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I R SPECTROSCOPY

A molecule, when it forms a bond, has a balance of forces. The attractive forces exist between nucleus of the first atom and electrons of the other atom and vice versa and repulsive forces exist between the nuclei of different atoms.

The molecules settle at an “in between” distance as both forces are balanced. An attempt to bring them closer sharply increases the repulsive force and an attempt to pull apart brings the attractive forces into play.

Thus, any attempt to change the equilibrium situation needs energy. We can plot the energy vs internuclear distance. (Figure 1). The minimum at the internuclear distance is referred to as the equilibrium distance r_{eq} or bond length.

Thus, a molecule, after bond formation, behaves like a spring and should obey Hooke’s Law

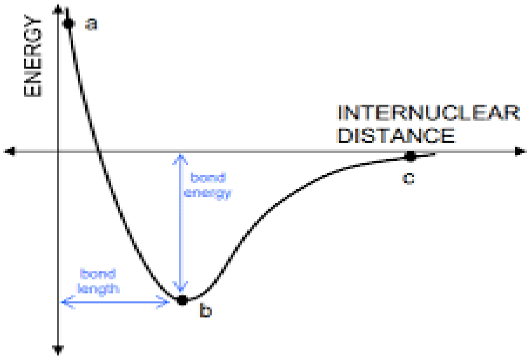

Figure 1. Figure showing the plot of energy vs internuclear distance in the formation of a molecule

In any spring, the restoring force is given by

$$f = -k\left(r - r_{eq}\right) \qquad (1)$$

Where f is the restoring force

k is the force constant

r is the internuclear distance

r_{eq} is the equilibrium distance

since the energy is parabolic it has the value

$$E = \frac{1}{2}k\left(r - r_{eq}\right),^2 \qquad (2)$$

This is the behaviour of a simple harmonic oscillator (SHO).

On increasing energy, the displacement is higher, but frequency remains the same.

this frequency is

$$w_{OSC} = \frac{1}{2\pi}\frac{\sqrt{K}}{\sqrt{\mu}} Hz \qquad (3)$$

$$\therefore\ \bar{w}_{OSC} = \frac{1}{2\pi c}\frac{\sqrt{K}}{\sqrt{\mu}} cm^{-1} \ldots\ldots \qquad (\text{as } \bar{w}_{OSC} = w_{OSC}/\text{c}) \quad (4)$$

Vibrational energy, like all other molecular energies, is quantized. The allowed vibrational energies are obtained by solving the Schrodinger wave equation for the simple harmonic oscillator. The value of vibrational energy from Schrodinger wave equation is

$$E_v = \left(v + \frac{1}{2}\right) h\, w_{OSC}\ joules \qquad (5)$$

Where *v* has a value 0,1,2, 3……. (*v* is the vibrational quantum number). Converting energy to wave number units, we get,

$$\mathcal{E}_v = \frac{E_v}{hc}\left(v + \frac{1}{2}\right) w_{OSC}\, cm^{-1}$$

$$= \left(v + \frac{1}{2}\right) \bar{w}_{OSC}\ cm^{-1} \qquad (6)$$

Putting the value of 0,1,2,3 …. in the above expression, we get

$$\mathcal{E}_0 = \frac{1}{2}\bar{w}_{OSC}\ cm^{-1}$$

$$\mathcal{E}_1 = \frac{3}{2}\ \bar{w}_{OSC}\ cm^{-1}$$

$$\mathcal{E}_2 = \frac{5}{2}\ \bar{w}_{OSC}\ cm^{-1}$$

we can see that the lowest vibrational energy is $\bar{w}_{OSC}$. This means that no molecule can ever have zero vibrational energy. The atoms in the molecule can never be at rest with respect to each other.

The value $\frac{1}{2}\bar{w}_{OSC}\ cm^{-1}$ is known as the **zero- point energy**. The values of vibrational energies are shown in Figure 2.

The prediction of zero-point energy was the only difference between classical mechanics and quantum mechanics.

