

electromagnetic spectrum.

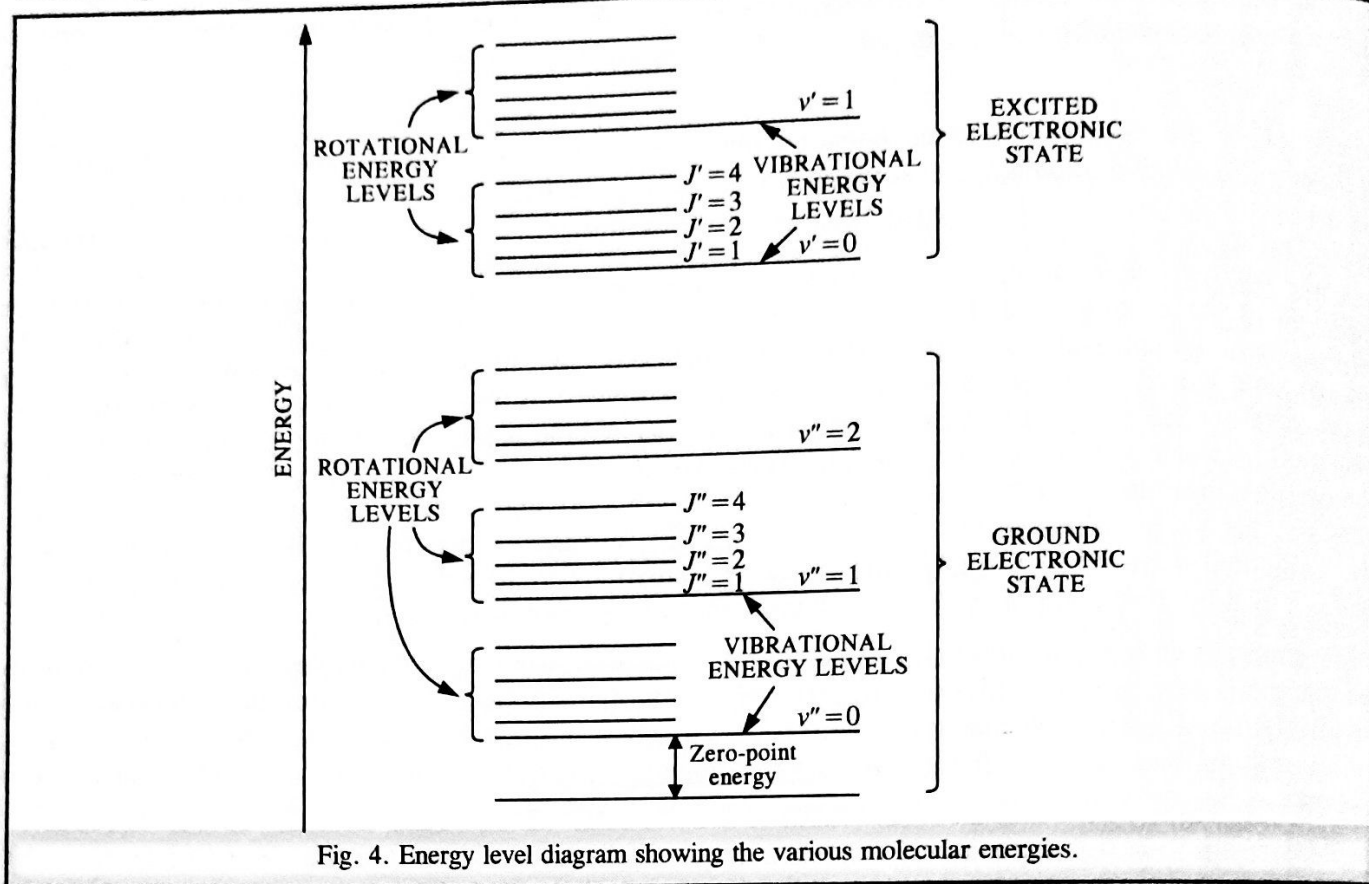


Fig. 4. Energy level diagram showing the various molecular energies.

The various types of spectra given by a molecule, the regions in which these spectra lie and the energy changes that take place in the molecule on absorption of radiation, are listed below.

1. Rotational (Microwave) Spectra. These spectra result from transitions between the rotational energy levels of a *gaseous* molecule on the absorption of radiations falling in the microwave region. These spectra are shown by molecules which *possess a permanent dipole moment*, e.g., HCl, CO, H₂O vapour, NO, etc. Homonuclear diatomic molecules such as H₂, Cl₂, etc., and linear polyatomic molecules such as CO₂, which do not possess a dipole moment, do not show microwave spectra. Microwave spectra occur in the spectral range of 1 – 100 cm⁻¹.

2. Vibrational and Vibration–Rotation (Infrared) Spectra. These spectra originate from transitions induced between the vibrational energy levels of a molecule on the absorption of radiations belonging to the infrared region. IR spectra are shown by molecules when vibrational motion is accompanied by a *change in the dipole moment of the molecule*. These spectra occur in the spectral range of 500 – 4000 cm⁻¹.

