

UNIT 2

MOLECULAR SPECTROSCOPY

Electromagnetic spectrum – Interaction of radiation with matter – Energy levels in molecules – Microwave spectroscopy – Principle – Classification of molecules based on moment of Inertia – Rotational energy expression (J levels) – Calculation of J for CO molecule – Vibrational spectroscopy – Normal modes of vibrations – Vibrations of polyatomic molecules (CO_2 and H_2O) – Determination of Force constant – Electronic transitions in organic molecules – Mathematical derivation of BeerLambert's law – Stimulated Emission – Lasers in action – Excimer laser, Diode laser and Gas laser.

2.1 INTRODUCTION

Spectroscopy is the branch of science dealing with the study of interaction of electromagnetic radiation with matter like atoms and molecules. The interaction of EMR with matter gives rise to two types of spectra namely atomic spectra and molecular spectra. Atomic spectrum arises from the transition of electrons from one energy level to another due to changes of energy in the atom. Molecular spectrum involves transition of electrons between rotational and vibrational energy levels in addition to electronic transition. Therefore molecular spectrum is much more complicated than the atomic spectrum. Moreover, molecular spectrum consists of bands composed of innumerable closely packed lines. Molecular Spectroscopy provides a clear image of how diatomic and polyatomic molecules interact by looking at the Frequency, Wavelength, Wave number, Energy, and molecular process also provides most useful information regarding the shape and size of molecules, the bond angles, bond lengths, strength of bonds and bond dissociation energies. Hence molecular spectroscopy is of great use in determining structure and constitution of

Molecular Spectroscopy

compounds. Before taking up their systematic study, it is necessary that the students must learn about electromagnetic spectrum and molecular energy levels.

2.2 ELECTROMAGNETIC RADIATIONS (EMR)

Electromagnetic radiation is a form of energy that is produced by oscillating electric and magnetic fields, traveling through a vacuum or matter. They propagate through space along a linear path and with a constant velocity. The oscillations in the electric and magnetic fields are perpendicular to each other, and to the direction of the wave's propagation. Figure 2.1 shows an example of plane-polarized electromagnetic radiation, consisting of a single oscillating electric field and a single oscillating magnetic field.

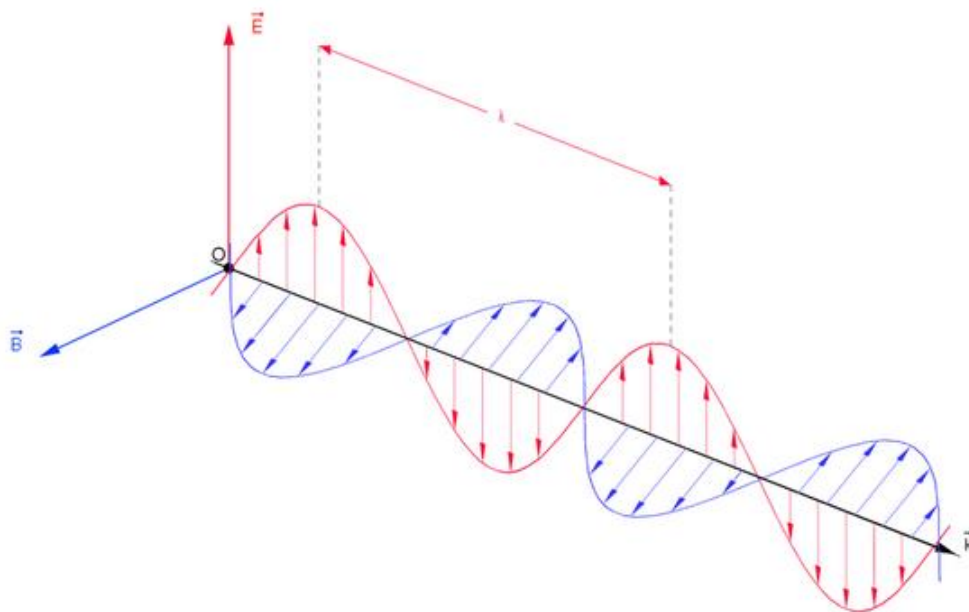


Fig 2.1 Electromagnetic radiation

Molecular Spectroscopy

2.3 CHARACTERIZATION OF EMR

The electromagnetic radiations are generally characterized by wavelength (λ), frequency(ν), wave number ($\bar{\nu}$) and energy(E).

Wavelength (λ): The linear distance between successive crests or trough of a wave is known as wavelength. It is usually expressed in centimetre or millimetres.

Frequency (ν): The number of vibrations or oscillations per second is known as frequency. It is expressed in Hertz.

Wave number ($\bar{\nu}$): The reciprocal of wavelength is known as wave number. It is expressed in cm^{-1} .

Energy of EMR (E): Electromagnetic radiations consist of particles having small packets of energies called quanta or photons. Photons possess the characteristic of wave and travel with the speed of light. The amount of energy corresponding to one photon is expressed by Planck's equation as

$$E = h\nu \text{ or } E = \frac{hc}{\lambda}$$

Where h – Planck's constant ($6.62 \times 10^{-34} \text{J}$)

ν - frequency in Hz

λ – wavelength in cm.

Unit conversion:

$$1 \mu\text{m} = 10^{-6} \text{m}$$

$$1 \text{ nm} = 10^{-9} \text{m} = 10 \text{ \AA}$$

2.3.1 Interaction of EMR with Matter

In order to interact with the electromagnetic radiation, the molecules must have some electric or magnetic effect that could be influenced by the electric or magnetic components of the radiation.

Molecular Spectroscopy

- i. In NMR spectroscopy, for example, the nuclear spins have magnetic dipoles aligned with or against a huge magnetic field. Interaction with radiofrequency of appropriate energy results in the change in these dipoles.
- ii. Rotations of a molecule having a net electric dipole moment, such as water will cause changes in the directions of the dipole and therefore in the electrical properties.
- iii. Vibrations of molecules can result in changes in electric dipoles that could interact with the electrical component of the electromagnetic radiation.
- iv. Electronic transitions take place from one orbital to another. Owing to the differences in the geometry, size, and the spatial organization of the different orbitals, an electronic transition causes change in the dipole moment of the molecule
- v. The above examples suggest that a change in either electric or magnetic dipole moment in a molecule is required for the absorption or emission of the electromagnetic radiation.

2.3.2 Electromagnetic spectrum

Electromagnetic spectrum is the arrangement of various types of electromagnetic radiations in order of their increasing wavelengths or decreasing the frequencies.

Regions of the electromagnetic spectrum

NMR	ESR	MICRO WAVE	INFRA RED	VISIBLE &UV	X- RAY	γ- RAY	Unit
10 m	100 cm	1 cm	100 μm	1 μm	10 nm	100 pm	Wavelength (λ)
10^{-1}	10^{-2}	1	100	10^4	10^6	10^8	Wave number (cm^{-1})
10^{-3}	10^{-1}	10	10^3	10^5	10^7	10^9	Energy (Joules/mole)

Molecular Spectroscopy

Since, cosmic rays have the highest frequencies while radio waves have the lowest frequencies. All the types of radiations of electromagnetic radiations travel with the same speed of light but they differ in their wavelength from each other. The arrangement of different types of emr with increasing order of their wavelength are cosmic rays < γ -rays < X-rays < ultraviolet rays < visible < infrared rays < micro waves < radio waves.

2.3.3 Energy levels in molecules

The electronic transitions in an atom are due to absorption or emission of electromagnetic radiation. We have further stated that electronic transitions in an atom are quantized and the resulting line emission spectra correlate with the difference between the electronic energy levels. There are more possibilities for transition between various energy levels in the polyatomic molecules than those in individual atoms. The total energy of a molecule is the sum of four different types of energy, viz., translational, rotational, vibrational and electronic. Therefore, absorption or emission of energy (electromagnetic radiation) may cause changes in some or all of these types of energy, and molecular spectra provide a method of measuring these changes. Before going into further details of molecular energy changes, their measurements and interpretation, let us first define the energy types present in molecules. Energy can be stored either as potential energy or kinetic energy, in a variety of ways including:

- **Translational energy (E_{trans}):** Translational Energy (E_{trans}) is concerned with the overall movement of the molecules along the three axes. It is significant only in gases and to a lesser extent for liquids. In solids, translational energy is minimum. Here small amounts of energy stored as kinetic energy. This is unquantized (can take any value) and hence is not relevant to spectroscopy.
- **Rotational energy (E_{rot}):** involves the spinning of molecules about the axes passing through their centre of gravity. Here, kinetic energy associated with the tumbling motion of molecules. This is quantized.

Molecular Spectroscopy

- **Vibrational energy (E_{vib}):** is associated with vibrations within a molecule such as the stretching or the bending of bonds. In stretching type, the bond length varies but in bending type, bond angle varies. Here, the oscillatory motion of atoms or groups within a molecule (potential energy \leftrightarrow kinetic energy exchange). This is quantized.
- **Electronic energy (E_{elec}):** involves changes in the distribution of electrons by the promotion of electrons to higher levels on absorption of energy. This is similar to electronic energy changes in atoms. Here energy stored as potential energy in excited electronic configurations. This is quantized.

If E is the energy of a molecule, it can be expressed as the sum of translational, rotational, vibrational and electronic contributions. $E = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}}$

The energies of molecules with spacing of energy levels of different types of energy as shown in fig.2.2. It is clear that electronic levels are much more widely spaced than vibrational levels, which in turn are more widely spaced than rotational levels.

