Fundamentals of Spectroscopy

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Lecture-35

Vibration of Polyatomic Molecules 3

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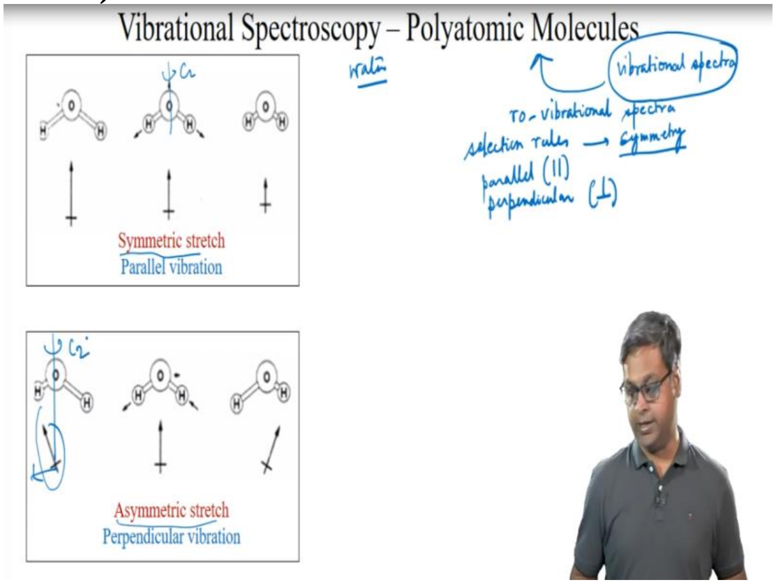

Vibrational Spectroscopy – Polyatomic Molecules

Symmetric stretch
Parallel vibration

Asymmetric stretch
Perpendicular vibration

water

vibrational spectra

ro-vibrational spectra
selection rules → symmetry
parallel (||)
perpendicular (⊥)

Hello everyone, welcome to the lecture. In the last couple of lectures, we have talked about the vibrational spectra of polyatomic molecules. In this lecture, we will discuss the ro vibrational spectra of polyatomic molecules, the selection rules of the rotational transitions. So the selection rules for this rotational transitions of the polyatomic molecules depend on the symmetry it depends on the symmetry of a particular vibration, if it is parallel which is shown by this symbol or perpendicular, which is shown by this symbol.

So, whether it is parallel or perpendicular of the particular vibration that the molecule is undergoing. We can illustrate what we mean by parallel or perpendicular using water molecule as the basis a parallel vibration is the one in which the dipole moment changes parallel to the principal axis of the molecule. If we take the example of symmetric stretch of water, it leads to the dipole moment changes that occur parallel to the principal axis or the C 2 axis of the molecule.

The perpendicular vibration is the one in which there is a component to the change in the dipole moment that is perpendicular to the principal axis. So, the asymmetric stretch of water illustrates this. As we can see from here, there is a component that is perpendicular to the C 2 axis. So, today we will start off with the ro vibrational spectra of linear molecules, such molecules can have either parallel or perpendicular vibrations. So, what are the selection rules for a parallel vibrational mode?

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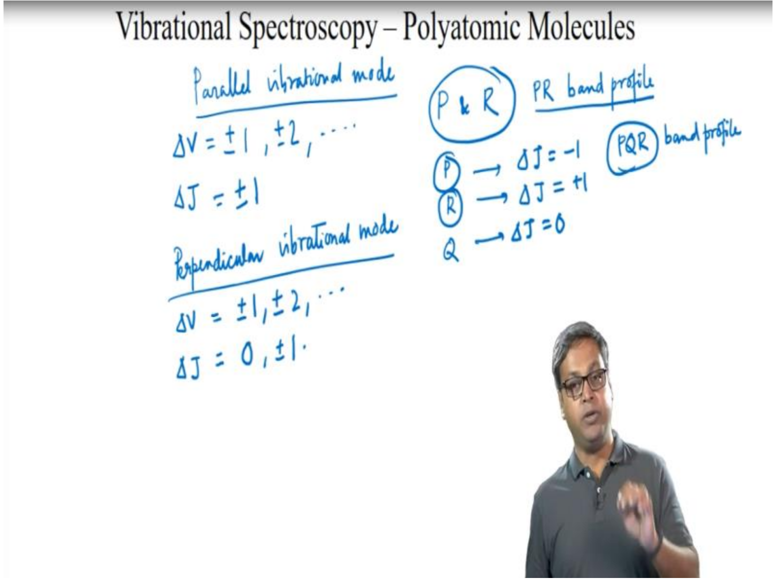

