DIRECTORATE OF DISTANCE & CONTINUING EDUCATION

MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI- 627 012

OPEN AND DISTANCE LEARNING (ODL) PROGRAMMES
(FOR THOSE WHO JOINED THE PROGRAMMES FROM THE ACADEMIC YEAR 2023–2024)

M. Sc. Chemistry Course material
Elective - II
Molecular Spectroscopy
Course Code SCHE12

Prepared by
Dr. S. L. Sathya Saibaba
Assistant Professor
Department of Chemistry
Manonmaniam Sundaranar University
Tirunelveli – 627 012

Semester - I

Course: Elective - II **Course Code** SCHE12

MOLECULAR SPECTROSCOPY

UNIT-I: Rotational and Raman Spectroscopy: Rotational spectra of diatomic and polyatomic molecules. Intensities of rotational spectral lines, effect of isotopic substitution. Non-rigid rotators. Classical theory of the Raman effect, polarizability as a tensor, polarizability ellipsoids, quantum theory of the Raman effect, Pure rotational Raman spectra of linear and asymmetric top molecules, Stokes and anti-Stokes lines. Vibrational Raman spectra, Raman activity of vibrations, rule of mutual exclusion, rotational fine structure-O and S branches, Polarization of Raman scattered photons.

UNIT-II: Vibrational Spectroscopy: Vibrations of molecules, harmonic and anharmonic oscillators- vibrational energy expression, energy level diagram, vibrational wave functions and their symmetry, selection rules, expression for the energies of spectral lines, computation of intensities, hot bands, effect of isotopic substitution. Diatomic vibrating rotor, vibrational-rotational spectra of diatomic molecules, P, R branches, breakdown of the Born-Oppenheimer approximation. Vibrations of polyatomic molecules – symmetry properties, overtone and combination frequencies. Influence of rotation on vibrational spectra of polyatomic molecule, P, Q, R branches, parallel and perpendicular vibrations of linear and symmetric top molecules.

UNIT-III: Electronic spectroscopy: Electronic Spectroscopy: Electronic spectroscopy of diatomic molecules, Frank-Condon principle, dissociation and predissociation spectra. $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions and their selection rules. Photoelectron Spectroscopy: Basic principles, photoelectron spectra of simple molecules, Xray photoelectron spectroscopy (XPS). Lasers: Laser action, population inversion, properties of laser radiation, examples of simple laser systems.

UNIT-IV: NMR and ESR spectroscopy: Chemical shift, Factors influencing chemical shifts: electronegativity and electrostatic effects; Mechanism of shielding and deshielding. Spin systems: First order and second order coupling of AB systems, Simplification of complex spectra. Spin-spin interactions: Homonuclear coupling interactions - AX, AX2, AB types. Vicinal, germinal and long-range coupling-spin decoupling. Nuclear Overhauser effect (NOE), Factors influencing coupling constants and Relative intensities. 13CNMR and structural correlations, Satellites. Brief introduction to 2D NMR – COSY, NOESY. Introduction to 31P, 19F NMR. ESR spectroscopy Characteristic features of ESR spectra, line shapes and line widths; ESR spectrometer. The g value and the hyperfine coupling parameter (A), origin of hyperfine interaction. Interpretation of ESR spectra and structure elucidation of organic radicals using ESR spectroscopy; Spin orbit coupling and significance of g-tensors, zero/non-zero field splitting, Kramer's degeneracy, application to transition metal complexes (having one to five unpaired electrons) including biological molecules and inorganic free radicals. ESR spectra of magnetically dilute samples.

UNIT-V: Mass Spectrometry, EPR and Mossbauer Spectroscopy: Ionization techniques- Electron ionization (EI), chemical ionization (CI), desorption ionization (FAB/MALDI), electrospray ionization (ESI), isotope abundance, molecular ion, fragmentation processes of organic molecules, deduction of structure through mass spectral fragmentation, high resolution. Effect of isotopes on the appearance of mass spectrum. EPR spectra of anisotropic systems - anisotropy in g-value, causes of anisotropy, anisotropy in hyperfine coupling, hyperfine splitting caused by quadrupole nuclei. Zero-field splitting (ZFS) and Kramer's degeneracy. Applications of EPR to organic and inorganic systems. Structural elucidation of organic compounds by combined spectral techniques. Principle of Mossbauer spectroscopy: Doppler shift, recoil energy. Isomer shift, quadrupole splitting, magnetic interactions. Applications: Mossbauer spectra of high and low-spin Fe and Sn compounds.

Recommended Text

1. C. N. Banwell and E. M. McCash, *Fundamentals of Molecular Spectroscopy*, 4th Ed., Tata McGraw Hill, New Delhi, 2000.
2. R. M. Silverstein and F. X. Webster, *Spectroscopic Identification of Organic Compounds*, 6th Ed., John Wiley & Sons, New York, 2003.
3. W. Kemp, *Applications of Spectroscopy*, English Language Book Society, 1987.
4. D. H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry,* 4th Ed., Tata McGraw-Hill Publishing Company, New Delhi, 1988.

R. S. Drago, *Physical Methods in Chemistry*; Saunders: Philadelphia, 1992.

Reference Books

1. P.W. Atkins and J. de Paula, *Physical Chemistry*, 7th Ed., Oxford University Press, Oxford, 2002.
2. I. N. Levine, *Molecular Spectroscopy*, John Wiley & Sons, New York, 1974.
3. A. Rahman, *Nuclear Magnetic Resonance-Basic Principles*, Springer-Verlag, New York,1986.
4. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and coordination Compounds*, PartB: 5th ed., John Wiley& Sons Inc., New York, 1997.
5. J. A. Weil, J. R. Bolton and J. E. Wertz, *Electron Paramagnetic Resonance*; Wiley Interscience, 1994.

UNIT-1

Rotational and Raman Spectroscopy

Rotational Spectroscopy

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 anotherdue 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.

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 the structure and constitution of compounds.

Classification of Molecules

The rotation of a three dimensional body may be quite complex and it is convenient to resolve it into rotational components about three mutually perpendicular direction through the centre of gravity - the principal axes of rotation. Thus a body has three principal moments of inertia, one about each axis, usually I_A, I_B and I_C.

Molecules may be classified into groups according to the relative values of their three principal moments of inertia I_A, I_B and I_C. In general A, B, C axes are selected in such a way that $I_A < I_B < I_C$. The molecules are usually classified into four groups based on the relative values of principal moments of inertia.

1. **Linear molecules**

As the name suggests, in this case, all the atoms of the molecules are arranged in a straight line. Some of the molecules of this category are HCl, CO_2, OCS, HCN, C_2H_2 etc. The three directions of rotation may be taken as

(a) about the bond axes

(b) end-over-end roation in the plane of the paper and

(c) end-over-end rotation at right angles to the plane. As the nuclei of the atoms which give the main contribution to the mass are situated in the axis A, the moment of inertia about this axis is approximately zero. *i.e.* $I_A = 0$. The moments of inertia I_B and I_C correspond to the end- over-end rotation of the molecule and therefore they are equal. Thus, for a linear molecule $I_A = 0$ and $I_B = I_C$.

2. **Symmetric tops**

In a symmetric top, two of the principal moments of inertia are equal and all the three are non zero. Examples CH_4, CH_3Cl etc in which the carbon has a tetrahedral coordination. The C–Cl bond axis (in CH_3Cl) having a three fold axis of symmetry in the A-axis and on this the centre of gravity of the molecules lies. The two mutually perpendicular B and C axis lie in a plane perpendicular to the A-axis. It is obvious $I_B = I_C$. A molecule of this type spinning about the A-axis resembles a spinning top and hence the name symmetric top. The molecule in this class are further subdivided into the groups prolate symmetric top and the oblate symmetric top. In prolate $I_B = I_C > I_A$ (e.g. CH_3Cl, CH_3F, CH_3CN, NH_3 etc.) and in oblate $I_B = I_C < I_A$ (e.g. BF_3, BCl_3 etc.)

3. Spherical tops

When all the three principal moments of inertia of a molecule are equal, it is called a spherical top (e.g. CH_4, OsO_4, SF_6, CCl_4 etc.) *i.e.* $I_A = I_B = I_C$.

4. Asymmetric tops

These molecules, to which the majority of substance belong, have all three momentsof inertia different is $I_A \quad I_B \quad I_C$. Some of the examples are H_2O, CH_3OH, $CH_2{=}CHCl$ etc.

Rotational Spectra of Rogod Diatomic Molecules

Rigid Rotator

Let us consider a diatomic molecule A—B in which the atoms A and B having masses m_1 and m_2 are joined together by a rigid bond of length $r_0 = r_1 + r_2$ (figure 1). The molecule A—B rotates about a point C, the centre of gravity: this is defined by the moment, or balancing, equation.

$$m_1 r_1 = m_2 r_2 \qquad \text{...(1.1)}$$

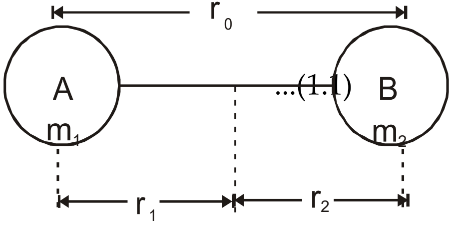


Fig. 1 : A rigid diatomic molecule A-B having atomic masses, m_1 and m_2, joined together by a rigid bond of length $r_0=r_1+r_2$ androtates about a point C.

The moment of inertia about C is defined by

$$I = m_1 r_1^2 + m_2 r_2^2 \qquad \left[m_1 r_1 = m_2 r_2 \right]$$

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

$$= r_2 r_1 \left(m_1 + m_2 \right) \qquad ....(1.2)$$

from eq$^{\underline{n}}$ (1) $m_1 r_1 = m_2 r_2 = m_2 \left(r_0 - r_1 \right)$

$$m_1 r_1 = m_2 r_0 - m_2 r_1$$

or $m_1 r_1 + m_2 r_1 = m_2 r_0$

or $r_1 \left(m_1 + m_2 \right) = m_2 r_0$

$$\Rightarrow \; r_1 = \frac{m_2 r_0}{m_1 + m_2} \text{ Similarly } \quad r_2 = \frac{m_1 r_0}{m_1 + m_2} \qquad ...(1.3)$$

Putting the value of $r_1 \,\&\, r_2$ from (3) in (2)

$$I = \frac{m_2 r_0}{\left(m_1 + m_2 \right)} \frac{m_1 r_0}{\left(m_1 + m_2 \right)} \left(m_1 + m_2 \right) = \frac{m_1 m_2 r_0^2}{m_1 + m_2} = \mu r_0^2 \qquad ...(1.4)$$

where μ is the reduced mass of the system i.e.

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad ...(1.5)$$

Equation (1.4) defines the moment of inertia conveniently in terms of the atomic masses and the bond length.

By the use of the Schrödinger equation it may be shown that the rotational energy levels allowed to the rigid diatomic molecule are given by the expression

$$E_J = \frac{h^2}{8\pi^2 I} J\left(J + 1 \right) \text{ Joules when } J = 0,\ 1,\ 2 \text{............................} (1.6)$$

In this expression h is Planck's constant, are I is the moment of inertia, either I_B or I_C, since both are equal. The quantity J, which can take integral values from zero upwards, is called the rotational quantum number and each level is (2J + 1) fold degenerate.

Often it is convenient to analyse the rotational energy spectrum in wave number units. Therefore we may write.

$$\varepsilon = {}^{E_J} = \frac{h}{8\pi^2 \; Ic} J\left(J+1\right) cm^{-1} \qquad \left[\, \underline{E} = \underline{1} \,\right]$$

$$= BJ\left(J+1\right) cm^{-1} \qquad J = 0,\ 1,\ 2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (1.7)$$

where B is the rotational constant and is given by

$$B = \frac{h/}{8\pi^2 Ic}\, cm^{-1} = \frac{h^2}{8\pi^2 I}\ Joule$$

Denoting the lower state by J´´ and the upper state by J´

$$\Delta\varepsilon_J = \varepsilon_{J'} - \varepsilon_{J''}$$

$$= BJ'\left(J'+1\right) - BJ'\left(J'+1\right)$$

$$B\left[J'\left(J'+1\right) - J'\left(J'+1\right)\right]$$

use of the selection rule $\left(\Delta J = \pm 1\right)$ or $J' - J' = 1$ gives the frequency of the absorption line as

$$v_J = \Delta\varepsilon_J = B\left[\left(J'+1\right)\left(J'+2\right) - J'\left(J+1\right)\right]$$

$$B\left(J'+1\right)2 \qquad \ldots(1.8)$$

$$J \longrightarrow J+1$$

$$\varepsilon_{J+1} = B\left(J+1\right)\left(J+2\right)$$

$$\varepsilon_J = B\,J\left(J+1\right)$$

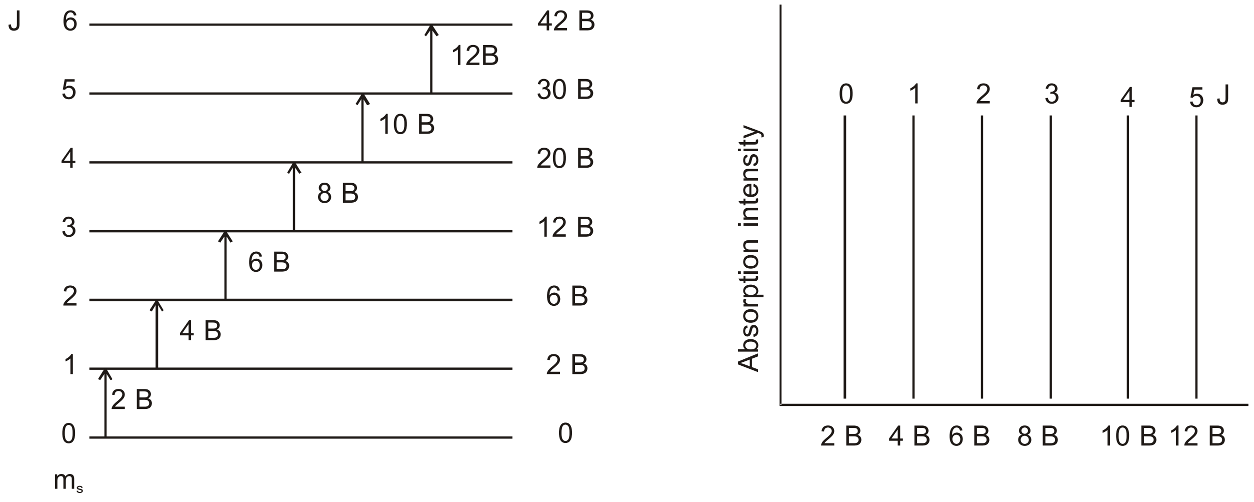
$$\overline{\Delta\varepsilon = B\left(J+1\right)\left(J+2-J\right)}$$

$$\Delta\varepsilon = 2B\left(J+1\right) cm^{-1} \quad where\ J = 0, 1, 2 \ldots.$$

The rotational constant B is assumed to be the same in both lower and upper rotational states and double prime is dropped from equ$^{\underline{n}}$ (1.8)

The allowed energy levels of a rigid diatomic rotor are illustrated in Fig. 2(a). Thus a step-wise raising of the rotational transitions result in an absorption spectrum consisting of spectral lines with a separation of 2 B, that is at 2B, 4B, 6B, (Fig. 2(b)). The lowering of stepwise energy results in identical emission spectrum.

Fig. 2(a) allowed energy levels of a rigid diatomic rotor showing electric dipole allowed transitions and (b) the resulting absorption spectrum.



(a) **(b)**

Fig. 2(a) allowed energy levels of a right diatomic rotor showing electric dipole allowed transitions and (b) the resulting absorption spectrum.

Selection Rule

The selection rule for a transition between any two rotational states is quantum chemically given by

$$\mu_{ij} = \int \psi_i \mu \Psi_j d\tau$$

where ψ_i and Ψ_j are the wave functions for the rotational states *i* and *j* and μ is the permanent dipole moment of the molecule. The dipole moment being a vector quantity can be expressed by its three components along the Cartesian coordinates axes, $\mu = \vec{\mu}_x + \vec{\mu}_y + \vec{\mu}_z$ and $\mu^2 = \mu_x^2 + \mu_y^2 + \mu_z^2$. The transition moment integral can be split in terms of the components of the dipole moment,

$$\left[\mu^x_{ij}\right] = \int \mu_i \, x \, \mu_j \, d\tau$$

$$\left[\mu^y_{ij}\right] = \int \mu_i \, y \, \mu_j \, d\tau$$

$$\left[\mu^z_{ij}\right] = \int \mu_i \, z \, \mu_j \, d\tau$$

If any one of the integrals is non zero, then the transition is allowed and forbidden otherwise. The intensity of an allowed rotational transition depends on the square of the transition dipole moment. Consequently, the intensity of the rotational line depends on the square of the permanent dipole moment of the molecule.

Schrödinger equation shows that for a diatomic rigid rotor (in the absence of an external electric or magnetic field) only transitions in which J changes by one unit, that is, $\Delta J = \pm 1$ are allowed and all other transactions are forbidden. Thus the selection rule for rotational spectra is $\Delta J = \pm 1$ (plus sign for absorption and minus sign for emission) and second, the molecule must have a permanent dipole moment (only hetronucelar diatomic molecules will exhibit the rotational spectrum since homonuclear diatomic molecules do not possess permanent dipole moment)

NON RIGID ROTOR

It is observed that in the pure rotational spectra of a diatomic molecule when the bond in it is considered as a rigid, the spacing between successive lines is same, i.e. 2 B cm^{-1}.However, the assumption that the bond is rigid is only an approximation. Actual bond is not a rigid bond and the bond length is not constant. It increases with rotations and is elastic. In a rapidly rotating molecule, there is always a tendency of the bond to stretch due to centrifugal effects. Hence, the moment of inertia increases with the rotational energy. This causes rotational levels to be same what closer as the J value increases.

It is evident that the separation between successive lines (and hence the apparent Bvalue) decreases steadily with increasing J.

we know $$B = \frac{h}{8\pi^2 Ic} = \frac{h}{8\pi^2 c\mu r^2}$$

$$B \propto \frac{1}{r^2}$$ [since all other quantities are independent of vibration

SPECTRUM OF A NON-RIGID ROTATOR

From Schrödinger equation for a non-rigid rotator in simple harmonic force field.

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 K} J^2 (J+1)^2 \ Joules$$ K = force constant

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h^2}{8\pi^2 Ihc} J(J+1) - \frac{h_4}{32\pi^4 I^2 r^2 Khc} J^2 (J+1)^2 \ cm^{-1}$$

$$BJ(J+1) - DJ^2(J+1)^2 \; cm^{-1} \qquad \dots \; (1.9)$$

when B is the rotational constant and D is the centrifugal distortion constant which is a positive quantity

$$B = \frac{h^2}{8\pi^2 Ihc}; \quad D = \frac{h^3}{32\pi^4 J^2 r^2 Kc} cm^{-1}$$

Relationship between B and D

$$B = \frac{h^2}{8\pi^2 Ihc} = \frac{h}{8\pi^2 Ic}$$

$$K = 4\pi^2 c^2 \bar{w}^2 \mu$$

$$D = \frac{h^4}{32\pi^4 I^2 r^2 Khc} = \frac{h^3}{32\pi^4 I^2 r^2 Kc} = \frac{h^3}{8 \times 2 \times 4 \times 8\pi^6 I^3 c^3} \frac{16\pi I c^2}{Kr^2}$$

$$= B^3 \times \frac{16\pi^2 I c^2}{Kr^2} \quad B^3 \times \frac{16\pi^2 \times \mu r^2 c^2}{4\pi^2 \bar{w}^2 c^2 \mu r^2} \quad \frac{B^3 \times 4}{\bar{w}^2} \quad \frac{4B^3}{\bar{w}^3}$$

$[\therefore \; w_{frequency} = \frac{\bar{w}}{c}$

$\omega = frequency$

$\bar{\omega} = wave\ number$

$\underline{\omega} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

$\therefore \; k = 4\pi^2 \bar{\omega}^2 mc^2]$

$[\; B^3 = \frac{h^3}{8 \times 8 \times 8\pi^6 I^3 c^3}]$

[$I = \mu r^2$; $k = 4\pi^2 \omega^2 c^2 \mu$] $\Delta J = \pm 1$ is of course still valid. The spectral line given by the

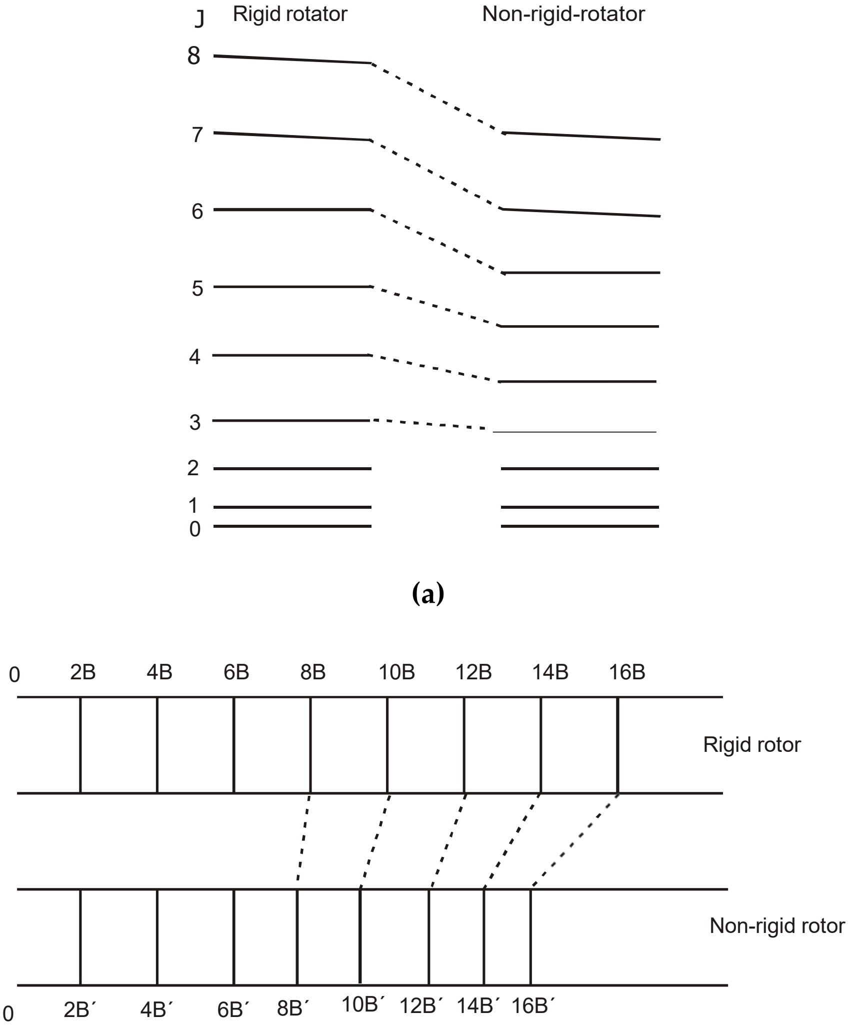
$$\therefore \; \boxed{D = \frac{4B^3}{\bar{w}^2}}$$

The selection rule equation is

$$BJ(J+1) - DJ^2(J+1)^2 \; cm^{-1}$$

$$\varepsilon_J = B_J(J+1) - DJ^2(J+1)^2 \; cm^{-1}$$

If D is neglected, the spectral lines occur at interval of 2B.



(a)

(b)

Fig. 3 (a) rotational energy levels and (b) allowed spectral lines for rigid andnon-rigid rotors.

For the an harmonic oscillator the expression (1.9) should be modified as

$$\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 \ cm^{-1} \qquad \ldots(1.10)$$

where the constants H, K etc, are dependent on the molecule. These constants H, K etc. are very small compared to D and hence can be neglected.

The value of D is also given by

$$D = \frac{16B^3\pi^2\mu c^2}{K} = \frac{4B^3}{\varpi^2}$$

The spectral line $\bar{v}_J$ is given by the equation

$$E_{J+1} - E_J = \bar{v}_J = 2B(J+1) - 4D(J+1)^3 \ cm^{-1} \qquad \ldots(1.11)$$

If D is neglected, the spectral lines occur at intervals of 2B. The rotational spectrum of a diatomic molecule such as HF, CO etc. can be fitted to the equation (1.11).

LINEAR POLYATOMIC MOLECULES

Linear polyatomic molecules can be treated like diatomic molecules. The rotational energy, E_J in this case is given by

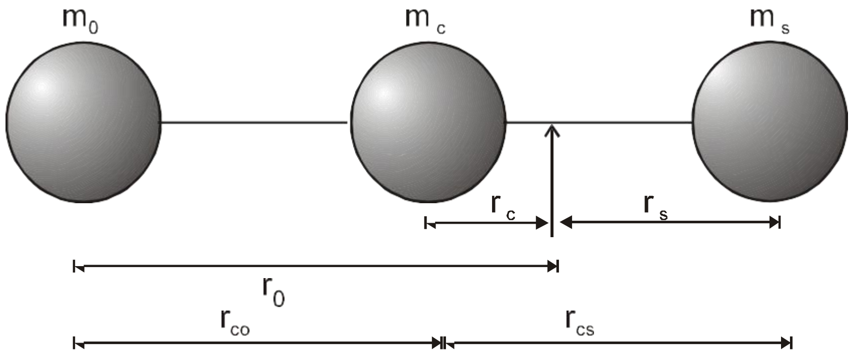
$$E_J = Bhc\ J(J+1)$$

The transition from one rotational state to other in rotational spectra is governed by –

1. Bohr quantum condition, $E = hv \ or \ hcv$
2. Molecule must have a permanent dipole moment
3. $\Delta J = \pm 1$

Thus, the rotational spectra of a linear polyatomic molecule will consist of a set of nearly equally spaced lines from which the rotational constant, B is determined. This value of B can be used to determine *I* and *r* in the molecule for a molecule. For a molecule with *n* atom, there are (*n* – 1) unknown inter nuclear distance to be determines. Thus for a triatomic molecule (OCS, HC ≡ CCl etc.) there are two bond distance to be determined. But only one moment of inertia for the end-over-end rotation can be obtained from the spectrum. It is impossible to obtain two unknown from one equation. This difficulty is overcome by obtaining the rotational spectra from (*n* – 1) different isotopic species for n- atom molecule to derive (n –1) different moments of inertia. The internuclear distance for the isotopic molecules are assumed to be the same. Consider linear unsymmetrical triatomic molecule such as OCS and HCN.

Let us consider the rotation of OCS molecule r_0, r_c and r_s represent the atoms from the centre of gravity



$$r_0 = r_{co} + r_c$$
$$r_s = r_{cs} - r_c$$

consideration of moments gives

$$m_0r_0 + m_cr_c = m_sr_s$$

$$\Rightarrow\ m_0\left(r_{co} + r_c\right) + m_cr_c = m_s\left(r_{cs} - r_c\right)$$
$$\Rightarrow\ m_0r_{co} + m_0r_c + m_cr_c = m_sr_{cs} - m_sr_c$$
$$\Rightarrow\ m_0r_c + m_cr_c + m_sr_c = m_sr_{cs} - m_0r_{co}$$
$$\Rightarrow\ \left(m_0 + m_c + m_s\right)r_c = m_sc_{cs} - m_0r_{co}$$
$$\Rightarrow\ Mr_c = m_sr_{cs} = m_0r_{co}$$

where M is the total mass of the molecule $\left(M = m_0 + m_c + m_s\right)$

$$\boxed{r_c = \frac{m_s r_{cs} - m_0 r_{co}}{M}} \qquad \text{...(1.12)}$$

The moment of inertia of the molecule about an axis passing through centre of mass will be given by

$$I = m_0 r_0^2 + m_c r_c^2 + m_s r_s^2$$

$$= m_0 \left(r_{co} + r_c\right)^2 + m_c r_c^2 + m_s \left(r_{cs} - r_c\right)^2$$

$$= m_0 r_{co}^2 + m_0 r_c^2 + 2m_0 r_{co} r_c + m_c r_c^2 + m_s r_{cs}^2 + m_s r_c^2 - 2m_s r_{cs} r_c$$

$$= \left(m_0 + m_c + m_s\right) r_c^2 + m_0 r_{co}^2 + m_s r_{cs}^2 + 2r_c \left(m_0 r_{co} - m_s r_{cs}\right)$$

$$= M r_c^2 + m_0 r_{co}^2 + m_s r_{cs}^2 + 2r_c \left(m_0 r_{co} - m_s r_{cs}\right)$$

$$= m_0 r_{co}^2 + m_s r_{cs}^2 + 2r_c \left(m_0 r_{co} - m_s r_{cs}\right) + M\left(\frac{m_s r_{cs} - m_0 r_{co}}{M}\right)^2 \qquad \text{[from (1.12)]}$$

$$= m_0 r_{co}^2 + m_s r_{cs}^2 + \frac{2\left(m_s r_{cs} - m_0 r_{co}\right)}{M}\left(m_0 r_{co} - m_s r_{cs}\right) + \frac{\left(m_s r_{cs} - m_0 r_{co}\right)^2}{M}$$

$$= m_0 r_{co}^2 + m_s r_{cs}^2 + \frac{\left(m_s r_{cs} - m_0 r_{co}\right)}{M}\left[2\left(m_0 r_{co} - m_s r_{cs}\right) + \left(m_s r_{cs} - m_0 r_{co}\right)\right]$$

$$= m_0 r_{co}^2 + m_s r_{cs}^2 + \left(\frac{m_s r_{cs} - m_0 r_{co}}{M}\right)\left(m_0 r_{co} - m_s r_{cs}\right)$$

$$= m_0 r_{co}^2 + m_s r_{cs}^2 - \left(\frac{m_o r_{co} - m_s r_{cs}}{M}\right)\left(m_o r_{co} - m_s r_{cs}\right)$$

$$= m_0 r_{co}^2 + m_s r_{cs}^2 - \left(\frac{m_o r_{co} - m_s r_{cs}}{M}\right)^2 \qquad \text{...(1.13)}$$

In order to obtain another equation of the type (1. 13), use of isotopes is made and an assumption that the internuclear bond distance do not change in isotopic substitution is also required.

$$I' = m_0' r_{co}^2 + m_s r_{cs}^2 - \frac{\left(m_0' r_{co} - m_s r_{cs}\right)^2}{M'}$$

From isotopic substitution, two moments of inertia are obtained. These two moments of inertia are used to calculate two bond lengths.

NON-LINEAR POLYATOMIC MOLECULES

Symmetric top molecules

The rotational spectra of symmetric top molecules are simple. This is because the rotation of a symmetric top rotor about its unique principle axis has no effect on its rotation about an axis perpendicular to this an vice- versa. So it is possible to separate the rotation about the principal axis from the other rotations for a symmetric top.

Consider a prolate symmetric top (CH_3Cl) where $I_B = I_c \neq I_A$ & $I_A \neq 0$. The

C—Cl bond is its molecular symmetry axis. Consequently we need two quantum numbers to describe he degree of rotation one for I_A and the other for I_B or I_C.

For the rigid prolate symmetric top, the solution of Schrödinger equation give the energy levels.

$$E_{J,K} = \frac{h^2}{8\pi^2 I_B} J(J+1) + \left(\frac{h^2}{8\pi^2 I_A} - \frac{h^2}{8\pi^2 I_B}\right) K^2 \text{ Joule}$$

$$\varepsilon_J = \frac{E_{J,K}}{hc} = BJ(J+1) + (A-B)k^2 cm^{-1} \qquad \text{...(1.14)}$$

For oblate

$$\varepsilon_J = BJ(J+1) + (C-B)k^2, \ k \le J \qquad \text{...(1.15)}$$

So that $(C—B)$ is positive

The rotational constant, A, B and C in cm^{-1} are

$$A = \frac{h}{8\pi^2 I_A c},\ B = \frac{h}{8\pi^2 I_B c},\ c = \frac{h}{8\pi^2 I_c C} \qquad \text{...(1.16)}$$

J = 0, 1, 2, 3 ......

k = 0, ±1, ±2, ±3 ... ± J

The quantum number J represents the total angular momentum of the molecule and K represents the projection of the total angular momentum upon the molecular symmetryaxis. Note that the energy depends on K^2, so that it is immaterial whether the top spins clockwise or anticlockwise, the energy is the same for a given angular momentum. For all k >0, therefore, the rotational energy levels are doubly degenerate. Selection rules (in the absence of external fields) for the rotational spectra of symmetric top molecules are

(i) The molecule must have a permanent dipole moment directed. Symmetry top molecules have their dipole moment directions among unique axis

(ii) The transition should obey $\Delta J = 0, \pm 1$ and $\Delta K = 0\,(K \neq 0)$, $\Delta J = \pm 1$ i.e. transitions with $\Delta J = 0$ do not occur. Thus transitions between different k levels are not allowed. k characteristics rotation about the unique axis. For a symmetric top, rotation about the unique axis does not change dipole moment and hence cannot interact with radiation.

Transition are identical to diatomic molecules and the spacing is also 2B

$J \to J+1$ (from (1.14)

$$\varepsilon_{J+1} = B(J+1)(J+2) + (A-B)k^2$$

$$\varepsilon_J = BJ\left(J+1\right) + \left(A-B\right)k^2\ cm^{-1} \qquad cm^{-1}$$

$$\Delta E = 2B\left(J+1\right)\ cm^{-1} \qquad .....1.17$$

equation (1.17) shows that the spectrum is just the same as for a linear molecule and that only one moment of inertia- that for a end-over-end rotation- can be measured. Planar symmetrical molecules such as BCl_3, SO_3, C_6H_6 do not exhibit rotational spectra. In symmetric top molecules bond lengths and bond angles can be determined using isotopic substitution method.

Effect of Isotopic Substitution

When a particular atom in a molecule is replaced by its isotope - an element identical except its atomic mass - the resulting substance is identical chemically with the original. In particular there is no appreciable change in internuclear distance on isotopic substitution. However, there is change in total mass and hence in the moment of inertia and B value for the molecule.

We have $B > B^I$. This change will be reflected in the rotational energy levels of the molecule.

Raman Spectroscopy

Introduction

Already we have studied that within a molecule, there are certain energy levelswhich are associated with rotation, vibration or electronic level. When a radiation of a particular wavelength falls on a molecule, there is absorption of radiation which results in transition between these energy levels. This technique is known as spectroscopy. Now a days, spectroscopy is a very vast topic in chemistry and constitute one of the subject in chemistry. It involve several spectra depending on the type of radiation absorbed. For example, if a molecule absorbs radiations falling in microwave region, there is a transition between rotational energy levels. This spectroscopy is known as pure rotational spectroscopy or microwave spectroscopy. Likewise, when a molecule absorbs radiations falling in infra-red region, the spectroscopy is known as vibrational spectroscopy in which there is transition between vibrational energy level of a molecule.

This chapter deals with Raman spectroscopy which was observed by C. V. Raman (Physicist) and for this he was awarded by Nobel Prize. It encompasses the concept of polarizability that changes on exposure to the radiations. Polarizability is defined as the ability of a non-polar molecule to acquire dipole moment in presence of an electric field. Further in this unit, we will discuss about the mechanism of Raman excitation, polarizability ellipsoids, selection rule (on the basis of which we decide whether the transition between energy levels are allowed or forbidden). In order to understand the unit more clearly, we will consider Raman spectra of a diatomic molecule which includes pure rotational and pure vibrational Raman spectra along with the law of mutual exclusion which play an important role in determining the structure of a molecule. Raman spectra is different from all the other type of spectra, as all other spectra involves absorption of radiation while in Raman spectra, there is scattering of radiation instead of absorption. The scattering is a two photon process. Therefore much focus has been given i As we have discussed earlier that there is scattering of radiation in Raman spectroscopy instead of absorption. We can obtain Raman spectra for solid, liquid and gaseous sample. Homo -diatomic molecules or molecules without permanent dipole moment like N , O , H etc also shown order to make the unit more interesting.

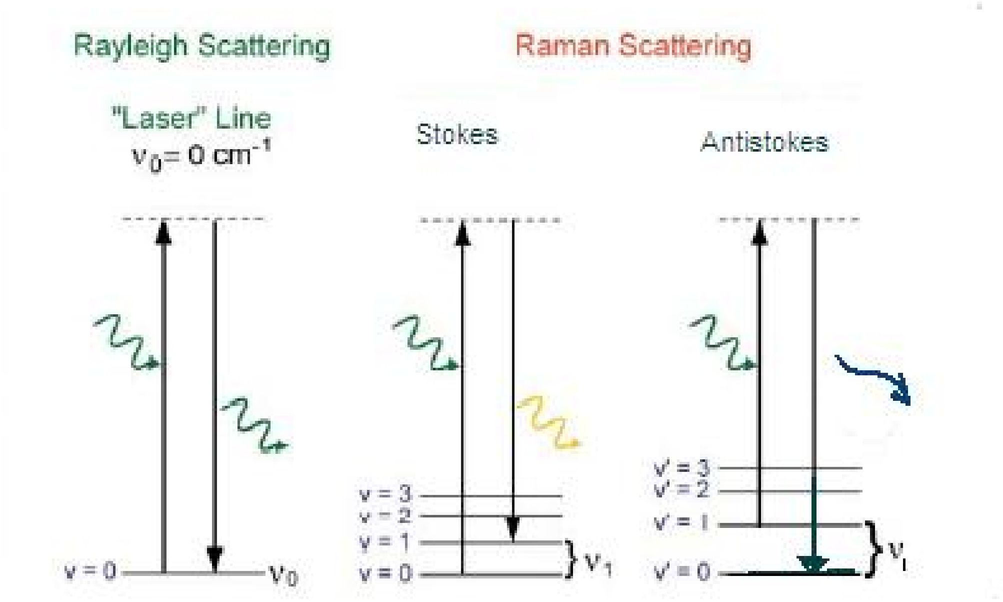
Raman spectra whereas for a molecule to be infra- red active, molecule must possess permanent dipole moment.In Raman spectroscopy, an intense beam of monochromatic light of visible region is allowed to pass through the molecule and the scattered light which is observed at right angle to the incident beam is observed. It has been seen that some of the scattered light have same frequency as that of the incident light while some scattered light have frequencies different (less or more) from the incident light. This is known as Raman effect or Raman shift. There are two theories that explain Raman scattering, one is classical theory of Raman scattering while other is a quantum theory of Raman scattering. The classical theory is known as the theory of polarizability. The quantum theory explains the mechanism of Raman excitation. According to the quantum theory of Raman scattering, there is a collision between the incident photon or radiation and the molecule. Let us consider a molecule having energy E_1. If an incident light of energy hυ (υ frequency of the incident radiation) falls on a molecule, its energy is raised to E_3.