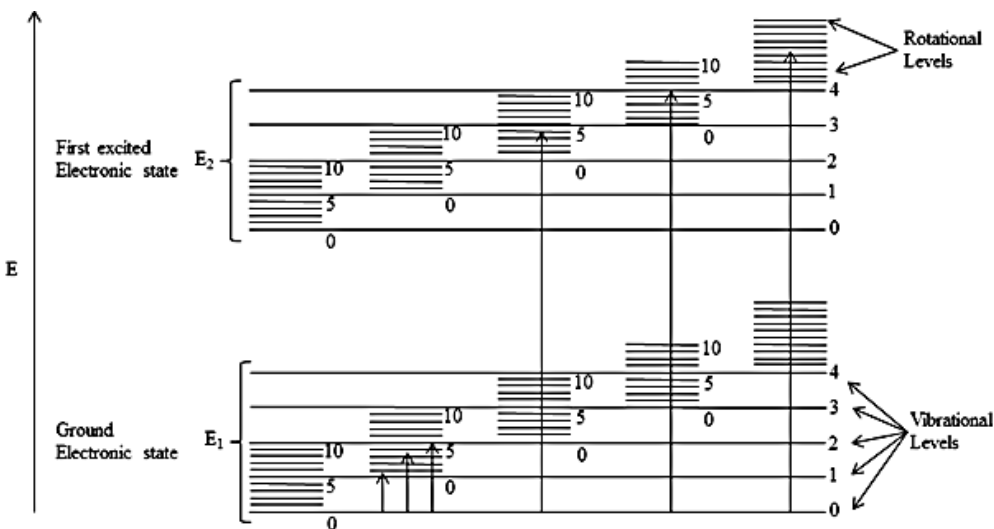


Fig 2.2. Representation of Electronic , Vibrational and Rotational energy levels

2.4. MICROWAVE SPECTROSCOPY

When a gas molecule is irradiated with microwave radiation, a photon can be absorbed through the interaction of the photon's electric field with the electrons in the molecules. For the microwave region this energy absorption is in the range needed to cause transitions between rotational states of the molecule. However, only molecules with a permanent dipole that changes upon rotation can be investigated using microwave spectroscopy. This is due to the fact that there must be a charge difference across the molecule for the oscillating electric field of the photon to impart a torque upon the molecule around an axis that is perpendicular to this dipole and that passes through the molecule's center of mass.

This interaction can be expressed by the transition dipole moment for the transition between two rotational states

$$\text{Probability of Transition} = \int \Psi_{\text{rot}(F)}^* \mu \Psi_{\text{rot}(I)} d\tau$$

Where $\Psi_{\text{rot}(F)}^*$ is the complex conjugate of the wave function for the final rotational state, $\Psi_{\text{rot}(I)}$ is the wave function of the initial rotational state, and μ is the dipole moment operator with Cartesian coordinates of μ_x , μ_y , μ_z . For this integral to be nonzero the integrand must be an even function. This is due to the fact that any odd function integrated from negative infinity to positive infinity, or any other symmetric limits, is always zero.

2.4.1 Selection Rule:

In addition to the constraints imposed by the transition moment integral, transitions between rotational states are also limited by the nature of the photon itself. A photon contains one unit of angular momentum, so when it interacts with a molecule it can only impart one unit of angular momentum to the molecule. This leads to the selection rule that a transition can only occur between rotational energy levels that are only one quantum rotation level (J) away from another.

$$\Delta J = \pm 1$$

Where J is the rotational quantum number

Molecular Spectroscopy

2.4.2 Degrees of Freedom

A molecule can have three types of degrees of freedom and a total of $3N$ degrees of freedom, where N equals the number of atoms in the molecule. These degrees of freedom can be broken down into 3 categories.

- **Translational:** These are the simplest of the degrees of freedom. These entail the movement of the entire molecule's center of mass. This movement can be completely described by three orthogonal vectors and thus contains 3 degrees of freedom.
- **Rotational:** These are rotations around the center of mass of the molecule and like the translational movement they can be completely described by three orthogonal vectors. This again means that this category contains only 3 degrees of freedom. However, in the case of a linear molecule only two degrees of freedom are present due to the rotation along the bonds in the molecule having a negligible inertia.
- **Vibrational:** These are any other types of movement not assigned to rotational or translational movement and thus there are $3N - 6$ degrees of vibrational freedom for a nonlinear molecule and $3N - 5$ for a linear molecule. These vibrations include bending, stretching, wagging and many other aptly named internal movements of a molecule. These various vibrations arise due to the numerous combinations of different stretches, contractions, and bends that can occur between the bonds of atoms in the molecule.

Each of these degrees of freedom is able to store energy. However, In the case of rotational and vibrational degrees of freedom, energy can only be stored in discrete amounts. This is due to the quantized break down of energy levels in a molecule described by quantum mechanics. In the case of rotations the energy stored is dependent on the rotational inertia of the gas along with the corresponding quantum number describing the energy level.

Molecular Spectroscopy

2.4.3 Classification of Molecules Based on Moment of Inertia:

Microwave rotational spectroscopy uses microwave radiation to measure the energies of rotational transitions for molecules in the gas phase only (due to intermolecular interactions hindering rotations in the liquid and solid phases of the molecule). It accomplishes this through the interaction of the electric dipole moment of the molecules with the electromagnetic field of the exciting microwave photon. In microwave spectroscopy, molecules may be classified into 5 categories based on their shape and the inertia around their 3 orthogonal rotational axes. These 5 categories include diatomic molecules, linear molecules, spherical tops, symmetric tops and asymmetric tops.

The moment of inertia I of any molecule about any axis through the centre of gravity is given by

$$I = \sum m_i r_i^2$$

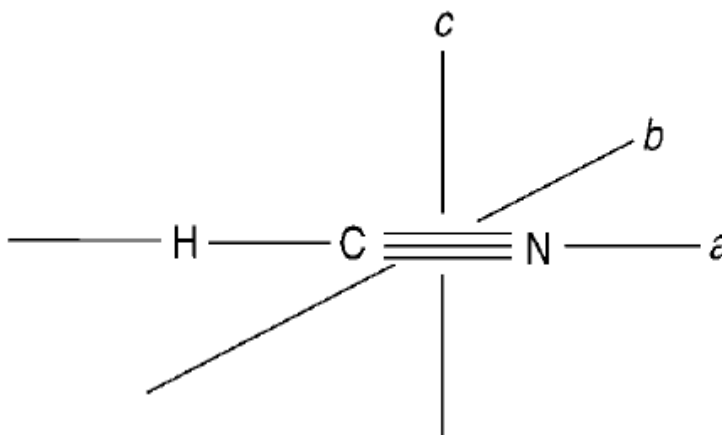
Where m_i and r_i are the mass and distance of atom i from the axis. There is one of these axes, conventionally labeled the c axis, about which the moment of inertia has its maximum value and a second axis, labeled the a axis, about which the moment of inertia has its minimum value. It can be shown that the a and c axes must be mutually perpendicular. These with a third axis, the b axis, which is perpendicular to the other two, are called the principal axes of inertia and the corresponding moments of inertia I_A , I_B and I_C are the principal moments of inertia. In general, according to convention $I_C \geq I_B \geq I_A$.

1. **Linear molecules:** In these molecules, atoms are arranged in a straight line, such as HCl, HCN, Carbon oxy sulphide ($O=C=S$) etc., the three directions of rotations may be taken as a) about the bond axis b) end-over-end rotations in the plane of the paper, and c) end-over-end rotation at right angles to the plane. It is evident that the moments of b and c are the same (i.e. $I_B = I_C$) while that of I_A is very small, taken as approximation, $I_A = 0$, For a linear

Molecular Spectroscopy

molecule the separation of lines in the rotational spectrum can be related directly to the moment of inertia of the molecule. Since the moment of inertia is quadratic in the bond lengths, the microwave spectrum yields the bond lengths directly, provided the atomic masses are known. Thus, for linear molecules we have

$$I_B = I_C, I_A = 0$$



2. **Symmetric tops:** In symmetric top, two moments of inertia are the same. For example, methyl fluoride, where three hydrogen atoms are bonded tetrahedrally to the carbon as shown below.

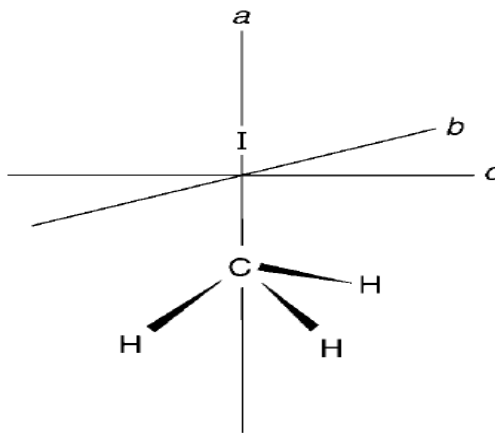
As in the case of linear molecules, the end-over-end rotation in, and out of, the plane of the paper are still identical and so we have $I_B = I_C$. The moment of inertia about the C-F bond axis is small, so such a system of molecules spinning about this axis can be imagined as a top.

$$\text{Symmetric tops: } I_B = I_C \neq I_A \quad I_A \neq 0.$$

There are two subdivisions of this class,

Molecular Spectroscopy

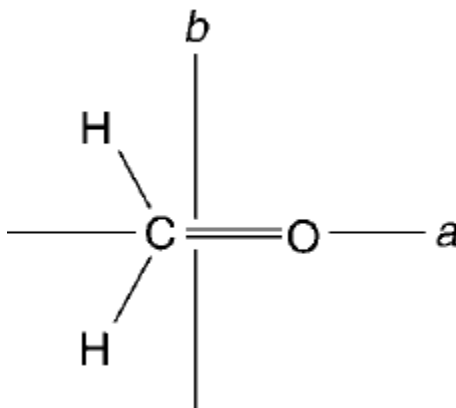
if $I_B = I_C > I_A$, then the molecule is said to be **prolate**. For example: Methyl fluoride, Methyl iodide, since the heavy iodine nucleus makes no contribution to I_a .



