PRINCIPLES OF MOLECULAR SPECTROSCOPY

Interaction of electromagnetic radiation with molecular systems

- -Scattering (molecules/particles) →O↗
- -Absorption (molecules/particles) →O
- -Emission (molecules/particles/surfaces) O→
- -Refraction →\↗
- -Reflection ↘/
  ↙/

Rayleigh Scattering- Compton Effect - Photoelectric Absorption - Pair Production Photons with energy greater than 1.024 MeV, under the influence of the electromagnetic field of a nucleus, may be converted into electron and positron.

Spectroscopy is the study of the interaction of electromagnetic radiation with matter involving either absorption, emission, or scattering of radiation by the system under study. The mechanism of interaction between electromagnetic radiation and matter relies on the interaction between the oscillating electric and magnetic fields of the radiation with the electric or magnetic dipole moment of an atom or molecule. Thus, a molecular system can experience a force as a consequence of the electrostatic interaction between its electric dipole moment and the oscillating electric field of the electromagnetic radiation. On the other hand, the interaction between the permanent magnetic moment of a nucleus or an electron and the magnetic field of the electromagnetic radiation is the foundation of nuclear magnetic resonance, electron spin resonance, and related spectroscopic techniques. According to this, the interaction between atoms or molecules and the electromagnetic radiation requires the existence of a permanent electric or magnetic dipole or the instantaneous creation of an electric dipole due to internal motions. Atomic and molecular spectra can provide detailed information about the structure and chemical properties of the system. Spectroscopic techniques are one of the main sources of molecular geometries, that is, bond lengths, bond angles, and torsion angles, and can also yield, as will be seen, significant information about molecular symmetry, energy level distributions, electron densities, or electric and magnetic properties

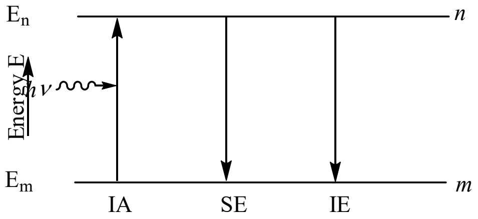
Atomic and molecular spectroscopies are mainly related to the absorption or emission of electromagnetic radiation and the changes taking place in those systems as a consequence of the energy of the radiation

Electromagnetic radiation includes radiation of longer and shorter waveengths. It contains both the electric and magnetic vectors orthogonal to each other, wit sinusoidal oscillating electric and magnetic field of strength E and H respectively of amplitude A.

$$E_y = A\sin(2\pi\nu t - kx)$$
$$H_z = A\sin(2\pi\nu t - kx)$$

The interaction of emr with matter is commonly through the electric component.

Absorption and Emission of Radiation:



m and *n* are stationary states

IA-Induced Absorption $M + h\nu \rightarrow M^*$

SE-Spontaneous Emission $M^* \rightarrow M + h\nu$

IE-Induced Emission $M^* \rightarrow M + 2h\nu$
Stimulated

Electromagnetic Spectrum:

Depending on its frequency or wavelength, an electromagnetic wave is divided into several regions called *electromagnetic spectrum*. The electromagnetic spectrum covers a large range of radiation frequencies, of which the visible region is only a small part. Each region can be usually related to particular technological applications certain spectroscopic method, the latter depending on the energy levels between which the radiation causes a transition or the processes that may occur in atoms or molecules exposed to that radiation. It must be noted, however, that the limits between regions are diffuse and that the type of energy transition associated with each spectroscopic region is only approximate.

Electromagnetic spectrum

Region	Frequency (s^{-1})	Wavenumber (cm^{-1})	Spectroscopy
Radio	$10^6 \rightarrow 3 \times 10^9$	300 m → 10 cm	Nuclear magnetic resonance
Microwave	$3 \times 10^9 \rightarrow 3 \times 10^{12}$	10 cm → 0.1 mm	Electron spin resonance and rotational spectroscopy
Infrared	$3 \times 10^{12} \rightarrow 3 \times 10^{14}$	0.1 mm → 1 µm	Rotational spectroscopy and vibrational spectroscopy
Visible	$4.3 \times 10^{14} \rightarrow 7.5 \times 10^{14}$	700 nm → 400 nm	Visible
Ultraviolet	$7.5 \times 10^{14} \rightarrow 3 \times 10^{16}$	400 nm → 10 nm	UV–visible

X-rays	$3 \times 10^{16} \rightarrow 10^{19}$	100 Å → 0.3 Å	Electronic transition (internal electrons)
γ-rays	$10^{19} \rightarrow 10^{22}$	0.3 Å → 0.003 Å	Nuclear transitions

a) Most commonly used spectroscopic units: Radio frequency radiation: MHz=10^6 Hz (Hz=s^{-1}). Microwave radiation: GHz=10^9 Hz. Infrared radiation: cm^{-1} (wavenumbers). Visible and ultraviolet radiation: nm =10^{-9} m. X-ray and γ-ray radiation: nm =10^{-9} m and Å =10–^{10} m

Einstein Transition Probability (IA, SE and StE)

Albert Einstein proposed that there are three processes occurring in the formation of an atomic spectral line. The three processes are referred to as spontaneous emission, stimulated emission, and absorption. Einstein A and B coefficients, f values (also called oscillator strength) and transition dipole moments are all atomic and molecular parameters related to the strength of transitions.

With each is associated an Einstein coefficient (which is a measure of the probability of that particular process occurring. Einstein considered the case of isotropic radiation of frequency ν, and spectral energy density ρ (ν)

Spontaneous emission is the process by which an electron "spontaneously" (i.e. without any outside influence) decays from a higher energy level to a lower one. The process is described by the Einstein coefficient A_{21} (s^{-1}) which gives the probability per unit time that an electron in state 2 with energy will decay spontaneously to state 1 with energy , emitting a photon with an energy $E_2 - E_1 = h\nu$. Due to the energy-time uncertainty principle, the transition actually produces photons within a narrow range of frequencies called the spectral line width. If n_i is the number density of atoms in state i then the change in the number density of atoms in state 2 per unit time due to spontaneous emission will be:

$$\left(\frac{dn_2}{dt}\right)_{spontaneous} = -A_{21}n_2$$

The same process results in increasing of the population of the state 1:

$$\left(\frac{dn_1}{dt}\right)_{spontaneous} = A_{21}n_2$$

Stimulated emission (also known as induced emission) is the process by which an electron is induced to jump from a higher energy level to a lower one by the presence of electromagnetic radiation at (or near) the frequency of the transition. From the thermodynamic viewpoint, this process must be regarded as negative absorption. The process is described by the Einstein coefficient B_{21}(J^{-1} m^{3} s^{-1}), which gives the probability per unit time per unit spectral energy density of the radiation field that an electron in state 2 with energy E_2 will decay to state 1 with energy E_1, emitting a photon with an energy $E_2 - E_1 = h\nu$. The change in the number density of atoms in state 1 per unit time due to induced emission will be:

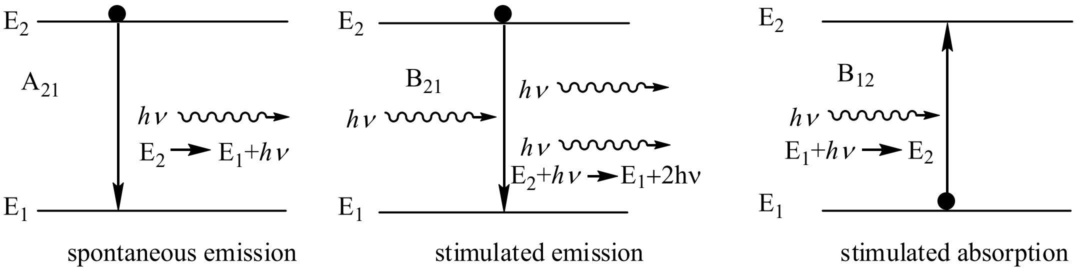
$$\left(\frac{dn_1}{dt}\right)_{neg\ absorb} = B_{21}n_2\rho(\nu)$$

where $\rho(\nu)$ denotes the spectral energy density of the isotropic radiation field at the frequency of the transition

Absorption is the process by which a photon is absorbed by the atom, causing an electron to jump from a lower energy level to a higher one. The process is described by the Einstein coefficient (J^{-1} m^{3} s^{-1}), which gives the probability per unit time per unit spectral energy density of the radiation field that an electron in state 1 with energy E_1will absorb a photon with an energy $E_2 - E_1 = h\nu$ and jump to state 2 with energy E_2. The change in the number density of atoms in state 1 per unit time due to absorption will be:

$$\left(\frac{dn_1}{dt}\right)_{pos\ absorb} = -B_{12}n_1\rho(\nu)$$

The $\boldsymbol{A_{ij}}$'s and $\boldsymbol{B_{ij}}$ and $\boldsymbol{B_{ji}}$'s are called the Einstein ***A*** and ***B*** coefficients.



Detailed balancing: At thermodynamic equilibrium, in which the net change in the number of any excited atoms is zero, being balanced by loss and gain due to all processes, with respect to bound-bound transitions, we will have detailed balancing as well, which states that the net exchange between any two levels will be balanced. This is because the probabilities of transition cannot be affected by the presence or absence of other excited atoms. Detailed balance (valid only at equilibrium) requires that the change in time of the number of atoms in level 1 due to the above three processes be zero:

$$n_1 B_{12} \rho(\nu) = n_2 A_{21} + n_2 B_{21} \rho(\nu)$$

Solving for ρ(ν) we get:

$$\rho(\nu) = \frac{\frac{A_{21}}{B_{21}}}{\left[\frac{B_{12}}{B_{21}}\right]\left[\frac{n_1}{n_2}\right] - 1}$$

Using the Boltzmann factor,

$$\frac{n_1}{n_2} = \frac{g_1}{g_2} e^{h\nu/k_B T}$$

$$\rho(\nu) = \frac{\frac{A_{21}}{B_{21}}}{\left[\frac{B_{12}}{B_{21}}\right]\frac{g_1}{g_2} e^{h\nu/k_B T} - 1} \qquad \rightarrow 1$$

If we regard the matter to be a blackbody and compare the above expression for the energy density with the corresponding energy density expression derived for the blackbody radiation, viz.,

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1} \qquad \rightarrow 2$$

Comparing 1 & 2

$$\frac{8\pi h\nu^3}{c^3} = \frac{\frac{A_{21}}{B_{21}}}{\left[\frac{B_{12}}{B_{21}}\right]\frac{g_1}{g_2}}$$

i.e., $\frac{B_{21}}{B_{12}} = \frac{g_1}{g_2}$; $g_2 B_{21} = g_1 B_{12}$ $\qquad \rightarrow 3$

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}; \; A_{21} = B_{21} \frac{8\pi \nu^2}{c^3} h\nu \qquad \rightarrow 4$$

Relation (3) shows that transition probability of absorption is equal to transition probability of induced emission. Equation (4) shows that A_{21}/B_{21} is proportional to ν^3. This is the ratio of Einstein's A coefficient of spontaneous emission and Einstein's B coefficient of induced emission.

- stimulated emission does occur and is consistent with the form of the blackbody spectrum
- the probability for stimulated absorption is equal to the probability stimulated emission
- the likelihood of spontaneous emission relative to stimulated emission increases rapidly with frequency

- one of the parameters A_{ji} , B_{ji} , B_{ij} we can determine the other ones

Transition dipole moment

In an atom or molecule, an electromagnetic wave (for example, visible light) can induce an oscillating electric or magnetic moment. If the frequency of the induced electric or magnetic moment is the same as the energy difference between one eigenstate Ψ_1 and another eigenstate Ψ_2, the interaction between an atom or molecule and the electromagnetic field is resonant (which means these two have the same frequency). Typically, the amplitude of this (electric or magnetic) moment is called the transition moment. In quantum mechanics, the transition probability of one molecule from one eigenstate Ψ_1 to another eigenstate Ψ_2 is given by $|\vec{\mu}_{21}|^2$.

$\vec{\mu}_{21}$ is called the transition dipole moment, or transition moment, from Ψ_1 to Ψ_2. In mathematical form it can be written as

$$\vec{\mu}_{21} = < 1|\hat{\mu}|2 > \neq 0$$

Transitions are electric dipole transitions – the oscillating electric field component of the radiation interacts with electrical charges, i.e. the positive nuclei and negative electrons that comprise an atom or molecule, and cause the transitions observed in uv-visible absorption and emission spectroscopes.

In general the transition dipole moment is a complex vector quantity that includes the phase factors associated with the two states. Its direction gives the polarization of the transition, which determines how the system will interact with an electromagnetic wave of a given polarization, while the square of the magnitude gives the strength of the interaction due to the distribution of charge within the system. The SI unit of the transition dipole moment is the Coulomb-meter (Cm); a more conveniently sized unit is the Debye (D).

- In order to obtain the strength of interaction that causes a transition between two states, the transition dipole moment is used rather than the dipole moment.
- the transition dipole moment is a quantum mechanical quantity

- It couples the total molecular wavefunction of the initial Ψ_1 and final Ψ_2 states of the molecule via the molecular dipole moment μ.

$$\mu_{21} = < 1|\hat{\mu}|2 > \neq 0$$

- the transition dipole moment must be non-zero for a transition to occur (or for a peak to be present in an experimental spectrum)

- the transition dipole moment can be regarded as a measure of the size of the electromagnetic jolt given to a system

- If $\mu_{21} = 0$ then the interaction energy is zero and no transition occurs – the transition is said to be electric dipole forbidden. Conversely, if μ_{21} is large, then the transition probability and absorption coefficient are large.

- The intensity of the transition $\propto |<2|1>|^2$

Oscillator Strength:

In spectroscopy, **oscillator strength** is a dimensionless quantity that expresses the probability of absorption or emission of electromagnetic radiation in transitions between energy levels of an atom or molecule. An atom or a molecule can absorb light and undergo a transition from one quantum state to another.

The probability of a transition occurring is commonly described by the transition strength. To a first approximation, transition strengths are governed by selection rules that determine whether a transition is allowed or disallowed. In the classical theory of light absorption, matter consists of an array of charges that can be set into motion by the oscillating electromagnetic field of the light. Here, the electric dipole oscillators set in motion by the light field have specific natural characteristics, that is, frequencies, ni, that depend on the material. When the frequency of the radiation is near the oscillator frequency, absorption occurs, and the intensity of the radiation decreases on passing through the substance. The intensity of the interaction is known as the oscillator strength, f_{12}, and it can be thought of as characterizing the number of electrons per molecule that oscillate with the characteristic frequency, v_i. Therefore, practical measurements of the transition strength are usually described in terms of f_{12}. The oscillator strength of a transition is a dimensionless number that is useful for comparing different transitions. For example, a transition that is fully allowed quantum mechanically is said to have an oscillator strength of 1.0. Experimentally, the oscillator strength, f, is related to the intensity of absorption, that is, to the area under an absorption band plotted versus the frequency:

The oscillator strength f_{12} of a transition from a lower state |1> to an upper state |2> may be defined by

$$f_{12} = \frac{2}{3}\frac{m_e}{\hbar^2}\,(E_2 - E_1)\sum_{\alpha=x,y,z} |< 1m_1|R_\alpha|2m_2 >|^2$$

The magnitude of the oscillator strength (*f*) for an electronic transition is proportional to the square of the transition dipole moment produced by the action of electromagnetic radiation on an electric dipole.

$$f_{12} \propto \mu_{ge}^{2} = (8\pi mev / 3he^{2})\,|er|^{2}$$

The concept of oscillator strength comes from the classical viewpoint that when an electron is bound to a nuclear framework and possesses perfect oscillating properties that the excitation probability of the electron would have an oscillator strength of unity.

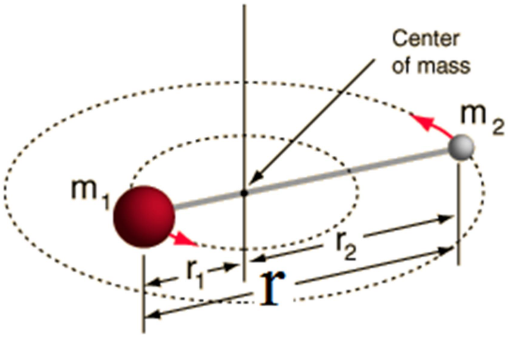
If we consider the molecule as a classical oscillating dipole, the oscillator strength (f) defined by the integral over the absorption band

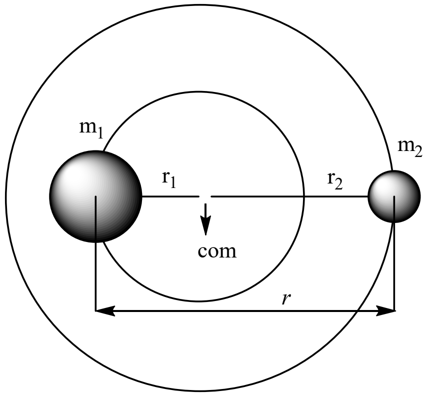
$$f = 4.3 \times 10^{-9} \int (\varepsilon)\, d\nu$$

Here ε is the extinction coefficient and ν is in wave numbers.

Rotational Spectra of Diatomic Molecules:

The rotation of a diatomic molecule can be described by the **rigid rotor** model. A diatomic molecule consists of two masses bound together. The distance between the masses, or the bond length, (*l*) can be considered fixed because the level of vibration in the bond is small compared to the bond length. As the molecule rotates it does so around its COM (as the intersection of R_1 and R_2) with a frequency of rotation of ν_{rot} given in radians per second.





Moment of Inertia(I) and Reduced Mass (μ)

The system can be simplified using the concept of reduced mass which allows it to be treated as one rotating body.

$m_1r_1 = m_2r_2$; $r = r_1 + r_2$; $r_1 = \frac{m_2 r}{m_1+m_2}$; $r_2 = \frac{m_1 r}{m_1+m_2}$

$$I = m_1r_1^2 + m_2r_2^2 = m_1r_1r_1 + m_2r_2r_2 = m_2r_2r_1 + m_1r_1r_2 = r_1r_2(m_2 + m_1)$$

$$I = r_1r_2(m_2 + m_1) = \frac{m_2 r}{m_1+m_2}\frac{m_1 r}{m_1+m_2}(m_2 + m_1) = \frac{m_1m_2}{m_1+m_2}r^2 = \mu r^2$$

$$I = \mu r^2$$

Reduced mass, $\mu = \frac{1}{N_A}\left(\frac{m_1m_2}{m_1+m_2}\right)$; $Moment\ of\ Inertia\ \ I = m_1r_1^2 + m_2r_2^2 = \ \mu r^2$; $r - bondlength$

By solving the Schrodinger's time independent wave equation the energy of the rigid rotator is found to be,

$$E_{rot} = \frac{h^2}{8\pi^2 I}J(J + 1)$$

J – Rotational Quantum No. *J* = 0, 1, 2, 3, ... The energy is quantized.

Rotational Constant:

If $B = \frac{\boldsymbol{h^2}}{\boldsymbol{8\pi^2 I}}$; Rotational constant in Hz

$B = \frac{\boldsymbol{h^2}}{\boldsymbol{8\pi^2 I}}x\ 10^{-6}$; Rotational constant in MHz

$\tilde{B} = \frac{\boldsymbol{h}}{\boldsymbol{8\pi^2 cI}}\ x\ 10^{-2}$ **;** Rotational constant in cm^{-1}

$$E_{rot} = \ B\,J(J + 1) or\ \varepsilon_J = \tilde{B}\,J\,(J + 1)\ \mathrm{cm}^{-1}$$

Selection rules for pure rotational spectrum

- Gross selection rule (diatomic, polyatomic linear/non-linear molecules with permanent μ)
  a. Molecule must have a non-zero *permanent dipole moment* to absorb energy in the microwave frequency range in which rotational transitions occur
  b. Homo-nuclear diatoms don't undergo transitions described here. (Raman spectroscopy used for such molecules)

- Specific selection rule(permit transitions between consecutive rotational levels

  $$\Delta J = \pm 1;\ \Delta M_J = 0,\ \pm 1;\ \ \Delta K = 0$$

- Origin of selection rules: The transition probability from state *n* to state *m* is only nonzero if the **transition dipole moment** μ_x^{nm} satisfies the following condition

  $$\boldsymbol{\mu_x^{nm}} = <\psi_m|\ \hat{\mu}\ |\ \psi_n> \neq 0$$

Energy of Rotational Transitions

When a molecule is irradiated with photons of light it may absorb the radiation and undergo an energy transition. The energy of the transition must be equivalent to the energy of the photon of light absorbed given by:

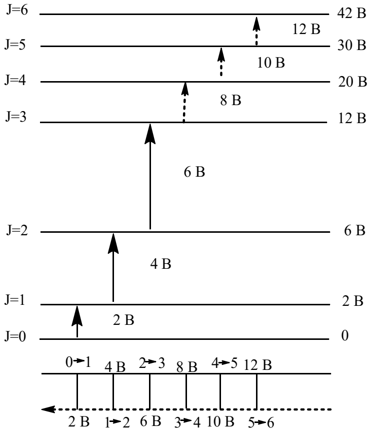
$$E=hv$$

For a diatomic molecule the energy difference between rotational levels (J to J+1) is given by:

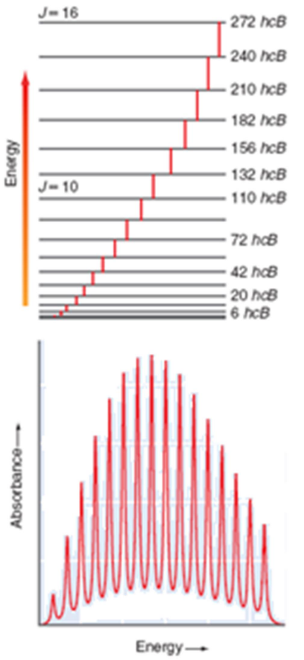
$$E_{J+1}-E_J = B(J+1)(J+2)-BJ(J=1) = 2B(J+1)$$

with J=0, 1, 2,...

Because the difference of energy between rotational levels is in the microwave region (1-10 cm^{-1}) rotational spectroscopy is commonly called microwave spectroscopy. In spectroscopy it is customary to represent energy in wave numbers (cm^{-1}), in this notation B is written as $\tilde{\boldsymbol{B}}$ To convert from units of energy to wave numbers simply divide by h and c, where c is the speed of light in cm/s (c=2.998e10 cm/s). In wave numbers $\tilde{B} = \frac{h}{8\pi^2 cI}$



The allowed rotational energy levels of a rigid diatomic molecule



<u>Geometrical Parameter</u>

From rotational spectrum of hetro-nuclear diatomic molecules the rotational contant and hence the bond length can be calculated, knowing the atomic masses.

Problem: The rotational spacing of $H^{35}Cl$ is found to be 21.18 cm^{-1}. Calculate the bond length of HCl molecule.

$$2\,\tilde{B} = 21.18\ cm^{-1}$$

$$\tilde{B} = 10.59\ cm^{-1}$$

$$\tilde{B} = \frac{h}{8\pi^2 cI};\ I = \frac{h}{8\pi^2 c\tilde{B}} = \frac{h}{800\pi^2 c10.59}$$

$$I = \frac{h}{8\pi^2 c\tilde{B}} = \frac{6.626\ x\ 10^{-34}}{800x9.8776x3x10^8x10.59} = 2.6393\ x\ 10^{-47} kg\ m^2$$

$$\mu = \frac{1x35}{36}x1.661x10^{-24} = 1.6149\ x10^{-24}$$

$$I\ =\ \mu r^2;\ r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{2.6393\ x\ 10^{-47}}{1.6149\ x10^{-27}}} = \sqrt{1.6343\ x10^{-2}}\ = 1.278x10^{-10}m$$

$H^{35}Cl$ bond length r_o = $\mathbf{1.278x10^{-10}m}$ or **1.278 Å**

In HI, the rotational spectrum is composed of equidistant lines separated by 384 GHz for small quantum numbers. Calculate the inter-atomic distance.

Effect of Isotopic substitution on rotational spectra:

For isotopic molecules, i.e. molecules that differ only by the mass of one or both of the nuclei but not by their atomic number (for example 1H 35Cl and 1H 37Cl), the rotational constants are obviously different.

Since the reduced mass is inversely proportional to the rotational constant B, molecules containing heavy isotopes have rotational lines corresponding to lower quantum energies and smaller line spacing

$$\tilde{B} = \frac{h}{8\pi^2 cI} = \frac{h}{8\pi^2 c\mu r^2} \dashrightarrow 1$$

$$\tilde{B}_i = \frac{h}{8\pi^2 cI_i} = \frac{h}{8\pi^2 c\mu_i r^2} \dashrightarrow 2$$

$$2/1, \quad \frac{\tilde{B}_i}{\tilde{B}} = \frac{I}{I_i} = \frac{\mu}{\mu_i} = \rho^2$$

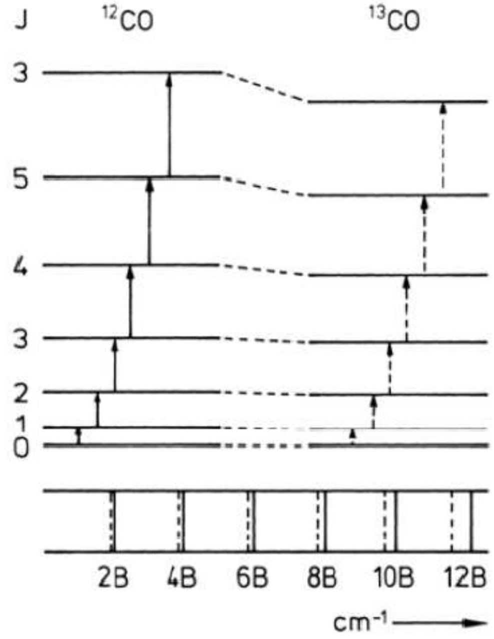
The internuclear distances in diatomic (and polyatomic) molecules are entirely determined by the electronic structure. They are therefore exactly equal in isotopic molecules as long as no vibration occurs. The rotational energies of the two isotopic molecules are thus connected by

$$\varepsilon_i = \tilde{B}_i J(J+1) = \rho^2 \tilde{B} j(j+1) = \rho^2 \varepsilon$$

Rotational levels of the heavier molecule have smaller energies. Furthermore, the separation of neighbouring lines in the rotational spectrum (which is $2\tilde{B}$ in first approximation) differs for isotopic molecules.

For example, for the ^{12}CO molecule, $2\tilde{B}$ is found to be 3.842 cm^{-1}, and for the ^{13}CO molecule containing the heavier isotope of carbon, 2B is found to be 3.673 cm^{-1}.

Figure shows the resulting differences in the rotational spectra of CO containing the isotopes ^{12}C and ^{13}C.



This helps to determine the isotopic mass as well as isotopic abundance by comparing the absorption intensities.

. Foe CO,

$$\tilde{B} = 1.921\ cm^{-1}$$

$$\tilde{B}_i = 1.837\ cm^{-1}$$

$$\boldsymbol{\frac{\tilde{B}}{\tilde{B}_i} = \frac{1.921}{1.837} = \frac{I_i}{I} = \frac{\mu_i}{\mu} = 1.046 = \frac{16m_i}{16 + m_i} x \frac{12 + 16}{12x16}}$$

$$\boldsymbol{1.046 = \frac{16m_i}{16 + m_i} x \frac{12 + 16}{12x16}}$$

$$\boldsymbol{m_i = 13.0005}$$

Molecules serve as a much more ideal tool to distinguish different isotopes than atoms. This is because the presence of more or less neutrons in the nucleus of a specific chemical element does not strongly modifying the electric field and thus has only a small influence on the electron configuration. The same is true for the electron configuration of molecules of course. However, the energy of nuclear motion in molecules due to vibration and rotation is influenced already to first order if the number of neutrons and thus the mass of the nucleus is changed. Thus, isotopic molecules have different frequencies of vibrations and rotations.

Intensity of Rotational Spectral lines:

a. Intensity of the lines is proportional to the square of the permanent electric dipole moment; so strongly polar molecules give rise to much more intense rotational lines than less polar molecules
Intensity of Transition $I \propto |\mu|^2$

b. The intensity of the lines depends on initial state/the Boltzman population density and degeneracy

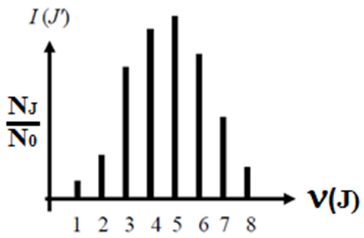
c. The ratio for value of *J* relative to the number in the ground state (*J*=0) can be calculated using the Boltzmann distribution:

$$\frac{n_J}{n_0} = \frac{g_J}{g_0} e^{-(\varepsilon_J - \varepsilon_0)/kT} = (2J+1)e^{-h^2 J(J+1)/2kT}$$

$$N_J = N_o(2J+1)e^{-B\ (J+1)/KT}$$

The rotational state with maximum intensity (as a function of J) will be determined by setting $\frac{dN_J}{dJ} = 0$ and solving for J.

Then the line with the maximum intensity $J_{max} = \sqrt{\frac{kT}{2B}} - \frac{1}{2}$ So transitions from very high / low J will have low intensities
The maximum is temperature dependent



Diatomic Non-Rigid Rotor,

Experimentally, it is found that the separation between adjacent lines decreases steadily with increasing J. The reason for the decrease is obviously due to the decrease in the $\widetilde{\boldsymbol{B}}$ value.

As molecules are excited to higher rotational energies they spin at a faster rate. The faster rate of spin increases the centrifugal force pushing outward on the molecules resulting in a longer average bond length. As consequence of centrifugal distortion, the interatomic distances can grow with increasing rotational frequency, i.e. the constant of rotation $\widetilde{\boldsymbol{B}}$ gets smaller as J gets larger. Looking back, $\widetilde{\boldsymbol{B}}$ and I are inversely related ($\tilde{B} = \frac{h}{8\pi^2 cI}$). Therefore the addition of centrifugal distortion at higher rotational levels decreases the spacing between rotational levels. The correction for the centrifugal distortion may be found through perturbation theory, using the complete Hamiltonian of non-rigid rotator. After some algebra the following equation would be obtained.

$$\varepsilon_J = \tilde{B}\,J\,(J+1) - \tilde{D}\,J^2(J+1)^2 \quad \rightarrow \text{A}$$

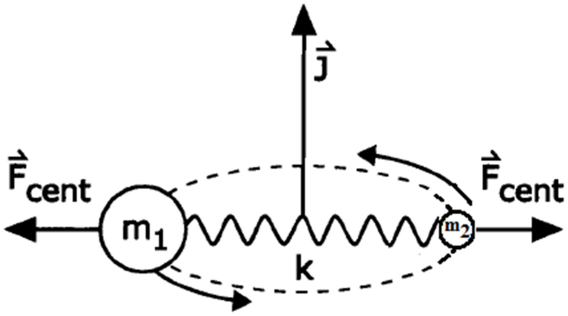
$\tilde{D}$ - Centrifugal distortion constant; +ve qty.

$$\tilde{D} = \frac{h^3}{32\pi^4 I^2 r^2 kc} = \frac{4\tilde{B}^3}{\nu_s^2}$$

The above equation A holds for simple harmonic force field only.If the force field is anharmonic the expression becomes:

$$\varepsilon_J = \tilde{B}\,J\,(J+1) - \tilde{D}\,J^2(J+1)^2 + \tilde{H}J^3(J+1)^3 + \tilde{K}J^4(J+1)^4 \quad \rightarrow \text{B}$$

$\tilde{H}, \tilde{K}$, etc., are small constants, varying with the geometry of the molecule. And are negligible comparing with$\tilde{D}$.



Because $\tilde{D} \propto \frac{1}{I^2}$. A large moment of inertia gives a small distortion
Because $\tilde{D} \propto \frac{1}{\nu_s^2}$. A large vibrational force constant gives a small distortion
As the selection rule is still *ΔJ* = ± *1* , the analytical expression for the transition is,

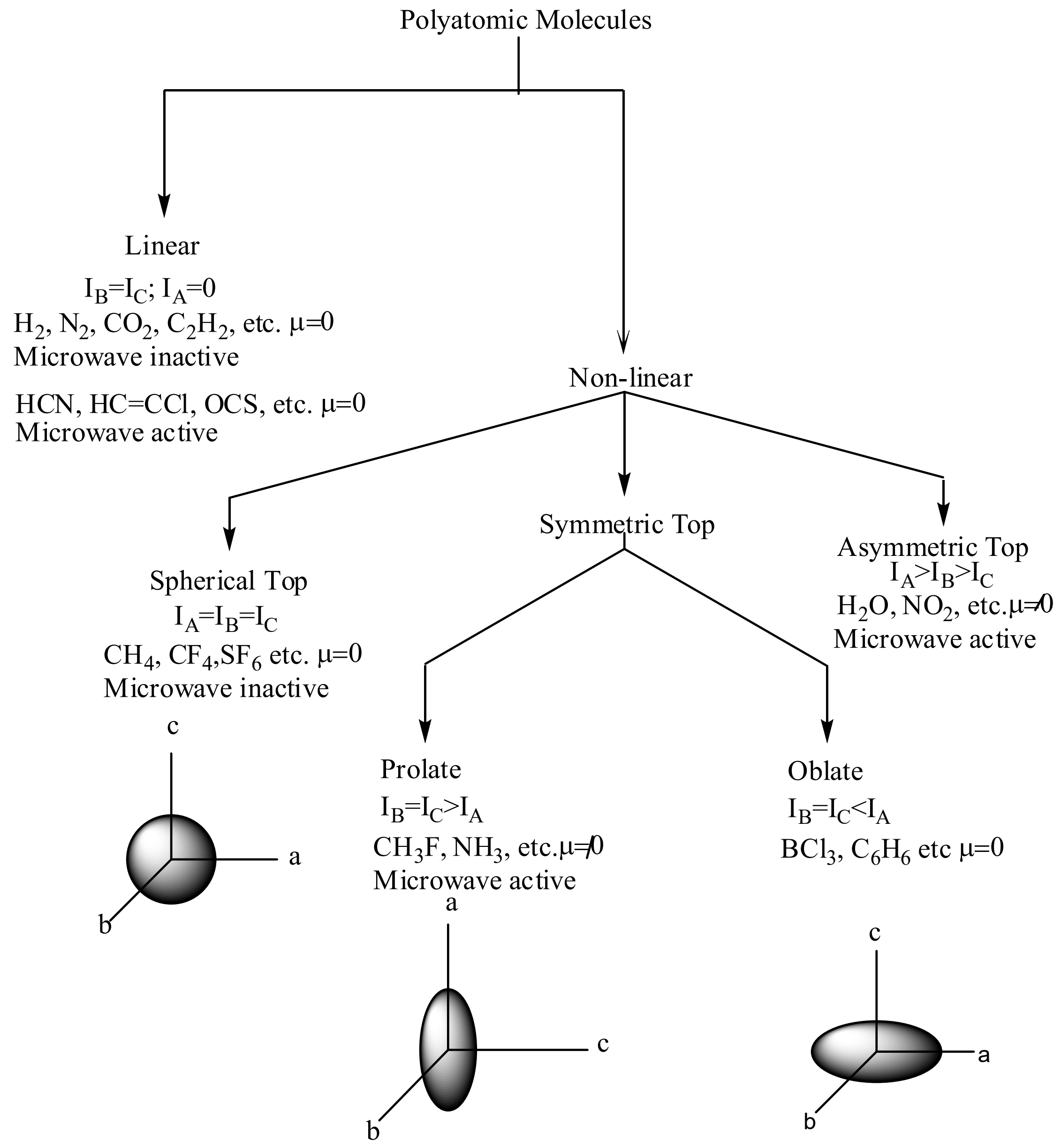
$$\varepsilon_{J'} - \varepsilon_J = \tilde{B}(J+1)\,(J+2) - \tilde{D}\,(J+1)^2(J+2)^2 - \tilde{B}\,J\,(J+1) + \tilde{D}\,J^2(J+1)^2$$

$$\Delta\varepsilon = \bar{\nu} = 2\tilde{B}(J+1) - \tilde{D}(J+1)^3\ cm^{-1}$$

Thus the spectrum of elastic (non-rigid rotator) is similar to that of the rigid molecule except that each line is displaced slightly to low frequency, the displacement increasing with $(J+1)^3$.

Measuring the consecutive lines$\tilde{B}$, $\tilde{D}$ $and\ J\ can\ be\ evaluated.$ From $\tilde{D}$ approximate $\bar{\nu}\ (vibration) can\ be\ obtained.$

Microwave Spectra of Polyatomic Molecules:



Linear Molecules:

Since $I_C=I_B;\ I_A=0,$ the energy levels are given by the formula identical with that of for diatomic molecules.

$$\varepsilon_J = \tilde{B}\,J\,(J+1) - \tilde{D}\,J^2(J+1)^2 + \tilde{H}J^3(J+1)^3 + \tilde{K}J^4(J+1)^4$$

The rotational spectrum will be similar to that of diatomic molecules, with the following observations:

a. As the moment of inertia corresponding to end-over-end rotation is greater than that for diatomics the $\tilde{B}$ values will be smaller with rotational lines more closely placed.
b. Must have permanent dipole moment.
c. For linear molecules with N atoms there would be N-1 bond lengths and they can be determined by isotopic substitution.