Thus E = E –hυ

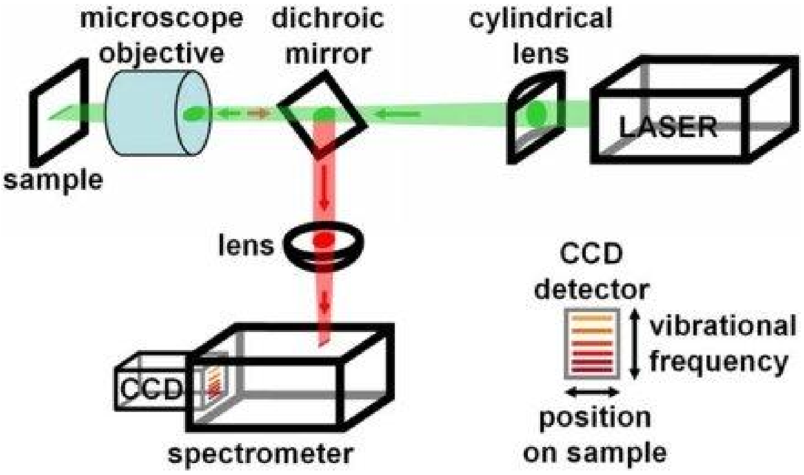
Putting the value of E in above equation we obtain: E = E +hυ –hυ

E – E = hυ –hυ h(υ –υ) = hΔυ

Where Δυ is Raman shift which is the difference in the frequency of the incident light and the scattered light. Therefore:Δυ = υ –υ . When the frequency of the scattered light is less than the frequency of the incident light (υ >υ), Stokes Raman lines are produced. Here Raman shift is positive. When the frequency of the scattered light is more than the frequency of the incident light i.e. υ <υ , we obtain anti-Stokes Raman lines. Here Raman shift is negative. When the frequency of the scattered light is equal to the frequency of the incident light (υ =υ), Rayleigh Raman lines are obtained. All these scattered Raman lines are shown in Figure. It is important to remember that Raman shift (Δυ) is independent of the frequency of the incident radiation but it depends on the characteristic of the molecule showing Raman effect. Raman shift lies in the region of near and far infra- red radiation. Finally it is concluded that for a molecule to show Raman effect, there must be at least three different energy levels within the molecule. Here in this case discussed above, E and E represents the energy of the initial and final state respectively while E2 represents the energy of the intermediate state. The experimental setup consist of a cell into which a sample is taken. One end of a cell is horn like while the other end is provided with optically glass plate. A beam of monochromatic radiation is allowed to fall on the cell containing



the sample. Sample must be colorless, pure and clean solid, liquid or gas molecule. Concentrated samples are taken so that the Raman lines produced possess high intensity. The source of a monochromatic radiation is helium tube which was used in previous time but now a day's mercury arc is used. This mercury arc is placed close to the cell so that the cell receive radiations of high intensity. The scattered radiations emerges through the optically plane glass plate. There is a lens that direct the scattered radiations on the spectrograph. Spectrograph possess short focus camera, prism having high resolving power and large light gathering power. The complete experimental setup for Raman spectra is shown in Fig.



As we have discussed above that when monochromatic light is scattered by a molecules, the scattered light having frequency equal to the frequency of the incident light is known as Rayleigh line or Rayleigh scattering. Some of the scattered light possess frequency lower than the frequency of the incident light, this give rise to Stokes lines in Raman spectra. This decrease in frequency is due to the transfer of some amount of energy of incident light to the molecule. As a result there is decrease in energy causing decrease in frequency. The part of energy absorbed by the molecule is used in the transition to higher energy states. For Stokes lines, Raman shift or Raman effect which is represented by Δυ is positive. Out of three types of lines (Stokes, anti-Stokes and Rayleigh) obtained after scattering of light in infra-red and far infra-red region, Stokes lines possess intensity more than the intensity of anti- Stokes lines but less than that of Rayleigh line. The wavelength of Stokes lines is more than that of the wavelength of the incident light.

Some of the scattered light possesses frequency higher than the frequency of the incident light, this give rise to anti-Stokes lines in Raman spectra. This increase in frequency is due to the transfer of molecular energy to the incident photon which results in the increase of energy or frequency of the scattered light. The part of energy lost by the molecule results intransition from higher energy or excited vibrational state to lower energy or ground state. For these lines, Raman shift or Raman effect (Δυ) is negative. The intensity of anti-Stokes lines are lower than that of Stokes lines. This can be explained on the basis of Boltzmann distribution law. According to which the intensity depends on the number of molecules present in the lower energy state or ground state before irradiation. As it is clear from above that in case of Stokes lines, there is transition of molecule from lower energy level to higher energy level whereas in case of anti- Stokes lines, there is transition from higher energy state to lower energy state. Therefore, the number of molecules is more in the ground state prior to irradiation in case of Stokes lines in comparison to anti- Stokes lines. Hence more is the number of molecules or atoms in the ground state, more is the intensity of the scattered line. Thus Stokes lines are more intense than anti- Stokes lines. The wavelength of these lines is less than the wavelength of the incident light. These Raman lines are shown in Figure.

POLARIZABILITY ELLIPSOIDS

The classical theory of Raman scattering is also known as theory of polarizability. According to this theory, in the presence of an electric field, the electrons of a molecule (neutral) are attracted to the positive pole while nuclei of a molecule are attracted towards the negative pole. As a result, a dipole moment is induced or produced in the molecule. In this state, a molecule is said to be polarized. In this way electron cloud get distorted in the presence of an electric field. This ability of a molecule to gain dipole moment is called polarizability. The induced dipole moment (μ) is related to electric field (E) by an expression:

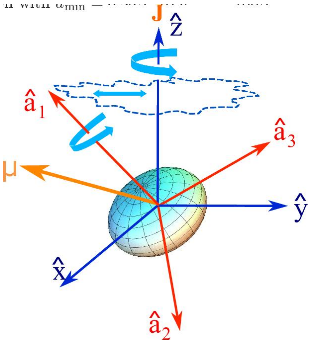
$$\mu = P\ E$$

where P is polarizability of the molecule. The value of μ (induced dipole moment) depends on the direction of the electric field. When the direction of the electric field is along the inter nuclear axis then the value of induced dipole moment is high. When the direction of electric field is perpendicular to the inter-nuclear axis then the value of induced dipole moment is low. In case of spherically symmetrical molecule, the direction of electric field is independent of the value of the induced dipole moment. For non- isotropic molecule for principle axis:

$$\mu' = P\ E\ ;\mu' = P\ E\ ;\ \mu' = P\ E\ z'z'\ z'$$

Here x′, y′ and z′ are three principle axis. If from the origin of the principle axis coordinate system, we draw lines of length proportional to the inverse of the square root of polarizability in any direction, then the locus of the points of lines form a surface. This surface is known as polarizability ellipsoid which is shown in Fig. The equation of an ellipsoid is:

$$Px'x'\ x'2 + Py'y'\ y'2 + Pz'z'\ z'2 = 1$$



Unit -II Vibrational spectroscopy

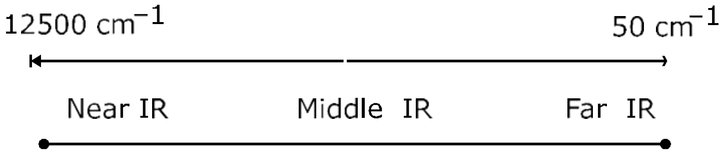
INTRODUCTION

Vibrational energy of a molecule corresponds to infrared frequency. The interaction of infrared radiation with molecular vibration gives infrared spectrum. If the average position and orientation of a molecule remains constant but the distance between the atoms in a molecule change, molecular vibrations are said to take place. Infrared spectroscopy is used in identification of functional groups in pure compounds.

Infra-red (IR) does not have sufficient energy to induce electronic transition as seen in UV spectroscopy. When molecule absorbed electromagnetic radiation in IR region, undergoes vibrational or a rotational transitions which causes net change in the dipole moment in the molecule (IR active, for example HCl, CO etc), if dipole moment does not change in molecules then they are IR inactive (for example: O_2, H_2, N_2 etc.) means they does not absorb IR radiation.

A vibrational spectrum is observed experimentally as Infrared as well as Raman Spectra. But the physical origin of two type of spectra are different. Infrared spectrum is associated with dipole moment (μ) of the bond whereas Raman spectra are associated with polarizability.

Either the wavelength (λ) or wave number ($\bar{\nu}$ in cm^{-1}) is used to measure the position of a given infrared absorption. The range of IR spectrum is as :



Wave number	:	$12500 - 4000\ cm^{-1}$	$4000\ cm^{-1} - 650\ cm^{-1}$	$650 - 50\ cm^{-1}$
Wave length	:	$0.8\,\mu - 2.5\,\mu$	$2.5\,\mu - 15\,\mu$	$15\,\mu - 200\,\mu$

where μ *is micron such that* $1\mu = 10^{-6}\ m = 10^{-8}\ cm$

Most studied absorption frequency in IR spectroscopy is 200 cm^{-1} 4000 cm^{-1}. It is fundamental frequency region. Greater than 4000 cm^{-1} requires very high energy. These are known as overtone bands. Overtones are multiple of fundamental frequencies (e.g. $2\nu_1, 2\nu_2, 3\nu_1, 3\nu_2$ *etc.*). Apart from fundamental & overtone, we also have combination bands $(\nu_1 \pm \nu_2)$

$\nu_1 + \nu_2$ Addition band

$(\nu_1 - \nu_2)$ Substraction band

MOLECULAR VIBRATION

A molecule is not a rigid assemble of atoms. A molecule can be considered as a system of balls of varying masses corresponding to atoms of molecules and spring of varying strengths, corresponding to the chemical bands of a molecule.

There are two types of fundamental vibration for molecules :

(i) Stretching vibration in which the distance between two atoms increases or decreases but the atoms remain in the same bond axis.

(ii) Bending or deformation, in which the position of the atom changes relative to the original bond axis.

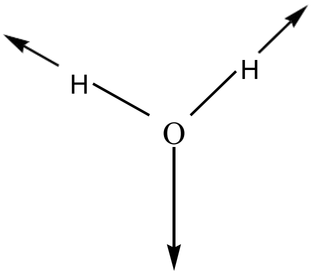
The various stretching and bending vibrations of a bond occur at a certain quantized frequencies. When infrared light of the same frequency is incident on the same molecule energy is absorbed and amplitude of that vibration is increased. When the molecule reverts from the excited state to the original ground state, absorbed energy is released as heat.

A nonlinear molecule that contains n atoms has 3n-6 possible fundamental vibrational modes that can be responsible for the absorption of infrared light. Thus, such simple molecules as methane (CH_4) and Benzene (C_6H_6) have theoretically, nine and thirty possible fundamental absorption bands, respectively.

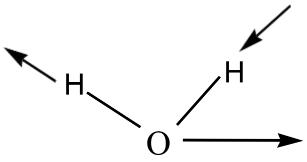
In order for a particular vibration to result in the absorption of infrared energy, that vibration must cause a change in the dipole moment of the molecule. Thus, molecules that contain certain symmetry elements will display somewhat simplified spectra. The C=C stretching vibration of ethylene ($H_2C = CH_2$) and the symmetrical C—H stretching of the few C—H bonds of methane (CH_4) don't result in a absorption band in the infrared region. The predicted number of peaks will not be observed also if the absorption occurs outside the region ordinarily examined.

Additional (non-fundamental) absorption bands may occur because of the presence of overtones (or harmonics that occur with greatly reduced intensity at $1/2$, $1/3$ ... of the wavelength (twice, thrice times the wave numbers) combination bands (the sum of two or more different wave numbers), and difference bond (the difference of two or more different wave numbers)

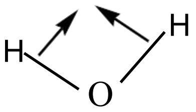
Obviously, there are many possible vibrations in a molecule. However, only those stretching vibrations which cause a change in dipole moment will show an IR absorption. Those which show no change in dipole moment may observed by raman spectroscopy. For example, H_2O. It is a bent molecule.



Symmetric stretching



Asymmetric stretching

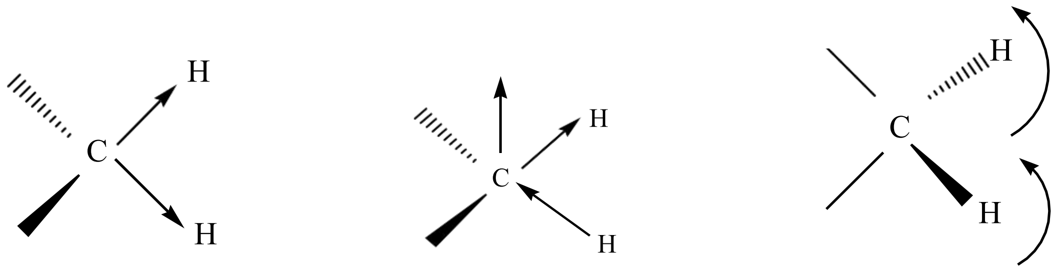


Scissoring

$$E_{\text{asy str.}} > E_{\text{sym. str.}} > E_{\text{sci}}$$

or $$V_{\text{asy st.}} > V_{\text{sym. st.}} > v_{\text{sci}}$$

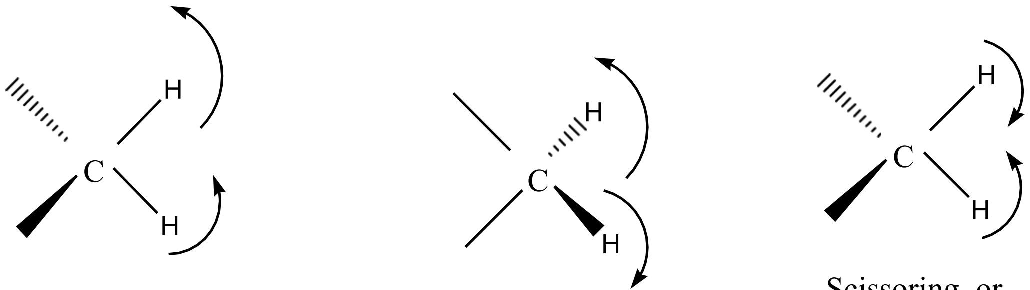
— **CH_2 group :**



Symmetric stretching

Assymetric stretching

Wagging or out of plane bending



Rocking or Asymmetric in plane bending

Twisting or out of plane bending

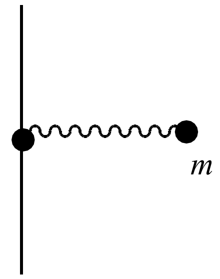
Scissoring or symmetic in plane bending

Fig. (2.1)

VIBRATION OF A SINGLE PARTICLE (CLASSICAL)

Let us consider a particle of mass attached to fixed position through a spring (tensionless).

Now, we consider the type of vibrational motion, the particle of mass m undergoes. The spring through which the body is fixed is such that if the particle is removed a distance from its equilibriums position, it experiences a restoring force (f_r) which is proportional to its displacement from the equilibrium position. A spring which behaves in this manner is said to obey Hooke's law.



For such behavior we can write $f_d \propto x$ where f_d = driving force, x = displacement from equilibrium position

$$\Rightarrow f_d = kx$$

where k = Proportionality constant called force constant

But $f_d = -f_r$ where f_r = restoring force.

$$\therefore \quad f_r = -kx$$

f_r is in opposite direction which tends to keep the particle in equilibrium position.

The force constant (k) which appears in the molecular problem measures the stiffness of the spring i.e. bond. It gives a restoring force (fr) for unit displacement from equilibrium position. The negative reign indicates that fr is directed opposite to x.

The potential energy (U) is work that must be done to displace the particle a distance dx.

Therefore, the potential energy is given by

$$dU = f_{app} \times dx = f_d \times dx$$

$$= -f_r dx$$

$$\Rightarrow \frac{dU}{dx} = -f_r$$

But from Hooke's law, we have

$$f_r = -kx$$

$$\therefore \quad \frac{dU}{dx} = -(-kx) = kx \quad \Rightarrow \text{ dU} = kxdx$$

If the equilibrium position is taken as that of zero potential energy

$$\therefore \int_0^U dU = \int_0^x kxdx \quad \Rightarrow \quad \boxed{U = \frac{1}{2}kx^2} \qquad ...(2.1)$$

This gives the expression for potential energy of vibrating particle.

From the expression for potential energy it is clear that is equation of a parabola. This is potential energy (U) of particle increases parabolically as the particle moves in either direction from equilibrium position.

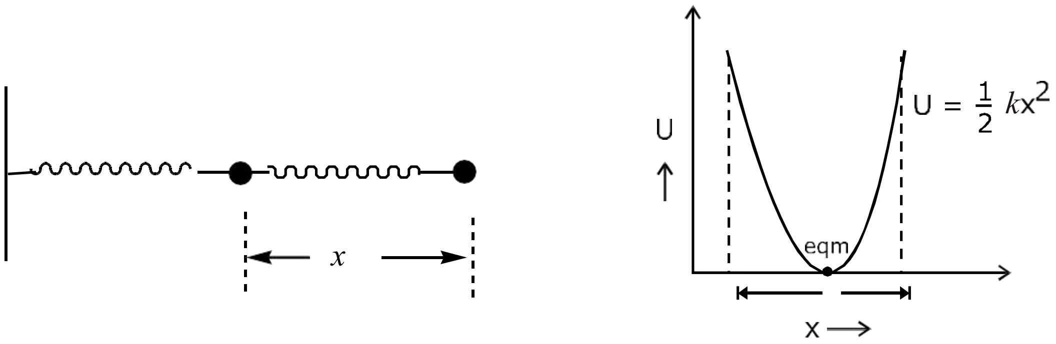


Fig. (2.2)

The equation describing the motion of the particle can be set up as :

From Newton's law, we know that

$$f = ma = m.\frac{d^2x}{dt^2} = m\ddot{x}$$

$$\text{Also} \quad f = -\frac{dU}{dx}$$

$$\therefore -\frac{dU}{dx} = m\ddot{x}$$

$$\Rightarrow \frac{dU}{dx} + m\ddot{x} = 0 \qquad ...(2.2)$$

$$\Rightarrow kx + m\ddot{x} = 0$$

This gives the equation for vibrational motion.

$$\Rightarrow \frac{dU}{dx} + m\frac{d}{dt}\left(\frac{dx}{dt}\right) = 0$$

$$\Rightarrow \frac{dU}{dx} + m\frac{1}{dt}\frac{d}{dt}(dx) = 0$$

$$\Rightarrow \frac{dU}{dx} + m\frac{1}{dt}d\dot{x} = 0$$

$$\Rightarrow dU + m\frac{dx}{dt}d\dot{x} = 0$$

$$\Rightarrow dU + m\dot{x}\,d\dot{x} = 0 \qquad ....(2.3)$$

This is required form of equation of motion for vibrating particle

Again, since $\frac{dU}{dx} = kx \qquad \Rightarrow dU = kxdx$

Equation (2.3) becomes as

$kxdx + m\dot{x}d\dot{x} = 0$

Now, we can integrate it to get potential energy (P.E.) and kinetic energy (K.E.) part of vibrational energy.

$$k\int xdx + m\int \dot{x}\,d\dot{x} = 0$$

$\Rightarrow \frac{kx^2}{2} + \frac{mx^2}{2} = E$; where E is Integration constant which gives total energy

$$\therefore \ E = \frac{1}{2}kx^2 + \frac{1}{2}m\dot{x}^2 \qquad ...(2.4)$$

$$\Rightarrow \ E = P.E. + K.E.$$

where $P.E. = \frac{1}{2}kx^2$ & $K.E. = \frac{1}{2}m\dot{x}^2$

Thus total energy associated with the vibrating particle is the sumn of KE. and P.E.

The expression for the vibrational frequency may be obtained as :

We know that equation for the vibrational motion is

$$\frac{dU}{dx} + m\ddot{x} = 0$$

$$\Rightarrow m\ddot{x} = -\frac{dU}{dx} = -kx$$

$$\Rightarrow m\ddot{x} + kx = 0 \qquad \text{...(2.5)}$$

It is a differential equation of second degree. It has solution of the form

$$x = A\cos(2\pi\nu t + \phi) \qquad \text{...(2.6)}$$

where A = amplitude of vibration

ν = vibrational frequency

ϕ = Phase angle

$$\dot{x} = \frac{dx}{dt} = A(-2\pi\nu).\sin\ (2\pi\nu t + \phi)$$

$$\& \quad \ddot{x} = \frac{d^2x}{dt} = A\left(-4\pi^2\nu^2\right)\cos(2\pi\nu t + \phi)$$

Putting the value of $\ddot{x}$ & x in equation (2.5), we get

$$mA\left(-4\pi^2\nu^2\right)C\text{ os }(2\pi\nu t + \phi) + kA\ Cos(2\pi\nu t + \phi) = 0$$

$$\Rightarrow A\ \mathrm{Cos}\,(2\pi\nu t + \phi)\ \left\{m\left(-4\pi^2\nu^2\right) + k\right\} = 0$$

$$\Rightarrow -4\pi^2\nu^2 m + k = 0$$

$$\Rightarrow 4\pi^2\nu^2 m - k = 0$$

$$\Rightarrow \nu^2 = \frac{1}{4\pi^2}\frac{k}{m}$$

$$\Rightarrow \nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad \text{...(2.7)}$$

$$\Rightarrow \bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{m}} \qquad \text{...(2.8)}$$

This equation is the important classical result for the frequency of vibration. It shows that a particle with mass m held by a spring with force constant k will vibrate according to equation (2.2) with frequency ν given by equation (2.7). Only this frequency is allowed. The energy with which the particle vibrate can be shown to depend upon the maximum displacement, i.e. amplitude *'A'* of the vibration.

SIMPLE HARMONIC OSCILLATOR

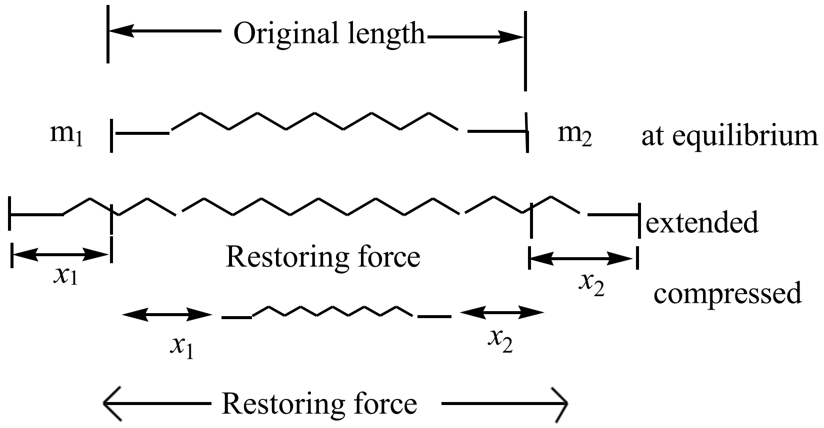


Fig. (2.3)

Let us consider conservative system of two particles having mass m_1 and m_2, joined by a massless perfectly elastic spring. On applying force (*f*) the particle move only along bond axis of the system with displacement x_1 and x_2 from equilibrium position. Such motions are assumed to be harmonic in nature giving rise to harmonic vibrations. The magnitude of the force that restores each particle to the equilibrium position is proportional to the extent of compression or extention of the bond (spring) i.e. Restoring force $f \propto -(x_2 - x_1)$

$$\Rightarrow \quad f = -k(x_2 - x_1) \qquad \boxed{f = -kx} \qquad \text{...(2.8)}$$

where k is characteristics of a bond called the force constant.

$x = (x_2 - x_1)$ = displacement with respect to mean position. The negative sign indicates that the restoring force (*f*) acts in a direction opposite to displacement. Also, if x is positive, it corresponds to extension and compression gives a negative value of x.

The work that must be done to displace the particles by a distance dx is $-fdx$. This work is stored in the system as potential energy (P.E.), dU so that

$$dU = -fdx \qquad \text{...(2.9)}$$

If zero potential energy is taken at the equilibrium position, then

$$\int_0^U dU = \int_0^x -fdx = \int_0^x kx\,dx$$

$$\Rightarrow U = \frac{1}{2}kx^2 = \frac{1}{2}k\left(x_2 - x_1\right)^2 \qquad \text{...(2.10)}$$

It complicates the system as it is no longer an equation of simple parabola. Similarly kinetic energy (K.E), T of the bond is given by

$$T = \frac{1}{2}\left[m_1 \left(\frac{dx_1}{dt}\right)^2 + m_2 \left(\frac{dx_2}{dt}\right)^2 \right] \qquad ...(2.11)$$

For each particle *i*, the Langrange equation can be written as

$$\frac{d}{dt}\left(\frac{dT}{dx}\right) + \frac{dU}{dx_i} = 0$$

For particle 1, $m_1 \frac{d^2 x_1}{dt^2} = -(-)\, K\left(x_2 - x_1\right) = K\left(x_2 - x_1\right)$

or $\quad m_1 \ddot{x}_1 = k\left(x_2 - x_1\right) \qquad$ ....(2.11(a))

and for particle 2

$$m_2 \frac{d^2 x_2}{dt^2} = -k\left(x_2 - x_1\right)$$

$$\Rightarrow m_2 . \ddot{x}_2 = -k\left(x_2 - x_1\right) \qquad ...(2.11(b))$$

The change in sign of two equation is due to their vibration in opposite direction.

Equation (2.11(a) has solution, $\quad x_1 = A_1\left(C\text{os}\, 2\pi \nu t + \phi\right)$

and equation (2.11(b)) has solution, $x_2 = A_2\left(C\text{os}\, 2\pi\, \nu t + \phi\right)$

$\therefore \quad x_1 = A_1\left(-2\pi\nu\right) S\text{in}\left(2\pi\nu t + \phi\right)$

and $\quad \ddot{x}_1 = A_1\left(-4\pi^2\nu^2\right) Cos\left(2\pi\nu t + \phi\right)$

$\therefore \quad m_1 A_1\left(-4\pi^2\nu^2\right) C\text{os}\left(2\pi\nu t + \phi\right) = K\left(A_2 - A_1\right) C\text{os}\left(2\pi\nu t + \phi\right)$

$$\Rightarrow m_1 A_1\left(-4\pi^2\nu^2\right) = k\left(A_2 - A_1\right)$$

$$\Rightarrow -4\pi^2\nu^2 m_1\, A_1 + kA_1 - kA_2 = 0$$

$$\Rightarrow (-4\pi^2\nu^2 m_1\ \nu^2 + k)\,\mathrm{A}_1 - KA_2 = 0 \qquad \text{...(2.12 (a))}$$

Similarly from equation (2.11 (b)), we get

$$m_2 \dot{x}_2 = -k\left(x_2 - x_1\right)$$

$$x_2 = A_2\left(C\mathrm{os}\, 2\pi\nu t + \phi\right)$$

$$\dot{x}_2 = \frac{dx_2}{dt} = A_2\left(-2\pi\nu\right)\, S\mathrm{in}\left(2\pi\nu t + \phi\right)$$

$$\ddot{x}_2 = \frac{d^2x_2}{dt^2} = A2\left(-4\pi^2\nu^2\right)\ C\mathrm{os}\ \left(2\pi\nu t + \phi\right)$$

$$\therefore\ m_2 A_2\left(-4\pi^2\nu^2\right) C\mathrm{os}\left(2\pi\nu t + \phi\right) = -k\left(A_2 - A_1\right) C\mathrm{os}\left(2\pi\nu t + \phi\right)$$

$$\Rightarrow m_2 A_2\left(-4\pi^2\nu^2\right) - kA_1 + kA_2 = 0$$

$$-kA_1 + \left(-4\pi^2\nu^2 m_2 + k\right) A_2 = 0$$

Thus equation (2.12(a)) (2.12(b)) are simultaneous equation of first degree

Solution : (i) $\mathrm{A}_2 = \mathrm{A}_2 = 0\ \therefore\ \nu = 0$

It is a trivial solution and so is meaningless

(ii) For non-trivial solution we construct secular determinant of A_1 & A_2

$$\begin{vmatrix} \left(-4\pi^2 m_1\nu^2 + K\right) & -K \\ -K & \left(-4\pi^2 m_2\nu^2 + K\right) \end{vmatrix} = 0$$

From this secular equation, we can obtain expression for frequency

$$\left(-4\pi^2\nu^2 m_1 + k\right)\left(-4\pi^2\nu^2 m_2 + k\right) - k = 0$$

$$\Rightarrow\ 16\pi^4\nu m^4 m_2 - 4\pi^2\nu^2 m_1 k - 4\pi^2\nu^2 m_2 k + k^2 - k^2 = 0$$

$$\Rightarrow 4\pi^2\nu^2\left(4\,\pi^2\nu^2 m_1m_2 - m_1k - m_2k\right) = 0$$

$$\Rightarrow\ 4\pi^2\nu^2\ m_1m_2 - \left(m_1 + m_2\right)k = 0$$

$$\Rightarrow\ 4\pi^2\nu^2\ m_1m_2 = \left(m_1 + m_2\right)k$$

$$\Rightarrow \nu^2 = \frac{1}{4\pi^2}\frac{k\left(m_1 + m_2\right)}{m_1m_2}$$

$$\Rightarrow\ \nu^2 = \frac{1}{4\pi^2}.\frac{k}{\mu}\ ; \quad \text{where } \mu = \frac{m_1m_2}{m_1 + m_2} \text{ is reduced mass}$$

$$\Rightarrow \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \text{...(2.13)}$$

It gives the expression for frequency of vibration of two particles and its relation with force constant (k) and reduced mass (μ) of the system. The frequency of the vibration is written as ν_{osc} in Hz and $\bar{\nu}_{osc}$ in cm^{-1} as :

then $\nu^2 = 0$ and hence $\nu = 0$

$$\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \text{... (2.13 a)}$$

$$\bar{\nu}_{osc} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \text{...(2.13 b)}$$

Also, if $4\pi^2\nu^2 = 0$

then $\nu^2 = 0$ and hence $\nu = 0$

It corresponds to the motion in which both particles are displaced by the same amount in same direction *i.e.* $x_1 = x_2$.

Thus $\nu = 0$ corresponds to translational motion

On substituting the ν_{osc} in equation (2.12 a) & (2.12 b), we get

$$\frac{A_1}{A_2} = \frac{m_2}{m_1} = \frac{x_1}{x_2} \qquad \text{...(2.14)}$$

If m_2 is lighter than m_1, the vibrational amplitude of m_2 will be correspondingly greater than that of m_1.

On substituting the value of force constant k = $4\pi^2\mu\nu_{osc}^2$ in equation (2.10),

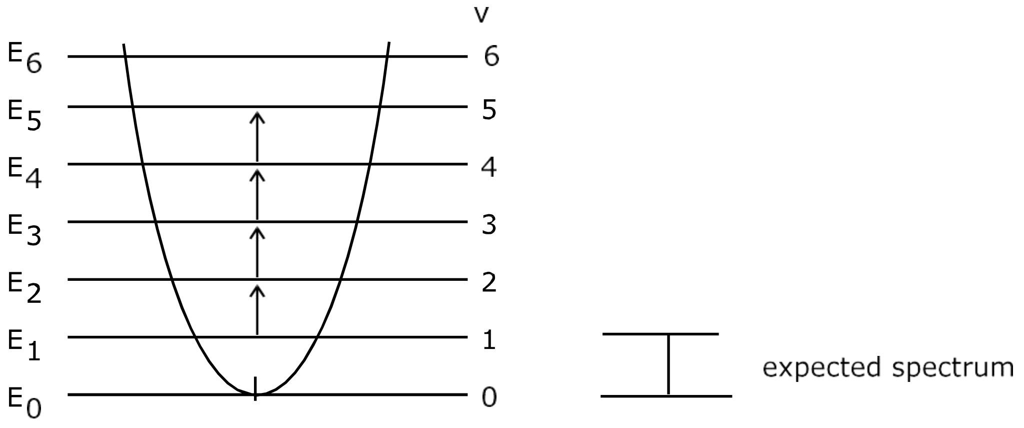
we get

$$U = \frac{1}{2}kx^2 = \frac{1}{2}4\pi\mu\nu_{osc}^2 x^2$$

$$\Rightarrow U = 2\pi^2\mu\nu_{osc}^2 x^2 \qquad \text{...(2.15)}$$

It shows that in simple harmonic motion (S.H.M) the potential energy (U) is proportional to the square the displacement of the centre of gravity of the molecule. The potential energy is parabolic.

The concept of reduced mass (μ) reduces the vibration of two atoms in a molecule to the vibration of a single mass point, whose amplitude equal the amplitude change (A_2-A_1) of the vibrating atoms in the molecule. An increase in energy will make the oscillations more vigorous, i.e. the degree of compression or extension will be greater but the vibrational frequency ν_{osc} will be the same. Such a model gives a vibrational frequency independent of the amount of bond distortion. However classical mechanics allows amplitudes and therefore the energy of vibration to attain any value contrary to the quantum nature of energy.



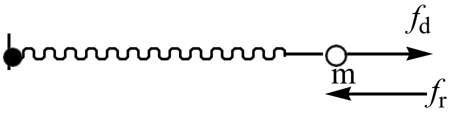
(Fig. 2.4): Some of the vibrational energy levels & allowed transition of H.O. diatomic molecule (NO)

SCHRÖDINGER EQUATION

There are a few simple systems where the potential energy is not constant, yet the Schordinger equation can be exactly solved. For example, vibration of a diatomic molecule and motion of an atom in a crystal lattice.

Let us consider a particle of mass '*m*' attached to a weightless spring and restricted in the same, way so that it can move only in the x-direction. The force acting on this particle is given by Hooke's law as :

$f_d \propto x$



Since direction of driving force (f_d) and restoring force (f_r) are opposite to each other,

$\therefore\ f_d = -f_r$

$\therefore\ f_r \propto -x$

$\Rightarrow\ f_r = -kx$ where k is proportionality constant known as force constant.

If f_r = 1 dyne, x = 1 cm $\therefore$ k = 1 dyne / cm.

It is defined as equal to force per unit displacement. This type of force is called harmonic. Whenever the motion of a particle can be described by the simple law known as Hooke's law, then the system is said to be harmonic oscillator.

The potential energy, U is given by $-\frac{dU}{dx} = f$

$$\Rightarrow -dU = fdx = -kxdx$$

$$\Rightarrow dU = kxdx$$

On integrating, we get

$$\int_0^U dU = k\int_0^x xdx$$

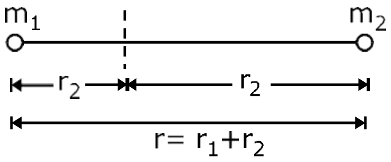
$$\therefore U = \frac{1}{2}kx^2$$

The kinetic energy, T is given by

$$T = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2 = \frac{1}{2m}m^2v^2 = \frac{1}{2}\frac{p_x^2}{m}$$

where $p_x\ (= mv)$ is linear momentum. For two particle system having mass m_1 and m_2, the kinetic energy, is given by

$$T = \frac{1}{2} m_1 \left(\frac{dr_1}{dt}\right)^2 + \frac{1}{2} m_2 \left(\frac{dr_2}{dt}\right)^2$$



$$\Rightarrow T = \frac{1}{2} m_1 \dot{r}_1^2 + \frac{1}{2} m_2 \dot{r}_2^2$$

The reduced mass, μ is given by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

$$\therefore\ T = \frac{1}{2}\mu x^2 = \frac{1}{2\mu} \times \mu^2 x^2 = \frac{p_{x^2}}{2\mu}$$

Total energy associated with the system is given as

$$H = T + U$$

$$\Rightarrow H = \frac{p_x^2}{2\mu} + \frac{1}{2}kx^2$$

This is expression of energy through classical mechanics
Classically the equation of motion is expressed as

$$m.\frac{d^2x}{dt^2} = -kx \text{ (Newton's law)}$$

which has the general solution as $x = x_0 \sin\left(\sqrt{\frac{k}{m}}\,t + \delta\right)$

where x_0 & δ are arbitrary constants, x_0 being the amplitude of the oscillation. According to classical mechanics, the particle oscillates from $x = x_0$ to $x = -x_0$

sinusoidally with the time at a frequency $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$

The energy then changes back and forth from the kinetic energy form to the potential energy form, being exclusively kinetic when $x = 0$ and exclusively potential when $x = x_0$. The total energy is constant given by $\frac{kx_0^2}{2}$. It can have any positive value, there being no limit on the value of x_0 . Now let us cansider the properties of such a system according to the law of quantum mechanics.

Let us first set up Hamiltonian operator for Harmonic oscillator (H.O.)

We know that

$$H = U + T = \frac{p_x^2}{2m} + \frac{1}{2}kx^2$$

$$\therefore\ \hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}k\hat{x}^2 = -\frac{{}^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2}k\hat{x}^2$$

$$\left(\hat{p}_x = -i\frac{\partial}{\partial x} \qquad \therefore\ \hat{p}_x^2 = \left(-i\frac{\partial}{\partial x}\right)^2 = i^2\,{}^2\frac{\partial^2}{\partial x^2} = -{}^2\frac{\partial^2}{\partial x^2}\right)$$

The schodinger equation for harmonic oscillator then may be written as : we know that S.E. in operator form is as

$$H\Psi = E\Psi$$

$$\Rightarrow \frac{-{}^2}{2\mu}\frac{\partial^2\Psi}{\partial x^2} + \frac{1}{2}kx^2\Psi = E\Psi$$

$$\Rightarrow \frac{\partial^2\Psi}{\partial x^2} + \frac{2\mu}{{}^2}\left(\frac{1}{2}kx^2\right)\Psi = \frac{2\mu}{{}^2}E\Psi$$

$$\Rightarrow \frac{\partial^2\Psi}{\partial x^2} + \frac{2\mu}{{}^2}\left(E - \frac{1}{2}kx^2\right)\Psi = 0 \qquad \text{....(2.16)}$$

This is Schrödinger equation for harmonic oscillator. The problem is now to find the well behaved functions which satisfy the equation (2.16) and the allowed energy levels.

The solution of this equation vanishes at infinite and is single valued and finite, and the energy is discontinuous but changes by integral value of the vibrational quantum number v given by

$$E_{osc} = \left(v + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \text{...(2.17)}$$

where v = 0, 1, 2, 3 .... known as vibrational quantum number (can take only positive integer values, including zero).

The quantum energy levels with the simple harmonic oscillator as a model are equidistant and have been represented in figure (2.4)

It should be particularly noted that energy at v = 0 is not zero but $\frac{1}{2}h\nu_{osc}$ and is called zero point energy. It has no counterpart in the classical approach. This is also in accordance with the Hiesenberg's uncertainty principle, i.e. at 0 K (–273°C) when even translational, rotational motion have been frozen, uncertainty of the position of the molecules still exist due to zero point energy and is equal to $\frac{1}{2}h\nu_{osc}$ per vibrational mode.

For example in case of NO,

$$\bar{\nu}_{osc} = 1904\, cm^{-1}$$

$$\text{zero point energy} = \frac{1}{2}h\nu = \frac{1}{2} \times 6.625 \times 10^{-34} \times 1904 \times 3 \times 10^{10}$$

$$= 18923 \times 10^{-24}\ \text{J}$$

It is conventional to express vibrational modes and energy levels in cm^{-1} as follows :

$$\frac{E_{osc}}{hc} = G(v) = \nu_{osc}\left(\nu + \frac{1}{2}\right) cm^{-1}$$

where G(v) is called term value, $\bar{\nu}_{osc}$ the molecular vibration in wave numbers, and v is the vibrational quantum number.

$$\text{Zero point energy in cm}^{-1} = \frac{\bar{v}_{osc}}{2}$$

$$\therefore \quad \text{zero point energy of NO in cm}^{-1} = \frac{1904}{2} = 952\, cm^{-1}$$

Again, $$E = \left(v + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

Thus the quantum mechanics requires that only certain discrete energies are assumed by the vibrator. The term

$$\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

appears in both classical as well as quantum mechanical treatment

Also, from classical mechanics treatment we know that

$$\nu_m = \frac{1}{2\pi}\sqrt{\frac{k}{m}} = \frac{1}{2\pi c}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}} \qquad ....(2.18)$$

From equation (2.17) and (2.18), we have

$$E = \left(v + \frac{1}{2}\right) h\nu_m \qquad ....(2.19)$$

where ν_m is the vibrational frequency of mechanical model.

If we now assume that transitions in vibrational energy levels can be brought about by radiation, provided the energy of radiation exactly matches the difference in energy levels ΔE between the vibrational quantum states and provided that the vibration causes a change in dipole. This difference is identical between any pair of adjacent levels, because *v* in equation (2.17) & (2. 19) can assume only whole numbers. That is ,

$$\Delta E = h\nu_m = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \qquad ...(2.20)$$

At room temperature majority of molecules use in the ground state (ν = 0). Thus

$$E_0 = \frac{1}{2} h\nu_m$$

In order to move to the first excited state with energy $E_1 = \frac{3}{2} h\nu_m$ requires radiation of energy $\left(\frac{3}{2} h\nu_m - \frac{1}{2} h\nu_m\right) = h\nu_m$

The frequency of radiation ν that will bring about this change is identical to the classical vibrational frequency of the bond ν_m. Thus,

$$E_{radiation} = h\nu = \Delta E = h\nu_m = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \qquad ...(2.21)$$

$$\Rightarrow \nu = \nu_m = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\ Hz \qquad ...(2.22)$$

This expression can also be written in terms of wave number of radiation.