Where as if $I_B = I_C < I_A$, then it is said to be **oblate**. For example: Boron trichloride which is planar and symmetrical. In this case, $I_A = 2I_B = 2I_C$.

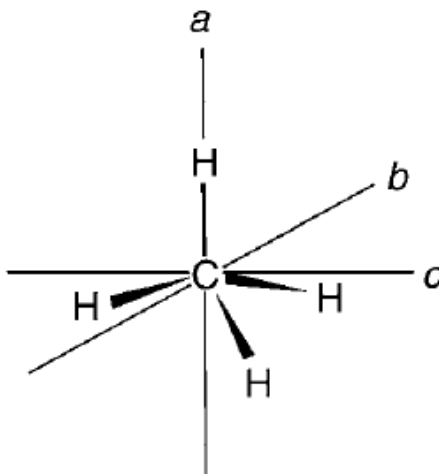
3. **Asymmetric tops:** These molecules have three orthogonal rotational axes that all have different moments of inertia and most molecules fall into this category. Unlike linear molecules and symmetric tops, these types of molecules do not have a simplified energy equation to determine the energy levels of the rotations. These types of molecules do not follow a specific pattern and usually have very complex microwave spectra. For example H_2O and vinyl chloride.

Molecular Spectroscopy



Asymmetric tops : $I_A \neq I_B \neq I_C$

4. **Spherical tops:** Spherical tops are molecules in which all three orthogonal rotations have equal inertia and they are highly symmetrical. This means that the molecule has no dipole and for this reason spherical tops do not give a microwave rotational spectrum. For example: Methane.



Spherical tops : $I_A = I_B = I_C$

2.4.4 Rotational Spectra of Diatomics

Consider a linear rigid diatomic shown in Fig.2.3.

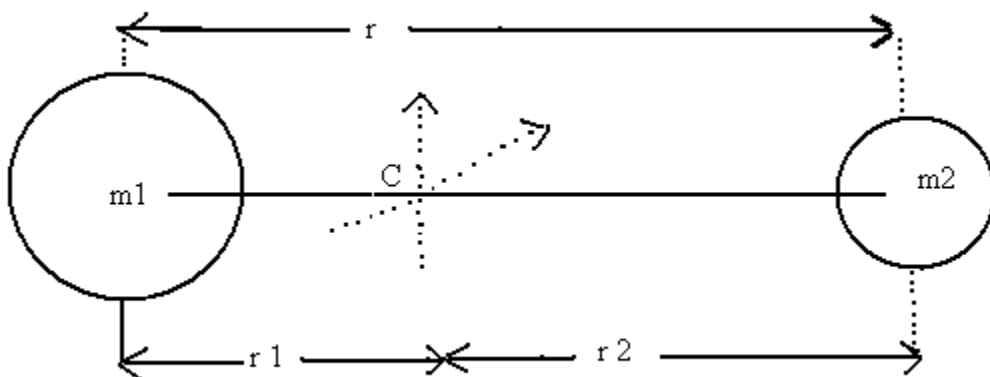


Fig 2.3 A rigid diatomic with masses m_1 and m_2 joined by a thin rod of length $r = r_1 + r_2$ the centre of mass is at C.

The two independent rotations of this molecule are with respect to the two axes which pass through C and are perpendicular to the “bond length” r . The rotation with respect to the bond axis is possible only for “classical” objects with large masses. For quantum objects, a “rotation” with respect to the molecular axis does not correspond to any change in the molecule as the new configuration is indistinguishable from the old one.

The center of mass is defined by equating the moments on both segments of the molecular axis.

$$m_1 r_1 = m_2 r_2 \quad (1)$$

The moment of inertia is defined by

Molecular Spectroscopy

$$I = m_1 r_1^2 + m_2 r_2^2 \quad (2)$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2$$

$$= r_1 r_2 (m_1 + m_2) \quad (3)$$

Since $m_1 r_1 = m_2 r_2 = m_2 (r - r_1)$, $(m_1 + m_2) r_1 = m_2 r$ Therefore,

$$r_1 = \frac{m_2 r}{m_1 + m_2} \quad \text{and} \quad r_2 = \frac{m_1 r}{m_1 + m_2} \quad (4)$$

Substituting the above equation in (3), we get

$$I = \frac{m_1 m_2 r^2}{(m_1 + m_2)} = \mu r^2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad (5)$$

Where μ , the reduced mass is given by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad (6)$$

The rotation of a diatomic is equivalent to a “rotation” of a mass μ at a distance of r from the origin C. The kinetic energy of this rotational motion is K.E. = $L^2/2I$ where L is the angular momentum, $I\omega$ where ω is the angular (rotational) velocity in radians/sec. The operator for L^2 is the same as the operator L^2 for the angular momentum of hydrogen atom and the solutions of the operator equations $L^2 Y_{lm} = l(l+1) Y_{lm}$, where Y_{lm} are the spherical harmonics.

The quantized rotational energy levels for this diatomic are

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \quad (7)$$

Molecular Spectroscopy

The energy difference between two rotational levels is usually expressed in cm^{-1} . The wave number corresponding to a given ΔE is given by

$$\nu = \Delta E / hc, \text{ cm}^{-1} \quad (8)$$

The energy levels in cm^{-1} are therefore,

$$E_J = B J (J + 1) \text{ where } B = \frac{h}{8\pi^2 I c} \quad (9)$$

The rotational energy levels of a diatomic molecule are shown in Fig. 2.4.

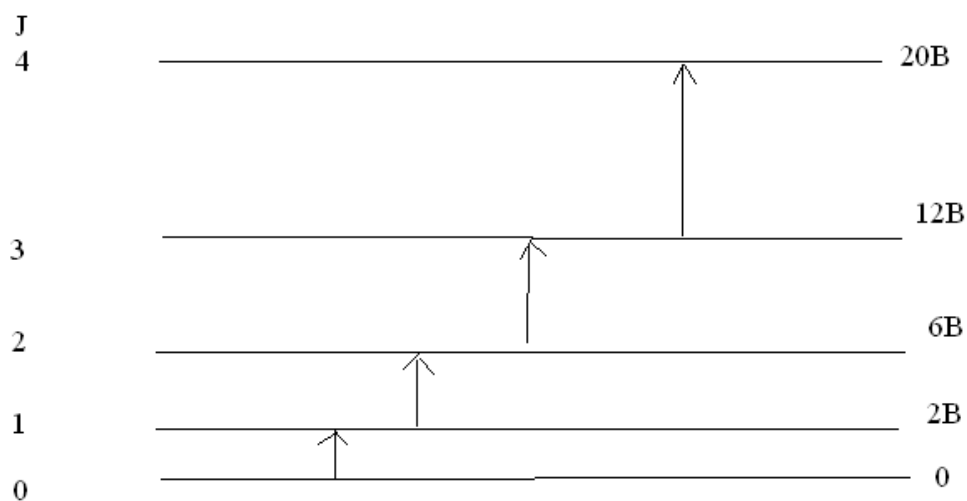


Fig 2.4 Rotational energy levels of a rigid diatomic molecule and the allowed transitions

The selection rule for a rotational transition is,

$$\Delta J = \pm 1 \quad (10)$$

Molecular Spectroscopy

In addition to this requirement, the molecule has to possess a dipole moment. As a dipolar molecule rotates, the rotating dipole constitutes the transition dipole operator μ . Molecules such as HCl and CO will show rotational spectra while H_2 , Cl_2 and CO_2 will not. The rotational spectrum will appear fig. 2.5 as follows

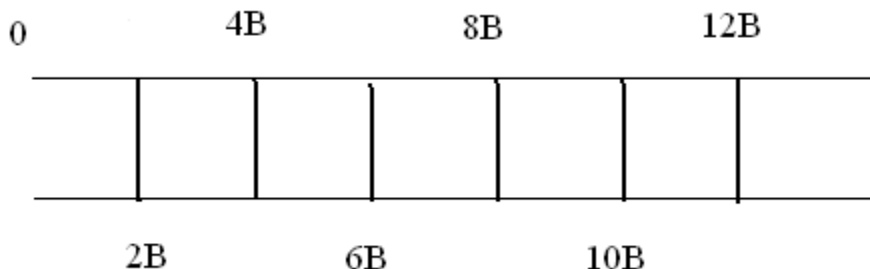


Fig 2.5 Rotational spectrum of a rigid diatomic. Values of B are in cm^{-1} . Typical values of B in cm^{-1} are 1.92118 (CO), 10.593 (HCl), 20.956 (HF), $^1\text{H}_2$ (60.864), $^2\text{H}_2$ (30.442), 1.9987 (N_2).

From the value of B obtained from the rotational spectra, moments of inertia of molecules I , can be calculated. From the value of I , bond length can be deduced.

2.4.5 Calculation of “J” for CO molecule

Example 1: Calculate J value of first three rotational transitions of CO molecule if its bond length is 112.8 pm. Given $\text{C}^{12} = 12.0001$ amu and $\text{O}^{16} = 15.9994$ amu.