<u>Selection rule (For diatomic molecule):</u>

1) $\Delta v = \pm 1$
2) molecule must have permanent dipole moment

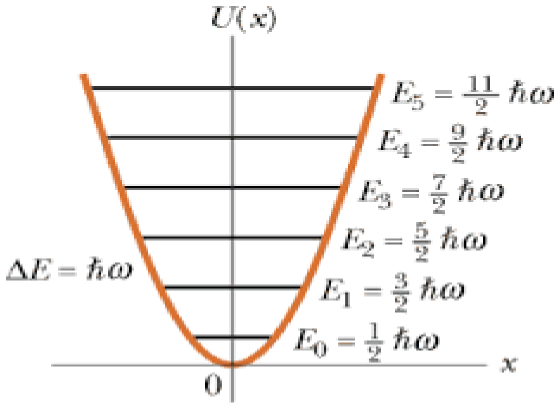

Figure 2.

When a molecule absorbs energy and goes from v^{th} to $v+1^{th}$ level, the energy absorbed will be

$$\mathcal{E}_{v+1}-\mathcal{E}_{v} = (v+1+1/2)\,\overline{w}_{OSC} - -(v+1/2)\,\overline{w}_{OSC}$$

$$= \overline{w}_{OSC} \qquad (7)$$

The difference between energy level directly gives wave number of spectral line absorbed or emitted

Thus, for a diatomic molecule, we can have two types of transmission.

1) Δv=+1, ΔJ= - 1 (8)
2) Δv=+1, ΔJ= + 1 (9)

For (8), $\Delta E_{J,V} = \overline{w}_{OSC} + 2B(J'' + 1)cm^{-1}$

For (9), $\Delta E_{J,V} = \overline{w}_{OSC} - 2B\,(J' + 1)\,cm^{-1}$

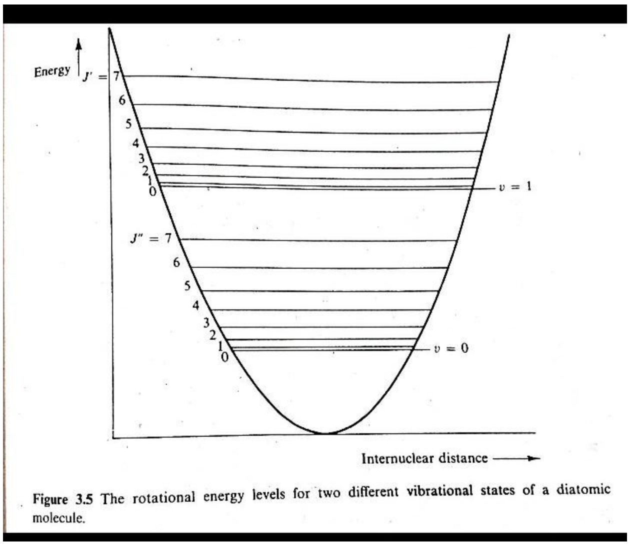

Figure 3.5 The rotational energy levels for two different vibrational states of a diatomic molecule.

Fig 3. Rotational energy levels for two different vibrational states of a diatomic molecule.

The two types of transitions mentioned above are show as below:

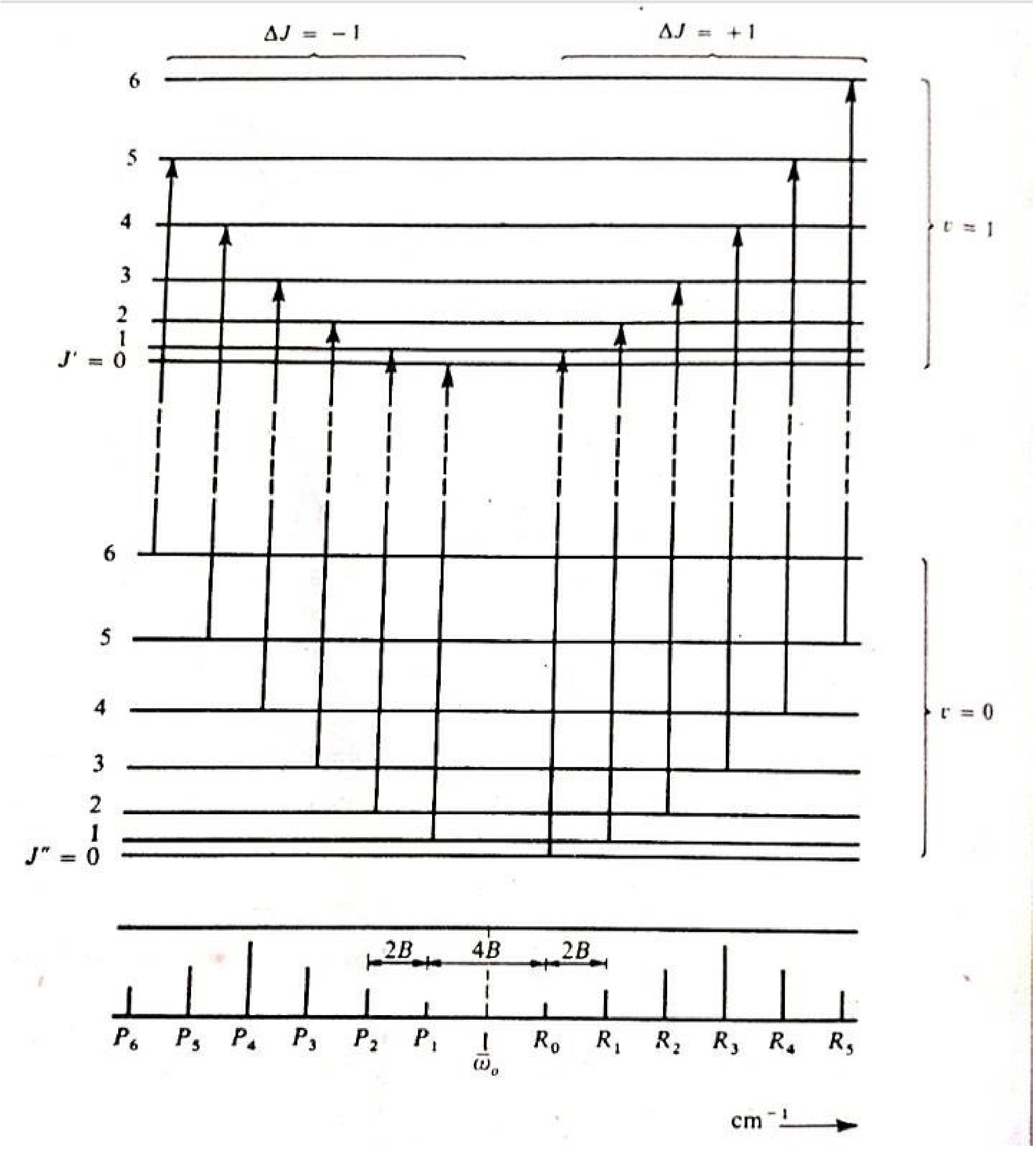

Figure 4. Transitions in a diatomic molecule between the vibrational energy levels, along with rotational transition according to the selection rules. Here $\overline{w}_{OSC}$ is called band origin or band centre.

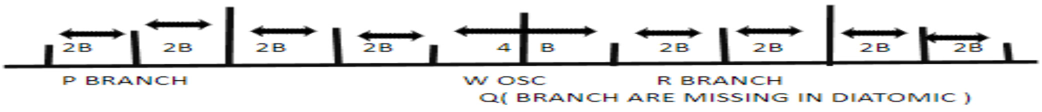

Figure 5. Spectrum that results from the transitions shown in Figure 4

In diatomic molecules, the band corresponding to ΔJ=0 is missing. The band corresponding to

ΔJ= -1 is called the P branch, the transition corresponding to ΔJ=0 is called the Q branch (which is missing in diatomic molecules) and the transition corresponding to ΔJ=+1 is called the R branch.