Spherical Top molecules:

For these molecules $I_C=I_B=I_A$. As these molecules do not have permanent dipole moment they are microwave inactive.

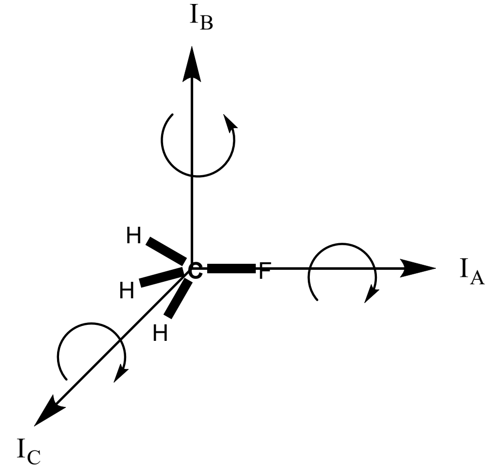
Eg. CH_4, SF_6

Symmetric Top Molecules:

For symmetric top molecules, $I_B=I_C\neq I_A$; $I_A\neq 0$

The two rotations, viz., rotation about the main symmetry axis and that perpendicular to this axis would absorb/emit energy. So two quantum numbers are needed.

Eg. CH_3F



J – Total angular momentum – 0, 1, 2, 3, ...

K – Angular momentum about main symmetry axis A: K ≤ J; J, J-1, J-2,...1, 0, -1, -2,...-J + & - allowed without change in energy → (2J+1) possibilities of K for each J. So for K>0, the rotational energy levels are doubly degenerate.

Then for rigid symmetric top molecules the allowed energy levels are given by,

$$\boxed{\varepsilon_{J,K} = \tilde{B}\, J\,(J+1) + (A-B)K^2\ cm^{-1}}$$

$$B = \frac{h}{8\pi^2 c I_B}\ ; A = \frac{h}{8\pi^2 c I_A}$$

$$(A-B) = \frac{h}{8\pi^2 c}\left(\frac{1}{I_a} - \frac{1}{I_B}\right) > 0 \text{ Prolate}$$

$$(A-B) = \frac{h}{8\pi^2 c}\left(\frac{1}{I_a} - \frac{1}{I_B}\right) < 0 \text{ Oblate}$$

Selection Rule: $\Delta J = \pm 1$; $\Delta M_J = \pm 1$; $\Delta K = 0$

The quantum number K may take values K = 0, 1,2, ... , J. The K cannot be greater than J. All levels with K > 0 are doubly degenerate which can be thought of, classically, as being due to the clockwise or anticlockwise rotation about the a axis resulting in the same angular momentum. For K = 0 there is no angular momentum about the ‘a’ axis and, therefore, no K-degeneracy.

The rotational transition, (J, K)→(J+1, K) is given by,

$$\varepsilon_{J+1,K} - \varepsilon_{J,K} = \Delta\varepsilon = \tilde{B}\,(J+1)\,(J+2) + (A-B)K^2 - [\tilde{B}\,J(J+1)\; + (A-B)K^2]$$

$$\Delta\varepsilon = 2\tilde{B}\,(J+1)cm^{-1}$$

For non-rigid rotator i.e., including centrifugal distortion the energy level expression is,

$$\boxed{\varepsilon_{J,K} = \tilde{B}\,J\,(J+1) + (A-B)K^2 - D_J J^2 (J+1)^2 - D_{J,K} J(J+1)K^2 - D_K K^4\ cm^{-1}}$$

D_J, D_K *and* $D_{J,K}$ are centrifugal distortion constants.

The transition frequencies are given by,

$$\varepsilon_{J+1,K} - \varepsilon_{J,K} = \Delta\varepsilon = \; 2\tilde{B}\,(J+1)\; - 4D_J(J+1)^3 - 2D_{J,K}J(J+1)K^2$$

Infrared Spectra – Diatomic Molecules:

Interaction of molecules in the IR region results inIR/vibrational spectrum. A basic IR spectrum is essentially a graph of infrared light absorbance (or transmittance) on the vertical axis vs. frequency or wavelength on the horizontal axis.

The infrared portion of the emr is divided into three regions:

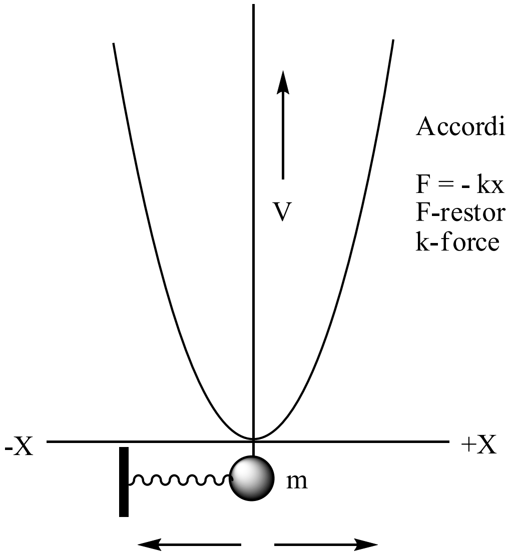
i) near-IR, approximately 14000–4000 cm^{-1} (0.8–2.5 μm wavelength) can excite overtone or harmonic vibrations. The

ii) mid-infrared, approximately 4000–400 cm^{-1} (2.5–25 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure.

iii) far-infrared, approximately 400–10 cm^{-1} (25–1000 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy.

Simple Harmonic Motion:

The movement of mass ‘m’ about the equilibrium position on either side along theX-axis under the influence of restoring force, which is directly proportional to the displacement from equilibrium rest position is called simple harmonic oscillator in one dimension. It is a periodic motion. This to and fro motion is the model system for vibrating diatomic molecules. So it can be used for the spectral analysis of vibrating diatomic as well as polyatomic systems.



According to Hook's law

F = - kx --> 1
F-restoring force
k-force constant

According to Newton’s law,

$$F = ma = m\frac{d^2x}{dt^2} \longrightarrow 2$$

From 1 & 2, $$kx + m\frac{d^2x}{dt^2} = 0 \rightarrow 3$$

Solution for 3 is,

$$x(t) = A\,Sin\,(2\pi\nu t + C) \rightarrow 4$$

From 3 & 4, $$\boxed{k = 4\pi^2\nu^2 m \quad or \quad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}; \; for\ two\ body\ system$$

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \quad cm^{-1}$$

Like all other energies vibrational energy is also quantised and eigen value equation is obtained by solving the Schrodinger′swave equation:

$$E_{vib} = \left(\mathrm{v} + \frac{1}{2}\right) h\nu \; joules$$

$$\varepsilon_{vib} = \left(\mathrm{v} + \frac{1}{2}\right) \bar{\nu} \; cm^{-1}; \quad \bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \quad cm^{-1}$$

v – vibrational quantum number; v = 0, 1, 2, 3, ...

for v = 0,

$$E_{vib} = \frac{1}{2} h\nu \; joules$$

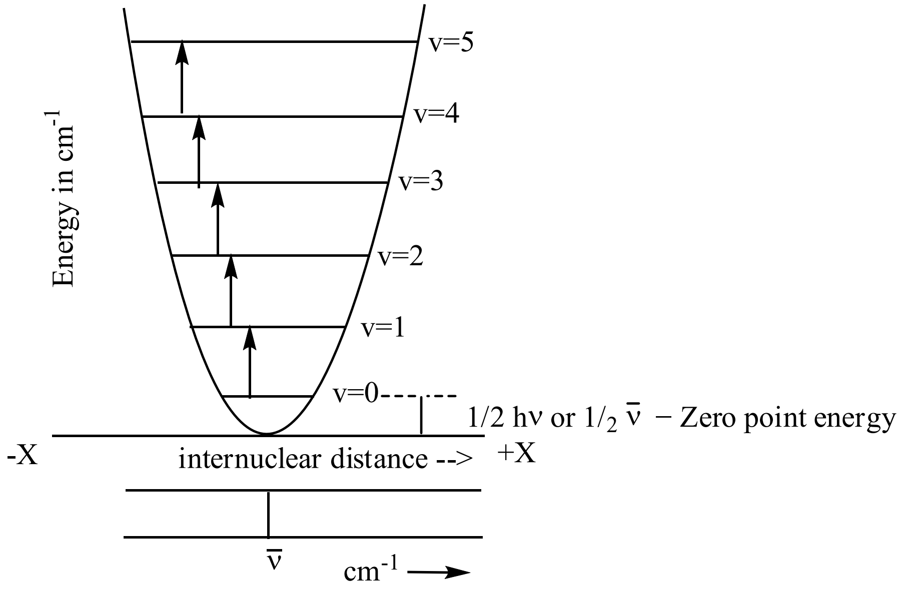
$$\varepsilon_{vib} = \frac{1}{2} \bar{\nu} \; cm^{-1}$$

i.e., the diatomic or any molecule will not have zero energy even at zero Kelvin and the energy possessed at v = 0, i.e., $\frac{1}{2}h\nu$ or $\frac{1}{2}\bar{\nu}$ is called zero point energy and above that the energy levels are equally spaced as shown in the figure giving a single absorption line for vibrational transition. The selection rule is Δv = ± 1.

The selection rule for diatomic molecule (harmonic oscillator):

i. the molecule must possess permanent dipole moment; i.e., only heteronuclear diatomic molecules would give vibrational spectrum

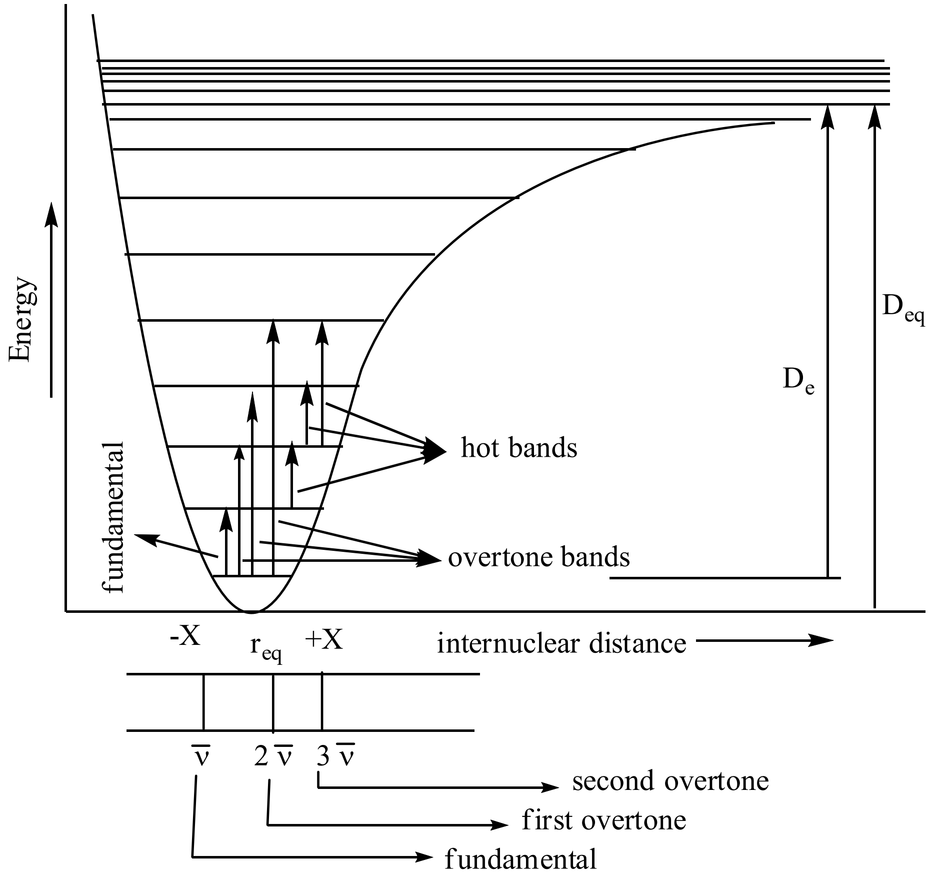
ii. the change in vibrational quantum number is ±1; i.e., Δv = ± 1



<u>Anharmonic oscillators:</u>

Real molecules elastic and anharmonic in its vibration. They deviate from Hooks law. Classically these can be explained by Morse function:

$$E = D_{eq}\left[1 - e^{-\alpha(r_{eq}-r)}\right]^2$$



D_{eq} – dissociation energy; α – constant for a particular molecule

$$X_{eq} = \frac{\bar{\nu}}{4D_{eq}}$$

Using the above equation in Schrodinger's wave equation and solving it gives,

$$\varepsilon_{vib} = \left(\mathrm{v} + \frac{1}{2}\right)\bar{\nu} - \left(\mathrm{v} + \frac{1}{2}\right)^2 \bar{\nu}x_e + \left(\mathrm{v} + \frac{1}{2}\right)^3 \bar{\nu}y_e + \cdots\ cm^{-1}$$

$Ignoring\ the\ higher\ terms$

$$\varepsilon_{vib} = \left(\mathrm{v} + \frac{1}{2}\right)\bar{\nu} - \left(\mathrm{v} + \frac{1}{2}\right)^2 \bar{\nu}x_e\ cm^{-1}$$

x_e , y_e – anharmonicity constants – small positive quantities. So vibrational levels unevenly come closer at higher 'v' values; consequently at higher 'v' values the vibrational levels coalesce with one another forming a continuum.

Anharmonicity now allows the transitions with,

$$\Delta v = \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \ldots$$
$$\Delta v = \pm 1\ fundamental;\ v_0 \rightarrow v_1$$
$$\Delta v = \pm 2\ first\ overtone;\ v_0 \rightarrow v_2$$
$$\Delta v = \pm 3\ second\ overtone;\ v_0 \rightarrow v_3$$
$$\Delta v = \pm 4\ third\ overtone;\ v_0 \rightarrow v_4$$

The overtones are not equal to the integral multiple of fundamental; but somewhat less.

The selection rule for diatomic molecule (anharmonic oscillator):

i. The diatomic molecule should be heteronuclear with permanent dipole moment

ii. The change in vibrational quantum number is, Δv = ±1, ±2, ±3, ±4,.....

Transitions (v_0 to v_1, v_2, v_3, v_4 etc.):

i. v=0 → v=1 (fundamental) with considerable intensity

$$\varepsilon_{v=1} - \varepsilon_{v=0} = \Delta\varepsilon = \left(1 + \frac{1}{2}\right)\bar{\nu} - \left(1 + \frac{1}{2}\right)^2 \bar{\nu}x_e - \left(0 + \frac{1}{2}\right)\bar{\nu} - \left(0 + \frac{1}{2}\right)^2 \bar{\nu}x_e$$
$$= \frac{3}{2}\bar{\nu} - \frac{9}{4}\bar{\nu}x_e - \frac{1}{2}\bar{\nu} + \frac{1}{4}\bar{\nu}x_e = \bar{\nu} - 2\bar{\nu}x_e$$

$$\boxed{\Delta\varepsilon = \bar{\nu}\,(1 - 2x_e\,)\ cm^{-1}}$$

ii. v=0 → v=2 (first overtone) with small intensity

$$\varepsilon_{v=2} - \varepsilon_{v=0} = \Delta\varepsilon = \left(2 + \frac{1}{2}\right)\bar{\nu} - \left(2 + \frac{1}{2}\right)^2 \bar{\nu}x_e - \left(0 + \frac{1}{2}\right)\bar{\nu} - \left(0 + \frac{1}{2}\right)^2 \bar{\nu}x_e$$
$$= \frac{5}{2}\bar{\nu} - \frac{25}{4}\bar{\nu}x_e - \frac{1}{2}\bar{\nu} + \frac{1}{4}\bar{\nu}x_e = 2\bar{\nu} - 6\bar{\nu}x_e$$

$$\boxed{\Delta\varepsilon = 2\bar{\nu}\,(1 - 3x_e\,)\ cm^{-1}}$$

iii. v=0 → v=3 (second overtone) with negligible intensity

$$\varepsilon_{v=3}-\varepsilon_{v=0}=\Delta\varepsilon=\left(3+\frac{1}{2}\right)\bar{\nu}-\left(3+\frac{1}{2}\right)^2\bar{\nu}x_e-\left(0+\frac{1}{2}\right)\bar{\nu}-\left(0+\frac{1}{2}\right)^2\bar{\nu}x_e$$

$$=\frac{7}{2}\bar{\nu}-\frac{49}{4}\bar{\nu}x_e-\frac{1}{2}\bar{\nu}+\frac{1}{4}\bar{\nu}x_e=2\bar{\nu}-6\bar{\nu}x_e$$

$$\boxed{\Delta\varepsilon=3\bar{\nu}\,(1-4x_e\,)\,cm^{-1}}$$

iv. v=0 → v=3 (third overtone) with very negligible intensity

$$\varepsilon_{v=4}-\varepsilon_{v=0}=\Delta\varepsilon=\left(4+\frac{1}{2}\right)\bar{\nu}-\left(4+\frac{1}{2}\right)^2\bar{\nu}x_e-\left(0+\frac{1}{2}\right)\bar{\nu}-\left(0+\frac{1}{2}\right)^2\bar{\nu}x_e$$

$$=\frac{9}{2}\bar{\nu}-\frac{81}{4}\bar{\nu}x_e-\frac{1}{2}\bar{\nu}+\frac{1}{4}\bar{\nu}x_e=4\bar{\nu}-20\bar{\nu}x_e$$

$$\boxed{\Delta\varepsilon=4\bar{\nu}\,(1-5x_e\,)\,cm^{-1}}$$

Diatomic Vibrating Rotator:

The rotational and vibrational energy levels and the corresponding absorption/emission spectra in far-IR/IR are discussed independent of each other. In fact, both the motions take place simultaneously in a molecule; consequently, rotational motion does affect the vibrational motion and vice versa perturbing each other's motion. There is an interaction between the two and therefore, for precise analysis of the infra red spectra, one needs to take the interaction into considerations.

Ignoring the interaction among rotational and vibrational motions, the overall energy level equation can be taken as the sum of the respective eigenvalue equation consistent with Born-Oppenheimer approximation.

Rotational Eigenvalue equation:

$$\varepsilon_J=\tilde{B}\,J\,(J+1)-\tilde{D}\,J^2(J+1)^2+\tilde{H}J^3(J+1)^3+\tilde{K}J^4(J+1)^4\ cm^{-1}\rightarrow\ 1$$

Vibrational Eigenvalue equation:

$$\varepsilon_{vib}=\left(\mathrm{v}+\frac{1}{2}\right)\bar{\nu}-\left(\mathrm{v}+\frac{1}{2}\right)^2\bar{\nu}x_e+\left(\mathrm{v}+\frac{1}{2}\right)^3\bar{\nu}y_e+\cdots\ cm^{-1}\qquad\rightarrow\ 2$$

Subsequent to the introduction of interaction, energy of a vibrating rotator molecule is given by the sum of vibrational energy (equation 2) and rotational energy manifested through equation 1.

That is

$$\begin{aligned}\varepsilon_{J,vib} = {} & \varepsilon_J + \varepsilon_{vib} \\ & = \tilde{B}\, J\,(J+1) - \tilde{D}\, J^2(J+1)^2 + \tilde{H}J^3(J+1)^3 + \tilde{K}J^4(J+1)^4 \\ & + \left(\mathrm{v}+\frac{1}{2}\right)\bar{\nu} - \left(\mathrm{v}+\frac{1}{2}\right)^2 \bar{\nu}x_e + \left(\mathrm{v}+\frac{1}{2}\right)^3 \bar{\nu}y_e + \cdots\ cm^{-1}\end{aligned}$$

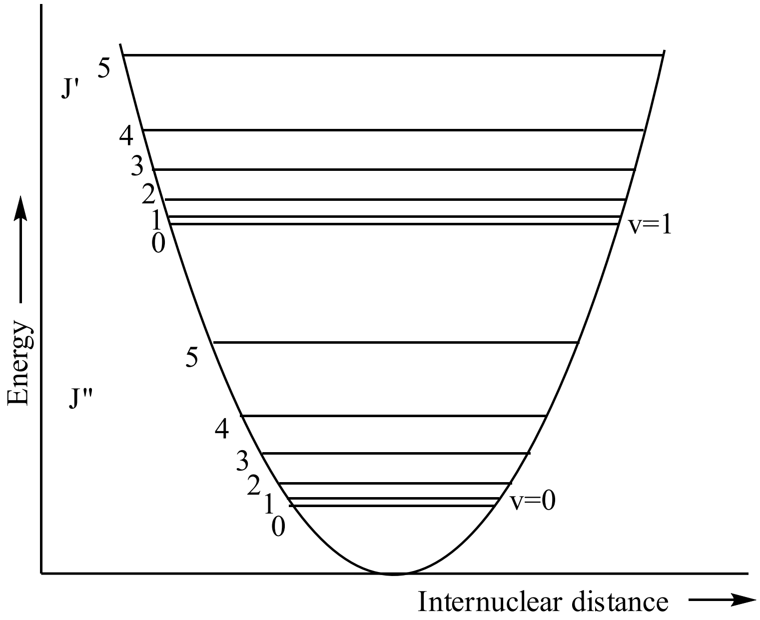
Ignoring the centrifugal distortion and higher anharmonic constants,

$$\varepsilon_{J,vib} = \tilde{B}\, J\,(J+1) + \left(\mathrm{v}+\frac{1}{2}\right)\bar{\nu} - \left(\mathrm{v}+\frac{1}{2}\right)^2 \bar{\nu}x_e\ cm^{-1}$$

The selection rule is,

i. Permanent dipole moment

ii. Δv = ±1, ±2, ±3, ±4,.....; ΔJ = ±1. Vibrational change occurs with simultaneous rotational change



Transition from lower to next upper level:

Assuming $\tilde{B}$ and $\tilde{D}$ same for v=0 and v=1 states, the following transitions are possible as per the selection rule: Δv = ±1, ±2, ±3, ±4,.....; ΔJ = ±1

Lower state – double prime; v”, J”

Upper state – single prime; v, J’

If J”=J, J’=J+1; v”=0, v’=1

$$\begin{aligned}\Delta\varepsilon_{J,vib} = {} & \varepsilon_{J'} - \varepsilon_{J''} \\ & = \tilde{B}\, J'\,(J+1) - \tilde{D}\, J'^2(J'+1)^2 + \left(\mathrm{v}'+\frac{1}{2}\right)\bar{\nu} - \left(\mathrm{v}'+\frac{1}{2}\right)^2 \bar{\nu}x_e \\ & - \left[\tilde{B}\, J''\,(J''+1) - \tilde{D}\, J''^2(J''+1)^2 + \left(\mathrm{v}''+\frac{1}{2}\right)\bar{\nu} - \left(\mathrm{v}''+\frac{1}{2}\right)^2 \bar{\nu}x_e\right]\end{aligned}$$

For Δv =1 and ΔJ =+1 i.e., (J’-J”) = +1; R-branch:

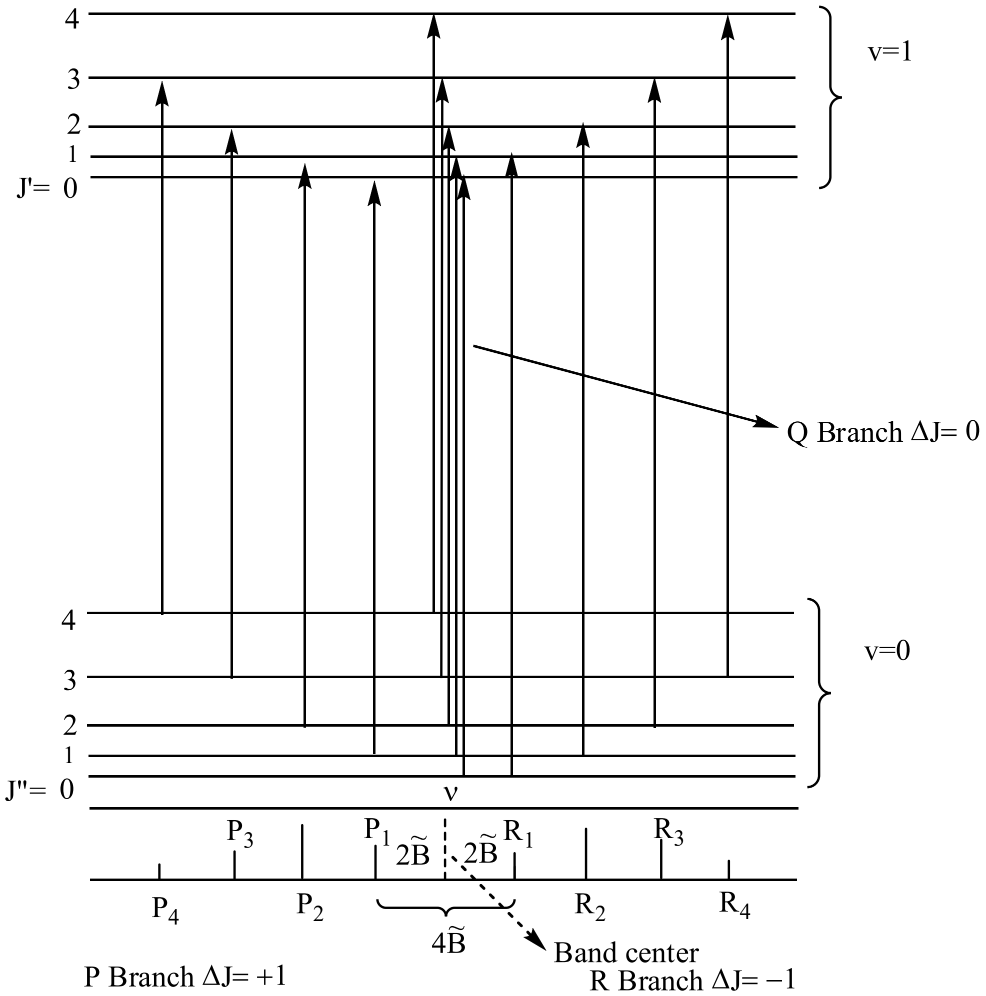
$$\Delta\varepsilon_R = \Delta\varepsilon_{J,vib} = \bar{\nu} + 2\tilde{B}(J''+1) - 4\tilde{D}(J''+1)^3\ cm^{-1}$$

J”=0, 1, 2, 3,...

For Δv =1 and ΔJ =-1 i.e., (J’-J”) = -1; P-branch:

$$\Delta\varepsilon_P = \Delta\varepsilon_{J,vib} = \bar{\nu} - 2\tilde{B}(J'+1) + 4\tilde{D}(J'+1)^3\ cm^{-1}$$

J”=0, 1, 2, 3,...



Diatomic transition of rotation-vibration levels

By measuring absorption splitting, we can get $\tilde{B}$. From that, the bond length can be calculated. From the band centre or band origin, which is the fundamental absorption frequency, the force constant can be evaluated.

Q-Branch

When ΔJ = 0, i.e. the rotational quantum number in the ground state is the same as the rotational quantum number in the excited state – Q branch (simple, the letter between P and R). To find the energy of a line of the Q-branch:

$$\Delta\varepsilon_P = \Delta\varepsilon_{J,vib} = \bar{\nu}_0 - \ band\ center;$$

The Q-branch can be observed in polyatomic molecules and diatomic molecules with electronic angular momentum in the ground electronic state, e.g. nitric oxide, NO.

Types of Bands:

Fundamental – ν_i the i^{th} vibrational mode; Δv = v'-v"=1 for the i^{th} mode

Overtones - occur when a vibrational mode is excited from 0ν=0 to ν=2, 3,..etc.
First overtone - $2\nu_i$; Δv = v'-v"=2 for the i^{th} mode
Second overtone - $3\nu_i$; Δv = v'-v"=3 for the i^{th} mode

Combination bands: Due to changes in multiple quantum numbers.

Combination bands are observed when more than two or more fundamental vibrations are excited simultaneously. One reason a combination band might occur is if a fundamental vibration does not occur because of symmetry.

$\nu_1 + \nu_2$: $\Delta v_1 = \Delta v_2 = 1$, i.e., v_1 and v_2 both increase by 1 for absorption or decrease by 1 for emission
$2\nu_1 + \nu_2$: $\Delta v_1 ==2$ and $\Delta v_2 = 1$

Difference bands: quantum numbers change with mixed sign.
$\nu_1 - \nu_2$; $v_{1,fina}-v_{1,initial} = \pm1$; $v_{2,fina}-v_{2,initial} = \mp1$; i.e., a unit increase in v_1 is accompanied by unit decrease in v_2 and vice-versa.

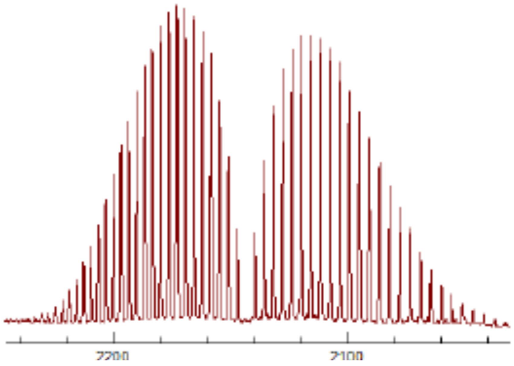
Fermi resonance is the shifting of the energies and intensities of absorption bands in an infrared or Raman spectrum. It is a consequence of quantum mechanical mixing. When a fundamental vibration couples with an overtone or combination band, the coupled vibration is called Fermi resonance. Fermi resonance is often observed in carbonyl compounds.

Hot band: If the sample has a high temperature, some population of n=1, n=2, or higher levels will lead to weak absorptions at nearly the same, but slightly lower energy as fundamental. A hot band will increase in intensity as the temperature of the sample is increased.

Vibration Spectrum of carbon monoxide:

Carbon monoxide, polar molecule with permanent dipole moment, as vibrating rotator would give the spectrum with P and R branches corresponding to the selection rules,

$\Delta v = \pm 1$ and $\Delta J = \pm 1$;
R branch : $\Delta J = +1$
P branch : $\Delta J = -1$



P-branch R-branch

Band center : 2143 cm^{-1}
Average line separation $2\tilde{B}$: 3.83 cm^{-1}

This value is in satisfactory agreement with the value (1.92118 cm^{-1}) from rotational spectrum of CO.

Interaction of Rotation and vibration:
(Breakdown of Born-Oppenheimer approximation)

In real diatomics the rotation and vibration are not independent of each other. They couple and the rotational-vibrational coupling is called rovibronic coupling/ Coriolis coupling. During rotation, the vibration causes average inter-atomic distance larger than equilibrium value ($r_{ave} > r_{eq}$), resulting reduction in $\tilde{B}$ ($\tilde{B} \propto \frac{1}{r_{eq}^2}$). Further enhanced vibrational energy increases vibrational amplitude. Thus $\tilde{B}$ is a function of vibrational quantum number 'v'. Then neglecting centrifugal distortion,

$$\varepsilon_{J,vib} = \varepsilon_J + \varepsilon_{vib} = \tilde{B}_v J\,(J+1) + \left(\mathrm{v} + \frac{1}{2}\right)\bar{\nu}$$

Vibrational-rotational coupling:

$$\tilde{B}_{\mathrm{v}} = \tilde{B} - \alpha(v + \frac{1}{2})$$

α – small positive constant; $\tilde{B}$- rotational term corresponding to equilibrium bond length.

With this energy expression, the allowed transition frequencies are as follows,

R – Branch: J →J+1; v=0 → v=+1

$$\tilde{\nu}_\mathrm{R} = \tilde{B}_1 (J+1)(J+2) + \left(1+\frac{1}{2}\right)\bar{\nu} - \tilde{B}_0 J (J+1) + \left(0+\frac{1}{2}\right)\bar{\nu}$$

$$\boxed{\tilde{\nu}_\mathrm{R} = \bar{\nu} + 2\tilde{B}_1 + \left(3\tilde{B}_1 - \tilde{B}_0\right)J + \left(\tilde{B}_1 - \tilde{B}_0\right)J^2}$$

P – Branch: J →J-1; v=0 → v=+1

$$\tilde{\nu}_\mathrm{P} = \tilde{B}_1 J(J-1) + \left(1+\frac{1}{2}\right)\bar{\nu} - \tilde{B}_0 J (J+1) + \left(0+\frac{1}{2}\right)\bar{\nu}$$

$$\boxed{\tilde{\nu}_\mathrm{P} = \bar{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + \left(\tilde{B}_1 - \tilde{B}_0\right)J^2}$$

$$I_{v=1} > I_{v=0}$$

$$\therefore\ \tilde{B}_1 < \tilde{B}_0$$

Then the coefficients of J^2 terms in P and R branch equations are negative resulting in nonconstant spacing in rotational-vibrational lines with asymmetry. This leads to further down to low frequency region than would be expected for $\tilde{B}_1 = \tilde{B}_0 = \tilde{B}$. The same trend is noticed in R-branch where the lines bunch up on the low frequency side; i.e., R-branch starts moving back to lower frequency for very high J values. This band is then said to have a band head.

Centrifugal distortion:

$$\widetilde{D}_\mathrm{v} = \widetilde{D} - \beta(v + \frac{1}{2})$$

Anharmonicity:

$$\varepsilon_{vib} = \left(\mathrm{v}+\frac{1}{2}\right)\bar{\nu} - \left(\mathrm{v}+\frac{1}{2}\right)^2 \bar{\nu}x_e + \left(\mathrm{v}+\frac{1}{2}\right)^3 \bar{\nu}y_e + \cdots\ cm^{-1}$$

So the energy of a rotational-vibrational level is,

$$\varepsilon_{J,vib} = \varepsilon_J + \varepsilon_{vib} = \tilde{B}_\mathrm{v} J (J+1) - \widetilde{D}_\mathrm{v} J^2 (J+1)^2 + \left(\mathrm{v}+\frac{1}{2}\right)\bar{\nu} - \left(\mathrm{v}+\frac{1}{2}\right)^2 \bar{\nu}x_e + \cdots\ cm^{-1}$$

The above facts shows the breakdown of Born-Oppenheimer approximation of non-interaction of rotation-vibration of molecules.

$$\tilde{\nu}_R \sim \tilde{\nu}_P = R_1 - P_2 \rightarrow \mathit{Rotational\ spacing\ in\ the\ lower\ vibrational\ level}\ v = 0$$

$$\tilde{\nu}_R \sim \tilde{\nu}_P = R_2 - P_1 \rightarrow \mathit{Rotational\ spacing\ in\ the\ upper\ vibrational\ level}\ v = 1$$

Thus $\tilde{B}_0$ and $\tilde{B}_1$ and hence $r_0 \mathit{and}\ r_1$can be calculated.

~~The interatomic potential is not exactly quadratic, so there should be deviations from the simple harmonic oscillator energies. If we view the connection between the atoms as a spring, it is obvious that the spring will stretch as the molecule spins, increasing the moment of inertia and decreasing the rotational level spacing. Additionally, in an anharmonic oscillator the average separation between atoms depends on the vibrational level, which in turn affects the moment of inertia and effectively couples the vibrational and rotational motions. We need to consider all these effects to get an accurate representation of the spectrum~~.

Influence of rotation on the spectrum of polyatomic molecules

Polyatomic molecules give complex rotation-vibration spectra that can be analysed under the categories of a) linear and b) non-linear (symmetric top) molecules in terms of parallel (||) and perpendicular (⊥) bands.

Linear Molecules

Two types of rotation-vibration bands occur for linear polyatomic molecules corresponding to the vibrational direction either parallel (||) or (⊥) perpendicular to the oscillating dipole moment along the molecular symmetry axis.

a) Parallel bands of linear molecules: The vibration of linear molecule results in oscillating dipole moment parallel to the molecular axis.

Selection Rules:
$\Delta J = \pm 1$; $\Delta v = \pm 1$ for simple harmonic motion (P and R branches with no Q-branch)

$\Delta J = \pm 1$; $\Delta v = \pm 1, \pm 2$,,, for simple anharmonic motion (P and R branches with no Q-branch)

The spectral analysis is as that for diatomic vibrating rotator. Thus $\tilde{B}_0$ and $\tilde{B}_1$ and hence $r_0 and\ r_1$can be calculated.

Linear symmetric molecules like CO_2, CH≡CH, etc with oscillating dipole moment would give vibration-rotation spectra even though no permanent dipole moment.

b) Perpendicular bands of linear molecules: The vibration of linear molecule results in oscillating dipole moment perpendicular to the molecular axis.

Selection Rules:
$\Delta J = 0, \pm 1$; $\Delta v = \pm 1$ for simple harmonic motion (P, Q and R branches

The spectral analysis is as that for diatomic vibrating rotator. Thus $\tilde{B}_0$ and $\tilde{B}_1$ and hence $r_0 and\ r_1$can be calculated. Eg. N_2O.