(Note: to convert amu in to mass multiplied by 1.66×10^{-24})

Solution:

$$I = \mu r^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{15.9994 \times 12.001}{15.9994 + 12.001} \times 1.66 \times 10^{-24}$$

Molecular Spectroscopy

$$\mu = 1.1383 \times 10^{-23} \text{g}$$

$$\text{therefore } I = 1.1383 \times 10^{-23} \text{g} \times (112.8 \times 10^{-10})^2 = 1.447 \times 10^{-39}$$

we know that

$$\begin{aligned} B &= h/(8\pi^2 I c) = 6.626 \times 10^{-34}/(8 \times (3.14)^2 \times 1.447 \times 10^{-39} \times 3 \times 10^{10}) \\ &= 1.9351 \text{ cm}^{-1} \end{aligned}$$

Therefore the rotational transition of CO molecule for first three transition levels is as follows

$$\begin{aligned} \Delta v (J = 0 \text{ to } J = 1) &= 2B \\ &= 2 \times 1.9351 = 3.870 \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta v (J = 1 \text{ to } J = 2) &= 4B \\ &= 4 \times 1.9351 = 7.7404 \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta v (J = 2 \text{ to } J = 3) &= 6B \\ &= 6 \times 1.9351 = 11.6106 \text{ cm}^{-1} \end{aligned}$$

2.4.6. Rotational Spectra of Polyatomics

Linear molecules such as OCS and $\text{HC}\equiv\text{CCl}$ have spectra similar to diatomics. In diatomics as well as linear triatomics, $I_A = I_B$; $I_C = 0$. I_A , I_B and I_C are the three moments of inertia of molecules along three independent axes of rotation. Just as any translation can be decomposed into three independent components along three axes such as x, y and z, any rotation can be decomposed into rotations along three axes A, B, and C. The way to choose these axes is to have the simplest values of I_A , I_B and I_C . Since triatomics are heavier than the constituent diatomics, their moments of inertia are larger and the values of rotational constants, B, are smaller, in the range of 1 cm^{-1} . The value of I_A or I_B determined from the B value gives the total length of the

Molecular Spectroscopy

triatomic. To determine the two bond lengths in the linear triatomic, we need to determine the moment of inertia I_A' of an isotope of the triatomic. From two values of I_A and I_A' , we can determine the two bond lengths.

The rotational spectra of asymmetric molecules for whom $I_A \neq I_B \neq I_C$ can be quite complicated. For symmetric tops, two moments of inertia are equal i.e.,

$$I_A = I_B \neq I_C; \quad I_C \neq 0$$

In CH_3Cl for example, the main symmetry axis is the C – Cl axis. We need two quantum numbers to describe the rotational motion with respect to I_A and I_C respectively. Let J represent the total angular momentum of the molecule and K the angular momentum with respect to the C – Cl axis of the symmetric top. J takes on integer values and K cannot be greater than J (recall that $m_l \leq |l|$ for orbital angular momentum). The $(2J + 1)$ “degeneracy” is expressed through the $2J + 1$ values that K can take.

$$K = J, J - 1, \dots, 0, \dots, -(J - 1), -J$$

The rotational energies of a symmetric top are given by

$$E_{J,K} / hc = BJ(J + 1) + (A - B)K^2, \quad \text{cm}^{-1}$$

The moments of inertia are related to B and A as

$$B = \frac{h}{(8\pi^2 I_c \cdot c)} \quad \text{and} \quad A = \frac{h}{(8\pi^2 I_A c)}$$

As the energy depends on K^2 , energies for states with $+K$ and $-K$ are doubly degenerate. Thus there will be $J + 1$ levels and $(2J + 1)$ states for each value of J .

The selection rules for the symmetric top are,

$$\Delta J = \pm 1 \text{ and } \Delta K = 0$$

Molecular Spectroscopy

It can be easily shown that

$$(E_{J+1, K} - E_{J, K})/hc = 2 B J (J + 1)$$

This implies that the spectrum is independent of the value of K. The physical meaning is as follows. K refers to the rotation about the symmetry axis such as the C - Cl axis. A rotation about this axis does not change the dipole moment. We mentioned in the section on the rotational spectra of diatomics that the molecular dipole moment has to change during the rotational motion (transition dipole moment operator of Eq 5) to induce the transition. Rotation along the axis A and B changes the dipole moment and thus induces the transition.

By using rotational or microwave spectroscopy, very accurate values of bond lengths can be obtained. For example, in HCN, the C-H length is 0.106317 ± 0.000005 nm and the CN bond length is 0.115535 ± 0.000006 nm. The principle of the microwave oven involves heating the molecules of water through high speed rotations induced by microwaves. The glass container containing water however remains cold since it does not contain rotating dipoles.

2.5 VIBRATIONAL SPECTROSCOPY

The pure vibrational spectra and the vibrational – rotational spectra are observed in near IR region. Since the energy changes in vibrational transitions are always larger than those in pure rotational transitions, so the molecules in the gaseous state exhibit vibrational-rotational spectra. This spectrum is shown only by molecules possessing either permanent dipole moment or the dipole moment arising due to vibration of atoms in molecules. These molecules are IR active for example CO, NO, HCl, CN etc. The homo nuclear diatomic molecules like O₂, N₂ and Cl₂ have no permanent dipole moment of their own however, when they are subjected to electromagnetic radiation it induces an oscillating dipole moment and excite them to undergo vibrational – rotational transitions. Pure vibrational spectroscopy can be observed only in liquid, where interaction between the molecules inhibit rotation. The

Molecular Spectroscopy

IR spectroscopy is highly useful in the determination of molecular structure and for identification of functional groups in organic compounds.

Definition: Interaction of Infrared radiation with matter

Spectral Range of IR Radiation:

Near IR: 12000 cm^{-1} to 4000 cm^{-1}

MID IR: 4000 cm^{-1} to 620 cm^{-1}

Far IR: 300 cm^{-1} to 10 cm^{-1}

Principle: Vibrational spectroscopy principle can be explained in two different approaches.

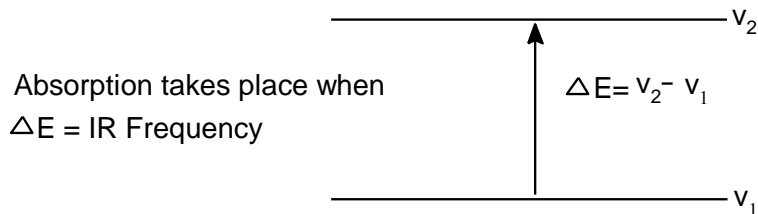
1. Classical Approach

Oscillating polar group produces stationary alternate electric fields (SAEF). These SAEFs can be presented in the form of frequency or energy. If the SAEF energy matches with IR radiation, the oscillating group absorbs energy and shows signal at corresponding frequency in the IR spectrum.

2. Quantum Approach

Irradiation of sample with IR radiation brings about changes in vibrational levels of molecules. The transition of molecule from lower vibrational energy level to higher vibrational energy level. The transition is induced by absorption of photon of IR light of appropriate frequency, which matches with energy gap between the two levels.

Molecular Spectroscopy



IR transition in a molecule

2.5.1 Vibrations of Diaatomic Molecules (Simple Harmonic Oscillator)

Taking the simple case where a diatomic molecule may be considered as a simple harmonic oscillator. Consider a diatomic molecule in which the atoms are linked by a covalent bond. The bond acts like a spring. The stiffness or elasticity of the spring (bond) is determined by a factor called force constant. The force constant is a measure of bond strength between two atoms.

An oscillator in which the restoring force(F) is directly proportional to the displacement, in accordance with Hooke's we have

$$F = -kx$$

Where x is the displacement and is equal to the distance to which the atoms have been stretched (R) minus equilibrium distance between the atoms (R_e) i.e. $x = R - R_e$, k in equation is called force constant. The negative sign indicates that the force is the restoring force, and has a direction opposite to that of the displacement. Thus if $x = 1 \text{ cm}$, $k = -F$. Hence **force constant** may be defined as the restoring force per unit displacement (or per cm) of a harmonic oscillator. It is found to be related to the equilibrium vibration frequency ω_e according to equation

$$\omega_e = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Where μ is the reduced mass of the system.

Molecular Spectroscopy

To calculate k, equation can be rewritten as follows:

$$k = 4\pi^2 \omega_e^2 \mu$$

$$k = 4\pi^2 \omega_e^2 \frac{m_1 m_2}{m_1 + m_2}$$

Where m_1 and m_2 are the masses of the oscillating atoms.

2.5.2 Vibration of Polyatomic Molecules

Degrees of freedom:

The number of variables required to describe the motion of molecule or atom

Translational motion:

The atom shifts from one point to another point in 3 dimensional space. It is a permanent displacement.

Rotational motion:

Roational of an atom through fixed axis.

Vibrational motion:

The motion brings change in bond angle and bond distance between connecting atoms

Normal mode:

It is a molecular vibration where some or all atoms vibrate together with the same frequency in a defined manner.

Poly atomic molecules show more than one fundamental vibrational absorption bands. The number of these fundamental bands is related to the degrees of freedom in a molecule. The number of degrees of freedom is equal to the sum of coordinates

Molecular Spectroscopy

necessary to locate all the atoms of a molecule in space. Each atom has three degrees of freedom corresponding to the three Cartesian coordinates (X, Y, Z) which necessary to describe its position on relative to other atoms in a molecule(fig 2.6.).

Therefore the total number of degrees of freedom in a molecule containing N-atoms is equal to $3N$ which includes rotational, vibrational and translation degrees of freedom.