Vibrational Spectroscopy – Polyatomic Molecules

Parallel vibrational mode

$\Delta v = \pm 1, \pm 2, \ldots$

$\Delta J = \pm 1$

Perpendicular vibrational mode

$\Delta v = \pm 1, \pm 2, \ldots$

$\Delta J = 0, \pm 1.$

P & R PR band profile

P $\rightarrow \Delta J = -1$

R $\rightarrow \Delta J = +1$

Q $\rightarrow \Delta J = 0$

PQR band profile

So, for a parallel vibrational mode, the selection rules are the change in the vibrational quantum number, that is delta v equals plus minus 1 plus minus 2, and so on. And the change in the rotational quantum number that is delta J is given by plus minus 1. So, we get a spectrum with a similar appearance to that we had for diatomic molecules. So, we will get P and R branches appearing in the ro vibrational spectrum. So, this is known as the PR band profile.

Just as the PR band profile we saw for hydrochloric acid or HCL. For HCL, we saw that there was a gap missing in the middle of the vibrational band that is when delta J = 0. This band does not occur as this band is not allowed for a parallel vibrational mode. For a diatomic molecule of course, there is only a parallel vibrational mode but for a polyatomic system, it is possible to have a perpendicular mode.

So, what difference does this perpendicular mode make to the selection rule? So, let us look into the selection rule for the perpendicular vibrational mode. So, the selection rule is delta v is plus minus 1 plus minus 2, and so on. But the main difference of the perpendicular vibrational mode of a linear molecule is that delta J = 0 and plus minus 1. So, for the perpendicular vibrational mode data J can be equal to 0.

So, we now can get another band appearing in the ro vibrational profile. So, we will have a P branch associated with delta J = - 1. We will also have an R branch associated with delta J = + 1. But additionally, we will also have a Q branch which is associated with delta J = 0. The Q branch will be right in the center of the P and R branches and all the Q branch transitions are going to be overlapping. So, we get what is called PQR band profile the Q branch appears because delta J = 0 is allowed. So, now, let us look into some real spectrum.

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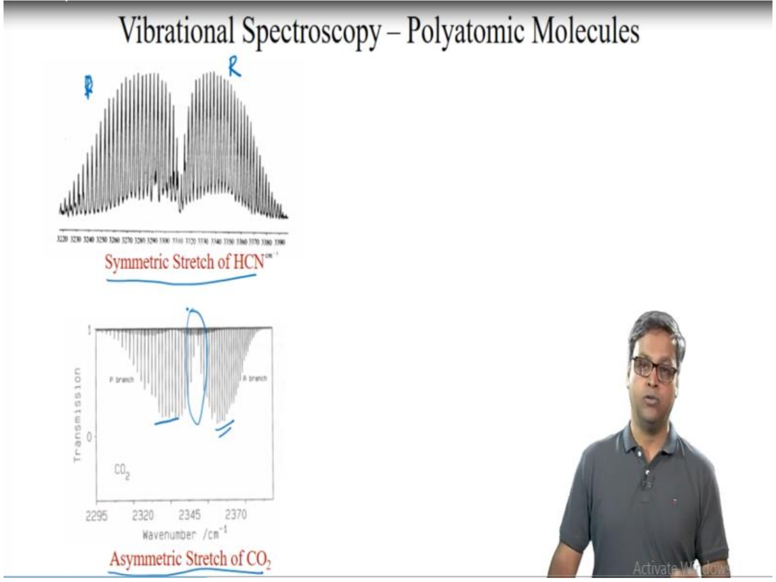

Vibrational Spectroscopy – Polyatomic Molecules

Symmetric Stretch of HCN

Asymmetric Stretch of CO_2

So here is the symmetric stretch of HCN which is a linear molecule. For this vibration, we get P and R branches. So, we get a PR band profile because we have both the PR branches here and nothing in the center. So, this must be therefore, our parallel vibration. So, here is another spectrum for the asymmetric stretch of carbon dioxide. So, on the left we have the P branch and on the right that is at higher frequencies or wave numbers, we have the R branch, we are missing a line in the center here, because that would be a transition for J = 0. Again, we have a PR band profile here. So, this has to be our parallel vibration.