Symmetric Top Molecules:

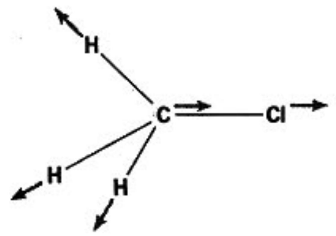
Symmetric top molecules have their oscillating dipole moment either parallel (||) or (⊥) perpendicular to the unique molecular axis. The rotational-vibrational energy level is given by,

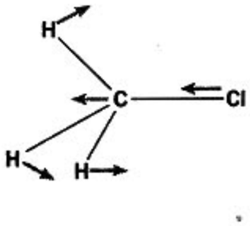
$$\varepsilon_{J,K} = \tilde{B}\, J\,(J+1) + (A-B)K^2$$

$$\varepsilon_{vib} = \left(\mathrm{v}+\frac{1}{2}\right)\bar{\nu} - \left(\mathrm{v}+\frac{1}{2}\right)^2 \bar{\nu}x_e$$

$$\varepsilon_{J,K,vib}\varepsilon_{J,K} = \tilde{B}\, J\,(J+1) + (A-B)K^2 + \left(\mathrm{v}+\frac{1}{2}\right)\bar{\nu} - \left(\mathrm{v}+\frac{1}{2}\right)^2 \bar{\nu}x_e$$

a) Parallel bands of symmetric top molecules: The vibration of symmetric top molecule results in oscillating dipole moment parallel to the molecular axis.





Selection Rules:

ΔJ = 0, ± 1; ΔK = 0 if K ≠ 0 ; Δv = ± 1 (P, Q and R branches)

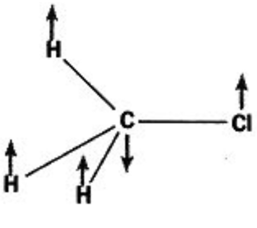
or

ΔJ = ± 1; ΔK = 0 if K = 0 ; Δv = ± 1 (P, and R branches)

This corresponds to the perpendicular bands for linear molecules with P, Q and R branches except for K = 0..

b) Perpendicular bands of symmetric top molecules: The vibration of symmetric top molecule results in oscillating dipole moment perpendicular to the molecular axis.

ΔJ = 0, ± 1; ΔK = ± 1; Δv = ± 1 (P, Q and R branches)



The perpendicular bands show all the ΔJ = 0, ± 1 transitions for agiven change in K.

For K=0 →1, the P, Q and R sub-bands result from the ΔJ = 0, ± 1 transitions.

Similar sub-bands occur for K=1 →0. For each K value except K=0,bands corresponding to ΔK = +1 and ΔK = -1 sub-bands would occur.

$\Delta J = 0$, $\Delta K = \pm 1$ - Q-branch

$$\varepsilon_{J,K} = \bar{\nu} + (A - B)(1 \pm 2K)cm^{-1}$$

$\Delta J = +1$, $\Delta K = \pm 1$ - R-branch

$$\varepsilon_{J,K} = \bar{\nu} + 2\tilde{B}\,(J + 1) + (A - B)(1 \pm 2K)cm^{-1}$$

$\Delta J = -1$, $\Delta K = \pm 1$ - P-branch

$$\varepsilon_{J,K} = \bar{\nu} - 2\tilde{B}\,(J + 1) + (A - B)(1 \pm 2K)cm^{-1}$$

Influence of nuclear Spin:

The intensity of P and R branch of rotational fine structure is influenced by the population and degeneracy of the rotational level. The population of the rotational level and hence the intensity is influenced by the nuclear spin. Then the overall wave function is,

$\Psi_{total} = \Psi_{electron}\ \Psi_{vibrational}\ \Psi_{rotational}\ \Psi_{nuclear\ spin}$

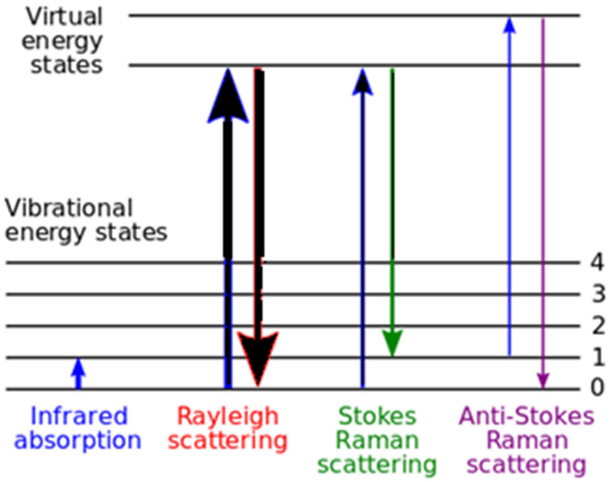
For homonuclear diatomic molecules, i.e., centrosymmetric, the total wave function is symmetric with respect to exchange of nuclei if bosons (zero or integral spin) or antisymmetric with respect to exchange of nuclei if fermions (half integral spin). Even J levels are symmetric, while odd J levels are antisymmetric

In the case of CO_2, both ^{12}C and ^{16}O have zero nuclear spins. The ground state CO_2 ($^1\Sigma_g^+$) is symmetric. Here rotational levels with odd J values have zero statistical weight and are completely absent. So transitions between even J values alone occur resulting in the line separation of 8B in rotational Raman spectrum.S

In general centrosymmetric linear molecules X2, XAX, XAAX, etc., with X – non-zero nuclear spin I and A – zero nuclear spin have odd and even rotational J levels with statistical weights (I+1):I or I:I+1) whether the nucleus has half integral or integral spins.

Raman Spectra

Raman spectroscopy relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The scattered photon has a slightly lower or higher energy, shifted by one quanta of either vibrational or rotational energy.



Selection Rule:

Roughly speaking the primary selection rule for a Raman transition is that the molecular polarizability must change during the molecular vibration

The polarizability of the molecule, is how hard or how easy it is for an electric field to change or distort the electron cloud in an atom or molecule. An atom in which the electron cloud is further away from the nucleus has a larger polarizability than an atom where the electron cloud is closer to the nucleus.

There are several useful generalities we can make concerning Raman & IR spectroscopy:

- symmetric vibrations lead to relatively strong Raman signals and no IR signals.
- asymmetric vibrations lead to much weaker Raman signals and are often quite strong in IR spectroscopy.
- bending vibrational modes lead to much weaker Raman signals and are often quite strong in IR spectroscopy.
- a molecule can have both IR and Raman signals at the same frequency, though if the Raman signal is strong, the corresponding IR peak will be weak and vice versa.

Rotational Raman Spectra

The rotational spectra of non-polar molecules can be observed and measured by Raman spectroscopy.

Linear Molecules:

Selection rule:

1.The molecule must be anisotropically polarisable. $\mu = \alpha E$; α-molecules polarizability

2.For linear rotors, ΔJ = 0, ±2;

ΔJ = 0 transitions do not lead to a change in the frequency of the scattered **photon**, and contribute to the unshifted Rayleigh radiation that passes unaltered through the sample.

ΔJ = ±2 does involve a change in rotational quantum number J, and therefore a change in the quantized rotational energy, E_J: (The end-over-end rotation of polarisable ellipsoid presents similar appearance twice when rotated through 360^o).

Spectrum:

ΔJ = J' – J" = ±2;

For pure rotational spectrum the J' should be necessarily higher than J'. Hence ΔJ= - 2 is neglected and ΔJ= + 2 only is considered (giving S- branch).

For rigid rotor,

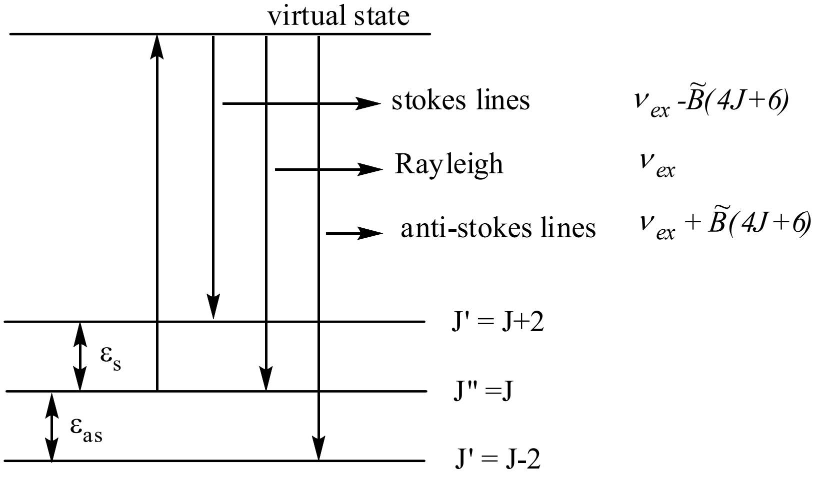
$$\Delta EJ = E_{J'} - E_{J''} = \varepsilon_J = \bar{\nu}_{ex} \pm [\tilde{B}\, J'(J'+1) - \tilde{B}J''(J''+1)]$$

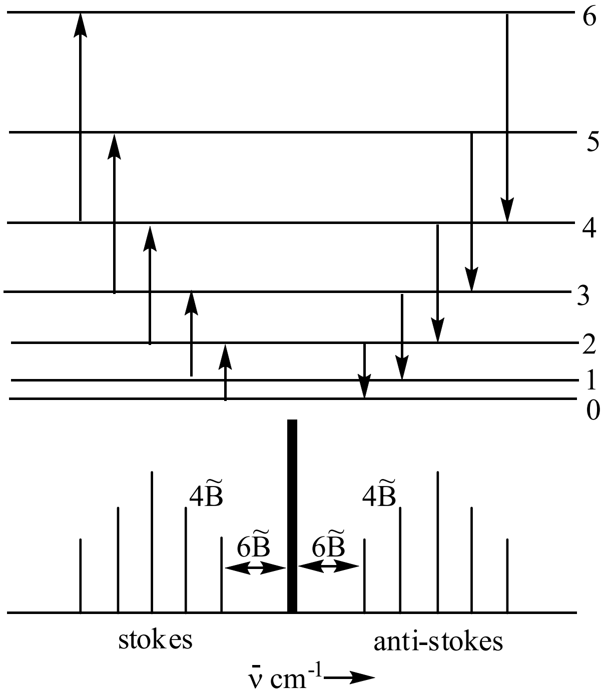
$$= \bar{\nu}_{ex} \pm [\tilde{B}\,(J+2)(J+3) - \tilde{B}J(J+1)]$$

$$= \bar{\nu}_{ex} \pm \tilde{B}\,(4J+6)\, cm^{-1} \qquad J = 0, 1, 2, 3, \ldots$$

$\bar{\nu}_{ex} + \tilde{B}\,(4J+6)$ - anti-stokes lines

$\bar{\nu}_{ex} - \tilde{B}\,(4J+6)$ - stokes lines





Symmetric Top Molecules:

Selection rule:

1. The molecule must be anisotropically polarisable. $\mu = \alpha E$; α-molecules polarizability
2. For symmetric top rotors, $\Delta J = 0, \pm 1, \pm 2$; $\Delta K = 0$

   Except for K=0states when $\Delta J = \pm 2$

   The energy level equation is

$$\varepsilon_{J,K} = \tilde{B}\, J\,(J+1) + (A-B)K^2\ cm^{-1}$$

$J = 0,1,2,3\ldots$; $K = \pm J, \pm(J-1), \pm(J-2)\ldots$

Spectrum:

If ΔJ is restricted to positive values only,

a. $\Delta J = +1$ R-branch

$$\Delta E_R = \varepsilon_R = 2\tilde{B}\ (J+1)\ cm^{-1}$$ $J = 1,2,3,\ldots$ $J \neq 0$

b. $\Delta J = +2$ S-branch

$$\Delta E_S = \varepsilon_S = \tilde{B}\,(4J+6)\ cm^{-1}$$ $J = 0,1,2,3,\ldots$

$$\bar{\nu}_R = \bar{\nu}_{ex} \pm \varepsilon_R = \bar{\nu}_{ex} \pm 2\tilde{B}\ (J+1)\ cm^{-1}\ ;\ J = 1,2,3,\ldots$$

$$\bar{\nu}_S = \bar{\nu}_{ex} \pm \varepsilon_S = \bar{\nu}_{ex} \pm \tilde{B}\ (4J+6)\ cm^{-1}\ ;\ J = 0,1,2,3,..$$

Vibrational Raman Spectra

Raman activity of vibrations:

i. Water – symmetric, bending and asymmetric stretching modes are Raman active

ii. CO_2 – symmetric stretching Raman active; asymmetric stretching and bending mode Raman inactive.

Symmetric vibrations produce strong Raman lines; non-symmetric vibrations give weak or no Raman lines.

Rule of Mutual Exclusion:

Vibrations of molecules or ions having an inversion center i are either infrared (asymmetric modes) or Raman active (symmetric modes).
Some or all vibrations of non-centro-symmetric molecules are both Raman and IR active.

Vibrational Raman Spectra:

The eigen value equation for Raman vibrational spectra is,

$$\varepsilon_{vib} = \left(\mathrm{v}+\frac{1}{2}\right)\bar{\nu} - \left(\mathrm{v}+\frac{1}{2}\right)^2 \bar{\nu}x_e$$

$$\mathrm{v} = 0,1,2,\ldots$$

$$x_e - anharmonicity\ constant$$

$$\Delta\mathrm{v} = 0, \pm1, \pm2, \pm3, \ldots$$

$$\mathrm{v}=0 \rightarrow \mathrm{v}=1: \Delta\varepsilon_{\text{fundamental}} = \bar{\nu}(1-2x_e)cm^{-1}$$

$$\mathrm{v}=0 \rightarrow \mathrm{v}=2: \Delta\varepsilon_{\text{overtone}} = 2\bar{\nu}(1-3x_e)cm^{-1}$$

$$\mathrm{v}=1 \rightarrow \mathrm{v}=2: \Delta\varepsilon_{\text{hot}} = \bar{\nu}(1-4x_e)cm^{-1}$$

Raman lines appear at a distance on either side (low frequency-stokes; high frequency-anti stokes) from ν_{ex}, viz., Rayleigh, given by

$$\nu_{spec} = \nu_{ex} \pm \Delta\varepsilon_{\text{fundamental}}\ cm^{-1}$$

Rotational fine structure:

The eigenvalue equation for vibration-rotation Raman spectrum is as that of IR spectrum (rigid rotor):

$$\varepsilon_{J,vib} = \varepsilon_J + \varepsilon_{vib} = \tilde{B}_{\mathrm{v}} J\,(J+1) + \left(\mathrm{v}+\frac{1}{2}\right)\bar{\nu} - \left(\mathrm{v}+\frac{1}{2}\right)^2 \bar{\nu}x_e\ cm^{-1}$$

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

Selection Rule: $\Delta\mathrm{v} = 0, \pm1, \pm2, \pm3, \ldots;\ \Delta\mathrm{J} = 0, \pm2$

Q – branch : $\Delta J = 0;\ \ \Delta\varepsilon_Q = \bar{\nu}_o\ cm^{-1}$ J= 0,1,2,..

S – branch $\Delta J = +2;\ \Delta\varepsilon_S = \bar{\nu}_o + \tilde{B}\,(4J+6)\ cm^{-1}$ J= 0,1,2,..

O – branch $\Delta J = -2;\ \Delta\varepsilon_O = \bar{\nu}_o - \tilde{B}\,(4J+6)\ cm^{-1}$ J= 2,3,4,..

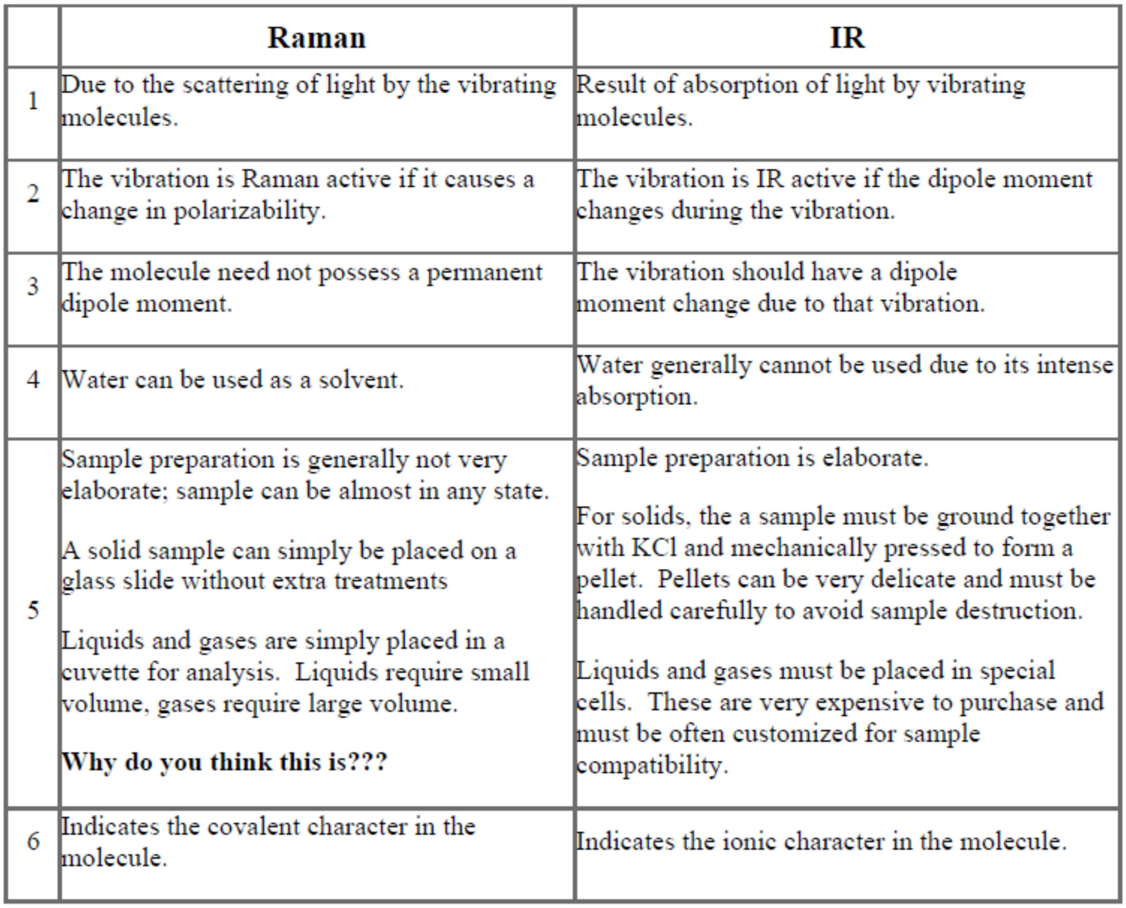
/or/

Q – branch : $\Delta J = 0;\ \ \Delta\varepsilon_Q = \bar{\nu}_Q = \bar{\nu}_{ex} - \bar{\nu}_o\ cm^{-1}$ J= 0,1,2,..

S – branch $\Delta J = +2;\ \Delta\varepsilon_S = \bar{\nu}_S = \bar{\nu}_{ex} - \bar{\nu}_o + \tilde{B}\,(4J+6)\ cm^{-1}$ J= 0,1,2,..

O – branch $\Delta J = -2;\ \Delta\varepsilon_O = \bar{\nu}_O = \bar{\nu}_{ex} - \bar{\nu}_o - \tilde{B}\,(4J+6)\ cm^{-1}$ J= 2,3,4,..

For larger molecules due to resolution factor rotational fine structure is neglected.



	Raman	IR
1	Due to the scattering of light by the vibrating molecules.	Result of absorption of light by vibrating molecules.
2	The vibration is Raman active if it causes a change in polarizability.	The vibration is IR active if the dipole moment changes during the vibration.
3	The molecule need not possess a permanent dipole moment.	The vibration should have a dipole moment change due to that vibration.
4	Water can be used as a solvent.	Water generally cannot be used due to its intense absorption.
5	Sample preparation is generally not very elaborate; sample can be almost in any state. A solid sample can simply be placed on a glass slide without extra treatments Liquids and gases are simply placed in a cuvette for analysis. Liquids require small volume, gases require large volume. **Why do you think this is???**	Sample preparation is elaborate. For solids, the a sample must be ground together with KCl and mechanically pressed to form a pellet. Pellets can be very delicate and must be handled carefully to avoid sample destruction. Liquids and gases must be placed in special cells. These are very expensive to purchase and must be often customized for sample compatibility.
6	Indicates the covalent character in the molecule.	Indicates the ionic character in the molecule.

Electronic spectra of diatomic molecules

Rotational spectra – molecules with permanent electric dipole moment

Vibrational spectra – molecules with oscillating electric dipole moment

Electronic spectra – all molecules

According to Born-Oppenheimer approximation,

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

The change in total energy is,

$\Delta E_{total} = \Delta E_{elec} + \Delta E_{vib} + \Delta E_{rot}$ J

$\varepsilon_{total} = \varepsilon_{elec} + \varepsilon_{vib} + \varepsilon_{rot}$ cm^{-1}

$\Delta\varepsilon_{total} = \Delta\varepsilon_{elec} + \Delta\varepsilon_{vib} + \Delta\varepsilon_{rot}$ cm^{-1}

So on the spectra of electronic transitions vibrational changes produce a coarse structure and rotational changes a fine structure.

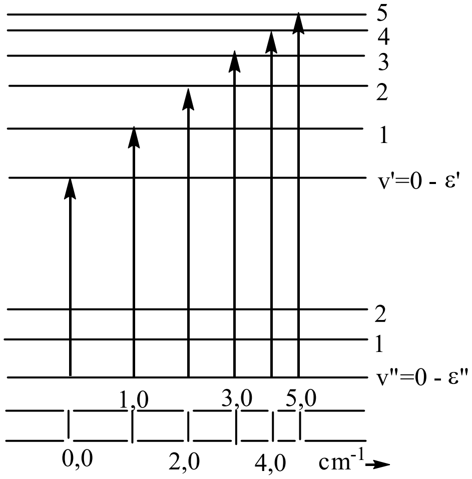
Vibrational coarse structure:

Neglecting rotational changes,

$\varepsilon_{total} = \varepsilon_{elec} + \varepsilon_{vib}$ cm^{-1}

$$\varepsilon_{total} = \varepsilon_{elec} + \left(v + \frac{1}{2}\right)\bar{\nu} - \left(v + \frac{1}{2}\right)^2 \bar{\nu}x_e \quad \text{cm}^{-1}$$

The electronic transitions with appreciable transition probabilities from v” to v’ are shown below. The set of transitions under low resolution appear to be a *band*. Each line in the set is broad and diffuse and is called v’ – *progression* as v’ increases by unity. Convergence at higher frequency is due to anharmonicity of the upper state.



$\Delta\varepsilon_{total} = \Delta\varepsilon_{elec} + \Delta\varepsilon_{vib}$

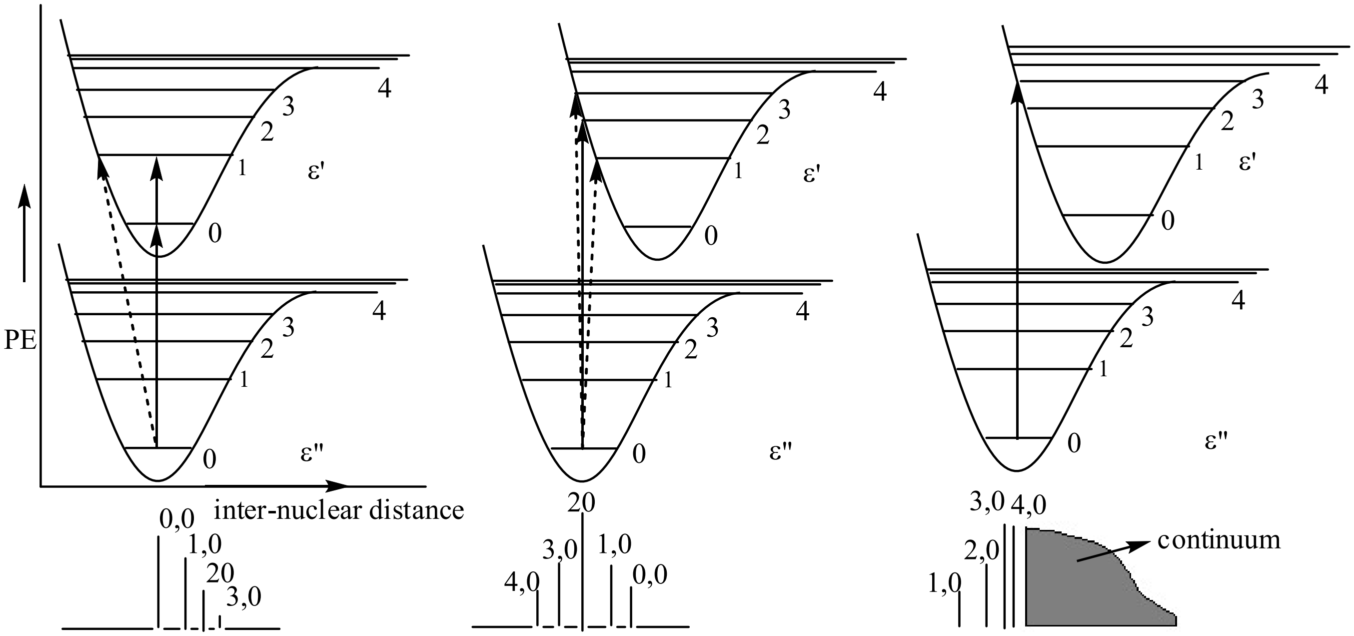
$$\bar{\nu}_{spec} = (\varepsilon' - \varepsilon'') + \left[\left(v' + \frac{1}{2}\right)\bar{\nu}' - \left(v' + \frac{1}{2}\right)^2 \bar{\nu}'x'_e\right] - \left[\left(v'' + \frac{1}{2}\right)\bar{\nu}'' - \left(v'' + \frac{1}{2}\right)^2 \bar{\nu}''x_e\right]$$

Ground state can undergo several excitations resulting in corresponding spectrum.

Intensity of vibrational lines in electronic spectra:

Vibronic spectra involve simultaneous changes in the vibrational and electronic energy states of a molecule, resulting in vibrational progression. The vibrational lines in a progression are not of the same intensity. The different patterns are shown in the figure. The intensity of allowed vibronic transitions is governed by the Franck–Condon principle:

> "An electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck–Condon state, and the transition involved, is a vertical transition".



(a) (b) (c)

(a). The potential curves of the two electronic states are drawn in such way that their minima lie very nearly one above the other. The physical meaning is that in both the electronic states, the equilibrium inter-nuclear distances are same. This is the most probable transition (0,0), with maximum intensity. (1, 0) transition is less probable and hence the weak intense line and so on (2, 0), (3, 0) etc.

(b).The minimum of the potential curve of the upper electronic state is shifted to higher intermolecular distance than that of the ground state. The physical meaning of this is that the bond length of the upper electronic state at the equilibrium is greater than that of the ground electronic state. The most probable transition is (2, 0) with maximum intensity. (4, 0), (3, 0), (1, 0) and (0, 0) transitions are less probable giving weak lines.

(c).The minimum of the upper electronic potential curve is further shifted to the higher side. In this case the vertical transition lies above the dissociation energy of the upper potential curve. This region corresponds to the continuous region of the vibrational spectrum. After this transition, molecule will dissociate. However, below the point the intensity of the vibrational bands will gradually increase up to the continuum.

Rotational Fine Structure of Electronic-Vibration Spectra:

The vibrational coarse structure of electronic spectra, on high resolution shows that each line is a cluster of many very close lines. This is the rotational fine structure.

By Born-Oppenheimer approximation, the total energy,

$$\varepsilon_{\text{total}} = \varepsilon_{\text{elec}} + \varepsilon_{\text{elec}} + \tilde{B}\text{J}(\text{J}+1)\ cm^{-1};\ \text{ignoring centrfugal distortion}$$

During electronic transition,

$$\Delta\varepsilon_{\text{total}} = \Delta\,(\varepsilon_{\text{elec}} + \varepsilon_{\text{vib}}) + \Delta[\tilde{B}\text{J}(\text{J}+1)]\ cm^{-1}$$

$$\bar{\nu}_{spec} = \bar{\nu}_{(v\prime,v")} + \Delta[\tilde{B}\text{J}(\text{J}+1)]\ cm^{-1}$$

The selection rule for rotational transition in the electronic transition is,

$\Delta\text{J} = \pm 1$; if the electron has no angular momentum in both the states
Characterised by P and R – branches

$\Delta\text{J} = 0, \pm 1$; if the electron has angular momentum in both or in any one of the states
Characterised by P, Q and R – branches; J"=0 →J'=0 transition is restricted

Then,

$$\bar{\nu}_{spec} = \bar{\nu}_{(v\prime,v")} + \tilde{B}'\text{J}'(\text{J}'+1) - \tilde{B}"\text{J}"(\text{J}"+1)\ cm^{-1}$$

$$\tilde{B}' < \tilde{B}"$$

1. P – branch $\Delta\text{J} = -1;\ \text{J}" = \text{J}' + 1$

$$\Delta\varepsilon = \bar{\nu}_P = \bar{\nu}_{(v\prime,v")} - (\tilde{B}' + \tilde{B}")(\text{J}'+1) + (\tilde{B}' - \tilde{B}")(\text{J}'+1)^2\ cm^{-1}$$

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

2. R – branch $\Delta\text{J} = +1;\ \text{J}' = \text{J}" + 1$

$$\Delta\varepsilon = \bar{\nu}_R = \bar{\nu}_{(v\prime,v")} + (\tilde{B}' + \tilde{B}")(\text{J}"+1) + (\tilde{B}' - \tilde{B}")(\text{J}"+1)^2\ cm^{-1}$$

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

P and R – branch equations canbe combined as,

$$\bar{\nu}_{P,R} = \bar{\nu}_{(v',v'')} + (\tilde{B}' + \tilde{B}'')\mathrm{m} + (\tilde{B}'\text{-}\tilde{B}'')\mathrm{m}^2 \ cm^{-1}$$

m = ±1, ±2, ±3, ... (m – can not be zero)

+ ve, m values for R – branch

- ve, m values for P – branch

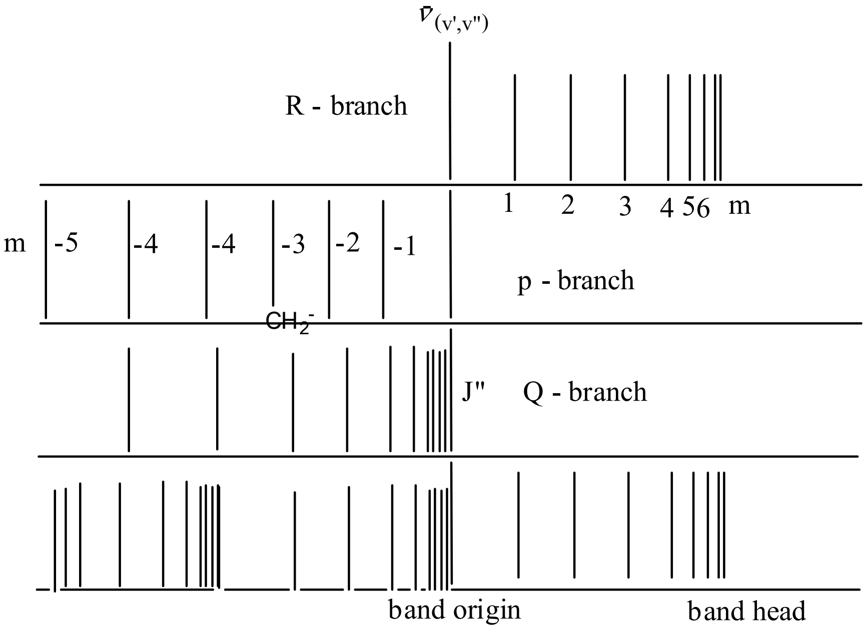
With this choice, P branches occur on the low wavenumber side of the band origin and the spacing between the lines increases with m. On the other hand the R branch appears on the high wavenumber of the origin and the line spacing decreases rapidly with m, so rapidly that the lines eventually reach a maximum wavenumber and then begin to return to low wavenumbers with increasing spacing. The point at which the R-branch separation reaches to zero is termed the band head

3. Q – branch $\Delta J = 0;\ J' = J'' \neq 0$

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

J" = 1, 2, 3, ...

The P, Q and R lines are shown in the figure:



Fortrat Diagram:

Consider the rotational fine structure equations,

$$\bar{\nu}_{P,R} = \bar{\nu}_{(v',v'')} + (\tilde{B}' + \tilde{B}'')\mathrm{p} + (\tilde{B}'\text{-}\tilde{B}'')\mathrm{p}^2 \ cm^{-1} \quad \rightarrow \mathrm{A}$$

p = ±1, ±2, ±3, ... (p – can not be zero)

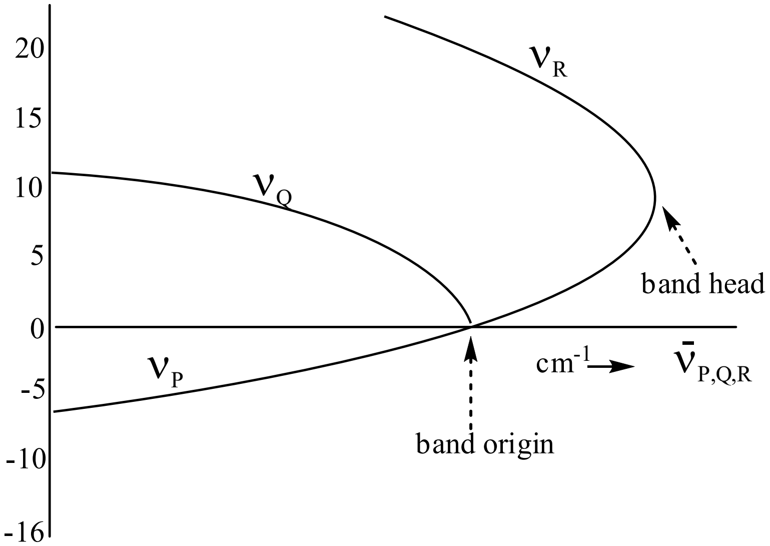
+ ve, p values for R – branch

- ve, p values for P – branch

$$\bar{\nu}_Q = \bar{\nu}_{(v',v")} + (\tilde{B}' - \tilde{B}")q + (\tilde{B}' - \tilde{B}")q^2 \ cm^{-1} \qquad \rightarrow B$$

q = +1, +2, +3, ...

Eqns. A and B represent a parabola. With $\tilde{B}' < \tilde{B}"$, and a difference of 10%, parabolae can be sketched and it is known as Fortrat Diagram.



The band head is at the vertex of P, R parabola. Differentiation at the vertex,

$$\frac{d\bar{\nu}_{P,R}}{dp} = (\tilde{B}' + \tilde{B}") + 2(\tilde{B}' - \tilde{B}")p = 0$$

$$p = \frac{\tilde{B}' + \tilde{B}"}{2(\tilde{B}' - \tilde{B}")}$$

Unit – III : Nuclear Magnetic Resonance

Basis:
Nuclei with spin are magnetically active. The empirical rule to identify magnetically active nuclei with non-zero spin is: (I – spin quantum number)

1. Even number proton + even number neutron – I = 0; magnetically inactive
   ^{4}He, ^{12}C, ^{16}O, etc.
2. Odd mass number – I = half-integral; ½, 1½ , 2½ , etc.
   ^{1}H (I=½), ^{13}C(I=½), ^{15}N(I=½), ^{17}O(I=2½), ^{31}P, etc
   Even number proton + odd number neutron
   Odd number proton + even number neutron
3. Even number mass number – I=integral 1, 2, 3, etc.
   Odd number proton + odd number neutron ^{2}H, ^{14}N, ^{10}B, etc.