Polyatomic molecules:

Selection Rule for Polyatomic molecules: Thus, a single line at the frequency of vibration is observed. However, since rotation also accompanies vibration, the selection rule becomes:

1) $\Delta v = \pm 1$, ΔJ=0, ±1
2) Dipole moment of the molecule must change with vibration.

(However, diatomic molecules do not have ΔJ=0)

Vibrational frequencies in a polyatomic molecule:

Each atom in a molecule can be described by three coordinates(x,y,z). For a molecule containing N atoms, there will be 3N coordinates, these are called degrees of freedom.

Once all coordinates have been specified, the bond distance and bond angles are also fixed. the molecule can move as whole in 3d space.

Thus, there will be 3 coordinates of centre of gravity. These account for the 3 degrees of freedom which are due to translation. Thus, out of 3N degree of freedom, 3N-3 remain.

There are three rotational degrees of freedom for a non-linear molecule, so 3N-3-3=3N-6 degrees of freedom for vibration modes are left.

However, in linear molecule there are only 2 degrees of freedom of rotation (rotation along bond axis is not considered). Therefore, for a linear molecule, there will be 3N-3-2=3N-5 vibrational degrees of freedom.

In both, linear and non-linear molecules, which are acyclic, if there are N Atoms, there are N-1 bonds, so, out of the vibrational degrees of freedom, there are N-1 stretching frequencies. Hence, there will be (3N-6) - (N-1) =2N-5 bending frequencies for non-linear molecule and (3N-5) - (N-1) =2N- 4 bending frequencies for linear molecules.

We can summarise the above discussion in the following way:

There are three types of motion in a molecule, translation, rotation, and vibration. The sum of these degrees of freedom should be 3N.

Since the molecule moves about the centre of gravity, the C.G can be described by three coordinates

$$\text{Trans} + \text{Rot} + \text{Vib} = 3N$$

Or, $$3 + 3(\text{non-linear}) + \text{Vib} = 3N$$

vibrational degrees of freedom for non-linear molecules= 3N-3-3=3N-6

And, for linear molecules, 3+2 (for linear)+ Vib = 3N

So, vibrational degrees of freedom for linear molecule= 3N-5

Non-linear molecules	linear molecules
3N-6 vibrational frequency	3N-5 vibrational frequency
N-1 stretching frequency	N-1 stretching frequency
(3N-6) -(N-1) = 2N-5 Bending frequency	(3N-5) -(N-1) = 2N-4 Bending frequency

CASE 1:

non-linear molecules: H_2O, SO_2

There will be 3N-6=3 Vibration modes

Out of these 3 vibrational modes, there will be 2(N-1) stretching modes and 2×3-5=1 bending mode.