3. Raman Spectra. Raman spectra relate to vibrational and/or rotational transitions in molecules but in a different manner. In this case, what we measure is the *scattering* and not the absorption of radiation. An intense beam of monochromatic radiation in the *visible region* is allowed to fall on a sample and the intensity of scattered light is observed at right angles to the incident beam. Most of the scattered light has the same frequency as the incident beam (this is called *Rayleigh scattering*). However, some of the scattered light has different frequencies than the incident beam. This is called *Raman scattering*. The energy differences between these weak lines and the main Rayleigh line correspond to vibrational and/or rotational transitions in the molecule under investigation. Raman spectra are observed in the visible region, viz., 12,500 – 25,000 cm⁻¹.

4. Electronic Spectra. Electronic spectra arise from electronic transitions in a molecule by absorption of radiations falling in the visible and ultraviolet regions. While electronic spectra in the visible region span $12,500 - 25,000 \text{ cm}^{-1}$, those in the ultraviolet region span $25,000 - 70,000 \text{ cm}^{-1}$. Since electronic transitions in a molecule are invariably accompanied by vibrational and rotational transitions, the electronic spectra of molecules are highly complex.

5. Photoelectron Spectra (PES). These spectra help in the determination of ionization energies of molecules. If a light photon falling on a molecule possesses very high energy, it can cause ionization of the molecule, *i.e.*, the removal of the electron from the molecule. If the energy of the incident photon is greater than the ionization energy, the ejected electron will possess excess kinetic energy. In PES, a beam of photons of known energy is allowed to fall on the sample and the kinetic energy of the ejected electrons is measured. The difference between the photon energy and the excess kinetic energy gives the binding energy of the electron. PES offers one of the most accurate methods for determining the ionization energies of molecules. Photoelectron spectra can be studied either using the X-ray photons or the UV photons. In the former case, they are called X PES spectra and in the latter case, the UVPES (or UPES) spectra.

6. Nuclear Magnetic Resonance (NMR) and Nuclear Quadrupole Resonance (NQR) Spectra. NMR spectra result from transitions induced between the nuclear spin energy levels of a molecule in an applied magnetic field. NQR spectra result from the transitions between the nuclear spin energy levels of a molecule arising from the interaction of the unsymmetrical charge distribution in nuclei with the electric field gradients (EFG) which arise from the bonding and non-bonding electrons in the molecule. NMR and NQR spectra span the radiofrequency regions, *viz.*, 5 - 100 MHz.

7. Electron Spin Resonance (ESR) or Electron Paramagnetic Resonance (EPR) Spectra. ESR spectra result from transitions induced between the electron spin energy levels of a molecule in an applied magnetic field. These spectra are exhibited by systems which contain odd (unpaired) electrons such as free radicals, transition metal ions and rare-earth ions. Molecules such as nitric oxide and oxygen and other paramagnetic systems also show ESR spectra. This branch of spectroscopy falls in the microwave region, *viz.*, 2 - 9.6 GHz.

8. Mössbauer Spectra (also called Nuclear Gamma Resonance Fluorescence (NRF) Spectra). Mössbauer spectra constitute a type of nuclear resonance spectra like nuclear magnetic resonance spectra. However, while NMR spectra result from absorption of low energy photons of frequency around 60 MHz, Mössbauer spectra result from absorption of high energy γ -photons of frequency around 10^{13} MHz by the nuclei. Gamma ray spectra have been used specifically for the study of compounds of iron and tin. In this case, γ -radiations from ^{57}Co source are allowed to fall on a sample in which the iron nuclei are in an environment identical with that of the source atoms. This results in resonant absorption of γ -rays. The splittings in Mössbauer lines are found to be of the same order as in NMR spectroscopy.

ROTATIONAL (MICROWAVE) SPECTRA OF DIATOMIC MOLECULES

Consider a diatomic molecule in which m_1 and m_2 are the masses of the two atoms and r is the equilibrium bond length, rotating about an axis passing through its centre of gravity, c.g. (Fig. 5).

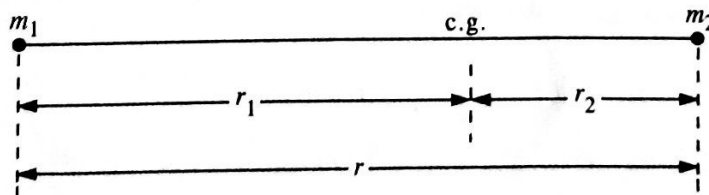


Fig. 5. Rotation of a diatomic molecule about its centre of gravity.