Nuclei obeying rule 2 and 3 with non-zero spin quantum number are magnetic nuclei. Nuclei with I=½ are suitable for NMR measurement. These nuclei possess angular momentum P given by,

$$P = \sqrt{I(I+1)}\,\hbar$$

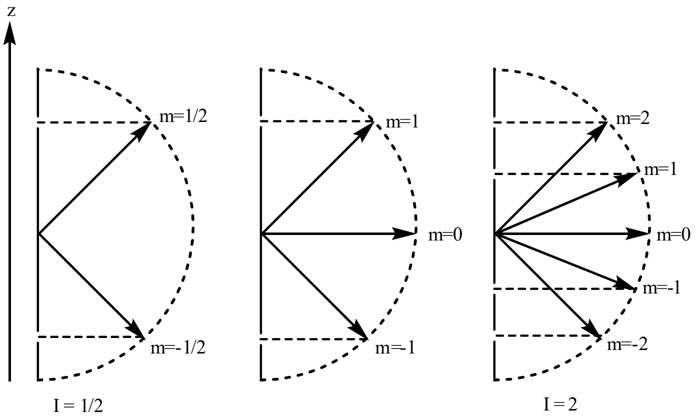
Nuclei with angular momentum has magnetic moment μ,

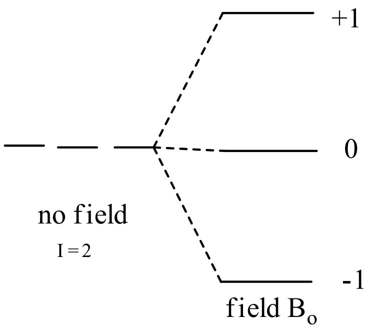
$$\mu = \gamma P \qquad \gamma \text{ - magnetogyric ratio}$$

When this nucleus is placed in a magnetic field B_o (along z-axis) P would take up one of (2I+1) orientations. The allowed projections P_z along z-axis are,

$$P_z = m\hbar$$

m = I, I-1, I-2, ...-I i.e., (2I+1) – orientations





$$\mu_z = \gamma P_z = \gamma m\hbar$$

The interaction energy of the magnetic nucleus with μ_z in a magnetic field B_o is (Zeeman interaction) then given by,

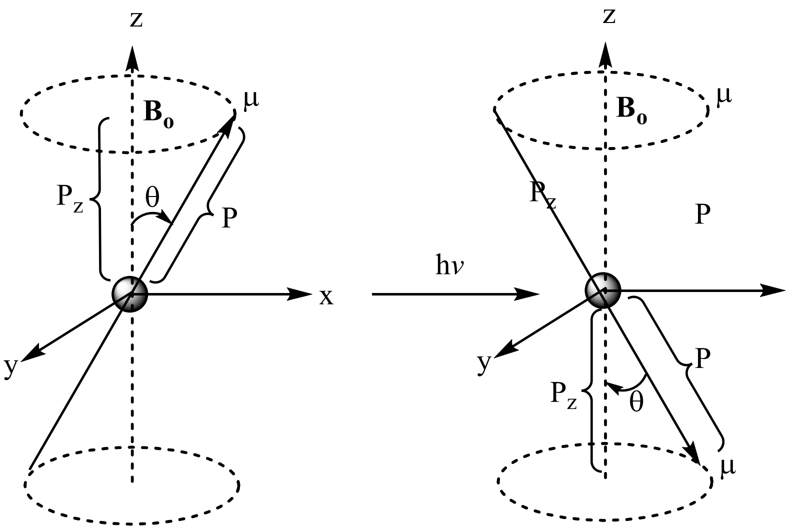
$E = -\mu_z B_o = -\gamma m\hbar B_o$ (Zeeman energy)

Quantum mechanically, Δm = ±1

For I = ½ , m_I = + ½ , - ½ ; m_I = + ½ is α-state; m_I = - ½ is

$$E_\alpha = -\frac{1}{2}\gamma\hbar B_o; \qquad E_\beta = \frac{1}{2}\gamma\hbar B_o; \qquad \Delta E_{\alpha\to\beta} = \gamma\hbar B_o = \frac{\mu_z}{P_z}\hbar B_o$$

$$\nu = \frac{\gamma B_o}{2\pi}; \quad 2\pi\nu = \gamma B_o; \quad \omega = 2\pi\nu; \quad \omega = \gamma B_o$$



ω – also known as Larmor precession frequency.
This Larmor precessional frequency is just the frequency separation between energy levels. A beam with precessional frequency applied perpendicular to the field direction will interact coherently with the spinning particle resulting in energy exchange. It is referred to nuclear magnetic resonance.

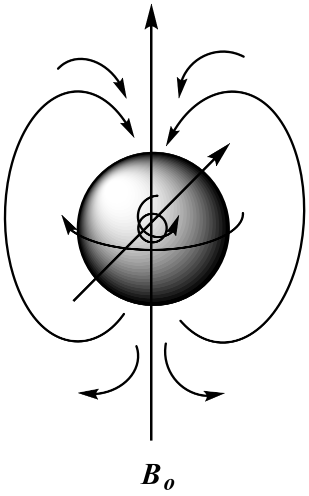
Experimentally there are two methods:

1. Frequency sweep method (CW) – the nuclei is exposed to fixed field strength (B_o) and the frequency of the incident radiation (ν) is changed continuously till it is equal to the Larmor precessional frequency (ω) at which resonance absorption occurs.
2. Field sweep method – the nuclei is exposed to a fixed frequency (ν) of the incident radiation and the field strength (B_o) is changed continuously till the Larmor precessional frequency (ω) of the nucleus is equal to ν at which resonance absorption occurs.

Shielding Constant:
When a magnetic nucleus is placed in an external magnetic field B_o, the surrounding electron cloud tends to circulate in such a direction as to produce a field opposing that applied field. So the total field experienced by the nucleus is:

$$B_{experienced} = Bo - B_{induced}$$
$$B_{induced} \propto Bo; \; B_{induced} = \sigma \, Bo$$
$$B_{experienced} = Bo(1 - \sigma)$$

Thus the nucleus is shielded from the applied fieldBo. The extent of shielding is given by σ - shielding constant, which varies with the density of the electron cloud around the nucleus in a given molecule.



Chemical Shift:
The chemical shift of a nucleus is the difference between the resonance frequency of the nucleus and a standard, relative to the standard. This quantity is reported in *ppm* and given the symbol delta δ.

$$\delta = \frac{\nu_{sample} - \nu_{ref}}{\nu_{ref}} \; x \; 10^6$$

In NMR spectroscopy, tetramethylsilane, $Si(CH_3)_4$, abbreviated TMS is often used as standard.

1. It is relatively inert with low b.pt. 26.5° C;
2. It has 12 chemically and magnetically equivalent h giving a sharp signal.
3. Its signal is at high field and most of organic compounds give signals at low field relative to it.
4. no overlapping with sample signal or solvent.
5. soluble in most organic liquids
6. TMS Less screened than TMS Low field High frequency {Most organic protons} 0 to +10δ

   More screened than TMS High Field Low frequency {Metal Hydrides} 0 to -10δ

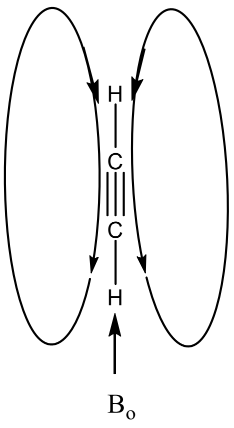
Factors affecting chemical shift:

1. Electronegativit/inductive effect

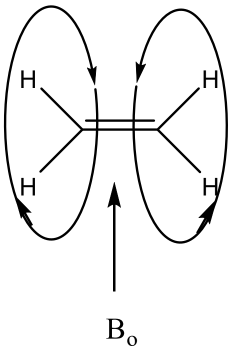
   Higher the electronegativity, higher the deshielding, higher the chemical shift δ and *vice-versa*.
2. Hybridization

   The deshielding of hybridized carbon is in the order $sp > sp^2 > sp^3$ hence higher the δ
3. Magnetic Anisotropic effect

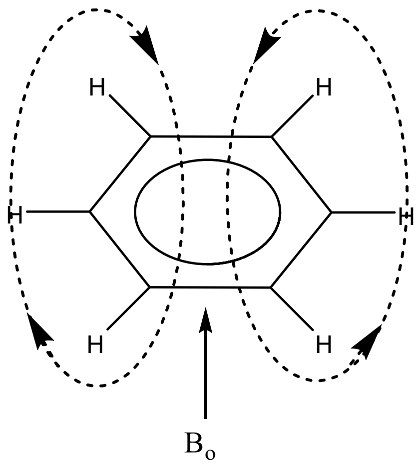
   Acetylinic protons shielded and lower δ values; olefinic protons are deshielded and higher δ values; aromatic protons are deshielded and higher δ values Hydrogen bonding; aldehydic proton deshielded and higher δ values



acetylinic shielded



olefinic deshielded

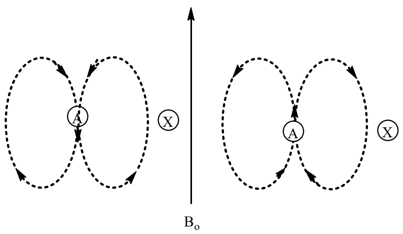


aromatic ring current deshielding

4. van der Waals deshielding
5. Hydrogen bonding deshielding and higher δ values

Coupling:
The interaction between two magnetically active nuclei is called coupling or interaction. There are two distinct types of magnetic interaction (coupling) between nuclei (A and X) with a non-zero spin - the direct interaction (dipole-dipole coupling: *D*) and the indirect or scalar coupling (spin-spin splitting: *J*).

1. Direct dipolar coupling (D): Any two hydrogen nuclei in different parts of a solid are sufficiently close together in space would exert an appreciable magnetic effect on each other. It is called direct or dipole-dipole coupling. (Shown in Fig.)

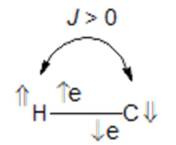


This type of coupling occurs for X in turn.

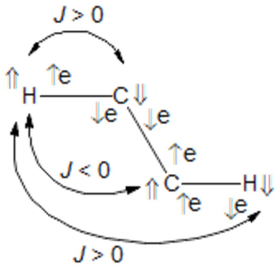
2. Scalar Coupling (J-coupling / indirect coupling):

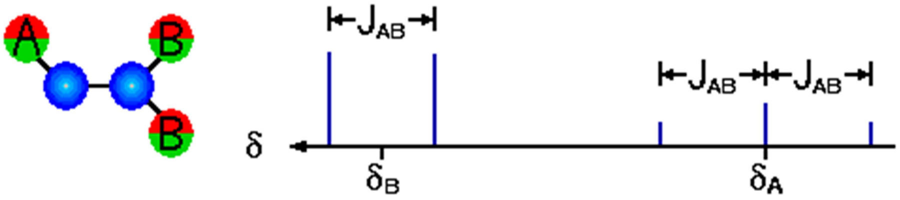
   Nuclei experiencing the same chemical environment or chemical shift are called equivalent. Those nuclei experiencing different environment or having different chemical shifts are non-equivalent. If the distance between non-equivalent nuclei is less than or equal to three bond lengths, this effect is observable. This effect is called spin-spin coupling or J – coupling or scalar coupling.

   The spin of one nucleus perturbs (polarizes) the spins of the intervening electrons, and the energy levels of neighboring magnetic nuclei are in turn perturbed by the polarized electrons. This leads to a lowering of the energy of the neighboring nucleus when the perturbing nucleus has one spin, and a raising of the energy whenwhen it has the other spin. The J coupling (*always* reported in Hz) is field-independent (i.e. J is constant at different external magnetic field strength), and is mutual (i.e. $J_{AX} = J_{XA}$). Because the effect is usually transmitted through the bonding electrons, the magnitude of J falls off rapidly as the number of intervening bonds increases. Coupling over one (^1J), two (^2J) and three (^3J) bonds usually dominates the fine structure of NMR spectra.



Positive one-bond coupling constant

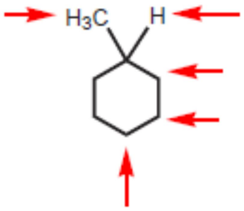




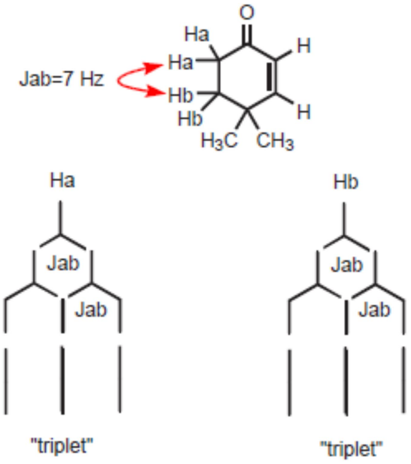
Multiplicity and Spin-Spin Splitting:

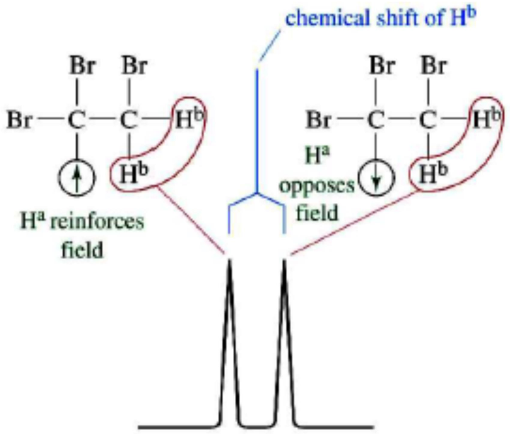
Each signal in a proton NMR spectrum may or may not be split into one or more peaks. This is called signal multiplicity and gives rise to names such as singlet, doublet, triplet, quartet, pentet, and multiplet. The most common concept associated with signal multiplicity is the n+1 rule. According to this rule, the signal for the proton under observation will be split into n+1 peaks by protons attached to adjacent carbons, where n is the number of such protons.

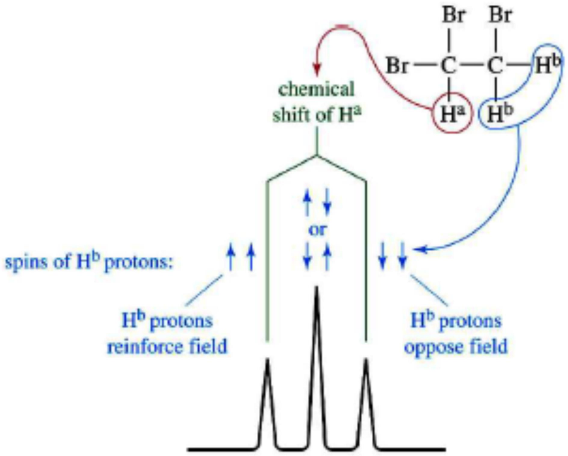
1 signal



5 signals







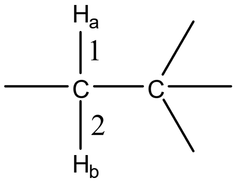
#of lines	ratio of lines	Term for peak	# of neighbors
1	-	singlet	0
2	1:1	doublet	1
3	1:2:1	triplet	2
4	1:3:3:1	quartet	3
5	1:4:6:4:1	quintet	4
6	1:5:10:10:5:1	sextet	5
7	1:6:15:20:15:6:1	septet	6
8	1:7:21:35:35:21:7:1	octet	7
9	1:8:28:56:70:56:28:8:1	nonet	8

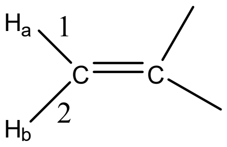
Coupling Constants:
The coupling constant is simply the difference, expressed in Hz, between two adjacent sub-peaks in a split signal.
For our doublet in the 1,1,2-trichloroethane spectrum, for example, the two subpeaks are separated by 6.1 Hz, and thus we write $^3J_{a\text{-}b} = 6.1$ Hz.

Factors affecting Coupling Constants:
Through bond distances between the coupling proyons
Angle between two C-H bonds
Electronegative substituents

Geminal proton-proton coupling ($^2J_{HH}$)

Germinal coupling generates through two bonds (Fig). Two proton having geminal coupling are not chemically equivalent.



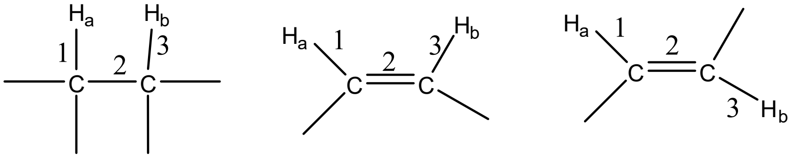


This coupling ranges from -20 to 40 Hz. $^2J_{HH}$depends on hybridization of carbon atom and the bond angle and the substituent such as electronegative atoms. When S-character is increased, Geminal coupling constant is increased : $^2J_{sp1}>^2J_{sp2}>^2J_{sp3}$ The bond angle(HCH) gives rise to change $^2J_{HH}$ value and depend on the strain of the ring in the cyclic systems. Geminal coupling constant determines ring size. When bond angle is decreased, ring size is decreased so that geminal coupling constant is more positive. If a atom is replace to an electronegative atom, Geminal coupling constant move to positive value.

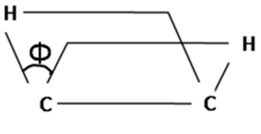
Vicinal proton-proton coupling ($^3J_{HH}$)

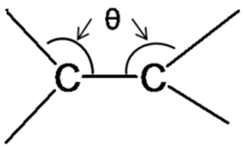
Vicinal coupling occurs though three bonds (Fig). The Vicinal coupling is the most useful information of dihedral angle, leading to stereochemistry and conformation of molecules. Vicinal coupling constant always has the positive value and is affected by the dihedral angle ($\angle$HCCH), the valence angle ($\angle$HCC), the bond length of carbon-carbon, and the effects of electronegative atoms. Vicinal coupling constant depending on the dihedral angle (Fig) is given by the Karplus equation.

$$^3J = 7.0 - 0.5cos\phi + 4.5cos^2\phi$$



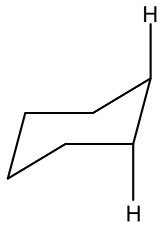
vicinal coupling $^3J_{H.H}$



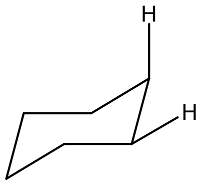


$^3J_{HH}$ is affected by φ and ϑ

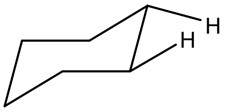
The coupling constant increases with the decrease of bond length. Electronegative atoms affect vicinal coupling constants so that electronegative atoms decrease the vicinal coupling constants. When the dihedral angle is 90°, the coupling is small. When the dihedral angle is 0° or 180°, the coupling is large. In general 180° gives a larger coupling than 0°Fig for ethane:



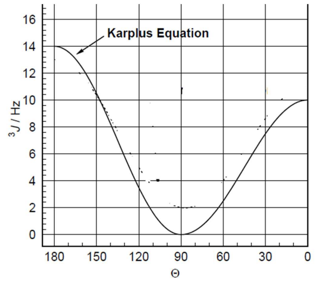
$^3J_{a,a} = 8 - 13$ Hz



$^3J_{a,e} = 1 - 6$ Hz



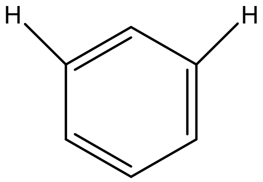
$^3J_{e<e} = 0 - 5$ Hz



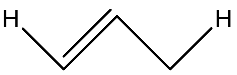
Long-Range (^{4} J and higher) Proton-Proton Couplings

^nJ; n>3 occur in rigid structures; alkenes, alkynes, aromatics, stained rings.

Proton-proton couplings over more than three bonds are usually too small to detect easily (< 1 Hz). However, there are a number of important situations where such couplings are present, and can provide useful structural information. Coupling across π-systems are the most frequently encountered 4 J couplings: the meta-coupling in aromatic compounds, and the 4-bond allylic, propargylic and allenic couplings. 4-Bond couplings across saturated carbons (sp3) or heteroatoms are rarer, and are usually seen only when there is a favorable geometric alignment along the H-C-C-C-H chain ("W-Coupling"). Longer range couplings (5 J and higher) are also observed, particularly in acetylenes and allenes

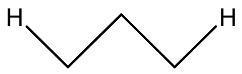


$^4J = 2$ to 3 Hz



allylic

$^4J = -3$ to +3 Hz



W - coupling

$^4J = -1$ to +3 Hz

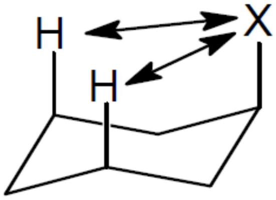
Chemical Shift and Stereochemistry:

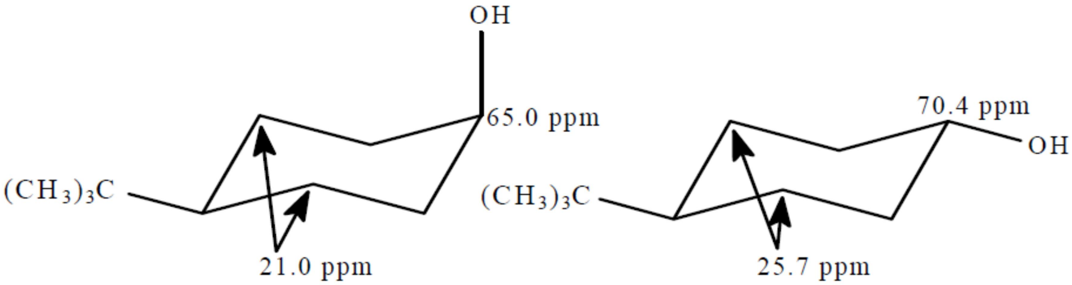
Chemical shift to a larger or lesser extent depends on stereochemical factors.

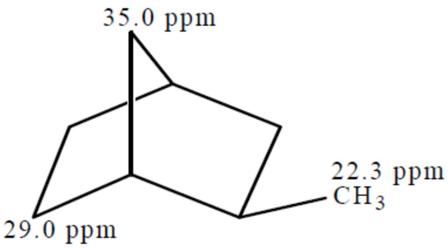
Steric effects

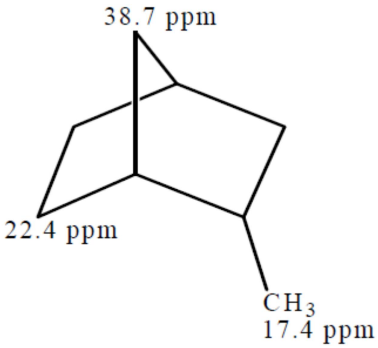
^{13}C chemical shifts are sensitive to molecular geometry. Carbons separated by several bonds s influence each other if they are spatially close.

γ-effect:

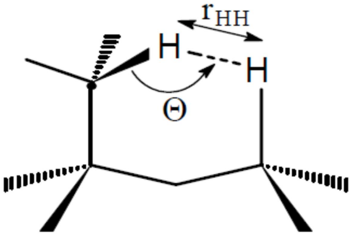








Upfield shifts are observed in all cases where the stereochemistry leads to van der Waals interactions of the type indicated above. In rigid molecules this effect can be as large as 10 ppm. Smaller γ effects are observed if there is free rotation about the C–C bonds. For X=CH_3:

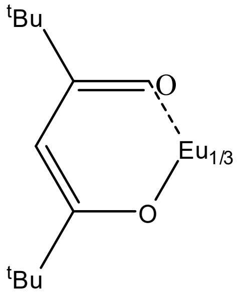


$\Delta\delta_{st} \sim F_{HH}(r)\cos\Theta$ {$F_{HH}(r)$ - the repulsive force between the protons}

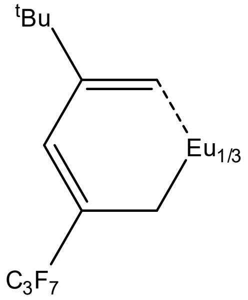
Depending on Θ, $\Delta\delta_{st}$ can have positive or negative values.

Chemical shift reagents:

Chemical shift reagents are organic complexes of paramagnetic rare earth metals from the lanthanide series. Of the lanthanides, europium is probably the most commonly used metal. Two of its widely used complexes are Tris (dipavalomethanato) europium and tris-(6,6,7,7, 8,8,8- heptafluoro-2,2-dimethyl-3,5-octanedionato) europium, frequently abbreviated Eu(dpm)3 and Eu(fod)3, respectively



$Eu(dpm)_3$



$Eu(fod)_3$

The Eu^{3+}-ion induces a spreading of the chemical shifts over a wider range according to the McConnell-Robertson equation

- The strength of the effect of the chiral shift reagent depends on:
  - The nature of the NMR shift reagent (metal and ligand)
  - The concentration of the NMR shift reagent
  - The proximity of the hydrogen atom to the metal ion
  - The solvent because it determines how strong the molecule is coordinated to the metal center
  - The temperature

When such metal complexes are added to the compound whose spectrum is being determined, there is a profound shifts in the various groups of protons. The direction of the shift (up field or downfield) depends primarily on which metal is being used. Complexes of europium, erbium, thulium and ytterbium shift resonances to lower field, while complexes of cerium, praseodymium, neodymium, samarium, terbium, and holmium generally shift resonances to higher field.

Interaction of chemical shift reagents: These lanthanide complexes interact with a relatively basic pair of electrons (an unshared pair) which can coordinate with Eu+3. Typically, aldehydes, ketones, alcohols, thiols, ethers and amines all interact.

The amount of shift a given group of protons experiences depends on the distance separating the metal (Eu^{3+})and that group of protons and the concentration of shift reagent in the solution. Hence it is necessary to include the number of mole equivalents of shift reagents used or its molar concentration when reporting a lanthanide shifted spectrum.

E.g:The spectra of 1- hexanol: In the absence of shift reagent, the spectrum shown Only the triplet of the terminal methyl group the triplet of the methylene group next to the hydroxyl are resolved in the spectrum. The protons (aside from O-H) are found together in a broad, unresolved group. With the shift reagent added each of the methylene groups is clearly separated and is resolved into proper multiplet structure.

Advantages of using chemical shift reagents - gives spectra which are much easier to interpret. No chemical manipulation of the sample is required with the use of shift reagents. more easily obtained.

Disadvantage shift reagents cause a small amount of line broadening At high shift reagent concentrations this problem becomes serious, but at most useful concentrations the amount of broadening is tolerable.

Chemical spin decoupling of rapidly exchangeable protons (OH, SH, COOH, NH, NH_2)

OH, NH protons are exchangeable (fast in NMR scale – no coupling, single peak or merged into background). The acidic H signal broadens, do not undergo coupling. H-N would couple to (3J) adjacent protons.
OH, SH, NH, H- bonded a. intermolecular (δ - solvent, concentration, temperature dependent) b. intramolecular
^{14}N (I=1, nuclear quadrupole interacts, lowers lifetime of H excited states, single broader peak or merged into bkg.)

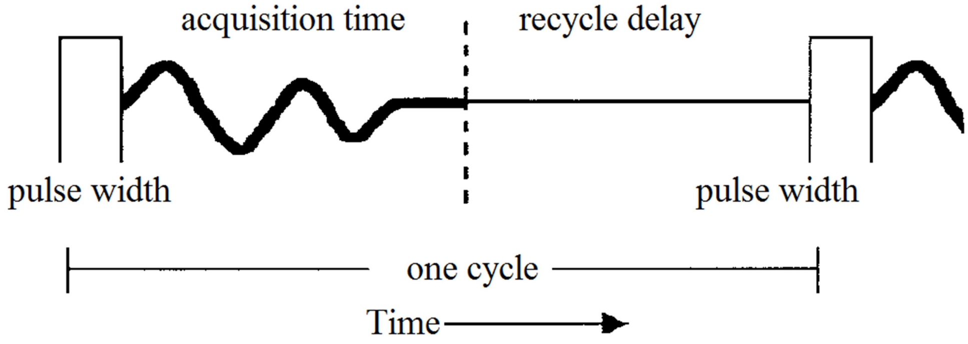
Detection of acidic (exchangeable) protons Acidic protons can be exchanged with deuterium ions. Mixing a compound with D_2O achieves this task. The H-NMR spectrum of the exchanged product would be absent of the acidic H peak. The exchanged product is HOD, the H of which appears at 4.7ppm as a single peak.

Carboxylic Acids. Most carboxylic acids are strongly hydrogen bonded in non-polar solvents, and the OH protons are correspondingly downfield shifted. Acetic acid dimer in Freon solvent (CDClF2/CDF3) at 128 K appears at δ 13.04, and the OH signals of acetic acid hydrogen bonded to a protected adenosine under conditions of slow exchange appear at even lower field

Amine N-H Protons. NH_2 protons of primary alkyl amines typically appear as a somewhat broadened signal at δ 1-2 in $CDCl_3$. The broadening is in part due rapid intermolecular exchange, and in part because of partially coalesced coupling to the quadrupolar 14N nucleus (I = 1), which usually has a short T_1. In the example below, the CH_2 group bonded to amino (δ 2.82) shows no sign of coupling to the NH_2 protons.

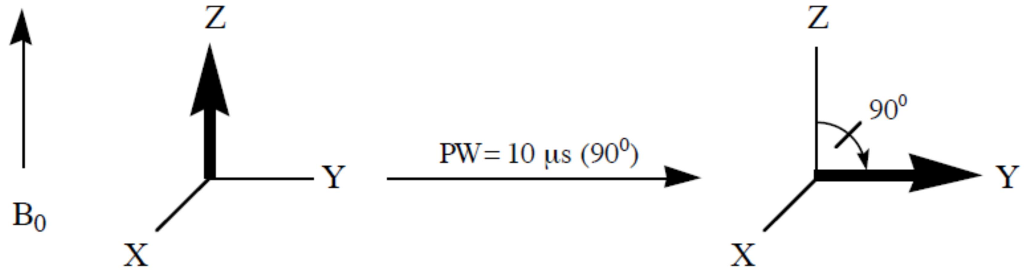
FT – NMR and its importance

In 1D pulsed FT-NMR a powerful, but short burst of energy, called pulse is used to excite all the magnetically active nuclei in a molecule simultaneously. Then the intensity of emission is measured with time and resolved to normal intensity vs frequency spectrum. The most basic and common pulse sequence in routine ^1H and ^{13}C acquisitions is as follows:



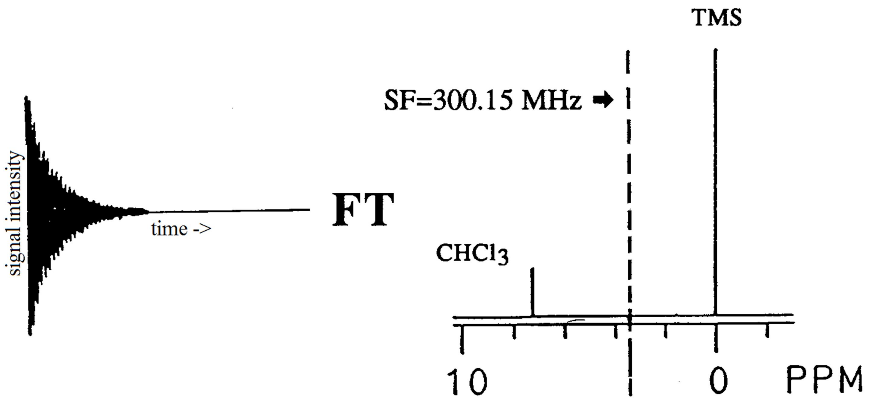
    1. Spectrometer Frequency [sfrq]
    2. Pulse Width [pw]
    3. Acquisition Time [at]
    4. Number of Points [np]
    5. Sweep Width [sw]
    6. Recycle Delay [d1]

1. The radio pulse that excites all the nuclei with different Larmor precessional frequency, has a characteristic frequency, called the spectrometer frequency (200 MHz/300 MHz, etc.)
2. Pulse width: The majority of nuclear spins are aligned parallel to the static magnetic field (B_0). The axis of alignment is typically designated the Z-axis and the bulk magnetization is shown as a bold arrow. Application of a short Rf pulse at the appropriate frequency will rotate the bulk magnetization by a specific angle. Pulses are generally described by this angle of rotation (also called flip angle). The angle of rotation is dependent on the intensity of the pulse (tpwr) and the width of the pulse (pw). The maximum measurable signal can be recorded following a 90º rotation or pulse. Thus, a 90º pulse width is defined as the amount of time the pulse of Rf energy is applied to the particular sample in order to flip the bulk magnetization from the Z-axis precisely into the X-Y plane.



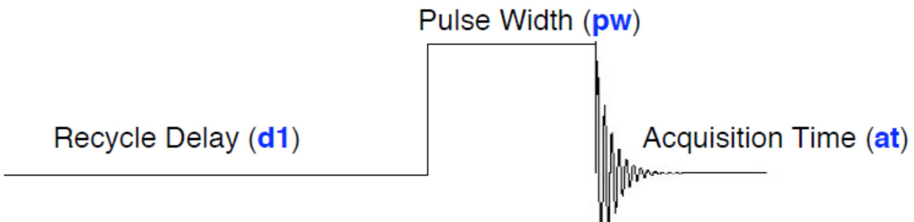
3. The nuclear spins are no longer at equilibrium and will eventually return to equilibrium along the Z-axis when the Rf pulse is cut off (after 10 μs). During this process the emitted energy (relaxation by emitting radiation) is measured with time as the signal dies off. It is in the form of decaying sine wave. The decaying sine wave represents this process of Free Induction Decay (FID), which is a plot of emitted radio intensity as a function of time. The time it takes to acquire the FID is called the acquisition time.
4. Number of points: the spectrometer represents the FID by a series of points on the FID curve. The ADC converts analog FID to FID envelope. It is called *time domain spectrum.*

5. The Fourier Transformation converts the time domain spectrum into a frequency domain spectrum, mathematically. Frequency domain spectrum has two characteristics, viz., spectrometer frequency and spectral width, erroneously called sweep width.

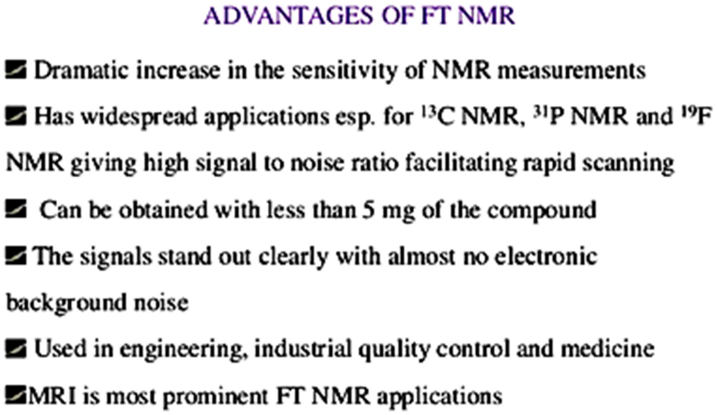


The sweep width (sw), number of points (np), and the acquisition time (at) are related by the following equations:
at = np / 2sw;
res = 1/ at = 2sw / np

6. The time for complete relaxation to equilibrium for all magnetically active nuclei in order to repeat the above process is called delay time.



Schematic representation of one pass of a simple '1-PULSE' pulse sequence.



ADVANTAGES OF FT NMR

- Dramatic increase in the sensitivity of NMR measurements
- Has widespread applications esp. for ^{13}C NMR, ^{31}P NMR and ^{19}F NMR giving high signal to noise ratio facilitating rapid scanning
- Can be obtained with less than 5 mg of the compound
- The signals stand out clearly with almost no electronic background noise
- Used in engineering, industrial quality control and medicine
- MRI is most prominent FT NMR applications

<u>Nuclear Overhauser Effect:</u>

➢ Consider a two channel experiment where one channel excites a spin X and the other saturates a spin A.

➢ Assume the spins X and A are spatially close enough to have a dipole-dipole coupling (the through-space interaction) and there is no spin-spin coupling (i.e. scalar coupling) among X and A.

- This experiment leads to the enhancement of the signal from spin X. This phenomenon is known as the Nuclear Overhauser Effect (NOE).

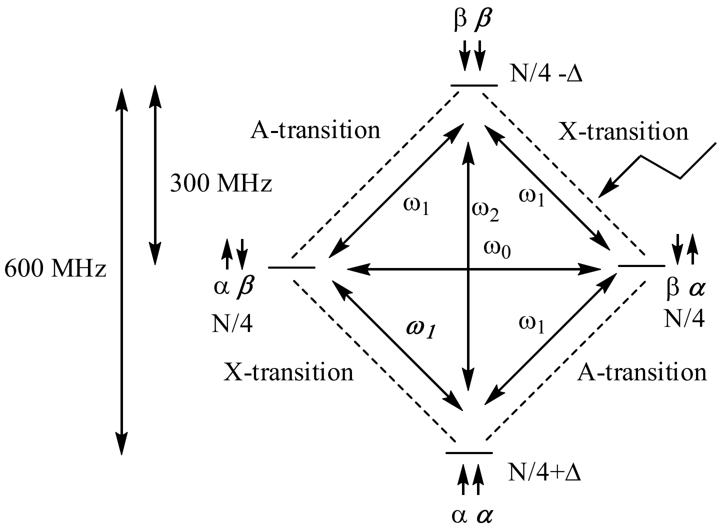
- This enhancement is due to the change in relative populations of the energy levels brought about by the saturation of A spins and the subsequent relaxation processes.