Thus, $$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi c}\sqrt{\frac{k\left(m_1+m_2\right)}{m_1 m_2}}\,cm^{-1} \qquad ....(2.23)$$

where, $\bar{\nu}$ = wave number of absorption peak in cm^{-1}

k = force constant (in dynes/cm)

c = velocity of light (3×10^{10} in cm/s)

m_1 & m_2 are masses of two atoms

The allowed vibrational energy levels and transition between them for a diatomic molecule undergoing simple harmonic motion may be shown as :

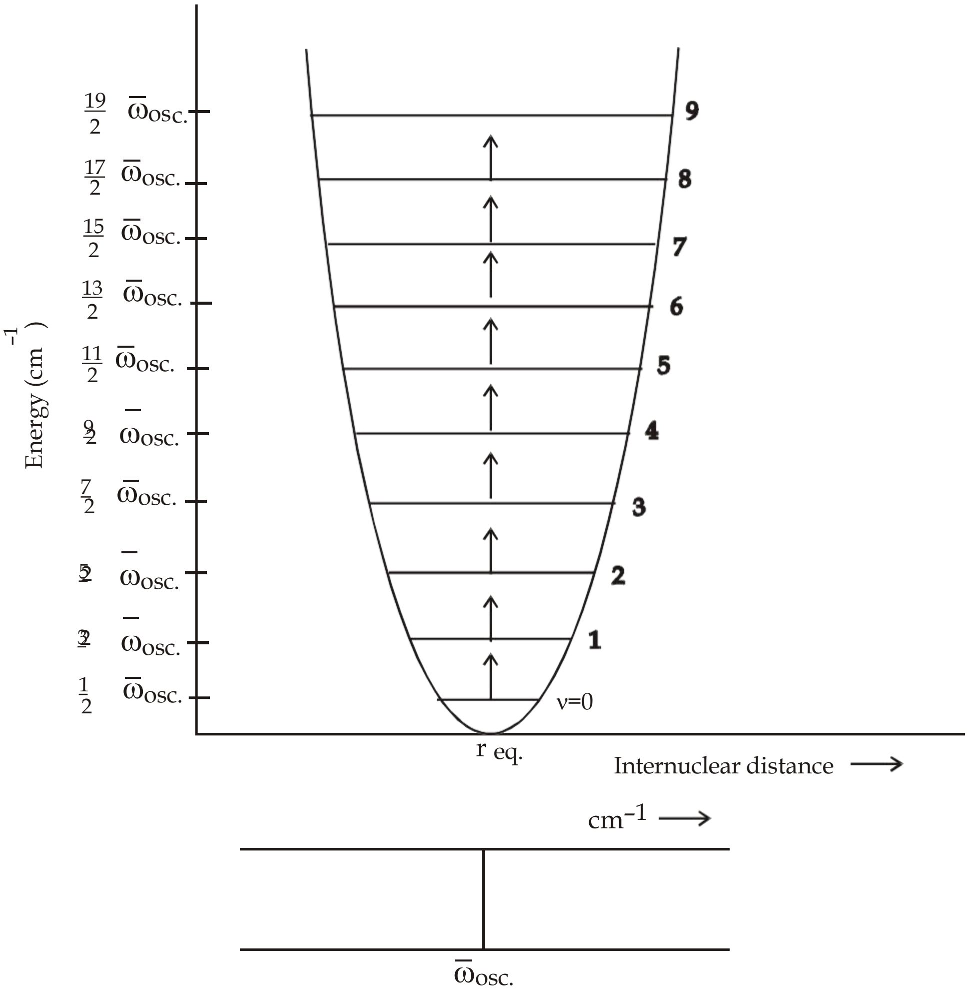


Fig. (2.5) The allowed vibrational energy levels and transition between them for a diatomic molecule undergoing simple harmonic motion.

ZERO POINT ENERGY

According to the old quantum theory, the energy levels of a harmonic oscillation were given by

$$En = n\,h\nu$$

If this were true, the lowest energy level would be that with n = 0, and would therefore have zero energy. This would be state of complete rest and represent the minimum in potential energy curve. The uncertainty principle does not allow such a state of complete defined position and completely defined momentum (in this case zero). As a result wave mechanical treatment show that the energy levels of the oscillator are given by

$$E_v = \left(v + \frac{1}{2}\right)h\nu_0 \qquad \text{...(2.24)}$$

where v is the vibrational quantum number which may take on the values, v=0, 1, 2, 3 The vibratory motion of the nuclei of a diatomic molecule can be represented as vibration of a simple harmonic oscillator. In such an oscillator the vibrational energy E_v is related to the fundamental vibrational frequency ν_0 by the above wave mechanical relationship. The above equation shows that such an oscillator retains the energy $E_0 = \frac{1}{2}h\nu_0$ in the lowest vibrational level v = 0. This residual energy, called zero point energy of the oscillator cannot be removed from the molecule even cooling it to 0 K (–273°C). The enrgy $E_0 = \frac{1}{2}h\nu_0$ must be added to the planck's expression for the mean energy of an oscillator.

The implication is that the diatomic molecule (and indeed any molecule) can never have zero vibration energy; the atoms can never be completely at rest relative to each other. The quantity $\frac{1}{2}h\nu_0$ Joules or $\frac{1}{2}\bar{\nu}_0\ cm^{-1}$, the zero point energy; depends only on the classical vibration frequency and hence on the strength of the chemical bond (k) and atomic masses (μ).

The prediction of zero point energy is the basic difference between the wave mechanical and classical approaches to molecular vibrations. Classical mechanics could find no objection to a molecule possessing no vibrational energy but wave mechanics insists that it must always vibrate to some extent, the latter conclusion has been amply borne out by experiment.

SELECTION RULE

Further use of the Schrödinger equation leads to the simple selection rule for the harmonic oscillator undergoing vibrational changes :

$$\Delta v = \pm 1$$

To this, we must of course add the condition that vibrational energy changes will only give rise to an observable spectrum if the vibration can interact with radiation, i.e. if the vibration involves a change in the dipole moment of the molecule. Thus the vibrational spectra will be observable only in hetronuclear diatomic molecules since homonuclear molecules have no dipole moment.

Applying the selection rule we have immediately :

$$E_{v\to v+1} = \left(v+1+\frac{1}{2}\right)\bar{\nu}_{osc} - \left(v+\frac{1}{2}\right)\bar{\nu}_{osc}$$

$$= \bar{\nu}_{osc}\ cm^{-1} \qquad \text{...(2.25)}$$

for absorption, whatever the initial value of v.

Such a simple result is also obvious from the figure given above; since the vibrational levels are equally spaced, transitions between any two neighboring states will give rise to the same energy change. Further since the difference between energy levels we expressed in cm^{-1} gives directly the wave number of the spectral line absorbed or emitted.

$$\bar{\nu}_{spectroscopic} = \varepsilon = \bar{\nu}_{osc}$$

This, again, is obvious if one consider the mechanism of a absorbing or emission in classical terms. In absorption for instance, the vibrating molecule will absorb energy only from radiation with which it can coherently interact and this must be radiation of its own oscillation frequency.

For example, NO (nitric oxide) molecule.

The expected vibrational energy levels for NO molecules are equally spaced. Transition between any two neighbouring states will give rise to the same energy change and thus only one line. The NO as harmonic oscillator should absorb at 1904 cm^{-1}

$$\text{or}\ \ \nu_{osc} = \frac{c}{\lambda} = c\bar{\nu}_{osc} = 3\times10^{10}\times1904s^{-1} = 5712\times10^{10}s^{-1}$$

The energy of this quanta of radiation is

$$E = h\nu_{osc} = 6.626\times10^{-34}\times5712\times10^{10}J = 37847\times10^{-24}J$$

It is the energy which must correspond to the energy difference, even for a

$v=0\to v=1$ transition.

THE ANHARMONIC OSCILLATOR

Though a simple harmonic oscillator gives a good picture, it does not explain the following points :

(i) The potential energy and therefore the restoring force increases infinitely with increasing distance from the equilibrium position. Therefore it places no limit on how far a bond can be stretched, while in an actual molecule, when atoms are at a great distance from one another, the attractive force is zero, the bond will break and correspondingly the potential energy has a constant value.

(ii) The summary of the potential energy curve (figure in the previous section) reflects that the restoring force for compression and extension is the same which is not the case. The bonds strongly resist compressing as revealed by relative incompressibility of solids.

Although for small compressions and extensions the bond may be taken as perfectly elastic for larger amplitudes say greater than 10% of the bond length, a much more complicated behaviour must be assumed. Figure given below shows, diagrammatically the shape of the energy curve for a typical diatomic molecule, together with (dashed) the ideal, simple harmonic parabola.

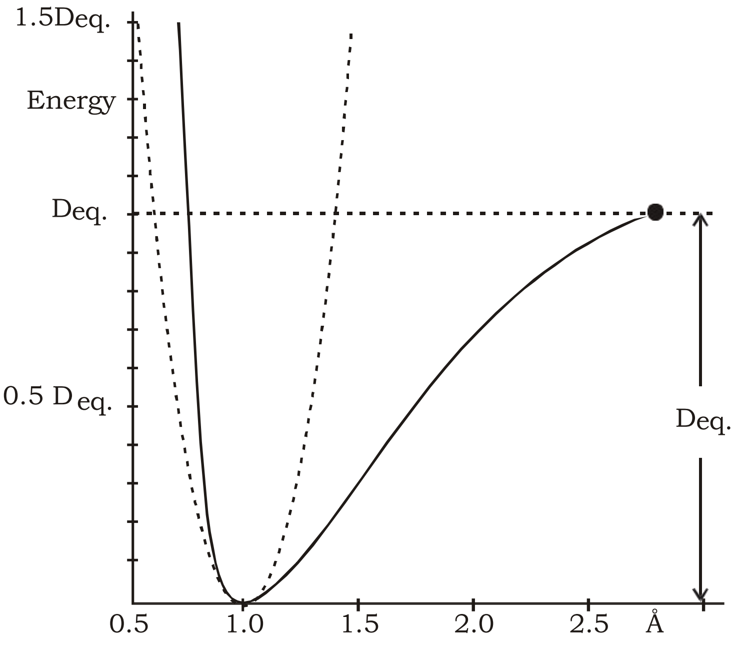


Figure (2.6) : The Morose Curve : the energy if a diatomic molecule undergoing anharmonic extensions and compression.

A purely empirical expression which fits this curve to a good approximation was derived by P.M. Morse, and is called Morse function

$$U(q) = \mathrm{De}\left(1 - e^{-\beta q}\right)^2 \qquad \text{...(2.27)}$$

where q measures the distortion of bond from the equilibrium length and β is a constant such that

$$\beta = \nu_{osc}\sqrt{\frac{2\pi^2 c\mu}{Deh}} = 1.2177 \times 10^7 \, \nu_{osc}\sqrt{\frac{\mu}{De}} \qquad \text{...(2.28)}$$

De = Dissociation energy of the molecule measured from equilibrium position, expressed in cm^{-1}. The constant β determines the narrowness and curvature of the curve. A plot of U(q) versus q gives an asymmetric curve, what is called he Mose potential curve. The Mose potential curve for the NO molecule is shown in the figure given below with potential energy U(q) in electron volts.

When equation $U(q) = De\ (1-e^{-Bq})^2$

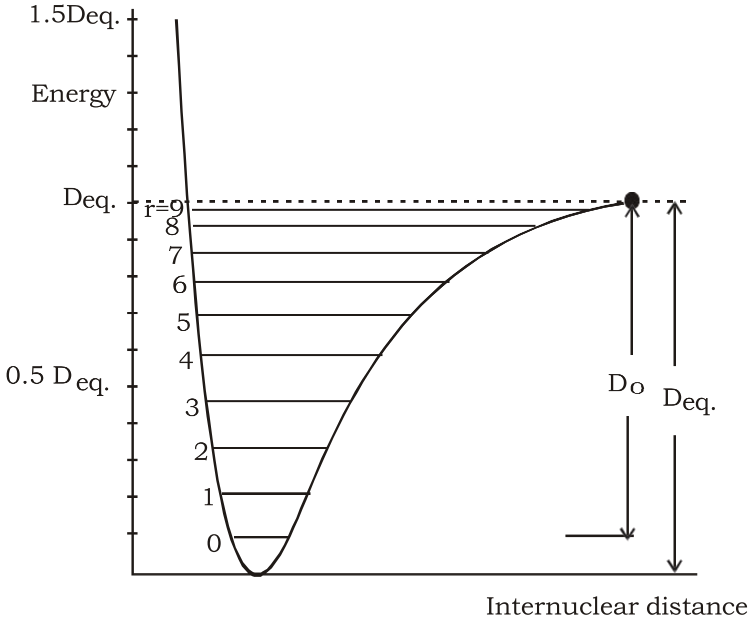
is used instead of $U(q) = \frac{1}{2}kq^2;\ q = r - r_{eq}$

in the Schrödinger equation, the pattern of the allowed vibrational energy levels is found to be

$$E_V = \left(v + \frac{1}{2}\right)\bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 \bar{\nu}_e x_e cm^{-1} \qquad \text{...(2.29)}$$

where v = 0, 1, 2, ...

and $\bar{\nu}_e$ is an oscillation frequency (expressed in wave numbers) which we shall define more closely below, and x_e is the corresponding anharmonicity constant which, for bond stretching vibrations, is always small and positive (≈ +0.01), so that the vibrational levels crowd more closely together with increasing v. Some of these levels are sketched in figure given below



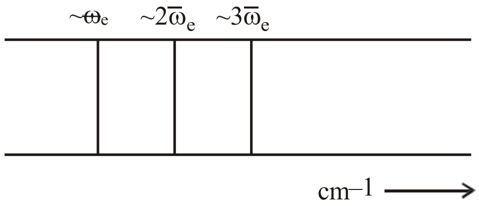


Fig. 2.7: The allowed vibrational energy levels and some transitions between them for a diatomic molecule undergoing anharmonic oscillations.

It should be mentioned that equation (2.29) like equation (2.27) is an approximation only; more precise expression for the energy levels require cubic, quartic etc. terms in $\left(v+\frac{1}{2}\right)$ with anharmonicity constant y_e, z_e etc. rapidly diminishing in magnitude.

These terms are important only at large values of *v*, and we shall ignore them

If we rewrite the equation (2.29), for anharnomic oscillator as

$$\varepsilon_v = \nu_e\left\{1 - x_e\left(v+\frac{1}{2}\right)\right\}\left(v+\frac{1}{2}\right) \qquad \text{...(2.30)}$$

and compare with the energy levels of the harmonic oscillation given as

$$\varepsilon_v = \left(v+\frac{1}{2}\right)\nu_{osc}\ \text{cm}^{-1} \qquad \text{...(2.31)}$$

we see that we can write

$$\nu_{osc} = \nu_e\left\{1 + x_e\left(v+\frac{1}{2}\right)\right\} \qquad \text{...(2.32)}$$

Thus the anharmonic oscillator behaves like the harmonic oscillator but with an oscillation frequency which decreases steadily with increasing *v*. If we now consider the hypothetical energy state obtained by putting $v = -\frac{1}{2}$ (at which, according to equation (2.30) $\varepsilon = 0$) the molecule would be at the equilibrium point with zero vibrational energy. Its oscillation frequency (in cm^{-1}) would be

$$\bar{\nu}_{osc} = \bar{\nu}_e$$

Thus we see that $\bar{\nu}_e$ may be defined as the (hypothetical) equilibrium oscillation frequency of the anharmonic system the frequency for infinitely small vibrations about the equilibrium point. For any real state specified by a positive integral *v* the oscillation frequency will be given by equation (2.32)

Thus in the ground state (v = 0) we would have

$$\bar{\nu}_0 = \nu_e\left(\ \frac{1}{2}\ e\right) cm^{-1}$$

and $$\varepsilon_0 = \frac{1}{2}\nu_e\left(\ \frac{1}{2}\ e\right) cm^{-1}$$

we see that zero point energy differs slightly from that of the harmonic oscillator $\left(\varepsilon_0 = \frac{1}{2}\nu_{osc}\ cm^{-1}\right)$

The selection rules for the anharmonic oscillator also change to

$$\Delta v = \pm 1\ , +2, \pm 3\ .....$$

Thus they are the same as for the harmonic oscillator, with the additional possibility of large jumps. These, however, are predicted by theory and observed in practice to be of rapidly of diminishing probability and normally only the lines of $\Delta v = \pm 1$ ±2 and ±3 at the most, have observable intensity. Further, the spacing between the vibrational levels is, as we shall shortly see, of the order 10^{-3} cm^{-1} and at room temperature we may use the Boltzmann distribution to show

$$\frac{N_{v=1}}{N_{v=0}} = \exp\frac{-hc\bar{\nu}}{kT} = \exp\left(-\frac{6.63\times10^{-34}\times3\times10^{10}\times10^{3}}{1.38\times10^{-23}\times300}\right)$$

$$\approx \exp^{-4.8} \approx 0.008$$

In other words, the population of the v = 1 state is nearly 0.01 or some one percent of the ground sate population. Thus, to a very good approximation, we may ignore all transitions originating at v = 1 or more and restrict ourselves to three transitions :

1. $v = 0 \to v = 1$, $\Delta v = +1$ with considerable intensity

$$\Delta\varepsilon = \varepsilon_{v=1} - \varepsilon_{v=0}$$

$$= \left(1+\frac{1}{2}\right)\bar{\nu}_e - x_e\left(1+\frac{1}{2}\right)^2\bar{\nu}_e - \left\{\frac{1}{2}\bar{\nu}_e - \left(\frac{1}{2}\right)^2 x_e\bar{\nu}_e\right\}$$

$$\Delta\varepsilon = \bar{\nu}_e\left(1-2x_e\right) cm^{-1} \qquad ...(2.33\ a\ )$$

2. $v = 0 \to v = 2$, $\Delta v = +2$ With small intensity

$$\Delta\varepsilon = \left(2+\frac{1}{2}\right)\bar{\nu}_e - x_e\left(2+\frac{1}{2}\right)^2\bar{\nu}_e - \left\{\frac{1}{2}\bar{\nu}_e\left(\frac{1}{2}\right)^2 x_e\bar{\nu}_e\right\}$$

$$\Delta\varepsilon = 2\bar{\nu}_e\left(1-3x_e\right) cm^{-1} \qquad ...(2.33\ b)$$

3. $v = 0 \rightarrow v = 3$, $\Delta v = +3$, with normally negligible intensity

$$\Delta\varepsilon = \left(3 + \frac{1}{2}\right)\bar{\nu}_e - x_e\left(3 + \frac{1}{2}\right)^2 \bar{\nu}_e - \left\{\frac{1}{2}\bar{\nu}_e - \left(\frac{1}{2}\right)^2 x_e\bar{\nu}_e\right\}$$

$$\Delta\varepsilon = 3\bar{\nu}_e\left(1 - 4x_e\right)cm^{-1} \qquad \text{...(2.33 c)}$$

These three transition are shown in the previous figure. To a good approximation, since $x_e \approx 0.01$, the three spectral lines lie very close to $\bar{\nu}_e$, $2\bar{\nu}_e$ & $3\bar{\nu}_e$. The line near $\bar{\nu}_e$ is called fundamental absorption, while those near $2\bar{\nu}_e$ and $3\bar{\nu}_e$ are called the first and second overtones respectively. The spectrum of HCl for example, shows a very intense absorption at 2886 cm^{-1}, a weaker one at 5668 cm^{-1}, and a very weak one at 8347 cm^{-1}. If we wish to find the equilibrium frequency of the molecule from these data, we must solve any two of the three equations :

$$\bar{\nu}_e\left(1 - 2x_e\right) = 2886$$

$$2\bar{\nu}_e\left(1 - 3x_e\right) = 5668$$

$$3\bar{\nu}_e\left(1 - 4x_e\right) = 8347 cm^{-1}$$

and we find $\bar{\nu}_e = 2990\, cm^{-1}$, x_e = 0.0174

Thus we see that, whereas for the ideal harmonic oscillator the spectral absorption occurred exactly at the classical vibrational frequency for real, anharmonic molecules the observed fundamental absorption frequency and the equilibrium frequency may differ considerably.

The force constant of the bond in HCl may be calculated directly by inserting the value of $\bar{\nu}_e$

$$k = 4\pi^2\bar{\nu}_e^2 c^2 \mu \quad Nm^{-1}$$

$$\therefore k = 4 \times (3.14)^2 \times 2990 \times 10^2 m^{-1} \times \left(3 \times 10^8\right)^2 1.64 \times 10^{-27}$$

$$= 516 \text{ Nm}^{-1}$$

Although we have ignored transitions from v = 1 to higher states we should note that, if the temperature is raised if the vibration has a particularly low frequency, the population of the v = 1 state may becomes appreciable. Thus at, say 600 K (*i.e.* about 300°C),

$\frac{N_{v=1}}{N_{v=0}}$ = $\exp^{-2.4}$ $\approx$ 0.09, and transition from v =1 to v =2 will be same 10 percent the intensity of those from v = 0 to v = 1. A similar increase in the excited state population would arise if the vibrational frequency were 500 cm^{-1} instead of 1000 cm^{-1}. We amy calculate the wave number of this transition as :

4. $v = 1 \rightarrow v = 2;\ \Delta v = +1$ normally very weak.

$$\Delta\varepsilon = 2\frac{1}{2}\nu_e - 6\frac{1}{4}x_e\nu_e - \left[\frac{1}{2}\nu_e - 2\frac{1}{4}x_e\nu_e\right]$$

$$= \bar{v}_e\left(1 - 4x_e\right) cm^{-1} \qquad \text{...(2.32 d)}$$

Thus, should this weak absorption arise, it will be found close to and at slightly lower wavenumber than the fundamental (since x_e is small and positive). Such weak absorption are usually called hot bands since high temperature is one condition for their occurrence. Their nature may be confirmed by raising the temperature of the sample and a true hot band will increase in intensity.

Therefore, the anharmonisity of the potential function has introduced the following points :

1. Earlier calculation had shown that only one absorption band will be observed corresponding to the oscillation frequency. Introduction of anharmonicity in molecular vibrations could explain the hot bands and overtones.
2. The zero point energy is not half of the oscillation frequency. As in NO molecule it is 978.66 cm^{-1} which is not half of $\bar{\nu}_{osc}$ = 1904.4 cm^{-1}.
3. The oscillation frequency and fundamental absorption band are not the same.

   The values for NO molecule are 1876.097 cm^{-1} and 1876.097 cm^{-1} respectively
4. The energy levels are not equally spaced but a decrease is observed with the increase in vibrational quantum number.
5. No vibration energy level is expected for $v \geq 40$ in the ground electronic state of the NO molecule but is expected to dissociates.

FUNDAMENTAL AND OVERTONE BANDS

The Infrared spectrum of diatomic molecules exhibit more than one bands. Some additional bands which occur at higher frequencies are attributed to anharmonisity. As such it need correction at high value of vibrational quantum number. As the vibrational quantum number v changes form 0 to 1, 1 to 2 etc. the spacing decreases. The former occurs at higher frequency than latter. The transition for $0 \rightarrow 1$ vibrational level is called fundamental vibration. It corresponds to one unit change $\Delta v = \pm 1$

Those transitions accompanying 2, 3 etc unit change occur in infrared region which are termed as overtone bands. The modified selection rules for anharmonic vibration are:

$\Delta v = \pm 1, \pm 2, \pm 3$ ....

The first three possible transition are

1. $0 \rightarrow 2$, $\Delta v = 2$; first overtone (second harmonic)
2. $0 \rightarrow 3$, $\Delta v = 3$; second overtone (third harmonic)
3. $0 \rightarrow 4$, $\Delta v = 4$; Third overtone (fourth harmonic)

The selection rule $\Delta v = \pm 1$ as discussed in the beginning breaks down and all transitions with Δv greater than 1 are classified as overtones. Actually the infrared spectrum comprises both fundamental and overtone bands. But the overtones are less probable and does out after $0 \rightarrow 3$ transition

The energy spacing for fundamental and overtones are given as:

1. $\nu = 0 \rightarrow v' = 1, \quad \Delta v = v' - v = 1$

$$\Delta E = E_1 - E_0$$

$$= \frac{3}{2} hc\nu_e \left(1 - \frac{3x_e}{2}\right) - \frac{1}{2} hc\nu_e \left(1 - \frac{x_e}{2}\right)$$

$$= hc\nu_e - \frac{9}{4} hc\nu_e x_e + \frac{1}{4} hc\nu_e x_e$$

$$= hc\nu_e - 2hc\nu_e x_e$$

$$= hc\nu_e (1 - 2x_e) cm^{-1}$$

$$= \bar{\nu}_{vib} (1 - 2x_e); \; where \; \bar{\nu}_{vib} = hc\nu_e$$

2. $v = 0 \rightarrow v' = 2, \quad \Delta v = v' - v = +2$

$$\Delta E = E_2 - E_0 = \frac{5}{2} hc\nu_e \left(1 - \frac{5}{2} x_e\right) - \frac{1}{2} hc\nu_e \left(1 - \frac{x_e}{2}\right)$$

$$= 2he\nu_e - \frac{25}{4} hc\nu_e x_e + \frac{1}{4} hc\nu_e x_e$$

$$= 2hc\nu_e - 6hc\nu_e x_e$$

$$= 2hc\nu_e\left(1-3x_e\right)$$

$$\overline{\Delta}E = 2\overline{\nu}_{vib}\left(1-3x_e\right); 1^{st} \text{ overtone}$$

$$\overline{\Delta}E = 3\overline{\nu}_{vib}\left(1-4x_e\right); 2^{nd} \text{ overtone}$$

3. $\nu = 0 \text{ to } \nu' = 3, \Delta\nu = \nu' - \nu = +3$

$$\underline{\Delta}E = \underline{E}_3 - \underline{E}_0 = \frac{7}{2}hc\nu_e\left(1+\frac{7}{2}x_e\right) - \frac{1}{2}hc\nu_e\left(1-\frac{x_e}{2}\right)$$

$$= 3hc\nu_e - 12hc\nu_e x_e$$

$$= 3hc\nu_e\left(1-4x_e\right)$$

$$= 3\overline{\nu}_{vib}\left(1-4x_e\right); \text{ 2nd overtone}$$

These three bands will occur at position $hc\nu_e\left(1-2x_e\right)$, $2hc\nu_e\left(1-3x_e\right)$ and $3hc\nu_e\left(1-4x_e\right)$.

For approximate work, these bands are located at ν_e, $2\nu_e$ & $3\nu_e$ cm^{-1} respectively. The line which is nearer to ν_e is fundamental band. The lines which occur at two or three time, the fundamental bands ($2\nu_e$ and $3\nu_e$) are overtones. Their intensities follow the order:

$$\nu_e > 2\nu_e > 3\nu_e$$

COMBINATION BANDS

Vibrational spectra are also complicated by the fact that two different vibrations in a molecule can interact to give absorption peaks with frequencies that are approximately the sums or differences of their fundamental frequencies. The combination bands are merely the sum of two or more fundamental frequencies or overtone ($\nu_1+\nu_2$; $2\nu_1+\nu_2$, $\nu_1+\nu_2+\nu_3$ etc.). While the difference bonds are differences of two or more fundamental frequencies or overtone (e.g. $\nu_1-\nu_2$, $2\nu_1-\nu_2$, $\nu_1+\nu_2-\nu_3$ etc.) The intensities of combination and difference peaks are generally low.

VIBRATION OF POLYATOMIC MOLECULES

NORMAL MODES OF VIBRATION

In case of polyatomic molecules, there can be a number of vibrational modes. We do not apply the selection rules regarding dipole moment of the molecule in vigorous manner. In even a non polar molecule (e.g. CO_2) with change in dipole moment during vibration gives the infrared active bands. The force constant values are different in polyatomic molecule and as a result of which the vibrational spectrum reveals a complicated structure. Consequently there is a direct way of assigning all their vibration . The only way is to calculate the degree of freedom associated with various molecular motion which determine the different types of vibration.

Molecules vibrate in a number of ways, we call them vibrational modes. These vibrations are attributed to the compression or extension of chemical bonds or bending (or deformation) of bond angles. Each vibration mode has got a characteristics frequency of vibration.

Let us consider a molecule containing N-atoms. We can refer to the position of each atom by specifying three coordinates (e.g. x, y & z certesian co ordinate). Thus the total number of coordinate values is 3N and we say the molecule has 3N degree of freedom. However, once all 3N coodinates have been fixed , the bond distances and bond angles of the molecule are also fixed and no further arbirary specification can be made.

Now, the molecule is free to move in three dimensional space, as a whole without change of shape. This translational movement uses three of 3N degrees of freedom leaving 3N -3.

In general, also the rotation of a non linear molecule can be resolved into components about three perpendicular axes. Specification of these axes also requires three degrees of freedom, and molecule is left with 3N-6 degree of freedom. The only other motion allowed to it is internal vibration, so we know immediately that a non linear N atomic molecule can have 3N-6 different internal vibrations.

Non linear molecule : 3N-6 fundamental vibration.

On the other hand, if the molecule is linear, there is no rotation about the bond axis, hence only two degrees of rotational freedom are required leaving 3N-5 degrees of vibrational freedom, one more than in case of non-linear molecule.

Thus, linear molecule : 3N -5 fundamental vibration

In both cases, since N-atomic molecule has N-1 bonds (acyclic) between its atoms, (N-1) of the vibrations are bond stretching motions.

The other 2N-5 (non linear) or 2N-4 (for linear molecule) are bending motions.

These 3N-5 (for linear molecules) and 3N-6 (for non-linear molecule) vibrational motion are also referred as normal modes of vibration. In general , a normal modes, of vibration is defined as molecular motion in which all the atoms move in phase and with the same frequency.

Now these normal vibrations are further classified as :

(a) Stretching mode :

In this mode, a molecule may vibrate by compression or extension of bonds. We call it bond stretching vibration. The distance between the vibrating atoms are periodically changing and thus the mean value is called bond length.

The different types of stretching mode are further classified as

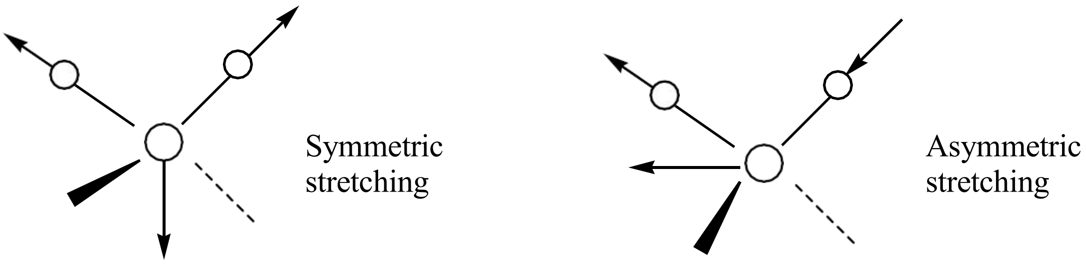
(i) Symmetric stretching and

(ii) Asymmetric stretching

In a symmetric stretching bonds one either compressed or elongated, so that the symmetry of the molecule is preserved.

In symmetric stretching one bond undergoes extension while the other is compressed.

For example, in the case of methylene group, H—C—H; the two H-atoms move away from the central carbon atom without change in bond angle in case of symmetric stretching. In case of asymmetric stretching one H-atom approaches carbon atom while the other H-atom moves away from the carbon atom.



Stretching vibrations

(b) Bending mode

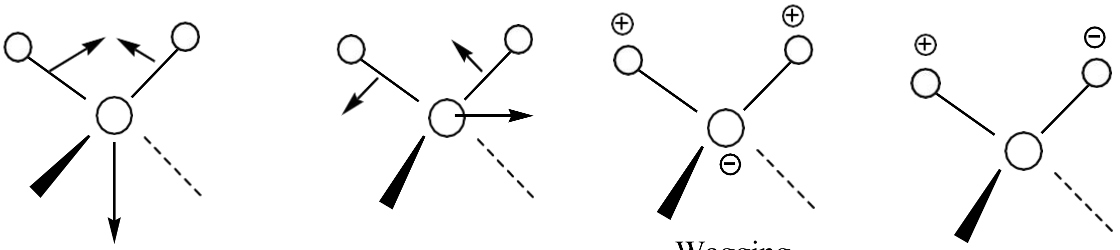
Such vibrations may consists of a change in bond angle between bonds with a common atom or the movement of a group of atoms with respect of the remainder of the molecule without movement of the atoms in the group with respect to one another. These are of four types :

(i) **Scissoring** : In scissoring the two atoms concerned to a atom move towards and away from each other with deformation of the valency angle (in plane bending)

(ii) **Rocking** : In rocking, the structural units swings back and forth in the plane of the molecule (in plane bending)

(iii) **Wagging** : wagging, the structural unit strong back and forth out of the plane of the molecular out of plane bonding)

(iv) **Twisting** : In twisting, the structural unit rotates about the bond which joins it to the remainder of the molecule fact of plane bending.



Scissoring (In plane bending) Rocking (In plane bending) Wagging (Out of plane bending) Twisting (Out of plane bending)

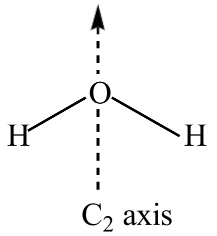
Fig. 2.8. (Bending vibrations)

In a molecule containing more than two atoms, all the four types of vibrations may be possible.

Let us consider the infrared spectrum of carbon dioxide (CO_2) which is a linear triatomic molecule and thus has a four normal nodes, i.e. 3N-5 = 3 × 3 – 5 = 4 modes of vibration.

Non linear triatomic molecules, such as H_2O, SO_2, N_2O etc have 3N- 6 = 3 × 3-6 =3 vibrational modes.

Examples : (a) H_2O



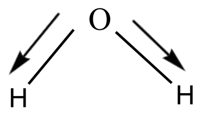
Let us consider water (H_2O) molecule. it is non linear (bent) and triatomic

∴ N = 3

∴ Normal modes of vibration = 3N — 6 = 3 × 3 – 6 = 3

Each of motion is described as stretching or bending depending upon the nature of change in molecular shape .

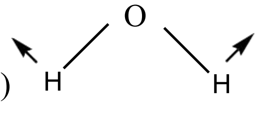
(a)



Symmetric stretching ν_1

Parallel (||)

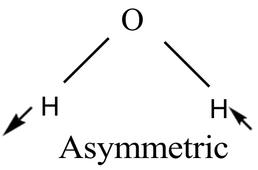
(b)



Bending ν_2

Parallel (||)

(c)



Asymmetric stretching ν_3

Perpendicular (⊥)

The IR spectrum of water shows the three bands at 1595 cm^{-1} 3652 cm^{-1} and 3756 cm^{-1}. The force constant for stretcing vibration is more than that of bending vibration and so it is easier to deforms or bend than to stretch it.

The stretching vibrations (ν_1 & ν_3) have frequency considerably larger than bending vibration (ν_2). Moreover, the asymmetric stretching (ν_3) occurs at larger frequency than the symmetric stretcing (ν_1). The three modes of vibrations corresponds to

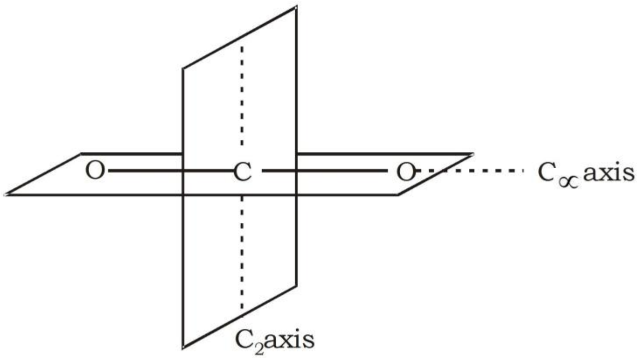
(i) 3652 cm^{-1} (ν_1) Symmetric stretching

(ii) 3756 cm^{-1} (ν_3) Asymmetric stretching

(iii) 1595 cm^{-1} (ν_2) Bending

Thus $\nu_2 > \nu_1 > \nu_2$

(b) CO_2



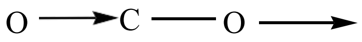
It is a linear triatomic molecule.

Here N = 3

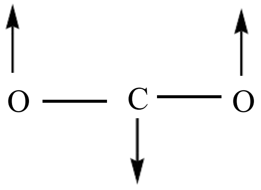
Normal modes of vibration = 3N– 5 = 3 × 3– 5 = 4

Its normal modes of vibration are shown in the figures given below

(i) Symmetric stretching
~ 1330 cm^{-1}
ν_1



(ii) Asymmetric stretching
or 2349.3 cm^{-1}
ν_3



(iii) Bending
or 667.3 cm^{-1}
$\nu_2 \perp$

It is non polar molecule with no permanent dipole moments ($\mu = 0$). The two stretching modes of vibrations are :

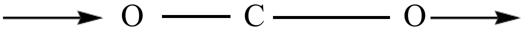
(i) Symmetric stretching : Here both covalent bonds are in same phase. The molecule remains symmetrical in course of vibration with no change in dipole moment. Therefore, symmetric stretching vibration is IR inactive.

$\mu = 0, \ \frac{d\mu}{dr} = 0$ IR inactive

$\nu_i = 1340\, cm^{-1}$

(ii) Asymmetric stretching :

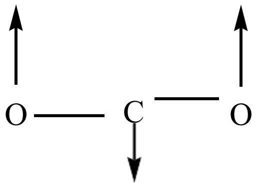
here one bond contracts and other expands. This leads to disappearance of initial symmetry of the molecule giving the formation of instantaneous dipole making the band IR active

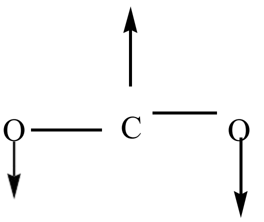


A bond which occurs at 2349 cm^{-1} for CO_2 is assigned to asymmetric stretching (ν_3)

(iii) Bending vibration : The molecule can bend in two independent directions at right angles to each other. They occur at the same frequency and so they give a doublet i.e. a double degenerate vibration. There is a loss of symmetry during bending vibration of the molecule giving the formation of instantaneous dipole and is IR active.

This absorption bond occurs at 667 cm^{-1}





If CO_2 is a linear molecule, two fundamental bands would be expected in infrared region. A doubly degenerate band at 667 cm^{-1} assigned to bending vibration and a high energy band at 2349 cm^{-1} is due to asymmetric vibration. The symmetric stretching (ν_1) is Raman active and it appears near 1340 cm^{-1}.

GROUP FREQUENCY

Due to 3N-6 and 3N-5 rules it is well evident that a complex molecule is expected to have an infrared spectrum that can exhibit a large number of normal vibrations. Each normal mode involves some displacement of all, or almost all the atoms in the molecule. However in some of the normal modes, all atoms may undergo approximately the same displacement while in other the displacement of a small group of atoms may be much more vigourous than the displacement of the remainder of atoms. Therefore the normal nodes can be divided into two classes.

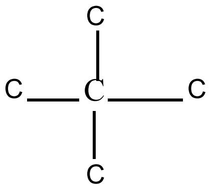
(i) Skeletal vibration

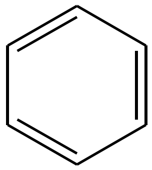
(ii) Characteristics group vibrations

Skeletal vibration :

It involves the displacement of all the atoms to the same extent. A linear or branched chain structure and molecular moiety gives the skeletal vibration and it usually falls in the range of 1400-700 cm^{-1}. Thus group such as

—C—O—C—





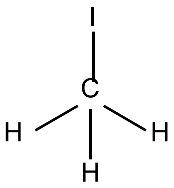
give rise to several skeletal modes of vibration and hence several absorption bonds. It is difficult to assign a particular band to a specific vibrational mode but the whole complex of bands observed is highly typical of a molecular structure. If changing a substituent results in a marked change in the chemcical nature, it is reflected in the change of absorption bands and vice versa.

These bands are generally known as the finger print bands, because the molecular or structure can often be recognized simply by the appearance of this part of the spectrum.

Characteristics Group frequency

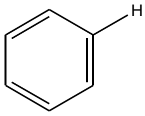
It involves only a small portion of the molecule, the remainder being more or less stationary. From the observation of the infrared spectra of a number of compounds having a common group of atoms, it is found that, regardless of rest of the molecule, this group absorbs over a narrow range of frequencies called the group frequency.