These vibrational modes are shown below in Figure

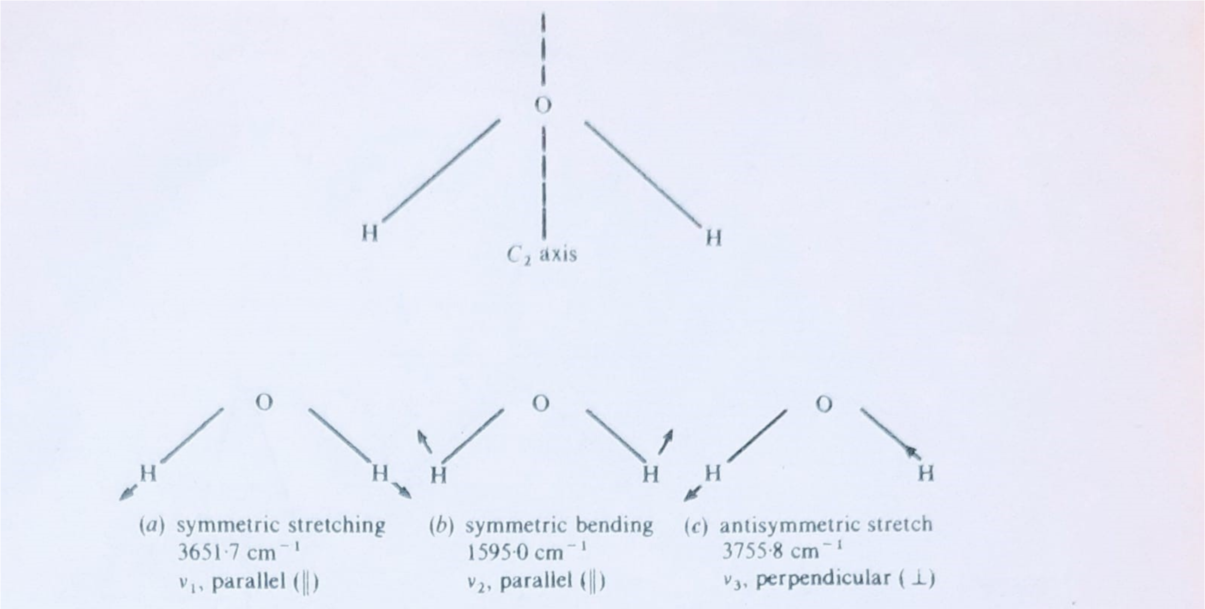

Figure 6. Depiction of the three vibrational frequencies of water. There are two stretching frequencies and one bending frequency

There is the symmetric stretch, the asymmetric stretch, and the bending frequency.

In order to identify which of these frequencies are IR active, we must observe the dipole moments of the molecule about the rotational axis C_2 about which the molecule rotates.

It is important to understand that in stretching frequencies the bond length changes without change in bond angle, while in bending frequency, only bond angle changes, without change in bond length.

In water, the dipole moment changes in the symmetric stretch, where both bonds stretch out and stretch in simultaneously. As the separation between the charges changes, so does the dipole moment. In the asymmetric stretch, one bond stretches out while the other one stretches in.

In this case, the direction of dipole moment undergoes a change as well as the size. (Remember that dipole moment is a vector). In the bending frequency, as the bond angle changes, the dipole moment also changes. (Also remember that dipole moment has a direction from positive to negative charge.) These changes in the dipole moment are shown in Figure 7.

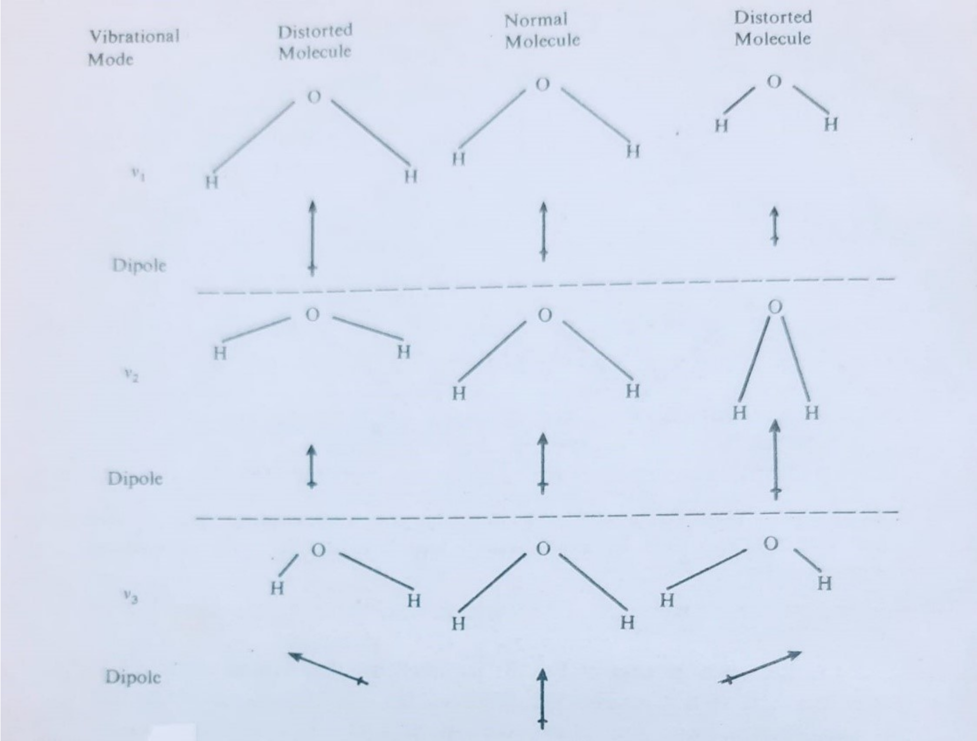

Figure 7. Change in dipole moment as the water molecule vibrates in different modes**.**

It is very clear that in all the vibrational frequencies of water, there is a change of dipole moment and thus, all vibrational frequencies of water are IR active.

CASE 2:

Taking the case of a linear molecule, which is represented by CO_2 , we can calculate the vibrational Frequencies as follows:

Linear molecule: CO2

Total degrees of freedom = 9 (3×3). Out of these degrees of freedom, the vibrational degrees of freedom = 3×3-5(remember, the molecule is linear, so 2 rotational degrees of freedom). Out of these 4 vibrational degrees, there are 3-1 =2 stretching frequencies and 2N-4 = 2 bending frequencies.

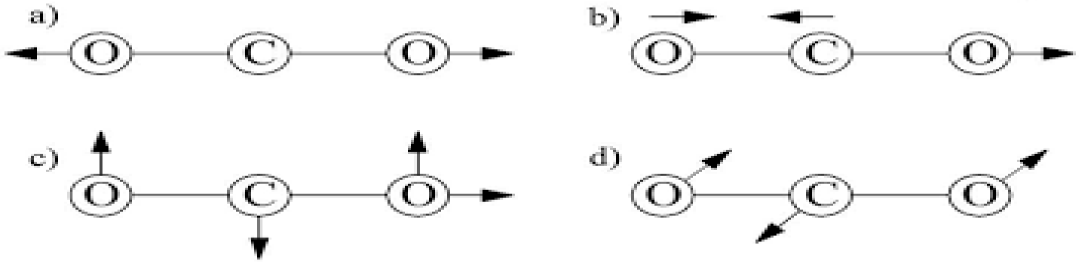

Figure 8. Vibrational frequencies of CO_2 molecule

In the symmetric stretch of CO_2 molecule, the dipole moment remains unchanged so this frequency is IR inactive. In the asymmetric stretch, the dipole moment changes direction as well as quantity, Therefore, this frequency is IR active. Considering the two degenerate bending frequencies of CO_2 molecule, it is very clear that the dipole moment changes, thus bending frequency is also IR active. We can calculate the number of vibrational frequencies of any molecule, provided we know the geometry of the molecule. The following table lists the vibrational frequencies of a few molecules. However, very often these frequencies merge with each other and only a few frequencies are seen in the IR spectrum.

S.No	Molecule	TOTAL DEGREES OF FREEDOM	TRANSLATIONAL DEGREES	ROTATIONAL DEGREES	VIBRATIONAL DEGREES
1	HBr	6	3	2	6-3-2=1
2	O_2	6	3	2	6-3-2=1
3	OCS	9	3	2	9-3-2=4
4	SO_2	9	3	3	9-3-3=3
5	BCl_3	12	3	3	12-3-3=6
6	C_2H_2	12	3	2	12-3-2=7
7	CH_4	15	3	3	15-3-3=9
8	CH_3I	15	3	3	15-3-3=9
9	C_6H_6	36	3	3	36-3-3=30

It should be easy to predict vibrational frequencies of a few simple molecules like HCN.
Since it is a triatomic but linear molecule, it will have 4 vibrational frequencies. All frequencies will be IR active, as, unlike CO_2, the symmetric stretch will also be IR active.

References

1.Wikipedia

2. Fundamentals of Molecular Spectroscopy by C N Banwell.

3. Physical Chemistry, Vol III, by Prof. Ajay Taneja