The centre of gravity is defined by the equality of the moments about it, *i.e.*,

$$m_1 r_1 = m_2 r_2$$

...(9)

The **moment of inertia** I of a molecule (rotating as a rigid rotor, not subject to centrifugal forces that tend to distort the molecular geometry and change the moments of inertia) is defined as

$$I = \sum_i m_i r_i^2 \quad \dots(10)$$

where r_i is the distance of the i th particle of mass m_i from the centre of gravity. Since a diatomic molecule has two atoms, we have

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \dots(11)$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2 \quad (\text{using Eq. 9})$$

$$= r_1 r_2 (m_2 + m_1) \quad \dots(12)$$

Also, as seen from Fig. 5,

$$r = r_1 + r_2 \quad \dots(13)$$

Therefore, from Eqs. 9 and 13,

$$m_1 r_1 = m_2 r_2 = m_2 (r - r_1) \quad \dots(14)$$

Hence,

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

Substituting the above values of r_1 and r_2 in Eq. 11, we have

$$I = \frac{m_1 m_2^2}{(m_1 + m_2)^2} r^2 + \frac{m_1^2 m_2}{(m_1 + m_2)^2} r^2 \quad \dots(15)$$

$$= \frac{m_1 m_2 (m_1 + m_2)}{(m_1 + m_2)^2} r^2 = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2 \quad \dots(16)$$

where $\mu = m_1 m_2 / (m_1 + m_2)$ is called the **reduced mass** of the molecule.

Classically, the angular momentum L of a rotating molecule is given by $L = I\omega$ where ω is its angular velocity. However, the angular momentum is quantized, being given by

$$L = \sqrt{J(J+1)} \hbar ; \quad J = 0, 1, 2, \dots \quad \dots(17)$$

where J is the rotational quantum number. The energy of a rotating molecule is given by $\frac{1}{2} I\omega^2$. Hence, the quantized rotational energy levels of a rigid diatomic rotor (rotating molecule) are given by

$$E_J = \frac{1}{2} I\omega^2 = (I\omega)^2 / 2I = L^2 / 2I \quad \dots(18)$$

Using the expression for L from Eq. 17, we have

$$E_J = J(J+1) \frac{\hbar^2}{2I} ; \quad \text{where } J = 0, 1, 2, \dots \quad \dots(19)$$

Eq. 19 is also obtained by solving the Schrödinger wave equation for a rigid diatomic rotor (Chapter 1). It is customary to express the energy in cm^{-1} rather than in joules. This is done by dividing energy in joules by hc when we get

Here Total rotational energy, written as

$$F(J) = E_J / hc = J(J+1) \frac{\hbar}{4\pi c I} ; \quad J = 0, 1, 2, \dots \quad \dots(20)$$

$F(J)$, is called the **rotational term**. Defining the **rotational constant** B as

$$B = \frac{\hbar}{4\pi c I} \text{ cm}^{-1}, \quad \dots(21)$$

we have

$$F(J) = B J (J + 1) ; \quad J = 0, 1, 2, \dots \quad \dots(22a)$$

and

$$E_J = \hbar c B J (J + 1) ; \quad J = 0, 1, 2, \dots \quad \dots(22b)$$

If we want to take into account **centrifugal distortion** whose effect on the diatomic rotor is to stretch the bond and hence to increase the moment of inertia, and thereby to reduce the rotational constant and hence bring the energy levels closer than in the rigid-rotor approximation, then the energy level expression (22a) becomes

$$F(J) = BJ(J+1) - D_J J^2(J+1)^2 \quad \dots(22c)$$

where D_J is the centrifugal distortion constant given by $D_J = 4B^3/\bar{\nu}^2$, where $\bar{\nu}$ is the vibrational frequency of the molecule.

Next we need a *selection rule* to determine the radiative transitions between the rotational energy levels. The derivation of the selection rule is a quantum-mechanical problem; its details need not concern us here. Suffice it to mention that the rotational transitions for a rigid diatomic molecule are governed by the selection rule

$$\Delta J = \pm 1 \quad \dots(23)$$

i.e., only those transitions are allowed in which the rotational quantum number changes by unity. The + sign refers to absorption and the - sign to emission of radiation. Microwave spectra are usually observed as absorption spectra so that the operative part of the selection rule is $\Delta J = +1$. For a transition taking place from J to $J+1$, the rotational frequency is given by

$$\nu_{(J \rightarrow J+1)} = B(J+1)(J+2) - BJ(J+1) \quad \dots(24)$$

$$= B(J^2 + 3J + 2) - B(J^2 + J) \quad \dots(25)$$

$$= 2B(J+1) \text{ cm}^{-1} \quad \dots(26)$$

Thus, $\nu_{(0 \rightarrow 1)} = 2B$; $\nu_{(1 \rightarrow 2)} = 4B$;

$\nu_{(2 \rightarrow 3)} = 6B$; $\nu_{(3 \rightarrow 4)} = 8B$, etc.

We see that the rotational spectrum of a rigid diatomic molecule consists of a series of lines at $2B$, $4B$, $6B$, $8B$, etc. Evidently, these lines are equally spaced by an amount of $2B$ (Fig. 6) called **frequency separation**.

Example 1. The internuclear distance (*i.e.*, bond length) of carbon monoxide molecule is 1.13 \AA . Calculate the energy (in joules and in eV) and angular velocity of this molecule in the first excited rotational level. The atomic masses are: $^{12}\text{C} = 1.99 \times 10^{-26} \text{ kg}$; $^{16}\text{O} = 2.66 \times 10^{-26} \text{ kg}$.