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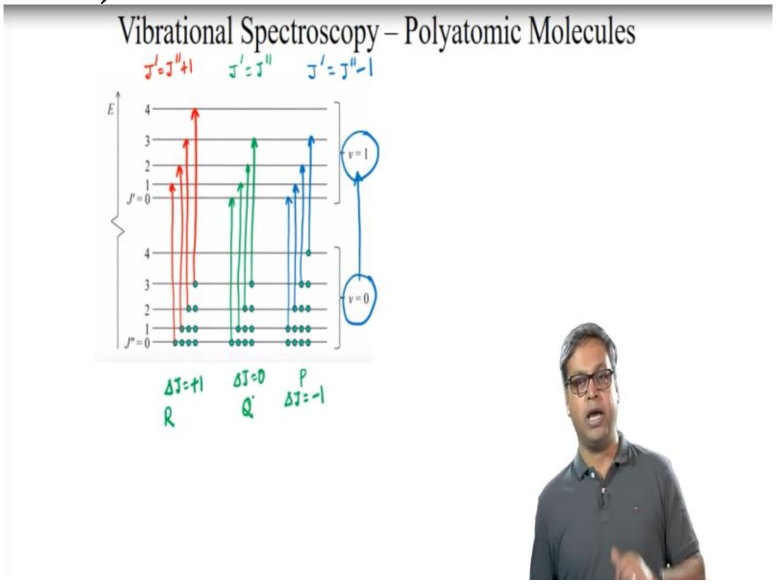

Vibrational Spectroscopy – Polyatomic Molecules

So, now, let us look into the perpendicular mode. As we now know, the selection rule for perpendicular mode is delta J = 0 or plus minus 1. So, let us draw the allowed transitions for a perpendicular mode. So, we have the energy levels here for v = 0 the different J levels. And for v = 1, the different J levels and we are considering the transition from v = 0 to v = 1. So let us first draw the P branch for which, if I start from v = 0 J = 1 it will go to v = 1 J = 0.

So, that means that J prime equals J double prime minus 1 for the P branch. So, let us draw the other transitions. We start from v = 0 J = 2 we end that v = 1 J = 1. So here we go from J = 3 to J = 2 and J = 4 to J = 3. So now if we draw the, R branch. So for the R branch, the J prime equals J double prime plus 1. So if we start from v = 0 J double prime = 0 I will end at v = 1, J prime = 1. Similarly, I will have 1 to 2 transitions, 2 to 3 transitions, and 3 to 4 transitions.

Now, if we draw the Q branch, for which I have J prime equals J double prime, so then I will have transitions from J = 0 to J = 0 J = 1 to J = 1 J = 2 to J = 2, J = 3 to J = 3, and so on. So, we can have our P branch for which delta J = - 1, we can have an R branch for which delta J = + 1. So this is the R branch and we can have a Q branch for which they delta J = 0. So this is my Q branch.

So we can see that the R branch transitions occur at frequencies that are higher than the fundamental frequency for the P branch there at lower frequencies than the fundamental however, If delta J does not change, that is from 0 to 0 or 1 to 1 or 2 to 2, the energy gap will almost be the same, it would be slightly different as v 0 is slightly different from v 1 as we have discussed in an earlier lecture. So, they will be slightly different, but will be pretty close. So, because of that all these lines associated with delta J = 0 will overlap with one another. So, the central spike associated with the Q branch will be quite intense.