Total number of degrees of freedom ($3N$) = Translational + Vibrational + Rotational

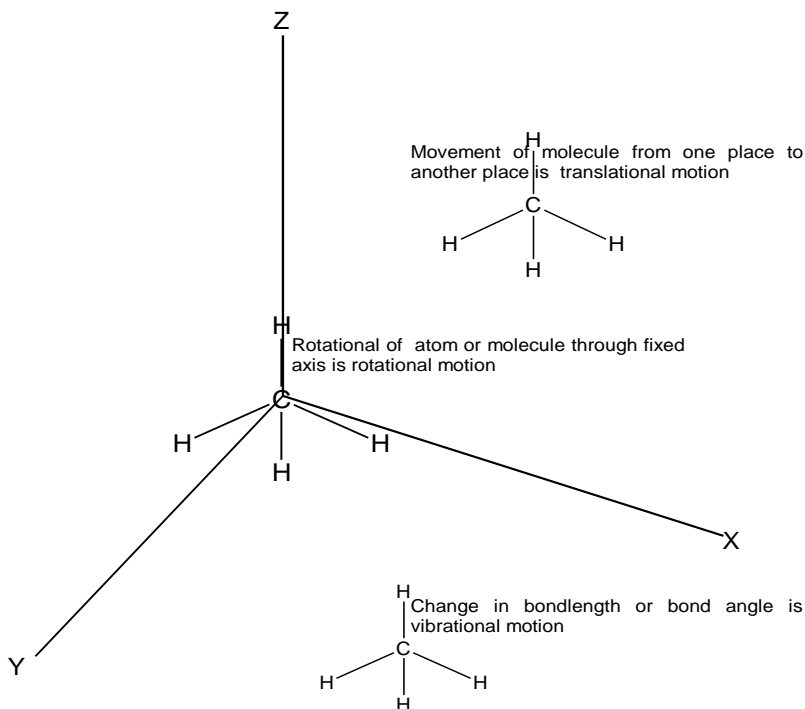


Fig 2.6 Representation of degrees of freedom of a methane molecule

Molecular Spectroscopy

S.No.	degrees of freedom	Monoatomic	Poly atomic	
			Linear molecule	Non linear molecules
1	Total	3	3N	3N
2	Translational	3	3	3
3	Rotational	0	2	3
4	Vibrational	0	3N-5	3N-6

We need 3-coordinates to specify the centre of gravity of a molecule in space. Hence the centre of gravity of the molecule has three independent translational degrees of freedom.

2.5.3 Vibrational Degrees of Freedom for Linear Molecule

If the molecule is linear then two independent modes of rotation about x and y axis are possible. Therefore the number of coordinates or degrees of freedom necessary to specify the vibrational transition is

Total degrees of freedom for polyatomic molecule = Translational + Rotational + Vibrational

$$3N = 3 + 2 + \text{Vibrational}$$

Vibrational Degrees of freedom = $3N-5$

For example: CO_2 , CO, HCl, Acetylene

Vibrational Degrees of freedom for CO = $3N-5 = 3 \times 2 - 5 = 1$

Vibrational Degrees of freedom for $\text{C}_2\text{H}_2 = 3N-5 = 3 \times 4 - 5 = 7$

Vibrational Degrees of freedom for $\text{CO}_2 = 3N-5 = 3 \times 3 - 5 = 4$

Molecular Spectroscopy

2.5.4 Degrees of Freedom of Vibration for Non-linear Molecule

In case of non-linear molecules, 3 rotational coordinates(x,y,z) are needed to specify the molecular orientation about the centre of gravity.

Total degrees of freedom for polyatomic molecule = Translational + Rotational + Vibrational

$$3N = 3 + 3 + \text{Vibrational}$$

$$\text{Vibrational degrees of freedom} = 3N - 6$$

$$\text{Vibrational Degrees of freedom for H}_2\text{O} = 3N - 6 = 3 \times 3 - 6 = 3$$

$$\text{Vibrational Degrees of freedom for CH}_4 = 3N - 6 = 3 \times 5 - 6 = 9$$

$$\text{Vibrational Degrees of freedom for NH}_3 = 3N - 6 = 3 \times 4 - 6 = 6$$

$$\text{Vibrational Degrees of freedom for C}_6\text{H}_6 = 3N - 6 = 3 \times 12 - 6 = 30$$

2.5.5 Types of Molecular Vibration

Vibration: Periodic displacement of atoms or nuclei from their equilibrium position is the vibration.

Classification: There are two types of molecular vibrations namely stretching and bending vibrations.

1. **Stretching Vibration:** The change in bond length between connecting atoms without altering the bond axis or bond angle is known as Stretching vibration. Stretching vibration are two types (Fig.)

a. Symmetric stretching vibration:

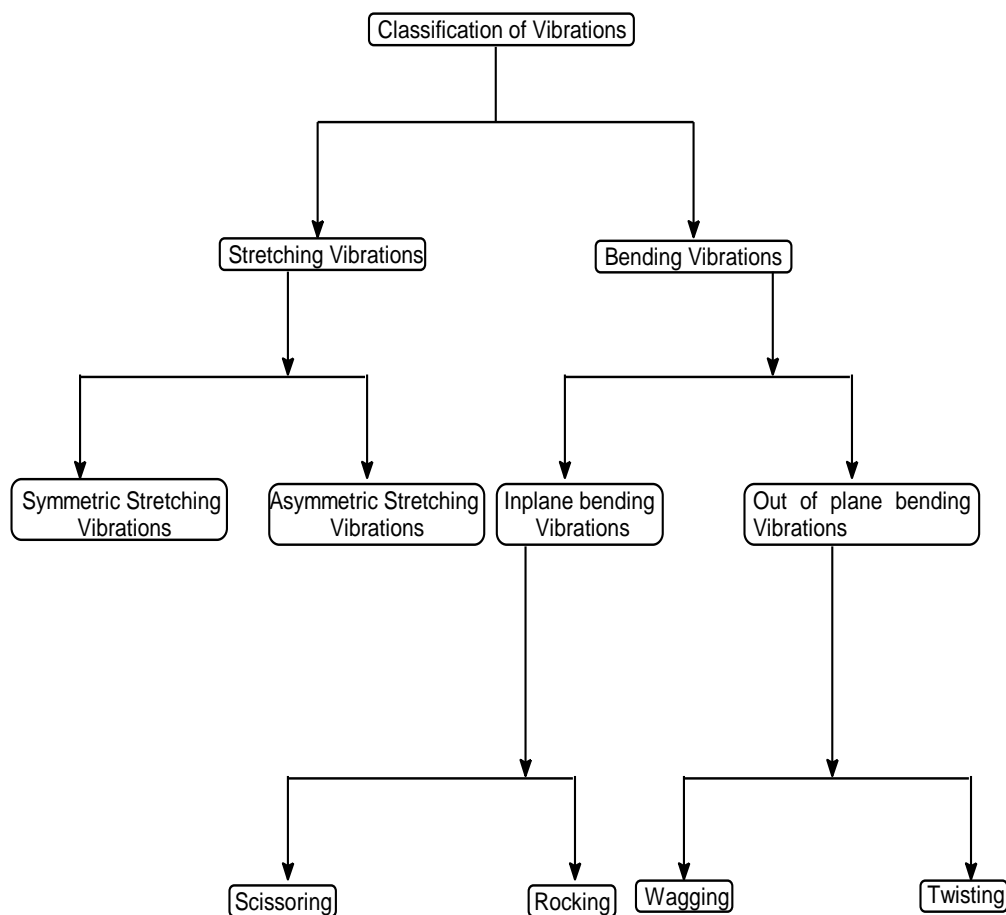
At the time of vibration reference bonds subjected to either expansion or compression (i.e. Opposite direction of movement)

Molecular Spectroscopy

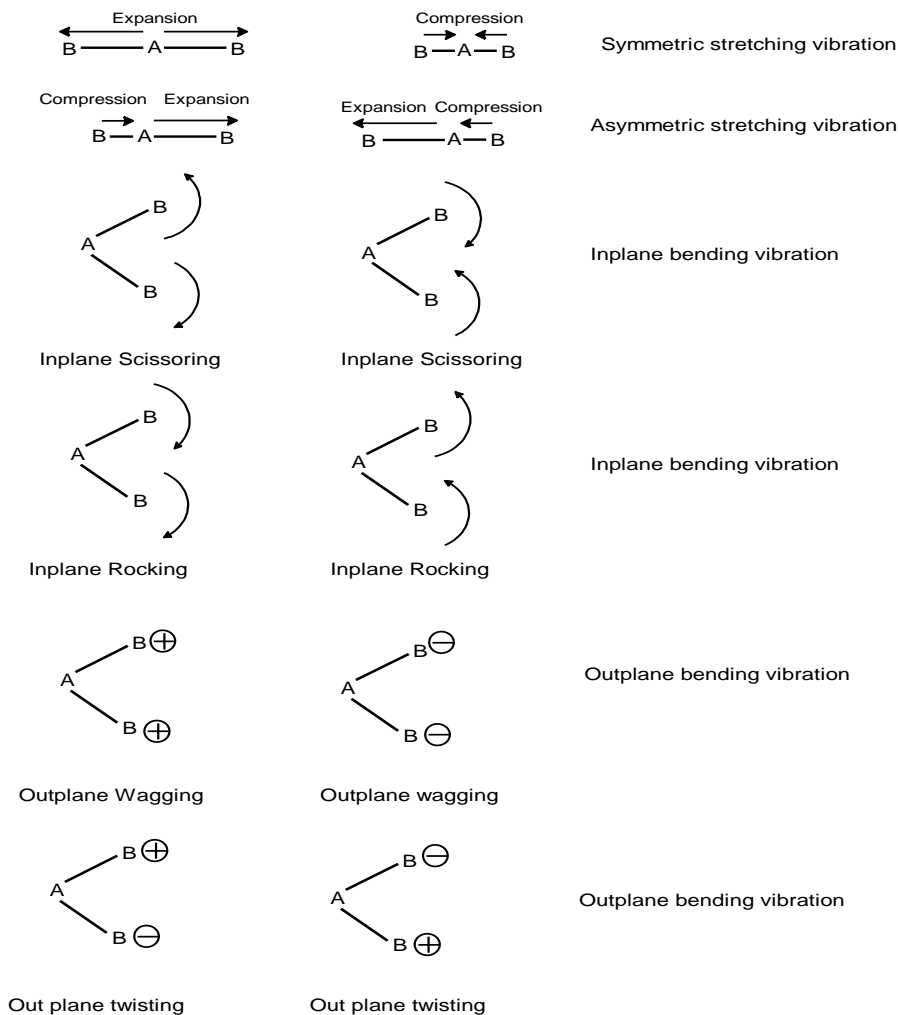
b. Asymmetric stretching vibration:

At the time of vibration reference bonds subjected to compressed and other is expanded (i.e. same direction of movement)

2. **Bending Vibrations:** The change in bond angle between connecting atom by changing the bond angle in and out of the bond axis plane is known as bending vibration. Bending vibration are four types (Figure).