The NOE effect occurs through space and is operational within a ~5Å sphere centered around the irradiated nuclei ("NOE range").
It does not enhance resonance signals away from "range" from the irradiated 'centre'.
NOE allows determination of the proximity of the nuclei to the irradiated ones, thus is an excellent technique to ascertain the inter-proton distances/stereochemistry of molecules.
Consider a pair of protons **AX**, close in space. Such a system has four energy states, corresponding to the αα, αβ, βα, and ββ spin states

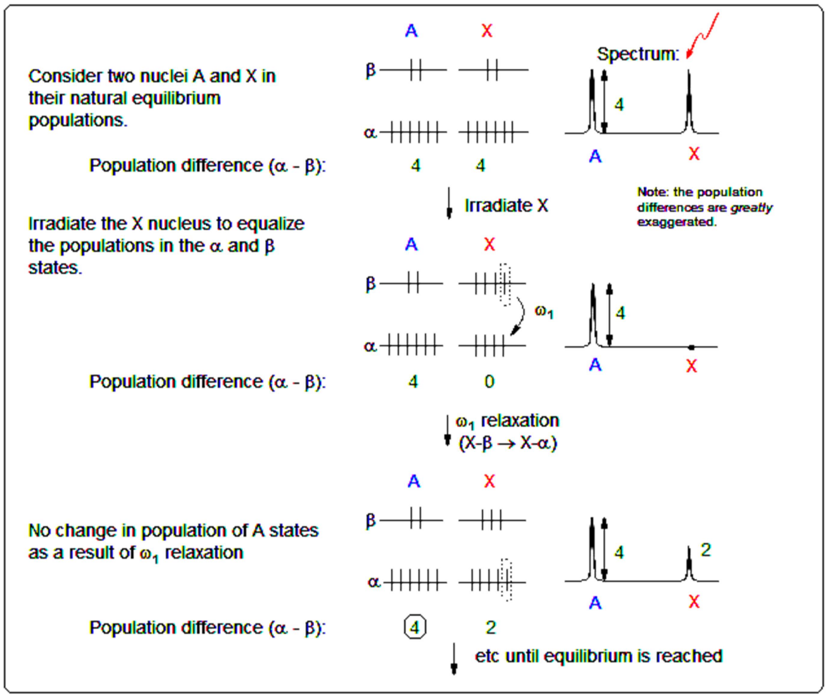
The DD interaction (dipole-dipole interaction) of the protons will cause T_1 relaxation between the spin states with the transition probabilities ω_1 (for the single quantum relaxation αα/αβ, αα/βα, αβ/ββ and βα/ββ), ω_2 (for the double-quantum relaxation αα/ββ) and ω_0(for the zero-quantum relaxation αβ/βα).

The ω_1 process simply re-establishes the normal population difference between the α and β states for the X nucleus. A is not affected.

- Now consider the situation when either the ω_0 or the ω_2 processes are the only ones operative. In the ω_0 process, the dipolar interaction between A and X causes an A nucleus to undergo an α → β transition when the X nucleus relaxes from β → α (αβ → βα). The net result is that as X returns to its normal population difference, it lowers the population difference for A. Thus, as the X intensity decreases, the A intensity decreases. If X is irradiated continuously then the signal for A will vanish (-100% NNOE). **This is a negative NOE.**



ω – transition probability
ω_0 – zero quantum
ω_1 – single quantum
ω_2 – double quantum
N - total no. of nuclei
Δ - excess population in the ground state



Consider two nuclei A and X in their natural equilibrium populations.

Population difference (α - β): 4 4

Note: the population differences are *greatly* exaggerated.

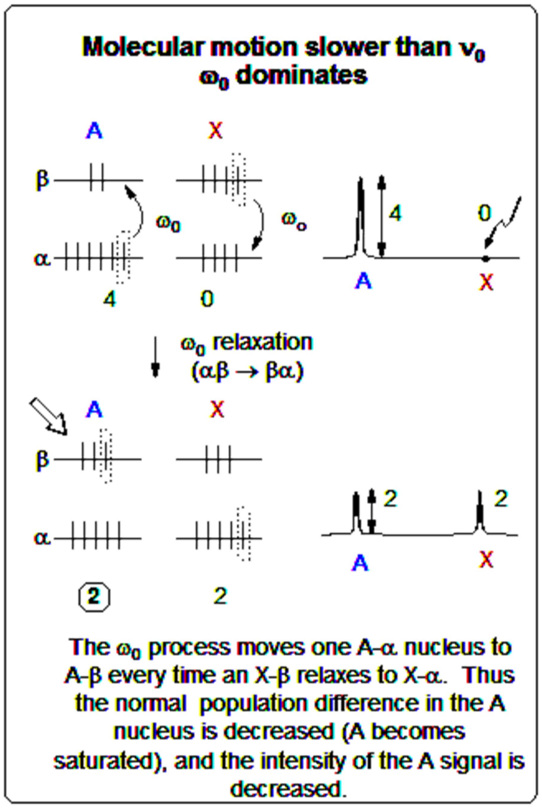
Irradiate the X nucleus to equalize the populations in the α and β states.

Population difference (α - β): 4 0

No change in population of A states as a result of ω_1 relaxation

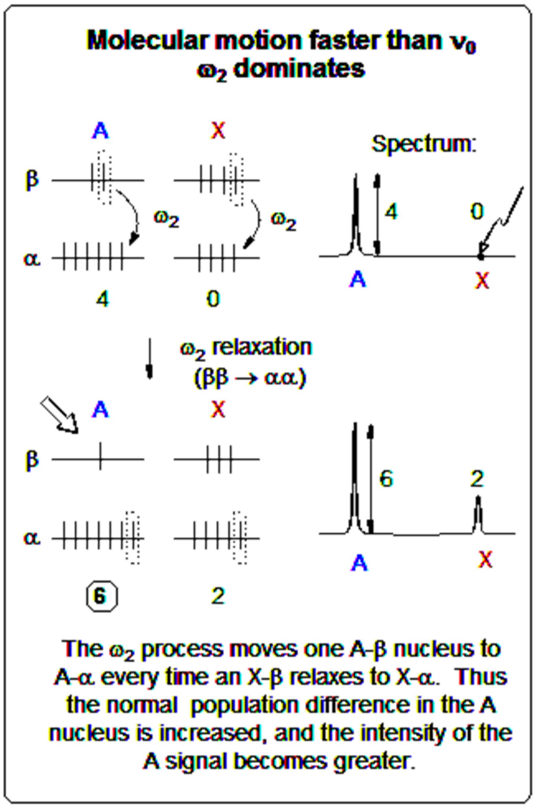
Population difference (α - β): ④ 2

etc until equilibrium is reached



Molecular motion slower than ν_0
ω_0 dominates

The ω_0 process moves one A-α nucleus to A-β every time an X-β relaxes to X-α. Thus the normal population difference in the A nucleus is decreased (A becomes saturated), and the intensity of the A signal is decreased.



Molecular motion faster than ν_0
ω_2 dominates

The ω_2 process moves one A-β nucleus to A-α every time an X-β relaxes to X-α. Thus the normal population difference in the A nucleus is increased, and the intensity of the A signal becomes greater.

For the ω₂ process, each time an X nucleus relaxes from β to α state, and A nucleus also undergoes a β to α transition (ββ → αα). This has the effect of increasing the population difference of A, i.e. an increase the area of A. **This is a positive NOE**. The phenomenon has sometimes been referred to as *spin pumping* - changing the population difference of X pumps A spins either from α to β or β to α.

$$NOE_{max} = \frac{1}{2}\left(\frac{\gamma_{irr}}{\gamma_{obs}}\right)$$

$Predicted\ intensity = 1 + NOE_{max}$

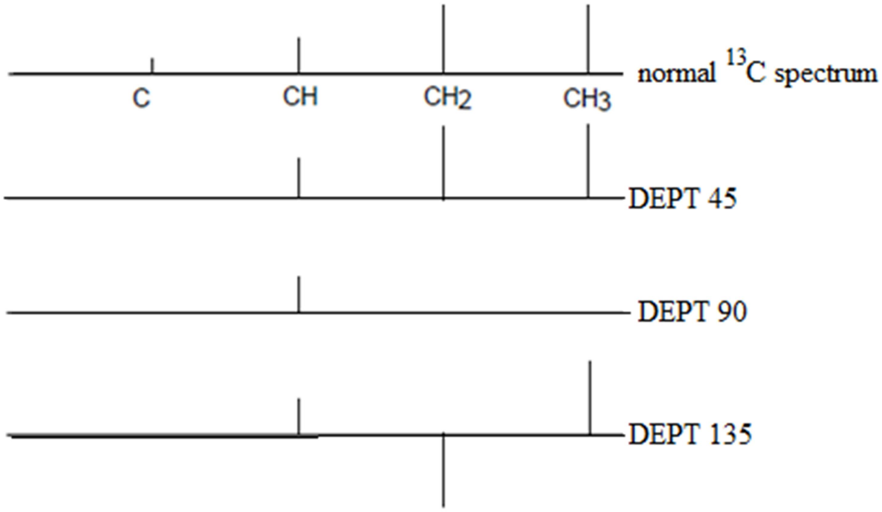
Explanation of DEPT spectra:

The aim - to increase sensitivity by transferring favourable NMR properties of the proton to another nucleus.

- DEPT is an acronym for ***D***istortionless ***E***nhancement by ***P***olarization ***T***ransfer. The result of this experiment is used for determining the presence of primary (methyl - CH_3), secondary (methylene - CH_2), tertiary (methine - CH) and quaternary carbon atoms.
- DEPT is a 1D experiment, but unlike decoupling and NOE, it involves a multiple pulse sequence. The experiment also requires that both protons and carbons are excited by the pulses.
- There are three types of DEPT spectra that can be acquired. They are noted by numbers.
- DEPT-45 (π/4) will give a positive1 signal for any carbon with an attached proton.
- DEPT-90 (π/2) spectra will give a positive signal for methine carbons.

- DEPT-135 ($3\pi/4$) spectra will give positive signals for methine and methyl carbons, and negative signals for methylene carbons.
- By a linear combination of these three spectra and the normal ^{13}C spectrum, the multiplicities of all of the carbons in a molecule may be determined.
- The example spectra below show the appearance of each type of carbon in the different DEPT spectra.
- DEPT- 45^o : CH, CH2 and CH3 peaks (all in positive phases); no quaternary carbons visible.
- DEPT - 90^o : CH peak only
- DEPT - 135^o : CH, CH2 and CH3 peaks (CH2 peak in negative phase)

- DEPT- 45^o - DEPT - 135^o = a subspectrum of just CH_2 peaks
- DEPT- 45^o + and 135^o = a subspectrum of CH and CH_3 peaks
- The 90^o subspectrum contains only the CH peaks,
- DEPT- 45^o + and 135^o - DEPT - 90^o = a subspectrum of CH_3 peaks.



Double Resonance Technique (Decoupling)

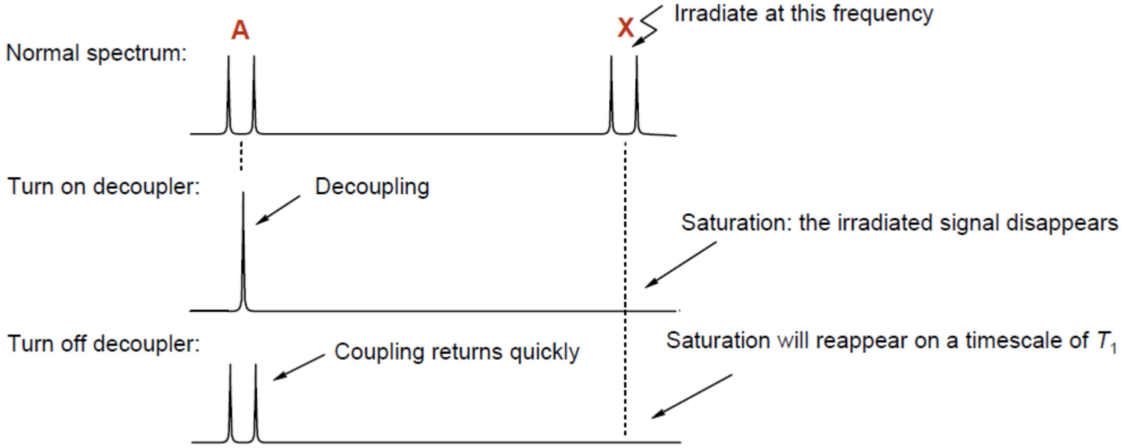
Decoupling is the process of removing specific kinds of J-coupling interactions in order to simplify a spectrum or identify which pairs of nuclei are involved in the J-coupling

In order for spin coupling to occur the life time τ_1 must satisfy the following condition: $\tau_1 > 1/J$ (s)

In order to prevent coupling between nuclei one needs to shorten the life time τ1. This can be achieved by simultaneously irradiating the nucleus to be decoupled by a second frequency ν2. Irradiation will saturate the particular nucleus.

In this technique the multiplets are merged back into a singlet by removing the spin-spin coupling between spins. This technique involves the irradiation of a proton or a group of equivalent protons with sufficiently intense radio- frequency energy to eliminate completely the observed coupling to the neighbouring protons.

When a proton is irradiated transitions between α and β states are induced, and the populations of the two states will tend to be equalized. The rate at which this occurs is a function of the strength of the decoupling field, but will in general be faster than *T*1 relaxation. If the field is powerful enough (i.e., if the induced transitions greatly exceed the rate of normal *T*1 relaxation), the populations of the α and β states will become identical and the signal will disappear (become *saturated*). If the decoupler is turned off, normal signal intensity will return as a function of *T*1 (the coupling will return to normal on a much shorter time scale).



Classification of Decoupling:

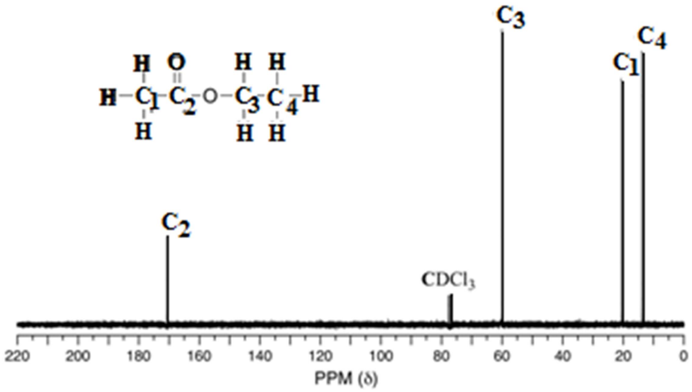
1. Homonuclear ($^1H - {}^1H$)

2. Heteronuclear ($^1H - {}^{13}C$)
3. Selective (Selective decoupling is accomplished by a very long pulse centered at the Larmor frequency of the signal of interest. Selective excitation of one signal or spin in an NMR spectrum leads to multiplate collapse and simplification of the spin- spin splitting patterns of the signals from the nuclei.)
4. **Broad Band Decoupling**

   Broadband decoupling is used in order to eliminate the coupling between two nuclei completely. For example, broadband ^1H decoupling while acquiring ^{13}C spectrum leads to singlets for each ^{13}C environment and a substantial increase in the sensitivity of the experiment.

   The resonances due to ^{13}C nuclei are split by neighbouring ^1H atoms. These splittings would complicate the appearance of the spectra making them harder to interpret. Therefore, in a "normal" ^{13}C spectra, these couplings are "removed" by applying a continuous second radio frequency signal of a broad frequency range that excites all the ^1H nuclei and cancels out the coupling patterns due to the interaction of the ^1H with the ^{13}C. This means that each ^{13}C is seen as a single line. Of course information is being lost by doing this, such as how many

^{1}Hs are attached to each ^{13}C. The convenient notation ^{13}C-{^{1}H} can be used to identify proton decoupled ^{13}C - NMR spectra; in the same way ^{31}P-{^{1}H} spectra are phosphorus-31 NMR spectra with all proton coupling to phosphorus removed by broad band or noise decoupling, and ^{15}N-{^{1}H} corresponds for nitrogen-15, etc. Ethyl acetate broad band nmr is shown below:

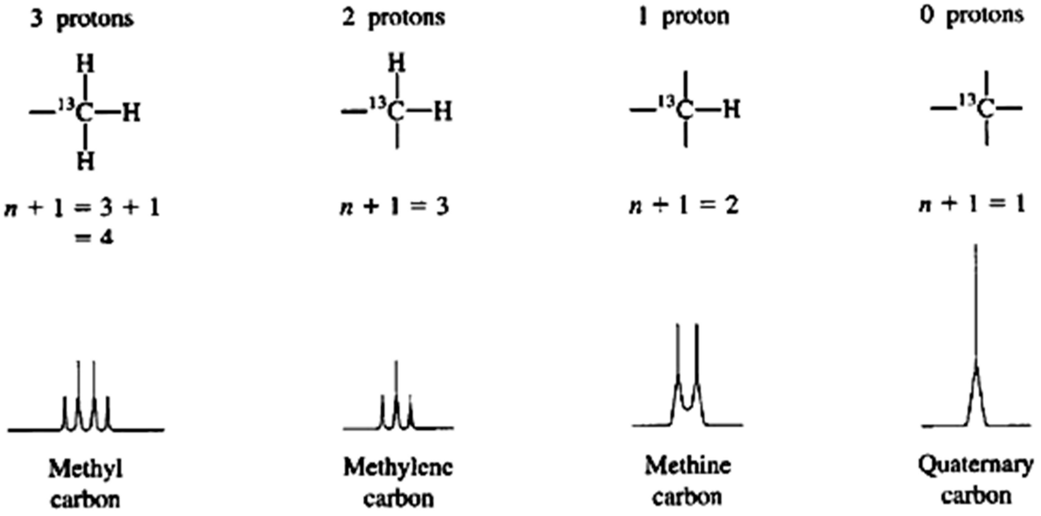


5. Gated broad band
6. Inverse gated broad band
7. **Off resonance**:
    - In an off resonance-decoupled ^{13}C spectrum, the coupling between each carbon atom and each hydrogen attached directly to it is observed. The n+1 rule can be used to determine whether a given carbon atom has three, two, one, or no hydrogen attached. However, when off resonance decoupling is used, the apparent magnitude of the coupling constants is reduced, and overlap of the resulting multiplets is a less frequent problem. The off-resonance-decoupled spectrum retains the couplings between the carbon atom and directly attached protons (the one-bond couplings) but effectively removes the couplings between the carbon and more remote protons.
    - Thus, a methine (CH) appears as a ***doublet*** no matter how many protons are on attached neighboring carbon atoms, a methylene (CH_2) appears as a ***triplet*** no matter how many protons are on attached neighbouring carbon atoms, and a methyl (CH_3)appears as a ***quartet*** and no matter how many protons are on attached neighbouring carbon atoms. If a carbon is not directly bonded to hydrogen [quaternary (C)], it appears as a ***singlet***.

- In this technique, the frequency of a second radiofrequency transmitter (the decoupler) is set either upfield or downfield from the usual sweep width of a normal proton spectrum (i.e. off resonance). In contrast, the frequency of the decoupler is set to coincide exactly with the range of proton resonances in a true decoupling experiment. Furthermore, in off resonance decoupling, the power of the decoupling oscillator is held low to avoid complete decoupling. The off resonance decoupled spectrum is usually obtained separately, along with the proton decoupled spectrum.

- Off resonance decoupled spectrum of 1-propanol, in which the methyl carbon atom is split into a quartet, and each of the methylene carbons appears as a triplet. The observed multiplet patterns are consistent with the n+1 rule. If TMS has been added, its methyl carbons would have appeared as a quartet centered at δ = 0 ppm.

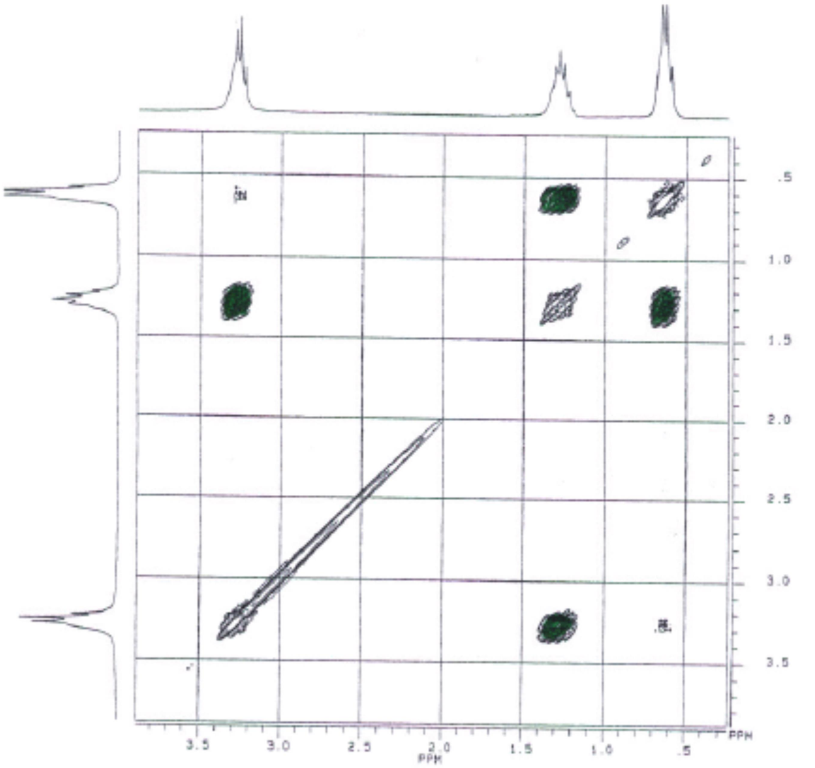
The 13C NMR spectra that we have signals which are "broad band decoupled" which means that all proton couplings have been removed.



8. Solvent suppression
9. Deuterium substitution

<u>COSY NMR Spectra</u> It is not intended that you tackle the theory behind two dimensional nmr spectra at this stage, but there is no reason why you cannot use the results of the technique! If a spectrum contains coupled resonances that are close together, the signals invariably become muddled to the point of not providing any useful information. In which case, a COSY spectrum may well provide the answer. Below is a brief summary of what happens in this type of experiment. The regular

pulse procedure for acquiring a spectrum is to have three different time intervals in each cycle of scans. The first interval is when nothing happens and the spins are allowed to settle to their natural distribution of states. The second is when a pulse of excitation energy is applied and the spins respond to the stimulus. The detector is then switched on and measurement is taken for a time t. The spectrum is obtained by transforming the data with respect to time t. In a 2D experiment, a series of spectra are collected where the time between stimulus and detection (t1) is increased by a small amount in each case. So not only can the spectra be transformed with respect to the detection time (t2) but also to t1. This results in a contour plot with the same (but rather crudely resolved) spectrum along each of two axes and a diagonal (bottom left to top right usually) of the contours of the regular spectrum. The interest lies in the off-diagonal contours. Where correlation between coupled resonances exists, a contour should appear in both halves of the spectrum. Values of coupling constants cannot be determined by this method (unless certain conditions are applied) but the fact that two resonances are coupled can aid in the interpretation of the spectrum. Figure 2 shows a COSY spectrum of 1-propanol containing three resonances. One is coupled to the other two, but they are not coupled to each other. This is reflected in the size of the contours (ie how big the blobs are!). VI-3 Figure 3: HETCOR of 1-propanol C-H Correlated Spectra including HMQC, HSQC & HMBC Essentially, this type of spectrum is the same as a COSY, with the correlation between two different nuclei. This means that there is no diagonal, but the correlation is signified by intensity at the cross point. Figure 3 shows the HETCOR of 1-propanol. Modern instruments do the same experiment but using different pulse programs. HMQC and HSQC both look at the correlation over 1 J (ie direct coupling). If correlations over several bonds must be observed, a filter is used to remove all 1 J coupling of J>10 Hz. This is known as HMBC, or longrange HETCOR.



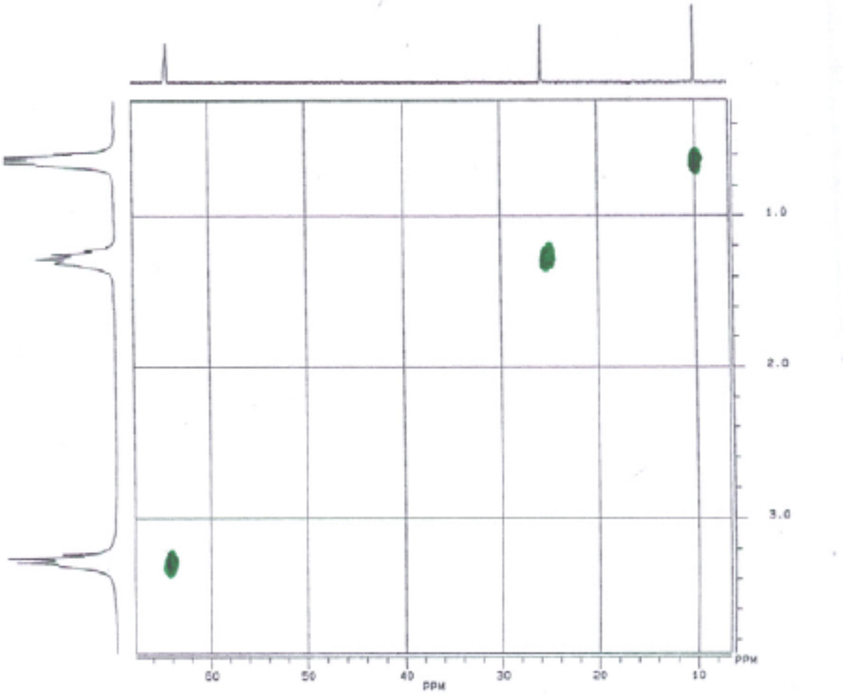


Figure 3: HETCOR of 1-propanol

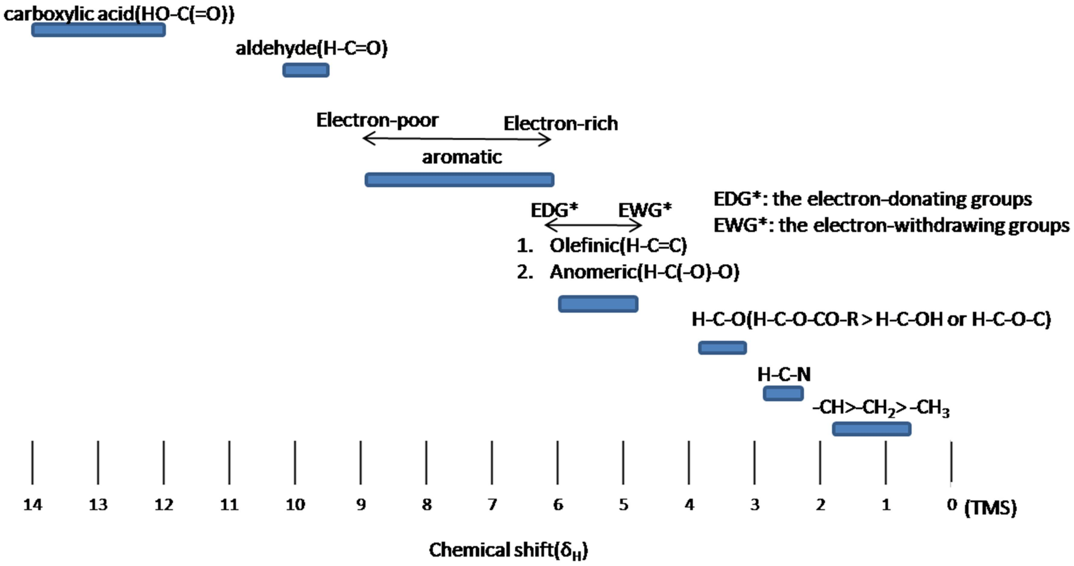
The Distortionless Enhancement by Polarization Transfer (DEPT) method is an instrumental mode that provides a way to acquire this information DEPT is an NMR technique for distinguishing among 13C signals for CH3, CH2, CH, and quaternary carbons

The DEPT method The DEPT methods uses a complex series ofʋ pulses in both the 1H and 13C ranges: a 45° pulse, a 90° pulse and a 135° pulse quaternary carbons give no signal 45° pul ll H se: all H-b i k iti bearing peaks are positiveʋ 90° pulse: only CH carbons are seenʋ 135° pulse: carbon signals show differentʋ phases signals for CH3 and CH carbons give positive signals signals for CH2 carbons give negative signals

Distortionless enhancement by polarization transfer (**DEPT**). is a **NMR** method used for determining the presence of primary, secondary and tertiary carbon atoms.

The 13C NMR spectra that we have signals which are "broad band **decoupled**" which means that all **proton** couplings have been removed. A number of assigned problems (13.24, 13.25, 13.26, 13.27, 13.28) give the multiplicity of the off resonance **decoupled** signals in parenthesis.

"off-resonance decoupling" in 13C NMR spectroscopy (p. 539 Carey). This technique removes all of the carbon-hydrogen coupling from a signal except those between nuclei that are directly bonded to one another. Thus, a methine (CH) appears as a doublet no matter how many protons are on attached neighboring carbon atoms, a methylene (CH2) appears as a triplet no matter how many protons are on attached neighboring carbon atoms, and a methyl appears as a quartet no matter how many protons are on attached neighboring carbon atoms. If a carbon is not directly bonded to a hydrogen, it appears as a singlet. The 13C NMR spectra that we have signals which are "broad band decoupled" which means that all proton couplings have been removed. A number of assigned problems (13.24, 13.25, 13.26, 13.27, 13.28) give the multiplicity of the off resonance decoupled signals in parenthesis. For example, in question 13.25c you are asked to identify the C4H10) isomer which has a 13 C NMR spectrum consisting of two signals, one at 31 ppm (quartet) and one at 69 ppm (singlet). From this information you can conclude that the signal at 31 ppm corresponds to the carbon atom of a methyl group and the signal at 69 ppm corresponds to a carbon atom with no hydrogens attached. The structure must be tert-butyl alcohol.



UV-Visible spectroscopy

Selection Rules for Electronic spectrum:

1. Spin Rule – Changes in spin multiplicity are forbidden
   Allowed Transitions: singlet → singlet; triplet → triplet
   Forbidden transitions: singlet → triplet; triplet → singlet
   Occurrence of singlet → trplet transition (inter system crossing) due to singlet state wavefunction containing a small fraction of triplet wavefunction and *vice-versa.*

2. Laporte rule: in an electronic transition there should be a change in parity (symmetry)
   g → u; u → g allowed
   g → g; u → u not allowed

- Light in the UV-VIS part of the spectrum (210 – 900 nm) is used to promote electrons from the ground state to various excited states.

- The transitions that result in the absorption of electromagnetic radiation in this region of the spectrum are transitions between electronic energy levels.

- Generally, the most probable transition is from highest occupied molecular orbital (HOMO) to lowest occupied molecular orbital (LUMO).

- The particular frequencies at which light is absorbed are affected by the structure and environment of the chromospheres (light absorbing species).

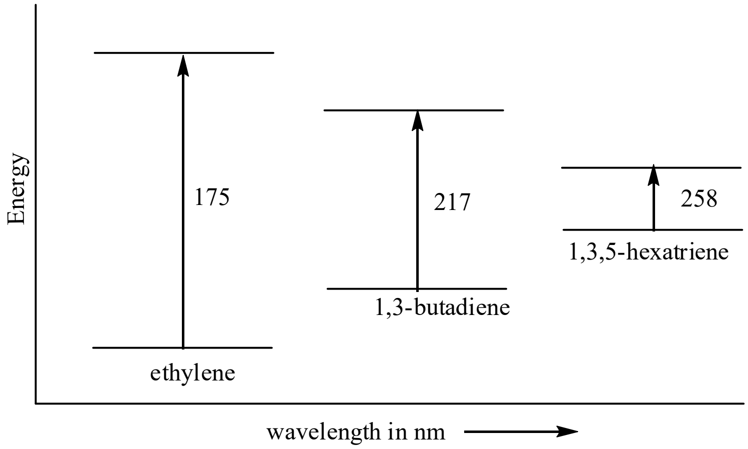
CHOMOPHORE. A covalently unsaturated group responsible for electronic absorption (for example, C=C, C=O, and NO2).

AUXOCHROME. A saturated group with nonbonded electrons which, when attached to a chromophore, alters both the wavelength and the intensity of the absorption

Bathochromic shift: (red shift): The shift of absorption to a longer wavelength due to substitution or solvent effect (a red shift).

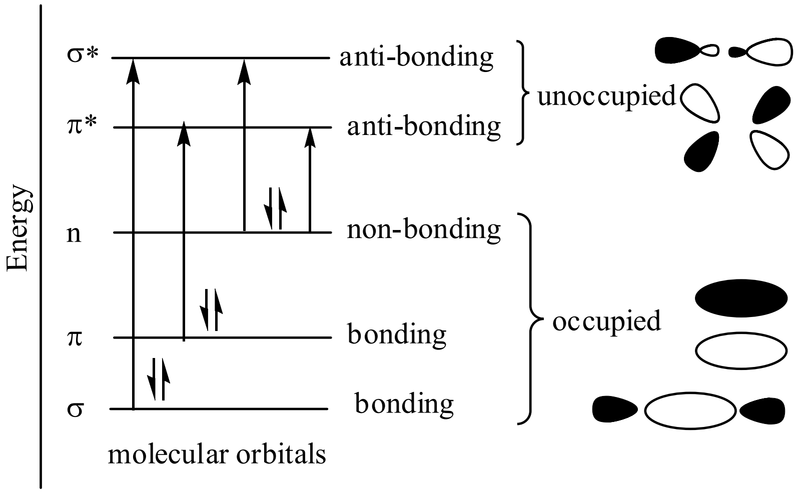
Hypsochromic shift: (blue shift): The shift of absorption to a shorter wavelength due to substitution or solvent effect (a blue shift).

Hyperchromic effect: An increase in absorption intensity.
Hypochromic effect: A decrease in absorption intensity.



Types of electronic transitions:

a. Transitions involving π, σ and *n* electrons (organics)
b. Transitions involving charge transfer (metal-ligand complexes)
c. Transitions involving *d* and *f* electrons (inorganic d – d)



$\sigma \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \sigma^* > n \rightarrow \pi^*$

~130 nm ~230 nm ~250 nm ~280 nm

C—C	C=C	C=O
σ σ*	σ σ*	σ σ*
	π π*	π π*
		n π*
		n σ*

σ→ σ* Alkanes
σ→ π* Carbonyl compounds
π →π* Alkenes, carbonyl compn, alkyne etc.
n→ σ* Oxygen, nitrogen, sulfur and halogen compounds
n →π* Carbonyl compounds

Introduction

Absorption of a particular wavelength of light depends upon the π-electron system of the molecule. The more the conjugation of the π-electron system within the molecule, the higher the wavelength of light it can absorb. Robert Burns Woodward and Louis Fieser put down a set of rules which allows one to calculate the wavelength of maximum absorption (λ_{max}) for a molecule empirically. These sets of rules to calculate the wavelength of maximum absorption or λ_{max} of a compound in the ultraviolet-visible spectrum, based empirically have been called the Woodward-Fieser rules or Woodward's-rules.

1. Conjugated Dienes and Polyenes

1. Woodward-Fieser Rules for Calculating the λ_{max} of Conjugated Dienes and Polyenes

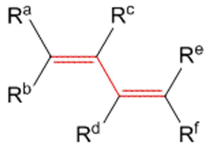
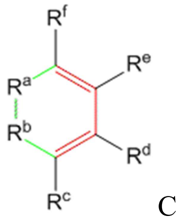
Conjugated dienes and polyenes are found in most organic compounds. For example, even a benzene ring is a conjugated polyene. Therefore it is useful to know how to utilize the **Woodward-Fieser rules** to calculate the wavelength of maximum absorption of conjugated dienes and polyenes.

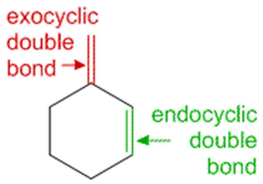
According to Woodward's rules the λ_{max} of the molecule can be calculated using a formula:

λ_{max} = ***Base value + Σ Substituent Contributions + Σ Other Contributions***

Here the base value depends upon whether the diene is a linear or heteroannular or transoid diene, or whether it is a cyclic or homoannular diene (each of these will be explained in greater detail below). The sum of all substituent contributions are added to the base value to obtain the wavelength of maximum absorption of the molecule.

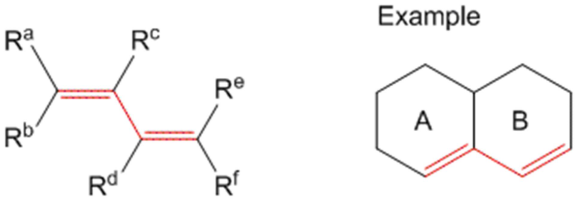
Table 1: Gives the values for the influence of different chromophores in conjugated diene systems as per Woodward-Fieser rules. The usage of these will become more evident in the examples which follow.