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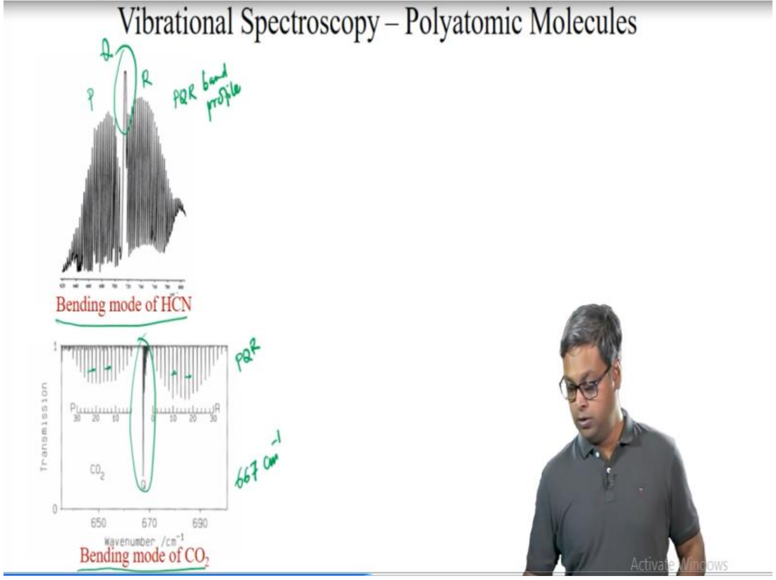

Vibrational Spectroscopy – Polyatomic Molecules

This is indeed what we see in the bending mode spectrum of HCN. This is a perpendicular vibrational mode. So, we have both this P and R branches and in the center, we have an intense Q branch. So, we can say this is a P Q R band profile for carbon dioxide, we will have a very similar spectrum. So, we are looking into the spectrum of the bending mode of carbon dioxide. So, this vibrational band is centered at 667 wave numbers.

So, apart from the P and R branches, there is this intense Q branch where all the lines are overlapping with one another the lines of P and R branches are separated. So, you can see these lines are all separated and they are not on top of one another. All the lines in the Q branch are on top of each other and thus the Q branch is very intense. So, this is again a PQR band profile which implies a perpendicular band.

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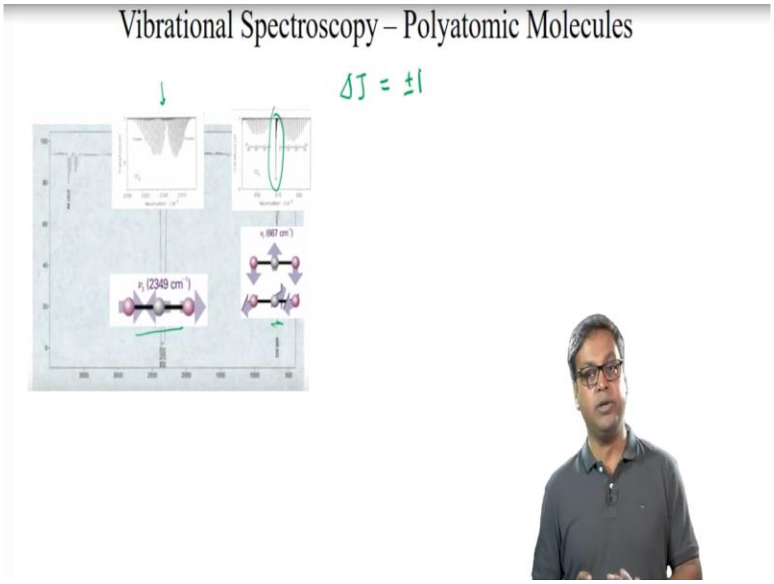

Vibrational Spectroscopy – Polyatomic Molecules

$\Delta J = \pm 1$

So, this is the ro vibrational spectrum of carbon dioxide that we showed in the previous lectures. So, we got a PR branch centered at 2350 wave numbers, but because this is a low resolution spectrum, we cannot see the rotational fine structures in the band but at high resolution, we can see the fine structure. So, for the asymmetric stretch, as shown here, the dipole moment is changing along the principal axis. But, for the bending mode as shown here, the dipole moment is changing perpendicular to the principal axis.

