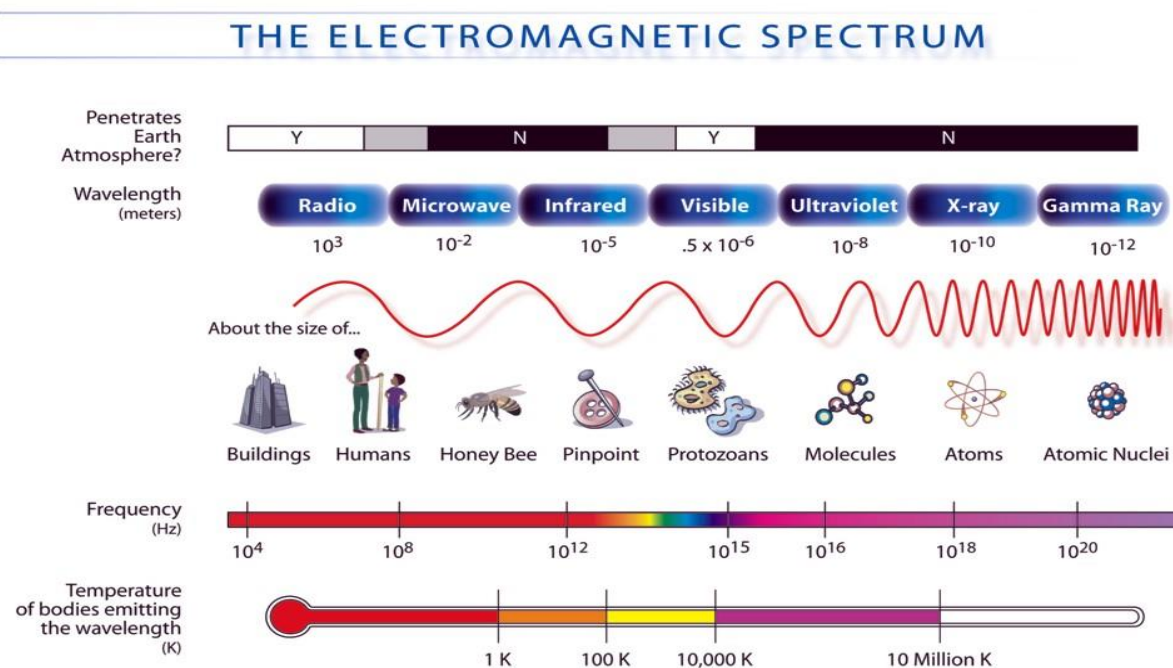


Vibrational Spectroscopy

It is the branch of spectroscopy which deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. Based on the relationship with the visible spectra IR is divided into Near, Mid and Far-Infrared.

- Near Infrared $14000\text{-}4000\text{ Cm}^{-1}$
- Mid Infrared $4000\text{-}400\text{ Cm}^{-1}$
- Far Infrared $400\text{-}10\text{ Cm}^{-1}$

These spectra originate from the transitions included between the induced between the vibrational energy levels of a molecule on the absorption of radiation belonging to the infrared region. A molecule can vibrate in many ways and each way is called vibrational mode.



What kind of sample absorbs IR radiation?

- Only vibration which alters molecule dipole moment and having the IR absorption frequency in the IR region .
- If the molecule is IR active ,it must be associated with change in the dipole.A permanent dipole is not necessary but a change in dipole is not necessary but change in dipole moment is required.

- Gas molecules such as O₂, H₂ and Cl₂ don't have a dipole moment, means no IR absorption occurs. H₂O have a dipole moment so it will give IR absorption. CO₂ in case of symmetric stretching IR inactive and in case of Asymmetric stretching it is IR active.

Theory of Infrared Absorption Spectroscopy

In order for IR absorbance to occur two conditions must be met:

1. There must be a change in the dipole moment of the molecule as a result of a molecular vibration (or rotation). The change (or oscillation) in the dipole moment allows interaction with the alternating electrical component of the IR radiation wave. Symmetric molecules (or bonds) do not absorb IR radiation since there is no dipole moment.
2. If the frequency of the radiation matches the natural frequency of the vibration (or rotation), the IR photon is absorbed and the amplitude of the vibration increases.

Significance of Force constant

When an particle is displaced from its equilibrium position, a force start acting on it in opposite direction, in order to restore it in equilibrium position. If 'x' be the displacement is given by then the restoring force is given by

$$F = -Kx \text{ -----1}$$

this law is known as Hook's law. k is a proportionality constant, which measures the 'stiffness' of the bond, hence also called the force constant for the bond. The negative sign in above equation is due to the direction of the restoring force being opposite to that of the displacement.