Schematic Representations of types of Vibrational Modes



- Scissoring:** The connecting atoms joined to a central atom move towards and away from each other in the same plane and change the bond angle.
- Rocking:** The connecting atoms joined to a central atom move back and forth in the same direction.

Molecular Spectroscopy

- c. **Twisting:** One of the atom moves up the plane while the other atom moves down the plane with respect to the central atom.
- d. **Wagging:** The two atoms move up or below the plane with respect to the central atom.

In pending vibrations, rocking and scissoring vibrations occur in the same plane (in plane vibrations) whereas twisting and wagging occur out of plane. In some cases, because of symmetry factors two or more vibrational modes may be identical with same energy. Such vibrations are generally referred to as degenerate modes

2.5.6 Vibration Modes of CO₂ Molecule

CO₂ is a linear triatomic molecule, therefore it has $3N - 5 = 3 \times 3 - 5 = 4$ fundamental modes of vibration. The four modes of vibration are symmetrical stretching, antisymmetrical stretching and two bending modes (fig 2.7.). During the stretching vibration, there is no change in the dipole moment. Hence, this symmetrical stretch will not absorb radiation, and hence it is IR inactive.

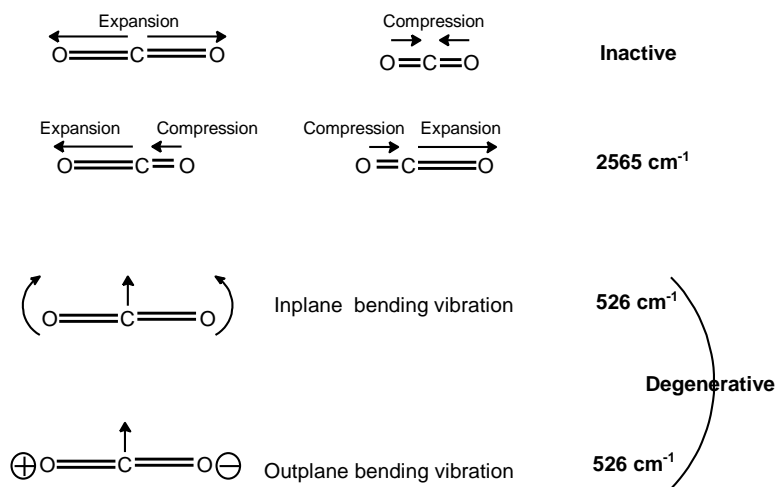


Fig 2.7 Representation of stretching and bending molecular vibrations of CO₂ Molecule

Molecular Spectroscopy

During the asymmetrical stretching, there is a change in the dipole moment and hence this mode is IR active. Two bending modes have the same energy and are said to be degenerate, i.e. only one absorption band is expected due to the two bending modes of vibrations. Therefore for linear CO_2 molecule we get total two absorption band in the spectrum.

2.5.7. Vibrations modes of H_2O molecule

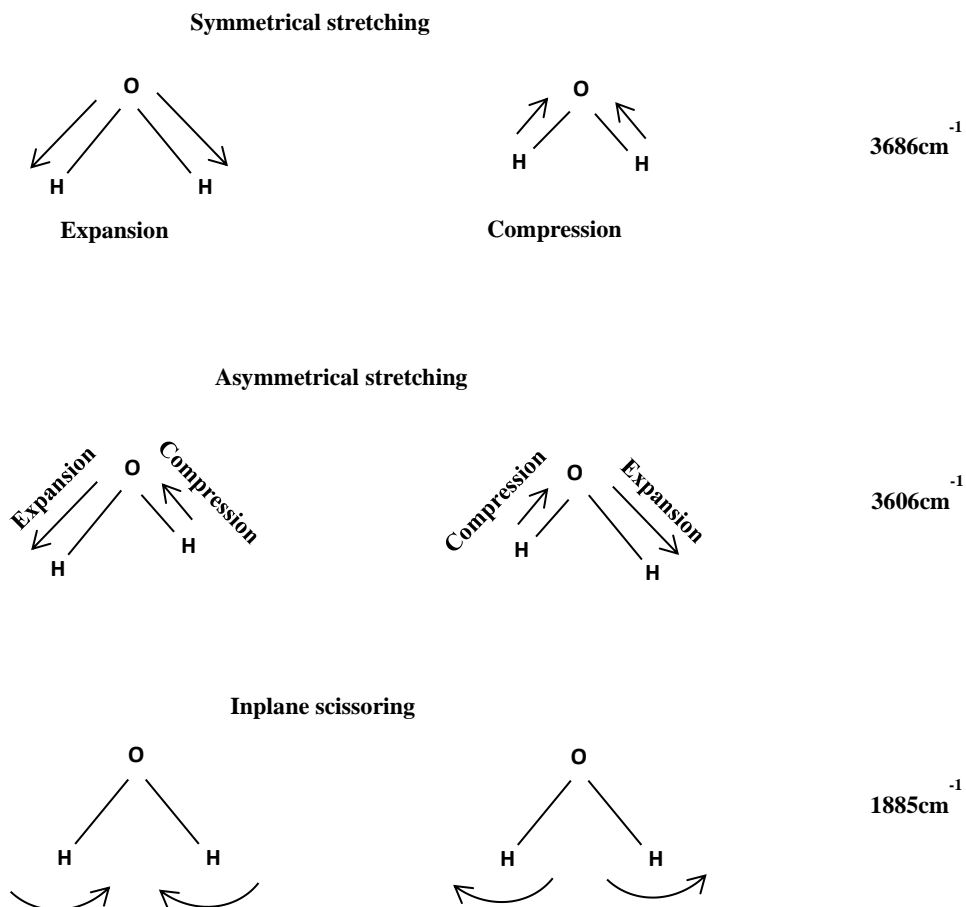


Fig 2.8 Representation of stretching and bending molecular vibrations of H_2O Molecule

Molecular Spectroscopy

Water is a bent, non-linear triatomic molecule. Therefore it has $3N - 6 = 3 \times 3 - 6 = 3$ fundamental modes of vibrations (fig 2.8.). The three modes of vibrations are a bending mode, a symmetrical stretching and an unsymmetrical stretching mode. All the three modes of vibration involve changing in dipole moment and hence they are IR active.

2.5.8 Determination of Force Constant

Calculate the force constant of CO molecule having $\bar{\nu} = 2143 \text{ cm}^{-1}$

For $\text{C} \equiv \text{O}$ molecule the $\bar{\nu} = 2143 \text{ cm}^{-1}$

In $^{12}\text{C} - ^{16}\text{O}$ the atomic mass of C = 12.00 amu and O = 16.00 amu

The reduced mass is calculated from $\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{192}{28} = 6.857 \text{ amu}$

1 amu = $1.66 \times 10^{-27} \text{ Kg}$

The reduced mass $\mu = 6.857 \text{ amu} \times (1.66 \times 10^{-27} \text{ Kg}) = 1.1383 \times 10^{-26} \text{ Kg}$

We know that $\nu = \frac{c}{\lambda} \Rightarrow \nu = c\bar{\nu} = (3 \times 10^{10} \text{ cm s}^{-1}) \times (2143 \text{ cm}^{-1})$

Thus $\nu = 6.429 \times 10^{13} \text{ s}^{-1}$

The angular frequency is given as $\omega = 2\pi\nu$

$$\omega = 2\pi\nu = 2 \times 3.14 \times 6.429 \times 10^{13} \text{ s}^{-1} = 4.037 \times 10^{14} \text{ s}^{-1}$$

From classical mechanics, the angular frequency ω is

$$\omega = \sqrt{\frac{k}{\mu}}$$

$$\omega^2 = \frac{k}{\mu}$$

Molecular Spectroscopy

$$\text{Thus } k = \mu\omega^2 = (1.1383 \times 10^{-26} \text{ Kg}) \times (4.037 \times 10^{14} \text{ s}^{-1})^2 = 1855 \text{ Kg s}^{-2}$$

$$\therefore 1 \text{ Newton} = 1 \text{ Kg m s}^{-2}$$

The force constant $k = 1855 \text{ Nm}^{-1}$

2.6 ELECTRONIC SPECTROSCOPY

The spectroscopy deals with study of electromagnetic radiation with matter. Thus it gives the information about the transition between rotational and vibrational energy levels with the addition of electronic energy levels. It is observed in the visible and ultraviolet region of spectrum. Absorption spectra are obtained when the electrons in the molecule are promoted from the lower electronic state to higher electronic excited state by the absorption of radiation. On the other hand, emission spectra are obtained from the transition of electrons from higher excited state to lower electronic state. An Electronic transition in molecules is accompanied by vibrational transition and the spectra consist of a series of bands. Each band has a number of lines due to rotational transition. Hence, the whole rotational – vibrational spectrum is superimposed on the electronic spectrum and this process produces a very complex band system.