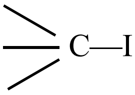
The group frequencies are usually almost independent of the structure of the molecule as a whole and, with a few exception fall in the region well above and well below that of the skeletal modes. We see that the vibrations of light atoms in terminal groups (for example —CH_3, —OH, —C ≡ N, > C = O etc.) are of high frequency, while those of heavy atoms (—C—Cl, —C—Br, metal - metal etc.) are low in frequency. Their frequencies and consequently their spectra, are lightly characteristics of the group, and can be used for analysis.

For example, the — CH_3 group gives rise to a symmetric C—H stretching absorption invariably falling between 2850 & 2890 cm^{-1}, an asymmetric stretching frequency at 2940 -2980 cm^{-1}, a symmetric deformation (*i.e.* the opening and closing of the  'umbrella') at about 1375 cm^{-1} and an asymmetic deformation at about 1470 cm^{-1}. Again, the > C = 0 group shows a very sharp and intense absorption between 1600 and 1750 cm^{-1}, depending largely on the other substituents of the group. For example, let us deduce the structure of thioacetic acid-acetic acid in which one oxygen atom is replaced by sulphur. It may be $CH_3CO.SH$ or $CH_3CS.OH$. The infrared spectrum gives a very clear picture. It shows a very sharp absorption at about 1730 cm^{-1}, and one at about 2600 cm^{-1} . These are consistent with the presence of $> C=O$ and $-SH$ groups respectively. Also there is little or no absorption at 1100 cm^{-1} (apart from the general background caused by the skeletal vibrations), thus indicating the absence of $> C = S$.

The table given below collects some of the data of characteristics streching frequency of some molecular groups :

Table 2.2

Group	**Approximate frequency (cm^{-1})**	**Group**	**Approximate frequency (cm^{-1})**
$-OH$	3600	$>C=O$	1750-1600
$-NH_2$	3400	$>C=C<$	1650
$\equiv CH$	3300	$>C=N-$	1600
	3060	$\geq C-C \leq$	1200-100
$=CH_2$	3030	$\geq C-N<$	
CH_3	2970 (asym. stretch)	$\geq C-O-$	
	2870 (sym. stretch)	$>C=S$	1100
	1460 (asym. deform.)	$\geq C-F$	1050
		$\geq C-Cl$	725
	1375 (sym. deform)	$\geq C-Br$	650

$-CH_2-$	2930 (asym. stretch)	 C—I	550
	2860 (sym. stretch)		
	1470 (deformation)		
$-SH$	2580		
$-C \equiv N$	2250		
$-C \equiv C-$	2220		

Unit – III Electronic Spectroscopy

Electronic Spectroscopy

In this region the transition are associated with the electronic energy levels of the compounds. Changes in electronic energy involve relatively large quanta, so there are simultaneous changes in the vibrational and rotational changes of the molecule. Consequently, the electronic spectra should be more complicated.

There are many closely spaced sub levels which make the electronic spectra of even gaseous polyatomic molecules to appear as broad absorption bands. In case of simple gaseous molecules, the fine structure obtained by the use of high resolution spectrometers, has been thoroughly studied. The electron in a molecule can be excited from an occupied molecular orbital to an empty or partially filled molecular orbital. This constituted what is known as electronic transition. The radiation required for the electronic transition lies in the visible or ultraviolet region. A molecule in each stable electronic level can execute vibrational and rotational motions. The total energy of the molecule is given as :

$$E_{total} = E_{electronic} + E_{vibration} + E_{rotation}$$

The electronic transitions are accompanied by changes in vibrational and rotational energy levels. The vibrational transitions appear as the coarse structure where as rotational transition as the fine structure. By the study of such highly resolved electronic spectra of simple molecule one can set quantitative idea of different excited electronic states of the molecule and vibrational rotational structure of spectrum can be used for calculation of bond distances, force constants and bond energies in the ground and excited states. Most of the measurements in chemistry are made in solution. In solution spectra, vibrational and rotational structures are lost and only broad absorption peaks result. The electronic spectra of molecules are found in the wavelength range 1000-8000 Ĺ of the electromagnetic spectrum. The visible region corresponds to the range of wavelength between 4000 - 8000 Ĺ. The ultraviolet region is subdivided into two spectral regions. The region between 2000 and 4000 Ĺ is known as near ultraviolet region and region below 2000 Ĺ is called the far or vacuum ultraviolet region. Commonly used units in this region are angustrum Ĺ (10^{-8} cm) nm (10^{-7} cm) and wave number (cm^{-1})

ELECTRONIC SPECTRA OF DIATOMIC MOLECULES

As a first approach to the electronic spectra of diatomic molecules, we may use the Born Oppenheimer approximation in the present context written as

$$E_{tot} = E_{elec} + E_{vib} + E_{rot}$$

It implies that the electronic, vibrational and rotational energies of a molecule are completely independent of each other. A change in the total energy of a molecule may then be written as :

$$E_{tot} = E_{elec} + E_{vib} + E_{rot}\ J$$

or

$$\ddot{A}\varepsilon_{tot} = \ddot{A}\varepsilon_{elec.} + \ddot{A}\varepsilon_{vib} + \ddot{A}\varepsilon_{rot}$$

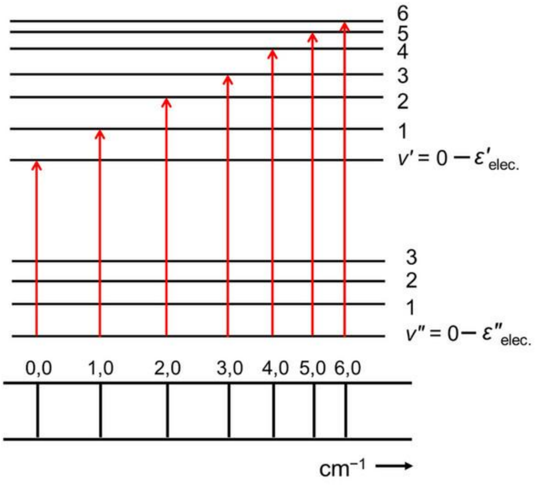
The approximate order of magnitude of these changes are :

$$\ddot{A}\varepsilon_{elec.} \approx 10^3 \text{x } \ddot{A}\varepsilon_{vib} \approx 10^6 \text{ x } \ddot{A}\varepsilon_{rot}$$

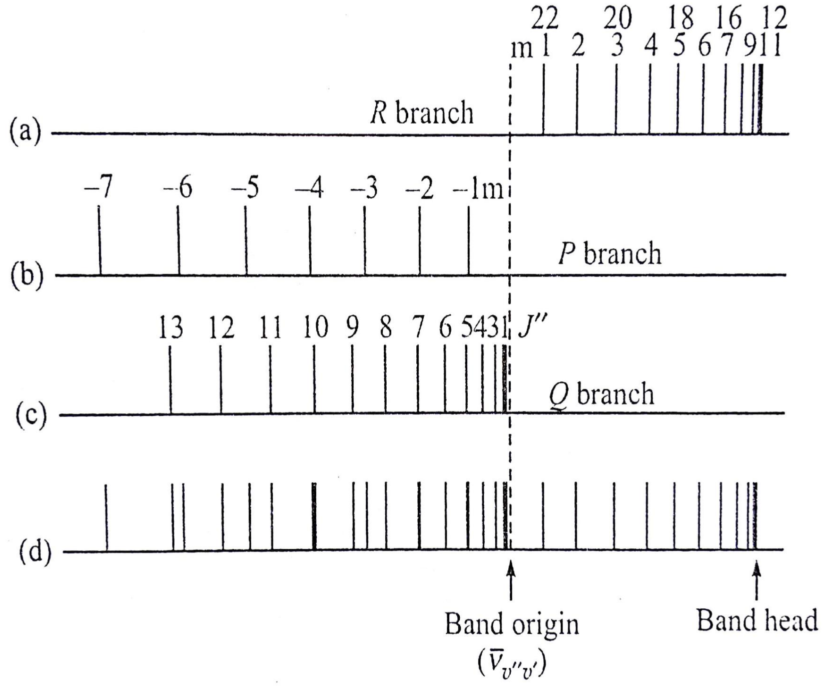
So the vibrational changes will produce a coarse structure and rotational changes a fine structure on the require of electronic transitions. The pure rotational spectra are shown only by molecules possessing a permanent electric dipole moment, and vibrational spectra require a change of dipole moment during motion, electronic spectra are given by all molecule since changes in the electron distribution in a molecule are always accompanied by a dipole change. It means that homonuclear molecules (e.g. H_2, N_2 etc.) which show no ratational or vibration rotational spectra, do give an electronic spectrum and show a vibrational and rotational structure in their spectra from which rotational constants (B) and bond vibration frequencies (νe) may be derived.

Vibrational Coarse Structure

For coarse vibrational spectra, rotational changes could be ignored . There is essentially no selection rule for v when a molecule undergoes an electronic transition. Transitions are conventionally labelled according to their(v',v") numbers (note:upper state first), that is(0,0),(1,0),(2,0),etc. Such a set of transitions is called ab and since, under low resolution, each line of the set appears somewhat broad and diffuse, and is more particularly called av' progression, since the value of v' increases by unit y for each line in the set.



Rotational fine structure



Electronic+Vibrational+Rotational Spectra In Molecule.

Including the vibrationalenergy, total molecular energy

$\varepsilon_{tot} = \varepsilon'_{el} + \varepsilon'_{vib} + B'J'(J'+1)\text{cm}^{-1}$,

$\varepsilon_{tot} = \varepsilon''_{el} + \varepsilon''_{vib} + B''J''(J''+1)\text{cm}^{-1}$.

Transition frequency/energy

$\bar{\nu} = \varepsilon'_{el} - \varepsilon''_{el} + \varepsilon'_{vib} - \varepsilon''_{vib} + B'J'('J+1) - B''J''(J''+1)\text{cm}^{-1}$.

$\bar{\nu} = \bar{\nu}_{v'v''} + B'J'('J+1) - B''J''(J''+1)\text{cm}^{-1}$.

Here v'v'' corresponds to any vibronic transitions,
Ex.: (0,0), (1,0), (0,1), (2,0), (0,2), etc

Spectrum has different'bands'based on J!! ($\Delta J = J' - J''$)

(i) R branch +1, (ii) P branch−1 & (iii) Q branch 0.

$\bar{\nu}_P = \bar{\nu}_{v'v''} + (B'-B'')('J+1) - (B'-B'')(J''+1)^2\text{cm}^{-1}$.

$\bar{\nu}_Q = \bar{\nu}_{v'v''} + (B'-B'')('J+1) - (B'-B'')(J''+1)^2\text{cm}^{-1}$.

$\bar{\nu}_Q = \bar{\nu}_{v'v''} + (B'-B'')(J''^2) + (B'-B'')J''cm^{-1}$.

Frequencies/energies of *P, Q, R* band spectra

$\bar{\nu}_{PR} = \bar{\nu}_{v'v''} + (B'-B'')P+(B'-B'')P^2cm^{-1}$

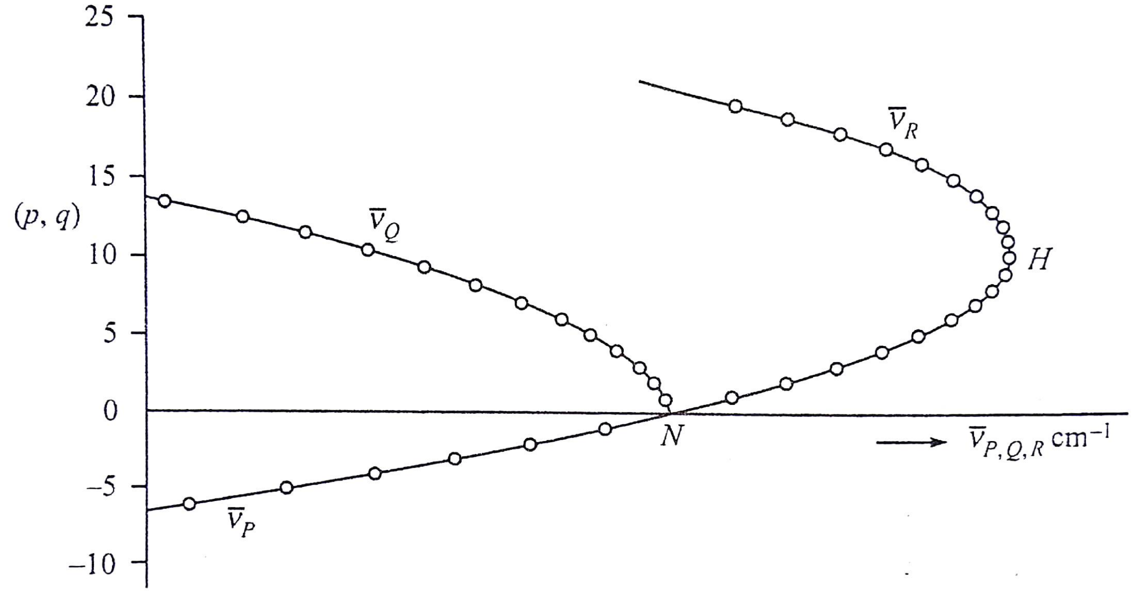
$\nu_Q = \bar{\nu}_{v'v''} + (B'-B'')q^2 + (B'-B'')q\ cm^{-1}$.

Here p = J'+1 and q = J''

d $\bar{\nu}_{PR}$/dp = B' + B''+2(B'-B'')p

Band head $P_{head} = -[B'+B''/2(B'+B'')]$

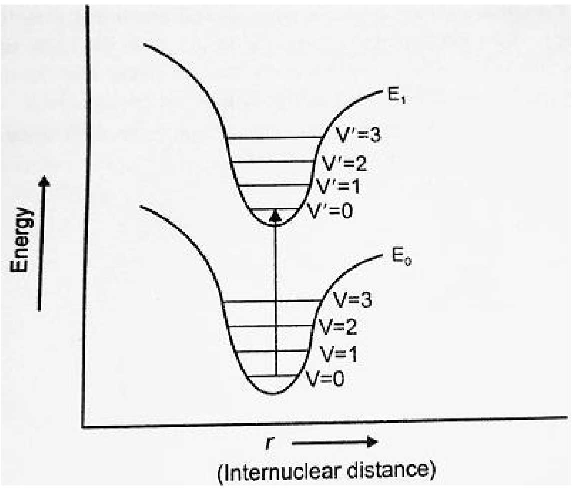
$\bar{\nu}_{PR} - \nu_{v'v''} = -[B'+B''/4(B'+B'')]$



Franck Condon Principle

The electronic transitions occur so quickly that a vibrating molecule does not change its internuclear distance appreciably during the transition.

It can be explained as below-



Consider a potential energy diagram where E_0 is the energy of the ground state and E_1 of the excited electronic state. The two curves show the variation in electronic energy with internuclear separation in the two states. The vibrational energy levels are shown as horizontal lines.

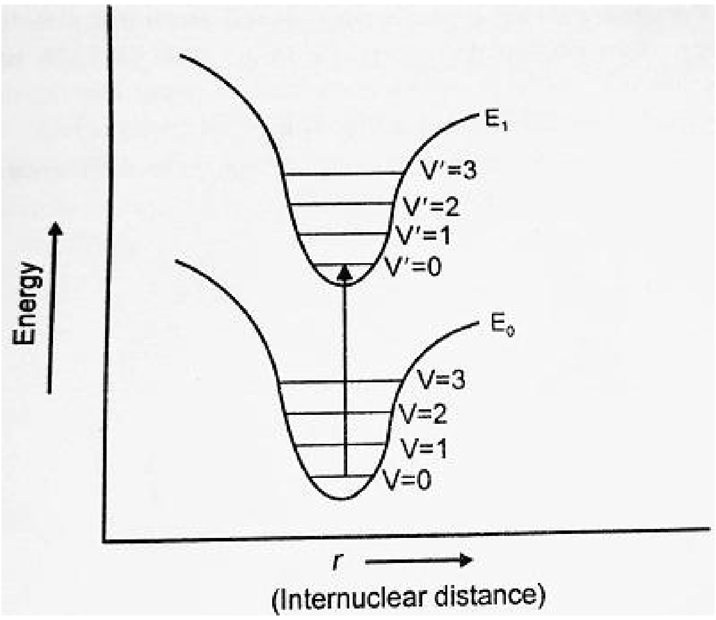
If a molecule absorbs quantum in the ground state E0, then its transition to excited state must occur along a straight line.

This is because nuclei are heavy and sluggish as compared to electrons. An electron undergoes a transition in about 10^{-16} sec, which is very short as compared to the period of vibration of atomic nuclei (i.e., 10^{-13} sec). So the internuclear distance in the excited electronic state remains the same as it was in the initial ground state before the time of electronic transition. So the transition is shown by a vertical line. An upward arrow is drawn for absorption of energy and a downward arrow for emission of energy.

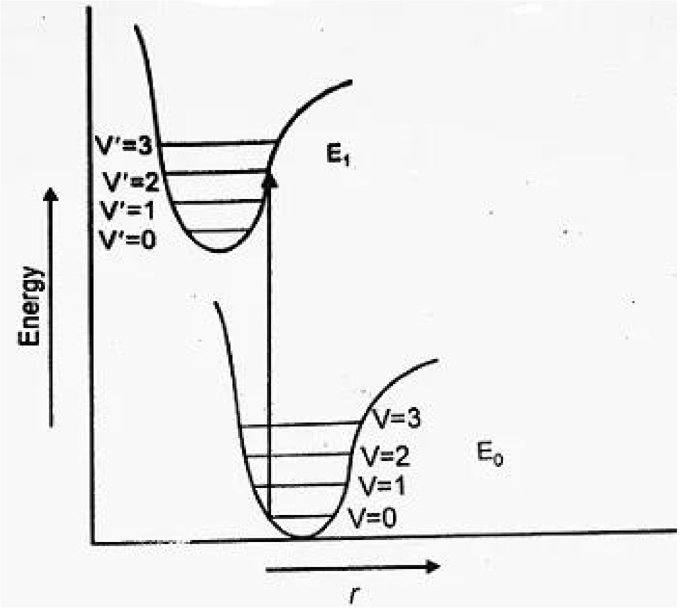
There are four possibilities w.r.t the internuclear distance.

(1) First Possibility- In this case upper electronic state (E_1) has the same internuclear distance as the lower electronic state (E_0). Now according to Franck Condon Principle transition occurs vertically along a straight line. If the molecule is in $V = 0$ vibrational level of lower electronic state E_0, then the strongest spectral line will be obtained if the molecule undergoes a transition to $V' = 0$ of upper electronic state (E_1).

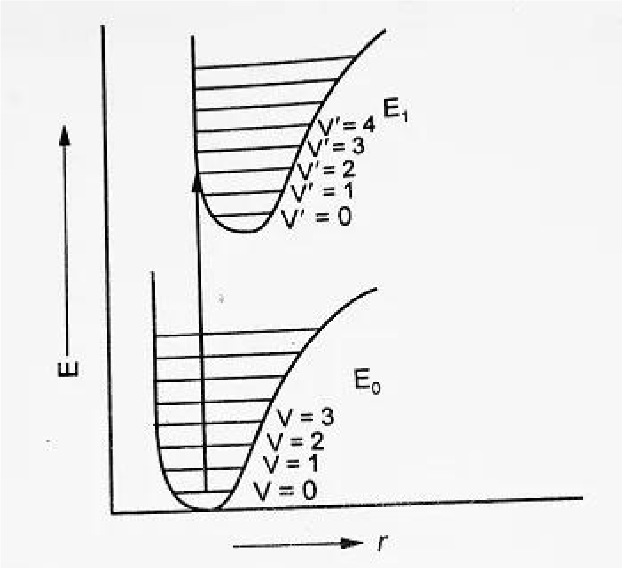
The transition of other levels gives rise to spectral lines that diminish rapidly in intensity.



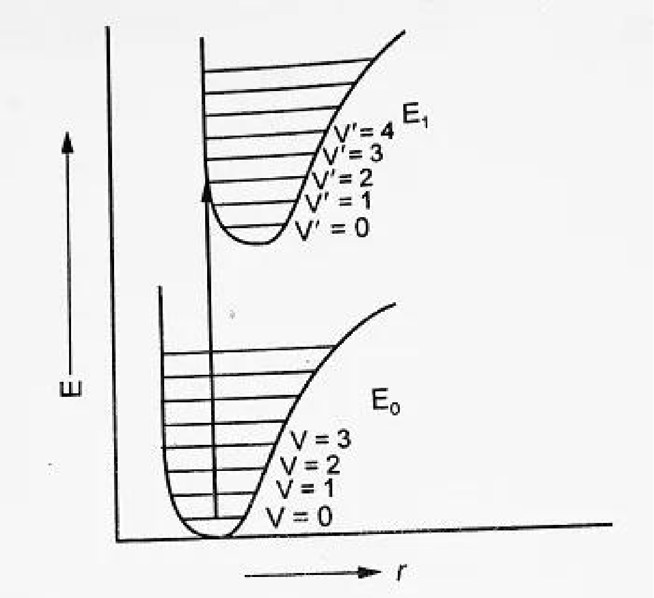
(2) Second Possibility- In this case, the upper excited electronic state has a slightly smaller internuclear distance than the lower electronic state (E_0). In such a case a vertical transition from V = 0 level will be most likely to occur into the upper vibrational level V' = 2 of E_1. The probability of transition to other levels is less. In general transitions to upper levels depend upon the difference between equilibrium separations in the lower and upper states.



(3) Third Possibility- In this case, the upper excited state has a slightly larger internuclear separation than the ground state. The resulting transitions and spectrum are similar as above.



(4) Fourth Possibility- In this case, the upper excited electronic state has considerably greater separation than that in the lower electronic state. In such a case transition will occur to a higher vibrational level (V') of the upper electronic state (E_1) from the lower electronic state (E_0).



Further transitions can now occur to a state where the excited molecules have energy greater than their own dissociation energy. From such states, the molecule will dissociate into atoms.

Fortrat Diagram

Normally Fortrat diagram is applicable in the diatomic molecules. The frequency in wave number for P,R,Q branches in terms of parameters p and q is

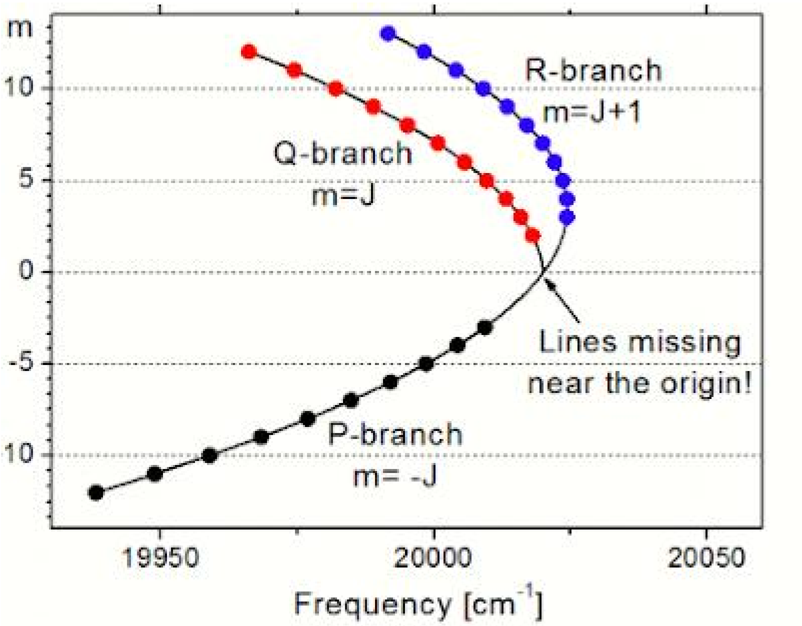
$\vartheta\bar{}P,R = (\vartheta\ )\bar{}(\vartheta',\vartheta'')+((\hat{a}'\ )\bar{} + (\hat{a}'\ )\bar{'})p+ ((\hat{a}'\ )\bar{} + (\hat{a}'\ )\bar{'})p2$ ------------------1 ϑ‾Q = = (ϑ)‾(ϑ',ϑ")+((â')‾+ (â')‾')q+ ((â')‾+ (â')‾')q2 -----------------------2

Each of these equations represents a parabola, p taking the both positive and negative values while q is positive only. These parabola are usually referred to as Fortrat parabola and these parabola are called the Fortart Diagram.

Fortrat diagram explain the multivariate nature of the rotational transition. The Fortrat diagram gives information regarding the rotational structure of the molecular spectra. This information is extremely important for the rotational chemistry. In general, the line of p-branch are densely distributed between the rotational quantum number to certain value and p-branch turns back thus more transition line form closer to the vertex of the parabola.

Symmetric and the dissymmetric properties of the molecules can be studied through the Fortrat diagram

The Fortrat diagram is as shown below:



X-Ray Photoelectron Spectroscopy

(Electron Spectroscopy for Chemical Analysis, ESCA)

X-ray photoelectron spectroscopy (XPS) is a surface sensitive, non-destructive technique used routinely to analyze the outermost ~10 nm (~30 atomic layers) of natural and engineered materials. XPS is routinely used to determine a) the composition of material surfaces (elemental identification), the relative abundances of these components on surfaces (semi-quantitative analysis), and c) the chemical state of polyvalent ions by measuring the binding energies of elements, which is related to the nature and strength of their chemical bonds. XPS is used to characterize the surfaces of diverse materials such as inorganic compounds (minerals), semiconductors, organic compounds, and thin films and coatings on natural and engineered materials. XPS is used to support research on surface-mediated processes such as sorption, catalysis, redox, dissolution/precipitation, corrosion, and evaporation/deposition type reactions. It is almost always the case that the surface composition and chemistry of materials, measured on the order of a few atomic layers (~10 nm), is different from the "bulk" composition determined by methods such as energy dispersive spectrometry (EDS) with excitation volumes that can extend as much as 3 microns into the material.

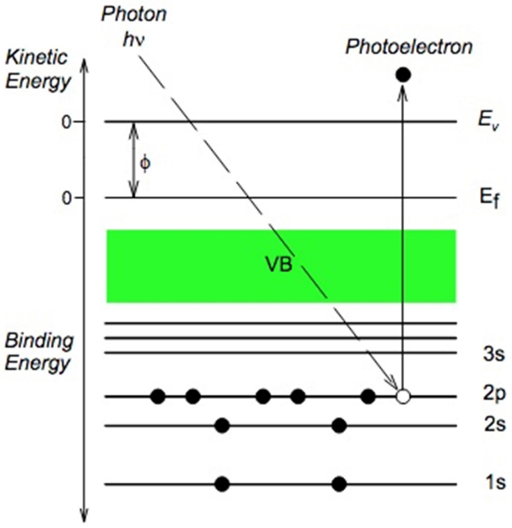
Principles of X-ray photoelectron spectroscopy

XPS is an application of the photoelectric effect described by Einstein in which electrons are emitted from atoms in response to impinging electromagnetic radiation. Einstein predicted that photoelectrons would be produced from a material when the energy of impinging photons exceed the binding energy of electrons in that material; the energy is proportional to the frequency ($h\nu$) not the intensity or duration of exposure to the incident electromagnetic radiation. The kinetic energy of an emitted electron is related to the binding energy of each electron, and because atoms have multiple orbitals at different energy states, the resulting response will be a range of emitted electrons with different binding energies (and kinetic energies) thus producing an XPS spectrum.

These relations are represented by the equation:

$$E_{kinetic} = E_{photon}\ (h\nu) - E_{binding} - \varphi$$

where $E_{kinetic}$ is the kinetic energy of the photoelectron measured by the instrument, E_{photon} is the energy of the incident photon (X-ray in this case, which is a known and fixed value), $E_{binding}$ is the binding energy of a given electron, and φ is the work function, the energy difference between the vacuum energy (E_v) level and the Fermi (E_f) level of a solid.



XPS instruments have the following components:

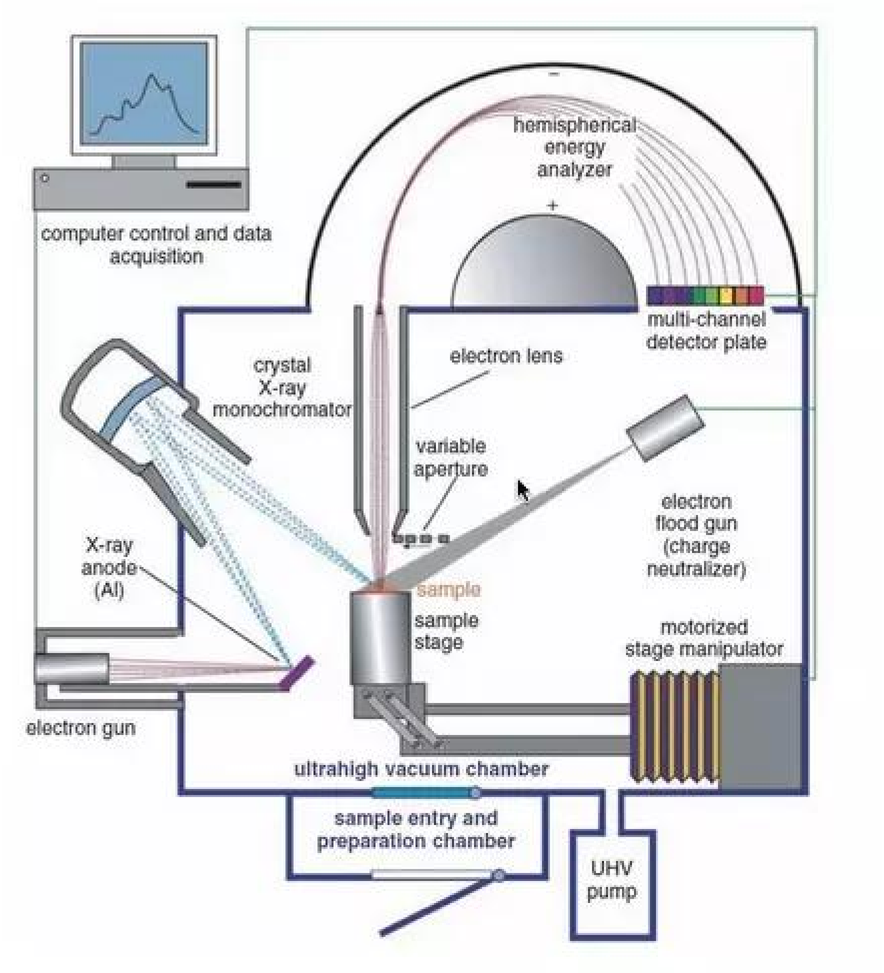
Ultrahigh vacuum system; typically operating conditions are at <10-9 Torr. This is required because the emitted photoelectrons have a relatively low energy and are readily absorbed by ambient atmosphere. In other words, photoelectrons have a relatively small mean free path between sample and detector as they are readily sorbed by gas molecules in the chamber.

X-ray source; Al Kα of Mgα X-rays are typically used to excite the sample; a monochrometer is used to permit only X-rays of this fixed energy to impinge on the sample.

An electron energy analyzer is used to discriminate among the energies of the photoelectrons that are produced. This is typically a Concentric Hemispherical Analyzer (CHA).

Ar ion gun is used a) to sputter material surfaces to "dust off" environmental contaminants (e.g., sorbed adventitious carbon from the atmosphere) off of material surfaces, and b) to obtain depth profiles across surface layers on the material surface.

Charge neutralization capability using an electron "flood gun" is used to minimize surface charging under the X-ray beam.

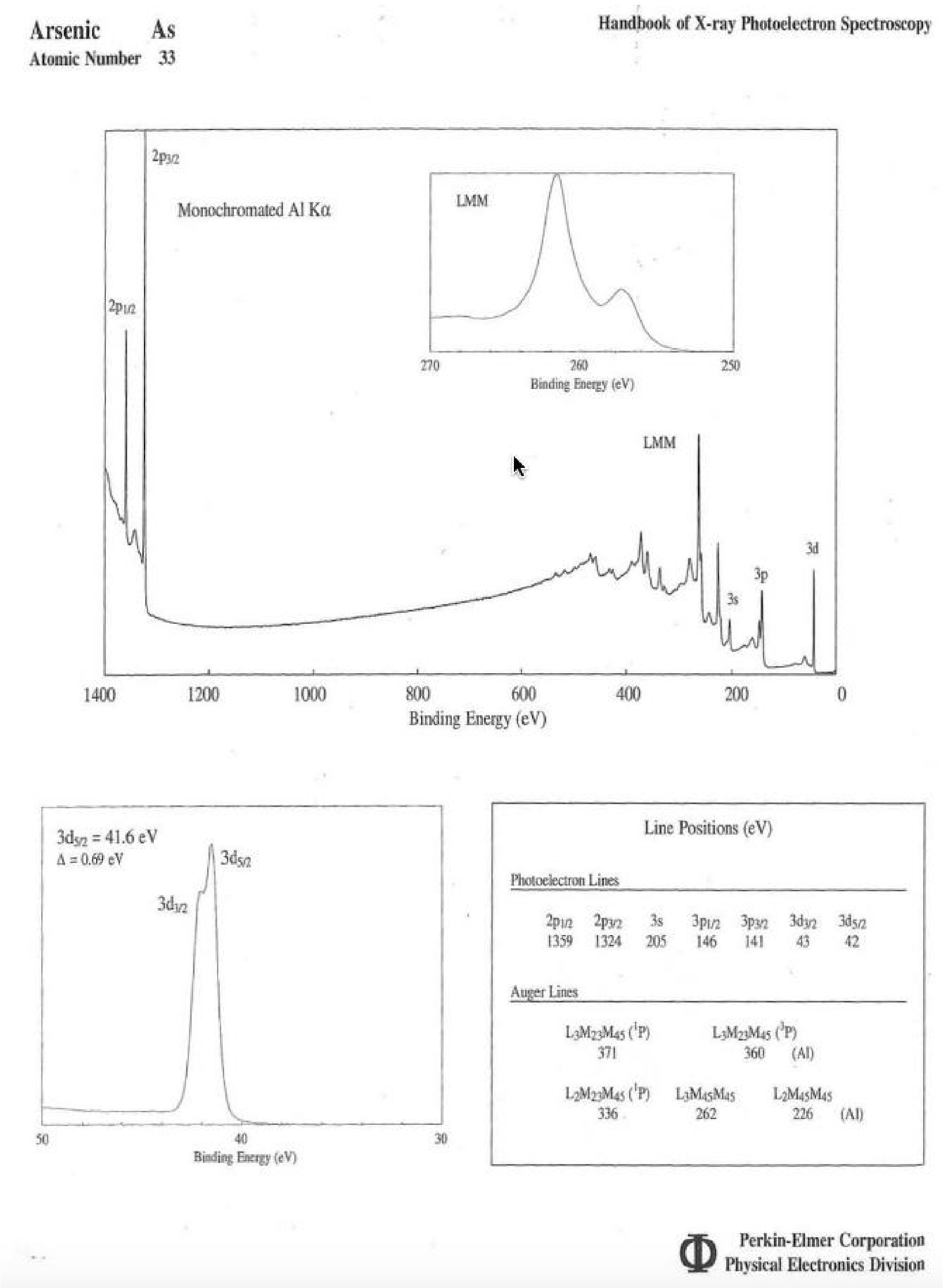


Schematic diagram of the components of an XPS Instrument.

XPS data are presented as spectra that plot Binding Energy (eV) on the X-axis vs. measured photoelectron counts on the Y-axis. Data are typically collected in a) Survey mode to obtain the complete inventory of elements on a material surface, and b) high resolution scans of peaks of interest to reveal the bound state (chemical bonds) involving elements of interest. The binding energies of the numerous photoelectrons emitted from a surface sample are used as a "fingerprint" to identify elements present. Chemical shifts in XPS spectra are observed when an element enters a different bound state, which results in changes in the binding energy of core electrons. In general, increased oxidation state (removal of valence electrons) increases the Binding Energy and addition of valence electrons decreases the Binding Energy.

For electrons in p, d, or f orbitals, two peaks are observed and the separation of these peaks is known as spin orbit splitting. The energy difference (in eV) and the ratio of areas under these split peaks is used to confirm the identity of the elements. Nomenclature for identifying peaks follows this form, nlj, where n is the period or principle quantum number, l is the type of orbital (with values l =0 for S, l=1 for P, l=2 for D, and l=3 for F orbitals), and j represents the spin angular momentum number where $j = l + s$ and s is ± 1/2. Thus, XPS peaks for As will be represented as 3s (a single peak)., 3p1/2 or 3p3/2, or 3d3/2 or 3d5/2. The spin-orbit splitting ratio is 1:2 for p levels, 2:3 for d levels and 3:4 for f levels. Note that Auger electron peaks are also generated, and these peaks are labeled as the LMM transition.

Reference XPS spectra for arsenic are presented below from the PHI Electronics Handbook of X-ray Photoelectron Spectroscopy.The spectrum on the left shows the survey of elemental arsenic. The binding energies of the As photoelectrons and Auger electrons are shown in the table in the lower right. The table at the bottom of the figure on the right shows the changes in Binding Energies for As occurring in different chemical species. The resolution of the Binding Energies is typically ±0.1 eV, so shifts of an eV or more are significant in interpreting the bound state of the element of interest. In general, reduced states of elements have a lower binding energy than their oxidized states.



Arsenic As

Atomic Number 33

Handbook of X-ray Photoelectron Spectroscopy

Line Positions (eV)

Photoelectron Lines

$2p_{1/2}$	$2p_{3/2}$	3s	$3p_{1/2}$	$3p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$
1359	1324	205	146	141	43	42

Auger Lines

$L_3M_{23}M_{45}$ (^1P) 371

$L_3M_{23}M_{45}$ (^3P) 360 (Al)

$L_2M_{23}M_{45}$ (^1P) 336

$L_3M_{45}M_{45}$ 262

$L_2M_{45}M_{45}$ 226 (Al)

Perkin-Elmer Corporation
Physical Electronics Division

For complex materials, such as organic compounds that have a variety of bond types (e.g., C-C, C=C, C-O, C-H, C-N, etc.), it is often necessary to obtain a high resolution scan and then deconvolute the spectrum to determine the binding energies that correspond to the various bond types, as numerous peaks will commonly contribute to a composite asymmetrical peak with numerous shoulders.

Merits and Limitations of XPS

Strengths of XPS include:

Non-destructive analysis of materials.

Ability to detect all elements except for H and He. XPS surveys will obtain inventories of all elements present on material surfaces.

Small shifts in binding energies can be measured (~0.1 eV) that provides information about the bound state of elements present. these data are obtained by collecting spectra over limited energy range to reveal the fine structure of XPS spectra for a given element.

Surface-sensitive analysis to determine composition of material surfaces a few atomic layers thick (~ 10 nm).

Surface contaminants are usually easily removed using ion (Ar) beam sputtering methods.

Semi-quantitative analyses can be obtained within ± 10% atomic concentration.

Depth profiles may be obtained to demonstrate chemical stratigraphy on the nm scale on material surfaces.

Little or no sample preparation is required.

X-ray beams produce relatively little charging effects compared with electron beam methods; charging can easily be addressed with charge compensation methods using an electron flood gun.

Some modern XPS instruments have imaging capabilities.

Mature XPS databases exist to rapidly identify elements and their chemical state.

Limitations of XPS include:

XPS uses an ultrahigh vacuum chamber (< 10-9 Torr) and some samples are either not stable or volatilize under UHV conditions.

X-ray beams cannot be focused in the same manner as electron beams; so the analyzed surface areas are significantly larger. Typically the analyzed area will be mm x mm or 10's or 100's of microns across at best--producing an averaged signal over these areas. Modern XPS instruments may have "small spot" capabilities, but this may be achieved by physically stepping down the beam size which reduces the count rate. Small spot XPS can be done via X-rays produced in a synchrotron source.

Although charge compensation is often effective, some samples may produce severe charging problems that compromise the quality of the analysis.

As a surface sensitive method, XPS is not an appropriate method for identifying bulk material substrates.

Unit IV NMR and ESR Spectroscopy
NMR Spectroscopy

Introduction

Nuclear Magnetic Resonance (NMR) spectroscopy takes advantage of the magnetic properties of certain nuclei and records the absorption of energy between quantized nuclear energy levels. In an NMR experiment, the spectrometer is tuned to the frequency of a *particular* nucleus and the spectrum reveals all such nuclei in the molecule being investigated. It is thus a very powerful technique, the closest analogy being a powerful microscope that allows the chemist to "see" the structure of molecules in solution.

Theory

NMR is possible owing to the magnetic properties of certain nuclei. In addition to charge and mass, which all nuclei have, various nuclei also possess a property called *nuclear spin*, which means that they behave as if they were spinning. Since nuclei have a charge, they generate a magnetic field with an associated *magnetic moment*.

There are useful empirical rules relating mass number, atomic number (Z) and *nuclear spin quantum number* (I):

Mass Number	Z	I
even	even	0
odd	even or odd	$^1/_2$, $^3/_2$, $^5/_2$, ...
even	odd	1, 2, 3, ...

Since NMR depends on the existence of a nuclear spin, nuclei with I = 0 have no NMR spectrum (*e.g.*, ^{12}C, ^{16}O, ^{18}O). From standpoint of generating NMR spectra, the most important class of nuclei are those with I = $^1/_2$. Nuclei with I >$^1/_2$ (*e.g.*, ^{11}B, I = $^3/_2$; ^{14}N, I = 1) have *quadrupole moments*, a non-spherical distribution of nuclear charge, which results in broad absorption lines and makes observation of spectra more difficult. The quadrupole moment can even affect the lineshape of neighbouring nuclei. For example, resonances of protons bonded to nitrogen or boron atoms are generally broad in ^1H NMR spectra. We shall thus be primarily concerned with nuclei where I = $^1/_2$, but the effect that quadrupolar nuclei can have on the NMR spectra of I = $^1/_2$ nuclei should be remembered. A listing of isotopes with I = $^1/_2$ is provided in Table 1.

Table 1: Natural abundances of isotopes with I = $^1/_2$.

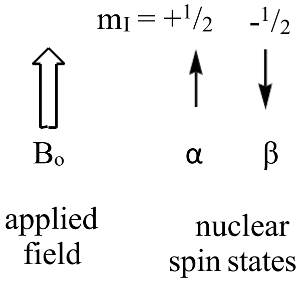
Isotope	Natural Abundance (%)	Isotope	Natural Abundance (%)	Isotope	Natural Abundance (%)
^{1}H	100	^{107}Ag	51.35	^{129}Xe	26.44
^{13}C	1.108	^{109}Ag	48.65	^{169}Tm	100
^{15}N	0.365	^{111}Cd	12.75	^{183}W	14.4
^{19}F	100	^{113}Cd	12.26	^{187}Os	1.64
^{29}Si	4.71	^{115}Sn	0.34	^{195}Pt	33.8
^{31}P	100	^{117}Sn	7.57	^{199}Hg	16.84
^{57}Fe	2.17	^{119}Sn	8.58	^{203}Tl	29.50
^{77}Se	7.58	^{123}Te	0.87	^{205}Tl	70.50
^{89}Y	100	^{125}Te	6.99	^{207}Pb	21.7
^{103}Rh	100				

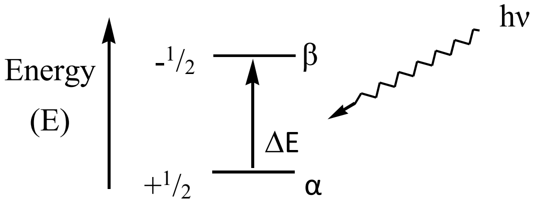
In an NMR experiment, the sample is placed in a strong magnetic field, B_o. Since the spins of the magnetic nuclei are quantized, they can have only certain well-defined values. If we have nuclei with I = $^1/_2$ (*e.g.*, ^{1}H, ^{31}P), the spins can orient only in two directions: either with ($m_I = +^1/_2$, α) or against ($m_I = -^1/_2$, β) the applied field. NMR transitions are allowed for cases where $\Delta m_I = \pm1$. There is an energy difference, ΔE, between the two states, and this is given by

$$\Delta E = h\nu = (h/2\pi\ \gamma)\ B_o \text{ or } \nu = (1/2\pi\ \gamma)\ B_o$$

where h is Planck's constant, γ is the gyromagnetic ratio (a constant characteristic of each nucleus)*, and B_o is the applied magnetic field. When the energy of the incoming radiation matches (is in *resonance* with) the energy difference between the spin states, energy is absorbed and the nucleus is promoted from the lower $+^1/_2$ to the higher $-^1/_2$ spin state. Since the sign of m_I changes, this is sometimes referred to as a "spin flip". NMR transitions occur in the *radio frequency* (rf) range of the electromagnetic spectrum. The absorption of rf energy is electronically detected and is displayed as an NMR spectrum.

The above equation is very important since it shows that ΔE depends only on γ and B_o. The gyromagnetic ratio, γ, is an intrinsic property of the magnetic nucleus. Therefore, each type of nucleus has a distinct and characteristic value of γ. Accordingly, the NMR experiment must be tuned for a *specific nucleus* and one must record a *different* NMR spectrum for each NMR active nucleus of interest. Conversely, you do not have to worry about observing signals from different nuclei on the same NMR spectrum. In order to gather all NMR knowledge about a molecule such as PH_3, we would record two different NMR spectra - a ^{1}H NMR spectrum to observe the ^{1}H nuclei and a ^{31}P NMR spectrum to observe the ^{31}P nucleus. We would not observe the ^{31}P nucleus in a ^{1}H NMR spectrum and *vice-versa*.


$m_I = +^1/_2$
$-^1/_2$
B_o
α
β
applied field
nuclear spin states


Energy (E)
$-^1/_2$
β
$+^1/_2$
α
ΔE
hν

The above equation also reveals that ΔE is directly proportional to B_o, the external magnetic field. The higher the external field, the greater is the energy separation between the α ($m_I = +^1/_2$) and β ($m_I = -^1/_2$) spin states. Recalling that $E = h\nu$, another way of saying this is that the *resonance frequency* of the nucleus increases with increasing B_o since if E increases, so does ν. This is shown in the following table.

B_o	Resonance Frequency (ν, MHz)				
(tesla)‡	^{1}H	^{13}C	^{11}B	^{19}F	^{31}P
2.35	100	25.2	32.1	94.1	40.5
4.70	200	50.4	64.2	188.2	81.0

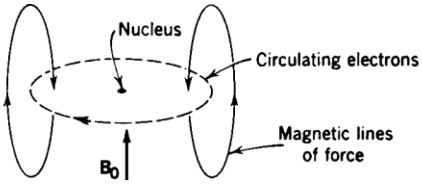
‡a *tesla* is a unit describing magnetic field strength

Note that *all $I = ^1/_2$ nuclei behave according to the same theoretical principles* - although ^{1}H NMR spectroscopy is the most commonly practiced, ^{19}F and ^{31}P NMR spectra are generated in exactly the same way as a ^{1}H NMR spectrum. The main difference between the different $I = ^1/_2$ nuclei is that the resonance frequency is changed when recording the spectrum.

Chemical Shift

The resonance frequency is determined only by γ and B_o, therefore, all atoms of a given nucleus in a molecule (*e.g.*, all ^{1}H nuclei) should resonate at the same frequency. If this were the case, the only thing NMR could tell us is whether a molecule contains NMR active nuclei (^{1}H, ^{31}P, ^{13}C, etc.). Fortunately, the frequency of the NMR absorptions of a given nucleus also depends on the *chemical environment* of the nucleus. The variation of the resonance frequency with chemical environment is termed the *chemical shift,* and herein lies the power of the NMR method.

The origin of the chemical shift can be traced to the electrons surrounding the nucleus, and the interaction of the electron cloud with the applied field, B_o. The reason for this is that circulating electrons also generate a magnetic field that orients itself in the *opposite direction* to the applied field.



The actual field (B_{local}) "felt" by a nucleus is thus *less* than B_o, and the ability of the electrons to alter the field felt at the nucleus can be expressed by θ, the *shielding constant.*

$$B_{local} = B_o(1-\theta)$$

Nuclei are said to be *shielded* or *deshielded* depending on the presence or absence of electron density surrounding them. For example, the introduction of an *electron* *withdrawing group* (*e.g.*, halogen, O, etc.) will reduce the electron density around a nucleus (*deshielding*; δ is small) and the resonance frequency will increase. Conversely, an *electron donating substituent* (*e.g.*, CH_x, SiH_x) will cause increased *shielding* (δ is large) and lower the resonance frequency.

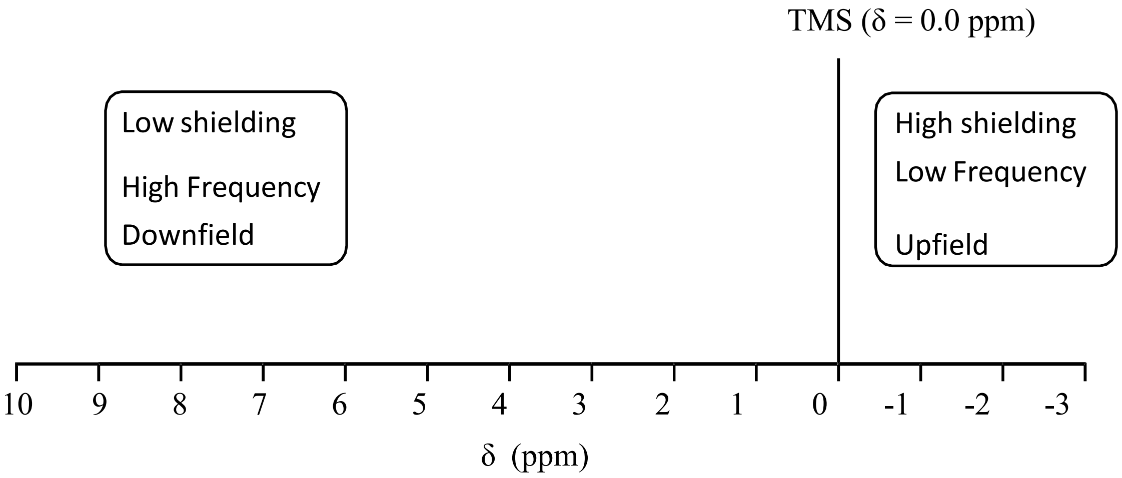
In reporting chemical shifts, one could use absolute field or absolute frequency, but this would be cumbersome and would result in the chemical shift being dependent upon the applied field. A simpler scale for chemical shifts has been devised. Chemical shifts (δ) are expressed in units of parts per million (ppm) of the spectrometer frequency with respect to a *reference material* whose position is arbitrarily assigned a value of 0.0 ppm.

$$\delta = \frac{\text{frequency of signal - frequency of standard}}{\text{spectrometer frequency}} \times 10^6$$

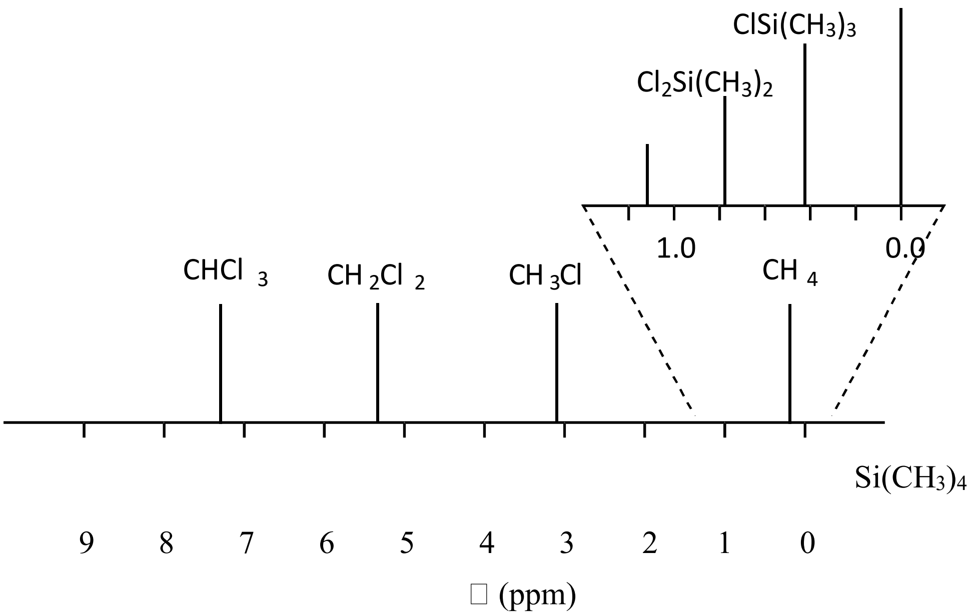
When expressed in such dimensionless units (δ in ppm), the chemical shifts are *invariant of the frequency of the spectrometer* and can be used as molecular parameters. For example, 1.0 ppmat 60 MHz is equal to a separation of 60 Hz, and at 200 MHz, 1.0 ppm equals 200 Hz. Thus, the same two resonances that are separated by 1 ppm at 60 MHz are still 1 ppm apart at 200 MHz, because δ = 60 Hz/60 MHz = 200 Hz/200 MHz = 1 ppm. Therefore, if the *same sample* is run at two different spectrometer frequencies, the chemical shifts of the resonances will be *identical*. Naturally, this statement is only true if the same reference material is used for each spectrum. Different references are used for different nuclei. The most widely accepted reference for ^{1}H and ^{13}C NMR is tetramethylsilane (Si(CH3)4 = TMS). For ^{11}B NMR, F3B•OEt2 is commonly used, as are CFCl3 for ^{19}F NMR and 85% H3PO4 for ^{31}P NMR spectroscopy.

In the past, NMR spectra were obtained by varying the applied field and measuring thechemical shift as a function of the field strength. This gave rise to the terminology of a *downfield shift* for nuclei that were *deshielded* (as they required a lower applied field to bring the nucleus into resonance) and *upfield shift* for *shielded* nuclei. For example, one would say that aresonance at δ 8.0 ppm is downfield of one at δ 2.0 ppm, and conversely that the signal at δ 2.0 ppm was upfield of the signal at δ 8.0 ppm.

More modern NMR spectrometers generate spectra by varying the frequency, γ, the magnetic field strength, B_o, constant. Nevertheless, the upfield/downfield terminology remains in common use. Unfortunately, this results in the confusing situation that δ is *positive* in the *downfield* direction (to the left of the standard on spectra) where *resonance* *frequencies are higher*. Resonances that are *upfield* of the reference appear at *lower frequencies* and have *negative* δ values.



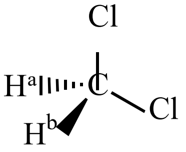
The concept of chemical shift is illustrated in Figure 8. As the hydrogens of methane are increasingly substituted by electron withdrawing chlorine atoms, the chemical shift of the remaining hydrogens shifts further *downfield* as the hydrogens become increasingly *deshielded*. Substitution of the methyl groups of tetramethylsilane (TMS) by chlorine has similar, but far less dramatic, results. In this case, the electron withdrawing chlorine atoms are separated from the hydrogens by carbon and silicon, resulting in less significant deshielding of the ^{1}H nuclei.



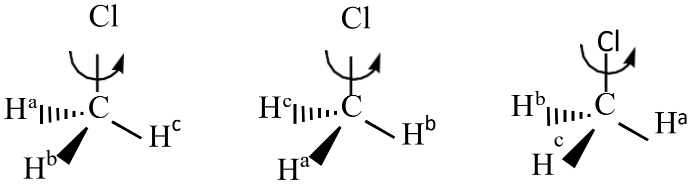
^{1}H NMR Spectra of CH_xCl_y and $Cl_ySi(CH_3)_x$.

One important consequence of chemical shift is that each *chemically different* type ofNMR-active nucleus in a molecule will give rise to *its own signal* in an NMR spectrum. Nuclei are thus referred to as *chemically equivalent* or *chemically inequivalent* in determining how many signals will be observed in an NMR spectrum. For example, both CH_3Cl and CH_2Cl_2

provided one resonance each in the ^1H NMR spectrum in the figure. From this, we can infer that the individual hydrogens in each of these molecules are *chemically equivalent*. From the viewpoint of chemical structure, the reason for this is that hydrogens are related by symmetry elements (reflection through a mirror plane or rotation about an axis) and are thus identical.



mirror in the plane of the page renders $H^a = H^b$



three-fold rotation axis demonstrates $H^a = H^b = H^c$

Sometimes, determining chemical equivalence or inequivalence is straightforward. The methyl hydrogens in ethanol (CH_3CH_2OH) are different from the methylene hydrogens and that both of these are different than the hydroxyl hydrogen; we would thus anticipate three signals in the ^1H NMR spectrum. When it is recognized that methyl groups rotate freely and rapidly, with the result that each hydrogen experiences the same overall chemical shift as it completes one rotation, a situation analogous to CH_3Cl described above. Therefore, all methyl groups generally give rise to one signal in ^1H NMR spectra. This concept can generally be applied to analogous groups such as *tert*-butyl, $C(CH_3)_3$, trimethylsilyl, $Si(CH_3)_3$, and trifluoromethyl, CF_3 (in ^{19}F NMR spectra).

The most general method of determining whether nuclei are chemically equivalent to other nuclei in a molecule is to determine whether they are in the same environment, and whether one nucleus can be related to the other through a symmetry transformation such as rotation or reflection through a mirror plane. Some examples are provided below for illustration.

$$CH_3CH_2—O—CH_2CH_3$$

The CH_2 groups are equivalent and the CH_3 groups are equivalent. 2 signals in either the ^1H or ^{13}C NMR spectra

$$CH_3CH_2CH_2Cl$$

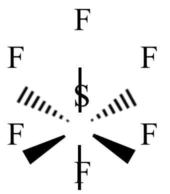
The CH_2 groups are inequivalent. 3 signals in either the ^1H or ^{13}C NMR spectra

$$CH_3CH_2—O—CH_3$$

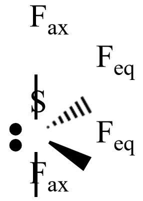
The CH_3 groups are inequivalent. 3 signals in either the ^1H or ^{13}C NMR spectra

$$ClCH_2CH_2CH_2CH_2Cl$$

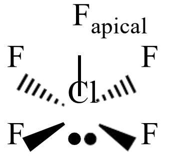
There are two distinct sets of CH_2 groups. 2 signals in either the ^1H or ^{13}C NMR spectra



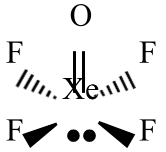
SF6 is a highly symmetrical octahedral molecule. 1 signal in the ^{19}F NMR spectrum



The axial (ax) and equatorial (eq) fluorines are chemically inequivalent2 signals in the ^{19}F NMR spectrum



The apical fluorine is chemically distinct from the four fluorines in the square base 2 signals in the ^{19}F NMR spectrum



The four fluorine nuclei in the square base are chemically equivalent 1 signal in the ^{19}F NMR spectrum

Integration

The area under each NMR absorption peak can be electronically *integrated* to determine the *relative number of nuclei* responsible for each peak. The integral of each peak can be provided numerically, and is often accompanied by a line that represents the integration graphically. Intensities of signals can be compared within a particular NMR spectrum only. For example, ^{1}H intensities cannot be compared to those of ^{19}F or ^{31}P nuclei. It is important to note that the integration of a peak is a relative number and does not give the *absolute number* of nuclei that cause the signal. Thus, the ^{1}H NMR spectrum of H3C–SiH3 will show two peaks in a 1:1 ratio, as will the ^{1}H NMR spectrum of (H3C)3C– Si(CH3)3. This is simply because the ratios 3:3 = 9:9 = 1:1. Nonetheless, the integrated intensities of the signals in an NMR spectrum are a vital piece of the puzzle.

The concept of integration, and also that of chemical shift, is illustrated by Figure 9. Determining integration ratios is an exercise in finding the greatest common divisor for the seriesof peaks (the largest whole number divisor that will produce a whole number ratio). In the above example, this value is either 1.4 cm or 9.9 integration units. It should be remembered that integration is a measurement that is subject to error; it is common for the error in integrated intensity to approach 5 - 10 %. The ratio of the integrated peak intensities is 1:3 = 3:9, allowing us to assign the resonance at δ 3.21 to the methyl group and that at δ 1.20 to the (CH3)3C group.It is important to note that the hydrogens of the (CH3)3C group are more *shielded* than the CH3 group. This occurs because the CH3 group is directly adjacent to the electron withdrawing oxygen, but the corresponding methyl protons in the (CH3)3C group are separated from oxygen by a second intervening carbon center.

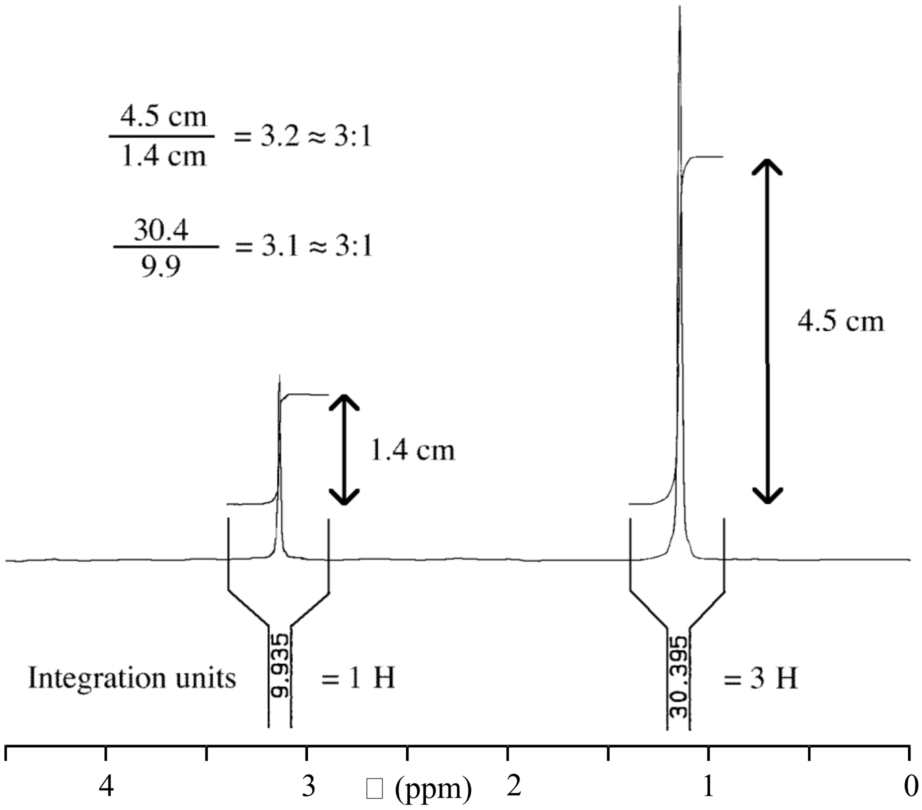


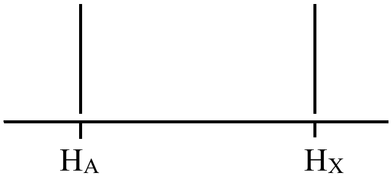
Figure 1. ^{1}H NMR Spectrum of $CH_3OC(CH_3)_3$.

At this stage, we can begin to appreciate how NMR resembles a molecular microscope. For example, at one frequency we could "see" the various protons, while the carbons, fluorines, phosphorus, and even certain metal nuclei could be observed at other frequencies. Within one spectrum, we can make use of the position (*chemical shift*) and *integrated intensity* of the different signals to assign particular molecular fragments responsible for them, and to build up a model of the molecule. There is one more aspect of NMR that is extremely helpful in determining how to connect the parts together.

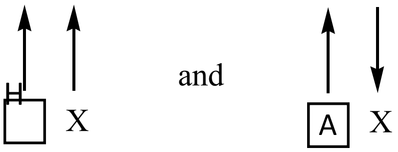
Spin-Spin Splitting (Coupling)

The appearance of a resonance may be very different when there are other *neighbouring* magnetic nuclei. The reason for this is that the nucleus under observation will interact with the magnetic spins of the different neighbouring nuclei.

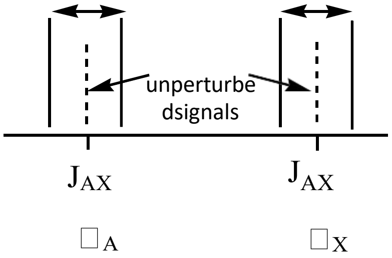
The simplest case is that of two protons having significantly different chemical shifts (designated A and X). Considering chemical shift and integration only, we could represent the spectrum as:



Both protons have a spin of $^{1}/2$, and both can exist in the $+^{1}/2$ and $-^{1}/2$ spin states. Now, it turns out that the magnetic environment of H_A is slightly different when H_X is in the $+^{1}/2$ state than when it is in the $-^{1}/2$ state. This can be represented pictorially with arrows (pointing either up or down) representing the two spin states of H_X.

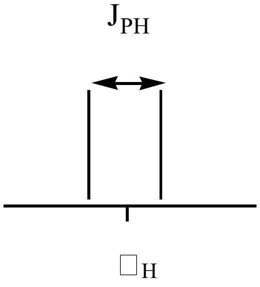


As a result, H_A will split into two lines, each half the intensity of the unperturbed signal. Similarly, H_A will influence H_X which becomes a *doublet* also. The *splitting*, or *coupling*, is symmetrical about the unperturbed resonances H_A and H_X, and is described by the means of a *coupling constant*, J_{AX}, which has units of Hz.



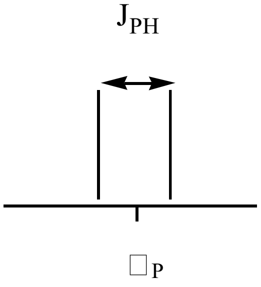
Note that the magnitude of J_{AX} is *identical* at both signals - coupled nuclei must share the *same* coupling constant.

In a similar way, the resonance of a proton attached to phosphorus will be a doublet, since the phosphorus nucleus has $I = ^{1}/2$ and may be in the $+^{1}/2$ or $-^{1}/2$ state. However, the key distinction here is that we are dealing with two different nuclei, and thus two different NMR spectra. *Each* NMR spectrum (^{1}H and ^{31}P) will show *one doublet* with a J_{PH} coupling constant that is identical in magnitude. Recall that we cannot "see" a ^{31}P nucleus in a ^{1}H NMR spectrum and vice-versa. Nonetheless, the splitting of the peaks into doublets in each spectrum tells us that the ^{1}H and ^{31}P nuclei are interacting.



^{1}H NMR Spectrum

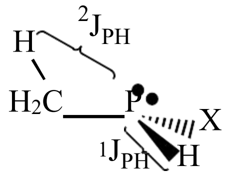
e.g., $HPCl_2$



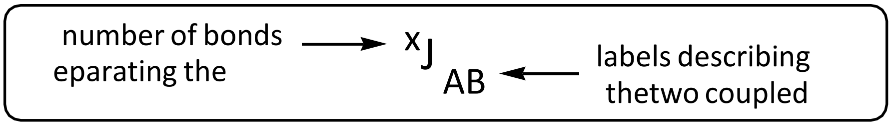
^{31}P NMR Spectrum

To review, the influence of the neighbouring spins is called *spin-spin coupling* and NMR peaks are split into *multiplets* as a result. The separation between the two peaks is called the *coupling constant*, J, which is expressed in Hz. Spin-spin coupling has the following characteristics:

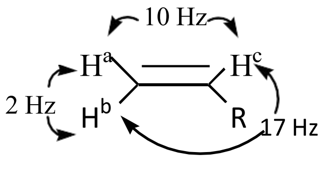
- the *magnitude* of J measures how strongly the nuclear spins interact with each other.
- coupling is normally a through-bond interaction, and is proportional to the product of the gyromagnetic ratios of the coupled nuclei. For example, $^1J_{CH}$ = 124 Hz for ^{1}H-^{13}C coupling in CH4, and $^1J_{SnH}$ = 1931 Hz for ^{119}Sn-H coupling in SnH4. This happens because δ (^{119}Sn) is much larger than δ (^{13}C).
- since coupling occurs through chemical bonds, the magnitude of J normally falls off rapidly as the number of intervening bonds increases. *e.g.*, $^1J_{PH}$ ~700; $^2J_{PH}$ ~20 Hz in



Coupling constants are thus labeled to show the *types of nuclei* and the *number of bonds separating the nuclei* that give rise to spin-spin splitting.



- since spin-spin coupling is a through-bond interaction, it is sensitive to the orientation of the bonds between two interacting nuclei. *This is particularly important for two-bond coupling constants.* The influence of the orientation of the two coupled nuclei can occasionally render $^2J < {^3J}$. For example,



$$^2J_{H^aH^b} << {^3J_{H^aH^c}} < {^3J_{H^bH^c}}$$

^{1}J is *not* affected by the orientation of the coupled nuclei, so it is generally true that ^{1}J >> ^{2}J or ^{3}J, but it is *not* always true that $^{2}J > {}^{3}J$.

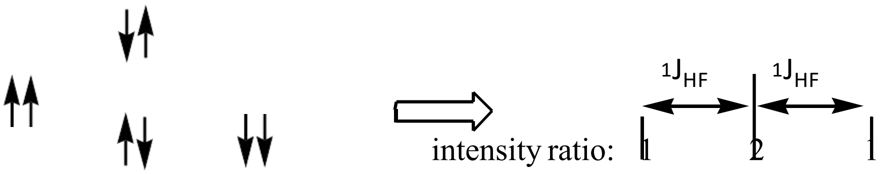
- spin-spin interactions are *independent of the strength of the applied field*. The spacing (in Hz) between lines at two different field strengths *will be the same if it is due to coupling*, but will be proportional to the field strength if it is due to a difference in chemical shift.

Table 2: Typical Coupling Constant Ranges (in Hz)

	Coupled Nuclei (AB in $^{x}J_{AB}$)			
x	HH	CH	PH[b]	PC[b]
1	–	115 - 250	630 - 710	120 - 180
2[a]	2 - 30	5 - 60	7 - 13	5 - 40
3	2 - 17	2 - 20	6 - 11	5 - 11
4	–	–	0 - 1	–

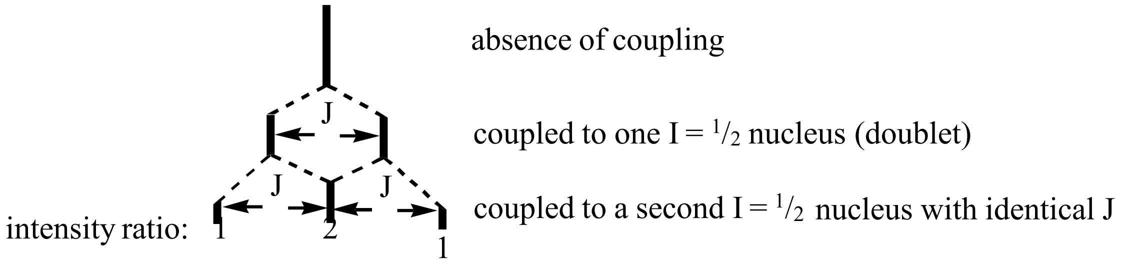
[a] Two bond couplings are particularly sensitive to the geometrical arrangement of the nuclei, which in some cases may render $^{2}J_{AB} < {}^{3}J_{AB}$. [b] Restricted to acyclic compounds.

Cases involving more than two nuclei with I = $^{1}/2$ are direct extensions of the above. However, because there are more nuclear spins interacting, the *pattern* of lines observed in the NMR spectrum becomes more complicated. For example, let's consider the ^{1}H NMR spectrum of the HF_2^- anion (*i.e.*, $[F{-}{-}H{-}{-}F]^-$). We are observing the ^{1}H nucleus, but it is coupled to two chemically equivalent ^{19}F (I = $^{1}/2$) nuclei. There are four ways that we can arrange the nuclear spins of the two fluorine nuclei, but only three different energy states are created, as is explained below:

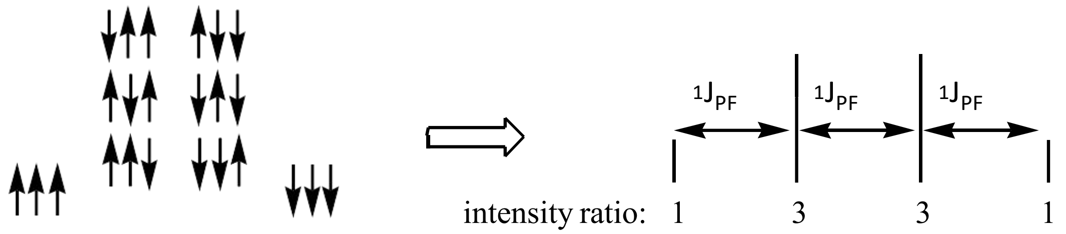


Extending what we learned about the generation of a doublet, we can clearly see that the ^{1}H environment where both ^{19}F spins are "up" is different from that where both ^{19}F spins are "down". However, we can also arrange things so that one ^{19}F spin is "up" and the other is "down". The latter case is *degenerate*; that is, there is more than one way of accomplishing an "up/down" arrangement of nuclei, but each "up/down" arrangement has the same energy. As a result, a pattern of three peaks (or *triplet*) with an intensity pattern of 1:2:1 is generated as shown above. It is important to note that each line in the triplet is separated by the same $^{1}J_{HF}$ coupling constant. As we would expect, the ^{19}F NMR spectrum of HF_2^- would show a doublet because the fluorine nuclei are chemically equivalent and couple to one ^{1}H nucleus.

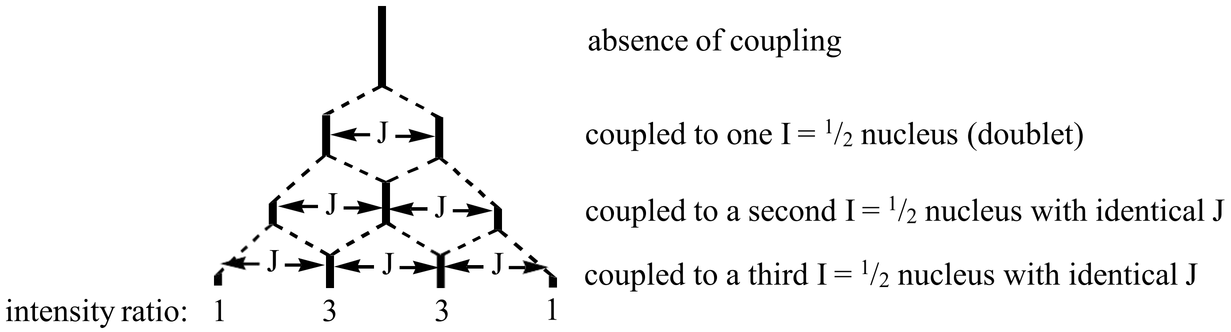
Another way of looking at this is to begin with a singlet for the ^{1}H nucleus and then couple each ^{19}F nucleus one step at a time. The coupling of the first ^{19}F nucleus generates a doublet. When each line in this doublet is *split again* into a doublet, they overlap identically at the center of the signal, generating a single line of intensity two relative to each outer line of intensity one:



When a similar exercise is undertaken for the ^{31}P NMR spectrum of PF3, the nuclearspins of the three equivalent ^{19}F nuclei can be arranged in four ways to generate a *quartet*

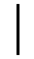
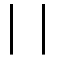
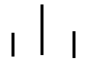
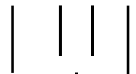
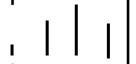
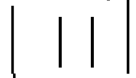


or we can split a singlet into doublets three times to accomplish the same transformation:



In this case, when each line at the triplet stage is split again into doublets, the intensity of the overlapping peaks is not identical; a signal of relative intensity two (from the middle peak) overlaps with a signal of intensity one (from the outer peak) to create a peak of intensity three.

Fortunately, the pattern of peaks generated by the interaction of I = $^{1}/2$ nuclei can be easily generated by remembering that *one nucleus is split by (n) equivalent nuclei into (n+1) peaks,* each separated by the coupling constant, ^{x}JAB. The number of peaks is referred to as the *multiplicity*. The intensity pattern is a direct consequence of the number of combinations of the various nuclear spins that are possible and is described by a series of binomial coefficients. In practice, it is easiest to determine the intensity pattern by use of a mnemonic device such as Pascal's triangle.

n	*n*+1	Intensity	Multiplicity	Pattern	Example
0	1	1	singlet (s)		$C\boldsymbol{H}_4$
1	2	1 : 1	doublet (d)		$(C\boldsymbol{H}_3)_2CHCl$
2	3	1 : 2 : 1	triplet (t)		$C\boldsymbol{H}_3CH_2Cl$
3	4	1 : 3 : 3 : 1	quartet (q)		$CH_3C\boldsymbol{H}_2Cl$
4	5	1 : 4 : 6 : 4 : 1	quintet		$^{29}\boldsymbol{Si}F_4$
5	6	1 : 5 : 10 : 10 : 5 : 1	sextet		$\boldsymbol{P}F_5$
6	7	1 : 6 : 15 : 20 : 15 : 6 : 1	septet		$(CH_3)_2C\boldsymbol{H}Cl$
			etc.		

The phenomenon of spin-spin coupling and its effect on the appearance and interpretation of NMR spectra is best described by example, several of which appear on the following pages.

Analyzing NMR Spectra and Reporting Results

NMR spectra contain a wealth of information and must be analyzed in a methodical way. Much like a jig-saw puzzle, all of the pieces (*i.e.*, chemical shift, integration, multiplicity, and coupling constants) must fit together properly. As with a puzzle, you may find that your initial conclusion is incorrect because several "pieces" are out of place. It is important to approach the problem in a creative way and investigate alternate solutions. The most straightforward method for analyzing NMR spectra is:

1) identify signals by chemical shift and determine their relative integration
2) identify the multiplicity of the peaks and calculate coupling constants.

Many students are tempted to "leap in" and attempt to analyze coupling patterns first, but the coupling pattern may not correlate if the integration ratio of the coupled multiplets has not already been deduced. Above all else, remember to double-check that the assignments make sense. It is often a good practice to use your results to generate a simple stick-diagram of the NMR spectrum. If the stick-diagram matches the actual spectrum exactly, then you have correctly analyzed the NMR spectrum. Chemical shifts should generally be reported to two decimal places. Multiplicities may be written out (*e.g.*, "triplet") or expressed in terms of common abbreviations (*e.g.*, "t"). Coupling constants are commonly reported as whole numbers, but may be expressed to one decimal place if the spectrum is of sufficiently high resolution. The coupling constants should be properly labeled (*i.e.*, ${}^{x}J_{AB}$) to show the nuclei that are coupled; if there is more than one NMR active isotope for a nucleus (*e.g.*, ${}^{117}Sn/{}^{119}Sn$), it should be clearly defined which is involved in the coupling interaction.

NUCLEAR OVERHAUSER EFFECT (NOE)

When we obtain a 13C{1H} NMR spectrum, the intensities of many of the carbon resonances increase significantly in comparison to the intensities observed in a proton-coupled experiment. Carbon atoms directly attached with hydrogen atoms are enhanced the most, and the enhancement increases (but not always linearly) as more hydrogens are attached to a particular carbon. This effect is known as the Nuclear Overhauser Effect NOE) and this is applied to the magnitude of the effect as well as to the phenomenon itself. Thus, NOE is the change in the intensity of the signal of a nucleus upon irradiation of a nearby nucleus and this operates through space. This effect can be either positive or negative, depending on types of atom are involved. In the case of 13C interacting with 1H, the effect is positive; irradiating the hydrogens increases the intensities of the carbon signals.

The magnitude of NOE depends on the balance of relaxation mechanisms, and its maximum value for an A{B} experiment in which the B nucleus is saturated is given by

$$\text{NOE max} = 1/2\ (\quad {}_{\text{irr}}/ \qquad)$$

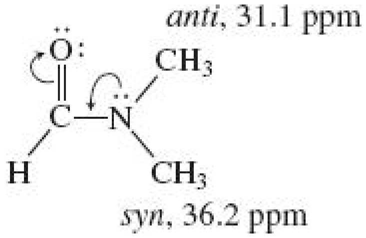
where, irr is the magnetogyric ratio of the irradiated nucleus (B), and obs is that of the observed nucleus (A). Remember that NOEmax is the enhancement of the signal, and it must be added to the original signal strength: Total predicted intensity (maximum) = 1 + NOEmax

For a ${}^{13}C\{{}^{1}H\}$ NMR spectrum, NOEmax = 1 /2 (267.52 67.28) = 1.988; indicating that the 13C signals can be enhanced up to 200% by irradiation of the hydrogens. Therefore, the total predicted intensity will be three. However, the maximum enhancement is 50% for homonuclear decoupling (e.g. 1H{1H}).

In a ${}^{13}C\{{}^{1}H\}$ NMR spectrum, the total NOE for a given carbon increases as the number of nearby hydrogens increases. Thus, we usually find that the intensities of the signals in a 13C spectrum (assuming a single carbon of each type) assume the order: $CH_3 > CH_2 > CH >> C$. Since, magnitude of NOE depends on relaxation mechanism and dipolar relaxation is particularly important for spin- 1/2 nuclei and, as the rate is inversely proportional to the sixth power of the distance between the nuclei, it is most significant when the nucleus being irradiated is directly bonded to the one being observed. Therefore, NOE decreases with the 6th power of the distance between the interacting nuclei (NOE is effective typically up to ~4 Å).

Signal enhancement due to NOE is an example of cross-polarization, in which a polarization of the spin states in one type of nucleus causes a polarization of the spin states in another nucleus. In a 13C{1H} spectrum, when the hydrogens in the molecule are irradiated, they become saturated and attain a distribution of spins very different from their equilibrium (Boltzmann) state. There are more spins than normal in the excited state. Due to the interaction of spin dipoles, the spins of the carbon nuclei "sense" the spin imbalance of the hydrogen nuclei and begin to adjust themselves to a new equilibrium state that has more spins in the lower state. This increase of population in the lower spin state of carbon increases intensity of the NMR signal.

The NOEs experiment is a very useful technique to determine the stereochemistry and structure of the molecule. For example, in dimethylformamide, the two methyl groups are nonequivalent, showing two signals at 31.1 and 36.2 ppm, because free rotation is restricted about the C–N bond due to resonance interaction between the lone pair on nitrogen and the -bond of the carbonyl group.



Irradiation of the aldehyde hydrogen leads to a larger NOE for the carbon of the syn-methyl group (36.2 ppm) than for that of the anti-methyl group (31.1 ppm), allowing the peaks to be assigned. The syn methyl group is closer to the aldehyde hydrogen.

ESR Spectroscopy

Electron Spin Resonance Spectroscopy ESR is used for the species having unpaired electron (one or more), free radical, biradical, transition metal complexes and unstable paramagnetic species. ESR is shown by molecules, atoms, ions, free radicals having at least one unpaired electron. It was discovered by Zavoisky in 1944. A molecule which is ESR active observed radiation in the microwave region (0.1 cm to 100 cm) or 9000-10000 MHz (9-10 GHz). With the help of ESR spectra we can obtain the following information:

1. Local environment of the molecule
2. Electron distribution within the molecule
3. Magnitude of magnetic moment
4. Identification of free radicals
5. Determination of structure of molecules

The basic concepts of ESR are analogous to those of NMR, but it is electron spins that are excited instead of spins of atomic nuclei. Because most stable molecules have all their electron paired. ESR technique is less widely used than NMR. However, this limitations to paramagnetic species also means that the ESR technique is one of great specificity. Since ordinary chemical solvents and materials do not give rise to EPR spectra.

Theory/origin of an ESR Signal:

Every electron has a magnetic moment and spin quantum number $s = 1/2$ with magnetic components $m_s = +1/2$ and $m_s = -1/2$. In the presence of an external magnetic field with B_0, the electrons magnetic moment align itself either parallel ($m_s = -1/2$) or antiparallel ($m_s = +1/2$) to the field. Each alignment has a specific energy due to Zeeman effect: $E = m_s g_e \mu_B B_o$. The parallel alignment corresponds to the lower energy state and the separation between it and the upper state is $\Delta E = g_e \mu_B B_o$; where g_e is the electrons so called g factor or spectroscopic splitting factor or gyromagnetic ratio and also the Lande g factor. μ_B is the bohr magneton. This equation implies that the splitting of the energy level is directly proportional to the magnetic fields strength as shown in below figure.

An unpaired electron can move between the two energy levels by either absorbing or emitting electron magnetic radiation of energy $\varepsilon = h\nu$ such that the resonance condition. $\varepsilon = \Delta E$ is obeyed substituting in $\varepsilon = h\nu$ and $\Delta E = g_e\mu_B B_o$ leads to the fundamental equation of ESR spectroscopy.

$$\boxed{\mathbf{h\nu = g_e\mu_B B_o}}$$

Experimentally, this equation permits a large combination of frequency and magnetic field values, but great majority of EPR measurements are made with microwaves in 9000-10000 MHz (9-10 GHz) region with field corresponding to about 3500 gauss (0.35 Tesla).

ESR spectra can be generated by either varying the photo frequency incident on a sample while holding the magnetic field constant or doing the reverse. In practice, it is usually the frequency which is kept fixed. A collection of paramagnetic centres such as free radicals is exposed to microwave at a fixed frequency.

By increasing an external magnetic field, the gap between the $m_s = +1/2$ and $m_s = -1/2$ energy states is widened (enlarged or expanded) until it matches the energy of the microwaves as represented by the double arrow in the above diagram. At this point the unpaired electron can moves between their two spin states. Since there are more electrons in the lower state due to the Maxwell Boltzmann distribution (see below); there is a net absorption energy and it is the absorption which monitored and converted into a spectrum.

As an example of how $h\nu = g_e\mu_B B_o$ can be used. Consider the case of a free electron which has $g_e = 2.0023$ and the simulated spectrum shown at the right in two different forms. For the microwave frequency of 9388.2 MHz; the predicated resonance position is a magnetic field about $B_o = h\nu/g_e\mu_B = 0.3350$ Tesla or 3350 Gauss as shown. The two forms of the same spectrum are presented in the figure. Most spectra are recorded and published only on first derivatives. Because of electron-nuclear mass differences the magnetic moment of an electron is substantially larger than the corresponding quantity for any nucleus, so that a much higher magnetic frequency is needed to bring about a spin resonance with an electron than with a nucleus at identical magnetic field strength. For example, for the field of 3350 Gauss as shown in figure below, spin resonance occurs near 9388.2 MHz for an electron compared to only about 14.3 MHz for ^1H nuclei (for NMR, the corresponding resonance equation is $h\nu = g_N\mu_N B_o$, where g_N and μ_N depend on the nucleus under study).

When a molecule or compound with an unpaired electron is placed in a strong magnetic field, the spin of the unpaired electron can align in two different ways creating two different spin states, $m_s = \pm 1/2$. The alignment can either be along the direction (parallel) to the magnetic field which corresponds to the lower energy states $m_s = -1/2$ or opposite (antiparallel) to the direction of the applied magnetic field $m_s = +1/2$. The two alignments have different energies and this difference in energy lifts 'the degeneracy of the electron spin states. The energy difference is given by

$\Delta E = E_{+1/2} - E_{-1/2} = h\nu = g_m\mu_B B$ where,

h = planks constant (6.624×10^{-34} J-sec)

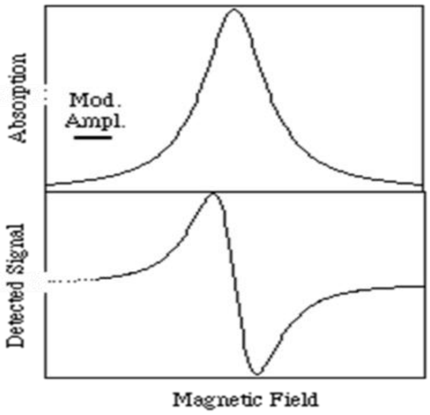
μ_B = Bohr magneton (9.274×10^{-24} JT^{-1})

B = strength of the magnetic field in Tesla

g = g factor (unit less)

ν = frequency of the radiation

$$B = \frac{eh}{4\pi mc}$$



Presentation of ESR spectra

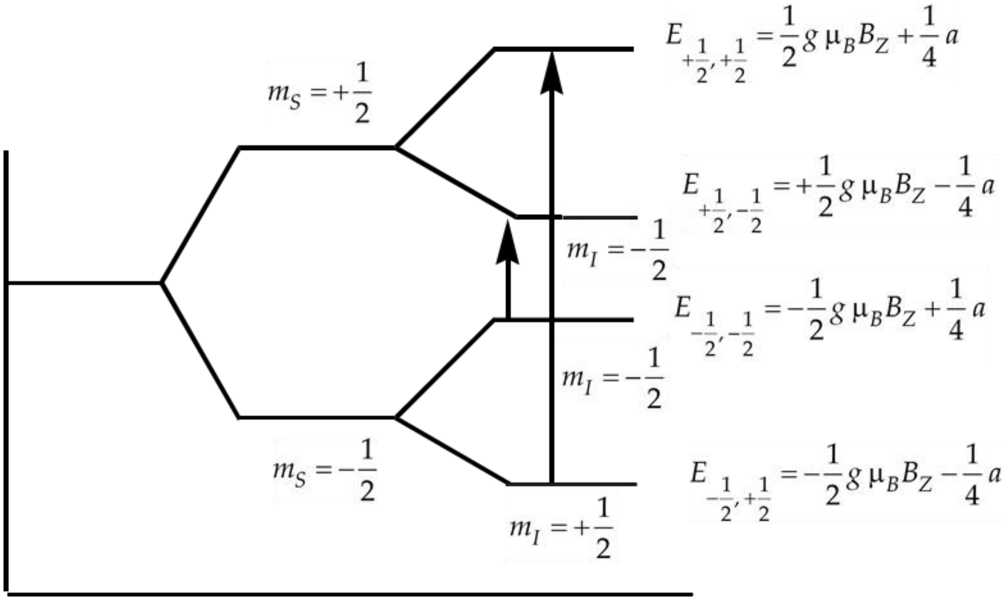
$$g = \frac{1+J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

$$g = 2.0023$$

$\mu_B = 9.274\times10^{-21}$ erg/gauss

Hyperfine splitting

When a nuclei having I (nuclear spin quantum number) active characteristics (I greater than zero) is present it will show definite nuclear spin and there will be an interaction between nuclear spin and electron spin thus the ESR peak given by electron (unpaired) is splitted (proton and magnetically active nuclei), this is called hyperfine splitting and interaction is called hyperfine interaction.



Selection Rule:

$\Delta MS = \pm 1$
$\Delta MI = 0$

Hyperfine splitting means
= +1/2 to +1/2
-1/2 to -1/2
For each I, state of nuclear spin = -I to +I

For e.g. if I = 1/2, then MI = +1/2, -1/2
I = 1, then MI = +1, 0, -1
I = 3/2, then MI = +3/2, +1/2, -1/2, -3/2
I = 5/2, then MI = +5/2, +3/2, +1/2, -1/2, -3/2, -5/2 Example:

(1) O_2^{16}, I = 0, 2nI + 1 = 2×1×0 + 1 = 1 peak

(2) Nitrogen, if I = 0

2nI + 1 = 2×0×1/2+1 = 1 line

If I = 1/2

ΔMI = 0,	ΔMS = ± 1,
+1/2 to +1/2 = 0	-1/2 to +1/2 = 1
-1/2 to -1/2 = 0	+1/2 to -1/2 = -1

2nI + 1 = 2×1×1/2+1 = 2 lines

The ESR spectra of $CH_3^{\bullet}$

I = 1/2, 2nI + 1 = 2×3×1/2+1 = 4 lines

(b) Give the ESR spectra of $CH_3^{\bullet}$

I = 1/2, 2nI + 1 = 2×3×1/2+1 = 4 lines

One H = 1/2 = I
if I = 3/2 = +3/2, +1/2, -1/2, -3/2 if
3H = 1/2×3 = 3/2
MI = +3/2 to +3/2 = 0
+1/2 to +1/2 = 0
-1/2 to -1/2 = 0
-3/2 to -3/2 = 0

Hyperfine Interaction: The resonance frequency of an electron depends upon the magnetic field at the electron. Previously the applied magnetic field was assumed to be the field at the electron. Actually the electron is affected by both the applied magnetic field, H_o and any local fields due to the magnetic fields of nuclei or other effects H_{local}, so that equation: $\Delta E = h\nu = g\mu_B H$ may be written as

$$h\nu = g\mu_B(H_o + H_{local})$$

This will cause transition between these energy levels. In distinction to other types of spectroscopy, in which the energy levels are essentially fixed, in ESR spectroscopy the splitting in energy levels and therefore, the frequency capable of causing transitions between these levels is a function of the magnetic field strength H.

The effect of the magnetic moments of nuclei on the ESR spectrum is called hyperfine interaction and leads to a splitting of the ESR line (hyperfine structure). Consider a hydrogen atom composed of an unpaired electron associated with a proton. Since the proton is a charged spinning particle with a nuclear spin I of 1/2, it has a magnetic moment and the electron will be affected by the magnetic field of the proton as well as that of the applied magnetic field.

The relative orientation of the nuclear magnetic moment and the electron magnetic moment causes a splitting of the original two levels to four levels (see figure below). Only two transitions are found between these states, so that transitions occur only between I = +1/2 or I = -1/2 states (i.e. the selection rule for the transition is $\Delta MI = 0$). The result is a splitting of the original line into a doublet.

The magnitude of the splitting usually given in gauss is called the hyperfine coupling constant, a. For the hydrogen atom aH is about 508 gauss.

In general, a single nucleus of spin I, will cause a splitting into (2I+1) lines, so that interaction with a single nitrogen nucleus (N^{14}, I = 1) will cause a splitting into three lines, and unpaired electron in manganese (II) (Mn^{55}, I = 5/2) interaction with the nucleus to form a six lines spectrum. Many common nuclei such as C^{12} and O^{16} have zero spin and do not interact with the electron.

For a system with the unpaired electron interacting with two equivalent protons a similar analysis shows that formation of a triplet occurs with relative intensities 1:2:1 (see figure below).

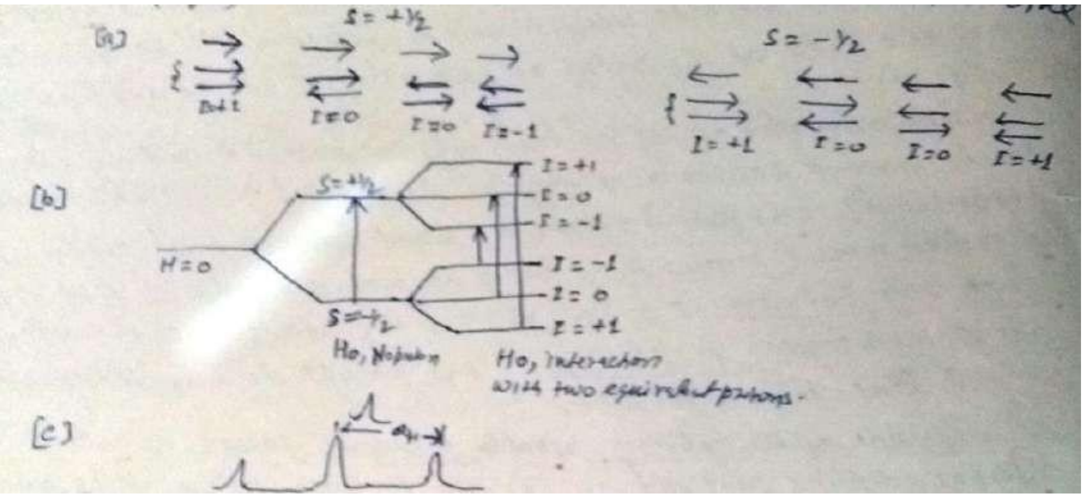


Fig.: Interaction of unpaired electron with two equivalent protons. [a] possible orientation of electron and nuclear magnetic moments. [b] splitting of energy levels. [c] splitting of spectral line.

The two protons may either both oppose or both act in the direction of the magnetic field causing the two extreme lines, or they may act opposite directions from one another, essentially canceling their effect on the electron, resulting in the line located at the same position as the unperturbed line. Since this latter condition can occur in either of two ways, this centre line is twice as intense as the two extreme lines. Continuing an analysis in this way results in the general conclusion that n equivalent protons cause a splitting into nH lines; the relative intensities of these lines follow the binomial expansion.

For non-equivalent nuclei, each will interact with the electron with a different coupling constant to produce a hyperfine splitting. For example, if the electron interacts with one proton (H_1) with a coupling constant a_1 and another proton (H_2) with a coupling constant a_2, assuming a_1 is much larger than a_2, a doublet due to interaction of H_1, split into a doublet due to H_2 will results (H_1 and H_2 hydrogen numbering) (see figure below). Similarly, the interaction of two equivalent hydrogens with a second pair of equivalent hydrogens results in a triplets for very different coupling constants.

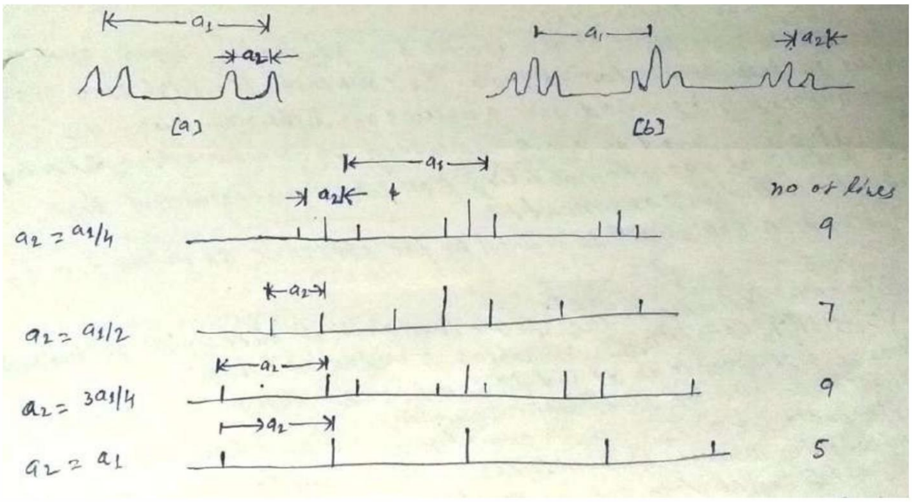


Fig.: A spectra due to interaction of unpaired electron with [a] two non-equivalent protons; [b] two non-equivalent sets of two equivalent protons; [c] variation of spectra for interaction of two sets of equivalent pairs of protons for different values of the coupling constants a_1 and a_2.

g-Value or factor affection g value: g-value in ESR is similar to chemical shift in NMR. For a free electron g = 2.0023. Transition metal complexes have extremely variable g values but broadly speaking less than 2.00 indicates the complex is electron poor often associated with higher oxidation states while greater than 2.00 is electron rich.

For example, in low spin Fe^{3+} the spectra one generally sharp and the g-value is close to 2.00. In contrast, the high spin (with 5 unpaired electrons) is broad and g-values are between 4.0-4.5. The g-value is affected by total electronic angular momentum, the orbital angular momentum and the spin angular momentum of the metal centre. The line pattern observed is temperature dependent. So the nature of magnetic coupling can been determined by temperature dependent measurement. The position of an ESR signal is defined by the effective g value i.e. by $g = \frac{h\nu}{\mu BB}$.

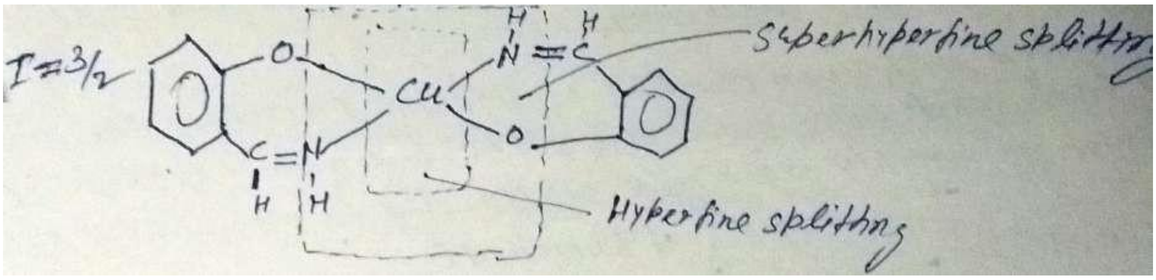
A very common reference is the stable free radical diphenylpicrylhydrazyl $(C_6H_5)_2NN^{\bullet}\{C_6H_2(NO_2)_3\}$ for which g value = 2.0036. g values of ESR spectra of d^n and f^n complexes can differ greatly from 2.00, because of spin-orbit coupling. The effective g for an electron in a d^n complex will depend upon how much orbital angular momentum contributes to the magnetic moment and whether this orbital contribution acts in parallel or is opposed to the spin angular momentum.

Example: V^{4+} (d^1) $g < 2.00$ (typically 1.9)
Cu^{2+} (d^9) $g > 2.00$ (typically 2.2)
Mn^{2+} (d^5) $g = 2.00$

Super hyperfine splitting

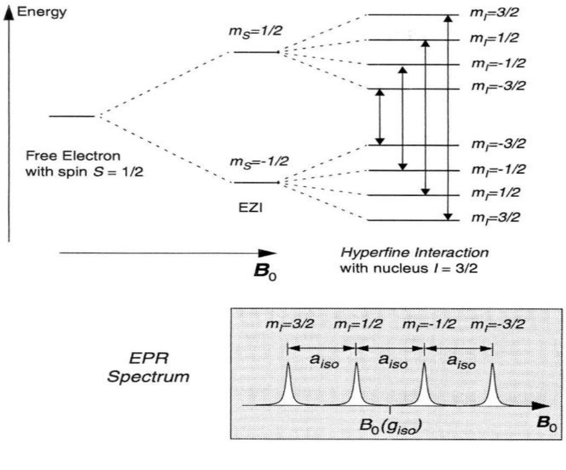
When nuclei and electron spin interacts then super hyperfine splitting takes place if further I active nuclei is present then hyperfine peaks are further splitted and this type of splitting is called super hyperfine splitting.

Ex: Give the ESR spectrum of *bis* salicyaldehyde Cu(II). I = 3/2



For this complex Cu is in Cu^{II} state thus there is d^9 configuration hence there is one unpaired electron.

For Cu^{II} (I = 3/2), thus they will be hyperfine splitting and four peaks will be obtained and since N is also I active (magnetically active) so it will further interacts called superfine splitting and each peak will be splitted give five signals. Hydrogen will further split each in three peaks, thus from one principle peak there should be 15 peaks but only 11 peaks are observed, it is due to overlapping between some peaks.



Cu has one unpaired electron = 2×1×3/2+1 = 4 N

= 2×1×1+1 = 3

But 2N = 2×2×1+1 = 5

For 2H = 2×2×1/2+1 = 3

5×3 = 15 lines

No. of peaks	Ratio	No. of peaks	Ratio
2	1:1	5	1:4:6:4:1
3	1:2:1	6	1:5:10:10:5:1
4	1:3:3:1	7	1:6:15:20:15:6:1

Zero field splitting and Kremer degeneracy

Zero field splitting is observed when system has d block element having more than one unpaired electron. When metal ion with two or more unpaired electrons is incorporated in the ligand field then the degeneracy of spin state is destroyed and it is taking place in absence of external magnetic field thus it is called zero field splitting and Kremer degeneracy.

For a system with even number of unpaired electrons the lowest energy level must take zero spin state and other higher state will exist as doubly degenerate sates due to zero field splitting.

	± 3	If 6 unpaired electrons
+2, +1, 0, -1, -2	± 2	If 4 unpaired electrons (doubly degenerate)
+1, 0, -1	± 1	If 2 unpaired electrons (doubly degenerate)
	0	single degenerate

For odd number of electrons (unpaired) all spin states exist as double degenerate state: 7e^- = ±7/2, 5e^- = ±5/2, 3e^- = ±3/2, 1e^- = ±1/2

The existence of double degenerate spin state due to zero field splitting is called Kremer degeneracy. By the application of external magnetic field, the degeneracy of doubly degenerate spin state is lifted and we will obtain singly degenerate state.

Selection rule, this step (into Kremer degeneracy) is $\Delta M_S = \pm 1$

If further active nuclei are present then hyperfine splitting will take place and we observe fine lines.

Selection rule, this step $\Delta M_I = 0$

Give the ESR lines:

(i) HOCH——COOH

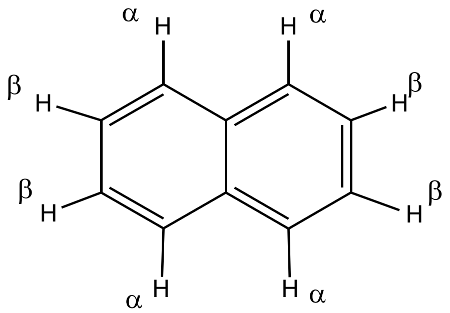
ACH > A(COH)

H-O-CH-COOH

Total lines = (2nI+1) (2nI+1)

$= (2\times1\times1/2+1)\ (2\times1\times1/2+1) = 2\times2 = 4$ lines

(ii) **Naphthalene (radical anion)**



$A\alpha = 4.90$

$A\beta = 1.89$

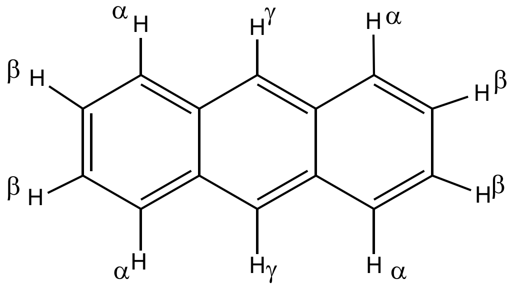
First splitting = 2nI + 1

n = Hα hydrogen = $2\times4\times1/2+1 = 5$

Hβ hydrogen = $2\times4\times1/2+1 = 5$

Total lines = $5\times5 = 25$ lines

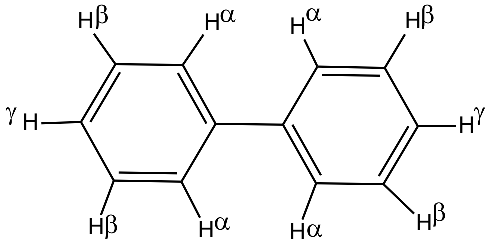
(iii) **Anthracene radical anion**



Total lines = (2nI+1) (2nI+1) (2nI+1)

= 75 lines

(iv) **Total lines and ESR in biphenyls radical anion**

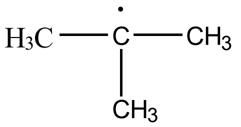


2γ> Hα > Hβ

$(2\times2\times1/2+1)\times(2\times4\times1/2+1)\times(2\times4\times1/2+1) =$

$3\times5\times5 = 75$ lines

(v) ESR lines and butyl radicals



$H_3C-\underset{\displaystyle CH_3}{\overset{\bullet}{C}}-CH_3$

Total lines = 2×9×1/2+1 = 10 lines

(vi) ESR lines for $^{13}CH_3^{\bullet}$

Total lines = (2×1×1/2+1) (2×3×1/2+1) = 2×4 = 8 lines

(vii) ESR lines in $CD_3^{\bullet}$

I = 1, Total lines = (2×3×1+1) = 7 lines

(viii) $CF_2H^{\bullet}$

I = 1/2, Total lines = (2×2×1/2+1) (2×1×1/2+1) = 2×3 = 6 lines

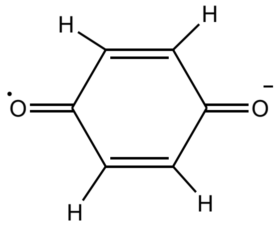
$^{13}CF_2H^{\bullet}$

Total lines = (2×1×1/2+1) (2×2×1/2+1) (2×1×1/2+1) = 2×3×2 = 12 lines

(ix) $CH_3CH_2^{\bullet}$

Total lines = (2×2×1/2+1) (2×3×1/2+1) = 3×4 = 12 lines

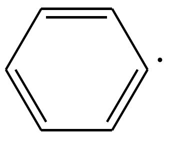
(x) Benzoquinone radical anions



Total lines = (2×4×1/2+1) = 5 lines

One unpaired electron interacts with H equivalent hydrogen atoms.

(xi) Benzene radical



Total lines = (2×6×1/2+1) = 7 lines

Instrumentation

An understanding of ESR instruments requires a general knowledge of the operation of microwave and other spectrometer components.

Spectrometer components

Klystrons (source): The source of the radiation ν is a klystron tube operating in the X-band (3 cm) region at about 9 G. The klystron can be turnover the range of about ± 0.5 gauss by a control which varies the dimensions of a resonant cavity inside the tube. The output frequency is also a function of a resonator and reflector voltages fed to the klystron by a power supply. It is generally stabilized against temperature fluctuations by immersion in an oil bath or by a feed-back Automatic Frequency Control (AFC) circuit. The power output of klystrons used in ESR spectrometer is generally about 300 milliwatts.

Wave Guide: A microwave radiation is conveyed to the sample and crystal by a wave guide, a hallow rectangular brass tube 0.9 inch x 0.4 inch.

Attenuators: The power propagated down the wave guide can be continuously decreased by interseting a variable attenuator consisting of a piece of resistive material into the wave guide. By the use of this attenuators, the power at the sample may be varied from the full power of the klystron to one attenuated by a factor of 100 or more.

Cavities: The sample is contained in a resonant cavity in which a standing wave is setup. The cavity is analogous to a tuned circuit (e.g. a parallel L-C combination) used at low frequencies. A measure of quality of the cavity is its "Q" or "Q-factor" which is defined as

$$Q = \frac{\text{Energy stored in cavity}}{\text{Energy lost}}$$

The sensitivity of a spectrometer is directly proportional to the value of Q. Two frequently used cavities are the rectangular TE102 cavity and the cylindrical TE011 cavity. Since the component of interest is the magnetic field; which interacts with the sample to cause spin resonance, the sample is placed where the intensity of the magnetic field is at its highest. The electric field, however, also interacts with the sample and if the sample has a high dielectric constant (i.e. lossy) the Q of the cavity may be drastically decreased.

Crystal detectors: The detector of the microwave radiations is usually a silicon crystal detector (which converts AC radiation to DC). An appreciable amount of noise is generated in a crystal detector; the magnitude of this noise is decreases with increasing frequency of the output signals. Therefore, the signal is usually modulated at a high frequency (6 k to 100 k) to decrease this source of noise.

Magic T's Bridge: Microwave bridges (which are analogous to impedance bridges in conventional circuits) can be of the "magic-T" variety.

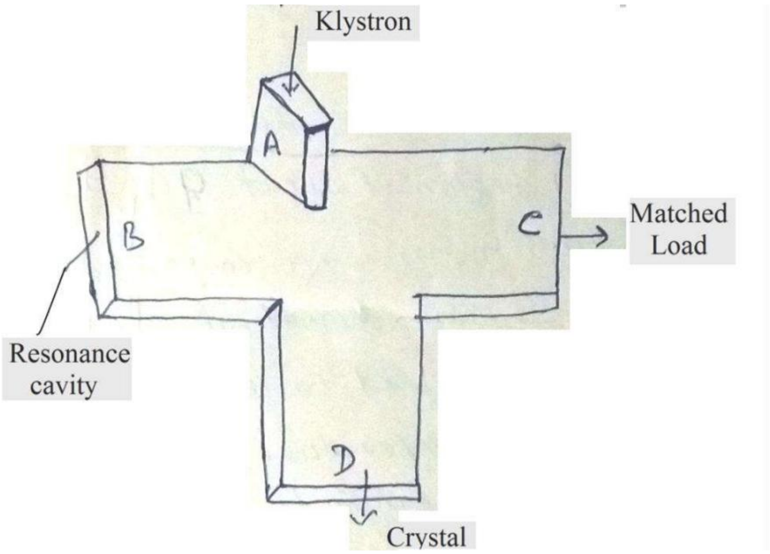


Fig.: Magic ‘T’ bridge.

Power entering arm A will divide between arms B and C if the impedances of B and C are the same, so that no power will enter in arm D. Under these conditions the bridge is said to be balanced. If the impedance of arm B changes, say because a resonant cavity coupled to the end arm B changes its Q because of the occurance of ESR absorption by a sample in it. The bridge becomes unbalanced and some microwave power enters into arm D containing the crystal detectors. In this way the ESR absorption occurs as an increase of a small signal rather than as a decrease in a large one.

Magnets: An electromagnet capable of producing field of at least 5000 gauss is required for ESR. The homogeneity of the field for solution studies should be about 50 milligauss over the ESR sample region. The ESR spectrum is recorded by slowly varying the magnetic field through the resonance conditions by sweeping the current supplied to the magnet by the power supply. This sweep is generally accomplished with a variable speed motor drive. Both the magnet and power supply may require water cooling.

Modulation Coils: The modulation of the signal at a frequency constant with good signal to noise (S/N) ratios in the crystal detector is accomplished by a small alternating variation of the magnetic field. The variation is produced by supplying an a.c. signal to modulation coils oriented with respect to the sample in the same direction as the magnetic field. For low frequency modulations (400 cycle per second or less) the coils can be mounted outside the cavity and even on the magnet pole pieces. High modulated frequencies (1 KV or more) cannot penetrate metal effectively and either the modulation coils must be mounted inside the resonant cavity or cavities constructed of a non-metallic materials (e.g. quartz with a thin silvered plating) must be employed.

Display devices: A cathode ray oscilloscope is used to adjust the spectrometer and sometimes to observe the signal.

Block diagram of ESR spectrometer:

The most widely used commercial ESR spectrometers are probably those made by Varian Associates. A simplified block diagram of the Varian V-4502 spectrometer is shown below:

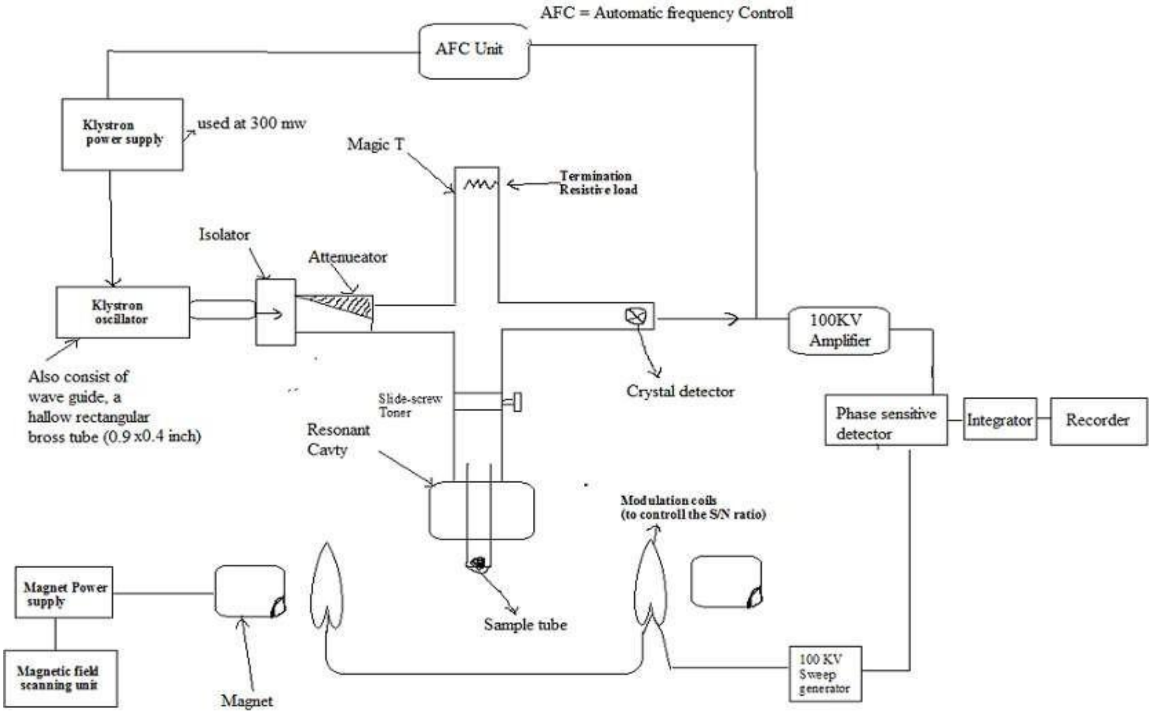


Fig.: Block diagram of a reflection ESR spectrometer incorporating 100 kV modulators and phase sensitive detector. The Varian Associates V-4502 spectrometer.

Although X-band is common, ESR spectrometers are available commercially in several frequency ranges. As particular matter, wave guides cannot be too big or too small (1 cm is a bit small and 10 cm a bit large). The most common choice called X-band microwaves has length (l) in the range 3.0-3.3 cm (n ~ 9-10 GHz); in the middle of X-band, the free electron resonance is found at 3390 gauss.

Designation	n (GHz)	l (cm)	$B_{electron}$ (Tesla)
S	3.0	10.0	0.107
X	9.5	3.15	0.339
K	23	1.30	0.82
Q	35	0.86	1.25
W	95	0.315	3.3

Application of ESR

The scope of application of ESR spectrometry to analysis is somewhat limited by the requirement that the substance being analyzed contains unpaired electrons. A few methods for transition metals and free radicals have been reported. The widest use for ESR in organic chemistry has been in the analysis of free radicals produced by chemical reaction or irradiations. These studies were usually associated with kinetic measurements or involved only qualitative identification of radicals. However, non-paramagnetic organic substances can be determined by a technique which converts them qualitatively or at a constant yield into free radicals which are then observed by ESR spectrometry. Techniques for producing free radicals include pyrolysis, adsorption on alumina or zeolites, photolytic methods and reductions or oxidations by chemical or electrolytic means. Classes of components which might be studied by this kind of techniques include aromatic hydrocarbons, ketones, quinoline, amines and phenols.

Analysis of Metals:

Analysis of vanadium in petroleum oils: Vanadium (IV) found in the ppm range in petroleum oils, leads to corrosions effects in combustion engines and furnaces using petroleum oils fuels and alters the catalytic cracking of the petroleum during processing. The analysis of Vanadium by ESR spectroscopy in such sample has been investigated by several groups and has been shown to be a rapid and convenient method of analysis. Vanadium (IV) yields an eight-line spectrum due to the interaction of an unpaired 3d electrons with a nucleus (I = 7/2). In highly viscous media, due to the anisotropy of the g-value; splitting into a greater number of lines occurs. A typical analysis involved using identical precession bore tubes of 3 mm. i.d. and using vandylitioporphyrine (I) dissolved in heavy oil distillate as a standard. The intensity measurements were made by measuring the peak-to-peak height on the first derivatives recording of a given hyperfine line. Peak height measurement rather than double integration can be used as long as lines widths and shapes remain constant. Quantities of Vanadium in the 0.1 to 50 ppm range were determined with results checking to within ± 20% in most cases with analysis performed by alternate method. No other constituents of oils interfered.

Organic Analysis

Analysis of polynuclear hydrocarbons: The determination of anthracene, perylene, dimethylanthracene and naphthalene by conversion to radical cations and determination by ESR spectrometry. When benzene or carbon disulphide solutions of these hydrocarbons are treated with an activated silica-alumina catalyst, they are quantitatively converted to the radicals and adsorbed on the surface of the catalyst. The procedure involved adding the polynuclear hydrocarbon sample in benzene or carbon disulphide and activated catalyst to 6 mm. Uniform pore tubes and measuring the peak heights. The standard deviation of a series of measurements of samples in the 10 μg range was about 5%. Benzene, naphthalene and other hydrocarbons which do not form radicals at the catalyst surface did not interfere.