Class	**Chromophore**	**Influence to λ_{max}**
Core Chromophore	 Transoid/Heteroannular Diene	+ 215 nm
	 Cisoid/Homoannular Diene	+ 253 nm (***Note***– Some text books mention it to be + 260 nm)
Substituent Effects	-R (Alkyl group)	+ 5 nm
	-OR (Alkoxy group)	+ 6 nm
	-X (-Cl, -Br, -halogen)	+ 10 nm
	-OC(O)R (Acyloxy/Ester)	+ 0 nm

	-SR (Sulfide)	+ 30 nm
	-NR_2 (Amine)	+ 60 nm
	– C=C (double bond extending conjugation)	+ 30 nm
	– C_6H_5 (Phenyl group)	+ 60 nm
Other Contributors	 If Exocyclic Double Bond (and not Endocyclic Double Bond)	+ 5 nm
	Solvent Effects	Negligible

Core Chromophores With Base Values

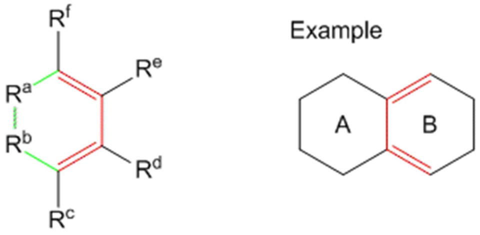
A. **Transoid Diene / Heteroannular diene / linear diene:** This type of diene generally involves the attachement of two trans dienes together. Since the two double bonds attached are trans, it leads to a linear diene which is also called a heteroannular diene as the diene cannot be placed within one ring system as it would cause the ring to become very unstable (5 – 6 carbon rings are most stable with very few exceptions). The base value for a heteroannular diene system is 215 nm according to the Woodward-Fieser rules. Examples of heteroannular dienes are shown below.



Transoid / Heteroannular Diene With an Example

In the above example, it can be seen that one of the double bonds belongs to ring A while the other double bond belongs to ring B, hence making the double bond heteroannular. Since both double bonds are trans with respect to substituents making the diene a transoid diene. In general, heteroannular dienes are transoid. If the diene is not a part of a ring then it is just transoid.

B. **Cisoid diene / Homoannular diene / cyclic diene:** This type of diene involves the conjugation of two cis dienes. Since the double bonds are cis to each other, the molecule often tends to form a closed ring system and therefore also called a cyclic or homoannular diene. The base value for homoannular diene system is 253 nm according to the Woodward-Fieser rules. Examples of homoannular dienes are shown below.



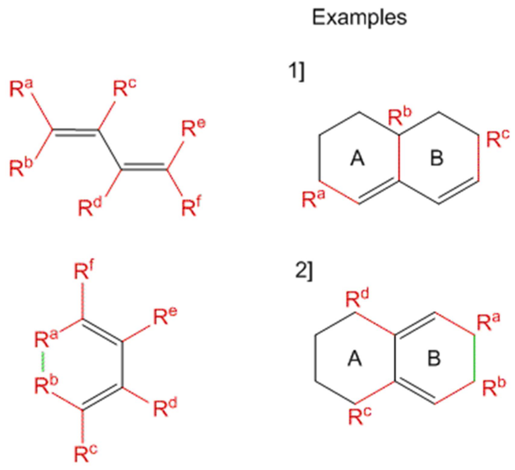
Cisoid / Homoannular Diene With An Example

In the above example, it can be seen that both the double bonds belong to ring B making this type of diene a homoannular diene. Since both double bonds are cis with respect to substituents making the diene a cisoid diene. In general, homoannular dienes are cisoid. If the diene is not a part of a ring (i.e. the green bonds do not exist) then it is just a cisoid diene.

Important Note- If a **molecule has both a homoannular diene and a heteroannular diene** the homoannular diene is taken as the core chromophore.

Substituent Effects

Only the substituents attached directly to the double bond diene systems can influence the ultraviolet visible absorption of the molecules. If the substituents are not directly attached to the carbons of the diene system, it will not affect the UV-Visible absorption spectrum of the molecule (as shown below).



The figure above highlights possible substituents in red given by the different -R groups. In the above examples 1 and 2, assignment of substituents must be given to all the atoms which are directly connected to the diene. Hence even though the structure has no substituents, the core carbon atoms have yet to be considered as alkyl-substituents. Hence in example 1, there are 3 alkyl substituents while in example 2, there are 4 alkyl substituents.

If one sees down the list of substituents an interesting factor in affecting the absorbance is whether the substituent directly has a heteroatom (with lone pairs) linked to the conjugated diene system. Below is the list of possible substituent effects.

Substituent	**Influence**
-R (Alkyl group)	+ 5 nm
-OR (Alkoxy group)	+ 6 nm
-X (-Cl, -Br, -halogen)	+ 10 nm
-OC(O)R (Acyloxy/Ester)	+ 0 nm
-SR (Sulfide)	+ 30 nm
-NR2 (Amine)	+ 60 nm

– C=C (double bond extending conjugation)	+ 30 nm
– C_6H_5 (Phenyl group)	+ 60 nm

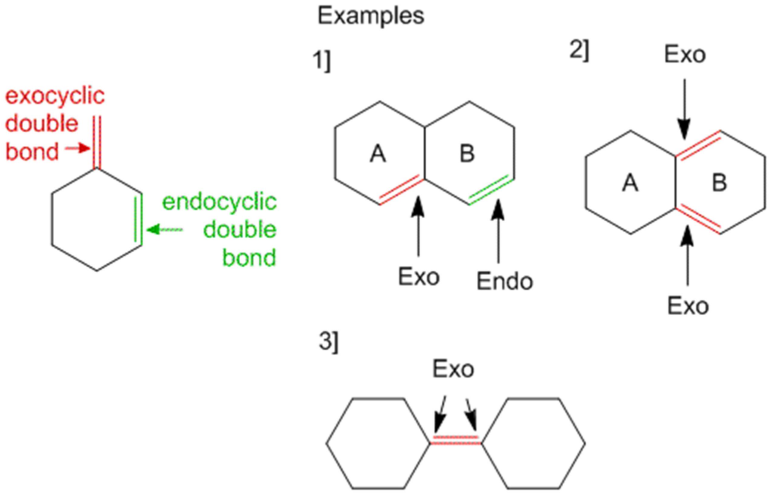
Important Note- In case of double bond extending conjugation the substituents on the extended double bond must also be counted for the calculation.

Other Contributors

1] Exocylcic Double Bonds

Exocyclic doube bond by definition is a double bond where one of the participating carbon atoms is a part of a ring, while the other carbon atom is not part of the same ring. From the name we can understand that exo-cyclic would stand for a double bond outside the ring and endo-cyclic would stand for a double bond within the ring.

For each exocyclic double bond, we must add +5 nm to obtain the λ_{max}. Below are a few examples as to what are exocyclic and what are endocyclic double bonds.

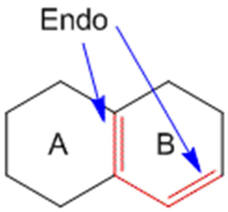


Examples of Exocyclic and Endocyclic Double Bonds

The above figure differentiates between exocyclic (shown in red) and endocyclic (shown in green) double bonds.

1. In example 1, the double bond present within ring A is exocyclic to ring B as it is attached to an atom which is shared between ring A and ring B, while the double bond present in ring B is not connected to any ring A atoms and is within just one ring, hence making it endocyclic.
2. In example 2, both double bonds are present within ring B with connections to shared carbon atoms with ring A, making both the double bonds exocyclic.
3. In example 3, there is a single double bond which is exocyclic at two points to two different rings. In such a case, the influence would be 2 times + 5 nm (i.e + 10 nm).

Note: Double bonds which are common to two rings are endocyclic. Below we give an example of a double bond which although has carbon atoms shared between two rings (A and B), it is considered endocyclic as at any given time the double bond will only belong to one ring.



2] Solvent effects
Since the conjugated diene base is relatively non-polar, contribution due to different solvents is very minor and can be ignored in most cases.

<u>λmax of Polyenes</u>

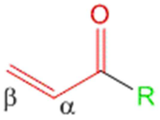
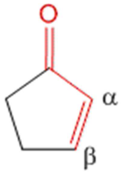
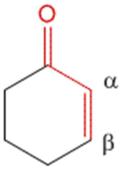
The Woodward's rules work well only for conjugated polyenes having four double bonds or less. For conjugated polyenes with more than four double bonds the Fieser- Kuhn rules are used.

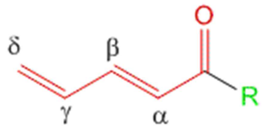
$\lambda max = 114 + 5M + n (48 - 1.7n) - 16.5 Rendo - 10 Rexo$

where n = no. of conjugated double bonds
M = no. of alkyl groups
Rendo = no. of endocyclic double bonds
Rexo = no. of exocyclic double bonds

Woodward-Fieser Rules for Calculating the λmax of Conjugated Carbonyl Compounds

Table 2: Gives the values for the influence of different chromophores in conjugated carbonyl systems as per Woodward-Fieser rules. The usage of these will become more evident in the examples which follow.

Class	Chromophore	Influence to λmax
Core Chromophore Base Value		
 α,β-unsaturated carbonyl compound	If R = -H (α,β-unsaturated aldehyde) If R = -Alkyl (α,β-unsaturated ketone) If R = -OR (α,β-unsaturated ester)	+ 210 nm + 215 nm + 195 nm
	Cyclopentenone	+ 202 nm
	Cyclohexenone	+ 215 nm

 α,β-γ,δ-diene carbonyl compound	If R = -H (α,β-γ,δ-diene aldehyde) If R = -Alkyl (α,β-γ,δ-diene ketone) If R = -OR (α,β-γ,δ-diene ester)	+210 + 30 =+240 nm +215 + 30 = +245 nm +195 + 30 = +225 nm
Substituent Effects at α-position	-R (Alkyl group)	+ 10 nm
	-OR (Alkoxy group)	+ 35 nm
	-Cl (Chloro group)	+ 15 nm
	-Br (Bromo group)	+ 25 nm
	-OH (alcohol/hydroxyl)	+ 35 nm
	-OC(O)R (Acyloxy/Ester)	+ 6 nm
Substituent Effects at β-position	-R (Alkyl group)	+ 12 nm
	-OR (Alkoxy group)	+ 30 nm
	-Cl (Chloro group)	+ 12 nm
	-Br (Bromo group)	+ 30 nm
	-OH (alcohol/hydroxyl)	+ 30 nm
	-OC(O)R (Acyloxy/Ester)	+ 6 nm
	-SR (Sulfide)	+ 85 nm
	-NR2 (Amine)	+ 95 nm
Substituent Effects at γ and δ-position	-R (Alkyl group) (both γ and δ)	+ 18 nm
	-OC(O)R (Acyloxy/Ester) (both γ and δ)	+ 6 nm
	-Cl (Chloro) (both γ and δ)	+ 12 nm
	-Br (Bromo) (both γ and δ)	+ 30 nm
	-OH (alcohol/hydroxyl group) (only γ)	+ 50 nm
	-OR (Alkoxy group) (only γ)	+ 30 nm
Further π-conjugation	– C=C (double bond extending conjugation)	+ 30 nm
	– C6H5 (Phenyl group)	+ 60 nm

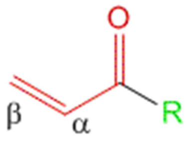
Other Contributors	Exocyclic Double Bond	+ 5 nm
	Homoannular cyclohexadiene	+ 35 nm
Solvent Effects	1] Water	– 8 nm
	2] Methanol/Ethanol	– 1 nm
	3] Ether	+ 6 nm
	4] Hexane / Cyclohexane	+ 7 nm

Let us discuss each of the above values and when to apply them in greater detail with examples:

Core Chromophores With Base Values

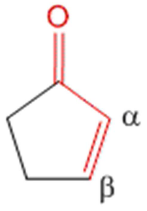
As Woodward and Fieser have listed, α,β-unsaturated carbonyl compounds have a range of influence on the λmax of the molecule depending upon:

1] The type of carbonyl functionality present. For example, ***α,β-unsaturated aldehyde contribute 210*** nm while ***α,β-unsaturated ketones contribute 215 nm*** and ***α,β-unsaturated esters contribute 195 nm***.

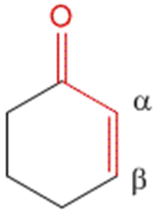


R= H = Aldehyde
R= Alkyl = Ketone
R= OAlkyl = Ester

2] If the core is a part of a cyclic ring. For example, ***cyclopentenone contribution is 202 nm*** while ***cyclohexenone is 215 nm***.

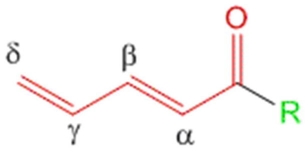


Cyclopentenone



Cyclohexenone

3] If the conjugation is extended to γ,δ-positions to form dienes. For example, in such cases, a simple addition of 30 nm to the base value of the α,β-unsaturated carbonyl compound gives appropriate estimates to the observed influences.



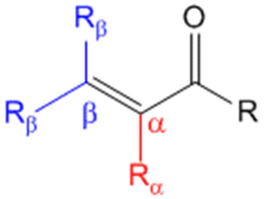
Extended Conjugation

R = H = Aldehyde = 240 nm
R = Alkyl = Ketone = 245 nm
R = OAlkyl = Ester = 225 nm

Note- In cases of α,β-γ,δ-diene carbonyl compounds like those shown above, the extended conjugation at the α,β-γ,δ-positions is accounted for in the base value of the core chromophore and need not be added separately. If however there is another substituent at the α,β-γ,δ-positions, then you must add an additional + 30 nm for each. *Also* the bond shown as β-γ is not counted as β substituent but as a part of the core chromophore and need not be added separately.

Substituent Effects

According to Woodward, in case of α,β-unsaturated carbonyl compounds, the location of the substituent is significant in determining the influence on the wavelength of maximum absorption. Substituents can be located on either α, β positions. If the conjugation is extended to γ and δ positions, then substitutions at these position also play a vital role in determining the practical λmax.



1] Substituents at α-Position

As we can see the from table 3 below the effect of different substituent when placed on the α-position.

Table 3: Effect of substituents on the α-position of α,β-unsaturated carbonyl compounds

Substituent	**Influence**
-R (Alkyl group)	+ 10 nm
-OR (Alkoxy group)	+ 35 nm
-Cl (Chloro group)	+ 15 nm
-Br (Bromo group)	+ 25 nm
-OH (alcohol/hydroxyl)	+ 35 nm
-OC(O)R (Acyloxy/Ester)	+ 6 nm

2] Substituents at β-Position

As we can see the from table 4 below the effect of different substituent when placed on the β-position.

Table 4: Effect of substituents on the β-position of α,β-unsaturated carbonyl compounds

Substituent	**Influence**
-R (Alkyl group)	+ 12 nm
-OR (Alkoxy group)	+ 30 nm
-Cl (Chloro group)	+ 12 nm
-Br (Bromo group)	+ 30 nm
-OH (alcohol/hydroxyl)	+ 30 nm

-OC(O)R (Acyloxy/Ester)	+ 6 nm
-SR (Sulfide)	+ 85 nm
-NR2 (Amine)	+ 95 nm

3] Substituents at γ and δ-position
As we can see the from table 5 below the effect of different substituent when placed on the γ or δ position.

Table 5: Effect of substituents on the γ or δ position of α,β-γ,δ-diene carbonyl compound.

Substituent	**Influence**
-R (Alkyl group) (both γ and δ)	+ 18 nm
-OC(O)R (Acyloxy/Ester)(both γ and δ)	+ 6 nm
-Cl (Chloro) (both γ and δ)	+ 12 nm
-Br (Bromo) (both γ and δ)	+ 30 nm
-OH (alcohol/hydroxyl group)(only γ)	+ 50 nm
-OR (Alkoxy group) (only γ)	+ 30 nm

Other Contributors

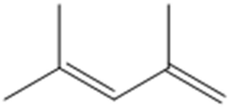
1] Exocyclic Double Bonds
In general exocyclic double bonds add an additional + 5 nm to the base value. In order to identify exocyclic double bonds we recommend you read the previous chapter on **how to use Woodward-Fieser rules to calculate the λmax of conjugated dienes and polyenes**. We have explained it extensively there.

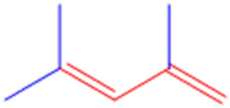
2] Solvent Effects
Since carbonyl functional groups have polarity, solvents play an important role in how the electronics of the structure play out. The rules are simple and straight forward:

Solvent	**Influence**
Water	– 8 nm
Methanol/Ethanol	– 1 nm
Ether	+ 6 nm
Hexane / Cyclohexane	+ 7 nm

3] Homoannular Cyclohexadiene
In a special case where you have α,β-γ,δ-diene carbonyl compound and both the double bonds are present within one ring system you get a homoannular or homocyclic cyclohexadiene carbonyl compound. In such a case you must add an additional 35 nm to the system.

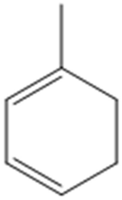
Example/Sample Problem 1

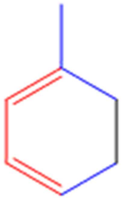




Name of Compound	2,4-dimethylpenta-1,3-diene
Woodward Component	**Contribution**
Core- Transoid/Heteroannular Diene	+ 215 nm
Substituents- 3 alkyl groups	3 x 5 = + 15 nm
Other Effects	0
Calculated λmax	**230 nm**
Observed λmax	234 nm

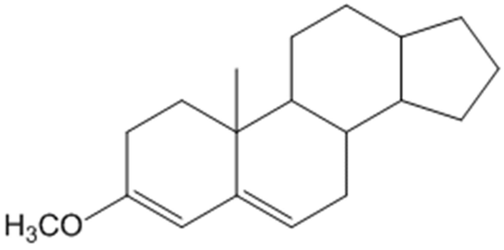
Example/Sample Problem 2

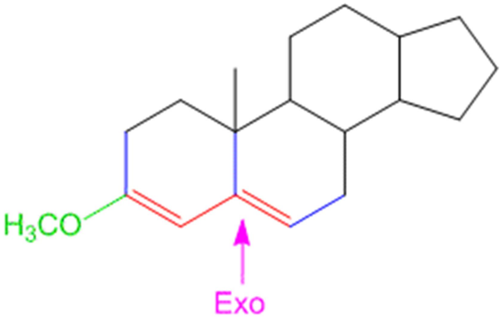




Name of Compound	1-methylcyclohexa-1,3-diene
Woodward Component	**Contribution**
Core- Cisoid/Homoannular Diene	+ 253 nm
Substituents- 3 alkyl groups	3 x 5 = + 15 nm
Other Effects	0
Calculated λmax	**268 nm**
Observed λmax	N/A

Example/Sample Problem 3



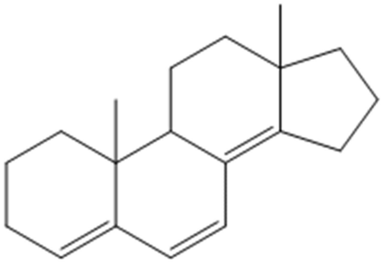


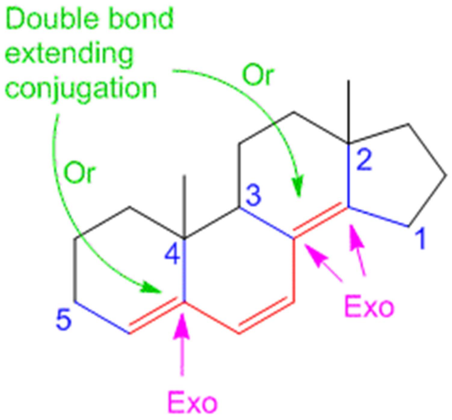
Name of Compound	3-methoxy-10-methyl-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-

cyclopenta[a]phenanthrene

Woodward Component	**Contribution**
Core- Transoid/Heteroannular Diene	+ 215 nm
Substituents- 3 alkyl groups 1 alkoxy group	3 x 5 = + 15 nm + 6 nm
Other Effects- Exocyclic Double Bond	+ 5 nm
Calculated λmax	**241 nm**
Observed λmax	N/A

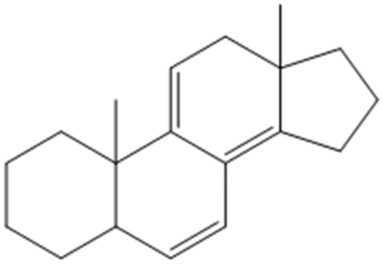
Example/Sample Problem 4





Name of Compound	10,13-dimethyl-2,3,9,10,11,12,13,15,16,17-decahydro-1H-cyclopenta[a]phenanthrene
Woodward Component	**Contribution**
Core- Transoid/Heteroannular	+ 215 nm
Substituents- 5 alkyl groups 1 Double bond extending conjugation	5 x 5 = + 25 nm + 30 nm
Other Effects- 3 Exocyclic Double Bond	+ 15 nm
Calculated λmax	**285 nm**
Observed λmax	283 nm

Example/Sample Problem 5

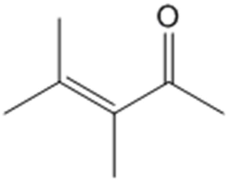


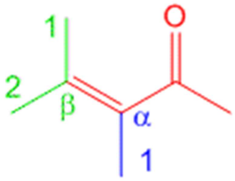
Note- In this example the molecule **<u>contains both, a homoannular diene system and a heteroannular diene</u>** system. In such a molecule the core chromophore is considered to be the homoannular system and accordingly the calculations are performed.

Homoannular system

Component	**Contribution**
Core- Homoannular/Cisoid diene	+ 253 nm
Substituents– 5 alkyl substituents	5 x 5 = + 25 nm
Double bond extending conjugation	+ 30 nm
Other Effects- 3 Exocyclic double bonds	3 x 5 = + 15 nm
Calculated λ$_{max}$	**323 nm**
Observed λ$_{max}$	n/a

Example/Sample Problem 6

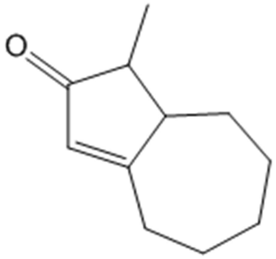




Name of Compound	3,4-dimethylpent-3-en-2-one
Component	**Contribution**
Core- α,β-unsaturated ketone	+ 215 nm
Substituents at α-position- 1 alkyl group	+ 10 nm
Substituents at β-position- 2 alkyl groups	2 x 12 = 24 nm
Other Effects	0

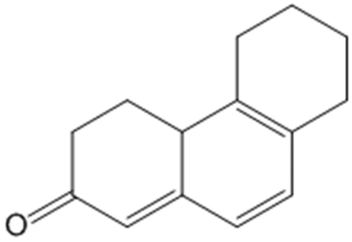
Calculated λ_{max}	**249 nm**
Observed λ_{max}	249 nm

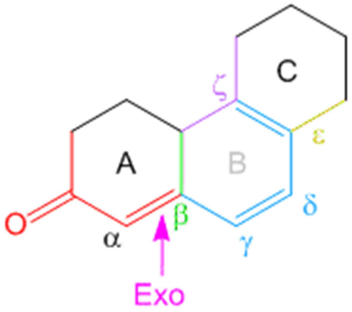
Example/Sample Problem 7



Name of Compound	1-methyl-4,5,6,7,8,8a-hexahydroazulen-2(1H)-one
Component	**Contribution**
Core- cyclopentenone	+ 202 nm
Substituents at α-position	0
Substituents at β-position- 2 alkyl groups	2 x 12= + 24 nm
Other Effects- 1 Exocyclic Double Bond	+ 5 nm
Calculated λ_{max}	**231 nm**
Observed λ_{max}	226 nm

Example/Sample Problem 8





Name of Compound	4,4a,5,6,7,8-hexahydrophenanthren-2(3H)-one
Component	**Contribution**
Core- cyclohexenone	+ 215 nm
Substituents at α-position:	0
Substituents at β-position: 1 alkyl group	+ 12 nm
Substituents at γ-position:	0

Substituents at δ-position:	0
Substituents at ε-position: 1 alkyl group	+ 18 nm
Substituents at ζ-position: 2 alkyl group	2 x 18 = + 36 nm
Other Effects: 2 Double bonds extending conjugation	2 x 30 = + 60 nm
Homoannular Diene system in ring B	+ 35 nm
1 Exocyclic double bond	+ 5 nm
Calculated λ_{max}	**381 nm**
Observed λ_{max}	388 nm

• In compounds where geometrical isomerism is possible. Example: trans - stilbene absorbs at longer wavelength [λmax=295 nm] (low energy) cis - stilbene absorbs at shorter wavelength [λmax=280 nm] (high energy) due to the steric effects. • Coplanarity is needed for the most effective overlap of the π - orbitals and increased ease of the π → π* transition. The cis-stilbene is forced into a nonplanar conformation due to steric effects.

<u>α,β-unsaturated acuds and esters:</u> Nielsen rule

Base value : 195 nm

Theory of EPR Spectroscopy

Differences between NMR and ESR

SNo.	Parameter	NMR	ESR
1	Spinning possible for	Nuclei	Electron
2	Observed Region	Radiofreuency	Microwave
3	Frequency range	300 – 1000 MHz	3 – 400 GHZ
4	Constant parameter	Magnetic field strength	Microwave frequency
5	Varied parameter	Radio freuency	Magnetic field strength
6	Sensitivity	1000 times less than ESR	1000 times more than NMR
7	Relaxation time	More for nuclei	Less for electrons
8	Parameter measured	Coupling constant J	Splitting constant g
9	G factor	Can be observed experimentally	G – may be calculated from L, S and J quantum numbers
10	Dipole	$\mu_z = G\mu_B I_z$	$\mu_z = -g\mu_B I_z$

An electron is a negatively charged particle with certain mass; it mainly has two kinds of movements. The first one is spinning around the nucleus, which brings orbital magnetic moment. The other is "spinning" around its own axis, which brings spin magnetic moment. Magnetic moment of the molecule is primarily contributed by unpaired electron's spin magnetic moment.

$$M_s = \sqrt{S(S+1)}\,\frac{h}{2\pi}$$

- M_s is the total spin angular moment,
- S is the spin quantum number and
- h is Planck’s constant.
-

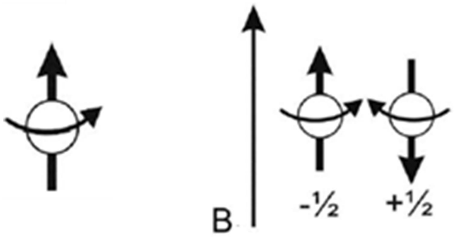
In the z direction, the component of the total spin angular moment can only assume two values:

$$M_{s_z} = m_s \frac{h}{2\pi}$$

The term m_s have (2S + 1) different values: +S, (S − 1), (S − 2),.....-S. For single unpaired electron, only two possible values for m_s are +1/2 and −1/2.

The Zeeman Effect

An isolated electron, all alone in space without any outside forces, still has an intrinsic angular momentum called "spin". Because an electron is charged, the angular motion of this charged particle generates a magnetic field. In other words, the electron due to its charge and angular momentum, acts like a little bar magnet, or magnetic dipole, with a magnetic moment μ_e.



The z-component of magnetic moment associated with the electron spin is

$$\mu_z = -g_e \mu_B m_s$$

The appearance of negative sign is due to the fact that the magnetic momentum of electron is collinear, but **antiparallel** to the spin itself. The term g_e is the magnetogyric ratio. The Bohr magneton, μ_B, is the magnetic moment for one unit of quantum mechanical angular momentum:

$$\mu_B = \frac{eh}{4\pi m_e}$$

where e is the electron charge, m_e is the electron mass, the factor g_e is known as the free electron g-factor with a value of 2.002 319 304 386 (one of the most accurately known physical constant).

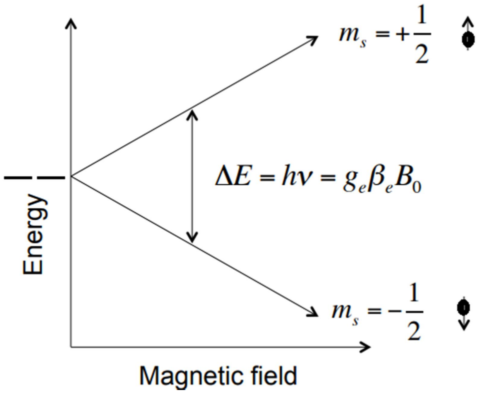
This magnetic moment interacts with the applied magnetic field. The interaction between the magnetic moment (μ) and the field (B) is described by

$$E = -\mu_z . B$$
$$E = g_e \mu_B m_s . B$$

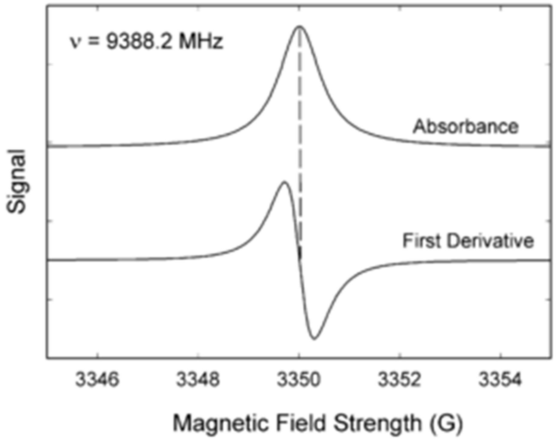
For single unpaired electron, there will be two possible energy states, this effect is called Zeeman splitting

$$E_{+1/2} = \frac{1}{2} g_e \mu_B . B$$
$$E_{-1/2} = -\frac{1}{2} g_e \mu_B . B$$
$$\Delta E = g_e \mu_B . B$$

In the presence of external magnetic field (Figure), the difference between the two energy states can be written as



With the intensity of the applied magnetic field increasing, the energy difference between the energy levels widens until it matches with the microwave radiation, and results in absorption of photons. This is the fundamental basis for EPR spectroscopy. EPR spectrometers typically vary the magnetic field and hold the microwave frequency. EPR spectrometers are available in several frequency ranges, and X band is currently the most commonly used.



Factors affecting the g-values:

$$\Delta E = g_e \mu_B . B$$
$$\frac{\Delta E}{\mu_B . B} = g_e = \frac{h\nu}{\mu_B . B}$$

For free electron g = 2.0023. In the case of free radicals and in some ionic crystals it varies in the range 0.2 – 8.0.

a. Operating frequency of the instrument – **b**. Concentration of unpaired e – **c**. Ground term of the metal ion present – **d**. Direction and temperature of measurement – **e**. Lack of symmetry – **f**. Inherent magnetic field in the crystals – **g**. Jahn – Teller distortion - **h**. ZFS

Hyperfine Structure (Hyperfine coupling)

The interaction between the unpaired electron and neighbouring nuclei leads to splitting of the energy levels and the spectrum. It is called *Hyperfine structure / Hyperfine coupling.*

$$h\nu = g_e\mu_B.(B + am_I); \quad m_I = \pm\frac{1}{2}; \; a - hyperfine\ coupling\ constant$$

In general, a spin-I nucleus splits the spectrum into 2I+1 hyperfine lines of equal intensity. If there are N equivalent protons, N+ 1 hyperfine line with a binomial intensity distribution will be obtained.

Methyl radical ($CH_3^{\cdot}$) would give four lines of intensities 1:3:3:1

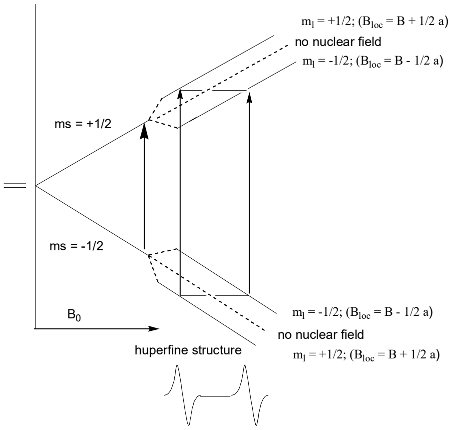
Benzene radical ($C_6H_6^{\cdot}$) would give 7 lines of intensities 1:6:15:20:15:6:1

Groups of equivalent nuclei give characteristic patterns of lines. The number of hyperfine lines, n_{hfs}, from a group of, n, equivalent nuclei of spin I is: nhf

$$n_{hfs} = (2nI + 1)$$

The total number of hyperfine lines, n, from several groups of equivalent nuclei:

$$n_{total} = \prod_i (2n_iI_i + 1)$$



Zero-Field Splitting

The splitting that occurs even in the absence of magnetic fieldis referred to as Zero-Field-Splitting (ZFS).

It occurs mainly in transition metal complexes where there are more than one unpaired electrons

It removes the degeneracy of transitions and more transitions are observed than expected, in the presence of external magnetic field

Fine structure in ESR spectrum is obtained

McConnel Euation:

McConnell equation describes the proportional dependence of the hyperfine splitting constant on the spin density (the probability of an unpaired electron being on a particular atom) in aromatic radical compounds such as benzene radical anion.

In aromatic radicals delocalisation causes the average unpaired spin population of a particular carbon 2pz orbital to be <1 and the amount of spin polarization it causes in the C-H bond depends upon its precise value. This is termed the 'π-electron spin density, ρ'. The McConnell equation states that the hyperfine coupling constant A is proportional to ρ:

$$A = Q \cdot \rho$$

where Q is a constant for the type of atom with the unpaired spin density. This important relationship allows a direct link between experiment and theory, for ρ can often be calculated quite simply by Huckel MO methods. The constant Q can be determined experimentally and for carbon atoms this is performed conveniently by observing the ESR spectrum of the benzene radical anion, C6H6 - . This spectrum has seven lines, equally spaced and with intensity ratios which disclose that the electron couples to six equivalent protons. This confirms that it occupies a molecular orbital delocalised over the ring - a nice demonstration of basic orbital theory. Symmetry requires all the carbon atoms to be equivalent so that the observed splitting of 3.75 gauss (0.375 mT) represents the value of A when $\rho = 1/6$.

Applications:

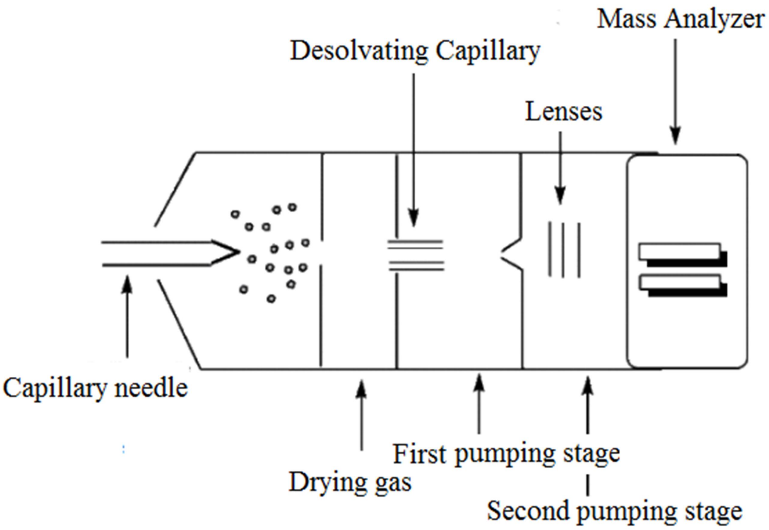
1. **Free Radicals**: Atoms, molecules or ions containing one unpaired electron either in the Solid, Liquid or Gaseous Phases
2. **Transition Ions Including Actinide Ions**: These routinely may have up to fiveor seven unpaired electrons
3. **Various 'Point' Defects in solids**: Localized Imperfections
4. **Systems with More than One Unpaired Electron**: Triplets state systems, biradicals and multiradicals
5. **Systems with Conducting Electrons**: Semiconductors and metals

Eiectron Spray Ioniation (ESI) Mass Spectrometry

Electrospray ionization is a soft ionization technique that is typically used to determine the molecular weights of proteins, peptides, and other biological macromolecule. This process does not fragment the macromolecules into smaller charged particles, rather it turns the macromolecule being ionized into small droplets. These droplets will then be further desolvated into even smaller droplets, which creates molecules with attached protons. These protonated and desolvated molecular ions will then be passed through the mass analyzer to the detector, and the mass of the sample can be determined. The spectrum is shown with the mass-to-charge (m/z) ratio on the x-axis, and the relative intensity (%) of each peak shown on the y-axis. Calculations to determine the unknown mass, M_r, from the spectral data can then be performed using

$$p = \frac{m}{z} \; ; \quad p_1 = \frac{M_r + z_1}{z_1} \; ; \quad p_2 = \frac{M_r + (z_1 - 1)}{z_1 - 1}$$

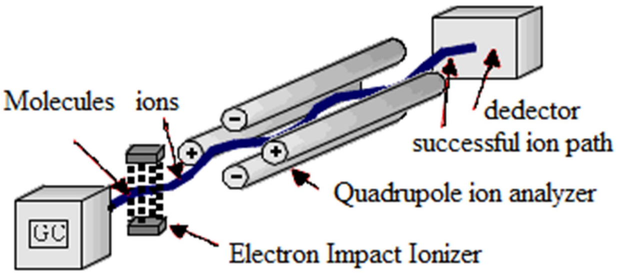
where p_1 and p_2 are adjacent peaks. Peak p_1 comes before peak p_2 in the spectrum, and has a lower m/z value. The z_1 value represents the charge of peak one. It should be noted that as the m/z value increases, the number of protons attached to the molecular ion decreases.