Solution :

$$r = 1.13 \text{ \AA} = 1.13 \times 10^{-8} \text{ cm} = 1.13 \times 10^{-10} \text{ m}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1.99 \times 10^{-26} \text{ kg})(2.66 \times 10^{-26} \text{ kg})}{(1.99 + 2.66) \times 10^{-26} \text{ kg}} = 1.14 \times 10^{-26} \text{ kg}$$

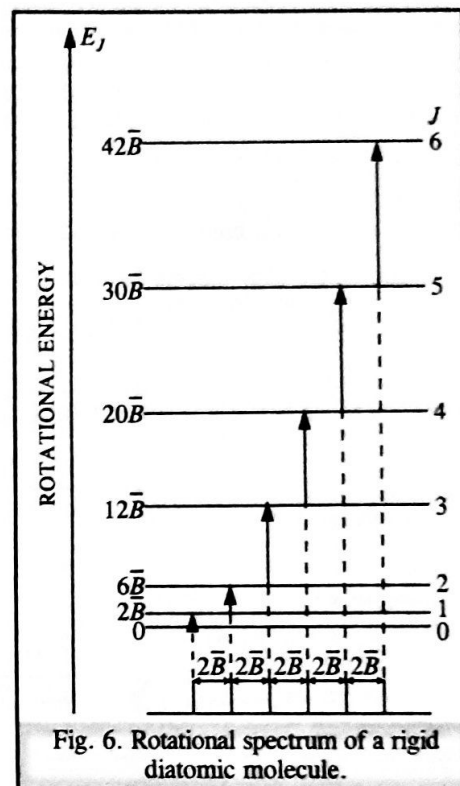
$$I = \mu r^2 = (1.14 \times 10^{-26} \text{ kg})(1.13 \times 10^{-10} \text{ m})^2 = 1.46 \times 10^{-46} \text{ kg m}^2$$

$$E_1 = \frac{h^2}{I} \text{ joule} \quad [\text{Eq. (19)}]$$

$$= \frac{(1.054 \times 10^{-34} \text{ Js})^2}{(1.46 \times 10^{-46} \text{ kg m}^2)} = 7.61 \times 10^{-23} \text{ joule} = \frac{7.61 \times 10^{-23} \text{ J}}{1.602 \times 10^{-19} \text{ J/eV}} = 4.76 \times 10^{-4} \text{ eV}$$

Since from Eq. 18, $E_1 = \frac{1}{2} I \omega^2$, where ω is the angular velocity, hence

$$\omega = \sqrt{\frac{2E_1}{I}} = \sqrt{\frac{2 \times (7.61 \times 10^{-23} \text{ J})}{1.46 \times 10^{-46} \text{ kg m}^2}} = 3.23 \times 10^{11} \text{ radians s}^{-1}$$



$$\frac{(1.673 \times 58.06) 10^{-27}}{59.73} \text{ kg} = 1.626 \times 10^{-27} \text{ kg}$$

Since $I = \mu r^2$, hence, $r = 1.29 \times 10^{-10} \text{ m} = 129 \text{ pm}$

Relative Intensities of Rotational Spectral Lines. The relative intensities of spectral lines depend upon the relative populations of the energy levels. As we see from Example 2, even at room temperature many of the diatomic molecules are present in the excited state energy levels. Since the energy level population is given by the Boltzmann distribution, the intensity of rotational lines is evidently proportional to the Boltzmann distribution of molecules in the rotational energy levels, *i.e.*,

$$\text{Intensity} \propto N_J/N_0 = e^{-E_J/kT} \quad \dots(27)$$

Rotational energy levels are, however, degenerate, their degeneracy (g_J) for a diatomic molecule being given by

$$g_J = 2J+1 \quad \dots(28)$$

In other words, for a given value of J , the energy level is $(2J+1)$ -fold degenerate. For $J=0$, $g_J=1$; for $J=1$, $g_J=3$; for $J=2$, $g_J=5$ and so on.

Thus, the intensity of the rotational spectral lines is determined by the product of the degeneracy factor and the Boltzmann exponential factor. Hence,

$$\text{Intensity} \propto N_J/N_0 = (2J+1)e^{-E_J/kT} \quad \dots(29)$$

Since $E_J = hcF(J) \quad \dots(30)$

and $F(J) = BJ(J+1), \quad \dots(31)$

hence, $N_J/N_0 = (2J+1)e^{-BJ(J+1)hc/kT} \quad \dots(32)$

The quantity N_J/N_0 is plotted versus J for a diatomic molecule at room temperature in Fig. 7.