Others Applications

EPR spectroscopy is used in various branches of science, such as chemistry and physics for the detection and the identification of free radicals and paramagnetic centres. EPR is sensitive, specific method for studying both radicals formed in chemical reaction and the reactions themselves. For example, when frozen water (solid H_2O) is decomposed by exposure to high energy radiation, radical such as H, OH and HO_2 are produced. Such radicals can be identical and studied by EPR. Organic and inorganic radicals can be detected in electrochemical system and in materials exposed to UV-light. In many cases, the reactions to make the radicals and the subsequent reaction of the radicals are of interest; while in other cases EPR is used to provide information on a radicals geometry and the orbital of the unpaired electrons.

Medical and biological applications of EPR also exist. Although radicals are very reactive and so do not normally occur in high concentrations in biology. Special reagents have been developed to spin-label molecules. These reagents are particularly useful in biological system. Specially designed non-reactive radicals molecules can attach to specific sites in a biological cells and EPR spectra can then give information on the environment of these so called spin-label or spin-probe.

EPR spectroscopy can only be applied to system in which the balance between radical decay and radical formation keeps the free-radical concentrations above the detection limit of the spectrometer used. This can be particularly severe problem in studying reactions in liquid. An alternative approach is to slow down reaction by studying samples held at cryogenic (freezing mixture) temperature, such as 77 K (liquid nitrogen) or 4.2 K (liquid helium). An example of this work is the study of the radical reactions in single crystals of amino acids exposed to X-ray; work that sometimes lead to activation energy and rate constants for radicals reactions. EPR also have been used by archaeologist for the dating of teeth. Radiation damage over long periods of times creates free radicals in tooth enamel, which can then be examined by EPR and after proper calibration dated. Alternatively, material extracted from the teeth of people during dental procedures can be used to quantity their cumulative exposure to ionizing radiation. People exposed to radiation from the chemobyl disaster have been examined by this method.

Radiation-sterilized foods have been examined with EPR spectroscopy, the aim being to develop methods to determine, if the particular food sample has been irradiated and to what dose. Because of its high sensitivity, EPR is used recently to measure the quantity of energy used locally during a mechanochemical milling process.

Unit – V

Mass and Mossbauer Spectroscopy

Mass Spectroscopy

Introduction

Mass Spectrometry is a powerful technique for identifying unknowns, studying molecular structure, and probing the fundamental principles of chemistry. Applications of mass spectrometry include identifying and quantitating pesticides in water samples, it identifying steroids in athletes, determining metals at ppq (Parts Per Quadrillion) levels in water samples, carbon-14 dating the Shroud of Turin using only 40 mg of sample (*1*), looking for life on M ars, determining the mass of an ^{28}Si atom with an accuracy of 70 ppt(*2*), and studying the effect of molecular collision angle on reaction mechanisms.

Mass spectrometry is essentially a technique for "weighing" molecules.* Obviously, this is not done with a conventional balance or scale. Instead, mass spectrometry is based upon the motion of a charged particle, called an ion, in an electric or magnetic field. The mass to charge ratio (*m/z*)* * of the ion effects this motion. Since the charge of an electron is known, the mass to charge ratio a measurement of an ion's mass. In mass spectrometry, one generates ions from a sample to be analyzed. These ions are then separated and quantitatively detected. Separation is achieved on the basis of different trajectories of moving ions with different mass/charge (m/z) ratios in electrical and/or magnetic fields.

Mass-spectrometry has evolved from the experiments and studies early in the 20th century that tried to explain the behavior of charged particles in magnetic and electrostatic force fields. Well-known names from these early days are J. J. Thompson *investigation into the behavior of ionic beams in electrical and magnetic fields* (1912), A. J. Dempster *directional focusing* (1918) and F. W. Aston *energy focusing* (1919). In this way a refinement of the technique was achieved that allowed important information concerning the natural abundance of isotopes to be collected.

The first analytical applications then followed in the early forties when the first reliable commercial mass spectrometers were produced. This was mainly for the quantitative determination of the several components in complex mixtures of crude oil.

In the beginning of the sixties the application of mass-spectrometry to the identification and structure elucidation of more complex organic compounds, including polymers and biomolecules, started. Since then the technique has developed to a powerful and versatile tool for this purpose, which provides information partly complementary to and overlapping with other techniques, such as NMR.

It is perhaps surprising that a technique that at first sight does not appear to give more information than the weight of a particle should be so important, since it is difficult to imagine a more prozaic property of a molecule than its molecular weight. The controlled fragmentation of the initial molecular ions yields interesting information that can contribute to structure elucidation. In addition the weights can now be determined with sufficient accuracy to allow elemental compositions to be derived.

Basic Principles

Though the principles of a modern analytical mass-spectrometer are easily understood this is not necessarily true for the apparatus. A mass spectrometer especially a multi-sector instrument is one of the most complex electronic and mechanical devices one encounters as a chemist.

Measurement principles.

In Figure the essential parts of an analytical mass spectrometer are depicted. Its procedure is as follows:

1. A small amount of a compound, typically one micromole or less, is evaporated. The vapour is leaking into the ionization chamber where a pressure is maintained of about 10^{-7} mbar.

2. The vapour molecules are now ionized by an electron-beam. A heated cathode, the filament, produces this beam. Ionization is achieved by inductive effects rather then strict collision. By loss of valence electrons, mainly positive ions are produced.

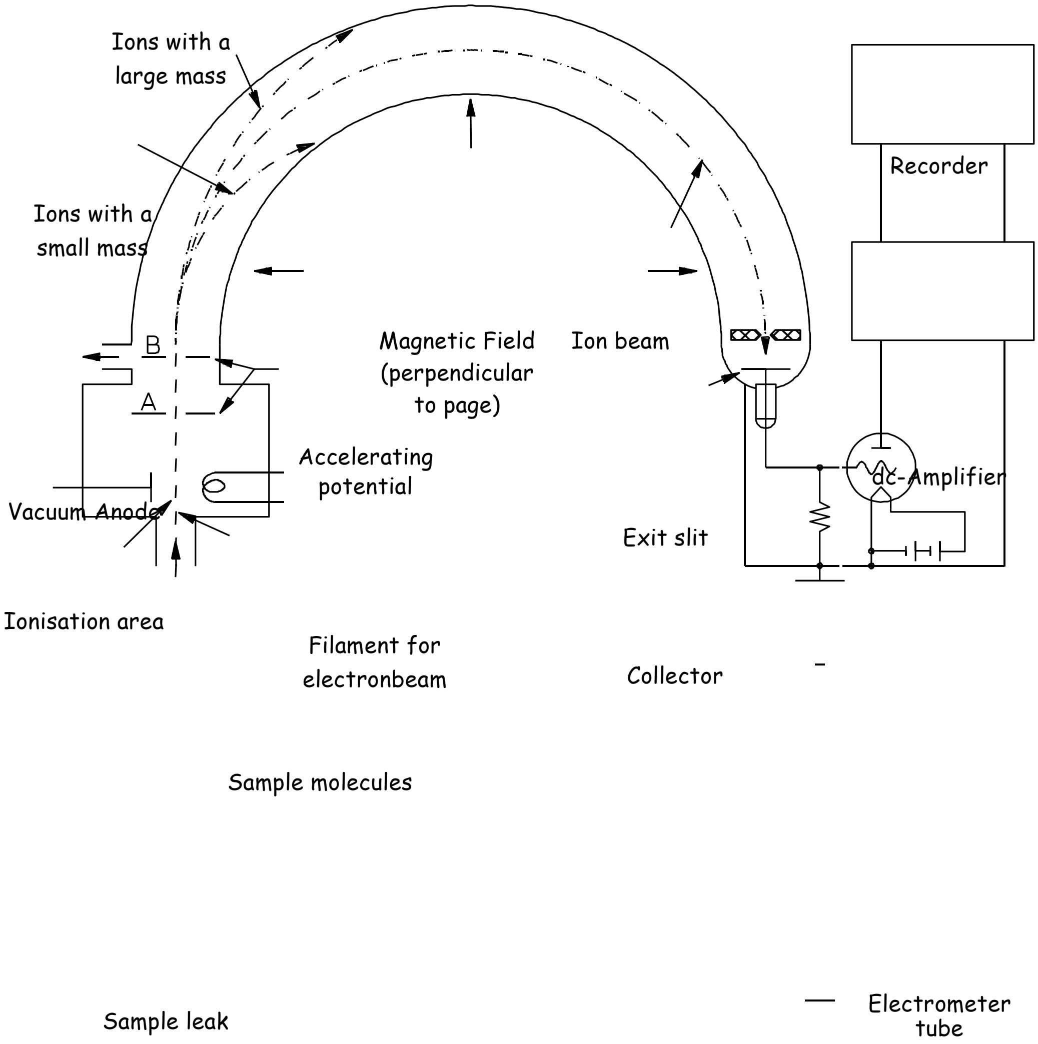
3. The positive ions are forced out of the ionization chamber by a small positive charge (several Volts) applied to the repeller opposing the exit-slit (A). After the ions have left the ionization chamber, they are accelerated by an electrostatic field (A>B) of several hundreds to thousands of volts before they enter the analyzer.

4. The separation of ions takes place in the analyzer, in this example a magnetic sector, at a pressure of about 10^{-8} mbar. A strong magnetic field is applied perpendicular to the motional direction of the ions. The fast moving ions then will follow a circular trajectory, due to the Lorentz acceleration, whose radius is determined by the mass/charge ratio of the ion and the strength of the magnetic field. Ions with different mass/charge ratios are forced through the exit-slit by variation of the accelerating voltage (A>B) or by changing the magnetic-field force.

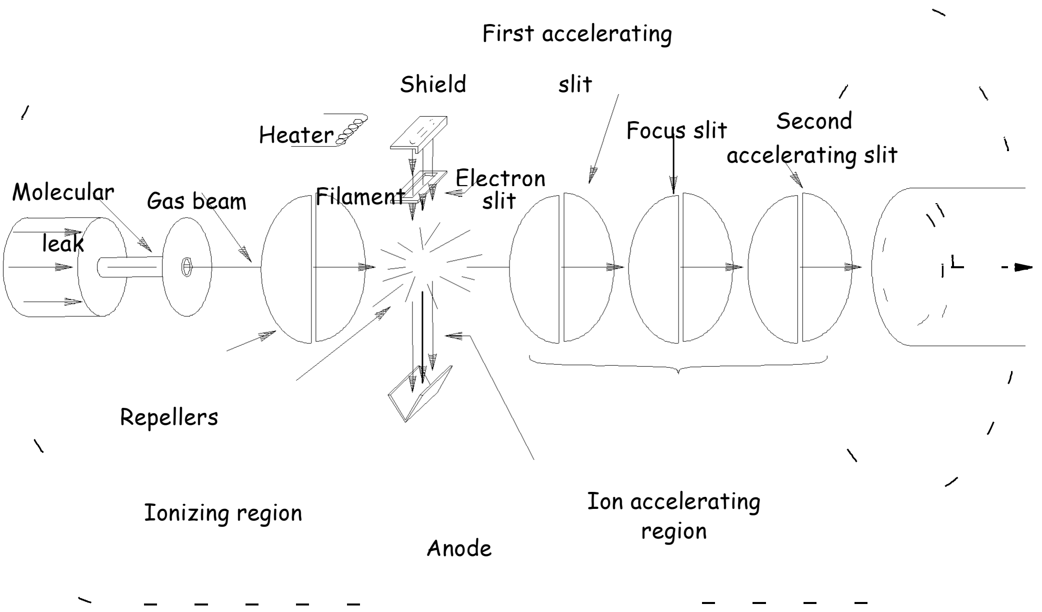
5. After the ions have passed the exit-slit, they collide on a collector-electrode. The resulting current is amplified and registered as a function of the magnetic-field force or the accelerating voltage. The applicability of mass-spectrometry to the identification of compounds comes from the fact that after the interaction of electrons with a given molecule an excess of energy results in the formation of a wide range of positive ions. The resulting mass distribution is characteristic (a fingerprint) for that given molecule. Here there are certain parallels with IR and NMR. Mass-spectrograms in some ways are easier to interpret because information is presented in terms of masses of structure-components.

Sampling. As already indicated a compound normally is supplied to a mass-spectrometer as a vapour from a reservoir. In that reservoir, the prevailing pressure is about 10 to 20 times as high as in the ionization chamber. In this way, a regular flow of vapour-molecules from the reservoir into the mass spectrometer is achieved. For fluids that boil below about 150 ^{o}C the necessary amount evaporates at room temperature. For less volatile compounds, if they are thermally stable, the reservoir can be heated. If in this way sampling cannot be achieved one passes onto to direct insertion of the sample.

The quality of the sample, volatility and needed amount are about the same for mass-spectrometry and capillary gas chromatography. Therefore, the effluent of a GC often can be brought directly into the ionization chamber. Use is then made of the excellent separating power of a GC in combination with the power to identify of the mass-spectrometer. When packed GC is used, with a much higher supply of carrier-gas, it is necessary to separate the carrier gas prior to the introduction in the mass-spectrometer (jet-separator).


Ions with a large mass
Ions with a small mass
B
A
Magnetic Field (perpendicular to page)
Ion beam
Recorder
dc-Amplifier
Accelerating potential
Vacuum Anode
Exit slit
Ionisation area
Filament for electronbeam
Collector
Sample molecules
Sample leak
Electrometer tube

The Ion source. In Figure the scheme of an ionization chamber, ion-source, typically electron impact, is presented. In this chamber in several ways, ions of the compound to be investigated can be produced. The most common way is to bombard vapour-molecules of the sample with electrons of about 70 eV. These electrons are generated by heating a metal wire (filament), commonly used are tungsten or rhenium. A voltage of about 70 Volts (from 5 to 100) accelerates these electrons towards the anode.



During the bombardment, one or more electron can be removed from the neutral molecule thus producing positively charged molecular radical-ions. Only about one in 10^3 of the molecules present in the source are ionized. The ionization probability differs among substances, but it is found that the cross-section for most molecules is a maximum for electron energies from approximately 50 to 100 eV. Most existing compilations of electron impact spectra are based on spectra recorded with approximately 70 eV electrons, since sensitivity is here close to a maximum and fragmentation is unaffected by small changes in electron energy around this value. During this ionization, the radical-ions on average gain an excess energy enough to break one or more bonds en hence producing fragment-ions. In Figure 1.3 the possible fragmentation of a molecule ABCD is presented. It should be stated here that this is a simplified presentation and that in real life a multitude of possible ways to form fragments even via re-arrangement reactions exists. Fragmentation of a molecular radical cation to give a neutral molecule and a new fragment radical cation is also possible.

Ionization Sources

The starting point for a mass spectrometric analysis is the formation of gaseous analyte ions, and the scope and the utility of a mass spectrometric method is dictated by the ionization process. The appearance of mass spectra for a given molecular species strongly depends on the method used for ion formation. Note that these methods fall into three major categories: *gas- phase sources, desorption sources*, and *ambient desorption sources.* With a gas-phase source, which includes the first three sources in the table, the sample is first vaporized and then ionized. With a desorption source, however, the solid- or liquid-state sample is converted directly into gaseous ions. An advantage of desorption sources is that they

Ambient sources allow desorption ionization with minimal sample pre treatment and without the enclosures of typical ionization sources. Currently, commercial mass spectrometers are equipped with accessories that permit interchangeable use of several ionization sources. Gas- phase sources are generally restricted to the ionization of thermally stable compounds that have boiling points less than about 500°C. In most cases, this requirement limits gaseous sources to compounds with molecular masses less than roughly

103 Da. Desorption and ambient sources, which do not require volatilization of analyte molecules, are applicable to analytes having molecular masses as large as 105 Da. Ion sources are also classified as being *hard sources* or *soft sources*. Hard ionization sources impart enough energy to analyte molecules to leave them in a highly excited energy state. Relaxation then involves rupture of bonds, producing fragment ions that have mass-to-charge ratios less than that of the molecular ion. Soft ionization sources cause little fragmentation. Thus, the mass spectrum from a soft ionization source often consists of the molecular ion peak and only a few, if any, other peaks. Both hard- and soft-source spectra are useful for analysis.

The many peaks in a hard-source spectrum provide useful information about the kinds of functional groups and thus structural information about analytes. Soft-source spectra are useful because they supply accurate information about the molecular mass of the analyte molecule or molecules.

Electron Ionization

Historically, ions for mass analysis were produced by *electron ionization,* formerly called electron-impact ionization. In this process, the sample is brought to a temperature high enough to produce a molecular vapor, which is then ionized by bombarding the resulting molecules with a beam of energetic electrons. Despite certain disadvantages, this technique is still of major importance and is the one on which many libraries of mass spectral data are based. Figure is a schematic of a basic EI source. Electrons are emitted from a heated tungsten or rhenium filament and accelerated by applying approximately 70 V between the filament and the anode. As shown in the figure, the paths of the electrons and molecules are at right angles and intersect near the center of the source, where collision and ionization occur. The primary product is singly charged positive ions formed when the energetic electrons approach molecules closely enough to cause them to lose electrons by electrostatic repulsion. Electron ionization is not very efficient, and only about one molecule in a million undergoes the primary reaction

$$M + e^- \rightarrow M^{\circ+} + 2e^-$$

Here, M represents the analyte molecule, and $M^{\circ+}$ is its molecular ion. The positive ions produced by electron ionization are attracted through the slit in the first accelerating plate by a small potential difference (typically 5 V) that is applied between this plate and the repellers shown in Figure. With magnetic sector instruments, high voltages (10^3 to 10^4V) are applied to the accelerator plates, which give the ions their final velocities before they enter the mass analyzer. Commercial EI sources are more complex than that shown in Figure and may use additional electrostatic or magnetic fields to manipulate the electron or ion beam.

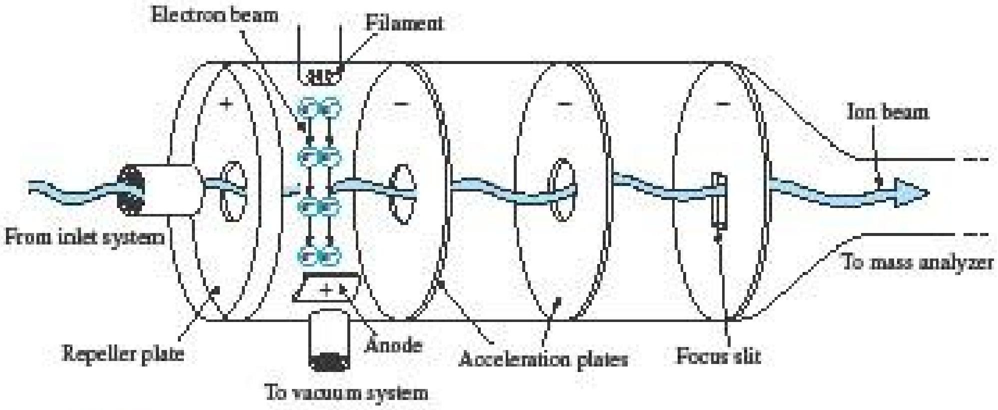


FIGURE 20-3 Diagram of an EI source. (Adapted from D. L. Pavia, G. M. Lampman, G. S. Kriz, and J. R. Vyvyanh, *Introduction to Spectroscopy*, 5th ed., Stamford, CT: Cengage Learning, 2015, p. 110.)

Advantages and Disadvantages of EI Sources

EI sources are convenient to use. They produce high ion currents, which lead to good sensitivities. The extensive fragmentation and resulting large number of peaks is also an advantage because it often makes unambiguous identification of analytes possible. Extensive fragmentation can also be a disadvantage, however, when it results in the disappearance of the molecular ion peak so that the molecular mass of analytes cannot be easily established. Another limitation of the EI source is the need to volatilize the sample, which may result in thermal degradation of some analytes before ionization can occur. The effects of thermal decomposition can sometimes be minimized by carrying out the volatilization from a heated probe located close to the entrance slit of the spectrometer. At the lower pressure of the source area, volatilization occurs at a lower temperature. Furthermore, less time is allowed for thermal decomposition to take place. As mentioned earlier, EI sources are applicable only to analytes having molecular masses smaller than about 10^3 Da.

Chemical Ionization Sources

Most modern mass spectrometers are designed so that electron ionization and chemical ionization can be carried out interchangeably. Such sources are called EI-CI sources. In CI, gaseous atoms of the sample (from either a batch inlet or a heated probe) are ionized by collision with ions produced by electron bombardment of an excess of a reagent gas. Usually, positive ions are used, but negative ion CI is occasionally used with analytes that contain very electronegative atoms. Chemical ionization is probably the second-most common procedure for producing ions for mass spectrometry.To carry out CI experiments, it is necessary to modify the electron beam ionization area shown in Figure by adding vacuum pump capacity and by reducing the width of the slit to the mass analyzer. These measures allow a reagent pressure of about 100 Pa (0.75 torr) to be maintained in the ionization area while maintaining the pressure in the analyzer below 1027 Pa. With these changes, a gaseous reagent is introduced into the ionization region in an amount such that the concentration ratio of reagent to sample is 103 to 104. Because of this large concentration difference, the electron beam reacts nearly exclusively with reagent molecules.

Desorption Sources

The ionization methods discussed so far require that the ionizing agents act on gaseous samples. Such methods are not applicable to non volatile or thermally unstable samples. A number of *desorption ionization* methods have been developed for dealing with this type of sample. These methods have enabled mass spectra to be obtained for thermally delicate biochemical species and species having molecular masses of greater than 100,000 Da. Desorption methods dispense with volatilization followed by ionization of the gaseous analyte molecules. Instead, energy in various forms is introduced into the solid or liquid sample in such a way as to cause direct formation of gaseous ions. As a consequence, spectra are greatly simplified and often consist of only the molecular ion or the protonated molecular ion. In most cases the exact mechanism of how ions are formed without fragmentation is not well understood.

Matrix-Assisted Laser Desorption/Ionization

Matrix-assisted laser desorption/ionization (MALDI) spectrometry is an ionization method that can be used to obtain accurate molecular mass information about polar biopolymers ranging in molecular mass from a few thousand to several hundred thousand Da. The method was first described nearly simultaneously in 1988 by two research groups, one German and the other Japanese Commercial instrumentation is available for MALDI. In the MALDI technique, a low concentration of the analyte is uniformly dispersed in a solid or liquid matrix deposited on the end of a stainless steel probe or placed on a metal plate. The plate is then placed in a vacuum chamber and a laser beam is focused onto the sample. In addition to the usual vacuum- chamber MALDI, atmospheric-pressure MALDI has also been described. The MALDI matrix must strongly absorb the laser radiation. The matrix and analyte are then desorbed and ionized, creating an ion plume. The overall process is illustrated in Figure. The most common type of mass analyser used with MALDI is the time-of- flight (TOF) analyzer.

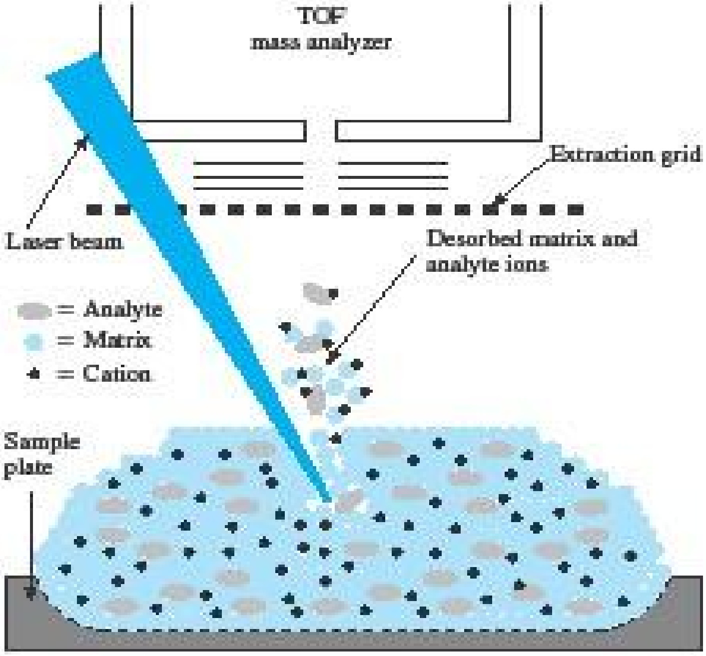


FIGURE 20-7 Diagram of the MALDI process. The analyte is uniformly dispersed in a matrix and placed on a metal sample plate. A pulsed laser beam strikes the sample causing desorption of a plume of matrix, analyte, and other ions. The analyte can be protonated, be deprotonated, or form adducts before entering the TOF analyzer.

A mass spectrum from a MALDI-TOF instrument is shown in Figure. Here, the matrix material was nicotinic acid, and the analyte was a monoclonal antibody from a mouse having a molecular mass of approximately 150,000 Da. Note that the spectrum is characterized by very low background noise and a complete absence of fragmentation of the large analyte ion. Multiply charged ions are present as well as peaks for dimer and trimer species. Although the mechanism of the formation of the MALDI ion plume is not completely understood, it is thought to involve absorption of the laser beam by the matrix, followed by transfer of the energy from the matrix to the analyte. Desorption of the analyte and the matrix then occurs. The analyte is thought to desorb as neutral molecules and then to be ionized by proton transfer reactions with protonated matrix ions in a dense phase over the surface containing the matrix. A series of photochemical reactions may produce the protonated matrix ions. Recently, the MALDI technique has been extended to imaging methods by scanning a localized laser beam over the dispersed sample. Mass spectral images of a variety of biopolymers have been obtained in this manner.

Fast Atom Bombardment Sources

Fast atom bombardment (FAB) sources, also called liquid secondary ion sources, were once very popular for producing ions for mass spectrometric studies of polar high-molecular-mass species. With this type of source, samples in a condensed state, usually in a viscous solution matrix, are ionized by bombardment with energetic (several keV) xenon or argon atoms. Both positive and negative analyte ions are sputtered from the surface of the sample in a desorption process. This treatment provide very rapid sample heating, which reduces sample fragmentation. The liquid matrix helps to reduce the lattice energy, which must be overcome to desorb an ion from a condensed phase, and provides a means of “healing” the damage induced by bombardment. Successful matrices include glycerol, thioglycerol, *m*-nitrobenzyl alcohol, crown ethers (18-crown-6), sulfolane, 2-nitrophenyloctyl ether, diethanolamine, and triethanolamine. A beam of fast atoms is obtained by passing accelerated argon or xenon ions from an ion source, or gun, through a chamber containing argon or xenon atoms at a pressure of about 10^{-3} Pa (10^{-5} torr). The high-velocity ions undergo a resonant electron-exchange reaction with the atoms without substantial loss of translational energy. Thus, a beam of energetic *atoms* is formed. The lower-energy ions from the exchange are readily removed by an electrostatic deflector. Fast atom guns are available from several commercial sources, and modern spectrometers offer FAB sources as accessories. The many drawbacks of FAB have led to its decrease in popularity. These include the limited molecular mass range of FAB, the need for larger sample quantities than many other ionization techniques and the necessity for finding an appropriate matrix in which the analyte is soluble. Also, FAB is best performed with double-focusing mass spectrometers. For these reasons, electrospray and MALDI methods have supplanted FAB techniques for many applications. Both of these are more sensitive and simpler to use than FAB methods.

Electrospray Ionization

Electrospray ionization–mass spectrometry (ESI/MS), which was first described in 1984, has now become one of the most important techniques for analyzing biomolecules, such as polypeptides, proteins, and oligonucleotides, having molecular weights of 100,000 Da or more. In addition, this method is finding more and more application to the characterization of inorganic species and synthetic polymers. For their development of soft desorption ionization methods, such as electrospray ionization, John B. Fenn and Koichi Tanaka shared the 2002

Nobel Prize in Chemistry. Electrospray ionization takes place under atmospheric pressures and temperatures in an apparatus such as that shown in Figure. A solution of the sample is pumped through a stainless steel capillary needle at a rate of a few microliters per minute. The needle is maintained at several kilovolts with respect to a cylindrical electrode that surrounds the needle. The resulting charged spray of fine droplets then passes through a desolvating capillary, where evaporation of the solvent and attachment of charge to the analyte molecules take place. As the droplets become smaller as a consequence of evaporation of the solvent, their charge density becomes greater until, at a point called the *Rayleigh limit*, the surface tension can no longer support the charge. Here a so-called *Coulombic explosion* occurs and the droplet is torn apart into smaller droplets. These small droplets can repeat the process until all the solvent is removed from the analyte, leaving a multiply charged analyte molecule. An interesting and useful feature of the electrospray process is that little fragmentation of large and thermally fragile biomolecules occurs because there is little extra energy retained by the analyte upon ionization. Furthermore, the ions formed are multiply charged so that their m/z values are small enough to make them detectable with a quadrupole instrument with a range of 1500 or less. This important property is demonstrated by the mass spectra of four proteins of varying molecular mass (M) shown in Figure. In these spectra, adjacent peaks are for analyte ions that differ by one charge. A striking feature of the spectra for proteins, such as those in the figure, is that the average charge state increases in approximately linear fashion with molecular mass. The charge state corresponding to each peak can be determined from peak distribution, thus making it possible to determine the molecular mass of a protein from spectra such as those shown in Figure. An important characteristic of electrospray ionization is that it is readily adapted to direct sample introduction from high-performance liquid chromatography and capillary electrophoresis columns. That there is little fragmentation of the analyte makes structural elucidation a difficult task. Usually, tandem mass spectrometry is used for this purpose. Here, the ions from the original ionization process are separated and the ion of interest is subjected to a fragmentation step before being mass analyzed.

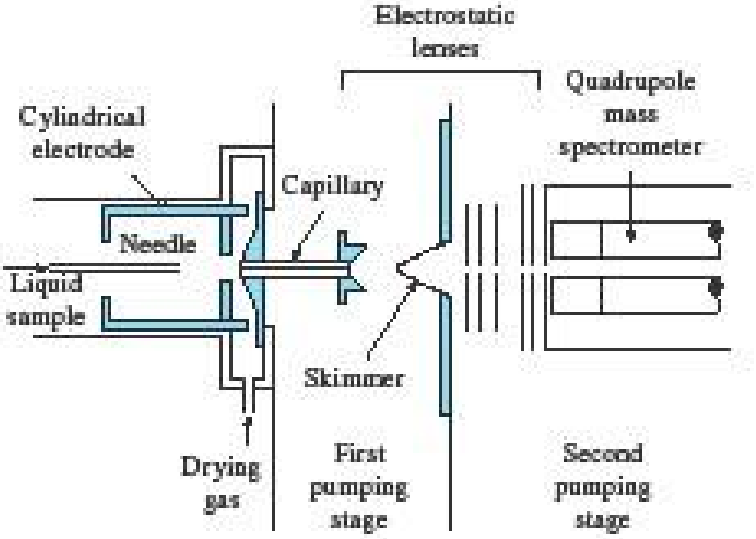


FIGURE 20-9 Apparatus for electrospray ionization. (From J. B. Fenn et al., *Science*, 1989, *246*, 64, DOI: 10.1126/science.2675315. Reprinted with permission.)

Isotopic Abundances

Most elements appear in nature as isotope mixtures. Thus, natural carbon is a mixture of 98.90 % of isotope 12C and 1.10 % of isotope 13C. Table lists the abundances of a few elements that are important in organic chemistry. These isotopes are responsible for the peaks in the mass spectrum appearing as isotopic clusters that are characteristic of the elemental composition. They provide important analytical data. Indeed, even without exact mass measurement, the possibilities for elemental composition determination can often be restricted by using isotopic abundance data. For example, the fragments $C_{10}H_{20}$ and $C_8H_{12}O_2$, both with a nominal mass of 140 u, produce peaks at mass 141 with 11 and 8.8 %, respectively, of the abundance at mass 140 u. This is the result of a different statistical probability of having 13C isotopes. These two elemental compositions can thus be distinguished in a mass analysis.

However, the actual possibilities are limited. Measurement artifacts can modify such percentages. In the case of fragments of heavier molecules, the observed intensity can result from several fragments with different compositions, all present in the isotopic cluster, such as C10H21 at mass 141 in the example above. In principle, this risk does not exist for the molecular peak. In fact, the contribution of a peak with composition (M H)+ associated to a molecular M•+ peak should never be excluded. This artefact can have high abundance in the case of compounds such as amides in electron ionization.

Table Isotopic abundances.

			Mean atomic mass	
Isotope	Relative abundance (%)	Mass (u)	Calculated	Measured
^{1}H	99.985	1.007 825	1.007 976	1.007 94
^{2}H	0.015	2.014 0		
^{12}C	98.90	12.000 000	12.011 036	12.011 1
^{13}C	1.10	13.003 355		
^{14}N	99.63	14.003 074	14.006 762	14.006 74
^{15}N	0.37	15.000 108		
^{16}O	99.76	15.994 915	15.999 324	15.999 43
^{17}O	0.04	16.999 131		
^{18}O	0.20	17.999 160		
^{19}F	100	18.998 403	18.998 403	18.998 4
^{23}Na	100	22.989 767	22.989 767	22.989 76
^{31}P	100	30.973 762	30.973 762	30.973 76
^{32}S	95.02	31.972 070	32.064 385	32.066 6
^{33}S	0.75	32.971 456		
^{34}S	4.21	33.967 866		
^{36}S	0.02	35.967 080		
^{35}Cl	75.77	34.968 852	35.452 737	35.452 79
^{37}Cl	24.23	36.965 903		
^{39}K	93.2581	38.963 707	39.098 299	39.098 31
^{40}K	0.0117	39.963 999		
^{41}K	6.7302	40.961 825		
^{79}Br	50.69	78.918 336	79.903 526	79.904 1
^{81}Br	49.31	80.916 289		

Mean value for the natural mixture of isotopes.

However, some atoms have isotopic compositions that are more obvious. This is the case for chlorine, bromine, selenium and sulfur, for example. The relative abundances of isotopes in a molecule or in a fragment result from their statistical distribution. Let us consider an example in order to explain the calculation of isotopic clusters. What are the relative intensities of the isotopic peaks accompanying themolecular peak of CS_2? Sulfur shows up as a mixture of three main isotopes with nominal masses 32, 33 and 34. These three isotopes occupy two possible positions in the CS_2 molecule. The total number of possible combinations is 3^2, that is 9:

^{32}S ^{32}S Total mass: 64, one combination. ^{32}S ^{33}S or ^{33}S ^{32}S Total
mass: 65, two combinations.^{32}S ^{34}S or ^{34}S ^{32}S Total mass: 66, two combinations.^{33}S ^{33}S
Total mass: 66, one combination. ^{33}S ^{34}S or ^{34}S ^{33}S Total
mass: 67, two combinations.^{34}S ^{34}S Total mass: 68, one combination.

Total: nine combinations.

Consider now the probability of observing each mass. Mass 64 results from the single possible combination of two isotope 32 atoms. This isotope amounts to 95.02 % in nature, so the probability of having two such atoms simultaneously is (0.9503)2, that is 90.31 %. Mass 65 results from two possible combinations of isotopes 32 and 33, which amount to 95.03 and 0.75 %, respectively. Each combination has a probability of occurring that is equal to (0.9503) (0.0075) 0.72 %, which must be multiplied by the number of combinations: 0.72 2 1.42 %.

Mass 66 can occur in either of two ways: either two isotopes 33, or one isotope 32 and one 34. 33S2 has a probability of (0.0075)2   0.005 62 %, in one combination, and 32S34S has a probability of (0.9503) (0.0422) 4.01 %, which must be multiplied by two for the number of possible combinations, that is 8.02 %. In total, the probability of observing mass 66 is equal to 8.02 + 0.00562 = 8.026 %. Mass 67 has a probability equal to (2 × 0.0075) × (0.0422) = 0.063 %, and mass 68 has (0.0422)2 = 0.1781 %.

In summary:

Mass	%	% of the predominant peak
64	90.31	100
65	1.42	1.572 4
66	8.026	8.889
67	0.063	0.069 75
68	0.1781	0.197 2

We now have the possible combinations of two sulfur atoms, and the relative abundances that are calculated are those which would be observed in the case of a fragment with composition S_2. We must now combine each of these with the carbon isotopes. As there is only one carbon atom in CS_2, we have 98.90 % of isotope 12 and 1.10 % of isotope 13. We must now look for all the possible combinations of both of the following isotope series, with their probabilities, while observing that the total mass is the sum of the masses and the probability is the product of the probabilities. Finally, we sum the probabilities of all the ions with equal masses:

S_2		C	
Mass	%	Mass	%
64	90.31	12	98.90
65	1.42	13	1.10
66	8.026		
67	0.063		
68	0.1781		

Mass S_2	Mass C	Total mass	Prob. S_2	Prob. C	Total probability
64	12	76	90.31	98.90	89.317
64	13	77	90.31	1.10	0.993 41
65	12	77	1.42	98.90	1.404
65	13	78	1.42	1.10	0.015 6
66	12	78	8.026	98.90	7.938
66	13	79	8.026	1.10	0.088
67	12	79	0.063	98.90	0.062
67	13	80	0.063	1.10	0.000 69
68	12	80	0.1781	98.90	0.176
68	13	81	0.1781	1.10	0.002

Total probability % 99.996 6

Gathering the identical masses, we obtain the abundances of the CS_2 peaks:

Mass	Total %	% of the predominant peak
76	89.31	100
77	2.3974	2.684
78	7.9536	8.9056
79	0.152	0.17
80	0.177	0.198
81	0.0019	0.002

If the molecule contains another element, we should combine its masses and abundances a new.

Note that this calculation does not take the sulfur isotope of mass 36 into account; it is0.017 % abundant and affects the result for the carbon sulfide of mass 80 u.

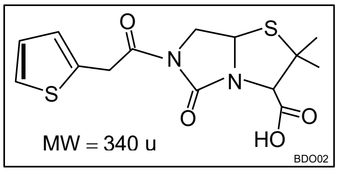
Mathematical methods for the calculation of theoretical relative abundances within the isotopic cluster, for comparison with experiment, usually rely on expansion of the polynomial expression based on an extension of the binomial probability distribution. Indeed, for an element with x isotopes and relative abundances I1, I2, .. ., Ix, and for n atoms of this element in the molecule, the problem consists of calculating, for every element, the terms of the following polynomial expression:

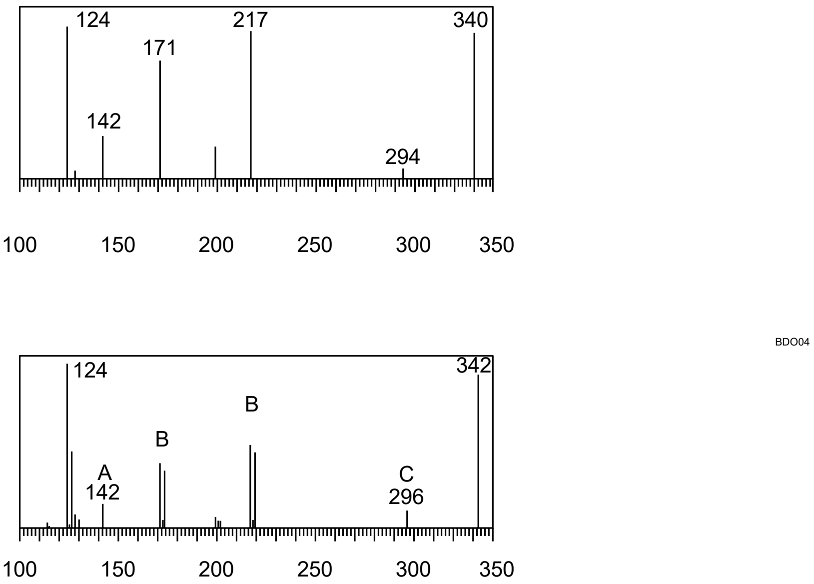
$$(I_1 + I_2 + \cdots + I_x)^n$$

The coefficient of the jth term then corresponds to the number of possible combinations that match a given distribution; the term itself corresponds to the probability of this combination. When considering several different types of atoms, we calculate the products for each term in these polynomials. We then match the right mass to each of these combinations, and we gather the identical masses.

This method uses Fourier transforms to do the multiple convolutions required to determine molecular isotope distributions and calculates ultrahigh-resolution distributions over a limited mass range. Because discrete Fourier transforms can be calculated very efficiently, this new way of looking at the problem has significant practical implications. Specifically, this method for calculating isotope distributions is very fast, accurate and economical in its use of computer memory and thus can be applied to extremely large molecules.

Even more information from isotopic abundances can be obtained by tandem mass spectrometry (MS/MS), as is shown in the following example.





Figure

Product ion spectra obtained from the fragmenta- tion of the molecular ion and of the correspond- ing (M 2) isotopic precursor shown above. (A) Unshifted ion, thus sulfurless. (B) Dedoubled ions, containing one of the two sulfur atoms. (C) Ions shifted two mass units: they contain both sulfur atoms.

The molecule shown in Figure contains two sulfur atoms and its molecular peak at 340 Th is thus accompanied by an isotopic peak at 342 Th. Its relative intensity is 2 × 4.21 = 8.42 %, if the participation of other elements' isotopes is neglected. The spectra of the ions derived from the fragmentation of the molecular ion and of the isotopic ion (M 2) are shown. The (M 2) ion contains one 34S and one 32S sulfur atom. If both sulfur atoms are kept in a fragment, then this fragment also contains one 34S and one 32S sulfur atom. It is shifted by 2 mass units. If it contains only one of the two sulfur atoms, the probability that the atom being retained is 34S is the same as the probability that it is 32S; the peak is therefore dedoubled. Finally, if the fragment does not contain sulfur atoms, it shows up at the same mass in both spectra. Such an approach therefore provides information on the elemental composition.

Mass and Electron Parities, Closed-Shell Ions and Open-Shell Ions

Electron Parity

Common molecules have an even number of electrons. Stable radicals are rare exceptions, such as NO. In classical chemistry, we most often meet active species that are ions with an even number of electrons, or radicals, an uncharged species with an odd number of electrons. In mass spectrometry, we observe ions with an even number of electrons, but we also often meet radical ions, a species uncommon in solution chemistry and having specific characteristics.

Mass Parity

The atomic masses used in common chemical calculations are based on averages resulting from mixtures of isotopes. In mass spectrometry, the calculation is based on the mass of the predominant isotope of each element. As the isotopes are separated in the spectrometer, we always face several peaks with different masses, and with intensity ratios defined as described earlier. Thus, for example, dichloromethane has a classical molecular mass equal to 12.01+2 +1.00×2 35=.45 84.91 Da. The molecular mass in mass spectrometry is (if mass defects are neglected) 12 2 2 35 84 u. Several isotopic peaks are observed in the spectrum, the second most important being observed at m/z 86 with an intensity equal to 64.8 % of that of the m/z 84 peak.

Organic molecules are normally made up of atoms of C, H, N, O, S, P and halogens, and we limit the following discussion to these elements. Molecular masses that are considered here are calculated by using the value of the atomic mass of the predominant isotope of each element, as usual in mass spectrometry.

The nitrogen rule requires that the molecular mass is always even when the number of nitrogen atoms is even or zero. This results from the fact that nitrogen has a different mass parity and valence electrons parity: mass 14 u, five peripheral electrons. Both of these parities are identical in the case of any other atom. It should be noted that this holds only if we consider the mass of the predominant isotope. Thus, the ‘chemical’ mass of bromine is 80 u, an even number, but its predominant isotope is that of mass 79 u, an odd mass. In the same way, isotopically labelled compounds do not always obey this rule.

Another approach to the problem consists of saying that adding one nitrogen atom in a molecular formula entails also adding one hydrogen to the ‘saturated’ formula. However, nitrogen has an even mass, and the number of new atoms with a unit mass is one. Thus, for example, CH3CH3 has a molecular mass of 30 u, while CH3NHCH3 has a mass of 45 u, an odd number.

Relationship Between Mass and Electron Parity

First, consider a molecule that contains no nitrogen and is ionized through electron ionization. The ionization process consists of expelling one electron in order to produce a radical cation:

$$M + e^- \longrightarrow M^{\bullet +} + 2e^-$$

At the beginning the molecule M has an even mass because, hypothetically, it contains no nitrogen, and has an even number of electrons. After ionization, the mass has not changed, but the number of electrons has decreased by one unit, and has become odd. We have obtained a radical cation, which is represented by a dot combined with a plus sign: $M^{\bullet +}$.

If this molecule M is ionized through chemical ionization, we obtain a protonated molecule, $(M + H)^{+}$. The protonated molecule has an odd mass: the mass, which is even, increased by one because of the new proton. The number of the ion electrons is the same as that of the neutral molecule that is even. It is a normal cation, not a radical cation. Thesame deductions apply to negative ions.

An odd number of nitrogen atoms brings about an odd molecular mass in daltons suchas is defined in mass spectrometry: NH_3 17, CH_3NH_2 31, and so on. Thus, in the case of an odd number of nitrogens, the earlier rule must be inverted: for the ion, the mass parity is the same as the electron parity.

From an analytical point of view, we see that an odd molecular mass, based on the predominant isotopes, indicates the presence of an odd number of nitrogen atoms.

When there are no or an even number of nitrogen atoms, any ion with an even mass has an odd number of electrons and is a radical cation or radical anion. Any ion with an odd mass, in turn, has an even number of electrons and is a cation or an anion. The reverse holds true for an odd number of nitrogen atoms. There is no exception within the C, H, N, O, S, P, alkali metal and halogen elements.

Fragmentation Reactions of Positive Ions

The terminology and the symbolism suggested by McLafferty [6, 7] are used here as they have become universal. Moreover, the name McLafferty is associated with a rearrangement that we will discuss later.

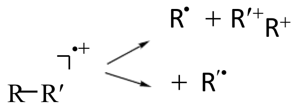
Fragmentation of Odd-Electron Cations or Radical Cations ($OE^{\bullet+}$)

In radical cations, the charge is delocalized over the whole molecule. The most favoured radical and charge sites in the molecular ion are assumed to arise from the loss of the electron of lowest ionization energy in the molecule. Consequently, when we write fragmentation reactions on paper, we represent the charge as localized on the site with the weakest ionization energy. As the following order $n > \pi > \sigma$-electrons is observed for ionization, the heteroatoms with weak ionization energies carry the charge preferentially. The symbol $^{\bullet+}$ at the end of the molecules means an odd-electron ion without specifying the localization of either the radical or the charge site. However, use of either $^{\bullet}$ or $^{+}$ within the molecule implies localization of the radical or the charge.

Positive charge and radical sites are electron-deficient sites. Cleavage reaction initiated by the positive charge site involves attraction of an electron pair because positive charge corresponds to the loss of an electron. The movement of an electron pair induces heterolytic cleavage with migration of the charge site. Cleavage reaction initiated by the radical site arises from its strong tendency for electron pairing. An odd electron is donated to form a new bond whereas the transfer of a single electron induces homolytic cleavage with migration of the site of the unpaired electron. Thus, the charge and the radical sites induce different cleavage reactions. The indication i and α involve all types of reactions initiated respectively at a charge or a radical site. The fragmentation of these radical cations without any rearrangement or without any cleavage of an even number of bonds such as occurs in rings necessarily leads to an even- electron, or closed shell, ion and to a neutral radical.

Direct Dissociation (σ) The expulsion of an electron from a σ bond can bring about the direct dissociation of the latter. We then speak of 'σ fragmentations'. One of the fragments keeps the charge, whilethe other is a radical:

$$R\_R' + e^- \;\_\_\_\_\_\_\; R \;\; R'^{\bullet+} + 2e^-$$



According to Stevenson’s rule, if two charged fragments are in competition to produce a neutral radical by electron attachment, the radical having the highest ionization energy will be produced. The other ion, whose corresponding neutral radical has a lower ionization energy, will hold its charge and will thus be the observed fragment. Indeed, this reaction can be considered as a competition between two cations to carry away the electron:

$$R+ \cdots e- \cdots Rr+$$

This rule is illustrated by the two examples in Figure. However, Stevenson’s rule must only be applied to the competitive formation of fragment ions. Further dissociation or additional formation by other pathways could respectively decrease or increase the abundance of the fragment ions and lead to erroneous interpretations.

Molecular Ion: The molecular ion provides the molecular mass of the analyte and is the first clue used to interpret a mass spectrum. The mass of the molecular ion is based upon the mass of the most abundant isotope for each element in the molecule. This is not the atomic weight from the periodic table. Since many mass spectrometers have unit mass resolution, the atomic mass is rounded to the nearest whole number, this is called the nominal mass. For example the molecular ion for CHBr3 is observed at m/z 250, not at the formula weight of 253.*

In many mass spectra, the molecular ion is easily identified as the ion with the highest mass to charge ratio. However, this assignment should be made with caution because the highest mass to charge ion be an impurity or an isotope of the molecular ion. In addition, many compounds fragment so easily that no molecular ion is observed in the 70 eV EI spectrum. It is important to clarify that the molecular ion is not necessarily the ion with the greatest abundance, the ion with the greatest abundance is the base peak. Table 1 lists several characteristics of molecular ions to help you identify them in a mass spectrum. Low energy EI or CI may be used to verify the molecular ion. As the ionization energy is reduced, the molecular ion often increases in intensity . In chemical ionization the adduct ion (M H+) is observed at *m/z* M +1.

Metastable ion

Sometimes fragmentation takes place during the flight rather than in the ionization chamber. The ions thus produced are called metastable ions. They have lower kinetic energy than the normal ions. The peaks due to these ions have the following characteristics:

1.They do not necessarily occur at the integral m/z value .

2. These are much border than the normal peaks

3. These are of relatively low abundance (of the daugher ions in 70 eV spectrum)10^{-2} or less than the parent or the molecular ions formed in the ionization chamber behave in one of the following ways

4. They decompose rapidly and completely in the ion source and never reach the collector (lifetime less than 10^{-5} sec

5. They survive long enough to reach the collector and be recorded there (lifetime longer than ~ 10^{-5} sec)

We also assumed that fragment ions are produced by decomposition of a proportion of the molecular ions in the ion source.

Depending upon the inherent stability of an ion, and on the amount of excitation energy absorbed on bombardment ion lifetimes will vary in a complex manner. Some molecular ion may have intermediate life times 10^{-5} s) and so leave the ionization chamber intact, but decompose during the flight. Of a larger number of M . produced, all will not possessed the same excitation energy and so some will have longer life time than others.

The ions with shorter lifetimes may decompose in the ionization chamber to stable daughter ions A+ and radicals $B^{\bullet}$, the daughter A+ will be detected at the collector normally. The M.+ ions that leave the ion source intact will be accelerated and then posses a translational energy eV. Some of these ions may survive upto the collector, but those which do not, will decompose to A+ and $B^{\bullet}$after acceleration. In such a case the translational M + energy of ion will be shared between A and B is proportions to their masses to conserve total momentum.The translational energy of the daugher ion (A+) must then be lower than that of the parent ion, an this ion A+ will arive at the collector differently from the ‘normal’ A+ ion produced in the ion source. This is called metastable ion. Thus the meta stable ion has the same mass as the corresponding normal daugher but less translational energy.

Of the metastable ions produced in the ion tube, only a fraction come to reasonable focus at the collector (unless by the use of special techniques), we must consider the successive regions of the ion tube to understand why this should be so.

The first field-free region in a double-focussing instrument, lies between the ion source and the electrostatic analyser. (This region has no counter-part in single focusing instruments). If a metastable ion is produced here, it will be focussed out by the electrostatic analyser because of its abnormal kinetic energy. Such ions, and any metastable ions formed in the analyser, will appear out of focus (randomly) at the collector as background current, and will be undetected.

The second field-free region (between two analyser)

Meta stables produced in this region will be focussed by the magnetic analyser but as a meta stable ion has the same mass with lower kinetic energy (less momentum) than the normal daugher ion, the metastable ion is deflected more easily than the normal daughter ion and will appear on the spectrum among ions of lower mass.

The third field-free region (between magnetic analyser and the collector)

Since no focusing takes place in this region, a parent ion is already immutably on path, and if it decomposes to the metastable A+, then this metastable will continue on the same path as the parent ion. The metastable ion is detected as the same m/z value as the parent ion.

***Fragmentation**:* Although the molecular ion is useful for identification, it does not provide any structural information about an unknown. The structural information is obtained from the fragmentation patterns of the mass spectrum. Identifying an unknown without analyzing the fragmentation patterns is like putting together a jigsaw puzzle without the picture. Fragmentation patterns are often complex, but they fit together like pieces of the puzzle to identify the structure of the molecule.

A) Electron Ionization

$ABCD + e^-$ $ABCD^+$ $+ 2 e^-$

B) Fragmentation

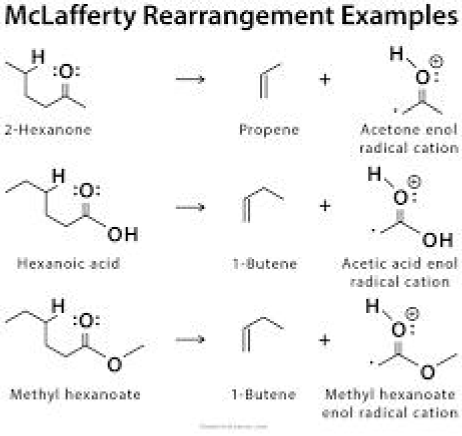
1) Direct Cleavage
$ABCD^+$ $AB^+ + CD$

2) Rearrangement

$ABCD^+$ AD^+ $+ B=C$

Fragmentation mechanisms

After a molecule is ionized, the molecular ion retains the excess ionization energy . If this excess energy is greater than the energy required to break a chemical bond, the molecule can fragment. The fragmentation processes are typically categorized as direct cleavage or rearrangement. Cleavage reactions are simply the breaking of a bond to produce two fragments. These reactions usually produce an even electron ion (AB^+). The even electron ion is detected at an odd *m/z* value (assuming no nitrogen) and a neutral odd electron radical.* Since the radical is a neutral fragment it is not observed in the mass spectrum. Rearrangements are more complex reactions that involve both making and breaking bonds. These reactions are thermodynamically favorable because they require less energy. However they also require a concerted mechanism that is not as kinetically favorable when compared to a simple cleavage reaction. Rearrangement ions easily identified because they are observed as odd electron ions with an even *m/z* value. These fragments often provide important clues about the location and identity of functional groups.



It involves cleavage of a -bond followed by a -hydrogen transfer. The rearrangement leads to the elimination of neutral molecules from amines, aldehydes, ketones, unsaturated compounds and substituent aromatics.

Generally a molecular ion with an even mass value cleaves to give fragment ions with odd mass values and vice-versa. But if the even mass molecular ion yields fragments of even mass and odd mass molecular ions yields fragments of odd mass, it indicates that a rearrangement has taken place.

In case the mass difference between expected and the observed fragment ion is of one unit, rearrangement involving migration of hydrogen atom can be expected. A rearrangement known as McLafferty rearrangement is commonly observed in the compounds having the following structure where x and y can be C, O, S, N and P.

The McLafferty rearrangement, is a classic example of a rearrangement reaction. This rearrangement results in formation of an intact neutral molecule and a radical ion with an even mass to charge ratio. This reaction is significantly different from the cleavage reaction. The McLafferty rearrangement is often observed for carbonyl compounds that contain a linear alkyl chain. If this alkyl chain is long enough, a six-membered ring forms from the carbonyl oxygen to the hydrogen on the fourth carbon. This spacing allows the hydrogen to transfer to the carbonyl oxygen via a six membered ring. The McLafferty rearrangement is energetically favorable because it results in loss of a neutral alkene and formation of a resonance stabilized radical cation. The McLafferty compliment is produced when the charge is transferred to the alkene fragment during the rearrangement. The mass spectrum of 2-hexanone is easily distinguished from *n*-hexanal because the McLafferty rearrangement breaks a different C-C bond. This results in loss of C_3H_6 and produces $C_3H_6O^+$ (*m/z* 58). The mass spectrum of 3-hexanone does not have any major even mass fragment ions so apparently the McLafferty rearrangement is not favorable. If the McLafferty rearrangement did occur, where would the ion be observed in this mass spectrum? What fragmentation would produce the major ions observed in the mass spectrum of 3-hexanone (*m/z* 29, 43, 57, and 71)? Based upon the discussion so far you should be able to identify many of the other fragments in these three mass spectra. Spend some time with a piece of scratch paper and see what you come up with.

Mossbauer Spectroscopy

Mössbauer spectroscopy, named after its discoverer Rudolf L. Mossbauer who received a Nobel prize in 1958 this work, is concerned with transitions between energy levels within the nuclei of atoms. The heavier elements formed by the radioactive decay of an isotope of the same or a different element are initially produced in an excited nuclear state, after a very short delay, the excited nucleus reverts to the ground state and emits energy of a very high frequency, usually in the γ-ray region of the spectrum.

Mössbauer spectrometry provides unique measurements of electronic, magnetic, and structural properties within materials. Mössbauer spectrometry looks at materials from the "inside out," where "inside" refers to the resonant nucleus. For one nucleus to emit a γ-ray and a second nucleus to absorb it with efficiency, both nuclei must be embedded in solids, a phenomenon known as the "Mössbauer effect."

"Mössbauer spectroscopy is the study of -ray absorption (or emission) spectra for transitions between nuclear states". It has applications in various fields, such as solid- state physics, metallurgy, chemistry and biochemistry.

The Mossbauer effect

Already we are familiar with the phenomenon of resonant absorption of electromagnetic radiation from the observation of light-induced electronic transitions. The most common reason for the electronic transitions in transition metal ions in inorganic coordination compounds is because of the absorption of the visible light at exactly the energies of the splitting of *d*-electrons or at the energies corresponding to metal-to-ligand charge transfer transitions. Only when the quantum energy of the light matches the energy gap between the electronic states involved does such resonant absorption occur. Such transitions are the primary reason of color in inorganic complexes.

Similar process is also possible for -radiation, for which nuclear states are involved as emitters and absorbers. In such experiments, the emission of the -rays is mostly triggered by a preceding decay of a radioactive precursor of the resonance nuclei with *Z* protons and *N* neutrons. The nuclear reaction (*i.e.* , or decay, or K-capture) yields the isotopes (*Z*, *N*) in the excited state (e) with energy E_e. The excited nucleus has a limited mean lifetime and will undergo a transition to its ground state (g) of energy E_g, according to the exponential law of decay. Such transition leads with a certain probability to the emission of a -photon with quantum energy $E_0 = E_e - E_g$, if the process occurs without recoil. The emitted -photon may be reabsorbed by the nucleus of the same kind in its ground state, whereby a transition to the excited state of energy E_e takes place. This phenomenon is known as the ***nuclear resonance absorption of -rays*** or the ***Mossbauer effect***.

The pictorial representation of the Mossbauer Effect is shown in figure.

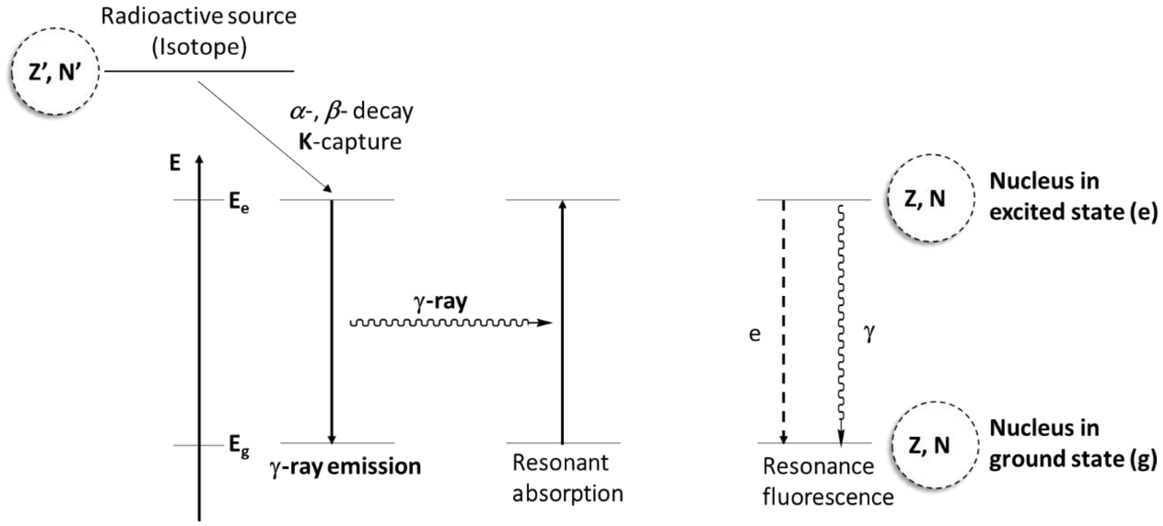


Figure: Nuclear resonance absorption of -rays (Mossbauer effect) for nuclei with *Z* protons and *N* neutrons. The Left part of figure shows the population of the excited state of the emitter by the radioactive decay of a source isotope (*Z*′, *N*′) via- - or -emission, or K- capture (depending of the isotope).The right part of the figure shows the de-excitation of the absorber by re-emission of a -photon or by radiationless emission of a conversion electron (thin arrows labelled " -" and "e", respectively).

Resonant -ray absorption is directly connected with nuclear resonance fluorescence. This is the re-emission of a (second) g-ray from the excited state of the absorber nucleus after resonance absorption. The transition back to the ground state occurs with the same mean lifetime t by the emission of a g-ray in an arbitrary direction, or by energy transfer from the nucleus to the K-shell via internal conversion and the ejection of conversion electrons. Nuclear resonance fluorescence was the basis for the experiments that finally led to R. L.Mossbauer's discovery of nuclear g-resonance in 191Ir and is the basis of Mossbauer experiments with synchrotron radiation which can be used instead of -radiation from classical sources. In order to understand the Mossbauer effect and the importance of recoilless emission and absorption, one has to consider a few factors that are mainly related to the fact that the quantum energy of the g-radiation used for Mossbauer spectroscopy(E0 10–100 keV) is much higher than the typical energies required in optical spectroscopy (1–10 eV). Although, the absolute line width of the energy levels involved in both spectroscopies are quite similar; however, the relative width of the nuclear energy levels is very small due to high mean energies (E/E0 10-13 or less). Consequently, the recoil connected with any emission or absorption of a photon is a particular problem for nuclear transitions in gases and liquids, because the energy loss for the -quanta is so large that emission and absorption lines do not overlap and nuclear g-resonance is virtually impossible.

Hyperfine interaction in Mossbauer spectroscopy

As we have been discussed that the interaction of magnetic moment of an unpaired electron with neighbouring magnetically active nuclei results in the splitting of energy levels which is known as the "Zeeman effect". Similarly, the nuclear states have spin, and associated magnetic dipole moments, and the spins can be oriented with different projections along a magnetic field. In presence of external magnetic field, the energies of nuclear transitions are therefore modified. The energy perturbations caused by this hyperfine magnetic field are sometimes called the “nuclear Zeeman effect,” analogous to the more familiar splitting of energy levels of atomic electrons when an atom is placed under the influence of external magnetic field. Three kinds of hyperfine interactions may be observed in a Mossbauer spectrum.

Electric monopole interaction: It is the interaction between the protons of the nucleus and s-electron penetrating the nuclear filed. The observable Mossbauer parameter is the “isomer shift”. The isomer shift values give information about the oxidation state, spin state, and bonding properties such as covalency and electronegativity.

(a). ***Magnetic dipole interaction***: It is the interaction between the nuclear magnetic dipole moment and a magnetic field at the nucleus. The observable Mossbauer parameter is the “magnetic splitting E_M. This quantity gives information on the magnetic properties of the material under study.

(b). ***Electric Quadrupole interaction***: It is the interaction between the nuclear quadrupole moment and a heterogeneous electric field at the nucleus. The observable Mossbauer parameter is the “quadrupole splitting E_Q”. The information derived from the quadrupole splitting refers to oxidation state, spin state and site symmetry.

Mossbauer energy levels with magnetic hyperfine splitting

The nucleus possessing a magnetic moment when placed under the influence of external magnetic field the energy levels get perturbed. In the presence of external magnetic field, the nuclear spin magnetic moment experiences a dipolar interaction with magnetic field. i.e., nuclear Zeeman effect. The magnetic field at the nucleus does not extend over the whole crystal but arises due to interaction of the nucleus itself with its own electrons. The internal magnetic field at the nucleus is

$$B = Bcontact + Borbital + Bdipole$$

$Bcontact$ arises due to the interaction of the nucleus with s-electrons, $Borbital$ is due to orbital magnetic moment of the atom, and $Bdipole$ is dipolar field due to spin of these electrons. The magnetic field is almost completely linked with the interaction of the nucleus with s-electrons, this is known as the Fermi contact term. The s-electrons are subject to the action of unpaired electron d electrons, which polarize the s-electrons even of the occupied shells. The greatest number of unpaired d-electrons (e.g., five d-electrons) in Fe+3 causes a strong polarization of the s-shell and large magnetic field ~40-60 T. Decrease in the number of unpaired d-electrons (e.g., four unpaired d-electrons in Fe^{+2}) leads to decrease of the magnetic field ~20-40T. When the nuclear magnetic moment $_n$, interacts with the field then the corresponding Hamiltonian (H) and Energy(E) is given by

$$H = -\mu_n B$$

$$H = -g_I \beta_N I B$$

Where $\mu_n = g_I \beta_N I$

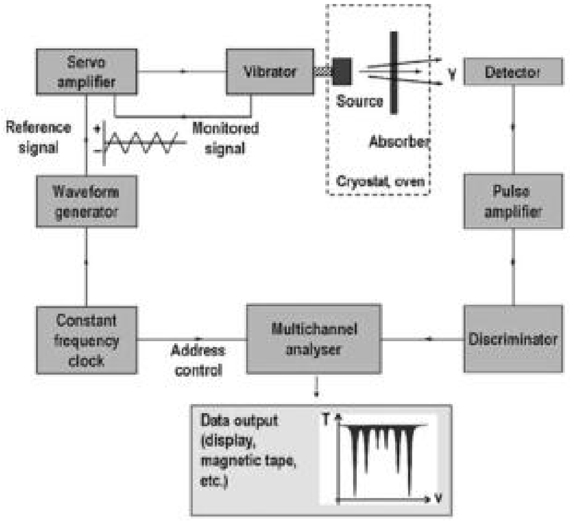
$$E = -g_I \beta_N m_I B$$

Where $m_I = I, I - 1 \ldots\ldots\ldots -I$.

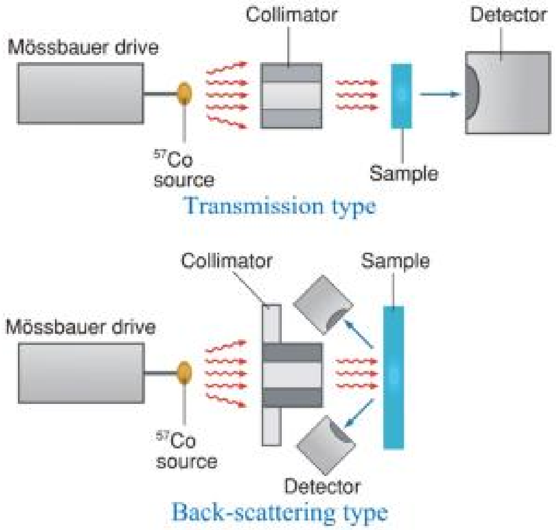
Thus magnetic field splits the nuclear level with spin I into 2I+1 components. For Fe^{57}, = 0.1806 and -0.1033 for ground state and the excited state, respectively. Figure shows the magnetic hyperfine splitting for Fe^{+3}. The transitions between these sublevels gives rise to six lines according to the selection rules Δ = 0,±1. The line positions are related to the splitting of the energy levels, but the line intensity is related to the angle between Mossbauer gamma rays and nuclear spin moment. The splitting of the nuclear levels in the magnetic field is quite similar to the splitting of the levels in nuclear magnetic resonance (NMR).

The Mössbauer Spectrometer

A schematic of the Mössbauer spectrometer is shown in Figure. The source is attached to a linear motor that sweeps through a range of velocities at constant acceleration. The motor is controlled with the S-700A Mössbauer drive circuit. The absorber is positioned between the source and a krypton gas proportional counter that counts the photons that are transmitted through the absorber and measures their energy. The pulses from the detector are amplified and analyzed with the MCS- pci card in the computer. A software gate is placed around the 14.4-keV peak in the photon energy spectrum and the number of 14.4-keV photons is plotted as a function of source velocity. When the Doppler shifted gamma rays have energy that corresponds to a nuclear transition energy, the photons will be absorbed and then re-emitted in all directions. At these velocities we will see a decrease in the number of gamma-ray counts in the detector. The correlation between the source velocity and the number of photons is controlled by the MCS-pci card and the velocity and drive signals between the linear motor and the Mössbauer drive circuit are monitored on an oscilloscope.



(a)



(b)

Mossbauer energy levels with quadrupole splitting

Quadrupole splitting is a salient feature of Mossbauer spectra. However, other techniques, such as perturbed-angular correlation spectroscopy, nuclear quadrupole resonance (NQR), solid-state nuclear magnetic resonance (NMR), and electron-paramagnetic or electron nuclear double resonance (EPR/ENDOR) spectroscopy, can also detect electric quadrupole interaction. Quadrupole splitting arises from the presence of electric field gradient at the Mossbauer nucleus, exactly as the Nuclear Quadrupole Resonance spectroscopy. This is due to the asymmetry of the electron cloud around the nucleus. Any effect that gives a different population in the pz orbital from that in the (p_x, p_y) orbitals, or in the dz^2, or dx^2-y^2 from (d_{xz}, d_{yz}) will produce a splitting of the spectrum which increases as the population imbalance increases. Such imbalance may occur directly through the presence of lone pairs of electrons, i.e., non-bonding electrons, or indirectly through the bonding electrons. The lone pairs of electronsmake the larger contribution to the electric field gradient, i.e., for example in Sn(II) or Sb (III) compounds. For transition metals atoms there is often an imbalance in the d-shell: in octahedral geometry only d^3, d^8, d^{10}, high-spin d^5 and low-spin d^6 configurations make no contribution to Quadrupole splitting. In Mossbauer spectra, the quadrupole splitting becomes apparent in the presence of two conditions:

a. When the Mossbauer nucleus displays the quadrupole moment in the ground state or excited state.

b. The presence of electric field gradient 'q' at the site of nucleus position.

The electric field gradient acting on the nucleus is given by

$$= \ (1 - \quad) + \quad (1 - \quad _{\infty})$$

Where; q = electric field gradient

q_v= Charge contributed by unfilled valance electron shell in transition element

q_L= Charge contributed by non-spherical charge distribution in lattice

(1-R) = Nucleus shielding factor

$(1 - \gamma_\infty)$ = Sternheimer factor

The interaction between the nuclear electric quadrupole moment Q and electric field gradient is expressed by the Hamiltonian

$$H = Q.\nabla E$$

And the energy is given by

$$E_Q = [e2qQ[3m1\ 2 - I(I + 1)]\ /4I(2I - 1)]\ eV$$

In ground state the Fe^{57} nucleus has a spin I = ½ and therefore have no quadrupole moment. In the excited state, Fe^{57} have a nuclear spin I = 3/2and therefore have a quadrupole moment. The isomer level (excited level with I = 3/2) splits into two sublevels with m_I= ±3/2, ±1/2. Reversal of the sign of m_I not changes the nuclear charge distribution. Therefore, electric field gradient will not completely lift the four-fold degeneracy of the I = 3/2 state. The quartet will split into two doublets while I = ½ state will remain degenerate. For I = 3/2, the energy of the sublevels m_I = ±3/2, ±1/2 are

$$E_{Q\,(\pm\,3/2)} = [e2qQ\ /\ 4\ ]\ eV$$

$$E_{\ Q\,(\pm\,1/2)} = [\ 2qQ\ /\ 4]\ eV$$

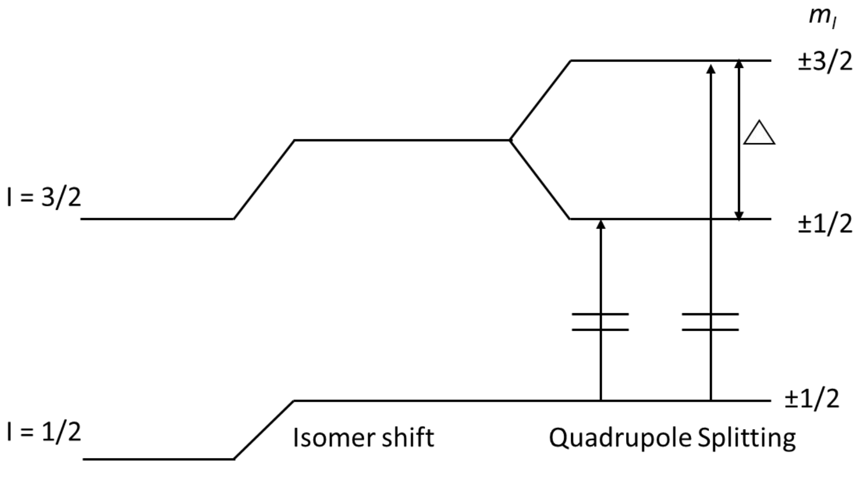
And

$$\Delta = E_{Q\ (\pm\,3/2)} - E_{Q\,(\pm\,1/2\,)}$$

$$\Delta = [e2qQ/2]V$$

The splitting of the level is shown in figure. The transition between these energy levels take place according to selection rule m_I = 0, ±1 and resulting in two lines. The separation between the transitions m_I= ±1/2 ↔ ±1/2 (-transition) and m_I= ±1/2 ↔ ±3/2 (-transition) can be calculated by the energy equations given above. The relative probability of the transitions m_I= ±1/2 ↔ ±1/2 and m_I= ±3/2 ↔ ±3/2 are identical, but shows an angular dependence. In monocrystal, for transitions m_I= ±3/2 ↔ ±1/2 the angular dependence is of the from 3/2(1+cos2┐) and from mI= ±1/2 ↔ ±1/2 is of the from (1+3/2 sin2┐).

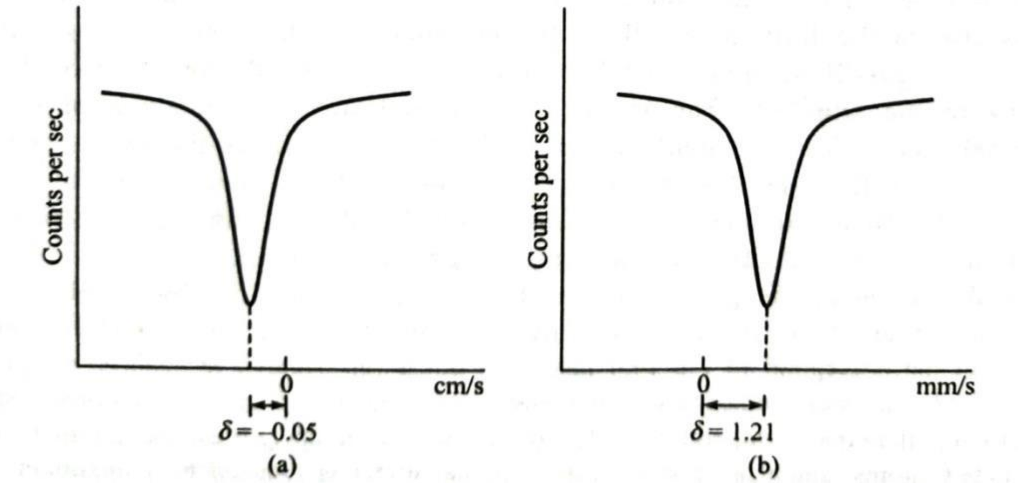
Quadrupole splitting in Fe^{57}



Chemical shift / Isomer shift

In a Mossbauer experiment, if the environments of the emitting and absorbing nucleiare different, the energy of the nuclear transition E_0 may differ by a small amount. This energy difference in known as the ***isomer shift* ( ) or *chemical shift*.**

The effect of isomer shift on the Mossbauer spectrum is the shift the resonance linefrom the zero position. The value of can be +ve or –ve depending on the sample. Isomershift is the term more widely used since this effect depends on the energy difference in theground and excited (isomeric) states.



Isomer shift in (a) $[Fe(CN)_6]^{-4}$ **(b)** $(C_6H_5)_4 S_n)$

Isomer shift arises because the nucleus of an atom is not a point charge as assumed, but hasa finite charge distribution. The electrostatic interaction between the nuclear charge distribution and the electron charge distribution brings about a change in the energy levels of the nucleus. The shift in the energy levels of the nucleus is given by

$$\Delta E = \frac{2\pi}{5} Ze^2 R^2 |\psi(0)|^2$$

Where $|\psi(0)|^2$ represents the total electron density at the site of the nucleus. The chargein energy $\delta(\Delta E)$ between the nuclear ground and first excited state . Hence,

$$\delta(\Delta E) = (\Delta E)_{ex} - (\Delta E)_{ga} = \frac{2\pi}{5} Ze^2 \, |\psi(0)|^2 \, (R_{ex}^{\ 2} - R_{gr}^{\ 2})$$

Writing R for radius of the equivalent sphere of uniform charge distribution and *dR* for

$$(R_{ex} - R_{gr})$$

$$(R_{ex}^{\ 2} - R_{gr}^{\ 2}) = 2R\,dR = 2R^2\,\frac{dR}{R}$$

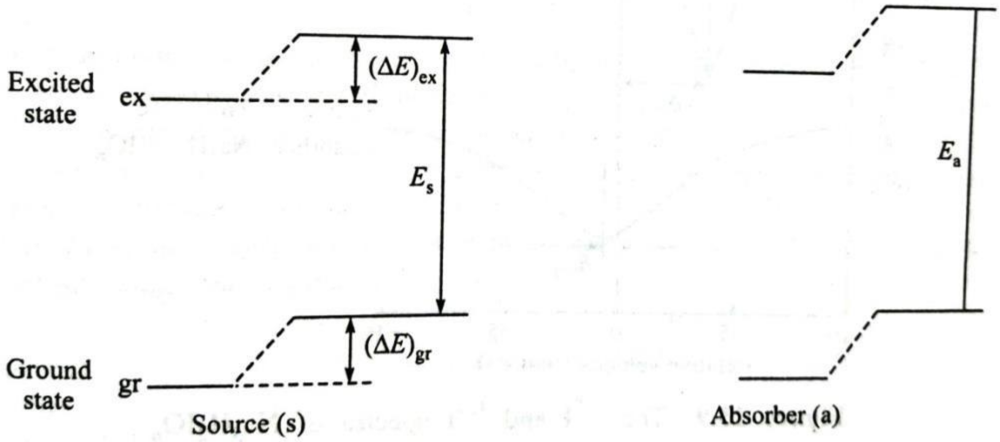


Fig. Representation of energy shifts responsible for isomer shift.

In the Mossbauer experiment, a source – absorber pair is involved and one measures onlya difference in the nuclear electrostatic energy changes of the source and the absorber. Hence, the isomer shift is given by,

$$\begin{aligned}\delta &= \delta\ (\Delta E)_a - \delta\ (\Delta E)_s \\ &= \frac{4\pi}{5} Ze^2\, R^2\ \frac{dR}{R}\left[\,|\psi(0)|_a^{\,2} - |\psi(0)|_s^{\,2}\,\right]\end{aligned}$$

Where subscripts ‘a’ and ‘s’ refer to the absorber and emitter (source) respectively. The chemical term represents the difference in the total electron densities at the absorber and source nuclei and hence is sometimes referred to as chemical isomer shift. Chemical isomer shift is the Mossbauer parameter that gives the maximum amount of chemical information.

Applications of Mossbauer Spectroscopy

1. It is used as a tool for studies in solid state and chemistry is mainly based on the observation of hyperfine structure.

2. The narrow line width of nuclear transitions is possible to investigate small interactions between nucleus and orbital electrons which cannot be studied by other methods.

3. Mossbauer spectroscopy is used in the analysis of electronic structure, molecular structure, magnetic structure and crystal symmetry of compounds.

4. It is also used in surface studies, adsorption and catalysis at solid-liquid and solid- gas interfaces.

5. It is useful in the field of geology for identifying the composition of iron-containing specimens including meteors and moon rocks.

6. Mossbauer spectroscopy has been widely applied to bioinorganic chemistry, especially for the study of iron-containing proteins and enzymes. Often the technique is used to determine the oxidation state of iron.