So, there is a Q branch in the bending mode at high resolution. The reason why delta J was plus minus 1 is because the angular momentum needed to be conserved. The photon had 1 unit of angular momentum. However, we did not know if it was plus 1 or minus 1 and the angular momentum of the molecule was associated with this rotational structure that is which J state it was in. So when the photon gets absorbed, it transfers its angular momentum to the molecule. So the angular momentum of the molecule either goes up by 1 or goes down by 1.

And for this reason, delta J was = plus minus 1. But where did the angular momentum of the photon go for the perpendicular band? When delta J equals zero? The angular momentum goes into the bending vibration. And this type of vibration, that is the bending vibration has angular momentum. When photon is absorbed, the angular momentum is not being lost, but it has been put into vibrational angular momentum.

And not rotational angular momentum. That is the reason why the Q band occurred for the bending mode for symmetric and asymmetric stretch, no angular momentum is associated with these vibrations. So far, we have looked into the vibrational and low vibrational spectra of triatomic molecules. However, if we now consider a polyatomic molecule consisting of more than 3 atoms.

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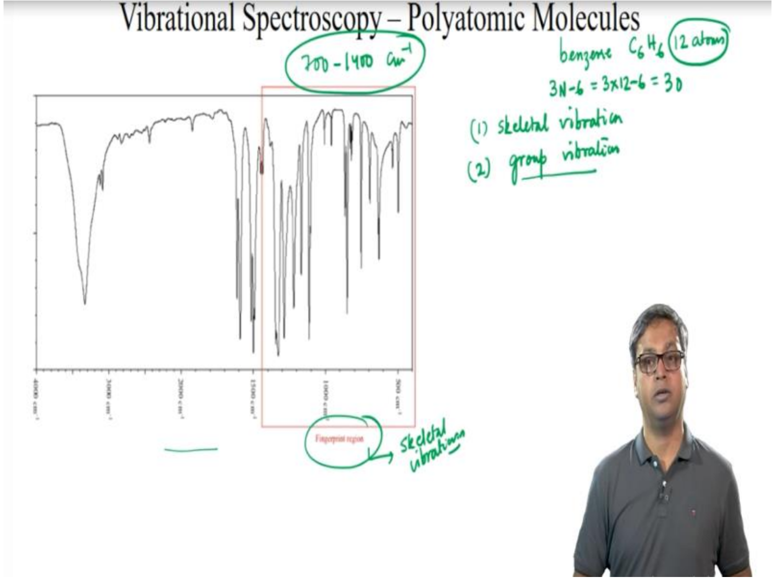

Vibrational Spectroscopy – Polyatomic Molecules

Let us say we have benzene. So the formula is C 6 H 6. So there are 12 atoms in total. So there are 6 carbon atoms and 6 hydrogen atoms. And this 12 atoms will give rise to 3N - 6 that is 3 times 12 - 6. So 30 modes of vibration there, it will be extremely difficult to underpin each individual vibration thus a complex molecule will have IR spectrum with large number of vibrations. So, these vibrations can be broadly divided into 2 classes, 1 is the skeletal vibration and number 2 we have what is known as group vibration.

The skeletal vibrations arise from strong coupling between stretching or bending motions of atoms in straight chains, branch chains or in a ring, many atoms are involved in skeletal vibrations, all undergoing approximately the same displacement. Whereas, the group vibrations involve a small part of the molecule with the remaining molecules or the remaining part of the molecules being more or less stationary.

In other words, the characteristic group vibrations are almost independent of the structure of the molecule as a whole and just depend on the structure of the group undergoing vibration. So, here is a typical IR spectrum of complex molecule so, we can see this 700 to 1400 wave numbers. So, this range normally shows the skeletal vibrations. This region is also known as the fingerprint region. So, fingerprint region is a region which shows the skeletal vibrations.

So, this is called the fingerprint region as the identity of the molecule can be recognized merely by the appearance of the spectral region. So, now, let us move on to group vibrations. If we consider 3 molecules.