Let us consider a diatomic molecule with atomic masses m and m joined by a chemical bond which vibrates as a one dimensional Simple Harmonic Oscillation. So classically, the vibrational frequency of mass point connected by a spring of force constant k is given by

- $\nu = \frac{1}{2\pi} \left[\frac{k}{m} \right]^{1/2} \text{ -----2}$

Vibrations take place in back and forth motion, relative to their centre of mass in the opposite direction. Vibrational frequency of a molecule is an analogue to eq 2, with mass m replaced by mass μ .

$$\nu = \frac{1}{2\pi} \left[\frac{k}{\mu} \right]^{1/2} \text{ S}^{-1}$$

To convert this S^{-1} to Cm^{-1} the unit most usually employed in vibrational spectroscopy, we must divide by the velocity of light C ,

$$\nu = \frac{1}{2\pi C} \sqrt{\frac{k}{\mu}} \text{ Cm}^{-1}$$

Units of force constant are Nm^{-1} . The potential energy of SHO as a function of displacement from equilibrium configuration is given by parabolic Hooke's law.

$$E = \frac{1}{2} k(x)^2$$

$$E = \frac{1}{2} k(r - r_{\text{eq}})^2$$

where $x = (r - r_{\text{eq}})$ is the displacement and r_{eq} is equilibrium bond length.

The solution of S.W equation for SHO gives the quantized vibrational energy levels.

$$E_v = \left(v + \frac{1}{2}\right) h \nu, \text{ where } \nu = 0, 1, 2, \dots$$

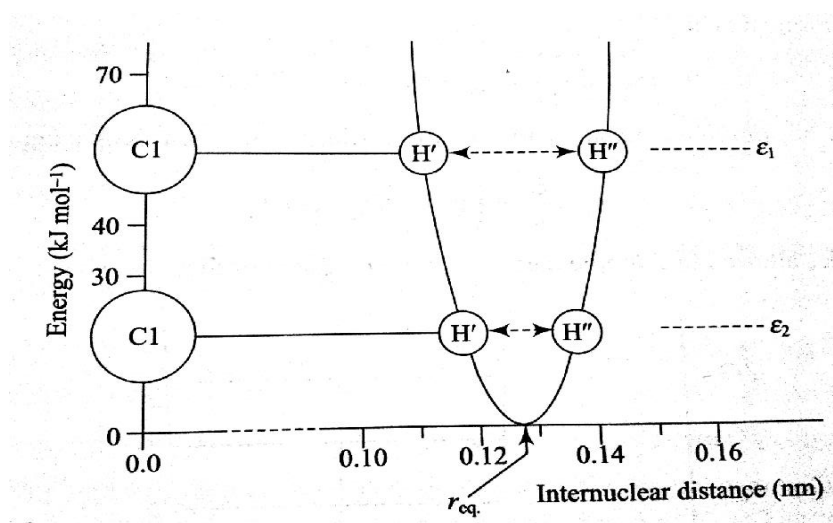
The energy of the lowest vibrational level of the oscillator is not zero but it is equal to $\frac{1}{2} h \nu$, this is called Zero-point energy. The energy levels of SHO are equally spaced, the spacing being equal to $h\nu$. To convert the energy from joules to Cm^{-1} we divide by hc , hence

$$G_v = E_v/hc = \left(v + \frac{1}{2}\right) \omega_e$$

ω_e = Equilibrium vib frequency, G_v = is called vibrational term.

Selection rule for a vibrational transition in SHO is $\Delta V = \pm 1$ (Vibrational quantum number changes by one unit)

Vibrational energy curve for Simple harmonic oscillator



To explain the harmonic oscillator let us consider a molecule. Ex HCl. In this one atom chlorine is considered to be stationary and the other molecule will oscillate between H^I and H^{II} . During the vibration, the heavy Chlorine atom stays virtually still and its lighter H atom which moves. If the energy of HCl molecule in fig 1, is increased to ϵ_1 the oscillation will become more vigorous—that is to say the degree of compression and extension will be greater—but the vibrational frequency will not change. An elastic bond, like a spring, has a certain intrinsic vibrational frequency, dependent on the mass of the system and force constant, but is independent of the amount of distortion. Oscillation frequency is represented by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \text{ S}^{-1}$$