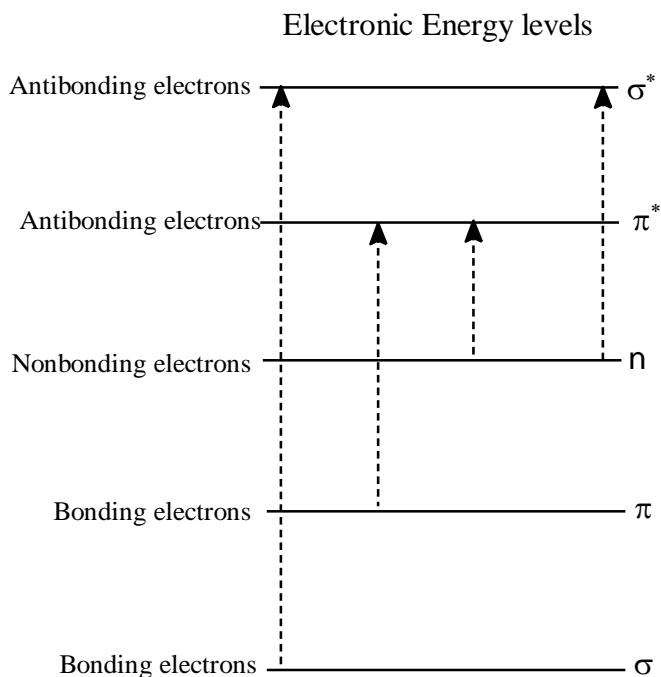
2.6.1 Types of Electronic Transitions in Organic Molecules

Electrons in a molecule can be classified into three different types

1. Bonding σ -orbital: electron in a single covalent bond is tightly bound and hence radiation of high energy is required to excite them.
2. Non-bonding n-orbital: electrons attached to atoms as loan pair. These electrons are not involved in bonds. For example: Oxygen, Nitrogen and Chlorine. The non-bonding electrons can be excited at a lower energy than tightly bound bonding electrons.
3. Bonding π -orbital: electrons in double or triple bond can be excited relatively easily. Molecules containing a series of alternating double bonds, the π -electrons are delocalized and require less energy for excitation.

Molecular Spectroscopy

According to molecular orbital theory, when a molecule is excited by the absorption of energy, its electrons are promoted from a bonding to anti bonding orbital (higher energy states). The anti bonding orbital associated with σ -bond is called σ^* orbital and the electron transition is represented as $\sigma - \sigma^*$. The anti bonding orbital associated with the π -bond is known as π^* orbital and the corresponding transition is denoted as $\pi - \pi^*$. Since non-bonding electrons are not directly involved in bonding, there is no corresponding anti-bonding orbital for them. So the major electronic transitions within the electronic transitions are $\sigma - \sigma^*$, $n - \sigma^*$, $\pi - \pi^*$ and $n - \pi^*$. When the selection rules are applied, the first three transitions are usually allowed whereas $n - \pi^*$ transition is forbidden. The energy required for various transitions follows the order $\sigma - \sigma^* > n - \sigma^* > \pi - \pi^* > n - \pi^*$.



Molecular Spectroscopy

Characteristics of electronic transitions:

1. Electronic transitions are appeared as broad bands due to their higher energy transitions.
2. During electronic transition there should be change in dipole moment (i.e. Ground state and Excited state dipole moment should not be the same)
3. During electronic transition retention of multiplicities is allowed
4. During electronic transition change in angular momentum should be zero or ± 1

2.6.2 Types of Electronic Transitions in Organic Compounds

1. $\sigma \rightarrow \sigma^*$ transition: The energy required for this transition is high (i.e. very short wavelengths; 150nm), which is not coming under UV spectral range. The saturated alkanes will undergo this type of transition.
2. $n \rightarrow \sigma^*$ transition: The saturated hydrocarbons attached to hetero atoms will undergo this type of transition. Example: Alcohols, amines, ether and water. The energy required for this transition is 180-190 nm.
3. $\pi \rightarrow \pi^*$ transition: The unsaturated hydrocarbons, carbonyl compounds, cyanides and azo compounds will undergo this type of transition. Ex: Alkenes, Alkynes, Aldehyde and Ketone. The energy required for this transition is very low (i.e. very longer wavelengths).
4. $n \rightarrow \pi^*$ transition: The carbonyl compounds will undergo this type of transition. Ex: Aldehydes, Ketone and cyanide.

The differences between $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$

Molecular Spectroscopy

S.No.	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
1	Allowed transition	Forbidden transition
2	High energy transition	Lower energy transition
3	Molar extinction coefficient (ϵ) value lies between 100 to 10000	Molar extinction coefficient (ϵ) value is < 100
4	More intense than $n \rightarrow \pi^*$	More intense than $\pi \rightarrow \pi^*$

2.6.3 Mathematical Derivation of Beer- Lambert's Law:

Beer- Lambert's law:

When a beam of monochromatic radiation passes through a transparent absorbing medium, the rate of decrease of intensity of radiation with the thickness of the absorbing medium is proportional to the intensity of incident radiation and concentration of the medium.

$$-\frac{dI}{dx} \propto cI$$

where $-\frac{dI}{dx}$ = decrease of intensity of radiation with the thickness of the absorbing medium

c = concentration of the absorbing medium

dI = Change in intensity of incident light (range is from I_0 to I)

dx = Change in thickness of medium (range is from 0 to b)

Molecular Spectroscopy

$$-\frac{dI}{I} = \epsilon c dx$$

ϵ = Molar extinction coefficient

$$-\frac{dI}{I} = c dx$$

$$\int_{I_0}^I \frac{dI}{I} = - \int_{x=0}^{x=b} \epsilon c dx$$

$$\log[I]_{I_0}^I = -\epsilon c [x]_0^b$$

$$\log I - \log I_0 = -\epsilon bc$$

$$\log \frac{I}{I_0} = -\epsilon bc$$

$$T = -\epsilon bc$$

T = Transmittance

$$\log \frac{I_0}{I} = \epsilon bc$$

$$A = \epsilon bc$$

A = Absorbance or Optical density

Beer – Lamberts Law:

The absorbance of a solution is directly proportional to the concentration of the medium when thickness of the medium is fixed and directly proportional to the thickness of the medium when the concentration is fixed.

2.7 LASER

LASER is an abbreviation for Light Amplification by Stimulated Emission of Radiation.

Properties of LASER light

1. **Coherence:** It is a crucial property of laser, that exists due to stimulated emission. It simply denotes that the wavelength of the waves of emitted light is in phase. When we talk about the ordinary light source for example LED, then it does not show the property of coherence because it gets generated due to the process of spontaneous emission of a photon.
2. **Monochromaticity:** A light emitted by the laser diode is monochrome in nature that means that it has a single wavelength.
3. **Brightness:** Brightness of a light is basically determined by the power per unit surface area per unit solid angle.
4. **Directionality:** A laser light is highly directional this means that the light emitted by a laser diode does not show much divergence.

2.7.1 Construction of Laser

Basically, every laser system essentially has an active/gain medium, placed between a pair of optically parallel and highly reflecting mirrors with one of them partially transmitting, and an energy source to pump active medium. The gain media may be solid, liquid, or gas and have the property to amplify the amplitude of the light wave passing through it by stimulated emission, while pumping may be electrical or optical. The gain medium used to place between pair of mirrors in such a way that light oscillating between mirrors passes every time through the gain medium and after attaining considerable amplification emits through the transmitting mirror.

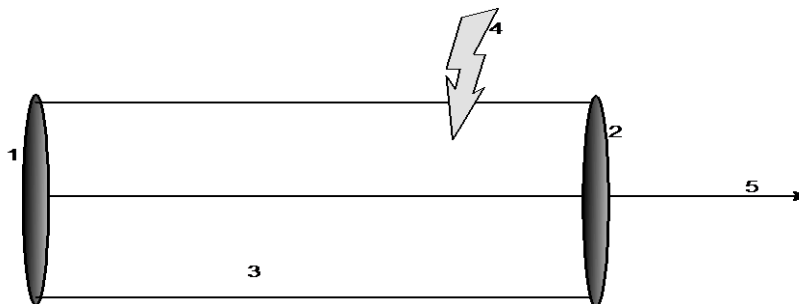


Fig 2.9 Basic geometry of laser cavity 1) 100% 2) 95% reflecting mirror 3) active medium 4) Pumping source and 5) Laser output

2.7.2 Stimulated Emission

Let us consider an active medium of atoms having only two energy levels: excited level E_2 and ground level E_1 . If atoms in the ground state, E_1 , are excited to the upper state, E_2 , by means of any pumping mechanism (optical, electrical discharge, passing current or electron bombardment), then just after few nanoseconds of their excitation, atoms return to the ground state emitting photons of energy

$$h\nu = E_2 - E_1.$$

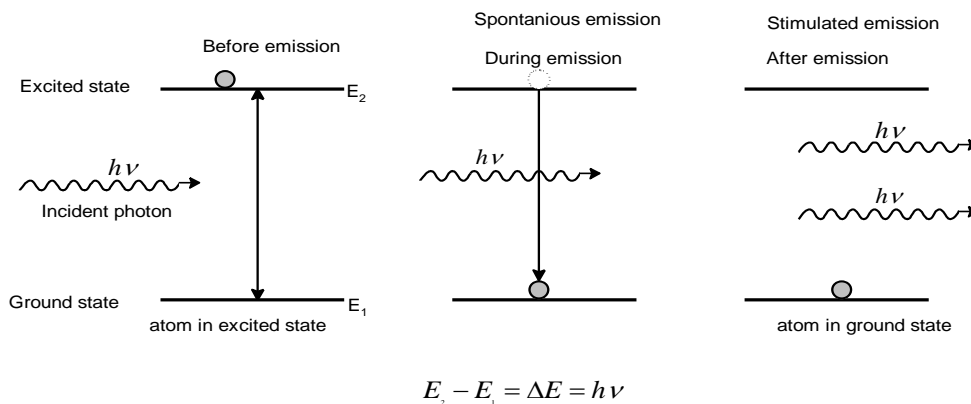


Fig 2.10 Representation of Spontaneous and Stimulated emission

Molecular Spectroscopy

According to Einstein's 1917 theory, emission process may occur in two different ways, either it may be induced by a photon or it may occur spontaneously.

The former case is termed as stimulated emission, while the latter is known as spontaneous emission. Photons emitted by stimulated emission have the same frequency, phase, and state of polarization as the stimulating photon; therefore they add to the wave of stimulating photon on a constructive basis, thereby increasing its amplitude to make lasing. At thermal equilibrium, the probability of stimulated emission is much lower than that of spontaneous emission (1 : 10³³), therefore most of the conventional light sources are incoherent, and only lasing is possible in the conditions other than the thermal equilibrium.

2.7.3 Laser Diode

A semiconductor device that generates coherent light of high intensity is known as a laser diode.

Semiconductor lasers also known as quantum well lasers are smallest, cheapest, can be produced in mass, and are easily scalable.

Construction of Laser Diode

The active layer of undoped GaAs is placed between the P and N type of AlGaAs layers. The thickness of this active layer is of few nanometers. The aim of sandwiching this layer in between p and n-type layers is to increase the area of electron and hole combination. Resultantly increasing the emitted radiation. The laser output is taken from the active region of the laser diode.

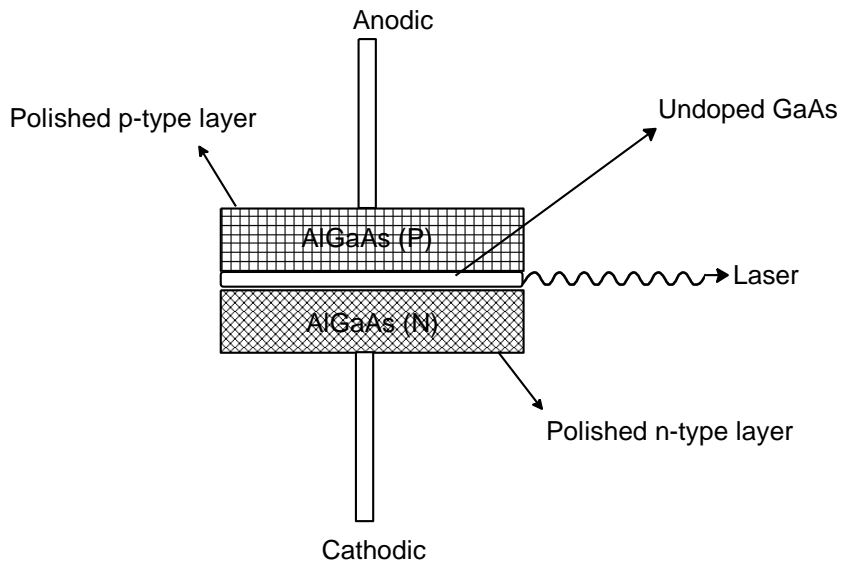


Fig 2.11 Laser Diode

The working of a laser diode involves 3 processes: absorption, spontaneous emission and stimulated emission.

1. **Absorption:** The ground state electron will absorb energy from pumping source and excites to the excited state. This is known as absorption.
2. **Spontaneous Emission:** The excited electron decays without external influence and emits a photon, that is called "spontaneous emission".
3. **Stimulated Emission:** The excited-state atom is perturbed by an electric field of frequency, it may emit an additional photon of the same frequency and in phase, thus augmenting the external field, leaving the atom in the lower energy state. This process is known as stimulated emission.

Molecular Spectroscopy

Advantages of laser diode

1. The operational power in case of laser diodes is less as compared to other light emitting devices.
2. It is small in size thus allows better handling.
3. Laser diodes generate light of high efficiency.

Disadvantages of laser diode

1. As it provides a light of high density, thus sometimes puts adverse effects on eyes.
2. It is expensive.

Applications of laser diode

1. Telecommunication and in defence industries.
2. Optical fiber communication also uses a laser beam for signal transmission as optical fibers requires highly focused beam.
3. It is highly used in laser printers also.

2.7.4 Gas Lasers

Gas lasers are widely available in almost all power and wavelengths and can be operated in pulsed and continuous modes. Based on the nature of active media, there are three types of gas lasers.

1. Atomic Gas lasers: He:Ne Laser
2. Ionic Gas lasers: Argon Ion Laser
3. Molecular Gas lasers: CO₂, N₂ Lasers, Excimer lasers

Molecular Spectroscopy

Most of the gas lasers are pumped by electrical discharge. Electrons in the discharge tube are accelerated by electric field between the electrodes. These accelerated electrons collide with atoms, ions or molecules in the active media and induce transition to higher energy levels to achieve the condition of population inversion and stimulated emission.

The argon-ion laser (Fig 2.12), one of a number of ‘ion lasers’, consists of argon at about 1 Torr, through which is passed an electric discharge. The discharge results in the formation of Ar^+ and Ar^{2+} ions in excited states, which undergo a laser transition to a lower state. These ions then revert to their ground states by emitting hard ultraviolet radiation (at 72 nm), and are then neutralized by a series of electrodes in the laser cavity. One of the design problems is to find materials that can withstand this damaging residual radiation. There are many lines in the laser transition because the excited ions may make transitions to many lower states, but two strong emissions from Ar^+ are at 488 nm (blue) and 514 nm (green); other transitions occur elsewhere in the visible region, in the infrared, and in the ultraviolet.

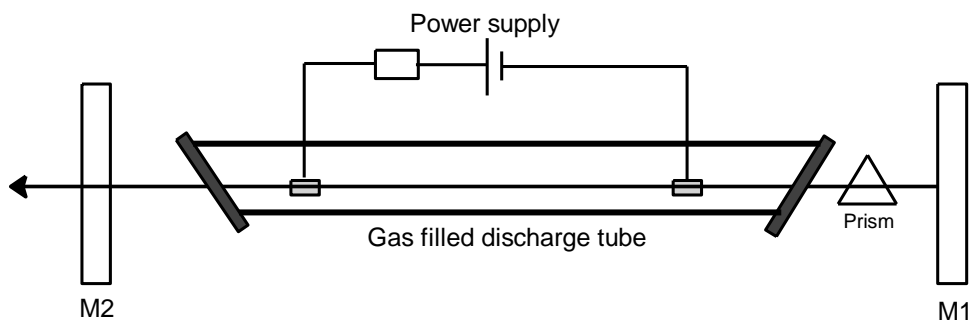


Fig 2.12 Construction of gas laser system (argon ion laser with prism-based wavelength tuning)

Molecular Spectroscopy

2.7.5 Excimer Laser

Excimers are molecules such as ArF, KrF, XeCl, and so on, that have repulsive or dissociating ground states and are stable in their first excited state. Usually, there are less number of molecules in the ground state; therefore direct pumping from ground state is not possible. Molecules directly form in the first excited electronic state by the combination of energetic halide and rare gas ions. Usually a mixture of halide such as F₂ and rare gas such as Ar is filled into the discharge tube. Electrons in the discharge tube dissociate and ionize halide molecules and create negative halide ions. Positive Ar⁺ and negative F⁻ ions react to produce ArF* molecules in the first excited bound state, followed by their transition to the repulsive ground state to commence lasing action. Various excimer lasers are developed in the wavelength range of 120–500 nm with 20–15% efficiency and up to 1 J peak and 200 W average powers. These lasers are widely used in materials processing and characterizations as well as for the pumping of dye lasers.

Applications:

1. Refractive surgery in ophthalmology
2. Gene manipulation in bioengineering.

Molecular Spectroscopy

Questions

Part A

1. What is an electromagnetic spectrum?.
2. Draw an electromagnetic spectrum with variable energy
3. What is rotational energy?
4. Define basic principle of microwave spectroscopy
5. Write down the selection rule for rotational spectroscopy
6. Define degrees of freedom
7. Which of the following diatomic molecules have a rotational microwave spectrum: IF, O₂, KCl, Cl₂.
8. Identify the molecules that will exhibit a pure rotational absorption microwave spectrum: N₂O, NO₂, CClF₃, NF₃, SF₆, CH₄, CO₂.
9. What are the various types of electronic transitions.
10. What is the necessary condition for a molecule to absorb infrared radiation?
11. Calculate vibrational degrees of freedom for CO₂.
12. Calculate fundamental bands for the linear molecules.
13. How many fundamental bands are observed in the IR spectrum of benzene?
14. Define spontaneous emission
15. Define stimulated emission
16. Differences between $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions
17. Define LASER

Molecular Spectroscopy

Part B

1. Explain in detail about the classification of molecules based on moment of inertia.
2. Explain rotational spectra of diatomic molecules with energy level spectrum.
3. Explain rotational spectra of polyatomic molecules.
4. Calculate J (1 to 3) values of CO molecule.
5. Explain the types of vibrations and its diagrammatic representation.
6. Calculate the force constant of CO molecule having $\bar{\nu} = 2143 \text{ cm}^{-1}$
7. Explain the construction, working principle and advantages and disadvantages of diode laser
8. Explain the electronic transitions in organic molecules with suitable examples.
9. Define Beer Lamberts law and derive its mathematical formulae.