Electron Impact (EI) Ionization

The charged particles (ions) required for mass analysis are formed by Electron Impact (EI) Ionization. The gas molecules exiting the GC are bombarded by a high-energy electron beam (70 eV). An electron which strikes a molecule may impart enough energy to remove another electron from that molecule. Methanol, for example, would undergo the following reaction in the ionizing region:

$$CH_3OH + 1 \text{ electron} \rightarrow CH_3OH^{+\cdot} + 2 \text{ electrons}$$



EI Ionization usually produces singly charged ions containing one unpaired electron. A charged molecule which remains intact is called the molecular ion. Energy imparted by the electron impact and, more importantly, instability in a molecular ion can cause that ion to break into smaller pieces (fragments). The methanol ion may fragment in various ways, with one fragment carrying the charge and one fragment remaining uncharged. For example:

$CH_3OH^{+\cdot}$(molecular ion) CH_2OH^{+}(fragment ion) + $H^{\cdot}$

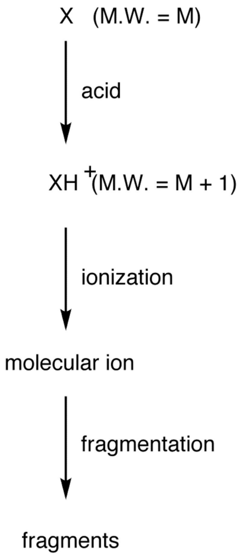
or

$CH_3OH^{+\cdot}$(molecular ion) CH_3^{+}(fragment ion) + $^{\cdot}OH$

Chemical ionization (CI)

Chemical ionization (symbol: CI) is a mass-spectroscopic technique, used when the peak with the highest mass-to-charge ratio in a mass spectrum is suspected not to be the molecular ion peak and, therefore, can not be used to determine the molecular weight of the compound. In chemical ionization mass spectroscopy, the sample molecule is first protonated in gas phase using a very strong acid. The resultant cation, which is not a free radical and, therefore, always gives rise to a peak in the mass spectrum, is subjected to ionization.

Consider the hypothetical compound X.



Fast Atomic Bombardment (FAB) Source

[Also known as liquid secondary ion mass spectrometry (LSIMS)]

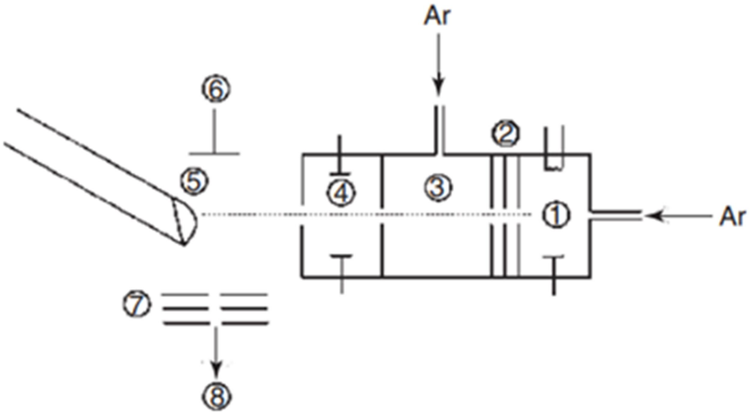
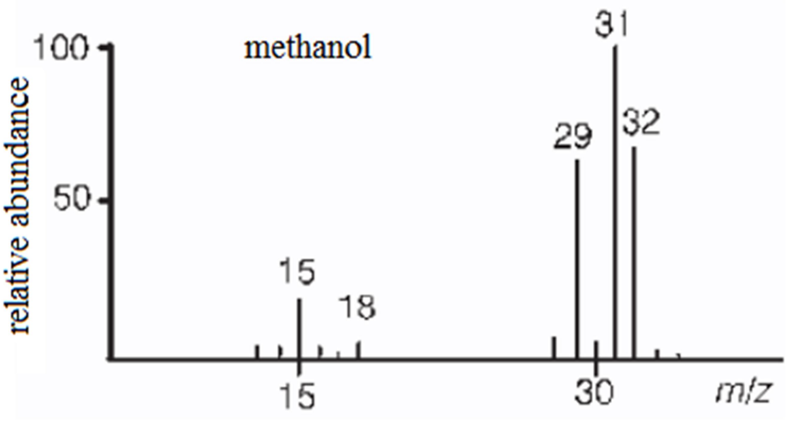


Diagram of an FAB gun. 1, Ionization of argon; the resulting ions are accelerated and focused by the lenses 2. In 3, the argon ions exchange their charge with neutral atoms, thus becoming rapid neutral atoms. As the beam path passes between the electrodes 4, all ionic species are deflected. Only rapid neutral atoms reach the sample dissolved in a drop of glycerol, 5. The ions ejected from the drop are accelerated by the pusher, 6, and focused by the electrodes, 7, towards the analyser, 8.

Base peak

A mass spectrum of the molecule is a plot of ion abundance versus mass-to-charge ratio. As illustrated in Figure 1, mass spectra can be presented as a bar graph or as a table. In either presentation, the most intense peak is called the base peak and is arbitrarily assigned the relative abundance of 100 %. The abundances of all the other peaks are given their proportionate values, as percentages of the base peak.



Molecular ion or Parent ion:

When a molecule is bombarded with electrons in high vacuum in Mass spectrometer, it is converted into positive ions by loss of an electron. These ions are called as Molecular or Parent ions.

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

Where, M – represents the Molecule; $M^{\circ+}$ – represents the Molecular or Parent ion The order of energy required to remove electron is as follows—

σ electrons > non-conjugated π > conjugated π > non bonding or lone pair of electrons.

Recognition of molecular ion The **molecular** formula is usually the most important piece of information which one drives from the mass spectrum of an organic compound. ... An extremely weak **molecular ion peak** or its absence indicates highly branched molecules, when the **molecular ion** fragments completely before detection.

Isotope peaks

Ionic fragments of the same chemical formula are usually represented by multiple adjacent peaks attributable to ions of different isotopic compositions. The number of isotope peaks and the relative intensity of each peak depend on the chemical formula of the ionic fragment and the natural isotopic composition of its constituent elements.

For example, the ion CH_3^+ consists of fragments with nominal mass ranging from 15 (for the "lighter" fragment $^{12}C^1H_3^+$) up to 19 (for the "heavier" fragment $^{13}C^2H_3^+$).

The natural isotopic abundance percentage for

^{12}C -98.90%

^{13}C - 1.10% ,

^{1}H -99.985%

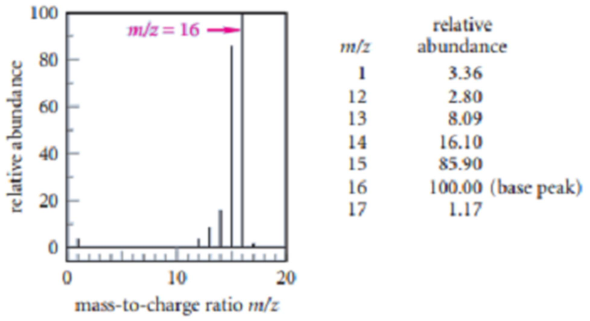
^{2}H - 0.015% ,

Therefore the more intense peak

M=15 is attributed to the more abundant $^{12}C^1H_3^+$.

The next in intensity peak (much smaller than peak M) is M+1=16, which is attributed to both $^{13}C^1H_3^+$ and $^{12}C^1H_2{}^2H^+$

The last peak M+4=19, attributed to $^{13}C^2H_3^+$, has practically zero intensity because of the extremely low probability of occurrence of all heavy isotopes in the same ionic fragment.



m/z	relative abundance
1	3.36
12	2.80
13	8.09
14	16.10
15	85.90
16	100.00 (base peak)
17	1.17

General Rules

Probablity of bond cleavage depends on stability of fragments produced. (3º > 2º > 1º > CH_3) (oxonium > carbocation) (allylic, benzylic > no resonance)

1. Increase branching → decrease M^+
2. Add carbons → decrease M^+
3. Cleave more likely at higher º C
4. Unsubst cyclic have strong M+ (especially aromatic)
5. Alkenes cleave to allylic species

6. R on cycloalkanes α cleave. Cyclohexenes do retro Diels-Alder.
7. R on aromatic rings β-cleave to benzylic
8. Bonds β to heteroatoms cleave
9. Loss of small stable molecules, H_2O, NH_3, C_2H_4, HCN, CO, H_2S,etc often occur

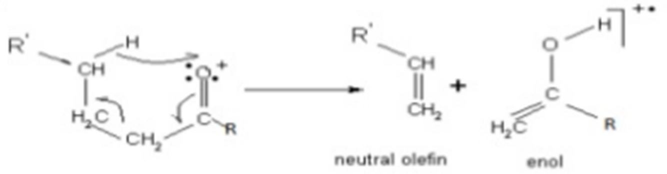
Mc Lafferty rearrangement:

Fragmentation due to rearrangement of Molecular or Parent ion:

Here cleavage of bonds in Molecular ion is due to the intramolecular atomic rearrangement. This leads to fragmentation whose origin cannot be described by simple cleavage of bonds. When fragments are accompanied by bond formation as well as bond for breaking, a rearrangement process is said to have occurred. Such rearrangement involves the transfer of hydrogen from one part of the molecular ion to another via, preferably, a six-membered cyclic transition state. This process is favoured energetically because as many bonds are formed as are broken

Compounds containing hydrogen atom at position gamma toSpectroscopy carbonyl group have been found to a relative intense peak. This is probably due to rearrangement and fragmentation is accompanied by the loss of neutral molecule. This rearrangement is known as McLafferty rearrangement. The rearrangement results in the formation of charged enols and a neutral olefins. To undergo McLafferty rearrangement, a molecule must posses a. An appropriately located heteroatom (ex.oxygen) b. A double bond c. An abstractable Hydrogen atom which is γ (gamma) to C=Osystem.

The rearrangement results in the formation of charged enols and a neutral olefins.



To undergo McLafferty rearrangement, a molecule must posses

a. An appropriately located heteroatom (ex.oxygen)
b. A double bond
c. An abstractable Hydrogen atom which is γ (gamma) to C=Osystem.

Electron Diffraction

Gas electron diffraction (GED) is one of the applications of electron diffraction techniques. The target of this method is the determination of the structure of gaseous molecules i.e. the geometrical arrangement of the atoms from which a molecule is built up.

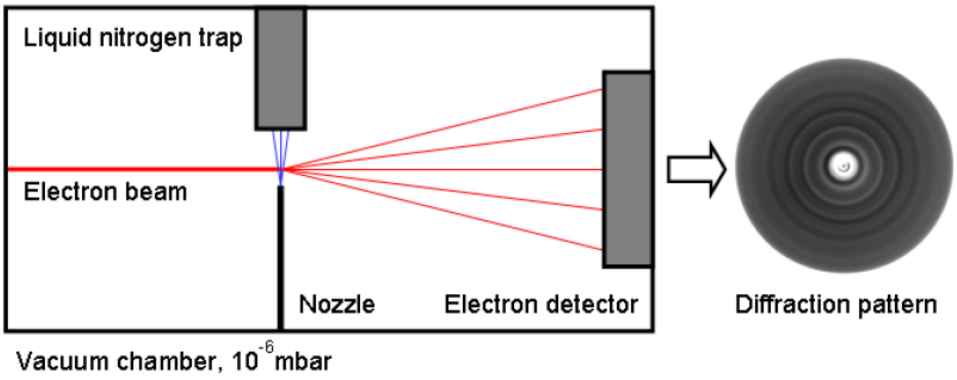
Diffraction occurs because the wavelength of electrons accelerated by a potential of a few thousand volts is of the same order of magnitude as internuclear distances in molecules

The total scattering intensity in GED is given as a function of the momentum transfer, which is defined as the difference between the wave vector of the incident electron beam and that of the scattered electron beam and has the reciprocal dimension of length. The total scattering intensity is composed of two parts: the atomic scattering intensity and the molecular scattering intensity.

$$I_{total} = I_{atom} + I_{mol}$$

I_{atom} decreases monotonically and contains no information about the molecular structure.

I_{mol} has sinusoidal modulations as a result of the interference of the scattering spherical waves generated by the scattering from the atoms included in the target molecule. It contains all the structural information. The interferences reflect the distributions of the atoms composing the molecules, so the molecular structure is determined from this part.



The diffraction pattern, captured on photographic film consists of diffuse, concentric rings due to the random orientation of the molecules in the diffraction chamber. Initially, patterns were interpreted by eye using the visual method.9,10 This consisted of measuring the diameters of rings with maximum and minimum intensities and comparing these with values calculated from a model. The best fit, determined by trial and error, gave the structure.

A universal variable‘s’ is used for the data reduction and refinement process. This is a function of both the scattering angle (ϑ) and the electron (de Broglie) wavelength (λ)

$$s = \frac{4\pi}{\lambda} sin\frac{\vartheta}{2}$$

It is an equation for the determination of intensity of an electron beam cattered through a specific angle by diffraction from a gas molecule. This is useful when dealing with complex molecules. To study larger molecules, or molecules which have no permanent dipole moment, GED must be employed.

$$I_S = \frac{L_{mol}}{I_{atom}} = \sum_{i}^{N}\sum_{j\neq i}^{N} Z_i Z_j \frac{\sin \boldsymbol{s}\, r_{i,j}}{\boldsymbol{s}\, r_{i,j}}$$

where I_S is the scattered electron intensity, Z is an atomic property, chosen as the atomic number, rij are the interatomic distances between the ith and jth atoms, and N is the number of atoms.

The original 'Wierl equation' (Equation 1.5) illustrates the relationship between the intensities and the bond distances, rij , 8 which can be rewritten in terms of the scattering function for each atom, Fi (Equation 1.7), shown in Equation 1.6.28 The scattering function is defined as the atomic number, Zi , minus the X-ray scattering factor, fi .

NEUTRON DIFFRACTION.

- Mass = 1.68×10^{-27} kg (photon mass = zero)
- Charge = zero (photon charge = zero)
- Spin = ½ (photon spin = 1)
- Magnetic dipole moment = -9.66×10^{-27} JT^{-1} (photon moment zero)

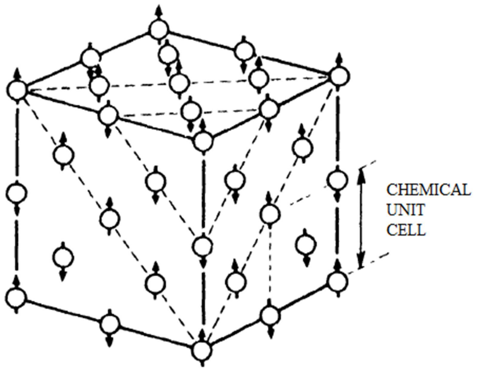
Neutron Scattering Requires Intense Sources of Neutrons

- Neutrons for scattering experiments can be produced either by nuclear fission in a reactor or by spallation when high-energy protons strike a heavy metal target (W, Ta, or U).
  - In general, reactors produce continuous neutron beams and spallation sources produce beams that are pulsed between 20 Hz and 60 Hz
  - The energy spectra of neutrons produced by reactors and spallation sources are different, with spallation sources producing more high-energy neutrons
  - Neutron spectra for scattering experiments are tailored by moderators
  - solids or liquids maintained at a particular temperature
  - although neutrons are not in thermal equilibrium with moderators at a short-pulse spallation sources

Neutrons From Reactors and Spallation Sources Must Be Moderated Before Being Used for Scattering Experiments

Not only X-ray and electron beams, but also beams of heavier particles may exhibit diffraction patterns when scattered from the regular array of atoms in a crystal. Neutron beams have proved to be especially useful for such studies. The wavelength is related to the mass and velocity by the Broglie equation, $\lambda = \frac{h}{mv}$. Thus a neutron with a speed of 3.9×10^5 cm sec^{-1} (kinetic energy 0.08 ev) would have a wavelength of 1 .0 Å. The diffraction of electron rays or X rays is caused by their interaction with the orbital electrons of the atoms in the material through which they pass; the atomic nuclei contribute practically nothing to the scattering. The diffraction of neutrons, on the other hand, is primarily caused by two other effects: (a) nuclear scattering due to interaction of the neutrons with the atomic nuclei, (b) magnetic scattering due to interaction of the magnetic moments of the neutrons with permanent magnetic moments of atoms or ions.

In the absence of an external magnetic field, the magnetic moments of atoms in a paramagnetic crystal are arranged at random, so that the magnetic scattering of neutrons by such a crystal is also random. It contributes only a diffuse background to the sharp maxima occurring when the Bragg condition is satisfied for the nuclear scattering. In ferromagnetic materials, however, the magnetic moments are regularly aligned so that the resultant spins of adjacent atoms are parallel, even in the absence of an external field. In antiferromagnetic materials, the magnetic moments are also regularly aligned, but in such a way that adjacent spins are always opposed. The neutron diffraction patterns distinguish experimentally between these different magnetic structures, and indicate the direction of alignment of spins within the crystal.

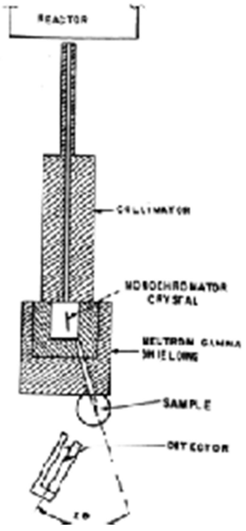


Magnetic structure of MnO as found by neutron diffraction. Note that the "magnetic unit cell" has twice the length of the "chemical unit cell."

For example, manganous oxide, MnO, has the rock-salt structure (Fig.), and is antiferromagnetic. The detailed magnetic structure as revealed by neutron diffraction is shown in Fig.. The manganous ion, Mn^{+2} , has the electronic structure $3s^2\ 3p^6 3d^5$.

The five 3d electrons are all unpaired, and the resultant magnetic moment is $2\sqrt{\frac{5}{2}\left(\frac{5}{2}+1\right)} =$ 5.91 Bohr magnetons. If we consider Mn^{+2} ions in successive (111) planes in the crystal, the resultant spins are oriented so that they are alternately positively and negatively directed along the [100] direction.

Another useful application of neutron diffraction has been the location of hydrogen atoms in crystal structures. It is usually impossible to locate hydrogen atoms by means of X-ray or electron diffraction, because the small scattering power of the hydrogen is completely overshadowed by that of heavier atoms. The hydrogen nucleus, however, is a strong scatterer of neutrons. Thus it has been possible to work out the structures of such compounds as UH_3 and KHF_2 neutron-diffraction analysis.



Magnetic Scattering

- The magnetic moment of the neutron interacts with B fields caused, for example, by unpaired electron spins in a material
  - Both spin and orbital angular momentum of electrons contribute to B
  - Expressions for cross sections are more complex than for nuclear scattering
- Magnetic interactions are long range and non-central

  - Nuclear and magnetic scattering have similar magnitudes
  - Magnetic scattering involves a form factor
  - FT of electron spatial distribution
- Electrons are distributed in space over distances comparable to neutron wavelength
- Elastic magnetic scattering of neutrons can be used to probe electron distributions
  - Magnetic scattering depends only on component of B perpendicular to Q
  - For neutrons spin polarized along a direction z (defined by applied H field):
- Correlations involving B z do not cause neutron spin flip
- Correlations involving Bx or By cause neutron spin flip
  - Coherent & incoherent nuclear scattering affects spin polarized neutrons
- Coherent nuclear scattering is non-spin-flip
- Nuclear spin-incoherent nuclear scattering is 2/3 spin-flip
- Isotopic incoherent scattering is non-spin-flip

The neutron has a magnetic moment. Just as two bar magnets either attract or repel one another, the neutron experiences a force of magnetic origin whenever it moves in a magnetic field, such as that produced by unpaired electrons in matter.

Ferromagnetic materials, such as iron, are magnetic because the moments of their unpaired electrons tend to align spontaneously. For many purposes, such materials behave as if small magnetic moments were located at each atomic site with all the moments pointing in the same direction. These moments give rise to ***magnetic Bragg scattering*** of neutrons in the same manner as the nuclear interactions. Because the nuclear and magnetic interactions experienced by the neutron are of similar magnitude, the corresponding Bragg reflections are also of comparable intensity.

One difference between the two types of scattering, however, is that the magnetic interaction, unlike the nuclear interaction is not isotropic. The magnetic interaction is dipolar, just like that between two bar magnets. And just like two bar magnets, the strength of the interaction between the neutron and a nucleus depends on the relative orientations of their magnetic moments and the line joining their centers. For neutrons, the dipolar nature of the magnetic interaction means that only the component of the sample's magnetization that is perpendicular to the scattering vector, Q effective in scattering neutrons. Neutron scattering is therefore sensitive to the spatial distribution of both the direction and the magnitude of magnetization inside a material.

The anisotropic nature of the magnetic interaction can be used to separate nuclear and magnetic Bragg peaks in ferromagnets, for which both types of Bragg peaks occur at the same values of Q . If the electronic moments can be aligned by an applied magnetic field, magnetic Bragg peaks for which Q is parallel to the induced magnetization vanish, leaving only the nuclear component. On the other hand, an equivalent Bragg peak for which Q is perpendicular to the magnetization will manifest both nuclear and magnetic contributions.

Neutron Scattering Requires Intense Sources of Neutrons

- Neutrons for scattering experiments can be produced either by nuclear fission in a reactor or by spallation when high-energy protons strike a heavy metal target (W, Ta, or U).
  - In general, reactors produce continuous neutron beams and spallation sources produce beams that are pulsed between 20 Hz and 60 Hz
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  - Neutron spectra for scattering experiments are tailored by moderators

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- – although neutrons are not in thermal equilibrium with moderators at a short-pulse spallation sources

Neutrons From Reactors and Spallation Sources Must Be Moderated Before Being Used for Scattering Experiments

Neutron diffraction – magnetic structure

•The positions of magnetic atoms within the unit cell
•The directions of their ordered magnetic moments
•The magnitudes of their ordered magnetic moments

Sources of neutrons

• natural sources of neutrons
– only radioactive elements, e.g. uranium
– neutron outside the nucleus will disappear after 18 minutes!
• artificial processes which produce neutrons
– (1) nuclear fission: sustained reaction of radioactive elements, e.g. uranium
– (2) spallation: disintegration of heavy elements, e.g. tantalum • artificial sources of neutrons
– (1) nuclear reactor source:
– (2) spallation source:

SEMESTER-II HOURS/WEEK: 6
CORE COURSE-V (CC-V) CREDITS: 5
PHYSICAL METHODS IN CHEMISTRY I

UNIT V:

X-Ray Diffraction X-Ray diffraction by single crystal method – space groups – systematic absences in X-ray data and identification of lattice types, glide planes and screw axes – X-ray intensities – structure factor and its relation to intensity and electron density – phase problem – structure solution by heavy atom method and direct method – determination of absolute configuration of molecules – a brief account of Cambridge Structural Database (CSD) and Protein Data Bank (PDB).

Electron diffraction by gases – scattering intensity vs. scattering angle, Wierl equation – measurement techniques. Neutron diffraction by crystals 0 magnetic scatterung - measurement techniques – elucidation of structure of magnetically ordered unit cell.

X-Ray diffraction by single crystal method

- It is a non-destructive analytical technique. It provides a detailed information about the internal lattice of crystalline substances, including unit cell dimensions, bond-lengths, bond-angles, and details of site-ordering. Directly related is single-crystal refinement, where the data generated from the X-ray analysis is interpreted and refined to obtain the crystal structure.

Fundamental Principles of Single-crystal X-ray Diffraction

- Generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays.

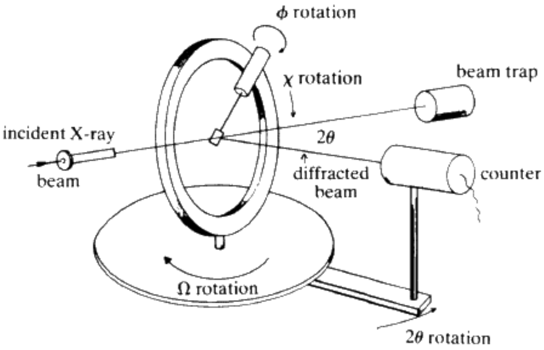
- Crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths.

- X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin\theta$). These diffracted X-rays are then detected, processed and counted.

- By changing the geometry of the incident rays, the orientation of the centered crystal and the detector, all possible diffraction directions of the lattice should be attained.

- Indices (*hkl*) may be assigned to each reflection, indicating its position within the diffraction pattern. This pattern has a reciprocal Fourier transform relationship to the crystalline lattice and the unit cell in real space. This step is referred to as the solution of the crystal structure. After the structure is solved, it is further refined using least-squares techniques.

Instrumentation



- In a cathode ray tube a filament is heated to produce electrons. They are accelerated toward a target by applying a voltage, and impact with the target material. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K_α and K_β. K_α consists, in part, of $K_{\alpha1}$ and $K_{\alpha2}$. $K_{\alpha1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha2}$. The specific wavelengths are characteristic of the target material. They are then mono-chromatized. $K_{\alpha1}$and $K_{\alpha2}$ are sufficiently close in wavelength such that a weighted average of the two is used. Molybdenum is the most common target material for single-crystal diffraction, with MoK_α radiation = 0.7107Å. These X-rays are collimated and directed onto the sample. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor. X-rays may also be produced using a synchotron, which emits a much stronger beam.

- Single-crystal diffractometers use either 3- or 4-circle goniometers. These circles refer to the four angles (2θ, χ, φ, and Ω) that define the relationship between the crystal lattice, the incident ray and detector. Samples are mounted on thin glass fibres which are attached to brass pins and mounted onto goniometer heads. Adjustment of the X, Y and Z orthogonal directions allows centering of the crystal within the X-ray beam.

- X-rays leave the collimator and are directed at the crystal. Rays are either transmitted through the crystal, reflected off the surface, or diffracted by the crystal lattice. A beam stop is located directly opposite the collimator to block transmitted rays and prevent burn-out of the detector. Reflected rays are not picked up by the detector due to the angles involved. Diffracted rays at the correct orientation for the configuration are then collected by the detector.

- Modern single-crystal diffractometers use CCD (charge-coupled device) technology to transform the X-ray photons into an electrical signal which are then sent to a computer for processing.

Strengths and Limitations of Single-crystal X-ray Diffraction

- Strengths
  - No separate standards required
  - Non-destructive
  - Detailed crystal structure, including unit cell dimensions, bond-lengths, bond-angles and site-ordering information
  - Determination of crystal-chemical controls on mineral chemistry
  - With specialized chambers, structures of high pressure and/or temperature phases can be determined
  - Powder patterns can also be derived from single-crystals by use of specialized cameras (Gandolfi)

- Limitations
  - Must have a single, robust (stable) sample, generally between 50—250 microns in size
  - Optically clear sample
  - Twinned samples can be handled with difficulty
  - Data collection generally requires between 24 and 72 hours

Data Collection, Results and Presentation

- **Data Collection**

Once the crystal is centered, a preliminary rotational image is often collected to screen the sample quality and to select parameters for later steps. An automatic collection routine can then be used to collect a preliminary set of frames for determination of the unit cell. Reflections from these frames are auto-indexed to select the reduced primitive cell and calculate the orientation matrix (which relates the unit cell to the actual crystal position within the beam). The primitive unit cell is refined using least-squares and then converted to the appropriate crystal system and Bravias lattice. This new cell is also refined using least-squares to determine the final orientation matrix for the sample.

After the refined cell and orientation matrix have been determined, intensity data is collected. Generally this is done by collecting a sphere or hemisphere of data using an incremental scan method, collecting frames in 0.1° to 0.3° increments (over certain angles while others are held constant). For highly symmetric materials, collection can be constrained symmetrically to reduce the collection time. Data is typically collected between 4° and 60° 2θ for molybdenum radiation. A complete data collection may require anywhere between 6-24 hours, depending on the specimen and the diffractometer. Exposure times of 10-30 seconds per frame for a hemisphere of data will require total run times of 6-13 hours. Older diffractometers with non-CCD detectors may require 4-5 days for a complete collection run.

- **Corrections for Background, Absorption, etc.**

After the data have been collected, corrections for instrumental factors, polarization effects, X-ray absorption and (potentially) crystal decomposition must be applied to the entire data set. This integration process also reduces the raw frame data to a smaller set of individual integrated intensities. These correction and processing procedures are typically part of the software package which controls and runs the data collection.

- **Phase Problem and Fourier Transformation**

Once the data have been collected, the phase problem must be solved to find the unique set of phases that can be combined with the structure factors to determine the electron density and, therefore, the crystal structure. A number of different procedures exist for solution of the phase problem, but the most common method currently, due to the prevalence of high-speed computers, is using direct methods and least-squares, initially assigning phases to strong reflections and iterating to produce a refined fit.

- **Structure Solution**

  Solution of the phase problem leads to the initial electron density map. Elements can be assigned to intensity centers, with heavier elements associated with higher intensities. Distances and angles between intensity centers can also be used for atom assignment based on likely coordination. If the sample is of a known material, a template may be used for the initial solution.

- **Structure Refinement**

  Once the initial crystal structure is solved, various steps can be done to attain the best possible fit between the observed and calculated crystal structure. The final structure solution will be presented with an *R* value, which gives the percent variation between the calculated and observed structures.

Systematization of Crystal Structures

Step 1: Crystal Systems : 7
(complete symmetry)

Step 2: Bravais Lattices : 14
(crystallographic PG)

Step 3: Crystal Classes : 32
(primitive + centered)

Step 4: Space Groups : 230
(metric + symmetry of UC)

Combination of 14 Bravais Lattices with 32 point groups and srew and glide symmetry gives 230 space groups

- Lattices in which the lattice points lie only at the vertices of the unit cell are Primitive lattices (P).

- In some cases, it is conventional to define the unit cell so that there are, in addition, lattice points at the centre of:

  One face (C) (the face opposite the c axis)

  All faces (F)

The unit cell (I, body centred). This is done so that the unit cell axes remain parallel to symmetry axes.

Space group

- **Space group**, in crystallography, any of the ways in which the orientation of a crystal can be changed without seeming to change the position of its atoms. These changes may involve displacement of the whole structure along a crystallographic axis (translation), as well as the point group operations of rotation about an axis, reflection in a plane, inversion about a centre, or sequential rotary inversion. As demonstrated in the 1890s, only 230 distinct combinations of these changes are possible; these 230 combinations define the 230 space groups. A crystal can be assigned to one of these groups after the arrangement of its atoms is studied, as by X-ray crystallography, thereby providing a definitive way of categorizing the inherent symmetry of the crystal.

- The number of permutations of Bravais lattices with rotation and screw axes, mirror and glide planes, plus points of inversion is finite: there are only 230 unique combinations for three-dimensional symmetry, and these combinations are known as the 230 space groups.

- Set of symmetry elements (and respective operations) which completely describes the special arrangements of a 3D periodic pattern.

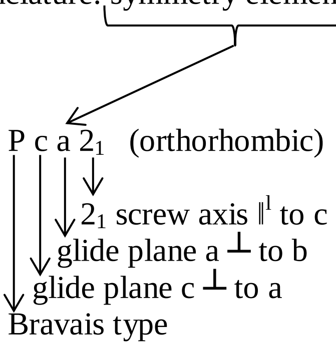
- A point group describes the symmetry of a finite object
- A lattice defines the translational symmetry
- Combining point group and Bravais lattice symmetries generates space group symmetry (but additional symmetry elements involving a translation need to be considered).

- The space group is a complete description of the symmetry of an (ideal) crystal. (Ideal implies infinite !)

- Knowing the space group, and the contents of the asymmetric unit, defines the positions of all atoms in the crystal.

- ➢ There are a total of 230 different space groups (first derived in nineteenth century), of which only 65 are possible for chiral molecules.

- ➢ Nomenclature: symmetry elements with respect to 3 given viewing directions



- ➢ The Hermann-Maguin system uses four symbols to uniquely specify the group properties of each of the 230 space groups. The first symbol is a single letter P, I, R, F, A, B, or C which refers to the Bravais lattice type. The remaining three letters refer to the point group of the crystal.

Bravais Lattice Conventions

- ➢ **ATOMS** assumes certain conventions for each of the Bravais lattice types. Listed here are the labeling conventions for the axes and angles in each Bravais lattice.
  - **Triclinic**: All axes and angles must be specified.
  - **Monoclinic**: B is the perpendicular axis, thus β is the angle not equal to 90.
  - **Orthorhombic**: A, B, and C must all be specified.
  - **Tetragonal**: The C axis is the unique axis in a tetragonal cell. The A and B axes are equivalent. Specify A and C in atoms.inp.
  - **Trigonal**: If the cell is rhombohedral then the three axes are equivalent as are the three angles. Specify A and α. If the cell has hexagonal axes, specify A and C. γ will be set to 120 by the program.
  - **Hexagonal**: The equivalent axes are A and B. Specify A and C in atoms.inp. γ will be set to 120 by the program.
  - **Cubic**: Specify A in atoms.inp. The other axes will be set equal to A and the angles will all be set to 90.

- ➢ The primitive Bravais lattices contain only one lattice point. The non primitive Bravais lattices contain more than one lattice point per unit cell (2 or 4), and are called centred lattices:

- Body-centred lattice (notation I for Innenzentrierung, new lattice point in a/2 + b/2 + c/2)

- Face-centred lattice (F, Flächenzentrierung, new lattice points a/2 + b/2 and + a/2 + c/2 and b/2 + c/2)

- Side-centred lattice (A, B or C, side centred on only some of the sides, e.g. a/2 + b/2. This is a C side centred lattice, which means that the centring are on the sides normal to the c direction/z axes)

Crystal system	Bravais lattice	Z
Cubic	P	1
	I	2
	F	4
Tetragonal	P	1
	I	2
Orthorhombic	P	1
	I	2
	C	2
	F	4
Monoclinic	P	1
	C	2
Triclinic	P	1
Rombohedral	R	1
Hexagonal	P	1

Systematic Absences and identification of lattice types

- The presence of a centered lattice leads to the systematic absence of certain types of peak in the diffraction pattern

  For I centered lattices: – h + k + l = 2n for a line to be present

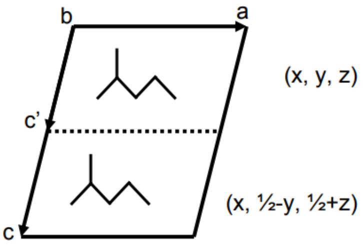
  For an F centered lattice: – h + k =2n, k + l = 2n and h + l = 2n

  For a C centered lattice: – h + k =2n

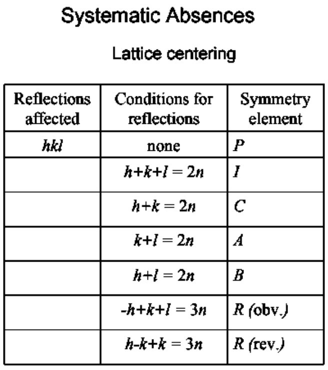
- Lattice centering and symmetry elements with translation (glide planes and screw axes) cause certain reflections to have zero intensity in the diffraction pattern. If, e.g., all reflections 0, k, 0 with odd values for k are absent, we know that we have a 21 axis along b. Other example: if all reflections h, 0, l with odd values for l are absent, we have a c glide plane perpendicular to b.

- Monoclinic cell, projection along b with c glide plane (e.g. Pc)

  In this two 2D projection the structure is repeated at c/2. Thus, the unit cell seems to be half the size: c’ = c/2 in this projection. (x, y, z)

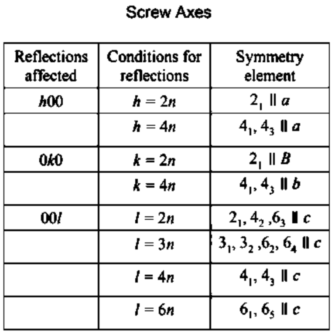


This doubles the reciprocal cell accordingly: $c^{*\prime} = 2c^*$. Therefore, the reflections corresponding to this projection (h, 0, l) will be according to the larger reciprocal cell. c That means h, 0, l reflections with $l \neq 2n$ are not observed.

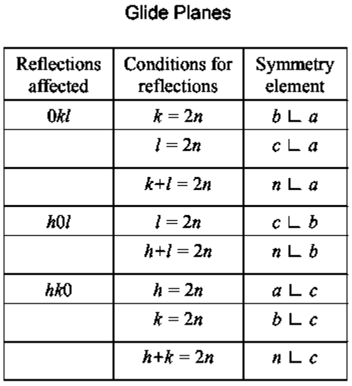

Systematic Absences

Lattice centering

Reflections affected	Conditions for reflections	Symmetry element
hkl	none	P
	$h+k+l = 2n$	I
	$h+k = 2n$	C
	$k+l = 2n$	A
	$h+l = 2n$	B
	$-h+k+l = 3n$	R (obv.)
	$h-k+k = 3n$	R (rev.)