To convert this S^{-1} to Cm^{-1} the unit most usually employed in vibrational spectroscopy, we must divide by the velocity of light C ,

$$\nu = \frac{1}{2\pi C} \sqrt{\frac{K}{\mu}} \text{ Cm}^{-1}$$

Like all molecular energies vibrational energies are quantized, and all the allowed vibrational energy for a particular system can be calculated using Schrodinger wave equation.

$$E_v = \left(v + \frac{1}{2}\right) h \nu, \text{ where } \nu = 0, 1, 2, \dots$$

When $\nu=0$, i.e. for the lowest vibrational energy then the above equation take the form

$$E_v = \left(\frac{1}{2}\right) h \nu \text{ joules } (\nu \text{ in Hertz})$$

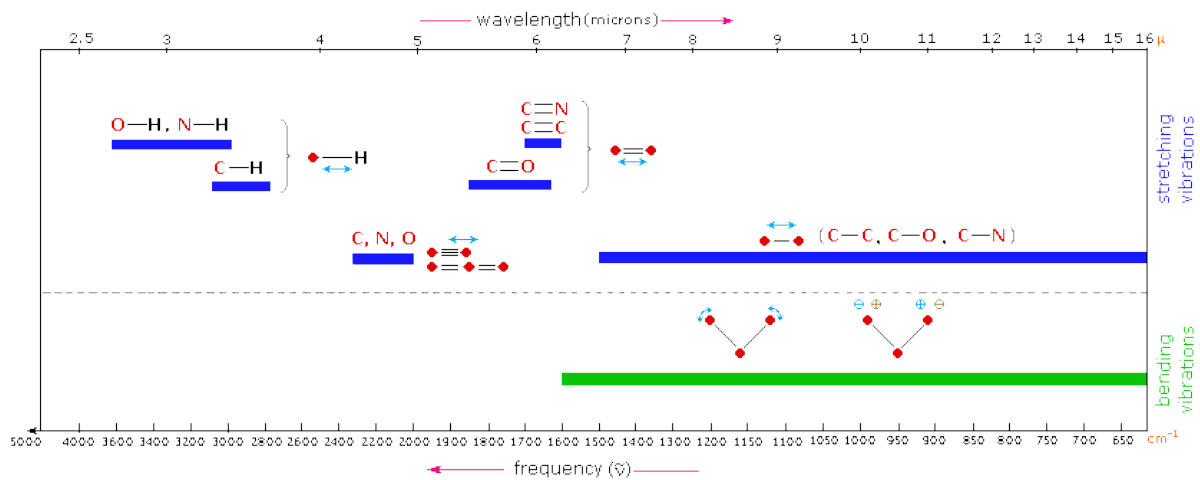
$$E_v = \left(\frac{1}{2}\right) h \nu \text{ Cm}^{-1}$$

The diatomic molecule can never have zero vibrational energy, the atom can never be completely at rest relative to each other it is equal to $\frac{1}{2} h \nu$, this is called zero point energy.

Use of the Schrodinger wave equation leads to the simple selection rule for harmonic oscillator undergoing vibrational changes:

$$\Delta \nu = \pm 1$$

Important Spectral region



4000-2500 Cm^{-1}	2500-2000 Cm^{-1}	2000-1800 Cm^{-1}	1800-1650 Cm^{-1}	1650-1550 Cm^{-1}	1550-650 Cm^{-1}
O-H N-H C-H	$\text{C}\equiv\text{C}$ $\text{C}\equiv\text{N}$	Rich information in metal carbonyls (Organo metallics)	Various types of C=O	C=C C=N N=O	C-Cl, C-O, C-N, C-C Finger print region

The fundamental IR region is divided to

- Group frequency region
 - Hydrogen stretching vibration
 - Double and
 - Triple bond region
- Finger print region

Group frequency region

- In the group frequency region absorption bands are characteristic of specific groups of atoms and relatively independent of composition of the rest of the molecule.
- It is extremely useful for diagnosing the presence or absence of certain functional groups.

Triple bond region

- 2500-2000 Cm^{-1}
- These bonds have high vibrational wave number because of the large force constant .

- The $C \equiv C$ group usually causes absorption between 2300 – 2050 but its absorption may be weak or absent because of the symmetry of the molecule.
- $C \equiv N$ groups absorb near 2300-2200

Stronger bonds are more difficult to stretch (higher force constant) and requires greater energy or higher frequency.

Hydrogen stretching vibration.