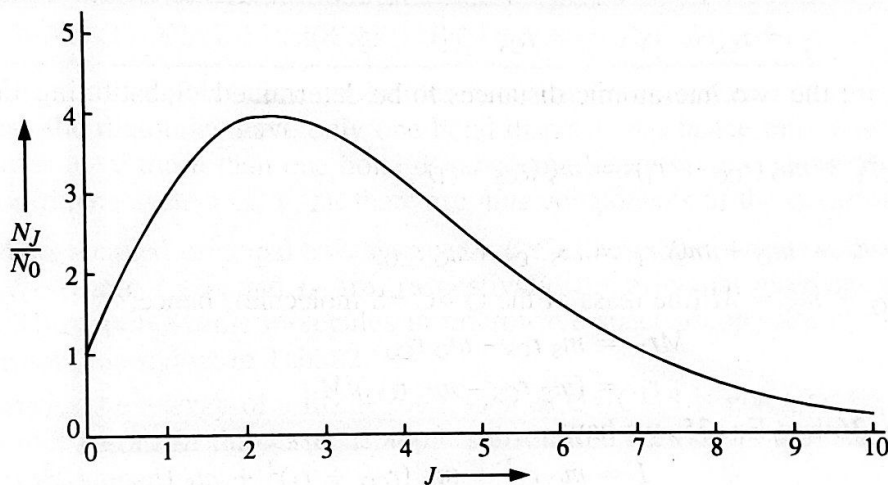


Fig. 7. Plot of the relative Boltzmann population versus J for a diatomic molecule.

We see that the relative intensity passes through a maximum. It can be shown that the value of J corresponding to the maximum in population is given by

$$J_{\max} = \left(\frac{kT}{2hcB} \right)^{1/2} - \frac{1}{2} \quad \dots(33)$$

The J_{\max} should be rounded off to the nearest integral value.

Example 5. Calculate J_{\max} for a rigid diatomic molecule for which at 300 K, the rotational constant is 1.566 cm^{-1} .

Solution :
$$J_{\max} = \left(\frac{kT}{2hcB} \right)^{1/2} - \frac{1}{2} \quad (\text{Eq. 33})$$

$$= \left[\frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}{2(6.626 \times 10^{-34} \text{ J s})(3 \times 10^{10} \text{ cm s}^{-1})(1.566 \text{ cm}^{-1})} \right]^{1/2} - \frac{1}{2} = 7.56 = 8$$

Application of Microwave Spectroscopy for the Determination of Bond Distances in Polyatomic Molecules. For the sake of simplicity, consider the gaseous linear triatomic molecule $\text{O}=\text{C}=\text{S}$ for which we want to determine the two bond distances $\text{O}-\text{C}$ and $\text{C}-\text{S}$. This can be done by **isotopic substitution method**. Consider first the molecule $^{16}\text{O}=\text{C}=\text{S}$ (Fig. 8).

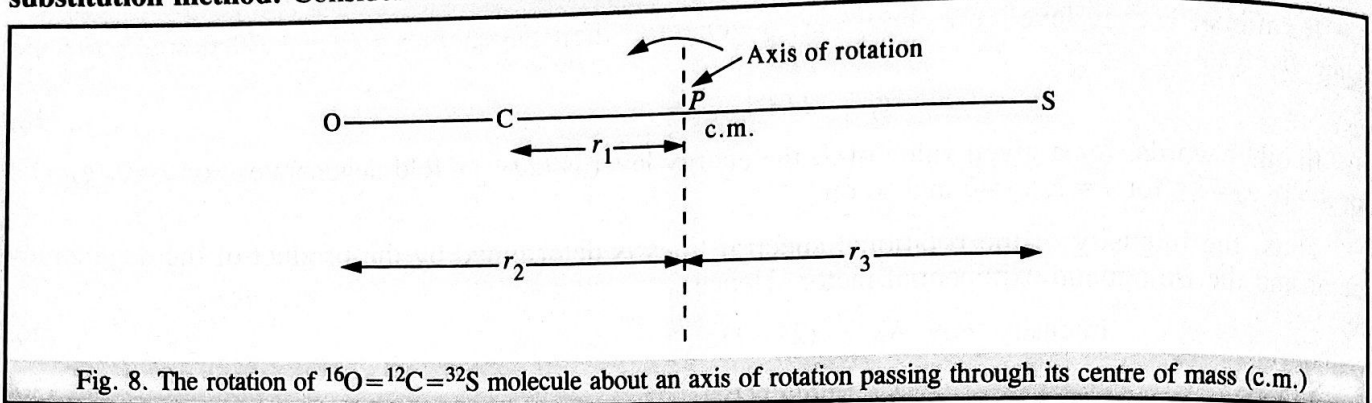


Fig. 8. The rotation of $^{16}\text{O}=\text{C}=\text{S}$ molecule about an axis of rotation passing through its centre of mass (c.m.)

