced in a molecule by an electromagnetic field $E(t)$:

$\mu(t) = \alpha(t)E(t)$ $\alpha(t)$ = polarizability,

Incident radiation with frequency ω

α of molecule changes between α_{min} and α_{max} at frequency ω_{int} as a result of its rotation or vibration

$$\mu(t) = (\alpha + \frac{1}{2}\Delta\alpha \cos\omega_{\text{int}} t)E_0 \cos\omega t$$

with a range of variation $\Delta\alpha = \alpha_{min} - \alpha_{max}$, the product expands to:

$$\mu(t) = \alpha E_0 \cos\omega t + \frac{1}{4}\Delta\alpha E_0 \{\cos(\omega + \omega_{\text{int}})t + \cos(\omega - \omega_{\text{int}})t\}$$

Rayleigh Stokes Anti-Stokes

So, one of the quantities which one should look at is the dipole moment, time dependent dipole moment related to the electric field and the object which it connects is the polarizability. Polarizability is what tensor this is a rank one which one will be, it will be binary basis or primary basis no.

So, it will be a binary basis. It is another like moment of inertia tensor. This will also be a tensor and basically you can see that the frequency with just in changes Rayleigh frequency which change as a Stokes and so, these are the three terms which turns out of this time dependent interaction term.

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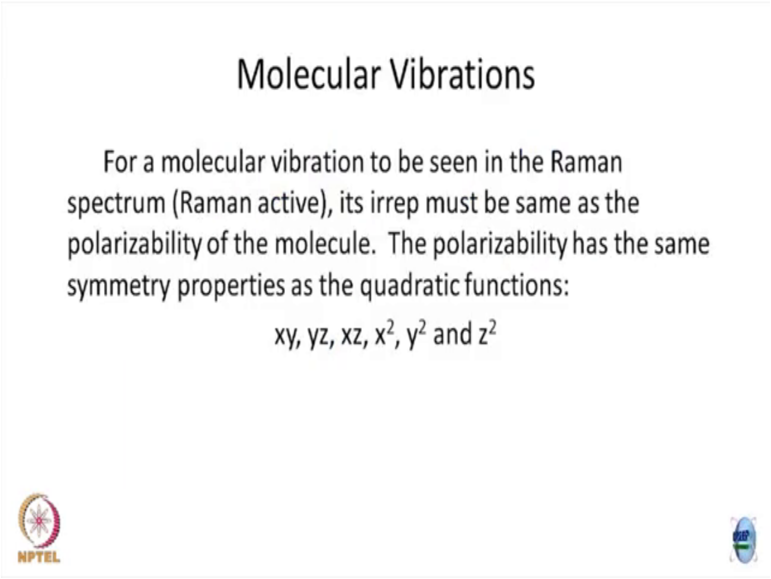

Molecular Vibrations

For a molecular vibration to be seen in the Raman spectrum (Raman active), its irrep must be same as the polarizability of the molecule. The polarizability has the same symmetry properties as the quadratic functions:

xy, yz, xz, x^2, y^2 and z^2

And what is going to be seen is look at the binary basis for the group symmetry. If the irreps has any of these basis, then you say it is also Raman active. That is all we do, ok. So, for a molecular vibration to be seen in the Raman spectrum it is irrep the vibrational irrep must be same as the polarizability of the molecule. The polarizability has the same symmetry properties has a binary basis or quadratic functions.

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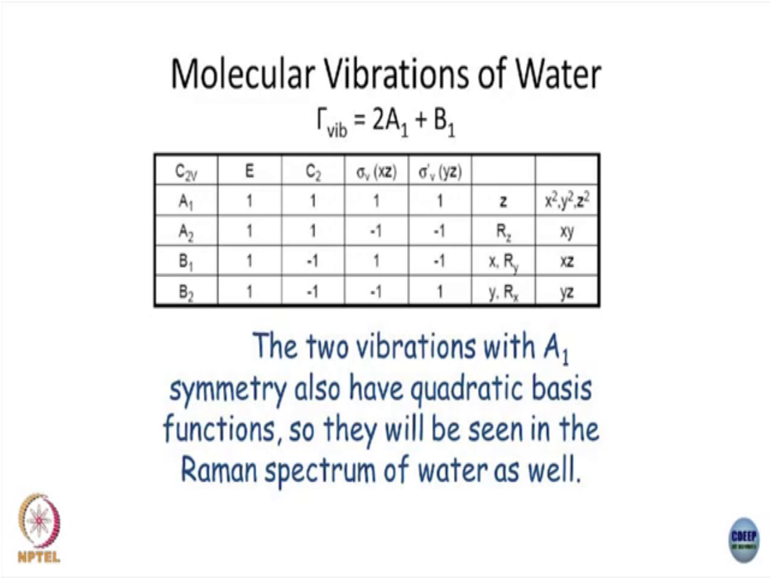

Molecular Vibrations of Water

$\Gamma_{vib} = 2A_1 + B_1$

C_{2V}	E	C_2	$\sigma_v (xz)$	$\sigma'_v (yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The two vibrations with A_1 symmetry also have quadratic basis functions, so they will be seen in the Raman spectrum of water as well.

So, you can look at here that the two vibrations with A 1 symmetry also has these quadratic basis, right. So, we can say that it should be the Raman spectrum as well and they do see in the Raman spectrum, those specific frequencies which they see in the infrared spectrum. So, that is kind of validating that you get the same frequencies and these are the three vibrational modes of the water molecule, ok.

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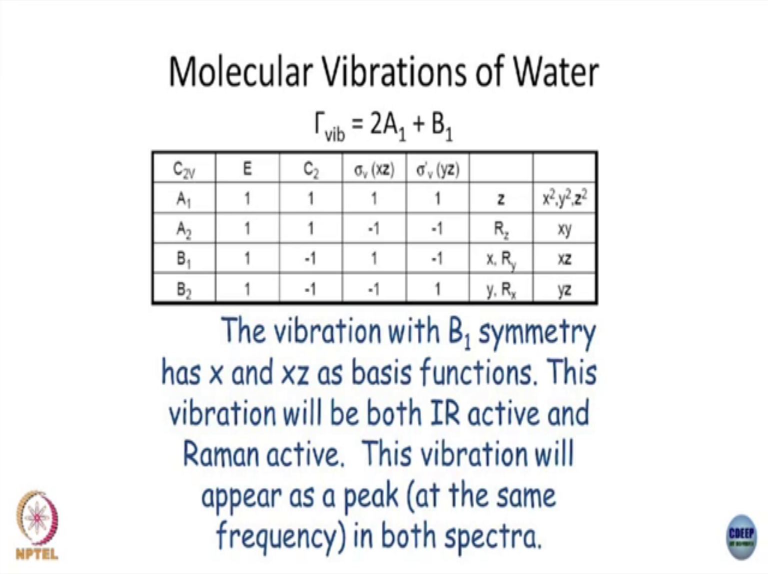

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A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The vibration with B_1 symmetry has x and xz as basis functions. This vibration will be both IR active and Raman active. This vibration will appear as a peak (at the same frequency) in both spectra.

What about B1? B 1 has x and x z as basis again the vibration will be both Infrared active and Raman active, ok. So, you do see this as a peak in both the spectra, Raman spectra as well as in the Infrared spectra. So, that is the summary and end of my discrete groups. Now I will start with continuous groups that does not mean you can forget whatever I have thought in discrete groups.

You will see a lot of parallel in understanding how there could be connections between what I have thought in the discrete groups. How it happens in the continuous groups? Of course, continuous groups are having a set of modified, you will have some modification because continuous groups are not finite order elements, right.

The group will have infinite elements and we need to handle it in a different way by introducing generators. In the discrete groups also we introduce generators. Even if we introduced generators, a number of generators and the number of elements are not significantly large that you need to worry. You could also write all the elements of the group and work with us.

But in the context of continuous groups, we have to work with generators and that will be the theme of how to see this in the rest of the semester. Any questions on this? I am going to get onto the board to give you a flavor today and next week onwards we will go more on SU 2 SU 3 and so on ok. So, that plan will be.

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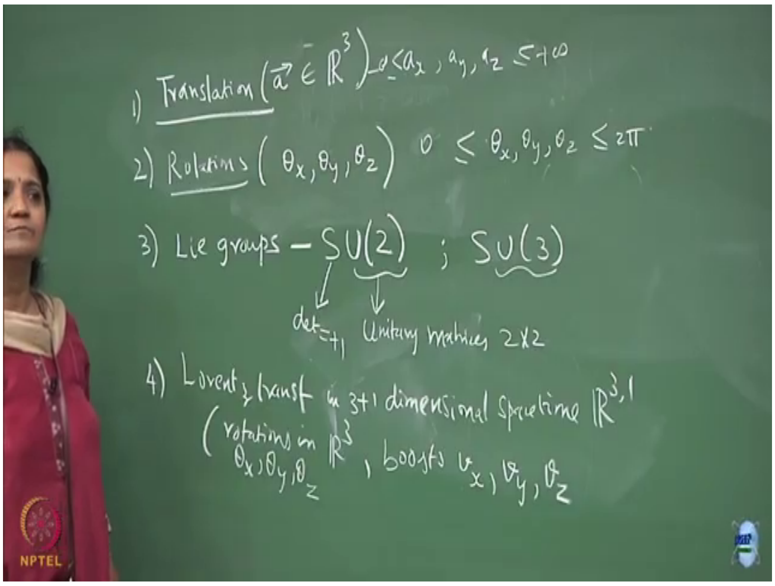

1) Translation $(\vec{a} \in \mathbb{R}^3)$ $-\infty \le a_x, a_y, a_z \le +\infty$

2) Rotations $(\theta_x, \theta_y, \theta_z)$ $0 \le \theta_x, \theta_y, \theta_z \le 2\pi$

3) Lie groups – $\underbrace{S}_{\det = +1}\underbrace{U(2)}_{\text{Unitary matrices } 2\times 2}$; $SU(3)$

4) Lorentz transf in 3+1 dimensional spacetime $\mathbb{R}^{3,1}$
(rotations in $\mathbb{R}^3$ $\theta_x, \theta_y, \theta_z$, boosts v_x, v_y, v_z

So, we will do a warm up on translation now and then a similar thing can be done for rotations. So, translation where you can translate by a vector a, any position where a could be any value what do I mean by that? This can lie in R 3 is what I would say technically what I mean is that a x a y az can lie between minus infinity and plus infinity.

That is the meaning of this right. This is like a three dimensional space unbounded a x translation which you want to do on an object can be any value between minus infinity and plus infinity, ok. Similarly rotations will involve theta x theta y theta z where the values are the rotation about x axis, y axis and z axis.

The values can lie between 0 to 2 pi, then I will slowly introduce groups which are lie groups. First I will do a warm up to get a clarification on the notations. So, the lie groups specially I will confine to this S denotes I will tell you what it is. S denotes that you write 2 cross 2 unitary matrices with determinant plus 1, ok.

So, this denotes this 1 denotes unitary matrices. If the lowest dimension has 2 cross 2 lowers non-trivial dimension is 2 cross 2 and this S denotes determinant to be equal to plus 1. The next thing I will do is SU 3 that will be again the same notation. The lowest non-trivial dimension is 3 cross 3 unitary matrices with determinant plus 1. Then we will get onto Lorentz transformations.

Lorentz transformation is on 3 space and 1 time, right. So, let me denote it by 3, 1. I have to remember that it is like R 3 space and then, you have one time coordinate which is having a slightly a different meaning. So, the Lorentz transformation will also involve various parameters. What are the parameters you will have?.

You will have rotations in, so let me write it space time which we call it as 3, 1. So, this will include rotations in R 3, right. This will include rotations in R 3. You will also have boosts. By boost I mean that you translate one inertial frame with respect to another inertial frame by introducing a velocity along the x direction.

So, these three rotations are theta x theta y and theta z. The boost are translatings or moving one inertial frame with respect to another inertial frame with velocity v x, v y and vz ok. You all know this I suppose. How many of you have not done basic relativity, special relativity, special theory of relativity. You have done this right, ok. So, what are the ranges you can see that theta x, theta y, theta z? The ranges will be 0 to 2 pi v x v y vz will be?.

Student: Minus.

Minus.

Student: C 2 plus c.

Minus c 2 plus c. That is because of special theory of relativity which says that no particle can, no frame can move with velocity greater than velocity of it.