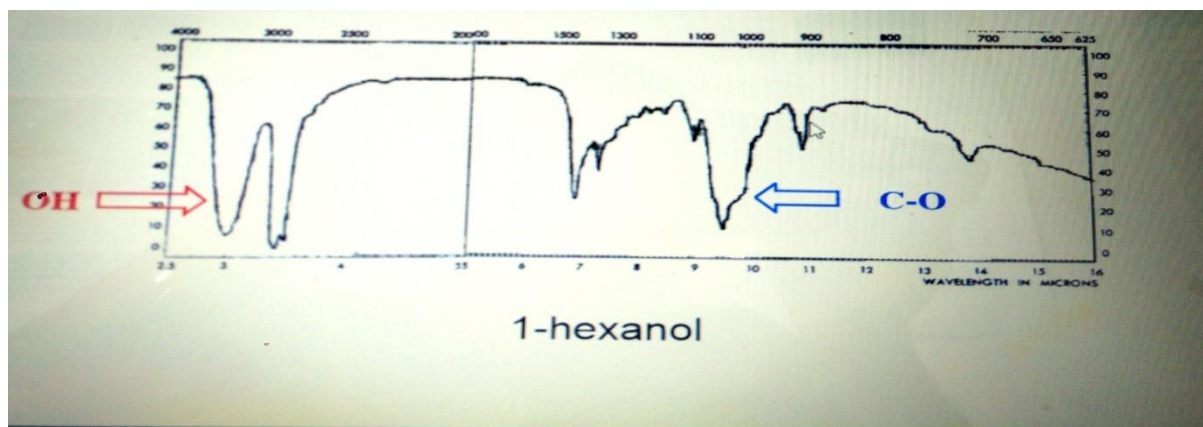
- 3700Cm^{-1} to 2500Cm^{-1}
- These vibrations occur at higher wave numbers because of the low mass of hydrogen atom.
- If H atom is replaced by D atom, the vibrational number falls by a factor of $1/\sqrt{2}$ because of the greater reduced mass of the deuterium molecule.
- The essential difference between the two types of H bonding is that, spectral shifts for inter molecular H-bonding show a strong concentration dependence, whereas spectral shifts for intra-molecular H-bonding are independent of concentration.

Double bond region

- $2000-2600\text{Cm}^{-1}$
- Absorption bands of substituted aromatic compounds fall in this range and are a good indicator of the position of the substitution.
- Carbonyl groups of ketones, aldehydes, acids etc are usually show strong absorption in the vicinity of 1700Cm^{-1}
- Alkenes may show absorption in the vicinity of 1650Cm^{-1}

Finger print region.

- Each trough in the IR spectra is caused because energy is being absorbed from the particular frequency of infrared radiation to excite the bonds in the molecule to a higher state of vibration – either stretching or bending.
- The complexity of infrared spectra in the 1450 to 600 cm^{-1} region makes it difficult to assign all the absorption bands, and because of the unique patterns found there, it is often called the **fingerprint** region. Every type of bond in a molecule has a unique natural vibrational frequency
- Therefore the IR spectrum of every molecule is unique as much as the finger print of human beings.
- By comparing IR spectra of two samples one can establish whether or not they are identical samples. If their IR spectra exactly match (coincide peak to peak) then they are likely to be same substance.
- The importance of this finger print region is that each different compound produces a different pattern of troughs in this part of the spectrum.
- IR spectrum of 1-hexanol



- The big trough in the right hand side of the spectrum indicate the C-O bond ,in the range of $1250-1050\text{ cm}^{-1}$

Vibration of polyatomic molecule

- Let us consider a molecule containing N atoms, in which we can refer the position of each atom by specifying three co-ordinates (x,y,z). Thus the total number of coordinate values is 3N we say that the molecules has 3N degree of freedom.
- For a non-linear molecule : $3N-6$ fundamental vibration For a linear molecule : $3N-5$ fundamental vibration.
- We need 3 coordinates to specify the centre of gravity of the molecule. Thus, centre of gravity of the molecule has 3 independent translational degrees of freedom. For a non-linear molecule in its equilibrium configuration, 3 rotational coordinated are needed to specify the molecular orientation about the centre of gravity. These can be the 3 angular coordinates specifying rotation about 3 mutually perpendicular axes, each passes through centre of gravity. Thus non-linear molecule has 3 independent rotational degrees of freedom. On the other hand ,a linear molecule has only two independent rotational degrees of freedom about the mutually perpendicular axes which are perpendicular to the molecular axes.

Water molecule

- For example water molecule has 3 degrees of vibrational freedom corresponding to two stretching mode and one bending mode of vibration. These are called fundamental modes or normal modes of vibration and they occur without change of center of gravity of the molecule



CO₂ molecule

- For example carbon dioxide molecule has 4 degrees of vibrational freedom corresponding to two stretching mode and two bending mode of vibration.