Since the centre of mass is at P (from where the various distances are measured),

$$\therefore m_C r_1 + m_O r_2 = m_S r_3 \quad \dots(34)$$

The moment of inertia is given by

$$I = m_C r_1^2 + m_O r_2^2 + m_S r_3^2 \quad \dots(35)$$

Also, $r_2 = r_{CO} + r_1$; $r_3 = r_{CS} - r_1$ (Fig. 8) $\dots(36)$

where r_{CO} and r_{CS} are the two interatomic distances to be determined. Substituting Eq. 36 into Eq. 34, we have

$$m_C r_1 + m_O (r_{CO} + r_1) = m_S (r_{CS} - r_1) \quad \dots(37)$$

or, rearranging,

$$(m_C + m_O + m_S) r_1 = m_S r_{CS} - m_O r_{CO} \quad \dots(38)$$

Since $m_C + m_O + m_S = M$ (the mass of the $\text{O}=\text{C}=\text{S}$ molecule), hence,

$$\begin{aligned} M r_1 &= m_S r_{CS} - m_O r_{CO} \\ r_1 &= (m_S r_{CS} - m_O r_{CO})/M \end{aligned} \quad \dots(39)$$

Substituting Eq. 36 into Eq. 35, we have

$$I = m_C r_1^2 + m_O (r_{CO} + r_1)^2 + m_S (r_{CS} - r_1)^2 \quad \dots(40)$$

Substituting for r_1 from Eq. 39 into Eq. 40 and simplifying, we obtain

$$I = (m_S r_{CS}^2 - m_O r_{CO}^2 + 2m_O m_S r_{CO} r_{CS} - m_S r_{CS}^2)/M \quad \dots(41)$$

Eq. 44 contains the unknowns r_{CO} and r_{CS} .

Now we make an important assumption *that isotopic substitution does not alter the interatomic distances*. Applying this assumption to the $^{16}\text{O}=\text{C}=\text{S}$ molecule, we obtain a similar expression for the moment of inertia I' of the molecule :

$$I' = (m_S' r_{CS}^2 - m_O r_{CO}^2 + 2m_O m_S' r_{CO} r_{CS} - m_S' r_{CS}^2)/M \quad \dots(42)$$

Thus, we can obtain both I and I' from the microwave spectra of $^{16}\text{O}=\text{}^{12}\text{C}=\text{}^{32}\text{S}$ and $^{16}\text{O}=\text{}^{12}\text{C}=\text{}^{34}\text{S}$ molecules and from these moments of inertia, the unknowns r_{CO} and r_{CS} can be determined.

The interatomic distances in gaseous $\text{O}=\text{C}=\text{S}$, using several pairs of isotopes are given in Table 1.

TABLE 1
Interatomic Distances in $\text{O}=\text{C}=\text{S}$ Molecule

Pairs of Isotopic Molecules	$r_{\text{C-O}}$ (in Å)	$r_{\text{C-S}}$ (in Å)
$^{16}\text{O}=\text{}^{12}\text{C}=\text{}^{32}\text{S}$ and $^{16}\text{O}=\text{}^{12}\text{C}=\text{}^{34}\text{S}$	1.1647	1.5576
$^{16}\text{O}=\text{}^{12}\text{C}=\text{}^{32}\text{S}$ and $^{16}\text{O}=\text{}^{13}\text{C}=\text{}^{32}\text{S}$	1.1629	1.5591
$^{16}\text{O}=\text{}^{12}\text{C}=\text{}^{34}\text{S}$ and $^{16}\text{O}=\text{}^{13}\text{C}=\text{}^{34}\text{S}$	1.1625	1.5594
$^{16}\text{O}=\text{}^{12}\text{C}=\text{}^{32}\text{S}$ and $^{18}\text{O}=\text{}^{12}\text{C}=\text{}^{32}\text{S}$	1.1652	1.5653

Notice that there are small differences in bond lengths caused by changing the isotopes. These differences are due to *zero-point vibrations* whose amplitudes depend upon the masses of the atoms. Thus, measured bond lengths change upon isotopic substitution.

Microwave Oven. In recent years, the microwave oven has become a very familiar and useful cooking device in the kitchen. Its mode of operation depends upon the absorption by the food of the microwave radiation in which it is placed. The water molecules in the food absorb the microwave radiation and are thereby raised to the higher rotational states. The biological molecules in the food, on the other hand, are far too big to be able to rotate. The heating in the microwave oven is entirely *internal*, in contrast to the conventional oven where the food is cooked by *external* heating. In internal heating, the water molecules in the food are excited and the excess rotational energy is re-emitted as heat with the help of which the food gets cooked.

Unfortunately, the microwave radiation also affects the human body. Hence, the door seal of the microwave oven must be in good condition to ensure that no radiation leaks out.

ROTATIONAL SPECTRA OF POLYATOMIC MOLECULES

The rotational spectra of polyatomic molecules show features not found in the spectra of diatomic molecules. Whereas the diatomics have only one bond distance and hence only one moment of inertia, polyatomic molecules have more than one bond distance and hence several moments of inertia. In fact, in the Cartesian coordinate system (x, y, z), there are *nine* components of the moment of inertia.

However, in the so-called principal axis system (A, B, C), these components reduce to three moments of inertia, I_A, I_B, I_C , where I_A, I_B and I_C are, respectively, the principal moments of inertia about the A, B and C axes. Thus, polyatomic molecules in microwave spectroscopy are classified into different types of rotators (rotors) as shown in Table 2.

1. Linear Rotor. The energy of a linear rotor such as $\text{O}=\text{C}=\text{S}$ is given by Eq. 22, *viz.*, the same as that for a diatomic rotor. In this case, isotopic substitution method is used to determine the bond distances, as discussed above.

TABLE 2
Classification of Polyatomic Molecules

Moment of Inertia	Type of Rotor	Examples
$I_A = I_B, I_C = 0$	Linear	HX, $\text{O}=\text{C}=\text{S}$, $\text{H}-\text{C}\equiv\text{N}$
$I_A = I_B = I_C$	Spherical top	$\text{CH}_4, \text{SF}_6, \text{UF}_6$
$I_A > I_B = I_C$	{ Prolate symmetric top Oblate symmetric top	$\text{NH}_3, \text{CHCl}_3, \text{CH}_3\text{Cl}$
$I_A < I_B = I_C$		
$I_A \neq I_B \neq I_C$	Asymmetric top	H_2O

2. Spherical Top Molecules. Since a spherical top molecule such as CH_4 or SF_6 does not possess a permanent dipole moment, it is not microwave-active and is of only academic interest.

3. Symmetric Top Molecules. The solution of the Schrödinger wave equation for a symmetric top molecule gives the following expression for the energy levels of this rotor :

$$E_{J,K} = BJ(J+1) + (A-B)K^2 \quad \dots(43)$$

where K is the component of J about the unique axis and the rotational constants A and B (in cm^{-1}) are defined as

$$A = h/(8\pi^2 I_A c) \text{ and } B = h/(8\pi^2 I_B c) \quad \dots(44)$$

For every value of J , there are $2J+1$ values of K given by

$$K = 0, \pm 1, \pm 2, \dots, \pm J \quad \dots(45)$$

The selection rules for rotational transitions are

$$\Delta J = 0, \pm 1; \Delta K = 0 \quad \dots(46)$$

4. Asymmetric Top Molecules. The solution of the Schrödinger wave equation for an asymmetric top rotor is a very difficult problem and there is no simple expression for the energy levels. We shall, therefore, not discuss this rotor here.

Stark Effect in Microwave Spectra. The splitting of molecular rotational energy levels in the presence of the external electric field E is called the **Stark effect**, after the German physicist, J. Stark (1874–1957) who was awarded the 1919 Physics Nobel Prize for his discovery of Doppler effect in canal rays and the splitting of spectral lines in electric fields. The shift of rotational frequency, $\Delta\nu$, for a linear gaseous molecule in the Stark effect is given by

$$\Delta\nu \propto (\mu E)^2 \quad \dots(47)$$

where μ is the electric dipole moment of the molecule. Thus, knowing E and measuring $\Delta\nu$, μ can be determined. The Stark effect is extremely useful for determining the dipole moments of gaseous molecules.

Other Applications of Microwave Spectroscopy

The two most important applications of microwave spectroscopy are the study of internal rotation and the inversion spectrum of NH_3 .

1. Internal Rotation. If a part of a molecule can rotate about a *single bond* then the internal potential energy of the molecule depends on the orientation of this part with respect to the rest of the molecule. Consider $\text{F}_3\text{C}-\text{CH}_3$ (*i.e.*, 1,1,1-trifluoroethane) molecule. The variation of the potential energy of this molecule when CF_3 group rotates about the C–C single bond, as a function of the angle θ is given by

$$V(\theta) = V_0 (1 - \cos 3\theta) \quad \dots(48)$$

where V_0 is the height of the potential energy barrier (Fig. 9). For low potential energy barriers, free rotation takes place. The potential energy barriers of a number of compounds have been determined using microwave spectroscopy. However, the origin of these barriers still remains obscure.

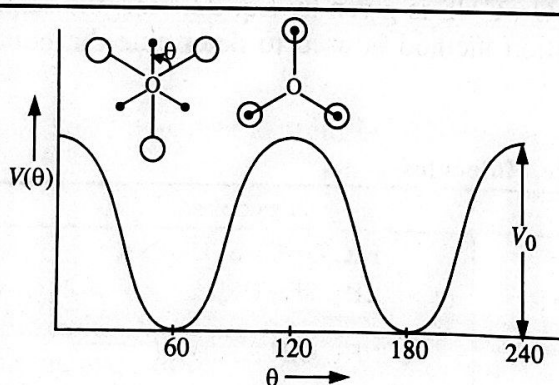


Fig. 9. Potential energy as a function of θ in internal rotation.

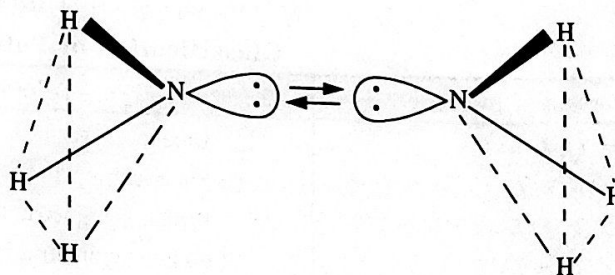


Fig. 10. The inversion of NH_3 molecule.

2. Inversion Spectrum of NH₃. Consider the inversion of the N atom through the plane of the three H atoms (Fig. 10).

The new configuration is the mirror image of the original configuration; it cannot be obtained by the rotation of the molecule. The two configurations have the same energy. A plot of the potential energy curve shows two minima with a hump in between (Fig. 11). The height of the hump, *i.e.*, the potential energy barrier, represents the *restriction to inversion*. Its value for NH₃ is about 25 kJ mol⁻¹.

Classically, it is impossible for the molecule to invert if it is in one of the first two vibrational levels. However, quantum mechanically it can 'tunnel' through the barrier. The inversion, in principle, is a vibrational motion. However, since it is hindered, it is observed in the microwave region. The splitting of the vibrational levels shown in Fig. 11 is a result of the *resonance interaction* between the two identical configurations. This **inversion doubling** causes the rotational lines to split.

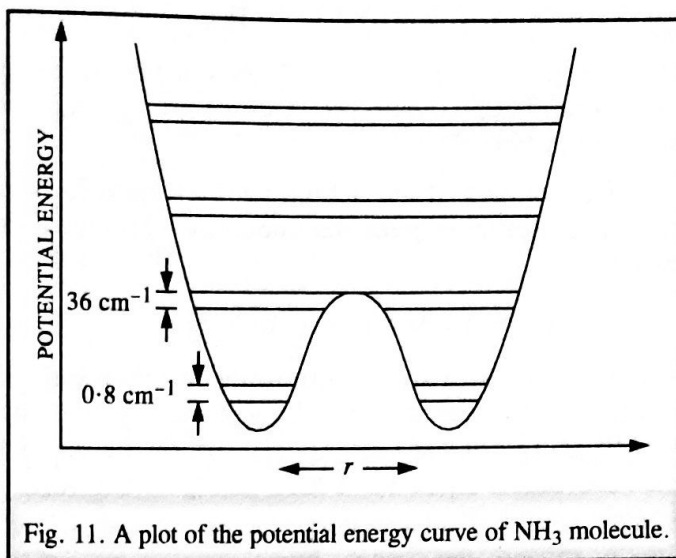


Fig. 11. A plot of the potential energy curve of NH₃ molecule.

VIBRATIONAL (INFRARED) SPECTRA OF DIATOMIC MOLECULES

A diatomic molecule with atomic masses m_1 and m_2 joined by a chemical bond vibrates as a one-dimensional simple harmonic oscillator (S.H.O.). Classically, the vibrational frequency of a mass point m connected by a spring of force constant k is given by

$$\nu = \frac{1}{2\pi} \left(\frac{k}{m} \right)^{1/2} \quad \dots(49)$$

In the case of a diatomic molecule, the masses m_1 and m_2 vibrate back and forth relative to their centre of mass in opposite directions (Fig. 12).

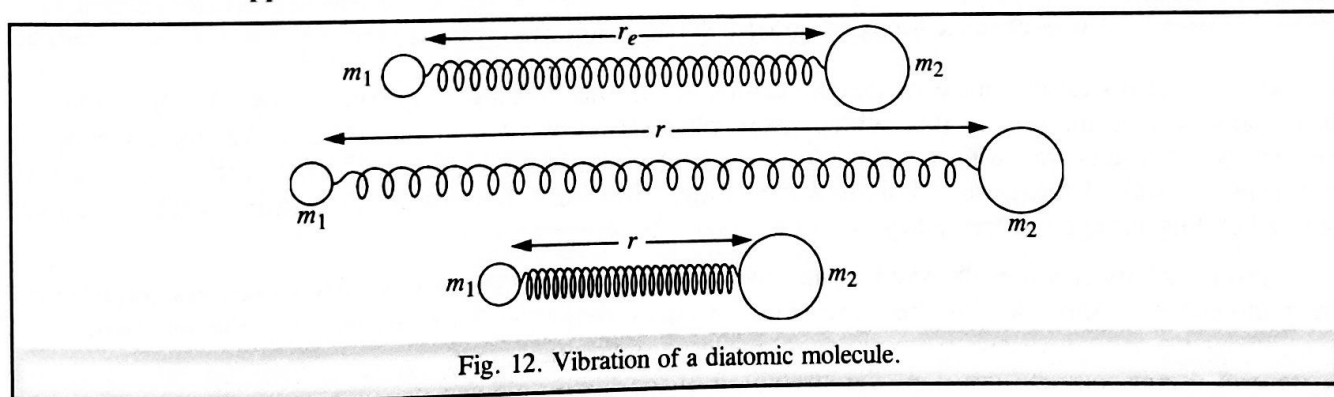


Fig. 12. Vibration of a diatomic molecule.

The two masses reach the extreme of their respective motions at the same time. The vibrational frequency of the molecule is given by a relation analogous to that of Eq. 49 with mass m replaced by the reduced mass μ :

$$\nu = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2} \text{ s}^{-1} \quad \dots(50)$$

To convert the frequency ν from s⁻¹ (hertz) to cm⁻¹, we divide by c , the velocity of light. Thus,

$$\bar{\nu} = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2} \text{ cm}^{-1} \quad \dots(51)$$