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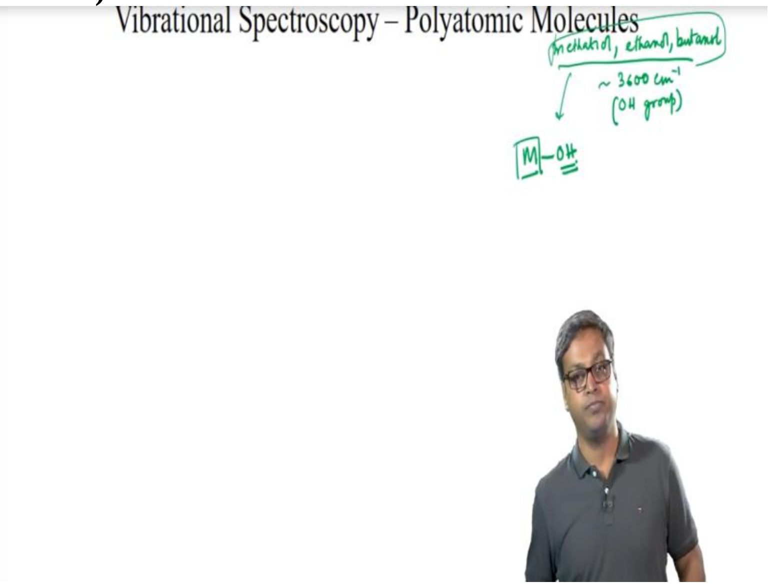

Vibrational Spectroscopy – Polyatomic Molecules

Let us say we have methanol ethanol and butanol all 3 of them show a broad band around 3600 wave numbers. So, this band arises from the OH group. So, this OH group is common to all the 3 alcohols. As far as the OH group is concerned, we can represent all these 3 alcohols as M OH where M, represents the other part of the molecule. So, to a first approximation, the vibrational frequency is independent of the overall size of the molecule and only depends on the vibrating group that is the OH functional group.

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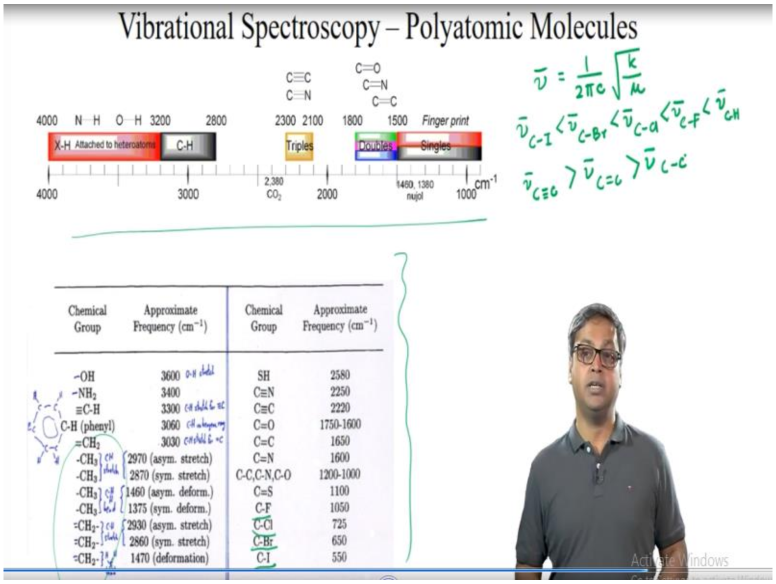

Vibrational Spectroscopy – Polyatomic Molecules

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

$$\bar{\nu}_{C-I} < \bar{\nu}_{C-Br} < \bar{\nu}_{C-Cl} < \bar{\nu}_{C-F} < \bar{\nu}_{CH}$$

$$\bar{\nu}_{C\equiv C} > \bar{\nu}_{C=C} > \bar{\nu}_{C-C}$$

Chemical Group	Approximate Frequency (cm^{-1})	Chemical Group	Approximate Frequency (cm^{-1})
$-OH$	3600	SH	2580
$-NH_2$	3400	C≡N	2250
≡C-H	3300	C≡C	2220
C-H (phenyl)	3060	C=O	1750-1600
$=CH_2$	3030	C=C	1650
$-CH_3$	2970 (asym. stretch)	C=N	1600
$-CH_3$	2870 (sym. stretch)	C-C,C-N,C-O	1200-1000
$-CH_3$	1460 (asym. deform.)	C=S	1100
$-CH_3$	1375 (sym. deform.)	C-F	1050
$=CH_2-$	2930 (asym. stretch)	C-Cl	725
$=CH_2-$	2860 (sym. stretch)	C-Br	650
$=CH_2-$	1470 (deformation)	C-I	550

The characteristic group frequencies of different functional groups are shown in this figure and also this is tabulated in this table. So, we can see that the different groups show up at different wave numbers in the IR spectrum. So, we also have a few general trends that exist in the group frequencies. So we can recall the relation that is nu bar = 1 / 2 pi c root over k / mu, where k is the force constant and mu is the reduced mass.

So increasing the mass of the atom undergoing vibration within the group will tend to decrease the frequency or the wave number. So, we can say nu bar of c iodine or c i is less than nu bar of c bromine bond, which is less than nu bar of c chlorine bond which is less than nu bar of c f that is c florin which is less than nu bar of c h. So, we can see here the c i is the least, then we have c br c cl c f and the c h are much higher frequencies also increase in the strength of the bond.

And hence the value of the force constant that is k increases the frequency. So we can write, let us say, nu bar c triple bond c is greater than nu bar c double bond c which is greater than nu bar c single bond c and this is true for other atoms. For example, we can have C triple bond N the frequency will be greater than C double bond N frequency which will be greater than C single bond N frequency. So, we can see thus increasing bond orders would lead to higher frequencies.

So, these frequencies can be theoretically estimated from quantum mechanical calculations and the vibrational normal modes can be visualized after the calculation using a visualizing software.

My co instructor, Anirban Hazra will discuss about this in more details in the next lecture. So, we will end this lecture by solving a couple of problems.

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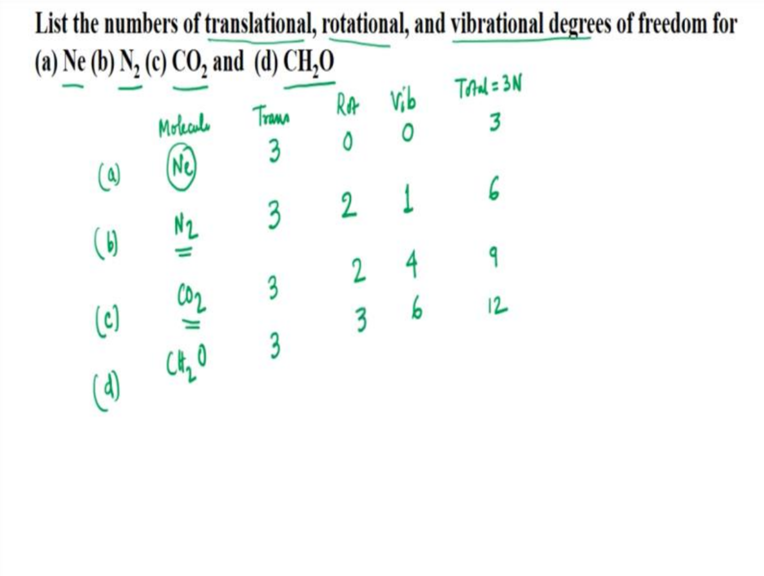

List the numbers of translational, rotational, and vibrational degrees of freedom for (a) Ne (b) N_2 (c) CO_2 and (d) CH_2O

	Molecule	Trans	Rot	Vib	Total = 3N
(a)	Ne	3	0	0	3
(b)	N_2	3	2	1	6
(c)	CO_2	3	2	4	9
(d)	CH_2O	3	3	6	12

So here we have the first problem, it says lists the number of translational, rotational and vibrational degrees of freedom for 4 cases one is neon, second is nitrogen third is CO 2, and fourth is CH 2 O, which is formaldehyde. So let us try to make a table. Let us say we have the molecule. Then we have the translational degrees of freedom. We have the rotational degrees of freedom. We have the vibrational degrees of freedom.

And we have that total degrees of freedom that is given by 3N. So for a, we have neon b we have nitrogen c, we have CO 2 and d we have CH 2 O. So for the first case, because it is just an atom, the total degrees of freedom we have is 3N, so 3 times 1 this is 3. And we know there are 3 translational degrees of freedom. So the rotation and vibration are 0, for the second case, is a diatomic molecule. So, 3N = 3 times 2 = 6, and we have 3 translational degrees of freedom.

And because this is a diatomic molecule with only one bond, we have only one vibrational degree of freedom. So, there are 2 rotations that are allowed. Now, for CO 2 this is a linear molecule. So, 3N = 3 times 3, that is 9. So there are 3 translational degrees of freedom, and 3N - 5, that is 9 - 5, that means 4 vibrations. So rotations equals 9 - 4 - 3, that is 2. And for CH 2 O, the total number of degrees of freedom is 12. That is 3 times 4. And we have 3 translations, 3N - 6, that mean 6 vibrations, and the rest are rotations. So we have 3 rotations.

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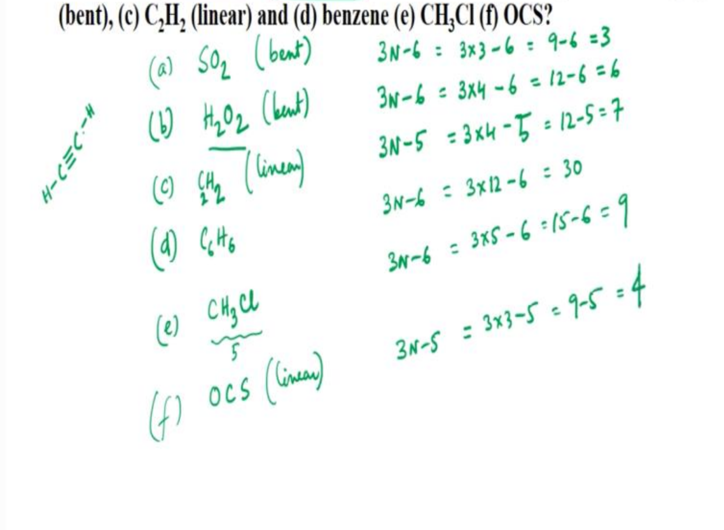

How many normal modes of vibration are there in for (a) SO_2 (bent), (b) H_2O_2 (bent), (c) C_2H_2 (linear) and (d) benzene (e) CH_3Cl (f) OCS?

$H-C\equiv C-H$

(a) SO_2 (bent) $3N-6 = 3\times3-6 = 9-6 = 3$

(b) H_2O_2 (bent) $3N-6 = 3\times4-6 = 12-6 = 6$

(c) C_2H_2 (linear) $3N-5 = 3\times4-5 = 12-5 = 7$

$3N-6 = 3\times12-6 = 30$

(d) C_6H_6 $3N-6 = 3\times5-6 = 15-6 = 9$

$3N-6$

(e) $\underset{5}{CH_3Cl}$ $3N-5 = 3\times3-5 = 9-5 = 4$

(f) OCS (linear)

So now that does look into the next problem. So the question is, how many normal modes of vibration are there for these different molecules so let us start with 1, the first 1 is SO 2. So SO 2 as given in the question is a bent molecule. So the number of normal modes will be 3N - 6. So that is 3 times 3 - 6 = 9 - 6 = 3. Now for the next molecule, we have H 2 O hydrogen peroxide. So this is also a bent molecule.

So we have 3N - 6 normal modes. So 3 times 4 because now we have 4 atoms minus 6, that is 12 - 6 = 6. The third one is acetylene. So C 2 H 2 so acetylene. As we know is a linear molecule with C triple bond C in between. So, acetylene. This is a linear molecule. So the number of normal modes is given by 3N - 5. So is 3 times 4 - 5. It is 12 – 5 = 7. The next molecule is benzene. So this is C 6 H 6. We have discussed this already in the lecture.

So, this is 3N - 6 that is 3 times 12 - 6 = 30. The other molecule that we have is CH 3 Cl. So, there are 5 atoms so it will be 3N - 6, that is 3 times 5 - 6 that is 15 - 6, so 9 normal modes. And the last molecule we have is OCS. Again, this is a linear molecule like CO 2. So we have 3N - 5 normal modes. So 3 times 3 - 5, so 9 - 5. So there are 4 normal modes.