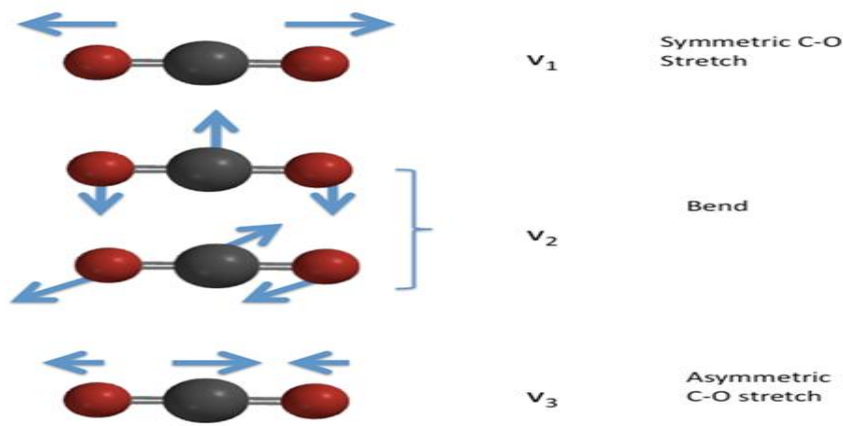


Fig. 1 Vibrational modes of CO₂

Expressions for fundamentals, overtone frequency

Fundamentals

- At the room temperature most of the molecule are in ground vibrational state.(V=0),so that the only transition of interest is that which takes place from V=0 to V=1.The vibrational frequency corresponding to this transition is called fundamental vibrational frequency. The intensity of the band is proportional to the probability of such transitions.

$$\omega = \left[\left(V + \frac{1}{2} \right) - \left(V + \frac{1}{2} \right)^2 x_g \right] - \left[\left(V + \frac{1}{2} \right) - \left(V + \frac{1}{2} \right)^2 x_g \right]$$

- $\omega_{0 \rightarrow 1} = \left[\left(1 + \frac{1}{2} \right) - \left(1 + \frac{1}{2} \right)^2 x_g \right] - \left[\left(\frac{1}{2} \right) - \left(\frac{1}{2} \right)^2 x_g \right]$

$$= 9(1-2x) \text{ Cm}^{-1}$$

Overtone frequency

- Bands corresponding to integral multiple of fundamental vibration. They are due to transition from ground state to higher vibrational states. They are very weak bands.

- **First overtone:**

$$\begin{aligned} \omega_{0 \rightarrow 2} &= \left[\left(2 + \frac{1}{2}\right) - \left(2 + \frac{1}{2}\right)^2 x \right] - \left[\left(\frac{1}{2}\right) - \left(\frac{1}{2}\right)^2 x \right] \\ &= 29(1-3x) \text{ Cm}^{-1} \end{aligned}$$

- This represents the double jump by the molecule from $v=0 \rightarrow 2$ and this
- Band occurs with small intensity. This is due to the fact that the number of molecules making such 'high jumps' is certainly low, and hence the band is low intensity.

Second overtone

- It represents a transition from $v=0 \rightarrow 3$ and such occurrences are less probable. Therefore the band corresponding to this transition is very weak in its intensity.

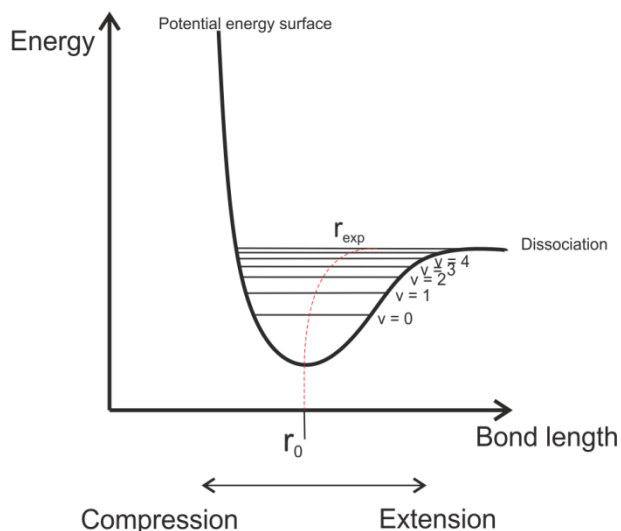
$$\begin{aligned} \omega_{0 \rightarrow 3} &= \left[\left(3 + \frac{1}{2}\right) - \left(3 + \frac{1}{2}\right)^2 x \right] - \left[\left(\frac{1}{2}\right) - \left(\frac{1}{2}\right)^2 x \right] \\ &= 39(1-4x) \text{ Cm}^{-1} \end{aligned}$$

- **Combination bands:** Two vibrational frequencies in a molecule couple to give a new frequency within the molecule. This band is a sum of the two interacting bands.

- Difference bands: Similar to combination bands. The observed frequency is the difference between the two interacting frequencies.
- Fermi resonance: When a fundamental vibration couples with overtone or combination Band, the coupled vibration is called a Fermi resonance.

An Harmonic oscillator

The Anharmonic Oscillator



- Compression Extension

Real molecules do not obey exactly the laws of simple harmonic motion.

Real bonds although elastic, are not so homogeneous as to obey Hook's law.

If the bond between atoms is stretched, for instance, there comes a point at which it will break-the molecule dissociates into atoms.

Thus for the smaller compressions and extensions the bond may be taken as perfectly elastic, for amplitude nearly 10% of the bond length, a much more complicated behaviour must be assumed.

Figure represents the energy curve for a typical diatomic molecule.

An empirical expression which suit this energy curve was derived by P.M.Morse and is called the Morse function

$$E = D_{eq} [1 - \exp\{a(r_{eq} - r)\}]^2$$

Where 'a' is a constant for a particular molecule and D_{eq} is the dissociation constant.

- When the above equation is used instead of $E = \frac{1}{2} k(r - r_{eq})^2$

In the Schrodinger equation, the pattern of the allowed vibrational energy levels is found to be

$$\epsilon_V = \left[\left(V + \frac{1}{2} \right) \omega_e - \left(V + \frac{1}{2} \right)^2 x \omega_e \right] \text{Cm}^{-1} \quad (V=0,1,2..)$$

- ω_e is an oscillation frequency

The selection rule for anharmonic oscillator are found to be $\Delta V = \pm 1, \pm 2, \pm 3$.

- **Note**

- $\Delta \epsilon_{J,V} = \omega_0 + 2Bm \text{Cm}^{-1}$ It represent combined rotation vibration spectrum. Since $m \neq 0$, the line at ω_0 itself will not appear.
- Lines to the low-frequency side of ω_0 , corresponding to negative m (that is $\Delta J = +1$) are referred to as the P branch.
- The higher frequency side (m positive, $\Delta J = -1$) are called R branch.

Vibrational-Rotational spectrum

As the energy required for rotation is much less than that required for vibration, the vibrational motion is always

accompanied by rotational motion & hence we do not have a pure vibrational spectra; instead we have a vibrational-rotational spectra.

As rotational motion & vibrational motion take place independent of each other, the total energy of the molecule may be taken as the sum of the rotational energy & vibrational energy.

$$E_{\text{total}} = E_r + E_v$$

$$\Delta \epsilon_{i,v} = \omega_0 + 2Bm \text{ Cm}^{-1} \rightarrow 1.$$

It represents combined rotational-vibrational spectrum, since

$m \neq 0$ the line at ω_0 itself will not appear. This wave number is called the band origin or band centre. Lines to the low frequency side of ω_0 corresponding to the negative m (that is $\Delta J = -1$) are preferred to as the P branch.

The higher frequency side (m positive, $\Delta J = +1$) are called R branch.

Vibrational-Rotational spectra of CO:

In the fundamental vibration-rotation band of CO, under high resolution, with some lines in the P & R branches numbered according to their J'' values. From the observed wave numbers of the first 5 lines in each branch, the band centre is about 2143 Cm^{-1} while the average line separation near the centre is 3.83 Cm^{-1} .

$$2B = 3.83 \text{ Cm}^{-1}, B = 1.915 \text{ Cm}^{-1}$$

This is in satisfactory agreement with the value

$B = 1.92118 \text{ Cm}^{-1}$ derived by microwave studies & we could, therefore have obtained quite good values for the rotational constant & hence the moment of inertia & bond length from IR data alone. The spectrum of CO under much poorer resolution,

when the rotational fine structure is blurred out to an envelope. By equation $J = \sqrt{\frac{KT}{2hcB}} - \frac{1}{2}$ that the maximum population of levels, & hence the maximum intensity of transition occurs at a J value of $\sqrt{\frac{KT}{2hcB}} - \frac{1}{2}$. Remembering that $m = J + 1$, substituting in equation (1) $m = \pm \sqrt{\frac{KT}{2hcB}} - \frac{1}{2}$ & we obtain

$$\nu_{\text{max intensity}} = \omega_0 \pm 2B\left(\sqrt{\frac{KT}{2hcB}} - \frac{1}{2}\right)$$

Where + & - sign refer to the R & P branches respectively.

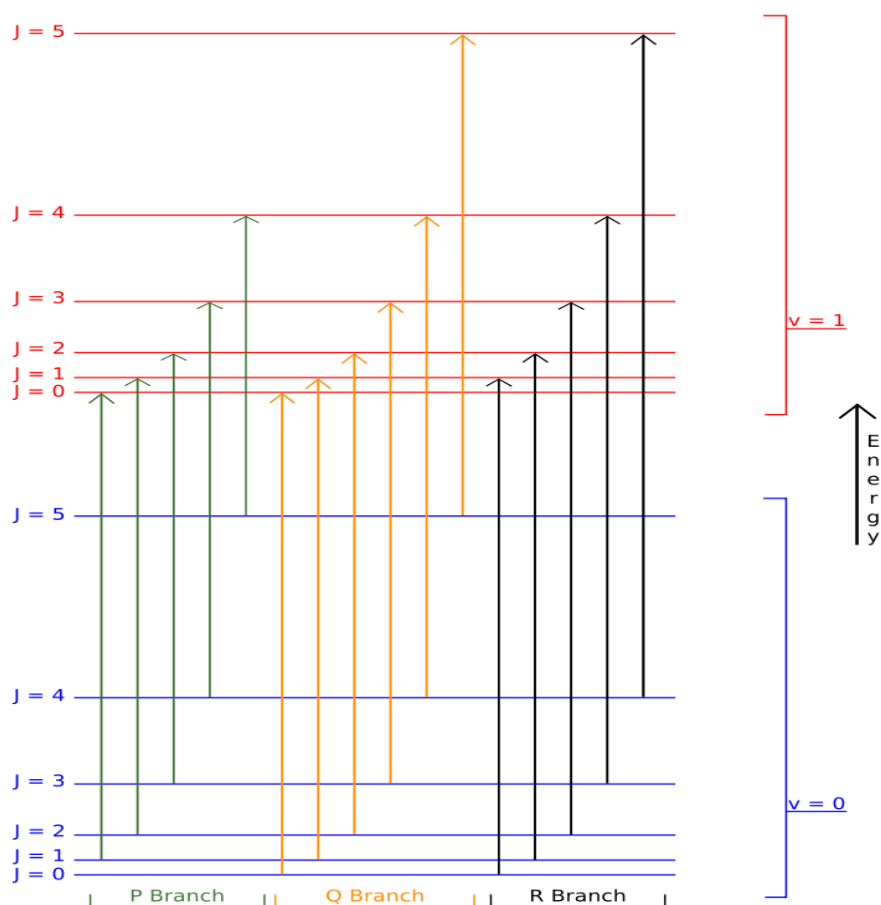


Fig: Rot-Vibrational energy level diagram for linear molecule

Parallel and perpendicular vibrations

Parallel vibration

The selection rule for these is identical with that for diatomic molecule,

$$\Delta J = \pm 1 \quad \Delta V = \pm 1$$

All the diatomic molecule are linear and hence they undergo only parallel vibration. The spectra will thus be similar in appearance, consisting of P and R branches with lines about equally spaced on each side, no line occur at band centre. If we consider a larger molecule then its mass is greater so, its moment of inertia is larger, the B value correspondingly smaller, and the P or R spacing will be less. The spacing of CO₂ is about 2.8-3.0 cm⁻¹. The spacing of CO is about 4 cm⁻¹. For still larger molecules, the value of B may be so small, that separate lines can no longer be resolved.

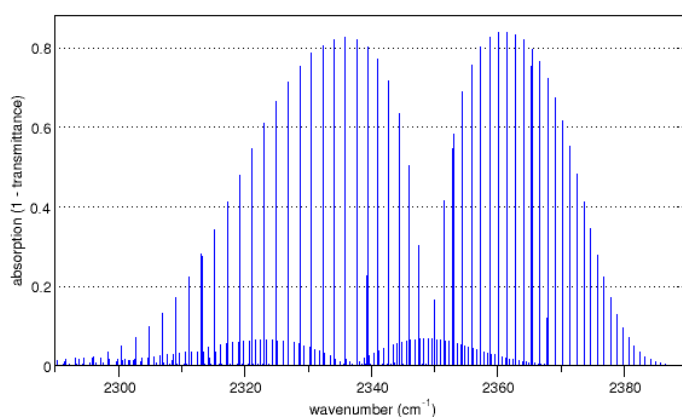


Fig: Spectrum of the asymmetric stretching (parallel) band of [carbon dioxide](#)

Perpendicular vibration

$$\Delta J=0, \pm 1 \quad \Delta V=\pm 1$$

This implies that for the first time, a vibrational change can take place with no simultaneous rotational transition. This result is illustrated in the below figure, which shows the same energy levels and transitions with the addition of $\Delta J=0$ transitions.

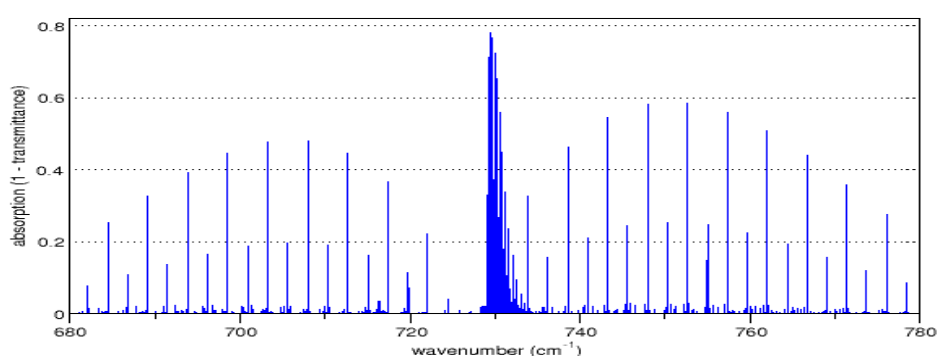


Fig: Spectrum of a perpendicular band from [acetylene](#)

Factors affecting group frequency

1. Electronic effect:

Change in the absorption frequencies for a particular group take place when the substituents in the neighbourhood of that particular group are changed.

It includes

Mesomeric effect Inductive effect *Field effect

Inductive effect :

The introduction of the alkyl group causes the +I effect which results in the lengthening or weakening of the bond. Hence the force constant is lowered and wave number of absorption decreases.

Let us compare the wave number of C=O absorption for the following compounds.

Formaldehyde - 1750cm^{-1}

Acetaldehyde - 1745cm^{-1}

Acetone - 1715cm^{-1}

Introduction of electronegative group causes -I effect, which results in bond order to increase. Hence the force constant increases and the wave number rises.

Mesomeric effect

It causes the lengthening or the weakening of a bond leading in the lowering of absorption frequency. As Nitrogen atom is less electronegative than oxygen atom, the electron pair on nitrogen atom in amide is more labile and participate more in conjugation. Due to the greater degree of conjugation, the C=O absorption frequencies is much less in amides as compared to esters.

2 Steric effects:

When atoms are put close to each other, there is a loss in energy. The electrons near the atom want to stay away from each other. Because of this interaction there is a steric hindrance which causes a change in the reactivity of the molecule. It may also change in the shape of the molecule. So because of the steric effect there is change in the stretching frequencies.

3 Ring strain

Ring strain is a type of instability that exists when bonds in the molecule form angles that are abnormal. Strain is mostly seen in lower cycloalkanes like cyclopropane, cyclobutanes, whose internal angles are substantially smaller than the idealized value of approximately 109° . Because of high strain, the heat of combustion for these small rings is elevated. Because of the ring strain there is a change in the stretching frequencies.

4 Hydrogen bonding

Hydrogen bonding, especially in O-H and N-H compounds, give rise to a number of effects in IR spectra, and the importance here can scarcely be overemphasized. Most of the polar solvents such as acetone or benzene will certainly influence O-H and N-H absorptions. Carbonyl groups or aromatic

rings in the same molecule as the O-H or N-H group may cause similar shifts by intramolecular action.

Carbonyl compounds: In carbonyl compounds hydrogen bonding will influence not only the O-H vibration frequency but also C=O vibration. The key factor is that the basicity of the C=O group. The more basic it is, the stronger will be the hydrogen bond that it can form. The extreme case of the protonation shows that the C=O bond has increased single-bond character and longer length. The same tendency occurs in hydrogen bonding, leading to a lowering of the vibration frequency.

KAVYA .H.V

ASSISTANT PROFESSOR

PG DEPARTMENT OF CHEMISTRY

JSS COLLEGE OF ARTS COMMERCE
SCIENCE, OOTY ROAD MYSURU.