Screw Axes

Reflections affected	Conditions for reflections	Symmetry element
$h00$	$h = 2n$	$2_1 \parallel a$
	$h = 4n$	$4_1, 4_3 \parallel a$
$0k0$	$k = 2n$	$2_1 \parallel B$
	$k = 4n$	$4_1, 4_3 \parallel b$
$00l$	$l = 2n$	$2_1, 4_2, 6_3 \parallel c$
	$l = 3n$	$3_1, 3_2, 6_2, 6_4 \parallel c$
	$l = 4n$	$4_1, 4_3 \parallel c$
	$l = 6n$	$6_1, 6_5 \parallel c$

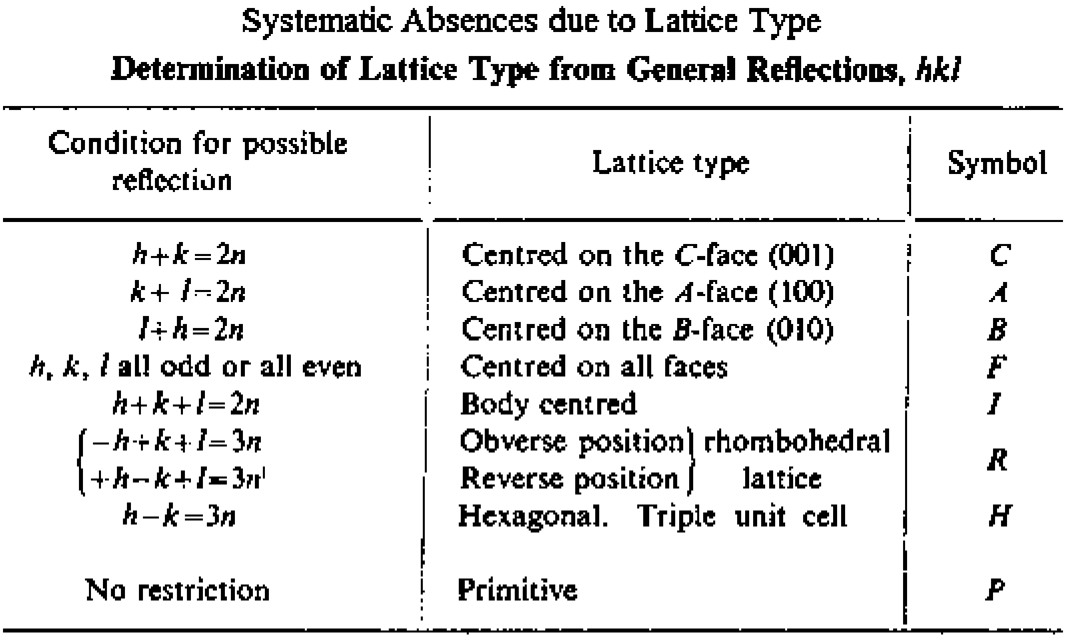

Glide Planes

Reflections affected	Conditions for reflections	Symmetry element
$0kl$	$k = 2n$	$b \llcorner a$
	$l = 2n$	$c \llcorner a$
	$k+l = 2n$	$n \llcorner a$
$h0l$	$l = 2n$	$c \llcorner b$
	$h+l = 2n$	$n \llcorner b$
$hk0$	$h = 2n$	$a \llcorner c$
	$k = 2n$	$b \llcorner c$
	$h+k = 2n$	$n \llcorner c$

- Any symmetry element with a translational component — including cell centring vectors — will produce *systematic absences* from a diffraction pattern: peaks whose intensity is zero.

  Systematic absences (or systematic extintions) in *hkl* reflections arise when symmetry elements containing translational components are present, such as in the following cases:

  a. lattice centering (translational operations derived from the lattice type),
  b. glide planes (mirror planes that imply reflection and an additional translation) and
  c. screw axes (symmetry axes that imply rotation and an additional translation).



Systematic Absences due to Lattice Type

Determination of Lattice Type from General Reflections, *hkl*

Condition for possible reflection	Lattice type	Symbol
$h+k=2n$	Centred on the *C*-face (001)	*C*
$k+l=2n$	Centred on the *A*-face (100)	*A*
$l+h=2n$	Centred on the *B*-face (010)	*B*
h, *k*, *l* all odd or all even	Centred on all faces	*F*
$h+k+l=2n$	Body centred	*I*
$-h+k+l=3n$ $+h-k+l=3n'$	Obverse position } rhombohedral Reverse position } lattice	*R*
$h-k=3n$	Hexagonal. Triple unit cell	*H*
No restriction	Primitive	*P*

Glide planes and screw axes

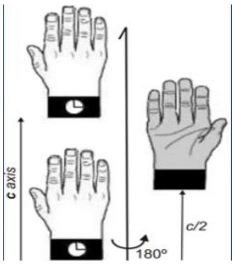
- There are special symmetry operations for a solid material formed by pairing certain symmetry operations (rotation and mirroring) with translation. Two new symmetry elements appear, glide planes and screw axes.

- A screw axis have the notation nm where n is the rotation axis “fold” and m/n is the translation given as a fraction of the unit translation parallel to the rotation axis.

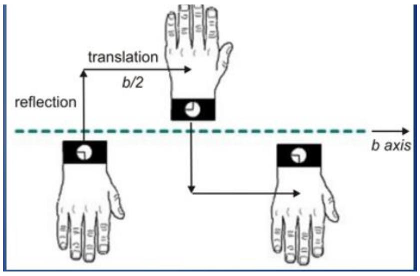
- There are several types of glide planes; axial, diagonal and diamond type. Axial glide planes involve mirroring combined with a translation ½ along an axis. The axial glide planes are called a, b or c. The mirror plane consist of the xz-plane and the translation is done along a. In a similar example with a coin the tail side will remain tail after the operation, but it will appear as a mirror image (right – left hand operation). Diagonal glide planes have the notation n, and diamond glide planes have the notation d.

- Screw Axes – combine a rotation with translation
  Combines rotation and translation
  - Designated as nm (e.g. 2_1 , 4_1 , 3_2 , 4_3)
  - Rotation as 360°/n
  - Symmetry element of the first kind
  - Translation as m/n of a unit cell (n > m)
  - Orientation of the screw axis given by its place in the H-M symbol

  - Causes systematic absences in axial (h00,0k0,00l) reflections
  - Certain pairs of screw axes correspond to right and left handed screws (e.g. 3_1 and 3_2) and are enantiomorphs



- Glide Planes – combine a reflection with translation
  - Combine reflection with translation
  - Symmetry element of the second kind
  - Designated as a, b, c, d, n and letter gives direction of translational component
  - Orientation of reflection plane given by place in the H-M symbol
  - Cause systematic absences in zero layers (0kl, h0l, and hk0) of the diffraction pattern



X-intensities

The high intensity nearly monochromatic K_α x-rays can be used as a radiation source for X-ray diffraction (XRD) studies ➢ a monochromator can be used to further decrease the spread of wavelengths in the X-ray

Target Metal	λ Of K_α radiation (Å)
Mo	0.71

Cu	1.54
Co	1.79
Fe	1.94
Cr	2.29

- When X-rays hit a specimen, the interaction can result in various signals/emissions/effects.
- The coherently scattered X-rays are the ones important from a XRD perspective.
- Usually, the unit cell of a crystal structure contains more than a single atom.
  Each sub-lattice of the structure, based on different atoms, can be imagined to diffract independently.
- All sub-lattices have the same periodicity, and thus the same d-spacings.
- While the incident beam is a coherent wave, the waves of the diffracted (sub-)waves will have phase shifts relative to each other, depending on the positions of the atoms in the unit cell.
- Different atom types have different scattering power, hence the diffracted (sub-)waves may also have different amplitudes.
- Due to these phase shifts and different amplitudes, various degrees of positive and negative interference between the diffracted sub-waves will result in an intensity modulation for the resulting total of the diffracted beam.
- In the special case of centered lattices (same atom type in the unit cell origin and (face or body) center), some reflections have exactly zero intensity (= systematic absence of reflections).
- This can be understood by realizing that both sub-lattices have exactly the same scattering power and a defined geometric relation to each other. As a consequence, the diffracted sub-waves of some lattice planes have the same amplitude and a phase shift of exactly half a period. Thus, the two sub-waves will cancel out completely.

The position of diffraction peaks and the d-spacings that they represent provide information about the location of lattice planes in the crystal structure. Each peak measures a d-spacing that represents a family of lattice planes. Each peak also has an intensity which differs from other peaks in the pattern and reflects the relative strength of the diffraction. In a diffraction pattern, the strongest peak is, by convention, assigned an intensity value of 100, and other peaks are scaled relative to that value. Although peak height may be used as a qualitative measure of relative intensity, the most accurate measure of intensity relationships in a pattern is obtained by measuring the area (minus background) under the peaks. Variations in measured intensity are related chiefly to variations in the scattering intensity of the components of the crystal structure and their arrangement in the lattice. Some of the most dramatic variations are related to interference between diffractions produced in the lattice; these can produce systematic extinctions or greatly reduced intensities of peaks from certain lattice planes.

Structure Factor

In diffraction, that is, the scattering in which the incident X-rays interact with a target atom, exciting it and causing it to be a secondary point source of X-rays of the same energy (wavelength). The intensity of that scattering is the result of a variety of processes the sum of which results in scattering which “looks” like it comes from the atom as a whole.

a. Scattering by an electron:

X-ray is electromagnetic radiation i.e. they have mutually perpendicular electric and magnetic fields. Electrons are negatively charged particles that are affected by these electric and magnetic fields. When X-rays interact with electrons it causes it to oscillate. The oscillating electron will in turn emit X-rays - this is called scattering.

Coherent scattering - emitted X-rays have the same wavelength (same energy) as the incident X-rays. This is also called elastic scattering and the scattered radiation has a definite phase relation with the incident X-rays. . For elastic scattering the scattered radiation is phase shifted from the incident beam by $\pi/2$ or has a path difference of $\lambda/2$.

b. Scattering by an atom:

An atom consists of electrons (loosely and tightly bound) and a nucleus. Nucleus is not involved in x-ray scattering. The scattering by all the individual electrons of the atom add up so that the total scattering by the atom is directly proportional to the atomic number (Z). Then, the total amplitude is Z times (elastic and all scattered radiations are in phase) scattering the amplitude from one electron. For scattering of x-rays by an atom, a scattering factor, f, is defined which is called atomic scattering factor. This is given by

$$f = \frac{\text{amplitude of wave scattered by atom}}{\text{amplitude of wave scattered by electron}} \leq Z$$

For $2\theta = 0$ $f = Z$.

c. Scattering by an unit cell (Structure Factor)

Unit cell has group of atoms in a periodic arrangement. This is extended in 3D. X-rays is diffracted in certain directions obeying Bragg's law. The intensity depends on the type and position of the atoms in the lattice. The total phase difference is then given by

$$\phi = 2\pi(hu + kv + lw)$$

u, v and w – fractional coordinates.

Combining this with the atomic scattering factor of the atoms located at different positions a new term called **the structure factor, F** is defined. The structure factor with an atom located at position (u, v, w) in a unit cell is given by

$$F = f \exp 2\pi i(hu + kv + lw)$$

If there are N atoms in the unit cell and the nth atom has structure factor fn and is located at ($u_n v_n w_n$) then the structure factor for the unit cell, for some plane (hkl) is given by

$$F = \sum_{n=1}^{N} f_n \exp 2\pi i(hu_n + kv_n + lw_n)$$

Putting this in words the structure factor is given as

$$F = \frac{\text{amplitude of wave scattered by unit cell}}{\text{amplitude of wave scattered by electron}}$$

The structure factor equation gives information about the whole crystal structure. The structure factor equation can be expressed in terms of electron density.

- Intrinsic amplitude of scattered X-ray from each type of atom depends on its electron density r(xyz) (described by atomic scattering factor *f*)
- f is used to describe scattering vector for each atom for one reflection (with Miller indices h,k,l)

- Sum of atomic scattering vectors is molecular scattering factor F, also called structure factor (can be calculated for a given structure):

  $\mathbf{F(hkl) = \int r(xyz)\ e^{-2pi(hx+ky+lz)}}$ Fourier Transformation

Phase problem in X-ray Diffraction

- The x-ray detector (as photographic plates or CCD) can only record intensities but not phases of the electromagnetic waves. This measurement is incomplete because a light wave has not only an amplitude (related to intensity), but also a phase, which is systematically lost in a measurement.

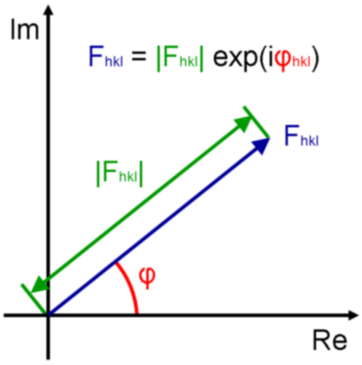
- Each reflection on the diffraction pattern or structure factor corresponds to a wave consisting of amplitude and a phase. The amplitude is easily calculated by taking the square root of the intensity, but the phase is systematically lost during the data collection. However, the phases contain vital information for the determination of the electron density distribution in the crystal.

- In x- ray crystallography, the diffraction data when properly assembled gives the amplitude of the 3D Fourier transform of the molecule's electron density in the unit cell.

- If the phases are known, the electron density can be simply obtained by Fourier synthesis.

- This is called ‘Phase Problem in X-ray Diffraction’.

  For easier representation a structure factor can be represented as a vector or complex number ‘F_{hkl}’ with the amplitude ‘$|F_{hkl}|$’ and the phase ‘φ_{hkl}’. The representation is called an Argand diagramme.



$$\rho(xyz) = 1/V \sum |F_{hkl}| \exp(i\alpha_{hkl}) \exp(-2\pi ihx + ky + lz)$$

Density (xyz)	=	1/Volume of unit cell	Structure Factor Amplitude (hkl)	α_{hkl} Phase associated with the structure factor amplitude	Wave scattered from the plane hkl

Structure solution by Heavy atom method

- Invented by W. L. Patterson for small molecules
- Patterson map is calculated with the square of structure factor amplitude and a phase of zero
- This is an interatomic vector map
- Each peak corresponds to a vector between atoms in the crystal
- Peak intensity is the product of electron densities of each atom

$$F(h,k,l) = |F(h,k,l)|^2$$

$$P(u,v,w) = \frac{1}{V}\sum_{h,k,l} |F(h,k,l)|^2 \cos[2\pi(hu + kv + lw)]$$

No. of spots =(No. of atoms)^2

- ❖ Once phases have been determined as accurately as possible, an e-density map (the Fourier transform of the structure factors with phases) is prepared and interpreted.
- ❖ Use observed structure amplitudes $|F_{obs}(hkl)|$ with best phases, $\alpha_{best}(hkl)$ to give experimentally derived structure factors, $F_{exp}(hkl)$:
- ❖ $F_{exp}(hkl) = |F_{obs}(hkl)| \ \exp[\, i\ \alpha_{best}(hkl)]$
- ❖ Fourier transform creates e-density $\rho_{exp}(xyz)$:

Direct methods

- ➢ Direct methods are based on the positivity and atomicity of electron density that leads to phase relationships between the normalized structure factors: Once the phases of some reflections are known, or can be given a variety of starting values, then the phases of other reflections can be bootstrapped.

- For small molecules there are methods to "guess" the phases of the structure factors. One possibility is the Patterson map. This is a map produced by setting all phases to zero. The amplitudes of each reflection still result in a map that contains information. This information can be interpreted as vectors between atoms, which allows to think of a molecule that explains the map. Using this method molecules up to 100 atoms can be solved by hand and up to 1000 atoms can be solved by progammes. This is not enough for proteins but enough to solve the heavy atom substructures for isomorphous replacement and anomalous dispersion, which in turn allows to solve the phases of the protein diffraction data. There are also other direct methods

- Direct methods determine the phases directly from the diffraction pattern without any knowledge about the nature of the sample. Several statistical equations relate the phase of a reflection to its intensity and the intensity and phase of other reflections in the dataset. This can be done with a certain probability. Many probability relations together with fast computers make it possible to determine the phases of many measured reflections with some accuracy. Direct methods usually do not use structure factors but operate in E-space (remember the normalized structure factors from the E2-1 statistics?). The advantage is, that the intensity of a normalized structure factor does not decline with the resolution; and direct methods assume atoms to be point scatterers anyway. Direct methods are used predominantly as “b

A Brief Account of Cambridge Structural Database (CSD)

- The Cambridge Structural Database is ‘a computer-based file containing both bibliographic information and numerical data abstracted from the literature and relevant to molecular crystal structures, as obtained by diffraction methods’

- The CCDC (Cambridge Crystallographic Data Centre)was established at the Department of Chemistry, Cambridge University, in **1965** to compile a database containing comprehensive information on small-molecule crystal structures, i.e. organics and metallo-organic compounds containing up to 500 non-H atoms, the structures of which had been determined by X-ray or neutron diffraction.

- A file format called CIF (now the Crystallographic Information Framework) is the standard for the interchange of crystallographic data. CIF is now ubiquitously used to capture the results of a diffraction experiment and enables streamlined publication of results alongside journal articles and in data repositories.

- Originally, it might best have been described as a secondary resource of data abstracted from the literature. Today, new source data files are almost always deposited directly into the CSD making it much more of a primary data resource. Indeed, many structures are published only and directly through the CSD as CSD Communications (previously known as Private Communications).

- A specific aim was to store the key numerical results of each analysis, namely the cell parameters, space group and atomic coordinates, making the **CSD one of the first numerical scientific databases in the world**, and the first to store experimental three-dimensional chemical structure information.

- It is continually updated with new structures and with improvements to existing entries, keeping fully informed of the latest research. This data update brings you 10,950 new entries and the total size of the CSD to just over 1,000,000+ in December, 2019.

    a. All database entries are identified uniquely by a six-letter reference code, or "refcode", which may be followed by two digits if the entry is a member of a family of entries. The refcode system allows to group together structures into families. The most obvious grouping is different data collections of the same crystal, for example at different temperatures or pressures. It also groups the same structure determined by different research groups, and add polymorphs of the same compound, too.

    Eg. For Adamantane-1,3,5,7-tetracarboxylic acid refcode is GEJVEW

    On deposition, each dataset is assigned an accession identifier referred to as a 'CCDC number' in the format CCDC 1234567 (older entries have six digits). This uniquely identifies the data associated with a particular structure determination and persists for the lifetime of the dataset. CCDC numbers are communicated to the depositor once it has been confirmed that the dataset is not a duplicate submission,

b. Due to the rising number of structures, depositions and transactions a new processing system, *CSD-Xpedite*, has been developed, automating most informatics processes required to manage depositions and process crystal structures into entries in the CSD.

The information stored in the CSD for each entry can be considered in three classes.

c. There is the text-based (and sometimes numeric) information, containing the bibliography (i.e. full literature reference, where appropriate), chemical names and formulae, some experimental information about the crystal structure determination procedure, and any other information that may be available (e.g. compound's use, color and shape of crystals, etc. etc.).

d. Secondly, there is chemical connectivity information in the form of a 2D structural diagram – it is this that forms the basis of much of the sophisticated search mechanisms for the CSD System.

e. Thirdly, there is the crystallographic information, consisting of unit cell dimensions and space group, and atomic coordinates (these are available for the vast majority of entries, although not all). It is in this third category where the true value of the Database lies.

CSD distribution and availability

a. The CCDC Web site **http://www.ccdc.cam.ac.uk/**, contains full current nformation about the availability of the Cambridge Structural Database system.
b. (i) pre-published archive,
c. (ii) published archive and
d. (iii) The distributed CSD archive, held in the CCDC's binary ASER format. This file contains all value-added data items, e.g.
e. chemical connection tables,

f. coordinates transformed to the c.c.u. basis,
g. processing flags and text etc., and
h. structured for search, analysis and display using CCDC software

Applications of CSD: Conformational preferences

a. If a particular molecular fragment containing a rotatable bond is observed in a series of crystal structures, it is likely that more **strained (higher energy) conformations will be observed less often** than relatively unstrained (lower energy) geometries.

b. Crystal conformers are close to *in vivo* environment.

c. A CSD-based compilation of the means, medians and standard deviations of many types of organic bond lengths has been very widely used for **model building** etc.

d. A crucial breakthrough in computational drug design came with the development of programs such as AIMB, CONCORD and CORINA that can convert a two- dimensional chemical structure into a reasonable three-dimensional geometry.

Knowledge-Based Libraries

CCDC has decided to expand the capabilities of the CSD System by including two knowledge-based libraries. These encapsulate much of the information on intermolecular interactions and on molecular geometry found within the CSD, which has been pre-extracted and is presented to the user in an easy to visualise form. One of these libraries, IsoStar, Mogul, SuperStar, GOLD etc., has been available for some years.

PROTEIN DATA BANK (PDB)

➢ The Protein Data Bank (PDB) [1] is a database for the three-dimensional structural data of large biological molecules, such as proteins and nucleic acids. The data, typically obtained by X-ray crystallography, NMR spectroscopy, or, increasingly, cryo-electron microscopy, and submitted by biologists and biochemists from around the world, are freely accessible on the Internet via the websites of its member organisations (PDBe,[2] PDBj,[3] RCSB,[4] and BMRB[5]). The PDB is overseen by an organization called the Worldwide Protein Data Bank, wwPDB.

- It is a “Single international repository for all information about the structure of large biological molecules.”

- History, growth and development of Protein Data Bank

PDB is freely and publicly available to the global community. It represents one of the earliest community-driven molecular-biology data collections.

PDB was first established in 1971 by W. Hamilton at Brookhaven National Laboratory in response to Community requirement for information about Biological macromolecular structures {seven entries}In 1977, the first paper was published about its existence and there were 77 entries then: Bernstein *et al.*, (1977) *Journal of Molecular Biology*, 112, 535-542.

Since 1971, the Protein Data Bank archive (PDB) has served as the single repository of information about the 3D structures of proteins, nucleic acids, and complex assemblies. The Worldwide PDB (wwPDB) organization manages the PDB archive of primary structural data of biological macromolecules. Many secondary sources of information are derived from PDB data. It is the starting point for studies in structural bioinformatics.

Initial use of the PDB had been limited to a small group of experts involved in structural biology research. Today, depositors to the PDB have expertise in the techniques of X-ray crystal structure determination, NMR, cryo-electron microscopy and theoretical modeling. A key component of the PDB is the ef®cient capture and curation of the data: data processing. Data processing consists of data deposition, annotation and validation. These steps are part of a fully documented and integrated data-processing system

- Data acquisition and processing

Content of the data collected by the PDB: Fixed format records to describe

a. Atomic coordinates

b. sequence information
c. Chemical and biochemical features
d. Experimental details of structure determination
e. Structural features: secondary structure assignments, hydrogen bonding, biological assemblies, active sites and disulphide bonds

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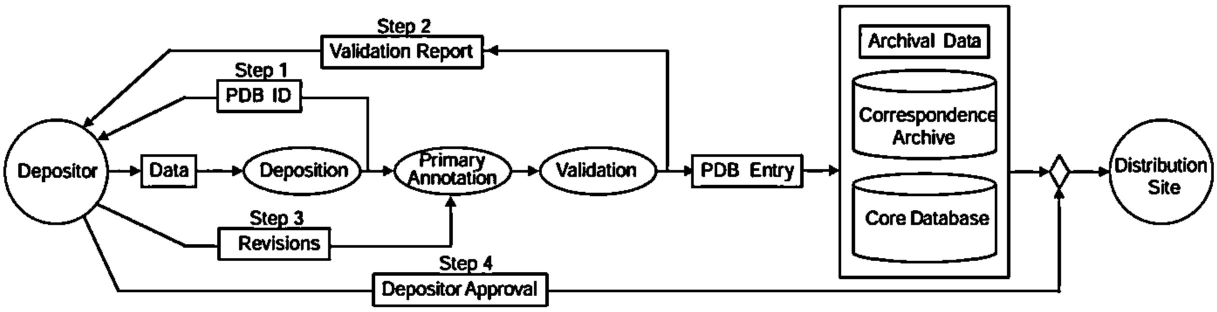
Validation and annotation Validation refers to the procedure for assessing the quality of deposited atomic models (structure validation) and for assessing how well these models ®t the experimental data (experimental validation). Annotation refers to the process of adding information to the entry that results from the validation process.

The following checks are run and are summarized in a letter that is communicated directly to the depositor.

a. Covalent bond distances and angles
b. Stereochemical validation
c. Atom nomenclature
d. Close contact
e. Ligand and atom nomenclature
f. Sequence comparison
g. Distant waters

Since October 1998, the PDB has been managed by the three members of the Research Collaboratory for Structural Bioinformatics (RCSB) ± Rutgers, The State University of New Jersey, the San Diego Supercomputer Center at the University of California, San Diego, and the National Institute of Standards and Technology.



The steps involved in PDB data processing. Ellipses represent actions and rectangles define content.

- User Communities

    a. Biologists (in fields such as structural biology, biochemistry, genetics, pharmacology)

    b. Other scientists (in fields such as bioinformatics, software developers for data analysis and visualization)

    c. Students and Educators (all levels)

    d. Media writers, illustrators, textbook authors

    e. General public

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- Ftp access

All structures, in PDB and mmCIF formats, are available for download from the PDB ftp site. Dictionaries, documentation and PDB-provided software are also available. Instructions and software for mirroring the PDB ftp archive as a local copy are available at http://www.rcsb.org/pdb/ ftpproc.final.html.

The structure files may be viewed using one of several free and open source computer programs, including Jmol, Pymol, VMD, and Rasmol.

- Distribution

As stated, the PDB distributes coordinate data in PDB and CIF formats, structure-factor files and NMR constraint files. In addition it provides derived data, documentation and software. The PDB files enjoy widespread usage by individual researchers and by databases of structural properties. New data officially become available at 2:00 AM PST each Wednesday.

As on date nearly 1, 60,233 number of structures can be viewed in PDB

Electron diffraction by gases

Gas electron diffraction (GED) is one of the applications of electron diffraction techniques. The target of this method is the determination of the structure of gaseous molecules i.e. the geometrical arrangement of the atoms from which a molecule is built up.

Diffraction occurs because the wavelength of electrons accelerated by a potential of a few thousand volts is of the same order of magnitude as internuclear distances in molecules

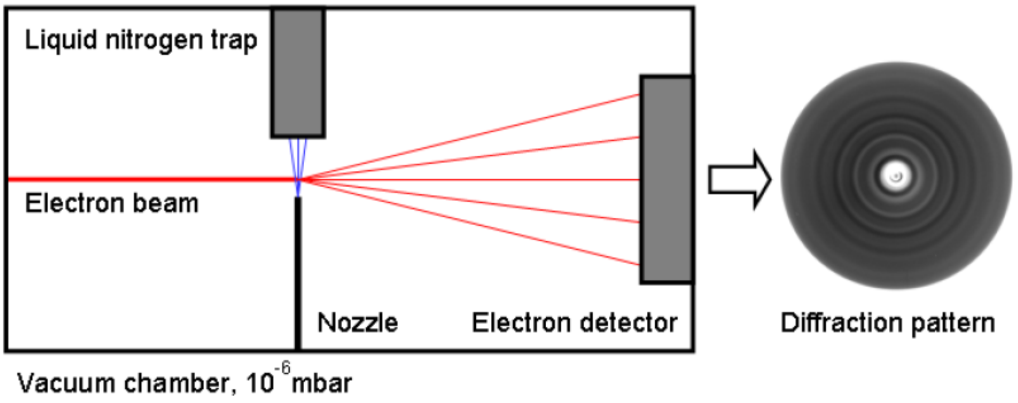
The total scattering intensity in GED is given as a function of the momentum transfer, which is defined as the difference between the wave vector of the incident electron beam and that of the scattered electron beam and has the reciprocal dimension of length. The total scattering intensity is composed of two parts: the atomic scattering intensity and the molecular scattering intensity.

$$I_{total} = I_{atom} + I_{mol}$$

I_{atom} decreases monotonically and contains no information about the molecular structure.

I_{mol} has sinusoidal modulations as a result of the interference of the scattering spherical waves generated by the scattering from the atoms included in the target molecule. It contains all the structural information. The interferences reflect the distributions of the atoms composing the molecules, so the molecular structure is determined from this part.

The diffraction pattern, captured on photographic film consists of diffuse, concentric rings due to the random orientation of the molecules in the diffraction chamber. Initially, patterns were interpreted by eye using the visual method.9,10 This consisted of measuring the diameters of rings with maximum and minimum intensities and comparing these with values calculated from a model. The best fit, determined by trial and error, gave the structure.



A universal variable‘s’ is used for the data reduction and refinement process. This is a function of both the scattering angle (ϑ) and the electron (de Broglie) wavelength (λ)

$$s = \frac{4\pi}{\lambda} sin\frac{\vartheta}{2}$$

It is an equation for the determination of intensity of an electron beam scattered through a specific angle by diffraction from a gas molecule. This is useful when dealing with complex molecules. To study larger molecules, or molecules which have no permanent dipole moment, GED must be employed.

$$I_S = \frac{L_{mol}}{I_{atom}} = \sum_{i}^{N}\sum_{j\neq i}^{N} Z_i Z_j \frac{\sin \boldsymbol{s}\, r_{i,j}}{\boldsymbol{s}\, r_{i,j}}$$

where I_S is the scattered electron intensity, Z is an atomic property, chosen as the atomic number, r_{ij} are the interatomic distances between the i^{th} and j^{th} atoms, and N is the number of atoms.

NEUTRON DIFFRACTION.

•Mass	= 1.68×10^{-27} kg (photon mass = zero)
•Charge	= zero (photon charge = zero)
•Spin	= ½ (photon spin = 1)
•Magnetic dipole moment	= -9.66×10^{-27} JT^{-1} (photon moment zero)

Neutron Scattering Requires Intense Sources of Neutrons

- Neutrons for scattering experiments can be produced either by nuclear fission in a reactor or by spallation when high-energy protons strike a heavy metal target (W, Ta, or U).

- In general, reactors produce continuous neutron beams and spallation sources produce beams that are pulsed between 20 Hz and 60 Hz
- The energy spectra of neutrons produced by reactors and spallation sources are different, with spallation sources producing more high-energy neutrons

- Neutron spectra for scattering experiments are tailored by moderators

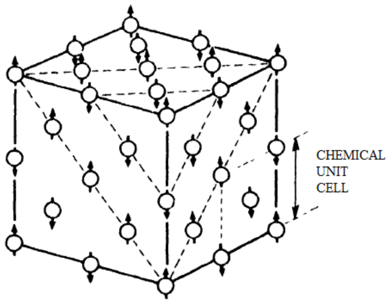
- solids or liquids maintained at a particular temperature

- although neutrons are not in thermal equilibrium with moderators at a short-pulse spallation sources

Neutrons from Reactors and Spallation Sources Must Be Moderated Before Being Used for Scattering Experiments

- Not only X-ray and electron beams, but also beams of heavier particles may exhibit diffraction patterns when scattered from the regular array of atoms in a crystal. Neutron beams have proved to be especially useful for such studies. The wavelength is related to the mass and velocity by the Broglie equation, $\lambda = \frac{h}{mv}$. Thus a neutron with a speed of 3.9 x 10^5 cm sec^{-1} (kinetic energy 0.08 ev) would have a wavelength of 1 .0 Å. The diffraction of electron rays or X rays is caused by their interaction with the orbital electrons of the atoms in the material through which they pass; the atomic nuclei contribute practically nothing to the scattering. The diffraction of neutrons, on the other hand, is primarily caused by two other effects: (a) nuclear scattering due to interaction of the neutrons with the atomic nuclei, (b) magnetic scattering due to interaction of the magnetic moments of the neutrons with permanent magnetic moments of atoms or ions.

- In the absence of an external magnetic field, the magnetic moments of atoms in a paramagnetic crystal are arranged at random, so that the magnetic scattering of neutrons by such a crystal is also random. It contributes only a diffuse background to the sharp maxima occurring when the Bragg condition is satisfied for the nuclear scattering. In ferromagnetic materials, however, the magnetic moments are regularly aligned so that the resultant spins of adjacent atoms are parallel, even in the absence of an external field. In antiferromagnetic materials, the magnetic moments are also regularly aligned, but in such a way that adjacent spins are always opposed. The neutron diffraction patterns distinguish experimentally between these different magnetic structures, and indicate the direction of alignment of spins within the crystal.

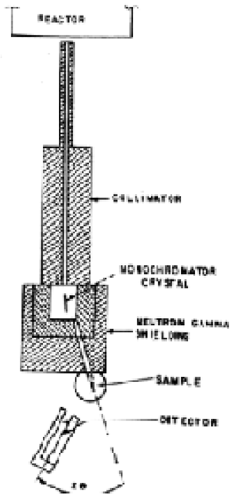


Magnetic structure of MnO as found by neutron diffraction. Note that the "magnetic unit cell" has twice the length of the "chemical unit cell."

For example, manganous oxide, MnO, has the rock-salt structure (Fig.), and is antiferromagnetic. The detailed magnetic structure as revealed by neutron diffraction is shown in Fig.. The manganous ion, Mn^{+2} , has the electronic structure $3s^2$ $3p^6 3d^5$.

The five 3d electrons are all unpaired, and the resultant magnetic moment is $2\sqrt{\frac{5}{2}\left(\frac{5}{2}+1\right)} =$ 5.91 Bohr magnetons. If we consider Mn^{+2} ions in successive (111) planes in the crystal, the resultant spins are oriented so that they are alternately positively and negatively directed along the [100] direction.

Another useful application of neutron diffraction has been the location of hydrogen atoms in crystal structures. It is usually impossible to locate hydrogen atoms by means of X-ray or electron diffraction, because the small scattering power of the hydrogen is completely overshadowed by that of heavier atoms. The hydrogen nucleus, however, is a strong scatterer of neutrons. Thus it has been possible to work out the structures of such compounds as UH_3 and KHF_2 neutron-diffraction analysis.



Magnetic Scattering

- The magnetic moment of the neutron interacts with B fields caused, for example, by unpaired electron spins in a material

  – Both spin and orbital angular momentum of electrons contribute to B
  – Expressions for cross sections are more complex than for nuclear scattering

- Magnetic interactions are long range and non-central

  – Nuclear and magnetic scattering have similar magnitudes
  – Magnetic scattering involves a form factor
  – FT of electron spatial distribution

- Electrons are distributed in space over distances comparable to neutron wavelength

- Elastic magnetic scattering of neutrons can be used to probe electron distributions

  – Magnetic scattering depends only on component of B perpendicular to Q
  – For neutrons spin polarized along a direction z (defined by applied H field):

- Correlations involving B z do not cause neutron spin flip
- Correlations involving Bx or By cause neutron spin flip
  – Coherent & incoherent nuclear scattering affects spin polarized neutrons
- Coherent nuclear scattering is non-spin-flip
- Nuclear spin-incoherent nuclear scattering is 2/3 spin-flip
- Isotopic incoherent scattering is non-spin-flip

The neutron has a magnetic moment. Just as two bar magnets either attract or repel one another, the neutron experiences a force of magnetic origin whenever it moves in a magnetic field, such as that produced by unpaired electrons in matter.

Ferromagnetic materials, such as iron, are magnetic because the moments of their unpaired electrons tend to align spontaneously. For many purposes, such materials behave as if small magnetic moments were located at each atomic site with all the moments pointing in the same direction. These moments give rise to ***magnetic Bragg scattering*** of neutrons in the same manner as the nuclear interactions. Because the nuclear and magnetic interactions experienced by the neutron are of similar magnitude, the corresponding Bragg reflections are also of comparable intensity.

One difference between the two types of scattering, however, is that the magnetic interaction, unlike the nuclear interaction is not isotropic. The magnetic interaction is dipolar, just like that between two bar magnets. And just like two bar magnets, the strength of the interaction between the neutron and a nucleus depends on the relative orientations of their magnetic moments and the line joining their centers. For neutrons, the dipolar nature of the magnetic interaction means that only the component of the sample’s magnetization that is perpendicular to the scattering vector, Q effective in scattering neutrons. Neutron scattering is therefore sensitive to the spatial distribution of both the direction and the magnitude of magnetization inside a material.

The anisotropic nature of the magnetic interaction can be used to separate nuclear and magnetic Bragg peaks in ferromagnets, for which both types of Bragg peaks occur at the same values of Q . If the electronic moments can be aligned by an applied magnetic field, magnetic Bragg peaks for which Q is parallel to the induced magnetization vanish, leaving only the nuclear component. On the other hand, an equivalent Bragg peak for which Q is perpendicular to the magnetization will manifest both nuclear and magnetic contributions.

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Neutron diffraction – magnetic structure
•The positions of magnetic atoms within the unit cell
•The directions of their ordered magnetic moments
•The magnitudes of their ordered magnetic moments

Sources of neutrons
• natural sources of neutrons
– only radioactive elements, e.g. uranium
– neutron outside the nucleus will disappear after 18 minutes!
• artificial processes which produce neutrons
– (1) nuclear fission: sustained reaction of radioactive elements, e.g. uranium
– (2) spallation: disintegration of heavy elements, e.g. tantalum • artificial sources of neutrons
– (1) nuclear reactor source:
– (2) spallation source: