LECTURE NOTES

UNIT-I

SYLLABUS

***Ultraviolet and Visible Spectroscopy**: Electronic spectra of diatomic molecules - laws of photochemistry - electronic absorption transitions-correlation of electronic structure with molecular structure - simple chromophoric groups - effects of conjugation - Woodward -Fisher rules for α, β unsaturated carbonyl compounds & dienes - aromatic systems with extended conjugation - applications to organic and inorganic compounds - Instrumentation*.

Vibronic spectroscopy

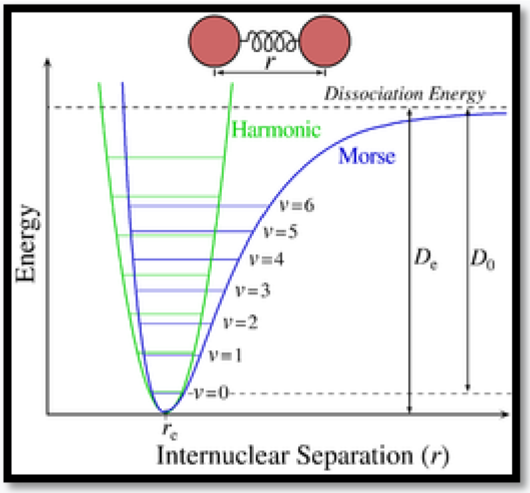
Vibronic spectra involve simultaneous changes in the vibrational and electronic energy states of a molecule. In the gas phase vibronic transitions are accompanied by changes in rotational energy also. Vibronic spectra of diatomic molecules have been analysed in detail; emission spectra are more complicated than absorption spectra. The intensity of allowed vibronic transitions is governed by the Franck–Condon principle. Vibronic spectroscopy may provide information, such as bond-length, on electronic excited states of stable molecules. It has also been applied to the study of unstable molecules such as dicarbon, C_2, in discharges, flames and astronomical objects.

Principles

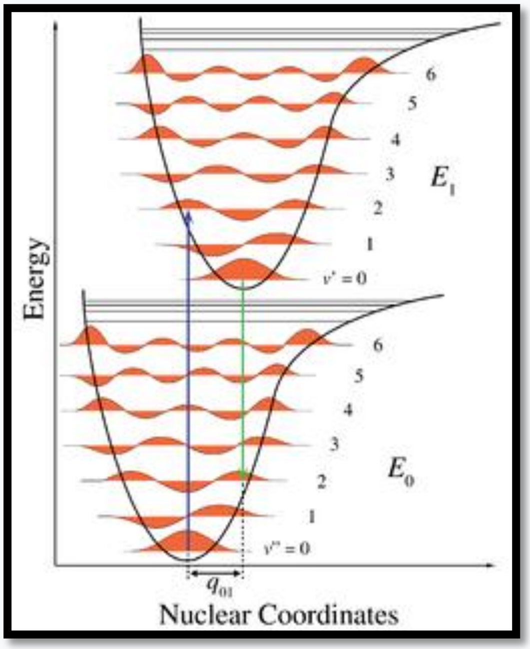
Electronic transitions are typically observed in the visible and ultraviolet regions, in the wavelength range approximately 200–700 nm (50,000–14,000 cm^{-1}), whereas fundamental vibrations are observed below about 4000 cm^{-1}. When the electronic and vibrational energy changes are so different, vibronic coupling (mixing of electronic and vibrational wave functions) can be neglected and the energy of a vibronic level can be taken as the sum of the electronic and vibrational (and rotational) energies; that is, the Born–Oppenheimer approximation applies. The overall molecular energy depends not only on the electronic state but also on vibrational and rotational quantum numbers, denoted v and J respectively for diatomic molecules. It is conventional to add a double prime (v", J") for levels of the electronic ground state and a single prime (v', J') for electronically excited states.

Each electronic transition may show vibrational coarse structure, and for molecules in the gas phase, rotational fine structure. This is true even when the molecule has a zero dipole moment and therefore has no vibration-rotation infrared spectrum or pure rotational microwave spectrum.

It is necessary to distinguish between absorption and emission spectra. With absorption the molecule starts in the ground electronic state, and usually also in the vibrational ground state $\upsilon^n=0$ because at ordinary temperatures the energy necessary for vibrational excitation is large compared to the average thermal energy. The molecule is excited to another electronic state and to many possible vibrational states $\upsilon^1=0,1,2,3....$. With emission, the molecule can start in various populated vibrational states, and finishes in the electronic ground state in one of many populated vibrational levels. The emission spectrum is more complicated than the absorption spectrum of the same molecule because there are more changes in vibrational energy level.



The **Morse potential** (blue) and harmonic oscillator potential (green). The potential at infinite internuclear distance is the dissociation energy for pure vibrational spectra. For vibronic spectra there are two potential curves (see Figure at right), and the dissociation limit is the *upper* state energy at infinite distance.



Energy level diagram illustrating the Franck–Condon principle. Transitions between $v'' = 0$ and $v' = 2$ are favored

For absorption spectra, the vibrational coarse structure for a given electronic transition forms a single *progression*, or series of transitions with a common level, here the lower level $\upsilon^n=0$. There are no selection rules for vibrational quantum numbers, which are zero in the ground vibrational level of the initial electronic ground state, but can take any integer values in the final electronic excited state. The term values G(υ) for a harmonic oscillator are given by

$$G(v) = \bar{\nu}_{electronic} + \omega_e(v + \frac{1}{2})$$

where *v* is a vibrational quantum number, ω_e is the harmonic wavenumber. In the next approximation the term values are given by

$$G(v) = \bar{\nu}_{electronic} + \omega_e(v + \frac{1}{2}) - \omega_e\chi_e(v + \frac{1}{2})^2$$

where χ_e is an anharmonicity constant. This is, in effect, a better approximation to the Morse potential near the potential minimum. The spacing between adjacent vibrational lines decreases with increasing quantum number because of anharmonicity in the vibration. Eventually the separation decreases to zero when the molecule photo-dissociates into a continuum of states. The second formula is adequate for small values of the vibrational quantum number. For higher values further anharmonicity terms are needed as the molecule approaches the dissociation limit, at the energy corresponding to the upper (final state) potential curve at infinite internuclear distance.

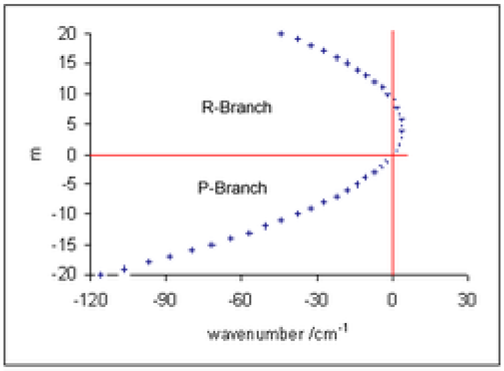
The intensity of allowed vibronic transitions is governed by the Franck–Condon principle. Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates, that is, when the transition is "vertical" on the energy level diagram. Each line has a finite linewidth, dependent on a variety of factors. Vibronic spectra of diatomic molecules in the gas phase have been analyzed in detail. Vibrational coarse structure can sometimes be observed in the spectra of molecules in liquid or solid phases and of molecules in solution. Related phenomena including photoelectron spectroscopy, resonance Raman spectroscopy, luminescence, and fluorescence are not discussed in this article, though they also involve vibronic transitions.

Diatomic molecules

The vibronic spectra of diatomic molecules in the gas phase also show rotational fine structure. Each line in a vibrational progression will show P- and R- branches. For some electronic transitions there will also be a Q-branch. The transition energies, expressed in wavenumbers, of the lines for a particular vibronic transition are given, in the rigid rotor approximation, that is, ignoring centrifugal distortion, by

$$G(J', J'') = \bar{\nu}_{v'-v''} + B'J'(J'+1) - B''J''(J''+1)$$

Here *B* are rotational constants and *J* are rotational quantum numbers. (For B also, a double prime indicates the ground state and a single prime an electronically excited state.) The values of the rotational constants may differ appreciably because the bond length in the electronic excited state may be quite different from the bond length in the ground state, because of the operation of the Franck-Condon principle. The rotational constant is inversely proportional to the square of the bond length. Usually $B' < B''$ as is true when an electron is promoted from a bonding orbital to an antibonding orbital, causing bond lengthening. But this is not always the case; if an electron is promoted from a non-bonding or antibonding orbital to a bonding orbital, there will be bond-shortening and $B' > B''$.



Fortrat diagram created with B′=0.8, B″=1, showing displacement of rotational lines from the vibrational line position (at 0 cm^{-1}). Centrifugal distortion is ignored in this diagram.

The treatment of rotational fine structure of vibronic transitions is similar to the treatment of rotation-vibration transitions and differs principally in the fact that the ground and excited states correspond to two different electronic states as well as to two different vibrational levels.

For the P-branch $J' = J'' - 1$, so that

$$\begin{aligned}\bar{\nu}_P &= \bar{\nu}_{v'-v''} + B'(J''-1)J'' - B''J''(J''+1)\\ &= \bar{\nu}_{v'-v''} - (B'+B'')J'' + (B'-B'')J''^2\end{aligned}$$

Similarly for the R-branch $J'' = J' - 1$, and

$$\begin{aligned}\bar{\nu}_R &= \bar{\nu}_{v'-v''} + B'J'(J'+1) - B''J'(J'-1)\\ &= \bar{\nu}_{v'-v''} + (B'+B'')J' + (B'-B'')J'^2\end{aligned}$$

Thus, the wavenumbers of transitions in both P- and R- branches are given, to a first approximation, by the single formula

$$\bar{\nu}_{P,R} = \bar{\nu}_{v',v''} + (B' + B'')m + (B' - B'')m^2, \quad m = \pm 1, \pm 2\ etc.$$

Here positive *m* values refer to the R-branch (with $m = +J'$) and negative values refer to the P-branch (with $m = -J''$). The wavenumbers of the lines in the P-branch, on the low wavenumber side of the *band origin* at $\bar{\nu}_{v',v''}$, increase with *m*. In the R-branch, for the usual case that $B' < B''$, as *J* increases the wavenumbers at first lie increasingly on the high wavenumber side of the band origin but then start to decrease, eventually lying on the low wavenumber side. The Fortrat diagram illustrates this effect. In the rigid rotor approximation the line wavenumbers lie on a parabola which has a maximum at

$$x = -\frac{B' + B''}{2(B' - B'')}$$

The line of highest wavenumber in the R-branch is known as the *band head*. It occurs at the value of *m* which is equal to the integer part of *x*, or of (*x*+1).

When a Q- branch is allowed for a particular electronic transition, the lines of the Q-branch correspond to the case $\Delta J=0$, $J'=J''$ and wavenumbers are given by

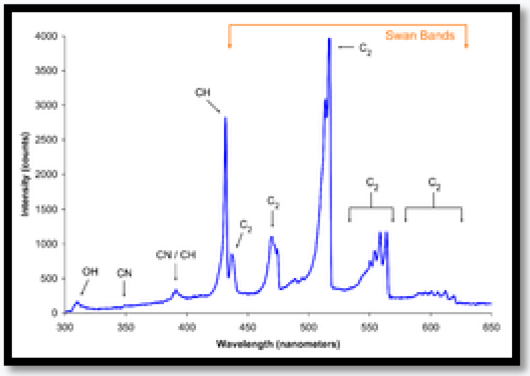
$$\bar{\nu}_Q = \bar{\nu}_{v',v''} + (B' - B'')J(J+1) \quad J = 1, 2\ etc.$$

The Q-branch then consists of a series of lines with increasing separation between adjacent lines as *J* increases. When $B'<B''$ the Q-branch lies to lower wavenumbers relative to the vibrational line.

Predissociation

The phenomenon of predissociation occurs when an electronic transition results in dissociation of the molecule at an excitation energy less than the normal dissociation limit of the upper state. This can occur when the potential energy curve of the upper state crosses the curve for a repulsive state, so that the two states have equal energy at some internuclear distance. This allows the possibility of a radiationless transition to the repulsive state whose energy levels form a continuum, so that there is blurring of the particular vibrational band in the vibrational progression.

Applications



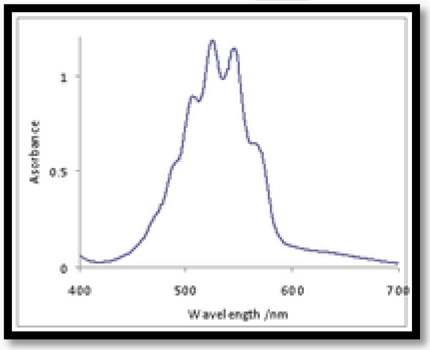
Spectrum of the blue flame from a butanetorch showing excited molecular radical band emission and Swan bands due to C_2.

The analysis of vibronic spectra of diatomic molecules provides information concerning both the ground electronic state and the excited electronic state. Data for the ground state can also be obtained by vibrational or pure rotational spectroscopy, but data for the excited state can only be obtained from the analysis of vibronic spectra. For example, the bond length in the excited state may be derived from the value of the rotational constant B'. In addition to stable diatomic molecules, vibronic spectroscopy has been used to study unstable species, including CH, NH, hydroxyl radical, OH, and cyano radical, CN.[14] The Swan bands in hydrocarbon flame spectra are a progression in the C-C stretching vibration of the dicarbon radical, C_2 for the $d\,^3\Pi_u \leftrightarrow a^3\,\Pi_g$ electronic transition. Vibronic bands for 9 other electronic transitions of C_2 have been observed in the infrared and ultraviolet regions.

Polyatomic molecules and ions

Formaldehyde

For polyatomic molecules, progressions are most often observed when the change in bond lengths upon electronic excitation coincides with the change due to a ″totally symmetric″ vibration. This is the same process that occurs in resonance Raman spectroscopy. For example, in formaldehyde (methanal), H_2CO, the n → π* transition involves excitation of an electron from a non-bonding orbital to an antibonding pi orbital which weakens and lengthens the C-O bond. This produces a long progression in the C-O stretching vibration.[16][17] Another example is furnished by benzene, C_6H_6. In both gas and liquid phase the band around 250 nm shows a progression in the symmetric ring-breathing vibration.[18]



Absorption spectrum of an aqueous solution of potassium permanganate

As an example from inorganic chemistry the permanganate ion, MnO^{-}_{4}, in aqueous solution has an intense purple colour due to an O → Mn ligand-to-metal charge transfer band (LMCT) in much of the visible region. This band shows a progression in the symmetric Mn-O stretching vibration. The individual lines overlap each other extensively, giving rise to a broad overall profile with some coarse structure.

Progressions in vibrations which are not totally symmetric may also be observed.

d-d electronic transitions in atoms in a centrosymmetric environment are electric-dipole forbidden by the Laporte rule. This will apply to octahedral coordination compounds of the transition metals. The spectra of many of these complexes have some vibronic character. The same rule also applies to *f-f* transitions in centrosymmetric complexes of lanthanides and actinides. In the case of the octahedral actinide chloro-complex of uranium(IV), UCl_6^{2-} the observed electronic spectrum is entirely vibronic. At the temperature of liquid helium, 4K, the vibronic structure was completely resolved, with zero intensity for the purely electronic transition, and three side-lines corresponding to the asymmetric U-Cl stretching vibration and two asymmetric Cl-U-Cl bending modes. Later studies on the same anion were also able to account for vibronic transitions involving low-frequency lattice vibrations.

Ultraviolet spectroscopy

We see a lot of colorful things around us. What exactly is the color and what make the things exhibit these colors? We know that the color we see is the visible region of the electromagnetic spectrum. We also know that matter can absorb the electromagnetic radiation of different energy (or wavelengths). The region of electromagnetic energy that is not absorbed is simply reflected back or gets transmitted through the matter. The colored compounds are colored because they absorb the visible light. The color that is perceived is called the complement color to the absorbed wavelength and is represented by a color wheel (Figure 4.1).

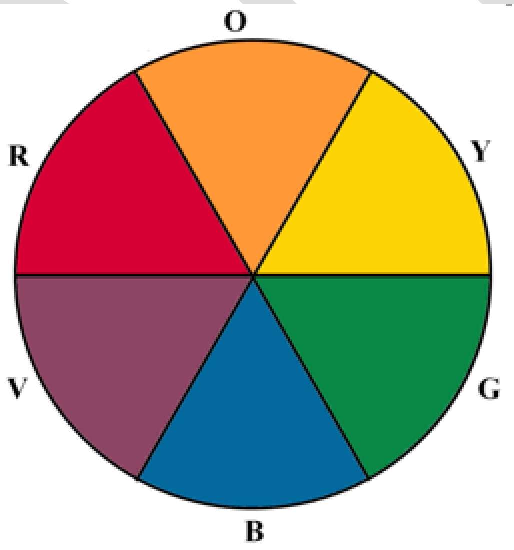


Figure 4.1 A simplified color wheel showing complementary colors. Green is interesting as it can arise from the absorption of radiation to either end of the visible spectrum.

Absorption of ultraviolet (UV) and visible radiation is one of the most routinely used analytical tools in life sciences research. The simplest application of UV/Visible radiation is to quantify the amount of a substance present in a solution. UV region of electromagnetic radiation encompasses the wavelengths ranging from ~10 nm – ~400 nm while visible region encompasses the wavelengths from ~400 nm – ~780 nm. For the sake of convenience in discussing the observations, UV region is loosely divided into near UV (wavelength region nearer to the visible region, λ ~ 250 nm – 400 nm), far UV region (wavelength region farther to the visible region, λ ~ 190 nm – 250 nm) and vacuum UV region (λ< 190 nm). The wavelength ranges defined for these regions are not strict and people use slightly different ranges to define these regions. We shall, however, stick to the wavelengths defined here . As has been discussed in the previous lecture, the absorption of UV and visible light is through the transition of an electron in the molecule from lower to a higher energy molecular orbital. The various electronic transitions observed in organic compound are shown in Figure 4.2.

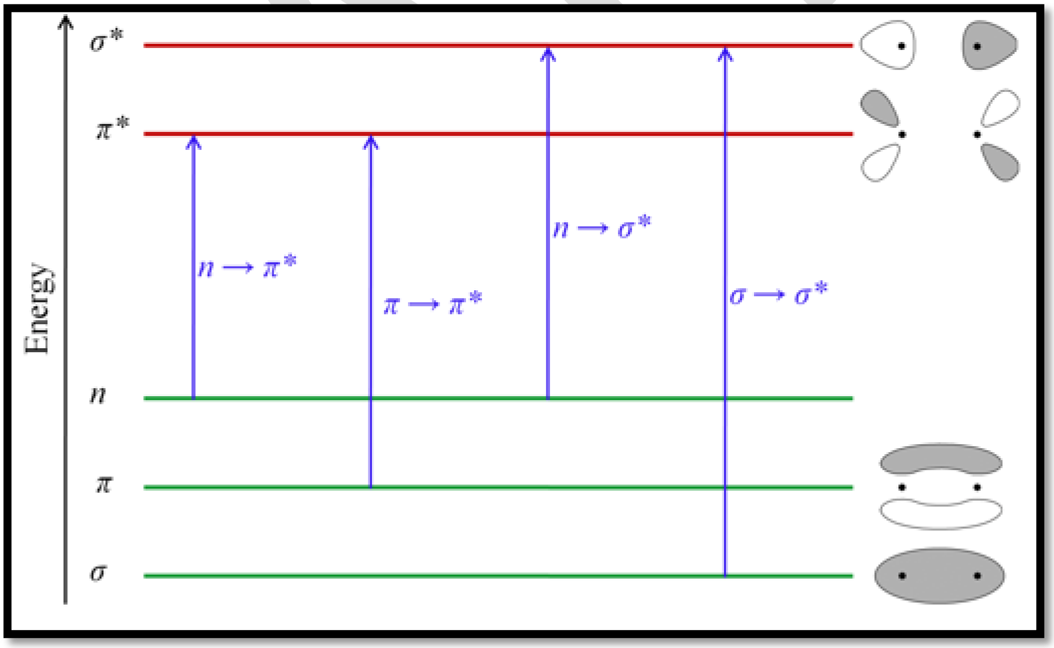


Figure 4.2 Schematic diagram showing energy levels of different orbitals and possible absorption transitions

As shown in figure 4.2, $\sigma \rightarrow \sigma^*$ transition is a high energy process and therefore lies in the vacuum UV region. Alkanes, wherein only $\sigma \rightarrow \sigma^*$ transition is possible show absorption bands ~150 nm wavelength. Alkenes have π and π^* orbitals and can show several transition; the lowest-energy transition, $\pi \rightarrow \pi^*$ gives an absorption band ~170-190 nm for non-conjugated alkenes (effects of conjugation on electronic transitions are discussed later). The presence of nonbonding electrons in a molecule further expands the number of possible transitions. The entire molecule, however, is not generally involved in the absorption of the radiation in a given wavelength range. In an aliphatic ketone, for example, the absorption band around 185 nm arises due to the $\pi \rightarrow \pi^*$ transition in the carbonyl group. Atoms that comprise the molecular orbitals involved in the electronic transitions constitute the molecular moiety that is directly involved in the transition. Such a group of atoms is called a **chromophore**. A structural modification in a chromophore is generally accompanied by changes in the absorption properties.

Instrumentation:

Figure 4.3A shows a schematic diagram of a single-beam spectrophotometer. The light enters the instrument through an entrance slit, is collimated and focused on to the dispersing element, typically a diffraction grating. The light of desired wavelength is selected simply by rotating the monochromator and impinged on the sample. The intensity of the radiation transmitted through the sample is measured and converted to absorbance or transmittance (discussed later). Double beam spectrophotometers overcome certain limitations of the single beam spectrophotometers and are therefore preferred over them. A double beam spectrophotometer has two light beams, one of which passes through the sample while other passes through a reference cell (Figure 4.3B). This allows more reproducible measurements as any fluctuation in the light source or instrument electronics appears in both reference and the sample and therefore can easily be removed from the sample spectrum by subtracting the reference spectrum. Modern instruments can perform this subtraction automatically. The most commonly used detectors in the

UV/Visible spectrophotometers are the photomultiplier tubes (PMT). Modern instruments also use photodiodes as the detection systems. These diodes are inexpensive and can be arranged in an array so that each diode absorbs a narrow band of the spectrum. Simultaneous recording at multiple wavelengths allows recording of the entire spectrum at once. The monochromator in these spectrophotometers is placed after the sample so that the sample is exposed to the entire spectrum of the incident radiation and the transmitted radiation is dispersed into its components.

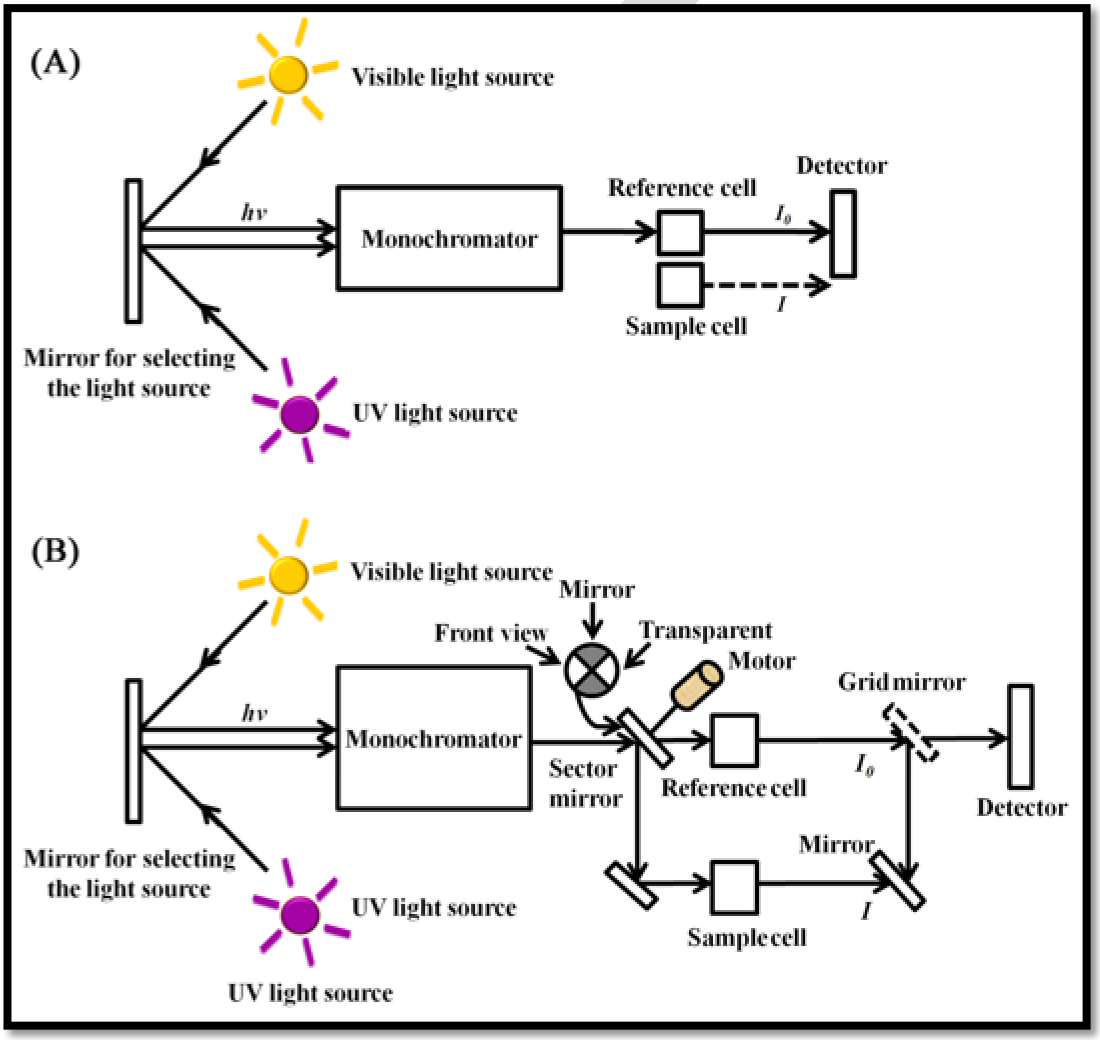


Figure 4.3 Schematic diagram showing a single beam (A) and a double beam (B) spectrophotometer

Beer-Lambert Law

It is quite intuitive that a higher concentration of the absorbing species in a sample would lead to higher absorption of the light. Furthermore, the higher thickness of the sample should result in higher absorption. Consider a cell (also called cuvette) of length, *l*, containing a solution of an absorbing molecule. The absorbing species in the sample can be represented by discs of cross-sectional area, σ. Now, let us consider a slab of infinitesimal thickness, *dx* and area, A (Figure 4.4). If an incident radiation of the resonance frequency (the frequency that causes maximum transition) having intensity I_o enters the sample cell, its intensity decreases as it penetrates the sample. Let us suppose that the intensity of the radiation before entering the infinitesimal slab is I_x.

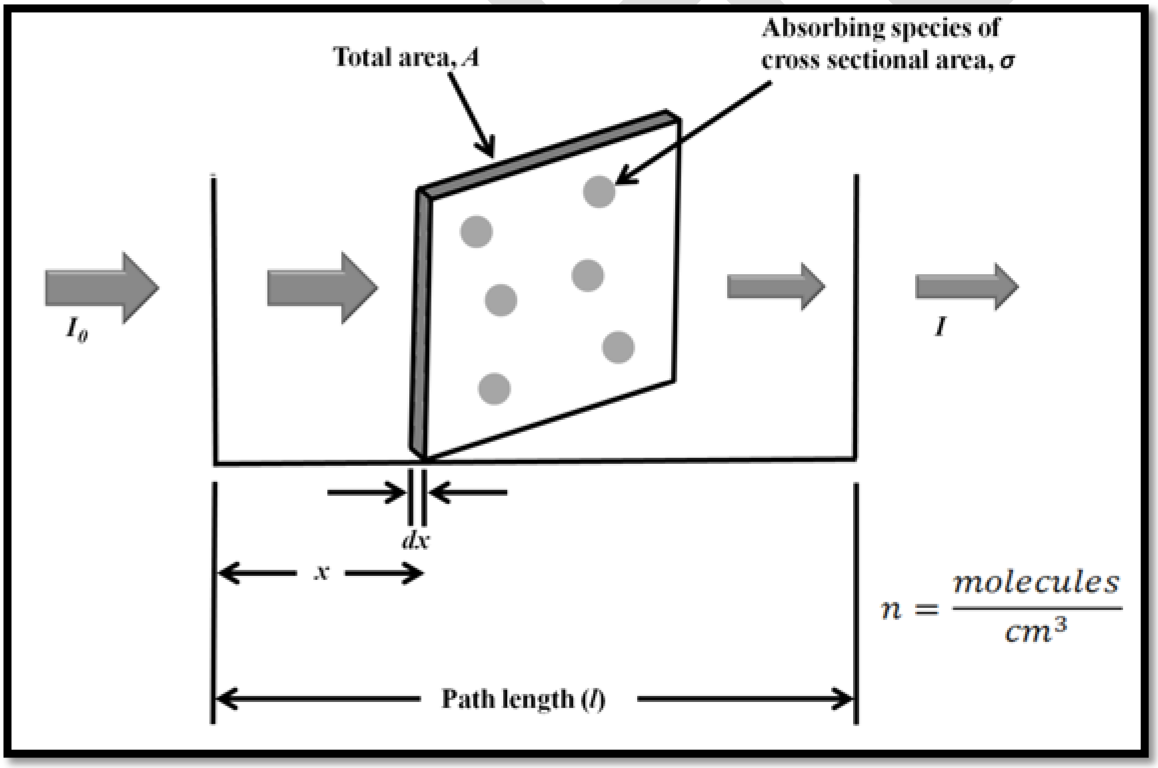


Figure 4.4 A diagrammatic representation of light absorption by sample molecules in an infinitesimal thin slab within the sample

If the concentration of the absorbing molecules = $n\,\frac{molecules}{cm^3}$, the fraction of the area occupied by the molecules in the slab = $\frac{\sigma \times n \times Volume\ of\ slab}{A} = \frac{\sigma \times n \times A \times dx}{A} = \sigma \times n \times dx$

Therefore, the fraction of the photons $(\frac{dI}{I_x})$ absorbed is proportional to $\sigma \times n \times dx$. Assuming the probability of absorption if a photon strikes the molecule to be unity,

$$\frac{dI}{I_x} = -\sigma \times n \times dx \quad \text{.........................} \ (4.1)$$

The negative sign represents a decrease in intensity

Integrating equation 4.1 from *x* = *0* to *x* = *l*

$$\ln I|_{I_o}^{I} = -\sigma \times n \times x|_0^l \quad \text{.........................} \ (4.2)$$

$$\ln I - \ln I_o = -\sigma \times n \times l \quad \text{.........................} \ (4.3)$$

$$-\ln\frac{I}{I_o} = \sigma \times n \times l \quad \text{.........................} \ (4.4)$$

Now, the molar concentration of the molecules, *c* can be given by:

$$c\left(\frac{\text{moles}}{\text{litre}}\right) = n\left(\frac{\text{molecules}}{\text{cm}^3}\right) \times \frac{1}{6.022 \times 10^{23}}\left(\frac{\text{mole}}{\text{molecules}}\right) \times 1000\left(\frac{\text{cm}^3}{\text{litre}}\right)$$

Substituting for *n* in equation 4.4 and converting natural logarithm, *ln* into $\log_{10}$ gives:

$$-2.303 \times \log\frac{I}{I_0} = \sigma \times \{c \times 6.022 \times 10^{20}\} \times l \quad \cdots\cdots\cdots\cdots (4.5)$$

$$-\log\frac{I}{I_0} = \sigma \times c \times \left(\frac{6.022 \times 10^{20}}{2.303}\right) \times l \quad \cdots\cdots\cdots\cdots (4.6)$$

$-\log\frac{I}{I_0}$ is defined as the absorbance and $\sigma \times \left(\frac{6.022 \times 10^{20}}{2.303}\right)$ is defined as the molar absorption coefficient, denoted by the Greek alphabet, ε. Therefore, equation 4.6 can be written as:

$$\text{Absorbance, } A = \varepsilon c l \quad \cdots\cdots\cdots\cdots (4.7)$$

This equality showing linear relationship between absorbance and the concentration of the absorbing molecule (or chromophore, to be precise) is known as the Beer-Lambert law or Beer's law.

Transmittance is another way of describing the absorption of light. Transmittance (T) is simply the ratio of the intensity of the radiation transmitted through the sample to that of the incident radiation. Transmittance is generally represented as percentage transmittance ($\%T$):

$$\%T = \frac{I}{I_0} \times 100$$

As is clear from the definition of absorbance and transmittance, both are dimensionless quantities. Absorbance and transmittance are therefore represented in arbitrary units (AU). The quantity of interest in an absorption spectrum is the molar absorption coefficient, ε which varies with wavelength (Figure 4.5). The wavelength at which highest molar absorption coefficient (ε_{max}) is observed is represented as λ_{max}. Area of cross-section of the absorbing species puts an upper limit to the molar absorption coefficient.

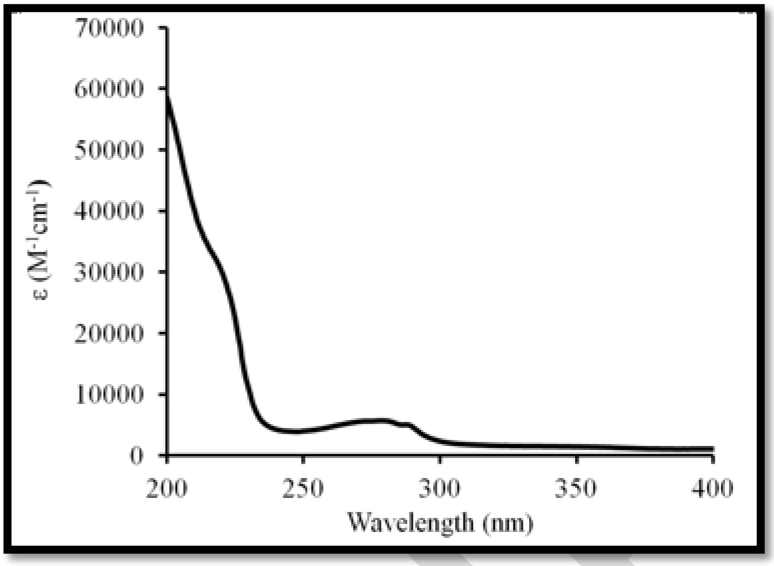


Figure 4.5 An absorption spectrum of N-acetyl-tryptophanamide

Deviations from Beer-Lambert law:

Beer-Lambert law can be used to determine the ε values of a compound by recording its absorption spectra at known concentrations. Alternatively, knowledge of ε enables the user to calculate the concentration of a compound in a given solution. It is, however, not uncommon to observe deviations from the Beer-Lambert law. Three major reasons that are responsible for the breakdown of linear relationship between absorbance and the concentration of the absorbing molecule are:

1. *High sample concentration*: The Beer-Lambert law generally holds good only for dilute solutions. At higher concentrations, the molecules come in close proximity thereby influencing their electronic properties. Although introduced as a constant at a particular wavelength for a compound, ε depends on the concentration of the compound and therefore results in deviation from linearity. At lower concentrations, however, ε can practically be assumed to be a constant.

2. *Chemical reactions*: If a molecule undergoes a chemical reaction and the spectroscopic properties of the reacted and unreacted molecules differ, a deviation from Beer-Lambert law is

observed. Change in the color of the pH indicator dyes is a classical example of this phenomenon.

3. *Instrumental factors*: As ε is a function of wavelength, Beer-Lambert law holds good only for monochromatic light. Use of polychromatic radiation will result in deviation for linearity between absorbance and concentration.

For practical purposes, the samples giving absorbance values between 0.05 – 0.5 are considered highly reliable. At lower concentrations , the signal to noise ratio is small while at higher concentrations, absorbance values underestimate the concentration of the compound as increase in absorbance no longer matches the increase in concentration. If the absorbance values are higher, a sample can be diluted or a sample cell with smaller path length can be used; usually dilution of sample is preferred.

In the following lecture, we shall discuss the various factors that influence the absorption spectra of molecules and look at the applications of UV/Visible absorption spectroscopy for studying the biomolecules.

In the previous lecture, we studied that UV/Visible radiation is absorbed by the molecules through transition of electrons in the chromophore from low energy molecular orbitals to higher energy molecular orbitals. We are interested in the transitions that lie in the far UV, near UV, and visible regions of the electromagnetic spectrum. The molecules that absorb in these regions invariably have unsaturated bonds. Plants are green due to unsaturated organic compounds, called chlorophylls. A highly unsaturated alkene, lycopene, imparts red color to the tomatoes (Figure 5.1).

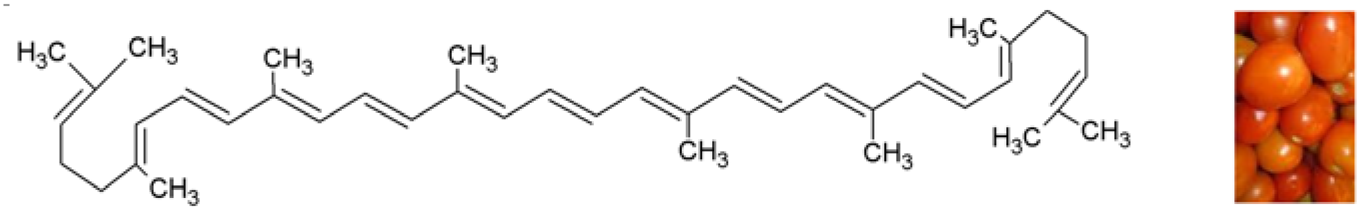


Figure 5.1 Structure of lycopene, the pigment that imparts red color to the tomatoes

As can be seen from its structure, lycopene is a highly conjugated alkene. As compared to the simple non-conjugated alkenes that typically absorb in vacuum UV region, absorption spectrum of lycopene is hugely shifted towards higher wavelengths (or lower energy). There can be factors that could shift the absorption spectra to smaller wavelengths or can increase/decrease the absorption intensity. Before understanding how conjugation causes shift in the absorption spectra, let us look at some important terms that are used to refer to the shifts in absorption spectra (Figure 5.2):

Bathochromic shift : Shift of the absorption spectrum towards longer wavelength

Hypsochromic shift : Shift of the absorption spectrum towards smaller wavelength

Hyperchromic shift : An increase in the absorption intensity

Hypochromic shift : A decrease in the absorption intensity

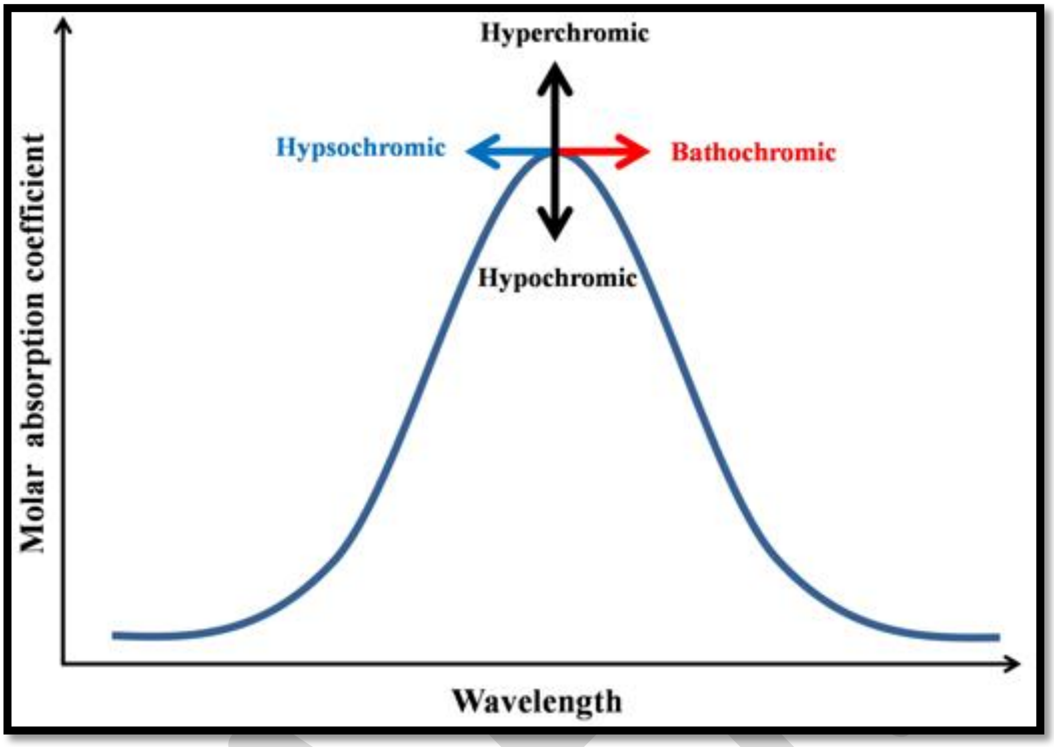
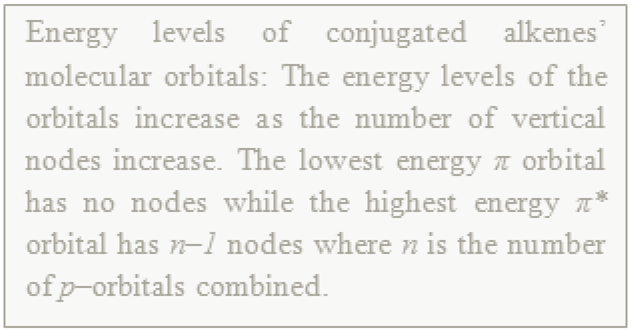


Figure 5.2 Terminology for shifts in absorption spectra

Conjugation: Conjugation brings about a bathochromic shift in the absorption bands. The higher the extent of conjugation, the more is the bathochromic shift. Such shift in absorption spectra can easily be explained using molecular orbital theory. Figure 5.3 shows the molecular orbitals drawn for ethylene; 1,3-butadiene; and 1,3,5-hexatriene on a qualitatively same energy scale for comparing their energies.

As is clear from the figure, the energy differences between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) decreases as the conjugation increases. This provides an explanation as to why an electronic transition is possible at lower energy (higher wavelength) as the conjugation increases



Energy levels of conjugated alkenes' molecular orbitals: The energy levels of the orbitals increase as the number of vertical nodes increase. The lowest energy π orbital has no nodes while the highest energy π^* orbital has $n-1$ nodes where n is the number of p–orbitals combined.

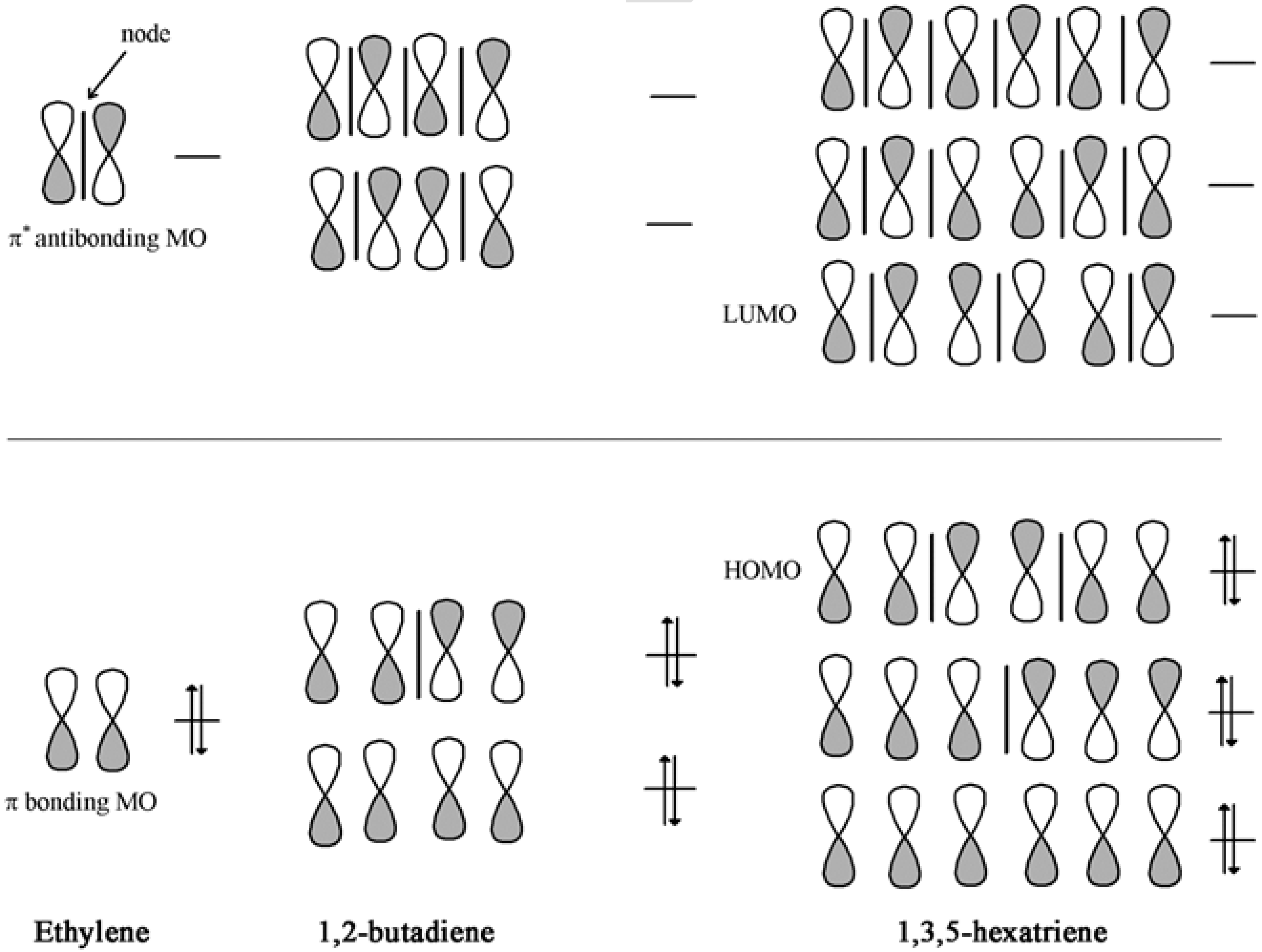
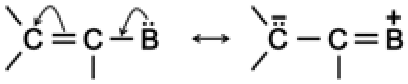


Figure 5.3 Molecular orbitals of ethylene; 1,3-butadiene; and 1,3,5-hexatriene. Notice the decrease in the energy gap of HOMO and LUMO as the conjugation increases.

Auxochrome: Auxochromes are the chemical groups that result in a bathochromic shift when attached to a chromophore. The strongest auxochromes like –OH, $–NH_2$, –OR, etc. possess nonbonding electrons. They exhibit bathochromism by extending conjugation through resonance.



The auxochrome modified chromophore is a new chromophore in real sense. The term auxochrome is therefore rarely used these days, and the entire group (basic chromophore + auxochrome) can be considered as a chromophore different from the basic chromophore. Alkyl groups also result in the bathochromic shifts in the absorption spectra of alkenes. Alkyl groups do not have non-bonded electrons, and the effect is brought about by another type of interaction called *hyperconjugation*.

Solvents: The solvents used in any spectroscopic method should ideally be transparent (non-absorbing) to the electromagnetic radiation being used. Table 5.1 shows the wavelength cutoffs (the lowest working wavelength) of some of the solvents used in UV/visible spectroscopy.

Table 5.1 Solvents commonly used in UV/visible spectroscopy

Solvent	**Wavelength cutoff**
Water	190 nm
Acetonitrile	190 nm
Cyclohexane	195 nm
Methanol	205 nm
95% ethanol	205 nm

Water, the solvent of biological systems, thankfully is transparent to the UV/visible region of interest *i.e.* the regions above $\lambda > 190$ nm. Solvents also play important role on the absorption spectra of molecules. Spectrum of a compound recorded in one solvent can look significantly different in intensity, wavelength of absorption, or both from that recorded in another. This is not something unexpected because energies of different electronic states will depend on their interaction with solvents. Polarity of solvents is an important factor in causing shifts in the absorption spectra. Conjugated dienes and aromatic hydrocarbons are little affected by the changes in solvent polarity. α,β-unsaturated carbonyl compounds are fairly sensitive to the solvent polarity. The two electronic transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respond differently to the changes in polarity. Polar solvents stabilize all the three molecular orbitals (n, π, and π^*), albeit to different extents (Figure 5.4). The non-bonding orbitals are stabilized most, followed by π^*. This results in a bathochromic shift in the $\pi \rightarrow \pi^*$ absorption band while a hypsochromic shift in $n \rightarrow \pi^*$ absorption band. Shift to different extents of the two bands will result in the different shape of the overall absorption spectrum.

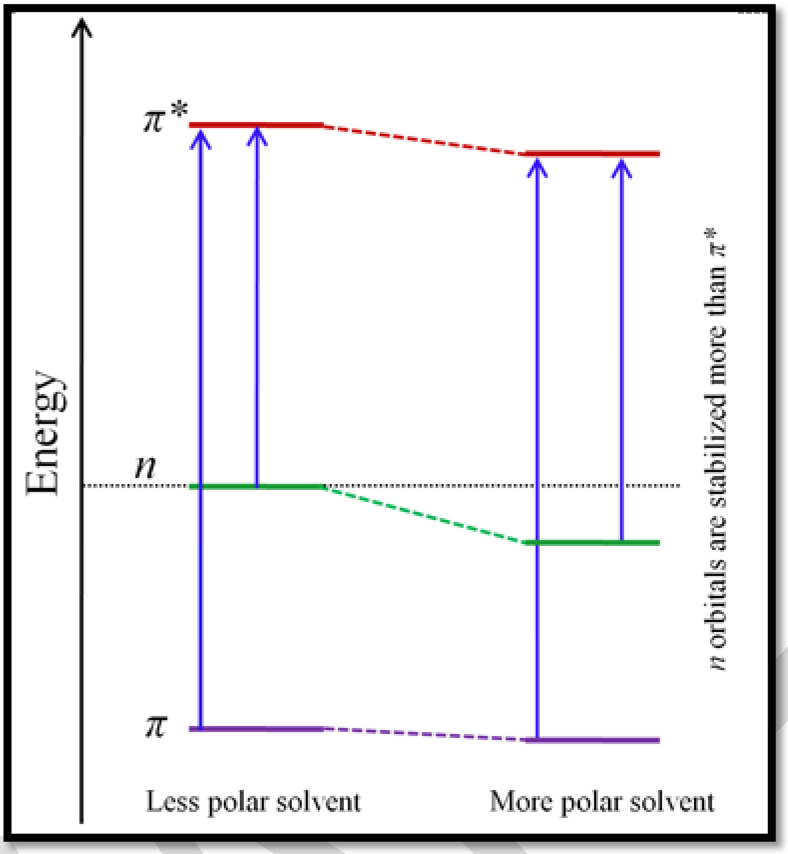


Figure 5.4 Differential stabilization of molecular orbitals in polar solvents

Biological chromophores

Amino acids and proteins: Among the 20 amino acids that constitute the proteins, tryptophan, tyrosine, and phenylalanine absorb in the near UV region. All the three amino acids show structured absorption spectra. The absorption by phenylalanine is weak with an ε_{max} of ~200 $M^{-1}cm^{-1}$ at ~250 nm. Molar absorption coefficients of ~1400 $M^{-1}cm^{-1}$ at 274 nm and ~5700 $M^{-1}cm^{-1}$ at 280 nm are observed for tyrosine and tryptophan, respectively. Disulfide linkages, formed through oxidation of cysteine resides, also contribute to the absorption of proteins in near UV region with a weak ε_{max} of ~300 $M^{-1}cm^{-1}$ around 250-270 nm. The absorption spectra of proteins are therefore largely dominated by Tyr and Trp in the near UV region. In the far UV region, peptide bond emerges as the most important chromophore in the proteins. The peptide bond displays a weak $n \rightarrow \pi^*$ transition ($\varepsilon_{max} \approx$ 100 $M^{-1}cm^{-1}$) between 210-230 nm, the exact band position determined by the H-bonding interactions the peptide backbone is involved in. A strong $\pi \rightarrow \pi^*$ transition ($\varepsilon_{max} \approx$ 7000 $M^{-1}cm^{-1}$) is observed around 190 nm. Side chains of Asp, Glu, Asn, Gln, Arg, His also contribute to the absorbance in the far UV region. Figure 5.5 shows an absorption spectrum of a peptide.

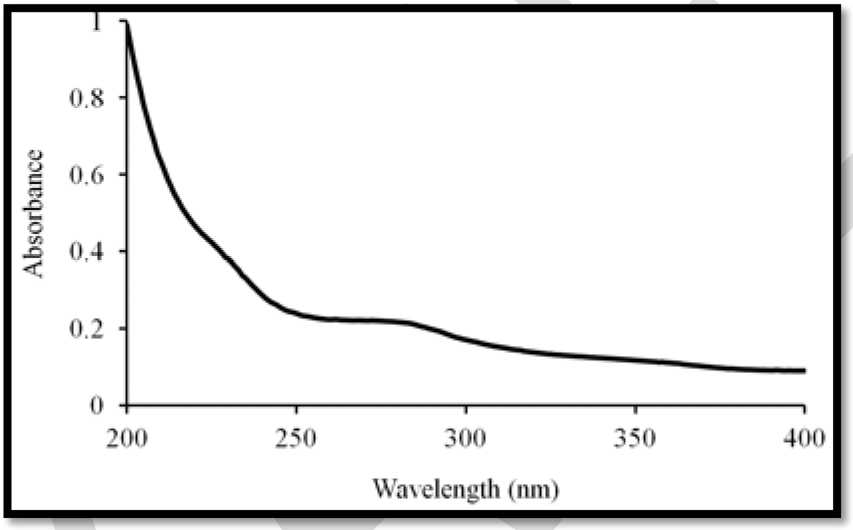


Figure 5.5 Absorption spectrum of a peptide. The absorption band ~280 nm is due to aromatic residues. Absorption band in the far UV region arises due to peptide bond electronic transitions.

Nucleic acids: Nucleic acids absorb very strongly in the far and near UV region of the electromagnetic spectrum. The absorption is largely due to the nitrogenous bases. The transitions in the nucleic acid bases are quite complex and many $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are expected to contribute to their absorption spectra. A 260 nm wavelength radiation is routinely used to estimate the concentration of nucleic acids. Though the molar absorption coefficients vary for the nucleotides at 260 nm, the average ε_{max} can be taken as ~10^4 M^{-1} cm^{-1}. It is important to mention that nucleotides show hyperchromicity when exposed to aqueous environment. The absorbance of the free nucleotides is higher than that of single stranded nucleic acid which is higher than that of the double stranded nucleic acid (assuming equal amount of the nucleotides present in all three).

Other chromophores: Nucleotides like NADH, NADPH, FMN, and FAD; porphyrins such as heme, chlorophylls and other plant pigments; retinal (light sensing molecule); vitamins; and a variety of unsaturated compounds constitute chromophores in the UV and visible region.

Having studied the principles of the UV/visible absorption spectroscopy and various factors that influence the electronic transitions, we can now have a look at its applications, especially the applications for analyzing the biological samples.

Applications:

i. *Determination of molar absorption coefficient*: From Beer-Lambert law, $A = \varepsilon c l$. It is therefore straightforward to calculate the molar absorption coefficient of a compound if the concentration of compound is accurately determined.

ii. *Quantification of compounds:* This is perhaps the most common application of a UV/visible spectrophotometer in a bioanalytical laboratory. If the molar absorption coefficient at a wavelength is known for the compound, the concentration can easily be estimated using Beer-Lambert law. The compounds can still be quantified if their molar absorption coefficients are not known. Estimation of total protein concentration in a given solution is an important example of this. As the given solution is a mixture of many different proteins, the ε is not available. There are, however, dyes that specifically bind to the proteins producing colored complex. The color produced will be proportional to the amount of the protein present in the solution. Performing the experiment under identical conditions using known concentrations of a protein gives a standard graph between absorbance of the dye and the amount of protein. This standard graph is then used to estimate the concentration of the given protein sample.

iii. *Quality control*: A given organic compound such as a drug can be studied for its purity. Comparison of spectrum with the standard drug will detect the impurities, if any. UV/Visible absorption is often used to detect the nucleic acid contamination in the protein preparations. Aromatic amino acids as well as the nucleotides show absorption band in the near UV region and there is a considerable overlap in the absorption spectra of aromatic amino acids and the nucleotides. A nucleic acid contamination in a protein, however, can be determined by measuring absorbances at 260 and 280 nm. A typical nucleic acid containing all four bases shows an absorption band centered ~260 nm while a protein having aromatic amino acids shows absorption band centered ~280 nm. It is possible to determine the purity of protein preparations by recording absorbances at both 260 and 280 nm. A ratio of the absorbance at 260 nm to that at 280 nm i.e. $\frac{A_{260}}{A_{280}}$ is a measure of the purity.

$\frac{A_{260}}{A_{280}}$ ratio is not useful in detecting protein contaminations in DNA preparations. This is because of the large difference in molar absorption coefficients of these molecules. To cause an appreciable change in the $\frac{A_{260}}{A_{280}}$ ratio, there should a large amount of protein present.

iv. *Chemical kinetics*: UV/visible spectroscopy can be used to monitor the rate of chemical reactions if one of the reactants or products absorbs in a region where no other reactant or product absorbs significantly.

v. *Detectors in liquid chromatography instruments*: UV/visible detectors are perhaps the most common detectors present in liquid chromatography systems. Modern instruments use photodiode array detectors that can detect the molecules absorbing in different spectral regions (Figure 5.6).

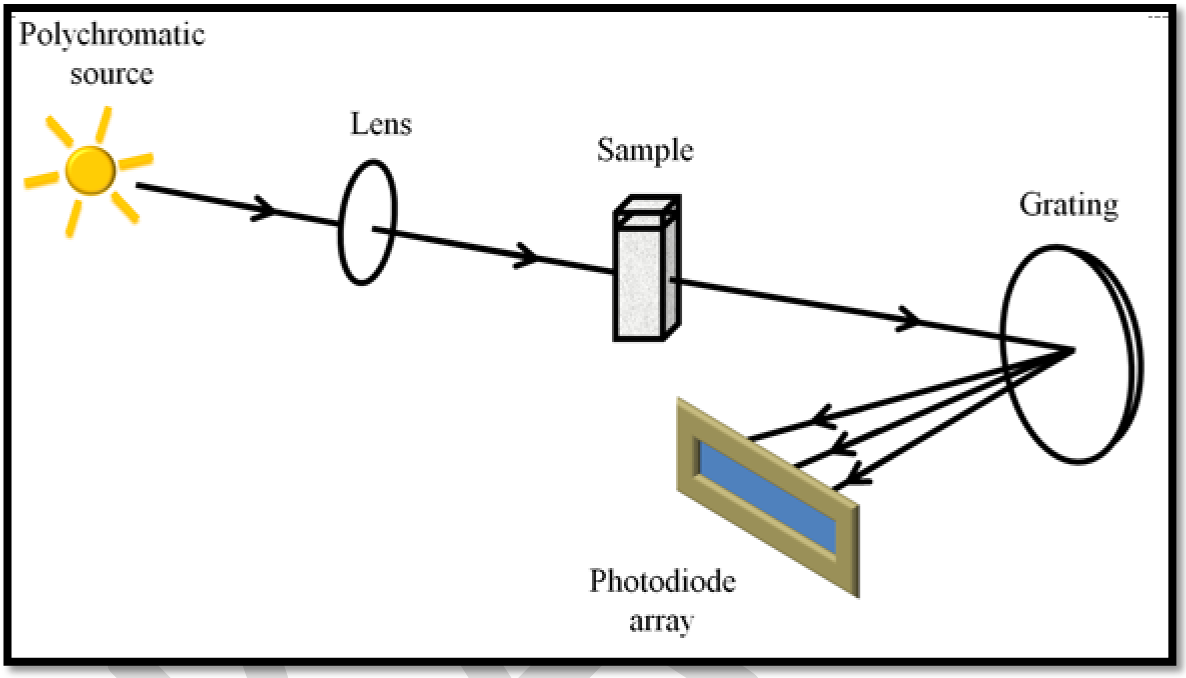


Figure 5.6 Diagram of a photodiode array detector

vi. *Determination of melting temperature of DNA*: A double stranded DNA molecule can be denatured into the single strands by heating it. Melting temperature, T_m is the temperature at which 50% of the DNA gets denatured into single strands. Denaturation of DNA is accompanied by hyperchromic shift in the absorption spectra in the near UV region. A melting curve (plot between temperature and absorbance at 260 nm) is plotted and T_m is determined (Figure 5.7).

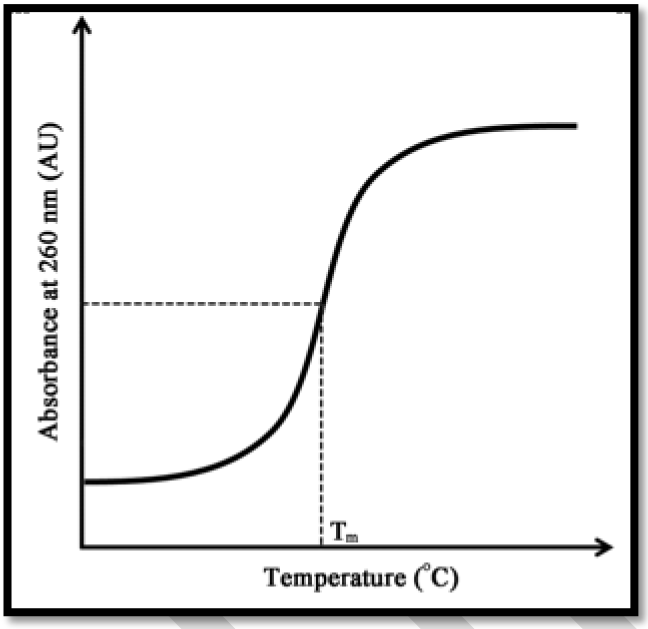
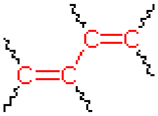
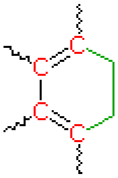
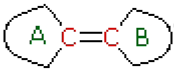


Figure 5.7 Thermal denaturation of a DNA sample; a plot of absorbance at 260 nm against the temperature allows determination of the melting temperature (T_m).

vii. *Microbial growth kinetics*: A UV/visible spectrophotometer is routinely used to monitor the growth of microorganisms. *The underlying principle behind this, however, is not absorbance but scattering*. As the number of microbial cells increase in a culture, they cause more scattering in light. The detector therefore receives less amount of radiation, recording this as absorbance. To distinguish this from actual absorbance, the observed value is referred to as the optical density.

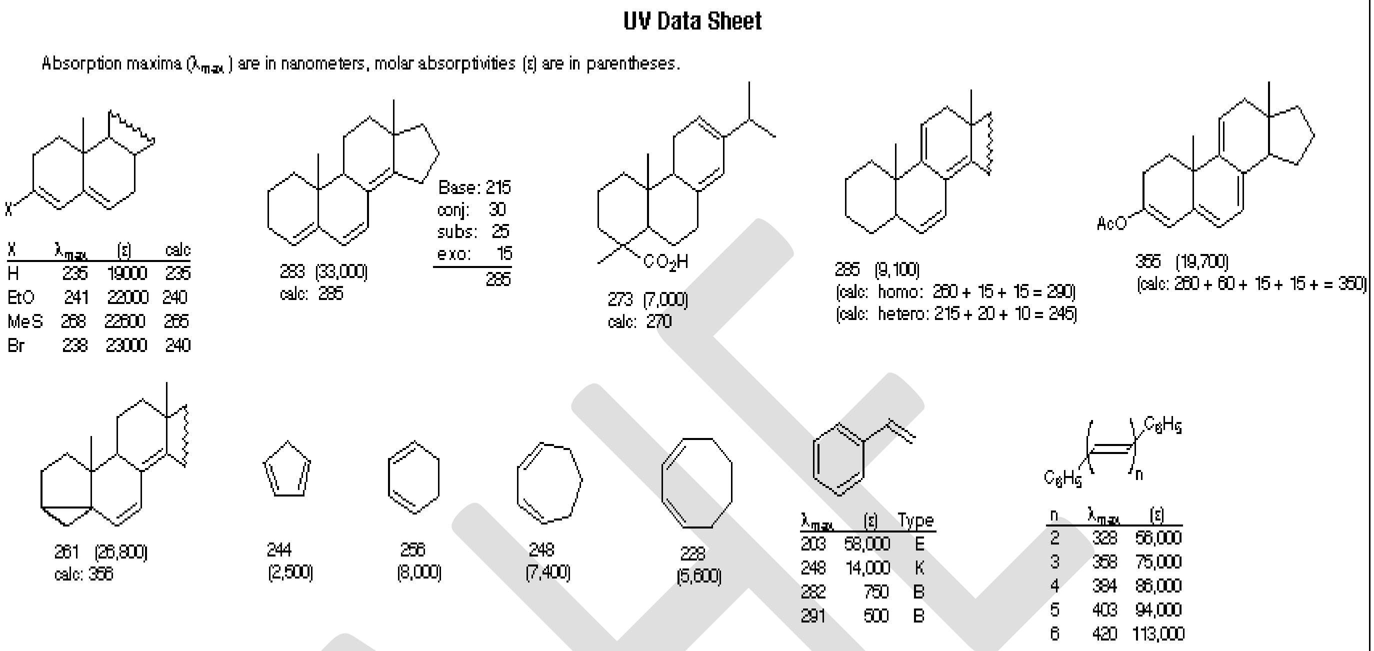
Empirical Rules for Absorption Wavelengths of Conjugated Systems

Woodward-Fieser Rules for Calculating the λ_{max} of Conjugated Dienes and Polyenes	
Core Chromophore	**Substituent and Influence**

<table>
<tr>
<td> Transoid Diene
215 nm</td>
<td rowspan="2">R- (Alkyl Group) .... **+5 nm**
RO- (Alkoxy Group) .. **+6**
X- (Cl- or Br-) .... **+10**
RCO_2- (Acyl Group) **0**
RS- (Sulfide Group) .. **+30**
R_2N- (Amino Group) .. **+60**
Further π -Conjugation
C=C (Double Bond) ... **+30**
C_6H_5 (Phenyl Group) ... **+60**</td>
</tr>
<tr>
<td> Cyclohexadiene*
260 nm</td>
</tr>
<tr>
<td colspan="2"> **(i)** Each exocyclic double bond adds **5 nm**. In the example on the right, there are two exo-double bond components: one to ring A and the other to ring B.
(ii) Solvent effects are minor.
***** When a homoannular (same ring) cyclohexadiene chromophore is present, a base value of 260 nm should be chosen. This includes the ring substituents. Rings of other size have a lesser influence.</td>
</tr>
</table>

λ_{max} (calculated) = **Base** (215 or 260) + **Substituent Contributions**

Some examples that illustrate these rules follow.



UV Data Sheet

Absorption maxima (λ_{max}) are in nanometers, molar absorptivities (ε) are in parentheses.

X	λ_{max}	(ε)	calc
H	235	19000	235
EtO	241	22000	240
MeS	268	22600	265
Br	238	23000	240

283 (33,000)
calc: 285

Base: 215
conj: 30
subs: 25
exo: 15
285

273 (7,000)
calc: 270

285 (9,100)
(calc: homo: 260 + 15 + 15 = 290)
(calc: hetero: 215 + 20 + 10 = 245)

355 (19,700)
(calc: 260 + 60 + 15 + 15 + = 350)

261 (26,800)
calc: 356

244
(2,500)

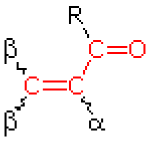
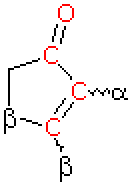
256
(8,000)

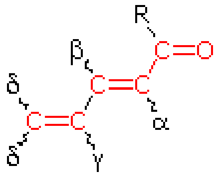
248
(7,400)

228
(5,600)

λ_{max}	(ε)	Type
203	58,000	E
248	14,000	K
282	750	B
291	500	B

n	λ_{max}	(ε)
2	328	56,000
3	358	75,000
4	384	86,000
5	403	94,000
6	420	113,000

Woodward-Fieser Rules for Calculating the π —> π* λ_{max} of Conjugated Carbonyl Compounds	
Core Chromophore	**Substituent and Influence**
 R = Alkyl **215 nm** R = H **210 nm** R = OR' **195 nm**	**α- Substituent** R- (Alkyl Group) **+10 nm** Cl- (Chloro Group) **+15** Br- (Chloro Group) **+25** HO- (Hydroxyl Group) **+35** RO- (Alkoxyl Group) **+35** RCO$_2$- (Acyl Group) **+6**
 Cyclopentenone **202 nm**	



β- Substituent

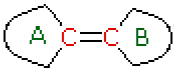
R-	(Alkyl Group)	**+12 nm**
Cl-	(Chloro Group)	**+12**
Br-	(Chloro Group)	**+30**
HO-	(Hydroxyl Group)	**+30**
RO-	(Alkoxyl Group)	**+30**
RCO_2-	(Acyl Group)	**+6**
RS-	(Sulfide Group)	**+85**
R_2N-	(Amino Group)	**+95**

γ & δ- Substituents

R-	(Alkyl Group)	**+18 nm** (both γ & δ)
HO-	(Hydroxyl Group)	**+50 nm** (γ)
RO-	(Alkoxyl Group)	**+30 nm** (γ)

Further π -Conjugation

C=C	(Double Bond) ...	**+30**
C_6H_5	(Phenyl Group) ...	**+60**



(i) Each exocyclic double bond adds **5 nm**. In the example on the right, there are two exo-double bond components: one to ring A and the other to ring B.

(ii) Homoannular cyclohexadiene component adds **+35 nm** (ring atoms must be counted separately as substituents)

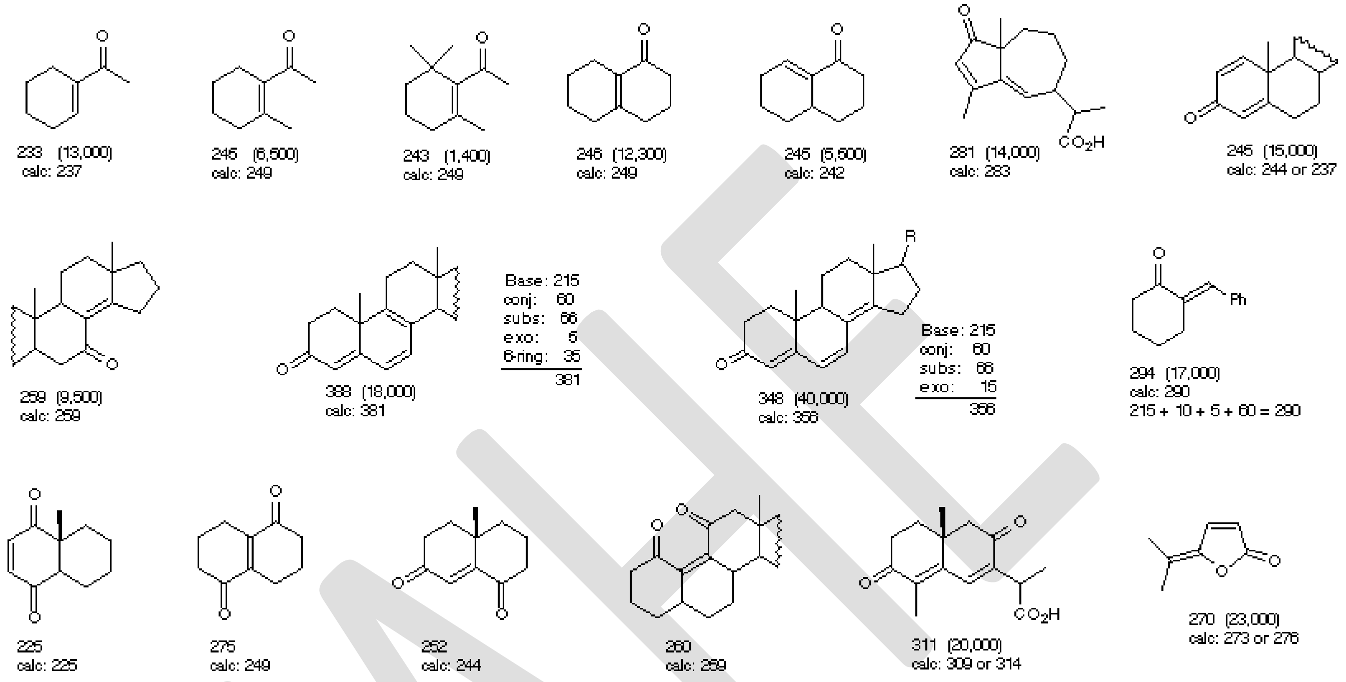
(iii) Solvent Correction: water = **–8**; methanol/ethanol = **0**; ether = **+7**; hexane/cyclohexane = **+11**

λ_{max} (calculated) = **Base + Substituent Contributions and Corrections**

Some examples that illustrate these rules follow.

UV Data Sheet

Absorption maxima (λ_{max}) are in nanometers, molar absorptivities (ε) are in parentheses.



References:

Text books:

T1- Y.R. Sharma, 2010, Elementary organic sectroscopy, S. Chand and company ltd.

POSSIBLE QUESTIONS

PART-A

MULTIPLE CHOICE QUESTIONS

(Each Question Carry One Mark)

1. UV absorption spectroscopy is powerful tool for ------------ analysis

a)**Quantitative** b)Qualitative c)Physical d)Environmental

2. As the number of double bonds in conjugation increases, λ_{max} --------

a) **Increases** b) Decreases c) Remains zero d)Zero

3. The alkyl subsitution in an alkene causes a ---------- shift

a)**Bathochromic** b)Hypsochromic c)Isomeric d)Chromophoric

4. What is the forbidden transition in the following?

a)σ- σ^* b)**n-π^*** c)n-σ^* d)π- π^*

5. In π- π^* transition, solvent polarity results in------------ shift

a) **Bathochromic** b) hypsochromic c) Isobestic point d)hyperchromic

6. In the case of alcohol λ_{max} small, the effect due to

a) Covalent bonding b) **Hydrogen bonding** c. Co ordinate bonding.

D. Ionic bonding

7. The arrangement of all type of electromagnetic radiation in the order of -------- wavelength is called electromagnetic spectrum.

a)**Increasing** b)Decreasing c)Same d)Approximate

8. Which of the following spectroscopy otherwise known as electronic spectroscopy

a) **UV** b) IR c) NMR d) ESR

9. Which of the energy not accounted in total energy state of electronic absorption by Born-oppenhiemer approximation?

a) E_{elec} b) E_{rot} c) $\mathbf{E_{trans}}$ d) E_{vib}

10. The relative intensity of molecular spectra both in absorption and emission may be interpreted in terms of

a)**Frank-condom principle** b)Hiesenberg principle c)Paulis principle d)Hooks law.

11. Beer-Lamberts law implies the fractional change in light intensity is proportional to

a)**concentration of solution and thickness of solution** b)concentration only c) thickness of the solution only d) intensity of emitted light.

12. Bathochromic shift also called

a)blue shift b)**red shift** c)yellow shift d)orange shift

13. Among the following electromagnetic radiations, which has the maximum wavelength?

a) IR b) UV c) **Radio wave** d) X-ray

14. Which of the following radiation has the maximum energy?

a) **UV** b) far IR c) visible d) near IR

15. Which of the following colours of visible light is bent most as it passes through a prism?

a) Yellow b) Red c) **Blue** d) Green

16. A frequency of 1000 cm^{-1} is in the ------ region

a)UV b**) IR** c) visible d) microwave

17. What is the calculated value for cyclohexa 1,3-diene

a) 261 mµ b) 262 mµ c) **263 mµ** d)264 mµ

18. Upon irradiation with UV-radiation, benzene displaces ---- bonds due to its transition

a) 1 b) 2 c**) 3** d) 4

19. If water used as solvent in UV absorption studies, ------ nm to be added with parent value.

a) -4 b) +4 c) + 8 d**) -8**

20. Cycles/sec is unit for

a) Wavelength b) Frequency c) Wave number d) **Energy**

PART-B

Each Question Carry Six Marks

1. (i)Explain the electronic transitions involved in UV spectroscopy?

   (ii). Explain the various parts and functions of a UV-visible spectrophotometer

2. Explain the Woodward-Fieser rules for calculating absorption maximum for α,β-unsaturated carbonyl compounds with examples.
3. (i). Explain the various applications of UV spectroscopy.

   (ii). Explain the absorption laws in detail.

4. Explain the Woodward-Fieser rules for calculating absorption maximum in dienes with examples.
5. Explain the instrumentation of UV spectrophotometer.

6. (i). Explain the various applications of UV spectroscopy.
   (ii). Explain the absorption laws in detail.

7. Explain the Woodward-Fieser rules for calculating absorption maximum in dienes and α,β-unsaturated carbonyl compounds with an examples.

8. Explain the applications of UV spectroscopy?

9. Discuss the following terms:

   (a)(i)Bathochromic shift (ii) hypochromic shift (iii) A chromophore (iv)Hyper chromic effect

   (b) On what effects do (i) and (ii) depend?

PART-C (Compulsory Question)

Ten Marks

1. (i)**.**Explain the description of double beam UV spectrophotometer.
   (ii). How will you determine the structure of α, β – unsaturated compounds and conjugated dienes by UV spectroscopy?

2. (i). Explain absorption and intensity shifts in detail.
   (ii). Explain the keto enol tautomerism in UV spectroscopy?

[19CHP104]

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-641021
(For the candidates admitted on 2019 onwards)
DEPARTMENT OF CHEMISTRY
I - SEMESTER
ORGANIC CHEMISTRY
OBJECTIVE TYPE QUESTIONS(EACH QUESTION CARRY ONE MARK)

Unit-1 Ultraviolet spectroscopy (19CHP104)

S.No	Question	option a	option b	option c	option d	answer
1	An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.This principle is known as	Paulis principle	Heisenberg principle	Franck condon principle.	Uncertinity principle	c. Franck condon principle.
2	Which among the following is the laws of Photochemistry	Hooks law	Beer-Lambertz law	Charls law	Avagdros law.	b.Beer-Lambertz law
3	Reciprocal of transmittance is called	Absorbance	Opacity	Incidence	Molar exinction coefficient	b. Opacity
4	The quantity Ecl is known as	Absorbance	Opacity	Transmittance	absorbtivity	a.Absorbance
5	Structural information deducible from UV spectra is mainly about	Inductive effect	Conjugation	Steric hiderance	Mesomeric effect	b.Conjugation
6	UV absorption spectroscopy is powerful tool for ------------ analysis	Quantitative	qualitative	physical	environmental	a. Quantitative
7	As the number of double bonds in conjucation increases, λ_{max} --------	increases	decreases	remains zero	zero	a. increases
8	The alkyl subsitution in an alkene causes a ---------- shift	Bathochromic	Hypsochromic	isomeric	Chromophoric	a.Bathochromic
9	What is the forbidden transition in the following	σ- σ*	n-π*	n-σ*	π- π *	b.n-π*
10	Saturated aldehyde exhibit ------- type of transition	both .n-π* and π-π*	both .σ- σ* and π-π *	both .σ- σ* and n-π*	only n- π *	A.both .n-π* and π-π*

11	Methyl chloride is an example for ------- type of transition	$n-\pi^*$	$\pi-\pi^*$	$\sigma-\sigma^*$	$n-\sigma^*$	d. $n-\sigma^*$
12	In $\pi-\pi^*$ transition, solvent polarity results in------------ shift	Bathochromic	hypsochromic	both	none	a. Bathochromic
13	In the case of alcohol λ_{max} small, the effect due to	Covalent bond	H-bonding	co ordinate bonding.	none	b.H-bonding
14	Transition in UV absorption depend on	size of the atom	Electronegativity	H-bonding	all the above	d.all the above
15	According to Woodward-Fieser rule, the value of absorbance depend on	no of alkyl sustituents	no of double bond	presence of polar group	all the above	d.all the above
16	Parent value for Buta diene system is	217mµ	218 mµ	219 mµ	220 mµ	a.217mµ
17	According to Woodward-Fieser rule, to correct strain correction in bicyclic system----- should be added	5 mµ	10 mµ	15 mµ	20 mµ	c.15 mµ
18	What is the λ_{max} for the 2,4-hexa diene	217 mµ	227 mµ	272 mµ	271 mµ	b.227 mµ
19	What is the calculated value for cyclohexa 1,3-diene	261 mµ	262 mµ	263 mµ	264 mµ	c.263 mµ
20	Upon irradiation with UV-radiation, benzene displaces ---- bonds due to its transition	1	2	3	4	3
21	If water used as solvent in UV absorption studies, ------ nm to be added with parent value.	7	4	#VALUE!	d.-8	d.-8
22	Cycles/sec is unit for	a. Wavelength	b.frequency	c.wave number	d.energy	d.energy
23	The arrangement of all type of electromagnetic radiation in the order of -------- wavelength is called electromagnetic spectrum.	a.increasing	b.decreasing	c.same	d.approximate	a.increasing
24	Which of the following spectroscopy otherwise known as electronic spectroscopy	a.UV	b.IR	c.NMR	d.ESR	a.UV

25	Greater value of Molar extinction coefficient indicates that the probability of transition-------	a.less	b.more	c. nil	d.zero	b.more
26	Molar extinction coefficient value less than ------- is called forbidden transition	a.1	b.10	c.100	d.1000	c.100
27	When electronegativity increases, λ_{max} -----------	a.increases	b.decreases	c.remains same	d.becomes zero	b.decreases
28	Increase of solvent polarity results in --------- of λ_{max} of absorption.	a.increase	b.decrease	c. increase and decrease	d.zero	b.decrease
29	Sufficient condition for absorption of energy of energy is that the interaction	a.dipole moment	b.frequency of oscillation	c.both the above	d.none	c.both the above
30	According to spin conservation rule,which of the following is allowed	a.singlet to singlet	b.singlet to triplet	c.triplet to singlet	d.none	a.singlet to singlet
31	The time taken for an electronic transition is very small compared to time taken for one vibration.This principle is	a.Paulis principle	b.Frank-condon principle	c.predissociation	d.Hunds principle	b.Frank-condon principle
32	In predissociation, some molecules dissociation occur at ------ energy	a.Higher	b.lower	c.zero	d.without	b.lower
33	Radiation source used in UV instrumentation is	a.Hydrogen	b.deuterium lamp	c. xenon discharge lamp	d.Hydrogen, deutrium and	d.Hydrogen, deutrium and xenon lamp
34	Which of the energy not accounted in total energy state of electronic absorption by Born-oppenhiemer approximation?	a.E_{elec}	b. E_{rot}	c. E_{trans}	d. E_{vib}	c. E_{trans}
35	The relative intensity of molecular spectra both in absorption and emission may be interpreted in terms of	a.Frank-condom principle	b.Hiesenberg principle	c.Paulis principle	d.Hooks law.	a.Frank-condom principle
36	Beer-Lamberts law implies the fractional change in light intensity is proportional to	a.concentration of solution and thickness of	b.concentration only	c.thickness of the solution only	d.intensity of emitted light.	a.concentration of solution and thickness of solution
37	Bathochromic shift also called	a.blue shift	b.red shift	c.yellow shift	d.orange shift	b.red shift
38	Water has the electronic transition	a. .n-π^*	b.π- π^*	c. .σ- σ^*	d. n-σ^*	d. n-σ^*

39	If a molecule exists in two tautomeric form,the preference of one form to another can be detected by -------	a.UV	b.IR	c,NMR	d.ESR	a.UV
40	Addition in unsaturation with the increase in the number of double bonds shifts the absorption to------- wavelength	a.shorter	b.longer	c.no change	d.maximum	b.longer
41	Which of the following is an electromagnetic radiation	a.alpha rays	b.beta rays	c.gammarays	d. anode rays	c.gammarays
42	Which of the following statements is true	a. X-rays are affected by electric field	b. X-rays are affectedby magnetic field	c. gamma rays are more energetic than X-rays	d.gamma rays are a stream of position	c. gamma rays are more energetic than X-rays
43	The wave length of x-rays is of the order of	a.10^{-8}m	b.10^{-8} cm	c. 10^{-23} cm	d. 40000A°	b.10^{-8} cm
44	The wave length of 1000 A° is in the ------ region	a. far UV	b.Visible	c.near UV	d. IR	a. far UV
45	Of the following radiations, which represents the visible region?	a. 0-100 nm	b. 100-200 nm	c.200-400 nm	d.400-800 nm	d.400-800 nm
46	Among the following electromagnetic radiations, which has the maximum wavelength?	a. IR	b.UV	c.radio wave	d. X-ray	c.radio wave
47	Which of the following radiation has the maximum energy	a.UV	b. far IR	c.visible	d. near IR	a.UV
48	Which of the following colours of visible light is bent most as it passes through a prism?	a. Yellow	b. Red	c. Blue	d. Green	c. Blue
50	A frequencyof 1000 cm^{-1} is in the ------ region	a.UV	b. IR	c.visible	d. microwave	b. IR
51	One electron- volt of energy is equivalent to a photon with a wave	a. 300 A°	b. 30 A°	c. 3000A°	d.12000A°	d.12000A°
52	Which among the following radiation will not ionise a gas?	a. X-rays	b. α-particles	c.β-particles	d. neutrons	d. neutrons

53	Radiation which has the least energy (among the following)	a.alpha rays	b.beta rays	c.gammarays	d. electrica; waves	d. electrica; waves
54	One nm is equal to	a. 10A°	b. 0.1 A°	c. 10^{-9} cm	d. 10^{-8} cm	a. 10A°
55	Which of the following transition require the least energy?	a. .n-π*	b.π- π*	c. .σ- σ*	d. n-σ*	a. .n-π*
55	Which of the following molecule has the shortest wavelength absorption band?	a. H_2O	b.CH_4	c. CH_3Cl	d. CH_3CHO	b.CH_4
56	Which compound does not involve the π-π* transition in UV spectroscopy	a. alkenes	b. azo compound	c. alcohols	c. cyanides	c. alcohols
57	Which one is acidic auxochromic group?	a. -OH	b. -NO_2	c. -OR	d.NH_2	b. -NO_2
58	What will be the theoritical number of vibrational degrees of freedom in benzene,CO_2, SO2 respectively	a. 12,4,3	b. 3,4,12	c. 30,4,3	d. 30,3,3	c. 30,4,3
59	The number of vibrational degrees of freedom in $C_6H_5CH_3$	a. 39	b. 15	c. 18	d. 40	a. 39
60	Which one is the correctbasic value of λ_{max} for a homoanular ddiene--	a.214	b.217	c.253	d.215	c.253

LECTURE NOTES

UNIT-II

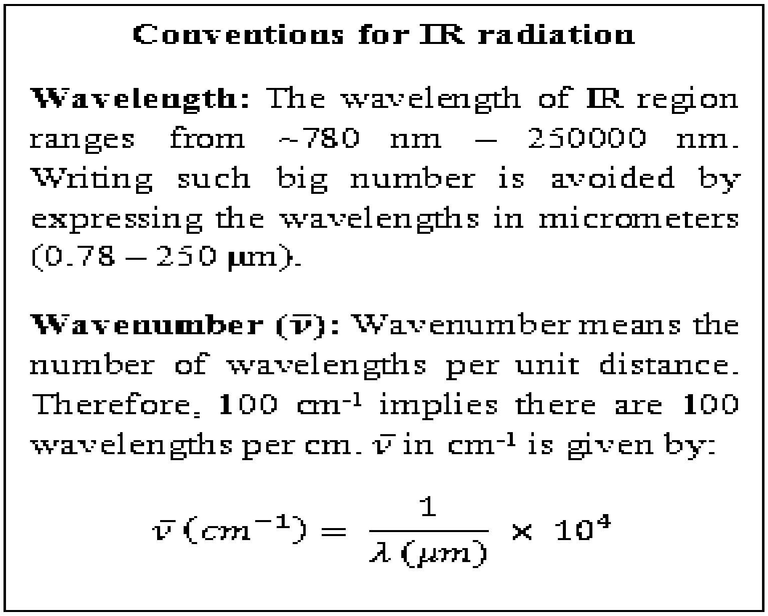
SYLLABUS

Infrared Spectroscopy: The vibrating diatomic molecules-the simple harmonic oscillator and anharmonic oscillator - the diatomic rotor - factors influencing vibrational frequencies - identification of fundamental groups. Fingerprint region-application to organic and inorganic compounds-Instrumentation**.**

Infrared Spectroscopy

Introduction

Infrared (IR) region of the electromagnetic spectrum lies between visible and microwave regions and therefore spans the wavelengths from 0.78 – 250 μm. The energies associated with molecular vibrations are smaller than those associated with electronic transitions and fall in the IR region. IR spectroscopy, therefore, is used to probe the vibrations in molecules and is also known as vibrational spectroscopy. Infrared region is usually divided into three regions: near infrared, mid-infrared, and far infrared (Figure 10.1). IR spectroscopists use wavenumbers $(\bar{\nu})$ to represent the IR spectra and we shall be following the same convention. Mid-IR region (λ = 2.5 -25 μm; $\bar{\nu}$ = 4000 – 400 cm^{-1}) is the region of interest for studying molecular vibrations.



Conventions for IR radiation

Wavelength: The wavelength of IR region ranges from ~780 nm – 250000 nm. Writing such big number is avoided by expressing the wavelengths in micrometers (0.78 – 250 μm).

Wavenumber ($\bar{\nu}$): Wavenumber means the number of wavelengths per unit distance. Therefore, 100 cm^{-1} implies there are 100 wavelengths per cm. $\bar{\nu}$ in cm^{-1} is given by:

$$\bar{\nu}\,(cm^{-1}) = \frac{1}{\lambda\,(\mu m)} \times 10^4$$

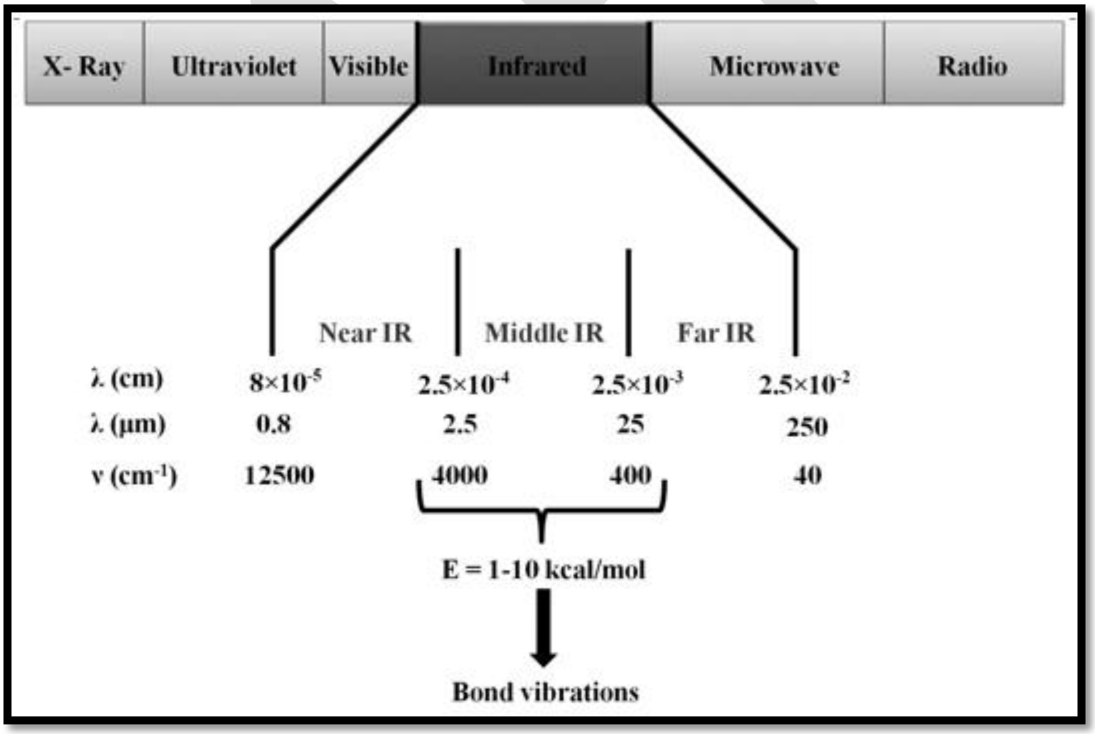


Figure 10.1 Infrared region of the electromagnetic spectrum

Degrees of freedom and molecular vibrations

At non-zero temperatures, *i.e.* temperatures above 0 K, all the atoms in a molecule are in motion. The molecule itself also is in translational and rotation motion. In a three dimensional space, an atom in isolation has 3 degrees of freedom, corresponding to the motion along the three independent coordinate axes. *A molecule composed of N atoms has a total of 3N degrees of freedom* (Figure 10.2).

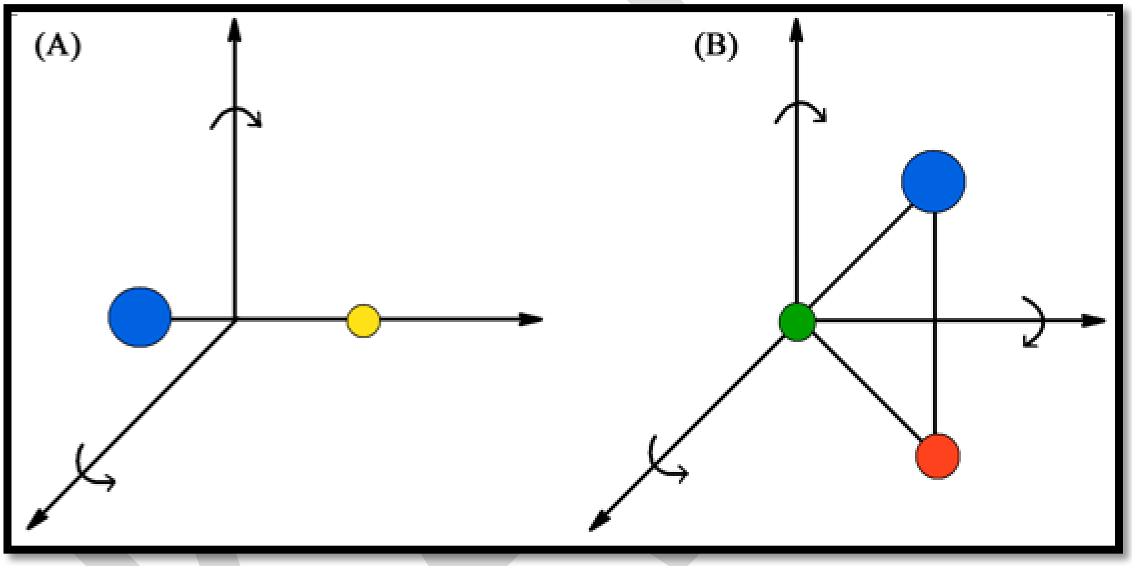


Figure 10.2 Degrees of rotational freedom for a diatomic (A) and a triatomic (B) molecule

For a non-linear molecule, three of these 3*N* degrees of freedom correspond to translational motion, three correspond to rotational motion while rest 3N-6 are the vibrational degrees of freedom. For a linear molecule, there are only two rotational degrees of freedom that correspond to the rotation about the two orthogonal axes perpendicular to the bond (Figure 10.2). A linear molecule, therefore, has 3*N*-5 vibrational degrees of freedom. Let us have a look at the degrees of freedom of a diatomic molecule. A diatomic molecule has a total of 3 × 2 = 6 degrees of freedom. *Three* of these *six* degrees of freedom correspond to translational motion of the molecule; *two* of them define rotational degrees of freedom; while *one* corresponds to the vibration of the atoms along the bond. The 3N-6 vibrational degrees of freedom (3N-5 for linear molecules) represent the true/fundamental modes of vibration of a molecule. The different types of vibrations are shown in Figure 10.3.

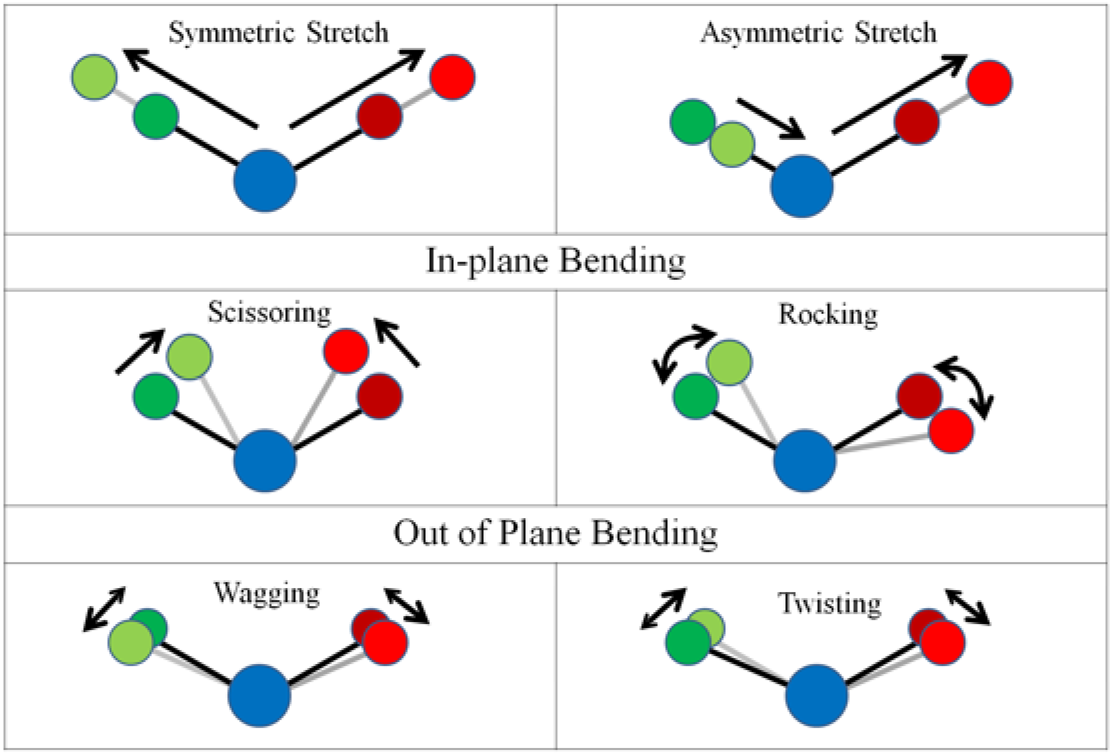


Figure 10.3 Stretching and bending vibrations in molecules

Hooke’s law and frequency of vibration

We have seen that the bonds are not static but vibrating in different ways. A vibrating bond can therefore be considered a spring with its ends tethered to two atoms (Figure 10.4).

Figure 10.4 Spring analogy of a bond vibration

If the masses of the atoms are m_1 and m_2, the frequency of stretching vibration of the diatomic molecule can be given by the Hooke's law:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \text{...(10.1)}$$

where, v is the frequency of vibration, k is the spring constant, and μ is the reduced mass *i.e.* $\frac{m_1 m_2}{m_1 + m_2}$

Dividing equation 10.1 by λ gives:

$$\frac{\nu}{\lambda} = \frac{1}{2\pi\lambda}\sqrt{\frac{k}{\mu}} \quad \text{...(10.2)}$$

$$\frac{1}{\lambda} = \frac{1}{2\pi(\lambda\nu)}\sqrt{\frac{k}{\mu}} \quad \text{...(10.3)}$$

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \quad \text{...(10.4)}$$

Anharmonic oscillator

Real molecules are anharmonic oscillators. Unlike harmonic oscillator wherein energy levels are equally spaced; energy levels in an anharmonic oscillator are more closely spaced at higher interatomic distances. A treatment for anharmonicity is beyond the scope of our discussion.

The spring constant, *k* is the measure of the bond strength. The stronger the bond, the higher the *k* , and consequently the higher is the frequency of vibration. This treatment implies that the diatomic molecule is a simple harmonic oscillator. The energy of a quantum harmonic oscillator is given by:

$$E = \left(n + \frac{1}{2}\right)hv \quad \text{...(10.5)}$$

where, *n* = 0, 1, 2, …… and *h* is the Plancks's constant

Absorption of infrared radiation

A molecular vibration is IR active i.e. it absorbs IR radiation if the vibration results in a change in the dipole moment. A diatomic molecule, that has one mode of vibration, may not absorb an IR radiation if the vibration does not accompany a change in the dipole moment. This is true for all the homonuclear diatomic molecules such as H_2, N_2, O_2, etc. Vibration of carbon monoxide (C=O), on the other hand, causes a change in dipole moment and is therefore IR active. Vibration of a bond involving two atoms that have large electronegativity difference is usually IR active.

An IR active vibration of a particular frequency absorbs the IR radiation of same frequency. Let us calculate the position of absorption band for carbonyl stretching vibration (frequency = 5.1 × 10^{13}vibrations/second) in acetone.

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}\ \text{cm}^{-1}$$

$$\bar{\nu} = \frac{5.1 \times 10^{13}\ sec^{-1}}{3 \times 10^{10}\ cm/sec} \quad = 1700\ \text{cm}^{-1}$$

Instrumentation

Two types of infrared spectrometers are commercially available: dispersive and Fourier Transform infrared (FTIR) spectrometers.

Dispersive spectrometer: A dispersive spectrometer is very similar in design to a UV/visible spectrophotometer. It has a radiation source, a grating monochromator, and a detector. The IR radiation generated by the source is dispersed into different frequencies by a monochromator. The selected frequencies go through sample and reference cells and the transmitted light is measured by the detector. The infrared sources are usually inert solids that are electrically heated to radiate infrared radiation. The detectors usually are either thermal sensors such as thermocouples and thermistors or the semiconductor materials that conduct following absorption of IR radiation (absorption of photon causes transition of electrons from the valence band to the conduction band).

Fourier Transform Spectrometer: A Fourier transform spectrometer uses an interferometer in place of the monochromator. An interference of polychromatic radiation is generated using an interferometer, usually a Michelson interferometer (Please see Box 10.1). Absorption of any particular wavelength will bring a change in the interferogram which gets detected. An interferogram is a time domain signal and is converted to frequency domain signal though Fourier Transformation.

Dispersive infrared spectrometers are still in use but FTIR spectrometers are slowly taking over. FTIR spectrometers have several advantages over the dispersive ones:

i. Better speed: FTIR spectrometers detect absorption of all the frequencies simultaneously; consequently, they are much faster than the dispersive spectrometers that scan the entire frequency range stepwise.

ii. Better sensitivity: Their speed of data acquisition makes FTIR spectrometers more sensitive. A large number of spectra can be recorded in small time thereby giving an improved signal to noise $\left(\frac{S}{N}\right)$ ratio.

$$\left(\frac{S}{N}\right) \propto \sqrt{n} \qquad \text{..(10.6)}$$

where *n* is the number of independent measurements

iii. More radiation energy: Dispersive spectrometers use slits that result in loss of radiation energy. FTIR spectrometers lack the slits as filtering of radiation is not required; this provides higher radiation energy for recording the absorbance.

iv. Simple design: As dispersion of the radiation and filtering are not required in the FTIR spectrometer , the movable mirror is the only moving part in the spectrometer.

v. Wavelength accuracy: The FTIR spectrometers usually have a He-Ne laser emitting light of 632.8 nm. This serves as an internal calibration for the wavelength and provides an accuracy of 0.01 cm^{-1} or better.

vi. **Attenuated Total Reflectance – Fourier Transform Infrared Spectrometer (ATR-FTIR)**

An ATR-FTIR works on the principle of total internal reflection and the evanescent field (Figure 10.5). The refractive index of the ATR crystal (usually Zinc selenide, diamond, Germanium) is significantly higher than that of the samples that are to be studied. An IR beam gets refracted at the interface of the ATR material and the sample (Figure 10.5A).

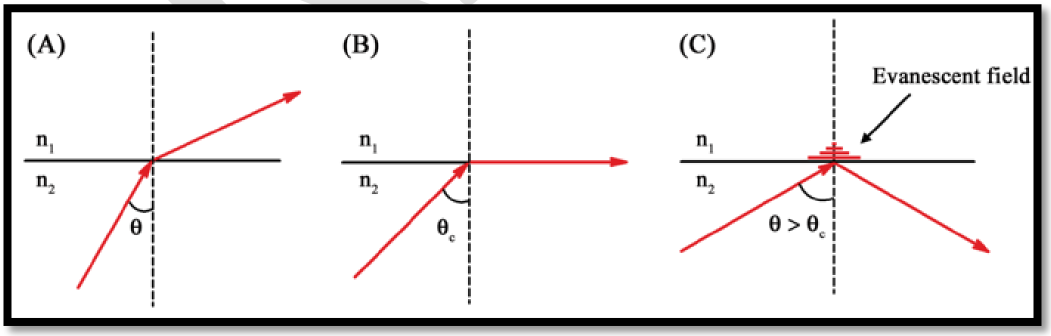


Figure 10.5 Phenomenon of total internal reflection. Notice the exponentially decaying evanescent field in the medium of lower refractive index (n_1)

vii. If the angle of incidence, θ is more than the critical angle, θ_c (Figure 10.5B and C), the beam gets totally internally reflected. Before getting totally reflected, however, an exponentially decaying field penetrates into the medium of low refractive index. This field is called an evanescent field and can interact with the molecules that are in the close proximity of the ATR crystal. If some part of the evanescent field is absorbed by the molecules, the reflected beam will be attenuated (become less intense) by this factor. The reflected beam will therefore be of lesser intensity implying absorption of radiation. The commercially available ATR instruments are FTIR spectrometers. ATR-FTIR allows studying the samples like thin films, powders, pastes by directly placing the sample on the ATR crystal.

viii. **Functional group region and fingerprint region**

The most common application of IR spectroscopy is perhaps to identify the functional groups. This is possible because different functional groups vibrate at different frequencies allowing their identification. The frequency of vibration, however, depends on additional factors such as delocalization of electrons, H-bonding, and substitutions at the nearby groups. The wavenumbers for some of the bonds are shown in Table 10.1.

Table 10.1 Typical vibrational frequencies of functional groups

Bond	**Molecule**	**Wavenumber (cm^{-1})**
C–O	Alcohols, ethers, esters, carboxylic acids, etc.	1300 – 1000
C=O	Aldehydes, ketones, esters, carboxylic acids	1750 – 1680
C=O	Amides	1680 – 1630
N–H (Stretching)	Amines and amides	3500 – 3100
–N–H (Bending)	Amines and amides	1640 – 1550
O–H	Alcohols	3650 – 3200
C–N	Amines	1350 – 1000
S–H	Mercaptans	2550

ix. The absorption bands in the 4000 – 1500 cm^{-1} region allows identification of functional groups ; this region therefore is also termed the functional group region of the IR spectrum (Figure 10.6). The lower energy portion of the mid-IR region (1500 – 400 cm^{-1}) usually contains a very complicated set of peaks arising due to complex vibrations involving several atoms. This region is unique to a particular compound and therefore is known as the fingerprint region of the IR spectrum. Though it is difficult to assign the vibrational modes to these peaks, these are useful to identify a compound if the spectrum of the compound is already known.

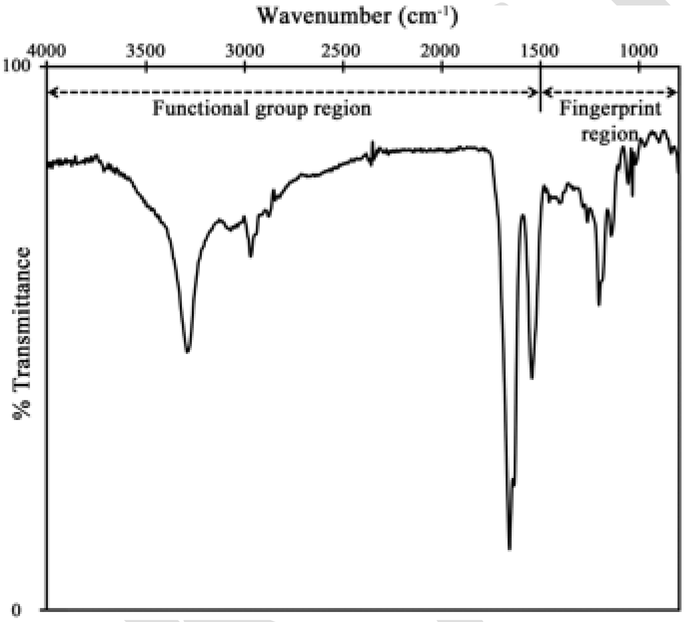


Figure 10.6. A typical IR spectrum showing functional group and fingerprint regions

Applications

i. *Identification of functional groups:* As has already been discussed, IR spectroscopy allows identification of functional groups. Carbonyl (C=O) is an interesting functional group worth discussing. Carbonyl is a double bond (high spring constant, *k*) with very high polarity. Stretching vibration of carbonyl group causes large changes in the dipole moment consequently resulting in a very intense absorption band. Furthermore, the frequency of carbonyl stretching does not differ significantly for aldehydes, ketone, carboxylic acids, and esters (Table 10.1). The large intensity and relatively unchanged frequency of carbonyl stretching allows easy identification of the carbonyl compounds (It is important to note that carbonyl stretching frequency can be much lower for amides and much higher for anhydrides and acid chlorides).

ii. *Identification of compounds:* The fingerprint region of the IR spectrum is unique to each compound. It is possible to identify a compound from its IR spectrum if the spectrum for the compound is already known and available for comparison. This is particularly useful in pharmaceutical research and development. A patented drug, if suspected to be synthesized by another pharmaceutical company, can easily be identified by comparing the IR spectra in the fingerprint region.

iii. *Presence of impurities:* Comparison of the IR spectra of the given compound with the spectra of pure compound helps in the assessment of its purity. It is important to ascertain the purity of the active molecule and the excipients used in preparing drug formulations.

iv. *Structural transitions in lipids:* Structural lipids are those that are organized in bilayers in biological membranes. Glycerophospholipids constitute the major class of the structural lipids (Figure 10.7). The lipids have several structural phases such as a gel phase with all-*trans*conformation and a liquid crystalline phase where *gauche* conformations are also present. Methylene ($–CH_2–$) stretching vibrations give the most intense absorption band in lipids as expected for a molecule having long hydrocarbon chains.

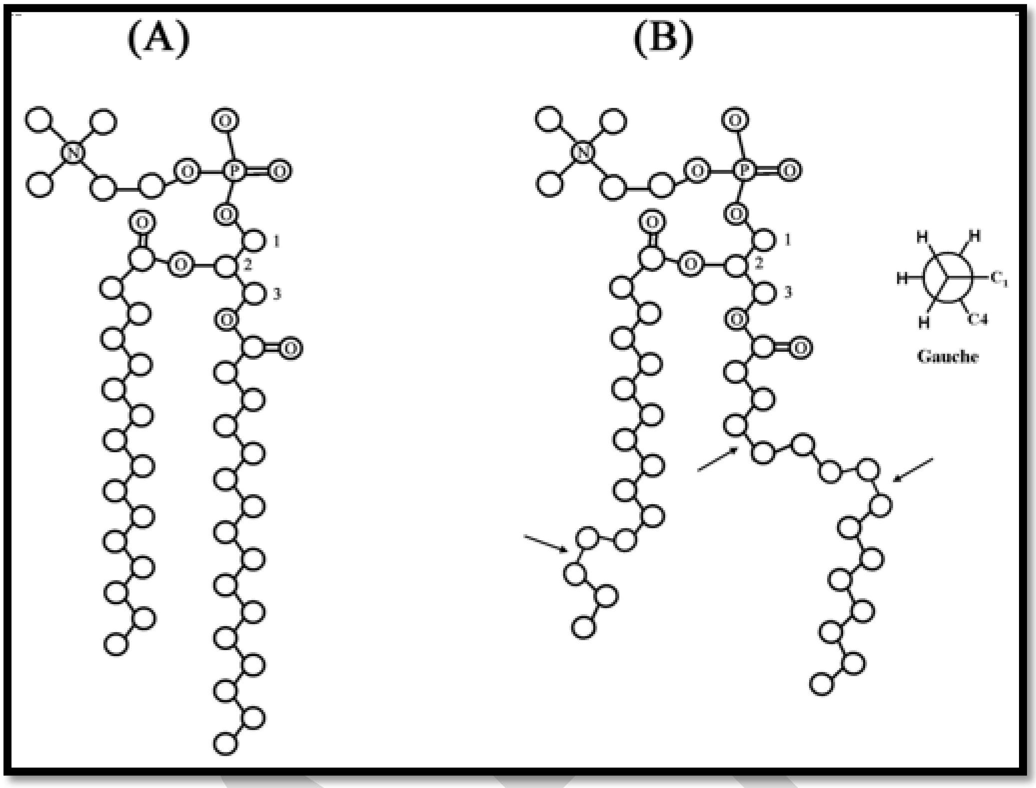


Figure 10.7. Structure of a glycerophospholipid: all-*trans* conformation (A); lipid with *trans* and *gauche* conformations (B), *gauche* conformations are indicated with arrows

Both –CH_2– stretching and bending vibrations are sensitive to the conformations of the lipids and therefore provide information about the transition of lipids between different phases. Vibration modes of the head group and the interfacial region also provide useful information about local acyl chain conformation. Carbonyl stretching vibration (1750 – 1700 cm^{-1}) in the ester bond is sensitive to the conformation of the local acyl chain conformation.

v. *Protein and peptide structure:* Infrared spectroscopy is routinely used to study the structures of proteins and peptides. Like CD spectroscopy, the region of interest in determining the conformation of the polypeptide backbone is the peptide bond. The peptide group results in nine distinct bands, labeled as amide A, B, and I-VII. Amide I is the most useful band in studying the polypeptide backbone conformation. Amide I band (1700 – 1600 cm^{-1}) arises largely due to the carbonyl stretching with small components of C–N stretching and N–H bending. The frequency of carbonyl stretching vibration is sensitive to the H-bonding, and therefore to the conformation of polypeptide backbone. The frequencies of absorption of different secondary structural elements are shown in Table 10.2

Table 10.2 Vibrational frequencies of the secondary structural elements of proteins in H_2O

Structure	Wavenumber (cm^{-1})
α-helix	1657 – 1648
β-sheet	1641 – 1623
Unordered	1657 – 1642
Antiparallel β-sheet	1695 – 1675

There is considerable overlap of the bands arising from α-helical and the unordered conformations. It is therefore generally difficult to assign the bands appearing in this region. Recording an IR spectrum in D_2O decreases this overlap to some extent. Dissolution a protein in D_2O results in the exchange of solvent exposed amide protons by deuterium. Hydrogens of the unordered amides are more easily exchanged as compared to those involved in the secondary structures. Despite this, it is not easy to unambiguously assign the bands arising in the 1657-1648 cm^{-1} region. Circular dichroism and IR spectroscopy therefore complement each other wherein α-helices are easily detected by CD and β-sheets by IR. Like CD, an IR spectrum of a protein can also be deconvoluted to determine the fractions of different secondary structural elements as shown in Figure 10.8.

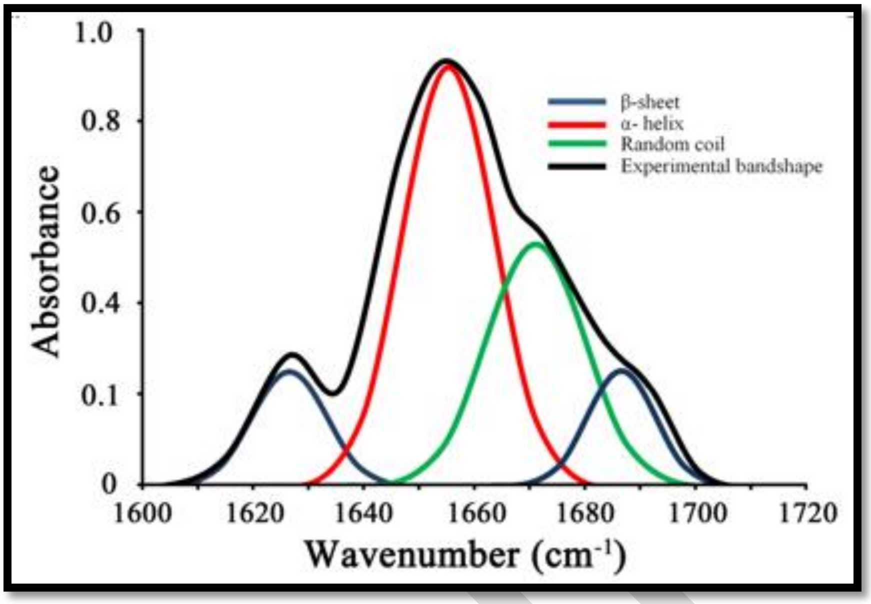
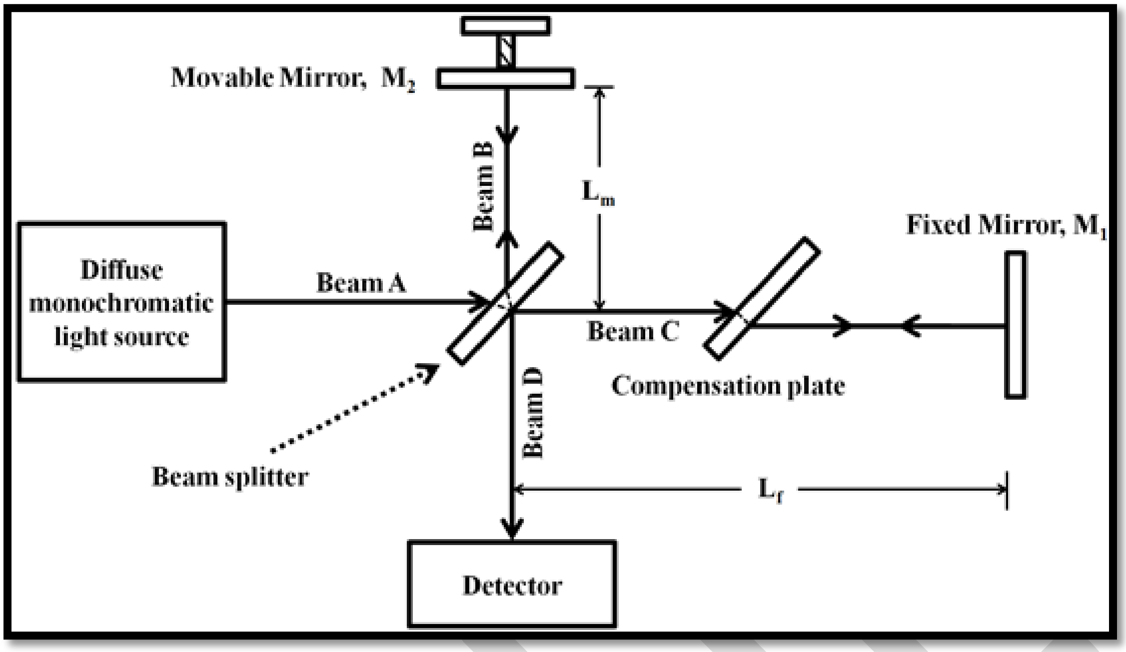


Figure 10.8. Deconvolution of Amide I band of a protein to identify the fractions of different structural elements

Michelson interferometer

A Michelson interferometer has a radiation source, a collimator, a beam-splitter, a movable mirror, a fixed mirror, a compensator, and a detector.



The radiation coming from the source is collimated and focused on the beam-splitter. 50% of the radiation gets transmitted while 50% gets reflected. The mirrors reflect back the radiation towards the beam splitter that again allows 50% transmission and 50% reflection. This allows the beams, B and C to interfere and give the beam D. As the beam, B travels through the beam-splitter twice while beam C does not travel through it even once, a compensation plate of same material (un-mirrored) and thickness as the beam-splitter is, is placed between the beam-splitter and the fixed mirror. This allows the beams, B and C to travel the equal distance. The motion of the movable mirror, M_2 causes the two beams to travel different distances thereby generating interference. Let us see what happens when a monochromatic radiation is used in the Michelson interferometer. If the beams, B and C travel the equal distance, they are in phase and will interfere constructively. If however, the M_2 moves, say towards the beam-splitter by a distance of $\frac{\lambda}{4}$, the beam B travels a distance of $\frac{\lambda}{2}$ less than that travelled by beam C. This allows a phase difference of 180° resulting in destructive interference. A continuous motion of the mirror M_2, therefore, will generate a sinusoidal signal through interference. The detector therefore detects a time domain signal. If a sample placed before the detector absorbs this radiation, the intensity of the light goes down. If a polychromatic light is used, the interference pattern generated carries all the wavelengths present in the polychromatic light. Absorption of any wavelength will result in a change in the interfering pattern. The interfering pattern, also known as interferogram is then Fourier transformed to obtain the frequency domain data.

Fingerprint region and Functional groups

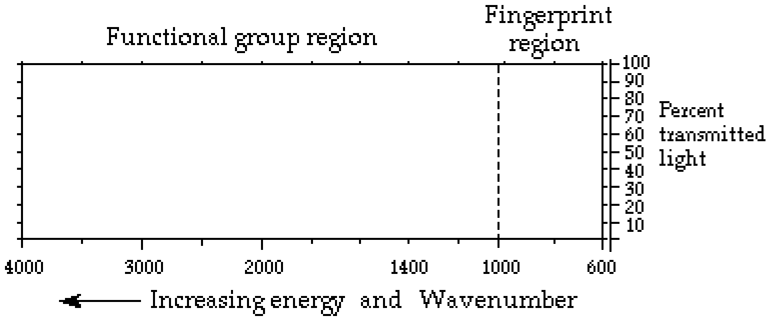
A molecule absorbs a unique set of IR light frequencies. Its IR spectrum is often likened to a person's fingerprints. These frequencies match the natural vibrational modes of the molecule. A molecule absorbs only those frequencies of IR light that match vibrations that cause a change in the dipole moment of the molecule. Bonds in symmetric N2 and H2 molecules do not absorb IR because stretching does not change the dipole moment, and bending cannot occur with only 2 atoms in the molecule. Any individual bond in an organic molecule with symmetric structures and identical groups at each end of the bond will not absorb in the IR range. For example, in ethane, the bond between the carbon atoms does not absorb IR because there is a methyl group at each end of the bond. The C-H bonds within the methyl groups do absorb.

In a complicated molecule many fundamental vibrations are possible, but not all are observed. Some motions do not change the dipole moment for the molecule; some are so much alike that they coalesce into one band.

Even though an IR spectrum is characteristic for an entire molecule, there are certain groups of atoms in a molecule that give rise to absorption bands at or near the same wavenumber, $\bar{\nu}$,

(frequency) regardless of the rest of the structure of the molecule. These persistent characteristic bands enable you to identify major structural features of the molecule after a quick inspection of the spectrum and the use of a correlation table. The correlation table is a listing of functional groups and their characteristic absorption frequencies.

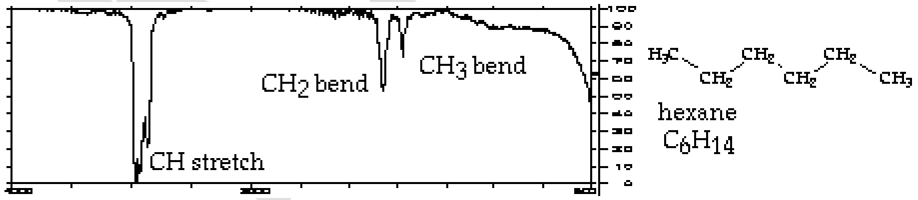
The infrared spectrum for a molecule is a graphical display. It shows the frequencies of IR radiation absorbed and the % of the incident light that passes through the molecule without being absorbed. The spectrum has two regions. The *fingerprint* region is unique for a molecule and the *functional group* region is similar for molecules with the same functional groups.



The nonlinear horizontal axis has units of wavenumbers. Each wavenumber value matches a particular frequency of infrared light. The vertical axis shows % transmitted light. At each frequency the % transmitted light is 100% for light that passes through the molecule with no interactions; it has a low value when the IR radiation interacts and excites the vibrations in the molecule.

A portion of the spectrum where % transmittance drops to a low value then rises back to near 100% is called a "band". A band is associated with a particular vibration within the molecule. The width of a band is described as broad or narrow based on how large a range of frequencies it covers. The efficiencies for the different vibrations determine how "intense" or strong the absorption bands are. A band is described as strong, medium, or weak depending on its depth.

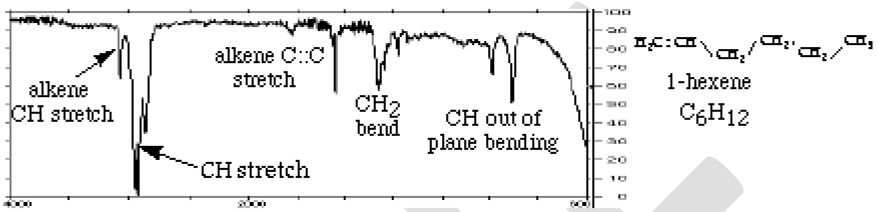
In the hexane spectrum below the band for the CH stretch is strong and that for the CH bend is medium. The alkane, hexane (C_6H_{14}) gives an IR spectrum that has relatively few bands because there are only CH bonds that can stretch or bend. There are bands for CH stretches at about 3000 cm^{-1}. The CH_2 bend band appears at approximately 1450 cm^{-1} and the CH_3 bend at about 1400 cm^{-1}. The spectrum also shows that shapes of bands can differ.



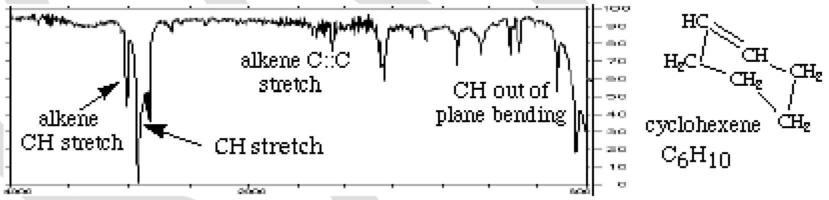
Procedure

Every molecule will have its own characteristic spectrum. The bands that appear depend on the types of bonds and the structure of the molecule. Study the sample spectra below, noting similarities and differences, and relate these to structure and bonding within the molecules.

The spectrum for the alkene, 1-hexene, C_6H_{12}, has few strong absorption bands. The spectrum has the various CH stretch bands that all hydrocarbons show near 3000 cm^{-1}. There is a weak alkene CH stretch above 3000 cm^{-1}. This comes from the C&emdash;H bonds on carbons 1 and 2, the two carbons that are held together by the double bond. The strong CH stretch bands below 3000 cm^{-1} come from carbon-hydrogen bonds in the CH_2 and CH_3 groups. There is an out-of-plane CH bend for the alkene in the range 1000-650 cm^{-1}. There is also an alkene CC double bond stretch at about 1650 cm^{-1} .

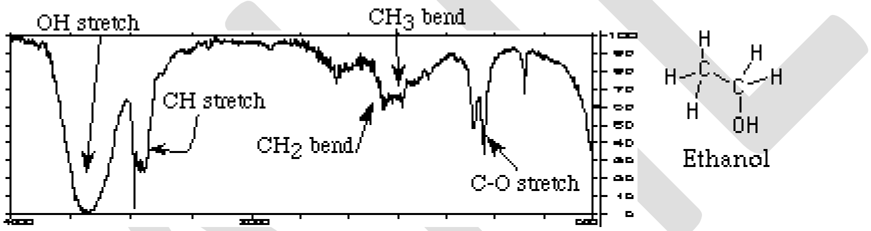


The spectrum for cyclohexene, (C_6H_{10}) also has few strong bands. The main band is a strong CH stretch from the CH_2 groups at about 3000 cm^{-1}. The CH stretch for the alkene CH is, as always, to the left of 3000 cm^{-1}. The CH_2 bend appears at about 1450 cm^{-1}. The other weaker bands in the range 1000-650 cm^{-1} are for the out of plane CH bending . There is a very weak alkene CC double bond stretch at about 1650 cm^{-1}.

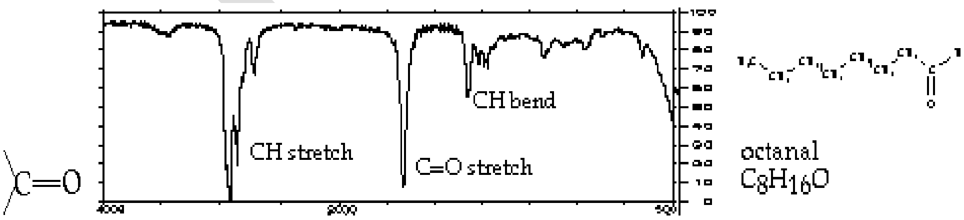


The IR spectrum for benzene, C_6H_6, has only four prominent bands because it is a very symmetric molecule. Every carbon has a single bond to hydrogen. Each carbon is bonded to two other carbons and the carbon-carbon bonds are alike for all six carbons. The molecule is planar. The aromatic CH stretch appears at 3100-3000 cm^{-1} .There are aromatic CC stretch bands (for the carbon-carbon bonds in the aromatic ring) at about 1500 cm^{-1}. Two bands are caused by bending motions involving carbon-hydrogen bonds. The bands for CH bends appear at approximately 1000 cm^{-1} for the in-plane bends and at about 675 cm^{-1} for the out-of-plane bend.

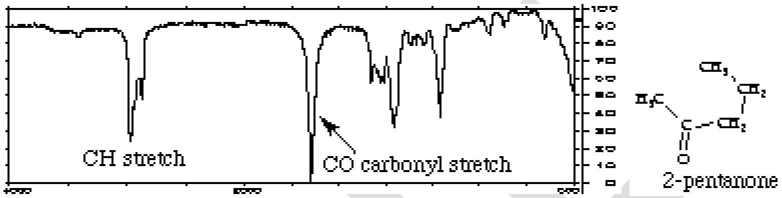
The IR spectrum for the alcohol, ethanol (CH_3CH_2OH), is more complicated. It has a CH stretch, an OH stretch, a CO stretch and various bending vibrations. The important point to learn here is that no matter what alcohol molecule you deal with, the OH stretch will appear as a broad band at approximately 3300-3500 cm^{-1}. Likewise the CH stretch still appears at about 3000 cm^{-1}.



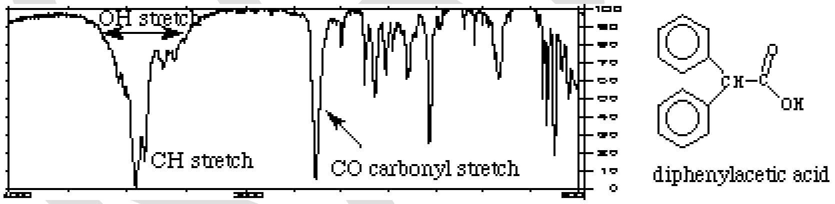
The spectrum for the aldehyde, octanal ($CH_3(CH_2)_6CHO$), is shown here. The most important features of the spectrum are carbonyl CO stretch near 1700 cm^{-1} and the CH stretch at about 3000 cm^{-1}. If you see an IR spectrum with an intense strong band near 1700 cm-1 and the compound contains oxygen, the molecule most likely contains a carbonyl group,



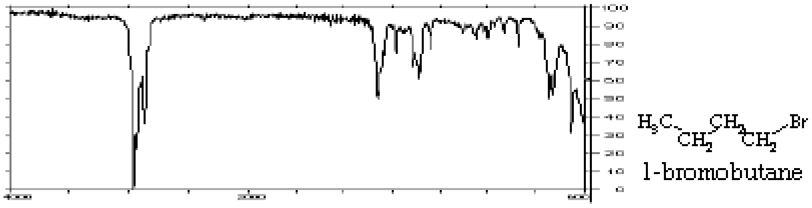
The spectrum for the ketone, 2-pentanone, appears below. It also has a characteristic carbonyl band at 1700 cm^{-1}. The CH stretch still appears at about 3000 cm^{-1}, and the CH2 bend shows up at approximately 1400 cm^{-1}. You can see the strong carbonyl CO stretch at approximately 1700 cm^{-1}. You can also see that this spectrum is different from the spectrum for octanal. At this point in your study of IR spectroscopy, you can't tell which compound is an aldehyde and which is a ketone. You can tell that both octanal and a 2-pentanone contain C-H bonds and a carbonyl group.



Carboxylic acids have spectra that are even more involved. They typically have three bands caused by bonds in the COOH functional group. The band near 1700 cm^{-1} is due to the CO double bond. The broad band centered in the range 2700-3300 cm^{-1} is caused by the presence of the OH and a band near 1400 cm^{-1} comes from the CO single bond . The spectrum for the carboxylic acid, diphenylacetic acid, appears below. Although the aromatic CH bands complicate the spectrum, you can still see the broad OH stretch between 2700-3300 cm^{-1}. It overlaps the CH stretch which appears near 3000 cm^{-1}. A strong carbonyl CO stretch band exists near 1700 cm^{-1}. The CO single bond stretch shows up near 1200 cm^{-1}.



The spectrum for 1-bromobutane, C_4H_9Br, is shown here. This is relatively simple because there are only CH single bonds and the CBr bond. The CH stretch still appears at about 3000 cm-1. The CH_2 bend shows up near 1400 cm^{-1}, and you can see the CBr stretch band at approximately 700 cm^{-1}.



IR spectra can be used to identify molecules by recording the spectrum for an unknown and comparing this to a library or data base of spectra of known compounds. Computerized spectra data bases and digitized spectra are used routinely in this way in research, medicine, criminology, and a number of other fields.

In this exercise you will try to identify the outstanding bands characteristic of certain bonds and functional groups in the spectra you examine. You are certainly not expected to identify all the absorption bands in each IR spectrum at this point in your work.

Table 1. A summary of the principle infrared bands and their assignments.

R is an aliphatic group.

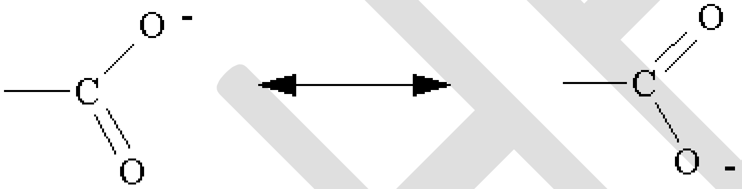
Functional Group	Type		Frequencies cm-1	Peak Intensity
C-H	sp3 hybridized	R3C-H	2850-3000	M(sh)
	sp2 hybridized	=CR-H	3000-3250	M(sh)
	sp hybridized	C-H	3300	M-S(sh)
	aldehyde C-H	H-(C=O)R	2750, 2850	M(sh)

N-H	primary amine, amide	RN-H2, RCON-H2	3300, 3340	S,S(br)
	secondary amine, amide	RNR-H, RCON-HR	3300-3500	S(br)
	tertiary amine, amide	RN(R3), RCONR2	none	
O-H	alcohols, phenols	free O-H	3620-3580	W(sh)
		hydrogen bonded	3600-3650	S(br)
	carboxylic acids	R(C=O)O-H	3500-2400	S(br)
CN	nitriles	RCN	2280-2200	S(sh)
CC	acetylenes	R-CC-R	2260-2180	W(sh)
		R-CC-H	2160-2100	M(sh)
C=O	aldehydes	R(C=O)H	1740-1720	S(sh)
	ketones	R(C=O)R	1730-1710	S(sh)
	esters	R(CO2)R	1750-1735	S(sh)
	anhydrides	R(CO2CO)R	1820, 1750	S, S(sh)
	carboxylates	R(CO2)H	1600, 1400	S,S(sh)
C=C	olefins	R2C=CR2	1680-1640	W(sh)

		R2C=CH2	1600-1675	M(sh)
		R2C=C(OR)R	1600-1630	S(sh)
-NO2	nitro groups	RNO2	1550, 1370	S,S(sh)

Effect of resonance and conjugation on infrared frequencies

Let's continue our discussion of the importance of resonance but shift from the nitro group to the carboxylate anion. The carboxylate anion is represented as a resonance hybrid by the following figure:

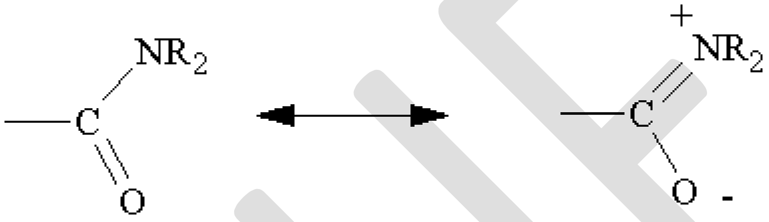


Unlike the nitro group which contained functional groups we will not be discussing, the carboxyl group is made up of a resonance hybrid between a carbon oxygen single bond and a carbon oxygen double bond. According to resonance, we would expect the C-O bond to be an average between a single and double bond or approximately equal to a bond and a half. We can use the carbonyl frequency of an ester of 1735 cm-1 to describe the force constant of the double bond. We have not discussed the stretching frequency of a C-O single bond for the simple reason that it is quite variable and because it falls in the fingerprint region. However the band is known to vary from 1000 to 1400 cm-1. For purposes of this discussion, we will use an average value of 1200 cm-1. The carbonyl frequency for a bond and a half would be expected to fall halfway between 1735 and 1200 or at approximately 1465 cm-1. The carboxyl group has the same symmetry as the nitro and CH2 groups. Both a symmetric and asymmetric stretch should be observed. The infrared spectrum of sodium benzoate is given in Figure 42. An asymmetric and symmetric stretch at 1410 and 1560 cm-1 is observed that averages to 1480 cm-1, in good agreement with the average frequency predicted for a carbon oxygen bond with a bond order of 1.5. While this is a qualitative argument, it is important to realize that the carboxylate anion does not show the normal carbonyl and normal C-O single bond stretches (at approximately 1700 and 1200 cm-1) suggested by each of the static structures above.

In the cases of the nitro group and the carboxylate anion, both resonance forms contribute equally to describing the ground state of the molecule. We will now look at instances where two or more resonance forms contribute unequally to describing the ground state and how these resonance forms can effect the various stretching frequencies.

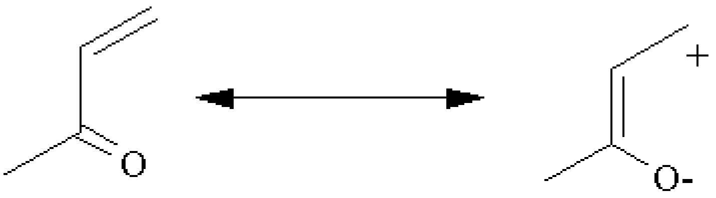
Carbonyl frequencies

Most carbonyl stretching frequencies are found at approximately 1700 cm-1. A notable exception is the amide carbonyl which is observed at approximately 1600 cm-1. This suggests that the following resonance form makes a significant contribution to describing the ground state of amides:

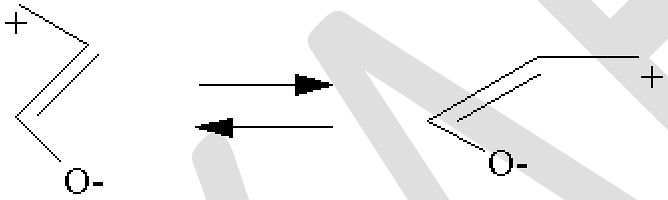


You may recall that resonance forms that lead to charge separation are not considered to be very important. However the following information support the importance of resonance in amides. X-ray crystal structures of amides show that in the solid state the amide functional group is planar. This suggests sp2 hybridization at nitrogen rather than sp3. In addition the barrier to rotation about the carbon nitrogen bond has been measured. Unlike the barrier of rotation of most aliphatic C-N bonds which are of the order of a few kcal/mol, the barrier to rotation about the carbon nitrogen bond in dimethyl formamide is approximately 18 kcal/mol. This suggests an important contribution of the dipolar structure to the ground state of the molecule and the observed frequency of 1600 cm-1, according to the arguments given above for the carboxylate anion, is consistent with more C-O single bond character than would be expected otherwise.

Conjugation of a carbonyl with a C=C bond is thought to lead to an increase in resonance interaction. Again the resonance forms lead to charge separation which clearly de-emphasizes their importance.



However this conjugative interaction is useful in interpreting several features of the spectrum. First it predicts the small but consistent shift of approximately 10 cm-1 to lower frequency, observed when carbonyls are conjugated to double bonds or aromatic rings. This feature is summarized in Table 4 for a variety of carbonyl groups. Next, the dipolar resonance form suggests a more polar C=C than that predicted for an unconjugated C=C. In terms of the change in dipole moment, contributions from this structure suggest that the intensity of infrared absorption of a C=C double bond would increase relative to an unconjugated system. Comparison of Figures 9, 10 and 35 with Figures 43, and 44-47 shows this to be the case. Conjugation is associated with an increase in intensity of the C=C stretching frequency. Finally, examination of Figures 43-46 reveals an intricacy not previously observed with simple non-conjugated carbonyls. The carbonyls of Figures 43-46 which are all conjugated appear as multiplets while those unconjugated carbonyls such as those in Figures 14 and 35 appear as single frequencies. Note however that not all conjugated carbonyls appear as multiplets (Figures 15 and 47. Resolution of this additional complicating feature can be achieved if we consider that conjugation requires a fixed conformation. For most conjugated carbonyls, two or more conformations are possible. The *s-cis* form is shown above and the *s-trans* form is shown below.



If the resonance interaction in these two forms differ, the effect of resonance on the carbonyl will differ leading to similar but different frequencies. The presence of multiple carbonyl frequencies is a good indication of a conjugated carbonyl. In some conjugated systems such as benzaldehyde

Table 4. The effect of conjugation on carbonyl frequencies.

Non-conjugated Compound	**Frequency cm-1**	**Conjugated Compound**	**Frequency cm-1**		**Frequency cm-1**
butanal	1725	2-butenal	1691	benzaldehyde	1702
2-butanone	1717	methyl vinyl ketone	1700, 1681	acetophenone	1685

propanoic acid	1715	propenoic acid	1702	benzoic acid	1688
ethyl propionate	1740	ethyl acrylate	1727	ethyl benzoate	1718
butanoic anhydride	1819, 1750	2-butenoic anhydride	1782, 1722	benzoic anhydride	1786, 1726
cis-cyclohexane-1,2-dicarboxylic anhydride	1857, 1786	1-cyclohexene-1,2-dicarboxylic anhydride	1844, 1767	phthalic anhydride	1852, 1762

and benzyl 4-hydroxyphenylketone (Figures 15 and 47), only one conformation by symmetry is possible and conjugation does not lead to any additional carbonyl frequencies. It should also be noted that in many of the examples given above, *cis-trans* isomerization about the carbon-carbon double bond is also possible. Some of the observed bands may also be due to the presence of these additonal isomers. Since the intensity of the peak is determined by the change in dipole moment, the presence of a small amount of geometric isomer can still lead to a detectable peak.

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Text books:

Sharma, Y. R. (2010). *Elementary Organic Spectroscopy: Principles and Chemical Applications* (V Edition). New Delhi: S. Chand & Company Limited

Jag Mohan, 2001. Organic Spectroscopy Principles and Applications. Narose Publishing House, New Delhi.

POSSIBLE QUESTIONS

Part-A

MULTIPLE CHOICE QUESTIONS
(Each Question Carry One Mark)

1. The most important region in IR is

a)15μ-200 μ b) **2.5 μ-15 μ** c) 0.8 μ-2.5μ d) 20μ–50μ

2. Stretching Vibrations require ---------- energy than bending vibration

a)Less b**) More** c) Same d) Equal

3. The vibrational frequency is given by

a)**$\upsilon = 1/2\pi c\sqrt{k/\mu}$** b) $\upsilon = 1/4\pi c\sqrt{\ \mu /R}$ c) $\upsilon/c = 1/2\pi c\sqrt{\ \mu /R}$ d) $\upsilon = 1/2\pi c * \mu /R$

4. The vibrational energy of a chemical bond is given by

a.)**Evib=[v+1\2]hv** b)Evib=[v+1]hv c)Evib=[v+1\2]3\2hv
d)Evib=[v_1\2]v

5. Zero point energy of diatomic S.H.O. of vibrational frequency ν is

a)**h ν** b) 1\2h ν c)1\4h ν d)0

6. The relation between De and Do the diossociation energies, of an S.H.O.is

a)**De=Do+h ν\2** b)Do=De+h ν\2 c)De=Do+h ν d)De=Do+2h ν

7. The selection rule for a vibrational transition in S.H.O.is

a)**$\Delta v = +1$** b) $\Delta v=+0$ c) $\Delta v=+$or-2 d) $\Delta n= 0$

8. Very important requirement for a molecule to show an I.R spectrum is that

a) **Change in dipole moment** b) Change in force constant c) Change in electronic energy d)Change in wave number

9. In IR C—H s tretching vibration occur at the region

a)1470—1430cm^{-1} b)**2960-2850cm^{-1}** c)1300-1800cm^{-1}
d)1000-1300cm^{-1}

10. In IR,C=C stretching has the frequency in the region

a)970—980cm^{-1} b)650-610cm^{-1} c)**1680-1620cm^{-1}**
d)995-985cm^{-1}

11. Absorbance is defined as

a)**$A=\log_{10}(1\backslash T)$** b)$A=e^{-}1\backslash T$ c)A=1\T d)A=2\T

12. For a non linear molecule there are ------degrees of vibrational degree of freedom

a)3n-2 b)**3n-6** c)3n-3 d)3n-4

13. The number of vibrational degrees of freedom of watermolecule is

a) 4 b) 9 c) 2 d) **3**

14. Which of the following molecules has the smallest spacing in the fine structure of IR spectrum?

a) HCl b) HBr c) CO d) **HI**

15. Carbonyl group shows a characteristic intense band in the IR. This high intensity is due to

a) high reactivity of the carbonyl group

b) the presence of lone pair of electrons which are easily excited

c) **high polarity of the group**

d) large force constant of the group

16. The vibrational frequency of HD is less than that of H_2becausce

a) H_2 has a higher force constant b) H_2 has a lower force constant

c) **HD has a higher mass** d) HD has a higher mass and lower force constant

17. The characteristic bond stretching frequency for C-Ois about---

a)10^4 cm^{-1} b) 10^5 cm^{-1} c) **10^3 cm^{-1}** d) $10^2 cm^{-1}$

18. In practical organic chemistry tetramethyl silane is used mainly for--

a) Making volatile derivatives of alcohols b) **A spectroscopic standard**

c) A solvent for IR spectra d) An antinock in gasolines

19. The spectra resulting from changes in vibrational energy levels for the same electronic state fall in which region of the spectrum

a) Microwave b)Visible c) UV d)**IR**

20. Which of the following isboth IR and microwave active?

a)Br_2 b)**HBr** c) CS_2 d) CO_2

Part-B

(Each Question Carry Eight Marks)

1. Write the expected infrared peaks for the following compounds.

   (i) Acetamide (ii) Benzophenone

   (ii). Discuss the features of the infrared spectra which could help in distinguishing the following pairs. $H_2N\ CH_2C_6H_4\ COCl$ and $H_2\ N\ C_6\ H_4\ CH_2\ COCl$.

2. (i).Obtain the selection rules for linear molecules, symmetric top molecules, asymmetric molecules for IR spectrum.

   (ii). Discuss briefly about the techniques employed for preparing solid samples in IR spectrum.

3. (i). Explain the following effects on vibrational frequency shift in IR spectrum.

   (a) Coupled vibration
   (b) Field effect and Bond angle

   (ii).What is the effect of ring size on carbonyl absorption in case of cycloketones?

4. How will you distinguish between the following pairs on the basis of IR spectroscopy?

   (i) Fundamental vibrations and overtones.
   (ii) Fermi resonamce and overtones
   (iii) Inplane bending and out of plane bending virbrations
   (iv) Inter and intramolecular hydrogen bonding.

5. (i). Compare the relative frequencies for C-C, C=C, and C≡C bonds.

   (ii). How can you distinguish among 1-hexane, l – hexene and l – hexyne on the basis of infrared spectroscopy.

6. Discuss in detail the various types of vibration and the factors influencing vibrational frequency.

7. (i)Explain the following effects on vibrational frequency shift in IR spectrum.

   (a) Coupled vibration
   (b) Field effect and Bond angle
   (ii) What is the effect of ring size on carbonyl absorption incase of cycloketones?

8. Explain the applications of IR spectroscopy in organic compounds?

9. (i). Compare the relative frequencies for C-C, C═C, and C≡C bonds.

   (ii). How can you distinguish among 1-hexane, l – hexene and l – hexyne on the basis of infrared spectroscopy.

10. Discuss in detail the various types of vibration and the factors influencing Vibrational frequency .

Part-C

Ten Mark Question(Compulsory Question)

1. (a) Write the expected IR peaks for the following compounds:

(i) p-nitro phenol (ii) p-nitro benzoic acid (iii) acetic anhydride

(b) An organic compound (a) with molecular formula C_3H_7NO gives absorption peak in the regions 3413 (m), 3236 (m), 3030-2899 (m), 1667 (s), 1634(s), and 1460 cm^{-1} (s). Give its possible structure.

[19CHP104]

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-641021
(For the candidates admitted on 2019 onwards)
DEPARTMENT OF CHEMISTRY
I- SEMESTER
ORGANIC AND INORGANIC SPECTROSCOPY

Unit-2 Infrared Spectroscopy (19CHP104)

S.No	Questions	Option a	Option b	Option c	Option d	Answer
1	The most important region in IR is	a)15μ-200 μ	b) 2.5 μ-15 μ	c) 0.8 μ-2.5μ	d) 20μ–50μ	b) 2.5 μ-15 μ
2	Stretching Vibration require ---------- energy than bending vibration	a)less	b) more	c) same	d) equal	b) more
3	The vibrational frequency is given by	a)υ = 1/2πc√k/μ	b) υ = 1/4πc√	c) υ/c = 1/2πc√ μ /R	d) υ = 1/2πc * μ /R	a)υ = 1/2πc√k/μ
4	The vibrational energy of a chemical bond is given by	a.)Evib=[v+1\2]h ν	b)Evib=[v+1]h ν	c)Evib=[v+1\2]3\2h v	d)Evib=[v_1\2]v	a.)Evib=[v+1\2]hν
5	The energy of fundamental band is	a)ΔEvib= hυ	b) ΔEvib=(	c) ΔEvib=3 hυ	d) ΔEvib= hυ\2	a)ΔEvib= hυ
6	The energy of first overtone is	a)ΔEvib= 2hυ	b) ΔEvib= hυ+3\2	c) ΔEvib= 3hυ	d) ΔEvib= hυ\2	a)ΔEvib= 2hυ
7	The number of vibrational degree of freedom for C_6H_6 is	a)40	b)60	c)30	d)10	c)30
8	The spectra caused in the IR region by the transition in vibrational levels in different modes of vibrations are called	a)rotational spectra	b)electronic spectra	c)vibrational spectra	d)absorption spectra	c)vibrational spectra
9	The IRspectra of a comgpound helps in	a)proving the identity of compounds	b)showing the presence of certain	c)neither of the above	d)both (a) and (b)	d)both (a) and (b)
10	The wave numbers are expressed in	a)sec	b)cmsec	c)cm	d)cmsec^{1}	c)cm
11	The internal energy of a molecule is its	a)rotational	b) vibrational	c)translational	d)all of these	d)all of these
12	The frequency and wavelength are related to each other by the formula	a) ν = c ν	b) ν=cν	c) ν=h ν	d) ν=h c/λ	d) ν=h c/λ
13	The molecule which is IR inactive but Raman active is	a)Hcl	b)N_2	c)SO_2	d)protein	d)protein

14	Number of translationa; rotational and vibrational degree of freedom in CO2 are respectively	a)3,2,4	b)3,4,2	c)3,3,3	d)4,3,2	a)3,2,4
15	Zero point energy of diatomic S.H.O. of vibrational frequency ν is	a)h ν	b) 1\2h ν	c)1\4h ν	d)0	a)h ν
16	The relation between De and Do the diossociation energies, of an S.H.O.is	a)De=Do+h ν\2	b)Do=De+h ν\2	c)De=Do+h ν	d)De=Do+2h ν	a)De=Do+h ν\2
17	The selection rule for a vibrational transition in S.H.O.is	a)Δv = +1	b) Δv=+0	c) Δv=+or-2	d) Δn= 0	a)Δv = +1
18	Very important requirement for a molecule to show an I.R.spectrum is	a)change in dipolemoment	b)change in force constant	c)change in electronic energy	d)change in wave number	a)change in dipolemoment
19	The rotational energy of a rigid rotar is	a)Erot =h^2 / 4л^{2}IJ(J+1)	b.E_{rot}-=h^2/8 л^{2}IJ(J+1)	c. E_{rot}=h/8 лIJ(J+1)	d.h/2I(J+1)	b.E_{rot}-=h^2/8 л^{2}IJ(J+1)
20	The IR spectrum od rigid rotator consist of ------- equally spaced lines with a spacing of each side of band origin	a)B	b)2B	c)4B	d)3B	a)B
21	The ΔJ=0 transition gives rise to a new group of lines called	a)R branch	b)S branch	c)Qbranch	d)Pbranch	c)Qbranch
22	To get parallel band in IR forCO2,the oscillating dipole moment is ------- to the molecular axis is	a)parallel	b)perpendicular	c)angular	d)linear	a)parallel
23	To get parallel band in IR the selection rule is	a)ΔV=+1, ΔJ=+1	b) ΔV= *1, ΔJ =+1*	*c) ΔV=+1, ΔJ* = _1	d) *ΔV=+2, ΔJ=+3*	a)ΔV=+1, ΔJ=+1
24	The selection rule to get the perpendicular band in spectrum is	a) ΔV=+1, ΔJ = -1	b) ΔV=+1, ΔJ = - 1,O	c) ΔV=O, ΔJ =+ -1	d) ΔV=+2 ΔJ =_1 2	b) ΔV=+1, ΔJ = - 1,O
25	Due to the +I effect of methyl group absorbtion takes place at ------- wave number in IR spectrum	a)higher	b)lower	c)same	d)none of above	b)lower
26	Introduction of electronegative atoms (or)groups-------the wave number absorption	a)increases	b)decreases	c)same	d)none of the above	a)increases

27	In IR C—H s tretching vibration occur at the region	a)1470—1430cm^{-1}	b)2960-2850cm$^{-1 -}$	c)1300-1800cm^{-1}	d)1000-1300cm^{-1}	b)2960-2850cm$^{-1 -}$
28	In IR,C=C stretching has the frequency in the region	a)970—980cm^{-1}	b)650-610cm^{-1}	c)1680-1620cm^{-1}	d)995-985cm^{-1}	c)1680-1620cm^{-1}
29	Absorbance is defined as	a)A=log10(1\T)	b)A=e^{-}1\T	c)A=1\T	d)A=2\T	a)A=log10(1\T)
30	For a non linear molecule there are ------ degrees of vibrational degree of	a)3n-2	b)3n-6	c)3n-3	d)3n-4	b)3n-6
31	Position of C—O stretching band for primary alcohol occur at ----in IR	a)1050cm^{-1}	b)1500cm^{-1}	c)1800cm^{-1}	d)200cm^{-1}	a)1050cm^{-1}
32	The O-H stretching of Phenol exibit a strong broad band in the range in IR	a)3600-3200cm^{-1}	b)1600-1700cm^{-1}	c)2300-2500cm^{-1}	d)900-100cm^{-1}	a)3600-3200cm^{-1}
33	The potential energy of an anhormonic oscillator is	a)Vr=De[1-expa(r-re)]^{2}	b)Vr=De[1-a(ro-r)]^{2}	c)Vr=De[1\ro-r]^{2}	d)Vr=a[Do-(r-ro)]^{2}	a)Vr=De[1-expa(r-re)]^{2}
34	μ/For a molecule to be IR active	a)dμ/dr=o	b) dr/dμ =o	c) dμ/dr not equal to 0	d) d¥/dc not equal to 0	c) dμ/dr not equal to 0
35	>C=O stretching of aldehudes occur in the region in the IR region.	a)2770-2700 cm^{-1}	b)1740-1720cm^{-1}	c)700-970cm^{-1}	d)3300-3400^{-1}cm	b)1740-1720cm^{-1}
36	The type of H-bonding which give rise to broad lines in IR Techinque is -----	a)Intermolecular	b)Intramolecular	c)C-H stretching	d)C-H bending	b)Intramolecular
37	The type of H-bonding which give rise to sharp lines in IR Techinque is ------	a)Sym.stretching	b)Anti.sym.stretching	c)Intramoleclulear	d)Intercular	a)Sym.stretching
38	In which region we get absorbtiion bands and shoulders	a)Far infradredf	b)near infrared	c)mid-infrared	d)finger print region	d)finger print region
39	N-H bending vibration for primary amines occurs in the region	a)700-900cm^{-1}	b)800-700cm^{-1}	c)1600-1500cm^{-1}	d)800-700cm^{-1}	c)1600-1500cm^{-1}
40	In a double beam instrument ,the beamspilts into-----parts	a)one	b)three	c)two	d)none of the above	c)two
41	The radiation used to study the vibrational spectra of a molecule is	a. microwave	b.radiowave	c.UV	d.IR	d.IR
42	The number of vibrational degrees of freedom of watermolecule is	a. 4	b.9	c.2	d. 3	d. 3

43	Which of the following molecules has the smallest spacing in thefine structureof Irspectrum?	a. HCl	b.HBr	c.CO	d.HI	d.HI
44	Carbonyl group shows a characteristic intenseband in the IR. This high intensity is due to	a. high reactivity of the carbonyl group	b. the presence of lone pair of electrons	c. high polarity of the group	d. largeforce constant of thegroup	c. high polarity of the group
45	The vibrational frequency of HD is less than that of H_2becausce	a. H_2 has a higher force constant	b. H_2has a lower force	c. HD has a higher mass	d. HD has a higher mass and lower	c. HD has a higher mass
46	Which one of the following spectroscopy is known as magnetic radiation absorption spectroscopy?	a. MS	b.NMR	c. IR	d. UV	c. IR
47	Which one of thefollowing region in IR is known as functional group region	a. 1300-4000 cm^{-1}	b. 900-1300 cm^{-1}	c. 650-900 cm^{-1}	d)1000-1300cm^{-1}	a. 1300-4000 cm^{-1}
48	Whatwill be the C=O stretching band in IR of CH_2=$CHCOCH_3$	a. 1700 cm^{-1}	b. 1710 cm^{-1}	c. 1680 cm^{-1}	d. 1780 cm^{-1}	c. 1680 cm^{-1}
49	Which one of thefollowing statement is false for IR spectroscopy	a. Conjugation decreases the C=O stretching frequency	b. higher the frequency if more strained the alicyclic	c. Electron releasing substituents decreases the frequency of C=O	d. Electran withdrawing subtituents decreases	d. Electran withdrawing subtituents decreases thefrequencyof C=O
50	An alcohol having mol-formula C_4H10O gives C-O stretching band at1120 cm^{-1} will be	a. 1-butanol	b.2.butanol	c. 2-methyl-2-propanol	d. isobutanol	b.2.butanol
51	Pedict thenumber of translational ,rotational and vibrational degree	a. 3,0,0	b. 3,1,0	c.3,0,1	d.3,1,1	a. 3,0,0
52	Which one of the following is microwave inactive?	a. HCl	b.HBr	c.Cl_2	d. NO	c.Cl_2
53	The rotational constant (B) of a diatomicmolecule is	a. $h/4\pi^2I$	b.$h^2/4\pi^2I$	c. $h^2/8\pi^2I$	d. $h/8\pi^2I$	d. $h/8\pi^2I$
54	The degree of degeneracy for a rid rotor in energy level with quantum number J	a.J	b.2J	c.2J-1	d.2J+1	d.2J+1

55	From the pure rotation spectrum of HF information can beobtained about	a. the force constant	b. The proton spin	c. The hydrogen bonding	d. the internuclear distance	d. the internuclear distance
56	The characteristic bond stretching frequency for C-Ois about---	a.10^4 cm^{-1}	b. 10^5 cm^{-1}	c. 10^3 cm^{-1}	d.$10^2$$cm^{-1}$	c. 10^3 cm^{-1}
57	In practical organic chemistry tetramethyl silane is used mainly for--	a. Making volatile	b. A spectroscopic	c. A solvent for IR spectra	d. An antinock in gasolines	b. A spectroscopic standard
58	The spectra resulting from changes in vibrational energy levels for the same electronic state fall in which region of thespectrum	a. microwave	b.Visible	c. UV	d.IR	d.IR
59	Which of the following isboth IR and microwave active?	a.Br_2	b.HBr	c.CS_2	d.CO_2	b.HBr
60	The symmetric C=C stretching ibration of €-2- butene is mesuredby which one of thefollowing spectroscopic methods	a. microwave	b.Visible	c. Raman	d.IR	c. Raman

LECTURE NOTES

UNIT-III

SYLLABUS

NMR Spectroscopy: Principle of NMR spectroscopy – description of the PMR instrument, factors affecting chemical shifts-chemical shift equivalence and magnetic equivalence - spin-spin coupling - first order and non first order spectra - Hetero nuclear coupling in ^{1}H NMR - deuterium exchange - high field spectra - double resonance-shift reagents-applications to organic and inorganic compounds. FT NMR.

^{13}C NMR spectroscopy-factors affecting the chemical shifts - broad band and off-resonance decoupling - applications in organic chemistry.

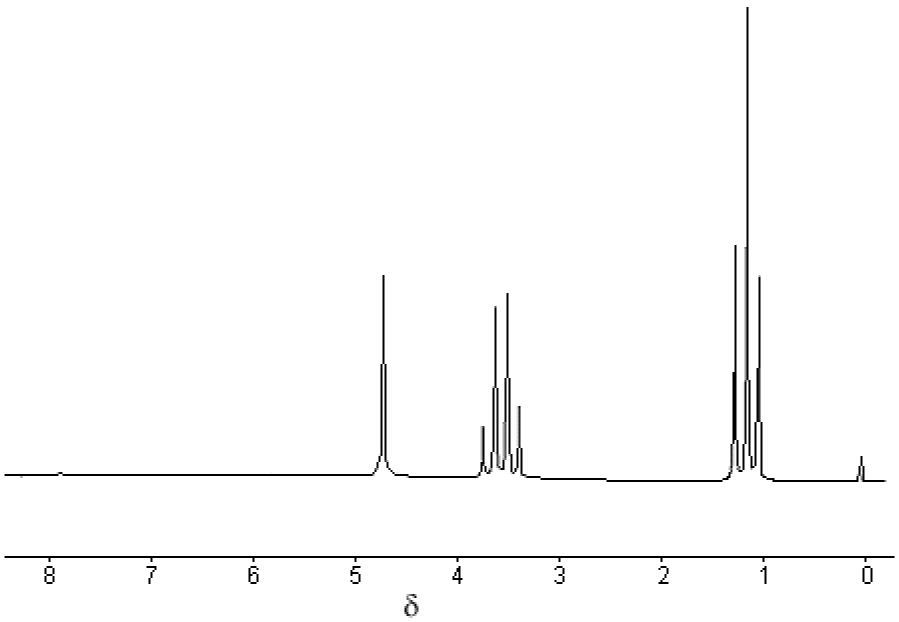
Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance (NMR) allows us to detect atomic nuclei and say what sort of environment they are in, within their molecule. Thus, the hydrogen of, say, propanol's hydroxyl group is different from the hydrogens of its carbon skeleton. NMR (actually ^{1}H, or proton, NMR) can easily distinguish between these two sorts of hydrogens. Moreover, it can also distinguish between all the other different sorts of hydrogen atoms present. Likewise, carbon (or rather ^{13}C) NMR can easily distinguish between the three different carbon atoms.

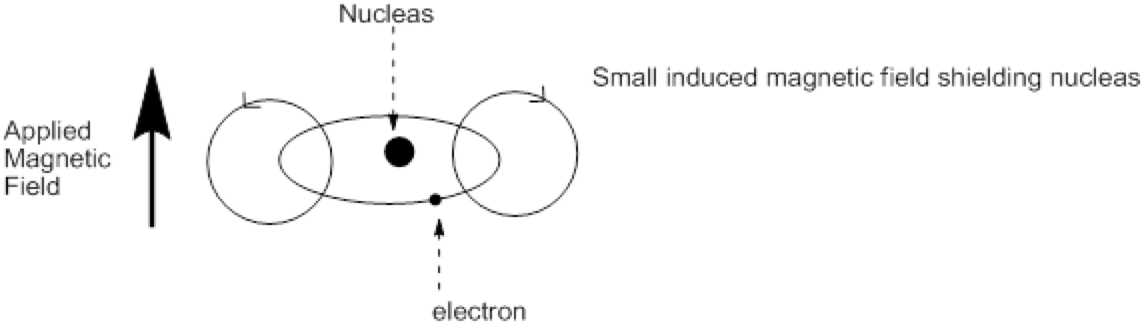
- Some atomic nuclei act like tiny compass needles and have different energy levels when placed in a magnetic field. Nuclear energy levels are quantized, just like the energy levels of an electron, and there are only certain specific energy levels it can adopt. Some nuclei (including ‘normal' carbon-12) do not interact with a magnetic field at all and cannot be observed in an NMR machine. ^{1}H and ^{13}C do interact and have just two different energy levels. When a magnetic field is applied to these nuclei, they can either align themselves with it, which would be the lowest energy state, or they can align themselves against the field, which is higher in energy. nucleus in a magnetic field, the difference in energy between the nuclear spin aligned with and against the applied field depends on how strong the magnetic field is, and also on the properties of the nucleus itself. The stronger the magnetic field we put our nucleus in, the greater the energy difference between the two alignments. However, the energy difference between the nuclear spin being aligned with the magnetic field and against it is really very small—so small that a very, very strong magnetic field is required to see any difference at all.

- Nuclei that interact with magnetic fields are said to possess nuclear spin. The exact number of different energy levels a nucleus can adopt is determined by this nuclear spin, I, of the particular isotope. The nuclear spin I can have various values such as 0, 1/2, 1, 3/2 and the number of energy levels is given by 2I+ 1. Some examples are: ^{1}H, I= 1/2; ^{2}H (= D), I= 1; ^{11}B, I= 5/2; ^{12}C, I= 0.
- The amount of energy needed to flip the nucleus can be provided by electromagnetic radiation of radiowave frequency. Radio waves flip the nucleus from the lower energy state to the higher state. The nucleus now wants to return to the lower energy state and, when it does so, the energy comes out again and this (a tiny pulse of radiofrequency electromagnetic radiation) is what is detected. The operation of a NMR machine is summarized below.
- The sample of the unknown compound is dissolved in a suitable solvent and put in a very strong magnetic field. Any atomic nuclei with a nuclear spin now have different energy levels, the exact number of different energy levels depending on the value of the nuclear spin.
- The sample is irradiated with a short pulse of radiofrequency energy. This disturbs the equilibrium balance between the two energy levels: some nuclei absorb the energy and are promoted to a higher energy level
- The energy given out when the nuclei fall back down to the lower energy level is detected using a sophisticated radio receiver.
- After lots of computational analysis involving complex mathematical operations, the results are displayed in the form of intensity (i.e. number of absorptions) against frequency. This is known as one dimensional NMR spectrum.

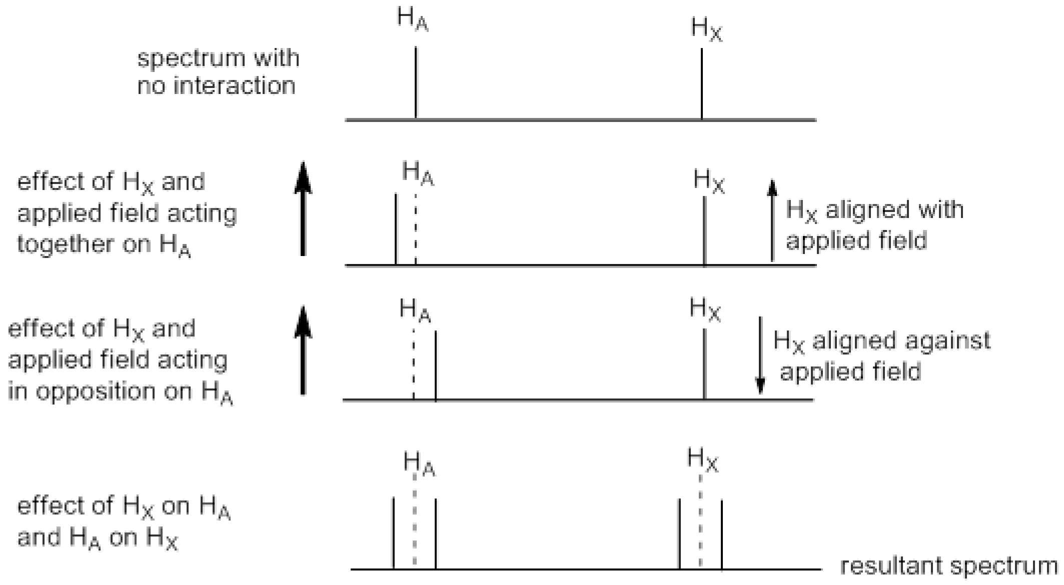
The proton NMR spectrum of ethanol is given below.



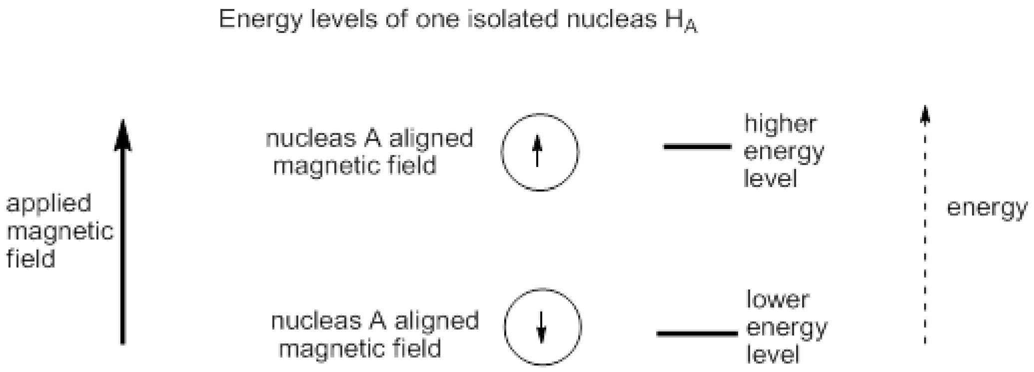
- In the spectrum, each line represents a different kind of carbon atom: each one absorbs energy (or resonates—hence the term nuclear magnetic resonance) at a different frequency. The reason that each carbon does not feel the same magnetic field is because of the electronic cloud around them. Each nucleus is surrounded by electrons, and in a magnetic field these will set up a tiny electric current. This current will set up its own magnetic field (rather like the magnetic field set up by the electrons of an electric current moving through a coil of wire or solenoid), which will oppose the magnetic field that is applied. The electrons are said to shield the nucleus from the external magnetic field. If the electron distribution varies from ^{13}C atom to ^{13}C atom, so does the local magnetic field, and so does the resonating frequency of the ^{13}C nuclei. A change in electron density at a carbon atom also alters the chemistry of that carbon atom. NMR tells us about the chemistry of a molecule as well as about its structure.



- In the spectrum above, the peak centred on 1ppm is for the CH_3 protons, the next are for CH_2 protons and the peak at around 5 ppm is for the OH proton. There are two things to be noted, the first is the so called “ppm” scale and second one is the splitting of the peaks in the proton signals. The splitting of the signal is due to coupling of the nuclear spins of one atom with another. An explanation can be provided for this phenomenon. If a molecule has two types of proton H_A and H_X having no interaction between them, then they can be aligned either along the external magnetic field or against it and only two lines are obtained. This can be seen 4,6-diaminopyrimidine-where there are only two single lines (called singlets). However, if there is an interaction between the two types of protons, then a different scenario arises. Now each proton, say, H_A , is near enough to experience the small magnetic field of the other proton H_X as well as the field of the magnet itself. The diagram shows the result.



- If each proton interacted only with the applied field two singlets only would be obtained. But proton H_A actually experiences two slightly different fields: the applied field plus the field of H_X or the applied field minus the field of H_X. H_X acts either to increase or to decrease the field experienced by H_A. The position of a resonance depends on the field experienced by the proton so these two situations give rise to two slightly different peak-a doublet as it is called. And whatever happens to H_A happens to H_X as well, so the spectrum has two doublets, one for each proton. Each couples with the other. The field of a proton is a very small indeed in comparison with the field of the magnet and the separation between the lines of a doublet is very small.
- The second explanation takes into account the energy levels of the nucleus. Electronic energy levels on neighbouring atoms interact with each other and splitting to produce new molecular energy levels, some higher in energy and some lower in energy than the original atomic energy levels. When hydrogen nuclei are near each other in a molecule, the nuclear energy levels also interact and split and produce new energy levels. If a single hydrogen nucleus interacts with a magnetic field there are two energy levels as the nucleus can be aligned with or against the applied magnetic field, there is one energy jump possible, and there is a resonance at one frequency.



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- This representation shows H_A protons independent of the influence of H_X. Each had two energy levels, each gave a singlet, and there were two lines in the spectrum. But, if each proton has hydrogen nucleus nearby and then there are now four energy levels. Each nucleus H_A and H_X can be aligned with or against the applied field. There is one most stable energy level where they are both aligned with the field and one least stable level where they are both aligned against. In between there are two different energy levels in which one nucleus is aligned with the field and one against. Exciting H_A from alignment with to alignment against the applied field can be done in two slightly different ways, shown as $A_1$and A_2 on the diagram given below. The result is two resonances very close together in the spectrum. If there are two slightly different energy jumps to excite H_A, there must also be two slightly different energy jumps to excite H_X. The difference between A_1 and A_2 is exactly the same as the difference between X_1 and X_2. Each proton now gives two lines (a doublet) in the NMR spectrum and the splitting of the two doublets is exactly the same. This situation is described as coupling. We say 'A and X are coupled' or 'X is coupled to A'(and vice versa, of course). Now look back at the spectrum of cytosine at the beginning of this section. Each is split by the same amount and the separation of the lines is the coupling constant and is denoted by J. Coupling constants J are measured in Hz because the same number regardless of the frequency of the spectrometer.

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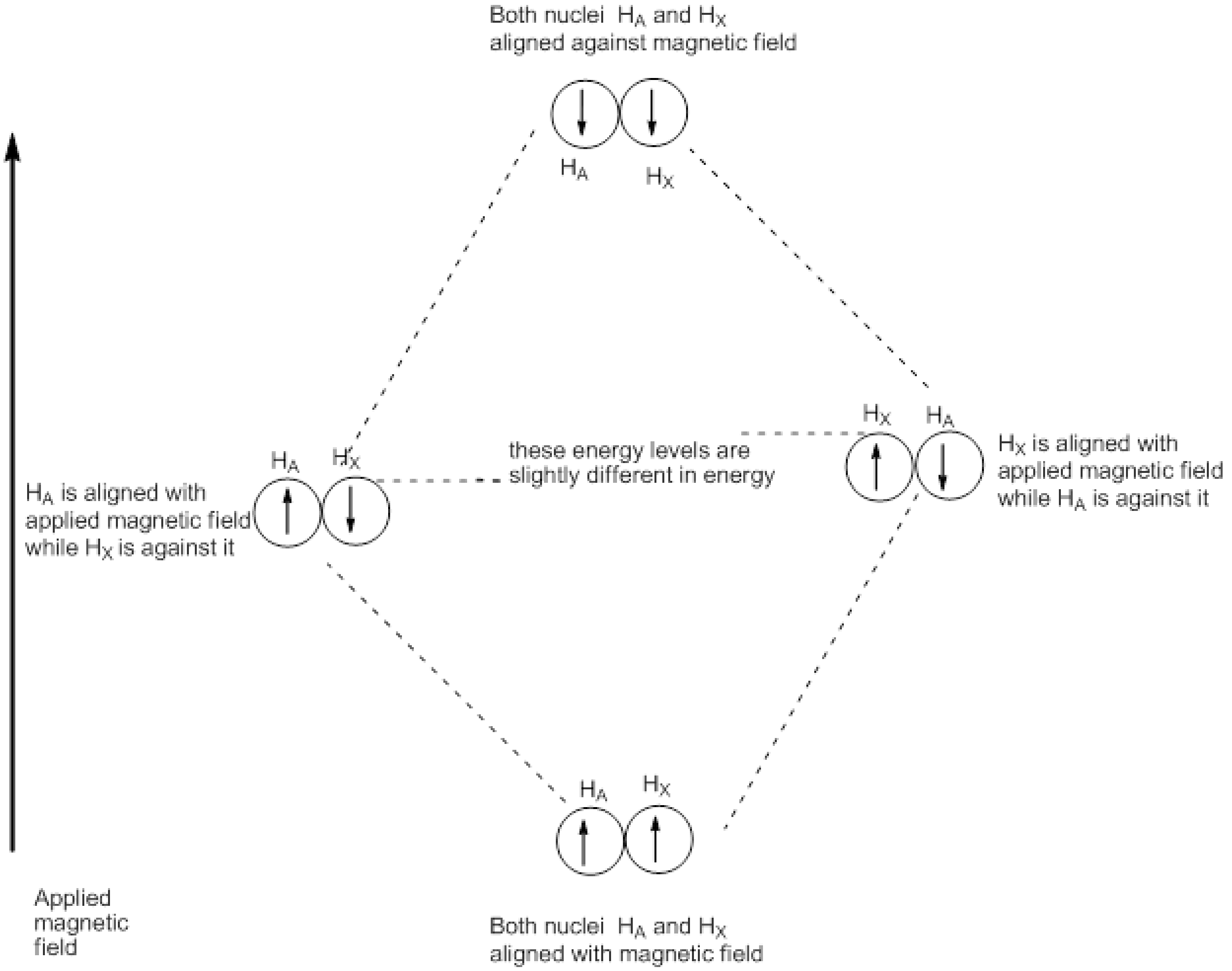
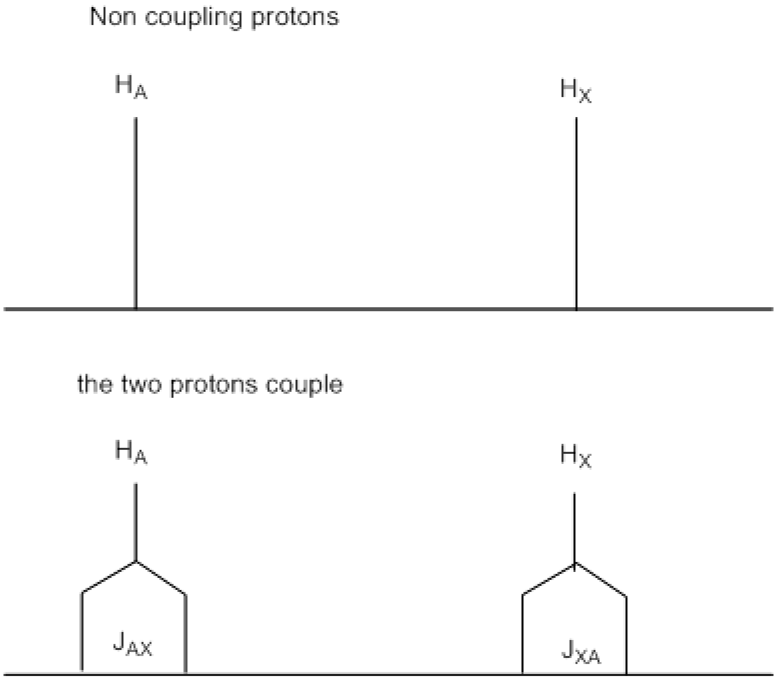
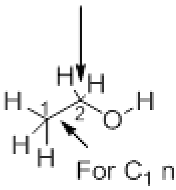

Both nuclei H_A and H_X aligned against magnetic field
H_A
H_X
H_A
H_X
H_A is aligned with applied magnetic field while H_X is against it
these energy levels are slightly different in energy
H_X
H_A
H_X is aligned with applied magnetic field while H_A is against it
H_A
H_X
Applied magnetic field
Both nuclei H_A and H_X aligned with magnetic field



The true spectrum has a pair of doublets each split by an identical amount. It is to be noted that no line appears at the true chemical shift, but it is easy to measure the chemical shift by taking the midpoint of the doublet. The multiplicity (splitting of peaks) can be determined by counting the protons on the carbons attached immediately to carbon to which the referred proton is attached and using the formula n+1. Thus for the CH_3 group in ethanol, there is a CH_2 group attached to it hence the formula gives (2+1) or 3 as multiplicity.



For C_2 number of hydrogens attached to C_1= 3 Hence multiplicity is (3+1) = 4

For C_1 number of hydrogens attached to C_2=2 Hence multiplicity is (2+1) = 3

- As for the ppm scale, the exact frequency at which the nucleus resonates depends on the external applied magnetic field. This means that, if the sample is run on a machine with a different magnetic field, it will resonate at a different frequency. It would be very difficult if as it couldn't be said exactly where the signal was, so instead how far it is from some reference sample, as a fraction of the operating frequency of the machine is mentioned. All protons resonate at approximately the same frequency in a given magnetic field and that the exact frequency depends on what sort of chemical environment it is in, which in turn depends on its electrons. This approximate frequency is the operating frequency of the machine and simply depends on the strength of the magnet—the stronger the magnet, the larger the operating frequency. The precise value of the operating frequency is simply the frequency at which a standard reference sample resonates. In everyday use, rather than actually referring to the strength of the magnet in tesla, chemists usually just refer to its operating frequency. A 9.4 T NMR machine is referred to as a 400 MHz spectrometer since that is the frequency in this strength field at which the protons in the reference sample resonate; other nuclei, for example ^{13}C, would resonate at a different frequency, but the strength is arbitrarily quoted in terms of the proton operating frequency. The compound we use as a reference sample is usually tetramethylsilane, TMS. The four carbon atoms attached to silicon are all equivalent and, because silicon is more electropositive than carbon, are fairly electron-rich (or shielded), which means they resonate at a frequency a little less than that of most organic compounds. The chemical shift, δ, in parts per million (ppm) of a given nucleus in our sample is defined in terms of the resonance frequency as:

$$\delta = \frac{\text{frequency (Hz)- frequency TMS (Hz)}}{\text{frequency TMS (MHz)}}$$

- No matter what the operating frequency (i.e. strength of the magnet) of the NMR machine, the signals in a given sample (e.g. ethanol) will always occur at the same chemical shifts. In ethanol the carbon attached to the OH resonates at 3.56 ppm whilst the carbon of the methyl group resonates at 0.98 ppm. By definition TMS itself resonates at 0 ppm. The proton nuclei in most organic compounds resonate at greater chemical shifts, normally between 0 and 10 ppm.

Similarly, the carbon nuclei in most organic compounds resonate at greater chemical shifts, normally between 0 and 200 ppm.

- In the ^{1}H NMR spectrum, it is also possible to obtain the number of protons that a particular signal corresponds to. Thus the signal at 0.98 corresponds to 3 protons for ethanol. This is because the area under each peak is directly proportional to the number of protons. This peak area is called integration value of the peak. Thus ^{1}H NMR spectra can be quantitative in nature but the same cannot be said for ^{13}C spectrum. For reasons beyond the scope of this text, they cannot be integrated to give the number of carbons.
- Similarly, the protons attached to particular type of carbon usually resonate in the same region. Thus, it is very useful to know the different regions on a ^{1}H spectrum.

protons on unsaturated carbons next to oxygen: aldehydes	protons on unsaturated carbons: benzene, aromatic hydrocarbons	protons on unsaturated carbons: alkenes	oxygen saturated CH_3 CH_2 CH next to oxygen	CH_2 CH_3 saturated CH not next to oxygen

10.0 8.5 6.5 4.5 3.0 0.0

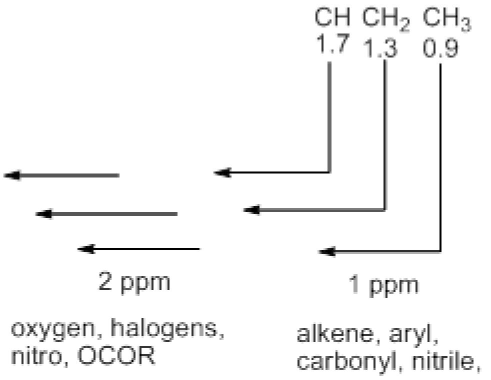
A similar region wise classification may be made for ^{13}C NMR spectrum.

Unsaturated Carbon next to O (C=O)	Unsaturated Carbon atoms (C=C and aromatic carbons)	Saturated atoms next to oxygen	Saturated carbon atoms (CH_3, CH_2 etc)

200 150 100 50 0.0

- If adding electronegative atoms are added to a carbon atom, electron density is progressively removed from it and the carbon nucleus and the hydrogen atoms attached to it are progressively deshielded. In general an oversimplified chart can be constructed regarding the values of chemical shifts in ^1H NMR. However, it should be kept in mind that such a chart is purely a simplication of the situation and therefore exceptions are very common. These chemical shifts are additive. This means that if in a molecule there are two factors that should lead to an increase in the value of chemical shift of the proton concerned, then the additive effect due to these is to be considered.

- Methyl groups are to be started at 0.9, methylenes (CH_2) at 1.3, and methines (CH) at 1.7 p.p.m. Any functional group is worth a one ppm downfield shift except oxygen and halogen for which the value goes two ppm downfield.



In order to determine the structure of an organic compound, it is advised to proceed in the following manner.

1. The history of the compound has to be determined. This includes the source from which the compound is obtained, or in case of a synthetic compound the series of steps which were carried out to obtain the compound.
2. The UV-Visible spectrum may be recorded and λ_{max} and its corresponding ε_{max} is to be determined. It may give information about the degree of conjugation in the molecule and well as information about certain functional groups like carbonyl group.
3. The IR spectrum also provides information about functional groups such as carbonyl group (aldehydes, ketones, carboxylic acid and its derivatives) and amine functionality.

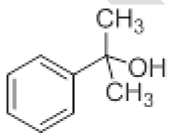
4. NMR spectrum provides the most exhaustive source of information regarding the structure of the molecule

As an example, if a $C_9H_{12}O$ compound has strong infrared absorption at 3300 to 3400 cm^{-1} . The ^{13}C NMR spectrum of this compound has six discrete signals. It's ^1H NMR spectrum has three sets of lines: singlets at δ1.1 (6H), 1.9 (1H) and 7.3 (5H) ppm.

In this case the molecular formula has been deduced by mass spectroscopy. A calculation to determine the degree of unsaturation is usually helpful. It is defined as follows.

$$\text{Degree of Unsaturation} = (\text{Number of carbon atoms}+1) - \frac{(\text{Number of monovalent atoms})-(\text{number of trivelent atoms})}{2}$$

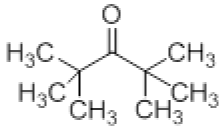
In this case the value comes out to be 4. This is indicative of a benzene ring or 4 double bonds or two triple bonds or a triple bond and a double bond. A strong absorption at 3300-3400 cm^{-1}indicates a O-H group. In the ^1H spectrum, the five 5 peaks at 7.3 ppm are indicative of the presence of monosubstituted benzene ring. Similarly, a singlet at 1.1ppm is indicative of two methyl groups which are not connected to each other. The peak at 1.9 could be due to the O-H proton. Hence the structure that could be deduced is-2-phenylpropan-2-ol.



Now in the ^{13}C NMR spectrum, this compound should show 6 signals which is same as observed. Hence the deduction is correct.

Similarly, if a compound $C_9H_{18}O$ has a strong infrared absorption at 1710 cm^{-1} . Its ^1H NMR spectrum has a single sharp peak (a singlet) at δ 1.2 ppm while ^{13}C NMR spectrum shows three lines at δ210, 45 and 25 ppm. The logic for the elucidation of structure may be as follows:

Degree of unsaturation is 1. This surely means there is only one double bond in the molecule. A strong IR absorption at 1710 cm^{-1} indicates a carbonyl group. A peak in ^1H spectrum at 1.2 ppm indicates the presence of a methyl group, however there must be multiple methyl groups with a symmetrical environment to satisfy the molecular formula. A further clue may be obtained from the ^{13}C spectrum that there are two peaks in the aliphatic region (45 and 25 ppm) but only one peak in ^{1}H spectrum. This means the other carbon (at 45 ppm) is a tertiary carbon. This overall scenario leads to the assumption of the presence of two t-butyl groups. Hence the compound is 2,2,4,4-tetramethylpentan-3-one.



Nuclear Magnetic Resonance Spectroscopy:

NMR is a physical phenomenon in which nuclei of a given substance under magnetic field absorb and re-emit electromagnetic radiation. This energy is at a particular resonance frequency which depends on the strength of the magnetic field and magnetic properties of the isotope of the atoms.

As nuclei with an odd mass or odd atomic number have nuclear spin (in a similar fashion to the spin of electrons), the spins of nuclei are sufficiently different that NMR experiments can be sensitive for only one particular isotope of one particular element.

The rules for determining the net spin of a nucleus are as follows:

1. If both the number of neutrons and the number of protons are even, then the nucleus has NO spin.

2. If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)

3. If the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

Note that the overall spin is important. Quantum mechanics shares that a nucleus of spin '/' has 2/+1 possible orientations, i.e., a nucleus with spin 1/2 will have 2 possible orientations. These orientations are of equal energy in the absence of external magnetic field, but the energy levels split once magnetic field is applied.

Nuclear Magnetic Resonance Spectroscopy:

The energy separation between the different nuclear spin states lies in the microwave spectral region and hence NMR transitions are excited by frequencies about 10^8 Hz and can be varied by applying a magnetic field.

The nucleus has a positive change and is spinning, resulting in a small magnetic field. As a result, the nucleus possesses a magnetic moment, which is proportional to its spin, *I*.

$$\mu = \frac{gIh}{2\pi}$$

The constant *g* is gyromagnetic ratio. The energy of a particular energy level is defined as

$$E = \frac{gh}{2\pi} mB$$

where **B** is the strength of the magnetic field at the nucleus.

Therefore, the difference in energy levels can be obtained in the form of

$$\Delta E = \frac{gh}{2\pi} B$$

This equation suggests that if the magnetic field **B** is increased, then the difference in the energy also increases.

Nuclear Magnetic Resonance Spectroscopy:

Since a nucleus is a charged particle in motion, it will develop a magnetic field. For instance, ^{1}H and ^{13}C have nuclear spins of ½. Hence, they would behave in a similar fashion to a simple, tiny bar magnet.

As shown in Figure 35.01, in the absence of magnetic fields, these are oriented randomly. On the other hand, the application of external magnetic field lines up them parallel to the application field, but either spin aligned or spin opposed.

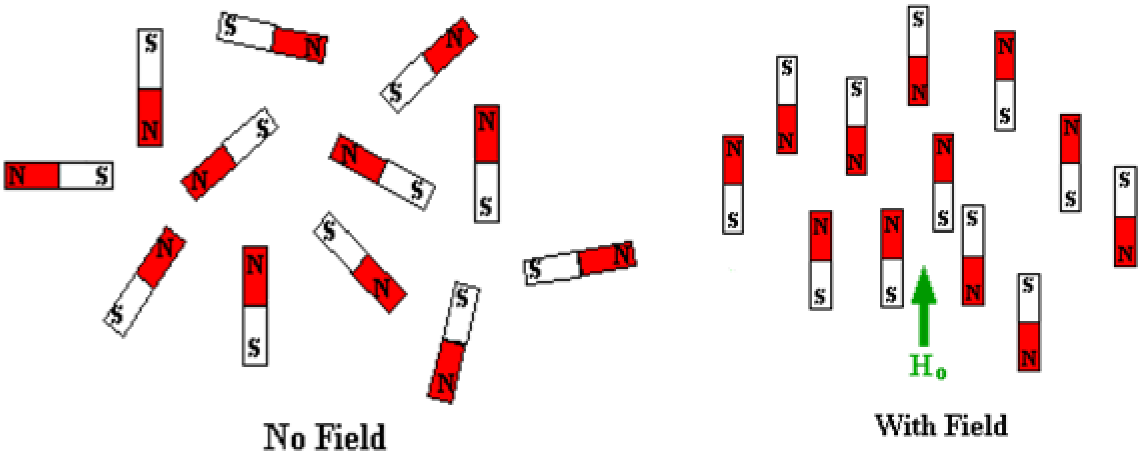


Figure 35.01: Schematic representation of nuclear spins or in the form of tiny magnets under zero and finite magnitude of external applied fields.

As displayed in Figure 35.02, the highly populated state is the lower energy spin aligned situation.

Nuclear Magnetic Resonance Spectroscopy:

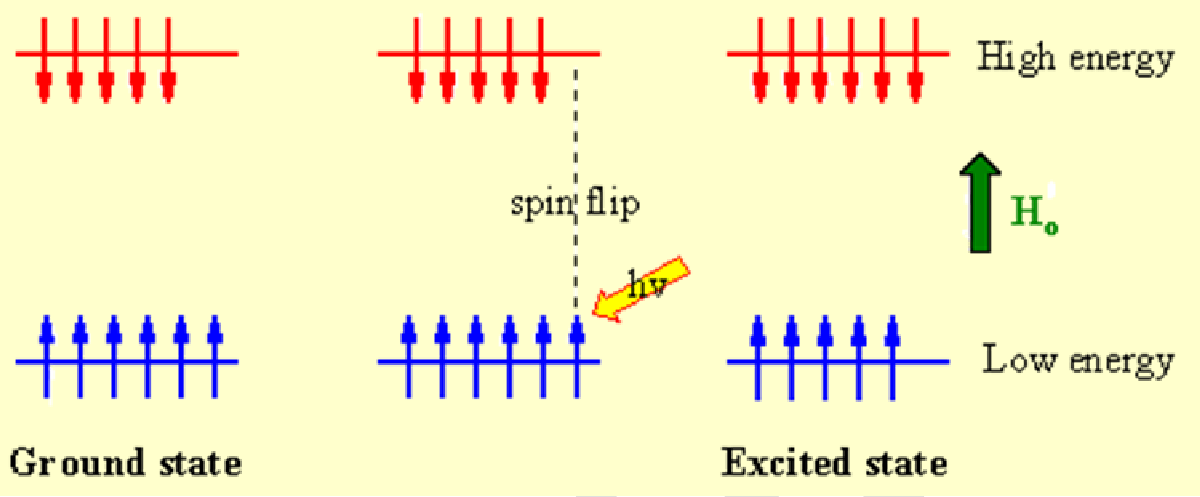


Figure 35.02: Schematic arrangements of spins in ground and excited states.

Upon radiating with microwaves, the alignment of nuclear spins from the low energy aligned state is flipped to the higher energy spin opposed state, resulting in an excited state. As derived earlier, the energy required for making this transition depends on the magnitude of the applied magnetic field, as demonstrated in Figure 35.03.

The two spin states have same energy when the external field is zero, but as the field increases so does the separation of energies of the spin states and therefore so does the frequency required to cause the spin-flip. At a field equal to H_0, the formula for the energy difference is given.

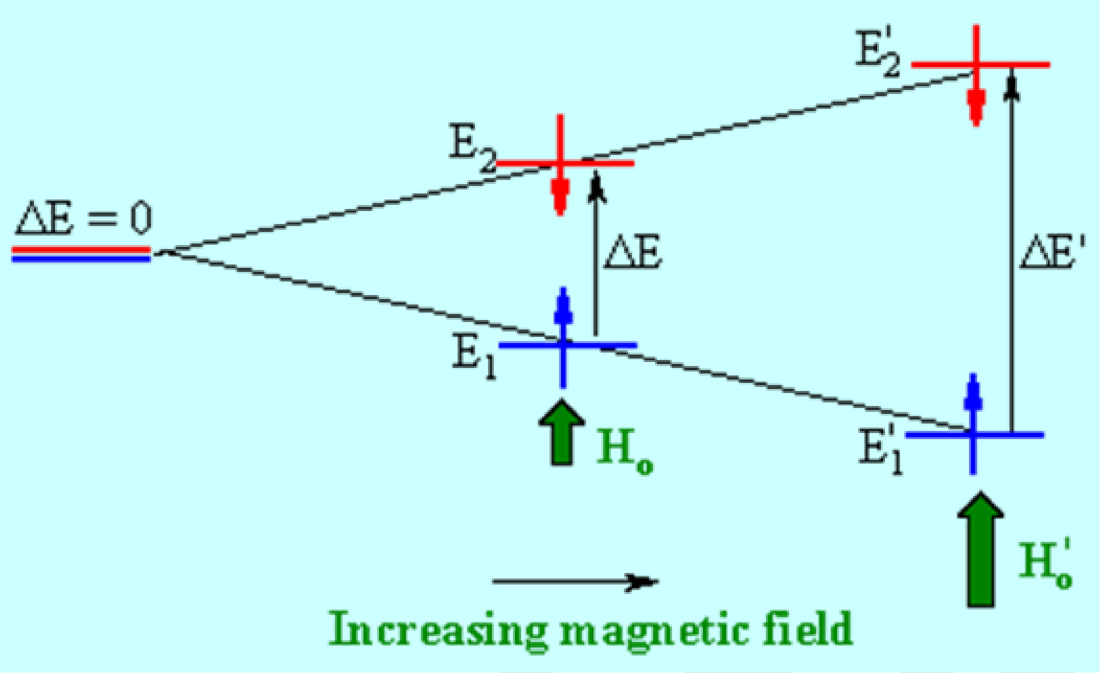


Figure 35.03: Schematic drawing of variation in energy required for flipping the spins with increasing applied magnetic fields.

Typically, one needs strong magnetic field in the range between 1 to 20 Tesla.

The basic arrangement of NMR spectrometer is shown in Figure 35.04. The sample is positioned in the applied magnetic field using electromagnet and microwaves are used in the radio frequency input circuit to excite the sample and to induce transitions between different nuclear spin states. This induces a radio signal in the output circuit, which generates an output signal.

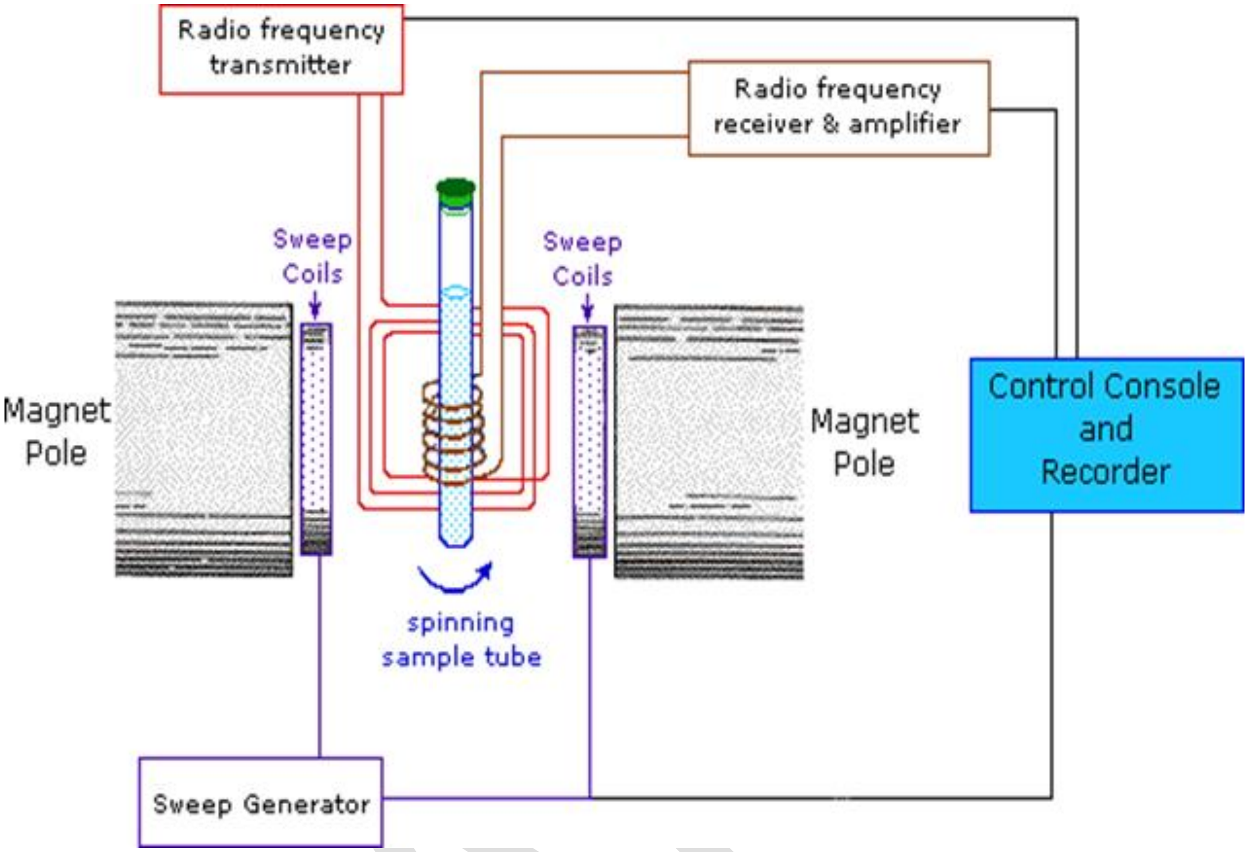


Figure 35.04: Basic arrangement of NMR Spectrometer.

Nuclear Shielding:

The power of NMR is based on the concept of nuclear shielding. The magnetic field at the nucleus is not equal to the applied magnetic field. This is because, every atom is surrounded by electrons, which orbit the nucleus. When charged particles move in a loop, they create a magnetic field. Hence, the field produced by the movement of electron is felt by the nucleus. Therefore, the field experienced by the nucleus is not same as applied field, known as shielding. Therefore, the change in the energy levels requires a different frequency to excite the spin flip. The shielding allows for structural determination of molecules.

Consider the s-electrons in a molecule as displayed in Figure 35.05. They have spherical symmetry and circulate in the applied field, producing a magnetic field which opposes the applied field. This means that the applied field strength must be increased in order for the nucleus to absorb at its transition frequency. This up-field shift is also termed diamagnetic shift.

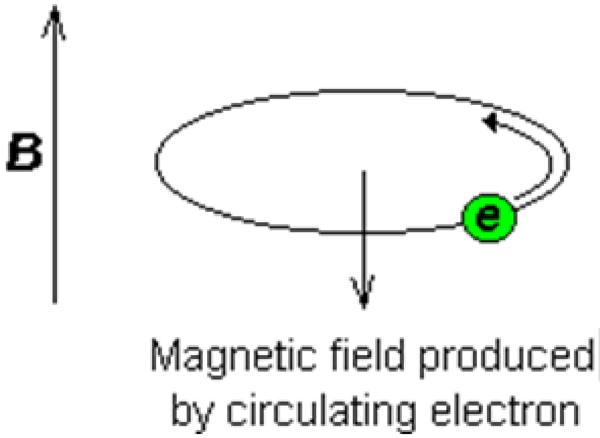


Figure 35.05: Schematic of nuclear shielding.

Similarly, electrons in p-orbitals having no spherical symmetry produce comparatively large magnetic fields at the nucleus giving a low-field shift and termed as a paramagnetic shift.

Chemical Shift:

1) NMR spectrum is a plot of the ratio of the frequency applied against absorption.

2) A signal in the spectrum is referred to as a resonance.

3) The frequency of a signal is known as its chemical shift.

The chemical shift is defined as

$$\text{chemical shift},\ \delta = \frac{\nu_{signal} - \nu_{reference}}{\text{spectrometer frequency}} \times 10^6$$

The shielding of the nucleus allows for chemically inequivalent environments to be determined by Fourier Transforming the NMR signal, which results in a spectrum.

- In general, the spectrum consists of a set of peaks in which each peak corresponds to a distinct chemical environment.

- The area underneath the peak is directly proportional to the number of nuclei in that chemical environment.

- The x-axis of an NMR spectrum is given in parts per million (ppm).

NMR Spectrum:

The 60 MHz proton NMR spectrum of pure methanol as shown in Figure 35.06 exhibits two signals located at 3.35 and 4.80 ppm. The higher-field methyl signal (magenta) being three times as strong as OH signal (orange) at a lower field.

Cooling the methanol to -45°C, the larger higher-field signal changes to a doublet (J = 5.2 Hz) having the same chemical shift. The smaller signal moves downfield to δ5.5 ppm and splits into a quartet (J = 5.2 Hz). However, the relative intensities of signals remain unchanged.

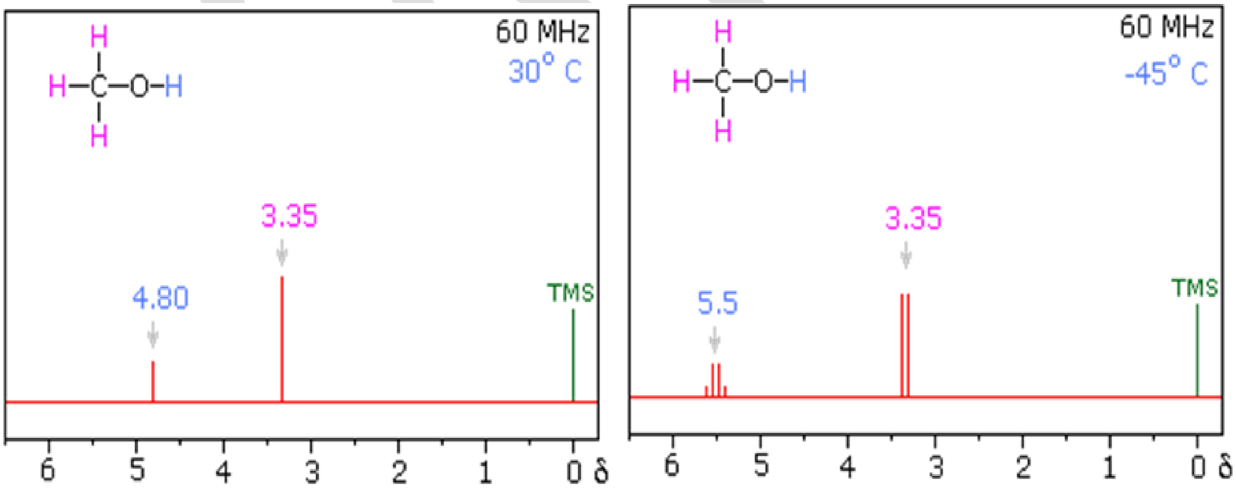


Figure 35.06:: NMR Spectra of pure methonal at 30°C (left) and -45°C [1].

Ref.[1]. https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/spectrpy/nmr/nmr2.htm.

Chemical Shift:

It is convenient to describe the relative positions of the resonances in an NMR spectrum. For instance, as shown in Figure 35.07, a peak at a chemical shift, δ, of 10 ppm is said to be downfieldor deshielded with respect to a peak at 5 ppm. Otherwise, the peak at 5 ppm is upfield or shielded with respect to the peak at 10 ppm.

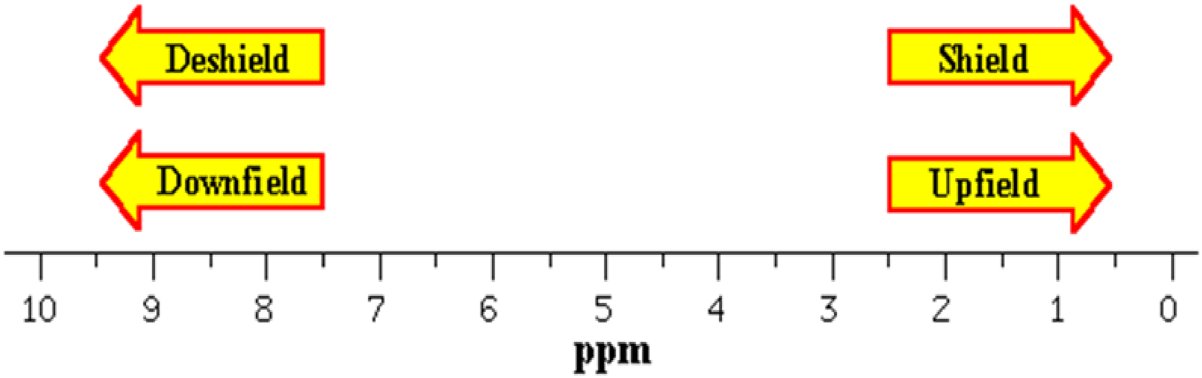


Figure 35.07: Schematic representation of de-shielded and shielded in NMR spectrum.

Taking the example shown in Figure 35.06, we can conclude that the peak at 4.8 is downfield or deshielded with respect to peak at 3.35 or the peak at 3.35 is upfield or shielded to peak at 4.8 ppm.

NMR Spectrum:

Figure 35.08 displays another NMR spectrum of CH_3Br. Since CH_3Br contains only a single type of hydrogen atom, only a single peak at 2.7 ppm was observed.

The position is slightly de-shielded due to the presence of the Br.

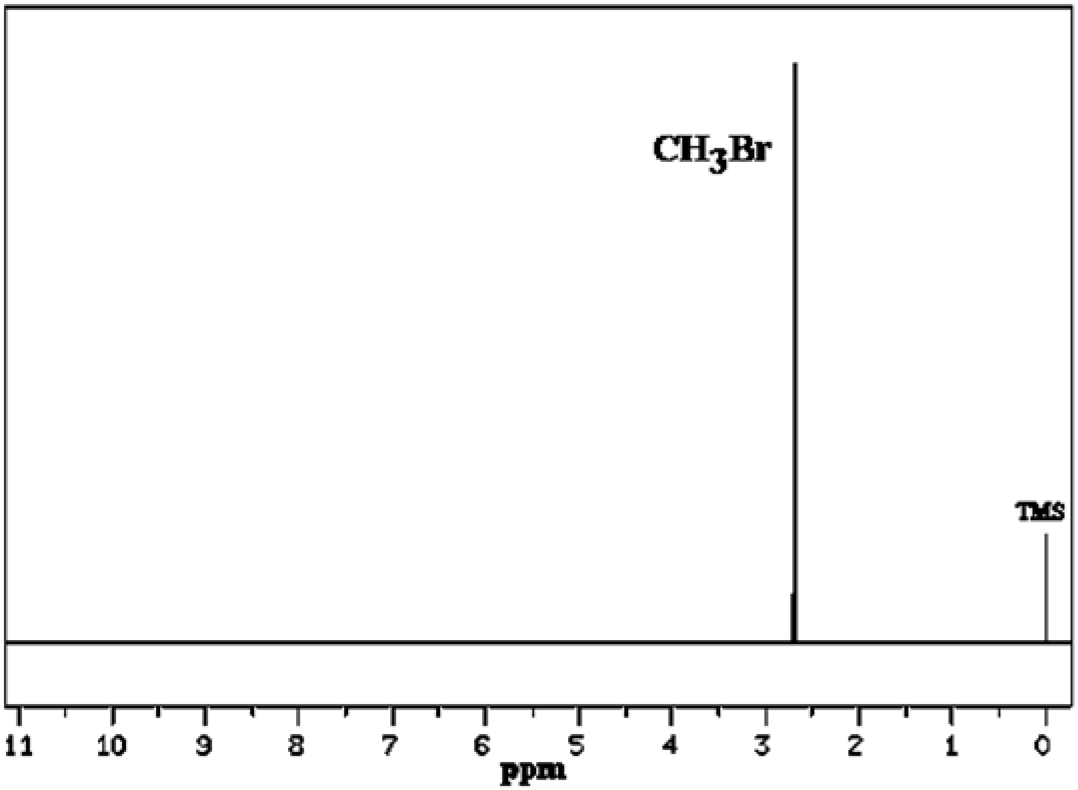


Figure 35.08: NMR Spectrum of methyl bromide.

Chemical Shift Equivalent And Magnetic Equivalent

In NMR, chemical and magentic equivalence plays important role in determining the number of peaks.

To learn more about number of peaks in NMR,see how to determine the number of NMR peaks

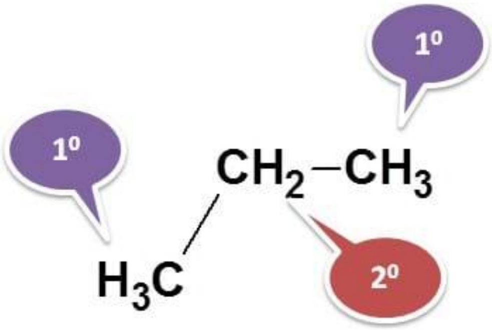
All nuclei which are magnetically equivalent will give single NMR signal. Similarly nuclei which are magnetically non-equivalent will produce different NMR signals.

Chemical equivalence

Let's start with chemical equivalence.

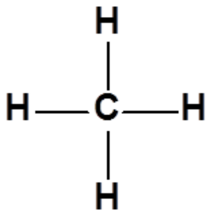
Chemical equivalnce means similar chemical environment. When nuclei are attached by similar linkage they are called as chemically equivalent.

Chemical equivalence=Identical linkage



Nuclei with different LINKAGE

Let’s take an example of methane.



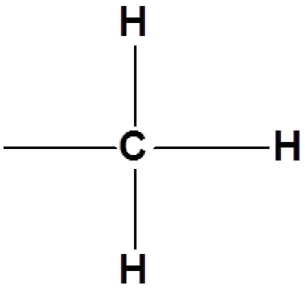
Methane

In methane, protons has spin quantum number I=1/2 and herefore can give NMR signal. Here all the protons are attached to carbon in similar way and hence chemically equivalent.

Remember

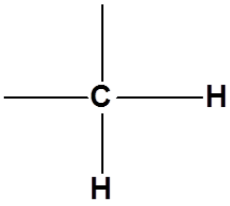
All the protons attached to carbon are always chemically equivalent.

In methyl group all protons are equivalent as they attached similary to the carbon.



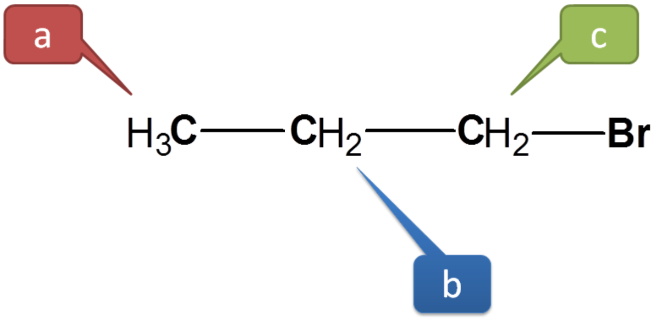
All protons are equivalent

Similarly in methylene group the two protons are equivalent.



All protons are equivalent

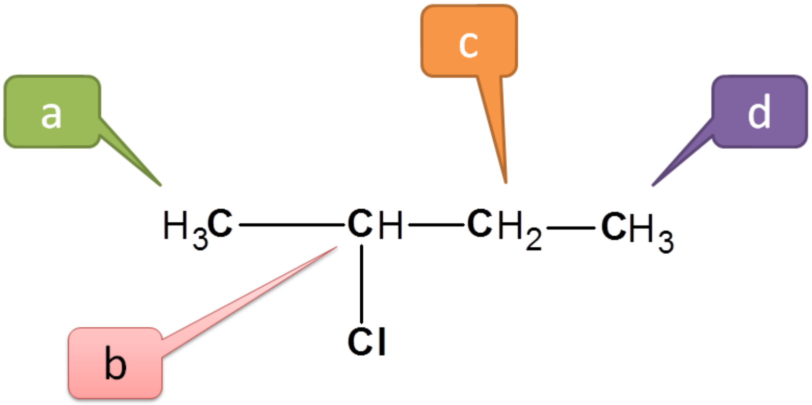
Now let’s take another example. Consider 1-bromopropane.



1-Bromo propane

Here CH3 protons are not equivalent with other protons hence indicated by ‘a’. Now we can see two types of –CH2 protons. Protons indicated by green color are not attached in similar way as the protons indicated by blue color. The protons indicated by green color are attached as –CH2Br whereas those with blue color as –CH2-. Hence all these protons are equivalent.

Now consider 2-chlorobutane.



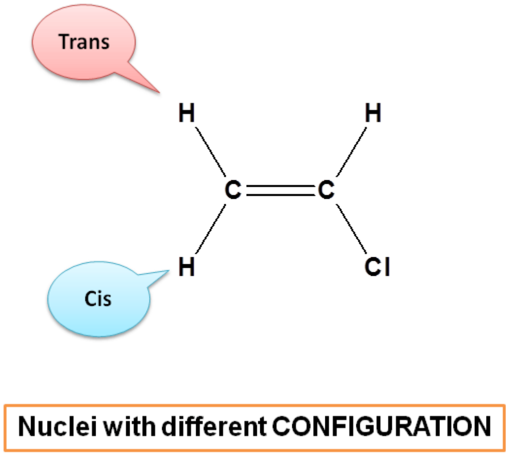
2-Chloro butane

Here CH3 indicated by blue and green color are not equivalent. Protons indicated by green are attached to –CHCl- where as protons indicated by blue are attached to –CH2-. Similarly protons –CHCl- and –CH2- are also non-equivalent. Hence all the protons above are non-equivalent.

Magentic equivalence

magnetical equivalence=Identical CONFIGURATION

When nuclei are arranged in similar way in the space they are called as magnetically equivalent.

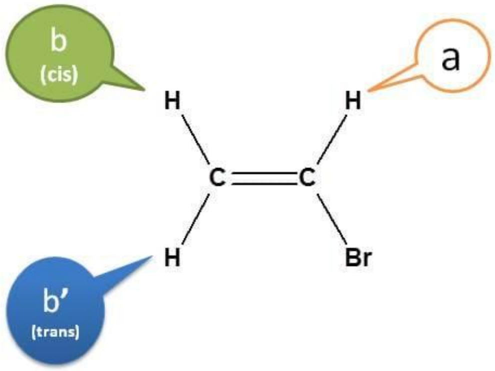


Nuclei with different CONFIGURATION

Here protons present in cis and trans position have siilar linkage but different configuration. cis-proton on the same side whereas trans-proton on opposite side of the double bond. Hence these protons are chemcially equivanet, but magntically not equivalent.

Compounds will have different configuration when they exhibit restricted rotation. Alkenes and cyclic compounds show restricted rotation hence may show magnetic non-equivalence.

Let's consider vinyl bromide.

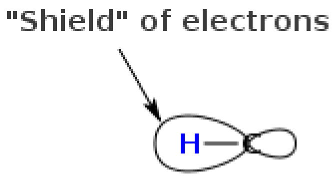


In vinyl bromide, the protons of –CH2– are not magnetically equivalent. The proton indicated by green is cis and blue is trans to other proton on -CHBr.

Chemical Shift

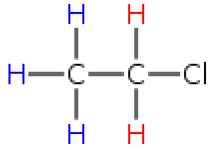
Shielding

If you were to take just a bare proton by itself (no electrons around it) and placed it in a magnetic field (B_o), the proton would experience or "feel" the entire field strength B_o. However most nuclei (H's and C's) are embedded in orbitals with electrons around them. Nuclei with more electrons around them feel less of the field B_o. A simplified picture that is useful for remembering this effect is "shielding". The electron density behaves like a shield, shielding the nuclei from the magnetic field. More electron density means more shielded and less electron density means deshielded. While this is a nice analogy that works well, the "real" physics is a bit more advanced.



Luckily for organic chemists different types of protons have different electron density, and we can tell them apart when we take an HNMR.

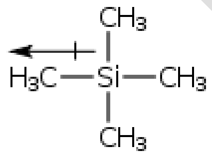
For example in chloroethane, there are 2 nonequivalent types of protons, colored blue and red.



Which protons would you think have greater electron density around them, red or blue? If you recall, chlorine withdraws electron density by induction and induction depends upon distance. The red protons feel the effect of the withdrawing group since they are closer and therefore have lower electron density. We would say the red protons are deshielded. The blue protons are further away and therefore have more electron density around them and are more shielded.

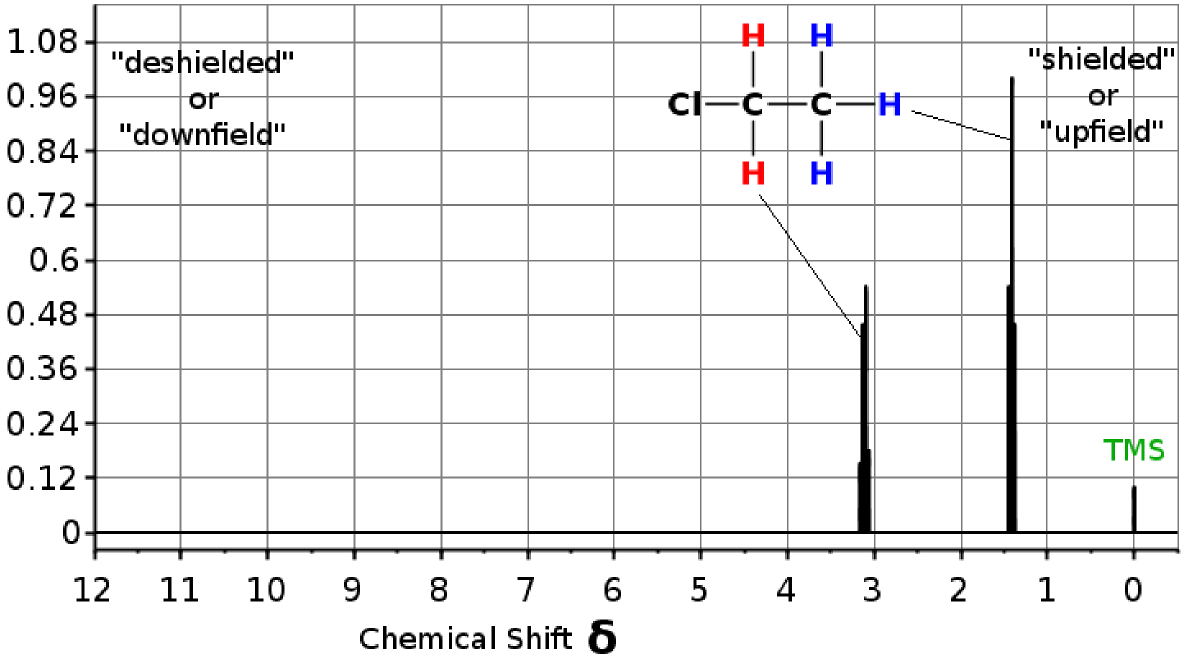
Chemical Shift is a measure of shielding!

Shielding is expressed in terms of a quantity called chemical shift (δ) and has units of parts per million (ppm) of the field strength. Chemical shift value are relative to an internal standard which is normally **t**etra**m**ethyl**s**ilane (TMS). The protons on TMS are more shielded than most other protons encountered in organic chemistry. Silicone is less electronegative than carbon, and also has electrons in diffuse d orbitals. TMS is given a chemical shift of 0 ppm and all other protons are relative to this. A useful mnemonic is TMS stands for "**T**he **M**ost **S**hielded". The most shielded end of the spectra is on the right where TMS is at 0 ppm, while the deshielded end is to the left on an NMR spectra.

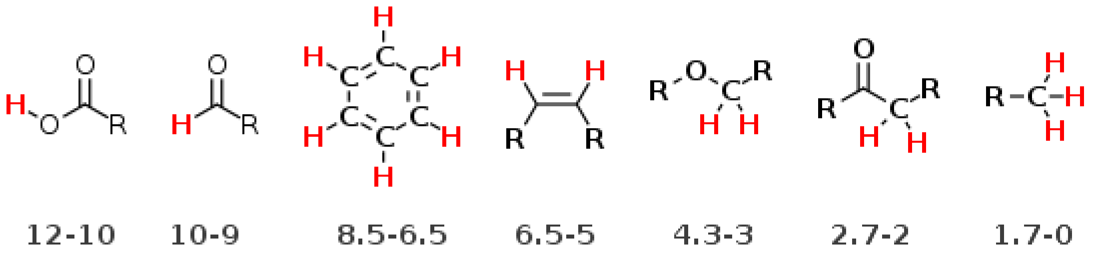


tetramethylsilane (TMS)
0 ppm

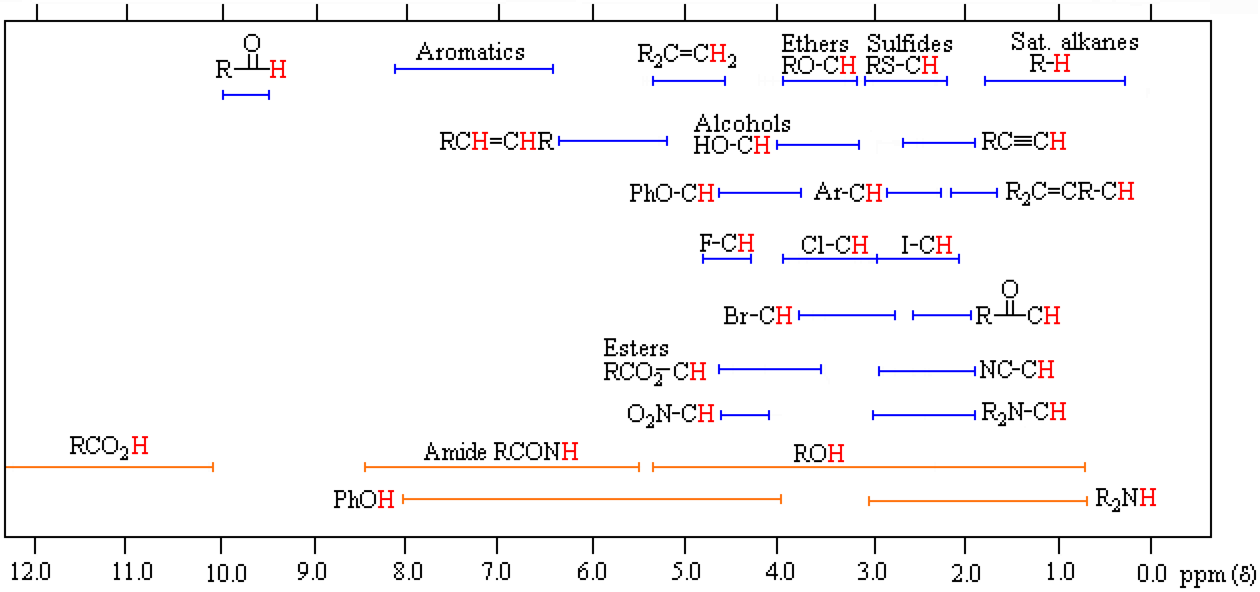
Proton chemical shifts of protons can vary from about -1 (highly shielded) to 13 (highly deshielded).



The chemical shifts for many types of protons have been tabulated. There are few very common proton chemcial shifts you should commit to memory and they are listed below.



The following more inclusive table or a the table from you textbook book should also prove useful.



Factors Affecting Chemical Shift

There are a number of factors which influence chemical shift.

- Inductive effects from adjacent EWG
- Magnetic anisotropy in structures with π systems
- Hydrogen bonding

Inductive effects from adjacent EWG.

The chemical shift of a proton is influenced by the electronegativity of the atoms attached to the carbons its attached to. The protons of fluormethane have a chemical shift of 4.3 ppm, due to the decreased electron density around its protons from the higly electronegative fluorine.

CH_3F	CH_3Cl	CH_3Br	CH_3I
4.3 ppm	3.1	2.7	2.2

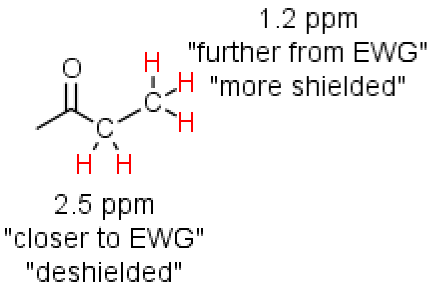
This effect is additive...the more electronegative groups, the more deshielding and the increase in chemical shift.

$CHCl_3$	CH_2Cl_2	CH_3Cl
7.3 ppm	5.3	3.1

A similar trend is observed going across the periodic table.

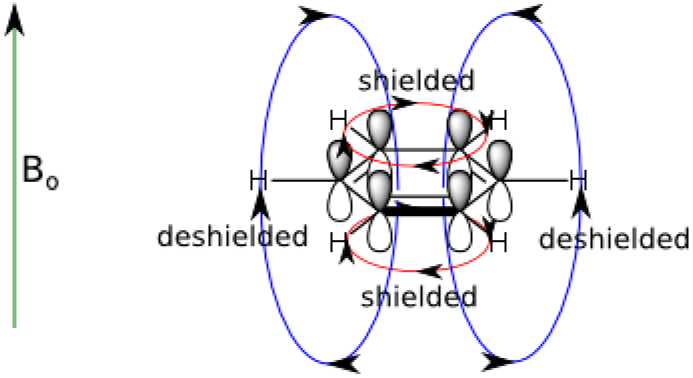
CH_3F	CH_3OCH_3	$(CH_3)_3N$	CH_3CH_3
4.3 ppm	3.2	2.2	0.9

This effect depends on the distance from the EWG. For example the protons adjacent to the carbonyl group are deshielded more so than the protons two carbons from it.



Magnetic Anisotropy

Electrons in molecules with π systems (e.g. aromatics, alkenes, alkynes and aldehydes) can circulate creating a ring current(red lines below) when place in the applied magnet field B_o. The ring current then induces or creates an induced magnetic field (blue lines). As a result, the protons around the outside of the ring are deshielded since the field lines oppose the Bo field in that region. Thus aromatic protons have a chemical shift of about 6.5-8.5 ppm. A similar effect explains the highly deshileded protons observed in aldehydes (9-10 ppm), carboxylic acid (-OH 10-12ppm) and alkenes (5-6.5 ppm)

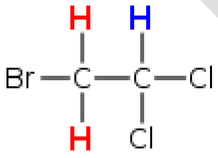


Hydrogen Bonding

Hydrogen bonding causes deshielding of protons. Since hydrogen bonding effects are concentration and temperature dependent you can usually recognize which protons are involved in hydrogen bonding by changing concentration or temperature. With the exception of carboxylic acid OH groups, protons attached to oxygen and nitrogen generally resonate between 0.5 - 5 ppm.

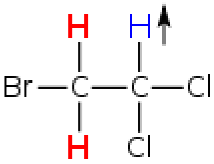
Spin-Spin Splitting

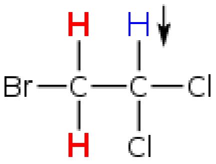
Consider 1-bromor-2,2-dichloroethane shown below. There are two distinct nonequivalent types of protons (blue and red), therefore there should be two signals in the HNMR. The blue protons are more deshielded since it's attached to a carbon with two highly electronegative Cl atoms and is at about 6 ppm on the spectra below. The ratio of the red to the blue protons is 2:1.



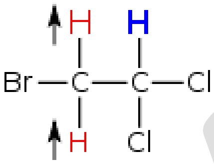
Imagine you shrink down to the size of the red protons. Lets think about the magnetic field you will experience or feel. Well, you will feel the B_o field, but it will be split into two fields created by the neighboring blue proton. In a given molecule the blue proton can only have one of two possible spin states, up or down. Don't forget we many molecules of 1-bromo-2,2-

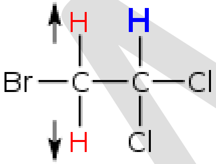
dichloroethane in the NMR tube. So if we had 100 molecules in our NMR tube half would be up and half would be down. Thus the red signal is slit into a doublet. This is known as the N+1 rule where N is the number of neighboring protons. The red protons have one blue neighboring proton therefore N=1 and N+1=2 a doublet.

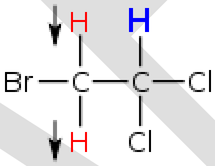


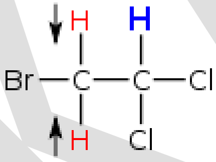


No image your the blue proton which experiences the two red protons. Below are the three possible spin states; 1) both soins up, 2) one up and one down (these two have the same resonance energy) and 3) both spins down. If you had 100 molecules you'd have a 25:50:25 ratio of molecues in teh trhee states and the NMR signal would appear as a triplet with a 1:2:1 relative intensity (see spectra above). In this case N=2 and N+1=3, a triplet is observed.









Applications of NMR Spectroscopy

NMR Spectroscopy is a technique used by most modern chemical laboratories. It has applications in a wide range of disciplines, and development of new applied methods for NMR is an active area of research. Methods in NMR spectroscopy have particular relevance to the following disciplines:

- Chemical research and development: organic, inorganic and physical chemistry
- Chemical manufacturing industry
- Biological and biochemical research
- Food industry

- Pharmaceutical development and production
- Agrochemical development and production
- Polymer industry

Common applications of NMR Spectroscopy include:

- Structure elucidation
- Chemical composition determination
- Formulations investigation
- Raw materials fingerprinting
- Mixture analysis
- Sample purity determination
- Quality assurance and control
- Quantitative analysis
- Compound identification and confirmation
- Analysis of inter- and intramolecular exchange processes
- Molecular characterisation
- Reaction kinetics examination
- Reaction mechanism investigation

REFERENCES

Jag Mohan, 2001. Organic Spectroscopy Principles and Applications. Narose Publishing House, New Delhi.

Kemp W., 2004. Organic Spectroscopy. III Edition, Pal Grave, New York.

POSSIBLE QUESTIONS

MULTIPLE CHOICE QUESTIONS

(EACH QUESTION CARRY ONE MARK)

1. What is precessional motion

a) **top moves around the vertical** b)moves away the horizontal

c) top moves away from the vertical d)moves around the horizontal

2. The gyromagnetic ratio is

a) **2 pi M/Hi** b) 2C pi M/hI c) hI/2 pi M d) hI/ 2C pi M.

3. What is flipping?

a) Energy **transfer within the molecule** b) Energy transfer outside the molecule c) Energy transfer from one energy d) No energy has been transfer

4. Acetone gives

a) **One signal NMR** b) Two signal NMR c) Three signal NMR d) Four signal NMR

5. Propanal gives

a) 1 NMR signal b) **2 NMR signal** c) 3 NMR signal d) 4 NMR signal

6. The DMSO is a

a) **Highly polar solvent** b) Highly non polar solvent c) Weakly polar solvent d) Weakly non polar solvent

7. NMR spectrum obtained in

a) Microwave region b) **Radiofrequency region**

c) IR region d) Far IR region

8. For NMR, (a) downfield due to deshielding (b) up field due to shielding

a) **both are true** b) a true b false

c) b true a false d)both are false

9. What is anisotropic effect

a. **δ for protons attached to C=C in alkenes** b. δ for protons attached to C=C in alkynes c. δ for protons attached to cyclo hexanes

d. δ for protons attached to para hexanes

10. The resultant spin of ^{1}H NMR is

a) 0-100 nm b) 1 c) ½ d) 3/2

11. The nucleus which gives NMR spectrum is

a) $^{16}_{8}O$ b) $\mathbf{^{10}_{5}B}$ c) ^{12}O d) $^{4}_{2}He$

12. The ^{1}H spectrum CH_2 (Cl)CH(Cl)OCH_3 would show

a) **a 3 proton singlet, I proton triplet and 2 proton doublet**

b) a 3 proton doublet 1 proton triplet and 2 proton singlet

c) a 3 proton triplet 1 proton doublet 2 proton doublet

d) a 3 proton singlet 1 proton singlet 2 proton doublet

13. The chemical shift of a proton on the δ scale is 4. The value of the τ scale is---

a) 14 b) **6** c) 2.5 d) 4

14. The fine structure and intensity ratios expected in the proton NMR spectrum of NH_4^+ ion (for ^{14}N, I=1) are

a) Singlet b) Doublet 1:1 c) **Triplet 1:1:1** d) triplet1:2:1

15. In the proton NMR spectrum of toluene, the resonance due to CH_3, group is expected to

a) δ 0.5 b) δ 1.25 c) **δ2.5** d) δ 3.5

16. How many NMR signals are found in cis dimethyl cyclopropane and trans dimethyl cyclopropane?

a) 2, 3 b) **3, 4** c) 1,2 d) 8,10

17. The nucleus which gives NMR spectrum is

a) $^{16}_{8}O$ b) $\mathbf{^{10}_{5}B}$ c) ^{12}O d) $^{4}_{2}He$

18. The $^{1}_{1}H$ spectrum CH_2 (Cl)CH(Cl)OCH_3 would show

a) **a 3 proton singlet,I proton triplet and 2 proton doublet**

b) a 3 proton doublet 1 proton triplet and 2 proton singlet

c) a 3 proton triplet 1 proton doublet 2 proton doublet

d) a 3 proton singlet 1 proton singlet 2 proton doublet

19. The chemical shift of $^{1}_{1}H$ on theδ scale is 2.56. The value on ϒ scale is

a) 12.56 b) **7.44** c) 2.56 d) 1.44

20. The bond length on NO is 0.116 nm. Its rotational constant is

a) $5.0^{30} \times 10^{10}$ sec b) 1.23×10^{10} sec

c) **5.030×10^{10} sec^{-1}** d) 1.23×10^{10} sec-1

Part-B

Each Question Carry Eight Marks

1. Describe with examples the various factors which affect the magnitude of the chemical shift in NMR spectra?.

2. What is double resonance and spin tickling? How these are helpful in simplifying the spectra?

3. Describe ^{13}C NMR spectroscopy. What are the advantages of it over proton magnetic resonance spectroscopy?

4. Explain (i). Qualitative analysis

(ii).Quantitative analysis using NMR spectra?

(iii). Explain heteronuclear coupling with examples?

5. (i). Explain first order and non-first order NMR spectra with example?

(ii).What are the factors that influencing germinal coupling (b) vicinal coupling (c) Long range coupling?

6. (i). What are lanthanide shift reagents and chemical shift reagents?

(ii). Explain spin-spin coupling and spin-spin splitting are resonance phenomenon?

7. Describe ^{13}C NMR spectroscopy. What are the advantages of it over proton magnetic resonance spectroscopy?

8. (i).Explain the qualitative analysis using NMR spectra?

(ii). Explain heteronuclear coupling with examples?

Part-C(COMPULSORY QUESTION)

TEN MARK QUESTIONS

1. (i). Explain first order and non-first order NMR spectra with example?

   (ii).What are the factors that influencing germinal coupling (b) vicinal coupling (c) Long range coupling?

2. (i). What are lanthanide shift reagents and chemical shift reagents?

   (ii). Explain spin-spin coupling and spin-spin splitting are resonance phenomenon?

3. Explain the application of NMR spectroscopy

[19CHP104]

KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-21

DEPARTMENT OF CHEMISTRY

M.SC CHEMISTRY 2019-2021 BATCH

I SEMESTER

ORGANIC AND INORGANIC SPECTROSCOPY

Unit-3 Nuclear Magnetic Resonance Spectroscopy (19CHP10 OBJECTIVE TYPE QUESTIONS EACH QUESTIONS CARRY ONE MARK

S.No	Questions	option a	Option b	Option c	Option d	Answer
1	What is precessional motion	a.top moves around the vertical	b.top moves away the vertical	c.top moves away from the vertical	d.none of the above	a.top moves around the vertical
2	The gyromagnetic ratio is	a.2 pi M/Hi	b.2C pi M/hI	c.hI/2 pi M	d.hI/ 2C pi M.	a.2 pi M/Hi
3	What is flipping	a.energy transfer within the molecule	b.energy transfer outside the molecule	c. .energy transfer from one energy	d.none of the above	a.energy transfer within the molecule
4	Acetone gives	a.one signal NMR	b. two signal NMR	c. three signal NMR	d. four signal	a.one signal NMR
5	Methyl cyclo propane gives	a.one signal NMR	b. two signal NMR	c. three signal NMR	d. four signal	c. three signal NMR
6	For non viscous system NMR gives	a.splitting signal	b.sharp signal	c.broad signal	d.none of the above	b.sharp signal
7	The relationship between delta value in ppm and frequency in hertz is fundamental	a.$\delta x = v_x - v_{TMS/V0}$	b. $\delta x = v_{TMS} - v_{x/V0}$	c.$v_0 / v_x - v_{TMS}$	d. $v_0 / v_{TMS} - v_x$	a.$\delta x = v_x - v_{TMS/V0}$
8	What is the rule of spectral multiplicity	a.I(n+1)	b.n(I+1)	C.n+1	d.n-1	C.n+1
9	Which compound gives AMX spectrum	a.poly styrene compound	b.poly ehylene compound	c.vinyl compound	d. polyvinyl compound	c.vinyl compound
10	What is karplus equation	a. Ǿ between 0° and 90° Jvic = 8.5COS^2 Ǿ-0.28	b. Ǿ between 0° and 90° Jvic = 9.5COS^2 Ǿ-0.28	c. Ǿ between 0° and 180° Jvic = 8.5COS^2 Ǿ-0.28	d. None of the above	a. Ǿ between 0° and 90° Jvic = 8.5COS^2 Ǿ-0.28
11	What is double resonance	a.At a time use of two radio frequency	b.alternate use of two radio frequency	c.simultaneous use of two radio	d.combined use of two radio	a.At a time use of two radio frequency
12	What is NOE signal	a.nucleous oriented energy level	b.nucleous over effect	c.nuclear over hauser effect	d.nucleous opposite energy	c.nuclear over hauser effect

13	How many double bond present in norborene	a.single	b.double	c.triple	d.multiplet	b.double
14	How many nitrogen present in imidazole	a.1	b. 2	c.3	d.5	b. 2
15	What is SPI	a.spin permittive intense peak	b.selective population inversion	c.selective possible interaction	d.spin pulse energy intensive	b.selective population inversion
16	(i)Magnetically equivalent protons are chemically equivalent (ii)each signal corresponds to a set of equivalent protons	a.(i) and (ii) are true	b.(i) true	c.(ii) true	d.(i) and (ii) false	a.(i) and (ii) are true
17	Propanal gives	a.1 NMR signal	b.2 NMR signal	c.3 NMR signal	d.4 NMR signal	b.2 NMR signal
18	The DMSO is a	a.highly polar solvent	b.highly non polar solvent	c.weakly polar solvent	d.weakly non polar solvent	a.highly polar solvent
19	NMR spectrum obtained in	a.microwave region	b.radiofrequency	c.IR region	d.none of the	b.radiofrequency
20	For NMR, (a) downfield due to deshielding (b)upfield due to shielding	a.both are true	b. a true b false	c.b true a false	d.both are false	a.both are true
21	What is Geminal coupling a.protons attached as the same carbon having different chemical environment b. protons attached as the same carbon having same chemical environment	a. a and b are true	b. a and d are flase	c. b and a flase	d. both are flase	a. a and b are true
22	I=0	a. NMR signals observed	b. NMR signals not observed	c. half NMR signals	d. none of the above	b. NMR signals not observed
23	How many gem methyl group present in ∝-pinene	a) one	b) two	c) three	d) zero	b) two
24	For NMR the aromatic character relates to cyclic delocalization of	a. (4n+2) π electrons	b. (2n+4) π electrons	c. (4n+π) 2 electrons	d. (2n+π) 4 electrons	a. (4n+2) π electrons
25	What is magnetic equivalence	a)chemical shift equivalence	b)coupling equivalence	c)chemical equivalence	d)magnetic equivalence	c)chemical equivalence

26	What is accidental equivalence	a.chemical shift of 2 proton are equal	b)environment of 2 protons are equal	c)coupling constants are equal	d)magnetic field of 2 protons are	a.chemical shift of 2 proton are equal
27	For NMR the number of orientatins is	a) (2m+I)	b) (2I+1)	c) (2n+1)	d) (2n+1)	b) (2I+1)
28	Oppose orientation most stable and alligned orientation least stable a)most stable b)least stale	a) both are true	b) a true b flase	c) both are flase	d) a flase b true	a) both are true
29	How many methyl group present I methanol	a) 2	b) 3	c) 4	d) 0	b) 3
30	Which is used as a lanthanide shift reagent	a) Europium	b) Tms	c) 6-methyl quinoline	d) combination of europium and	c) 6-methyl quinoline
31	What is the natural abundance of ^{13C} NMR	a) 1%	b) 0.1%	c) 1.1%	d) 11%	c) 1.1%
32	What is the chemical shift range of ^{1}H spectrum	a) 4ppm	b) 40 ppm	c) 80 ppm	d) none	c) 80 ppm
33	What is the chemical shift range of	a) 4ppm	b) 40 ppm	c) 80 ppm	d) 120 ppm	a) 4ppm
34	What is "CI DNP"	a. Chemically induced dynamic nuclear	b. Chemically induced dinuclear polarisation	c. Chemically induced dynamic number polarisation	d. magentically indued	a. Chemically induced dynamic nuclear
35	What is MRI	a)magnetic radio frequency imagine	b)magnetic resolution imagine	c)magnetic resonance imagine	d)none	c)magnetic resonance imagine
36	What is "COSY"	a)2D NMR-Shift correlation spectra	b)2D NMR-Shift corrected spectra	c)NMR shift corrected spectra	d)NMR shift correction spectra	a)2D NMR-Shift correlation spectra
37	The energy of free spin is related to give their envirnment is called as	a. spin-spin relaxation	b. spin-spin coupling	c. spin-lattice relaxation	d. spin-lattice coupling	c. spin-lattice relaxation
38	How many number of hydrogen present in annulene	a) 12H	b) 14H	c) 16 H	d) 18 H	d) 18 H
39	What is shielding	a. spin oppose to magnetic field	b. spin allign to magnetic field	c. spin lateral to magnetic field	d. spin oppose lateral to magnetic	b. spin allign to magnetic field

40	What is anisotropic effect	a. δ for protons attached to C=C in alkenes	b. δ for protons attached to C=C in alkynes	c. δ for protons attached to cyclo hexanes	d. δ for protons attached to para hexanes	a. δ for protons attached to C=C in alkenes
41	The resultant spin of$^{1}_{1}$H is	a. 0-100 nm	b. 1	c. 1/2	d.3/2	c. 1/2
42	The nucleus which gives NMR spectrum is	a. $^{16}_{8}$O	b. $^{10}_{5}$B	c.^{12}O	d. $^{4}_{2}$He	b. $^{10}_{5}$B
43	The $^{1}_{1}$H spectrum CH_2 (Cl)CH(Cl)OCH_3 would show	a. a 3 proton singlet,I proton triplet and 2 proton	b. a 3 proton doublet 1 proton triplet and 2 proton singlet	c. a 3 proton triplet 1 proton doublet 2 proton doublet	d. a3 proton singlet 1 proton singlet 2 proton	a. a 3 proton singlet,I proton triplet and 2 proton doublet
44	The chemical shift of $^{1}_{1}$H on theδ scale is 2.56. The value on ϒ scale is	a. 12.56	b. 7.44	c.2.56	d. 1.44	b. 7.44
45	The bond length on NO is 0.116 nm. Its rotational constant is	a. 5.0^{30} x 10^{10} sec	b. 1.23x 10^{10} sec	c. 5.030x10^{10} sec^{-1}	d. 1.23x 10^{10} sec-1	c. 5.030x10^{10} sec^{-1}
46	Among the following which does not give NMR spectra	a. $^{16}_{8}$O	b. $^{10}_{5}$B	c. $^{15}_{7}$N	d.$^{1}_{1}$H	a. $^{16}_{8}$O
47	The NMR spectroscopy is based on the magnetic momentby the spinning of a	a. Atom	b. Charged nucleus	c. Electron	d. neutrons	b. Charged nucleus
48	In the PMR spectrum FCH$_2$ CHF$_2$ would give	a. 4 signals	b. 3 signals	c. 2 signals	d.1 signals	c. 2 signals
49	In a NMR spectrum number of protons of each kind in a molecule is indicated by the	a. number of signals	b. Intensity of signals	c.Splitting of a signals	d. Charged nucleus	b. Intensity of signals
50	In a low resolution NMR spectrum of ethanol, the area under the peak corresponding to OH, CH$_2$ and CH$_3$ protons respectively will be in the ratio	a. 3:2:1	b. 1:3:2	c.3:1:2	d.1:2:3	a. 3:2:1

51	What is the spin number of thefollowing nuclei ^{11}B, ^{35}Cl, ^{79} Br, ^{81} Br?	a. 3/2	b. 1/2	c. 1	d. 5/2	a. 3/2
52	The spin angular momentum of thenucleus, H is----	a. root of 1/2x h/2π	b.root of 1/2x11/2	c. rootof 1/2x1 1/2xh/2π	d.root of 1/2	c. rootof 1/2x1 1/2xh/2π
53	The Bohr magneton is aunit of--- and it is nearly--- times the nuclear magneton	a. Magnetic field 1850	b. Magnetic moment,1850	c. Magnetic field 1/1850	d. Magnetic moment, 1/1850	b. Magnetic moment,1850
54	The proton magnetic resonance is studied in---	a. Radiofrequency	b. microwave region	c.IR region	d.Visible region	a. Radiofrequency
55	Underhigh resolution, ethanol containing acid inpurity gives--- PMR signals and the hydroxyl proton appears as a	a.3 triplet	b.3.singlet	c.2 singlet	d. 3 quintet	a.3 triplet
56	The chemical shift of a proton on the δ scale is 4. The value of the τ scale is---	a. 14	b.6	c. 2.5	d.4	b.6
57	The fine structure and intensity ratios expected in the proton NMRspetrum of NH$_4^+$ ion (for ^{14}N,I=1) are	a. singlet	b. Doublet 1:1	c. Trplet 1:1:1	d.triplet1:2:1	c. Trplet 1:1:1
58	In the proton NMR spectrum of toluene,the resonancedue to CH$_3$, group is expected to	a. δ 0.5	b.δ 1.25	c.δ2.5	d. δ 3.5	c.δ2.5
59	How many NMR signals are found in cis dimethyl cyclopropane and transdimethyl cyclopropane?	a. 2,3	b.3,4	c. 1,2	d. 8,10	b.3,4
60	In NMR spectroscopy the value of coupling constant(5)	a. Changes with ield strength	b. Changes with temperature	c.Changeswith solvent	d. Is independent to field strength, temperature and	d. Is independent to field strength, temperature and

LECTURE NOTES

UNIT-IV

SYLLABUS

Mass Spectroscopy: *Principles of mass spectrometry – resolution - description of single focusing and double focusing electron impact mass spectrometers - presentation and analysis of spectra - determination of molecular formulae - Nitrogen rule- Stevenson's rule - isotope abundance analysis - meta stable ions and peaks the molecular ion peak - fragmentation processes - Retro Diels - Alder rearrangement - McLafferty rearrangement - ortho effect - fragmentation associated with functional groups - aldehydes, ketones, carboxylic acids, esters, amides, alcohols, thiols, amine, ethers, sulphides and halides..*

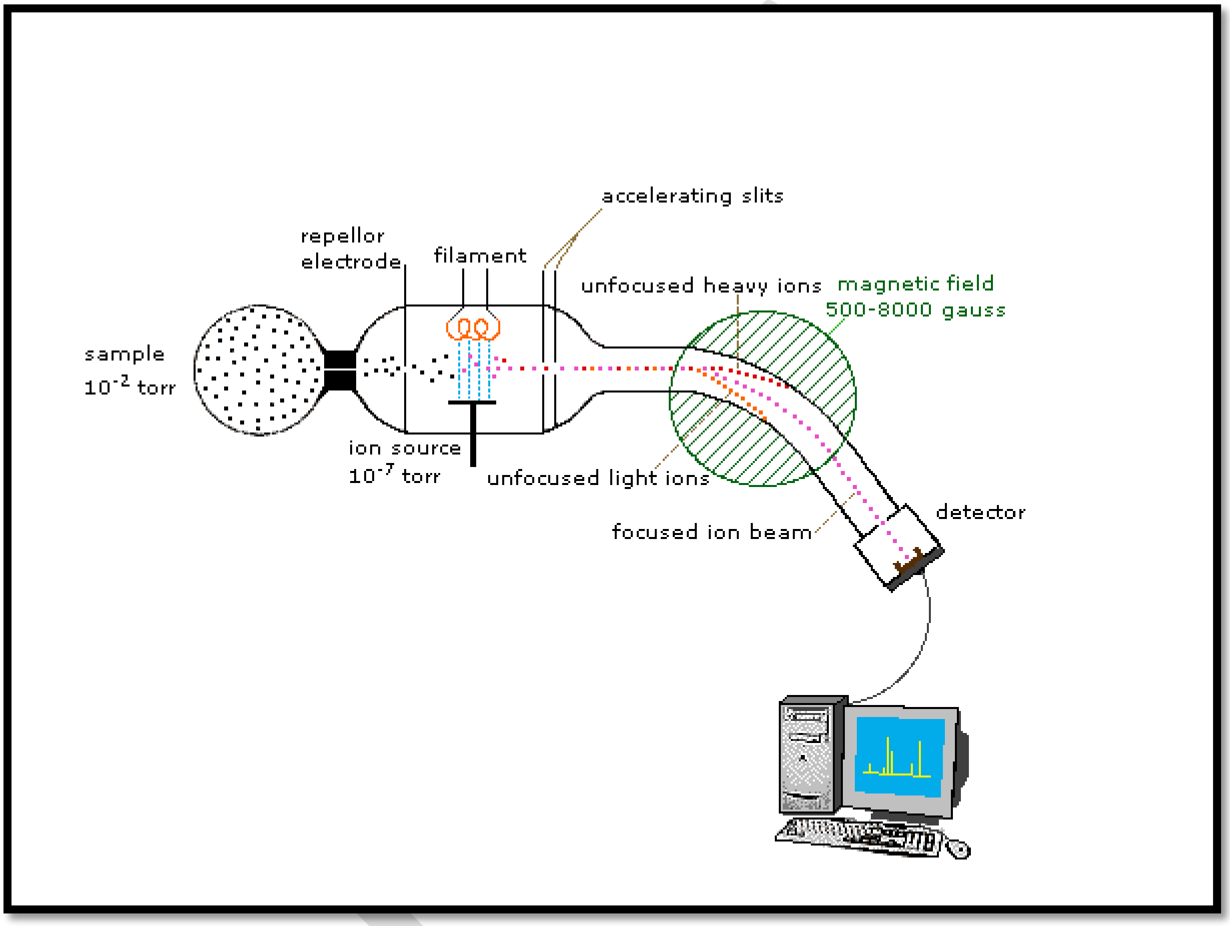
Mass Spectrometry

The Mass Spectrometer

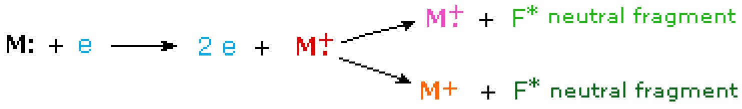
In order to measure the characteristics of individual molecules, a mass spectrometer converts them to ions so that they can be moved about and manipulated by external electric and magnetic fields. The three essential functions of a mass spectrometer, and the associated components, are:

1. A small sample is ionized, usually to cations by loss of an electron. **The Ion Source**
2. The ions are sorted and separated according to their mass and charge. **The Mass Analyzer**
3. The separated ions are then measured, and the results displayed on a chart. **The Detector**

Because ions are very reactive and short-lived, their formation and manipulation must be conducted in a vacuum. Atmospheric pressure is around 760 torr (mm of mercury). The pressure under which ions may be handled is roughly 10^{-5} to 10^{-8} torr (less than a billionth of an atmosphere). Each of the three tasks listed above may be accomplished in different ways. In one common procedure, ionization is effected by a high energy beam of electrons, and ion separation is achieved by accelerating and focusing the ions in a beam, which is then bent by an external magnetic field. The ions are then detected electronically and the resulting information is stored and analyzed in a computer. A mass spectrometer operating in this fashion is outlined in the following diagram. The heart of the spectrometer is the ion source. Here molecules of the sample (black dots) are bombarded by electrons (light blue lines) issuing from a heated filament. This is called an **EI** (electron-impact) source. Gases and volatile liquid samples are allowed to leak into the ion source from a reservoir (as shown). Non-volatile solids and liquids may be introduced directly. Cations formed by the electron bombardment (red dots) are pushed away by a charged repeller plate (anions are attracted to it), and accelerated toward other electrodes, having slits through which the ions pass as a beam. Some of these ions fragment into smaller cations and neutral fragments. A perpendicular magnetic field deflects the ion beam in an arc whose radius is inversely proportional to the mass of each ion. Lighter ions are deflected more than heavier ions. By varying the strength of the magnetic field, ions of different mass can be focused progressively on a detector fixed at the end of a curved tube (also under a high vacuum).

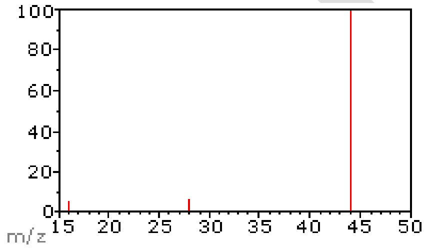


When a high energy electron collides with a molecule it often ionizes it by knocking away one of the molecular electrons (either bonding or non-bonding). This leaves behind a **molecular ion** (colored red in the following diagram). Residual energy from the collision may cause the molecular ion to fragment into neutral pieces (colored green) and smaller **fragment ions** (colored pink and orange). The molecular ion is a radical cation, but the fragment ions may either be radical cations (pink) or carbocations (orange), depending on the nature of the neutral fragment. An animated display of this ionization process will appear if you click on the ion source of the mass spectrometer diagram.

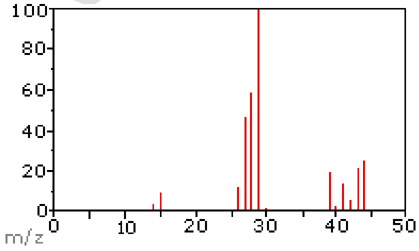


2. The Nature of Mass Spectra

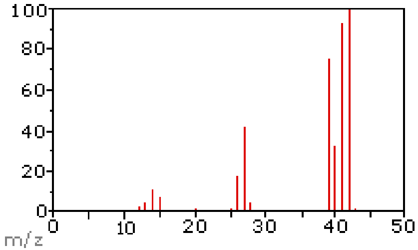
A mass spectrum will usually be presented as a vertical bar graph, in which each bar represents an ion having a specific mass-to-charge ratio (m/z) and the length of the bar indicates the relative abundance of the ion. The most intense ion is assigned an abundance of 100, and it is referred to as the **base peak**. Most of the ions formed in a mass spectrometer have a single charge, so the m/z value is equivalent to mass itself. Modern mass spectrometers easily distinguish (resolve) ions differing by only a single atomic mass unit (amu), and thus provide completely accurate values for the molecular mass of a compound. The highest-mass ion in a spectrum is normally considered to be the molecular ion, and lower-mass ions are fragments from the molecular ion, assuming the sample is a single pure compound.
The following diagram displays the mass spectra of three simple gaseous compounds, carbon dioxide, propane and cyclopropane. The molecules of these compounds are similar in size, CO_2 and C_3H_8 both have a nominal mass of 44 amu, and C_3H_6 has a mass of 42 amu. The molecular ion is the strongest ion in the spectra of CO_2 and C_3H_6, and it is moderately strong in propane. The unit mass resolution is readily apparent in these spectra (note the separation of ions having m/z=39, 40, 41 and 42 in the cyclopropane spectrum). Even though these compounds are very similar in size, it is a simple matter to identify them from their individual mass spectra. By clicking on each spectrum in turn, a partial fragmentation analysis and peak assignment will be displayed. Even with simple compounds like these, it should be noted that it is rarely possible to explain the origin of all the fragment ions in a spectrum. Also, the structure of most fragment ions is seldom known with certainty.



Carbon Dioxide



Propane



Cyclopropane

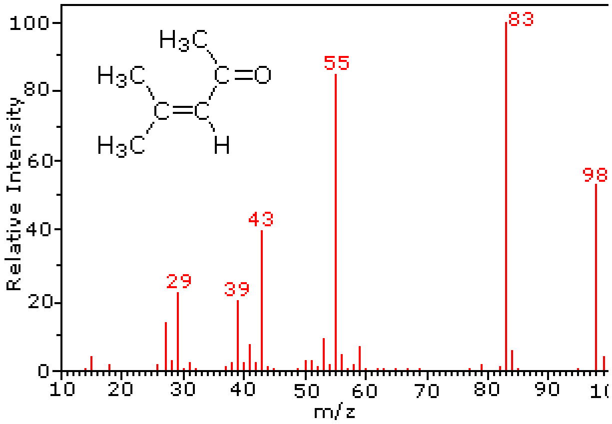
Since a molecule of carbon dioxide is composed of only three atoms, its mass spectrum is very simple. The molecular ion is also the base peak, and the only fragment ions are CO (m/z=28) and

O (m/z=16). The molecular ion of propane also has m/z=44, but it is not the most abundant ion in the spectrum. Cleavage of a carbon-carbon bond gives methyl and ethyl fragments, one of which is a carbocation and the other a radical. Both distributions are observed, but the larger ethyl cation (m/z=29) is the most abundant, possibly because its size affords greater charge dispersal. A similar bond cleavage in cyclopropane does not give two fragments, so the molecular ion is stronger than in propane, and is in fact responsible for the the base peak. Loss of a hydrogen atom, either before or after ring opening, produces the stable allyl cation (m/z=41). The third strongest ion in the spectrum has m/z=39 (C_3H_3). Its structure is uncertain, but two possibilities are shown in the diagram. The small m/z=39 ion in propane and the absence of a m/z=29 ion in cyclopropane are particularly significant in distinguishing these hydrocarbons.

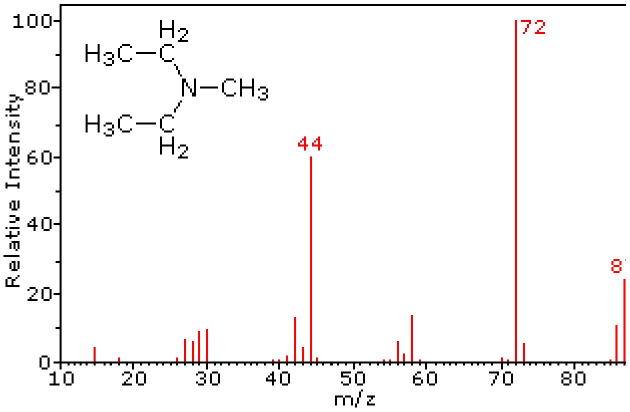
Most stable organic compounds have an even number of total electrons, reflecting the fact that electrons occupy atomic and molecular orbitals in pairs. When a single electron is removed from a molecule to give an ion, the total electron count becomes an odd number, and we refer to such ions as **radical cations**. The molecular ion in a mass spectrum is always a radical cation, but the fragment ions may either be even-electron cations or odd-electron radical cations, depending on the neutral fragment lost. The simplest and most common fragmentations are bond cleavages producing a neutral radical (odd number of electrons) and a cation having an even number of electrons. A less common fragmentation, in which an even-electron neutral fragment is lost, produces an odd-electron radical cation fragment ion. Fragment ions themselves may fragment further. As a rule, odd-electron ions may fragment either to odd or even-electron ions, but even-electron ions fragment only to other even-electron ions. The masses of molecular and fragment ions also reflect the electron count, depending on the number of nitrogen atoms in the species.

Ions with no nitrogen or an even # N atoms	odd-electron ions even-number mass	even-electron ions odd-number mass
Ions having an odd # N atoms	odd-electron ions odd-number mass	even-electron ions even-number mass

This distinction is illustrated nicely by the following two examples. The unsaturated ketone, 4-methyl-3-pentene-2-one, on the left has no nitrogen so the mass of the molecular ion (m/z = 98) is an even number. Most of the fragment ions have odd-numbered masses, and therefore are even-electron cations. Diethylmethylamine, on the other hand, has one nitrogen and its molecular mass (m/z = 87) is an odd number. A majority of the fragment ions have even-numbered masses (ions at m/z = 30, 42, 56 & 58 are not labeled), and are even-electron nitrogen cations. The weak even -electron ions at m/z=15 and 29 are due to methyl and ethyl cations (no nitrogen atoms). The fragmentations leading to the chief fragment ions will be displayed by clicking on the appropriate spectrum. Repeated clicks will cycle the display.



4-methyl-3-pentene-2-one

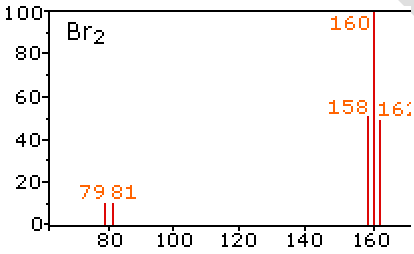


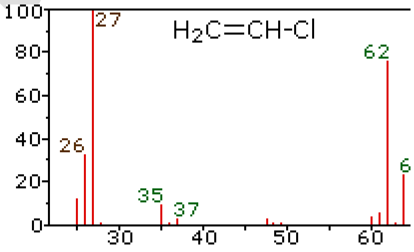
N,N-diethylmethylamine

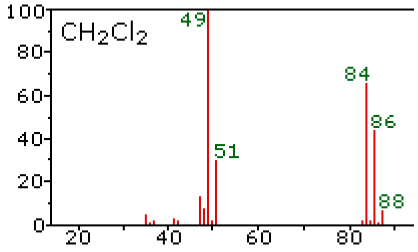
When non-bonded electron pairs are present in a molecule (e.g. on N or O), fragmentation pathways may sometimes be explained by assuming the missing electron is partially localized on that atom. A few such mechanisms are shown above. Bond cleavage generates a radical and a cation, and both fragments often share these roles, albeit unequally.

Isotopes

Since a mass spectrometer separates and detects ions of slightly different masses, it easily distinguishes different isotopes of a given element. This is manifested most dramatically for compounds containing bromine and chlorine, as illustrated by the following examples. Since molecules of bromine have only two atoms, the spectrum on the left will come as a surprise if a single atomic mass of 80 amu is assumed for Br. The five peaks in this spectrum demonstrate clearly that natural bromine consists of a nearly 50:50 mixture of isotopes having atomic masses of 79 and 81 amu respectively. Thus, the bromine molecule may be composed of two ^{79}Br atoms (mass 158 amu), two ^{81}Br atoms (mass 162 amu) or the more probable combination of ^{79}Br-^{81}Br (mass 160 amu). Fragmentation of Br_2 to a bromine cation then gives rise to equal sized ion peaks at 79 and 81 amu.







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bromine **vinyl chloride** **methylene chloride**

The center and right hand spectra show that chlorine is also composed of two isotopes, the more abundant having a mass of 35 amu, and the minor isotope a mass 37 amu. The precise isotopic composition of chlorine and bromine is:

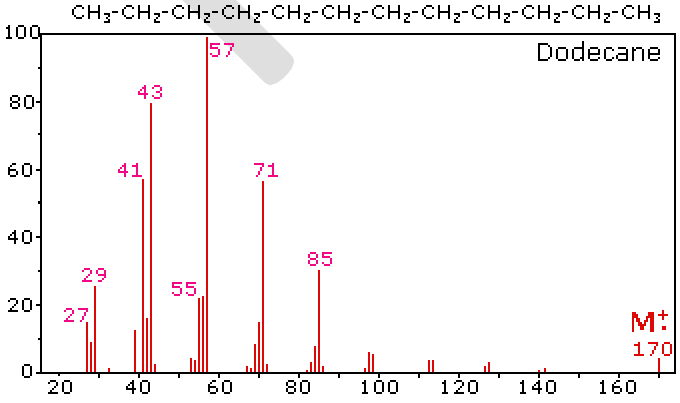
Chlorine:75.77% ^{35}Cl and 24.23% ^{37}Cl

Bromine: 50.50% ^{79}Br and 49.50% ^{81}Br

The presence of chlorine or bromine in a molecule or ion is easily detected by noticing the intensity ratios of ions differing by 2 amu. In the case of methylene chloride, the molecular ion consists of three peaks at m/z=84, 86 & 88 amu, and their diminishing intensities may be calculated from the natural abundances given above. Loss of a chlorine atom gives two isotopic fragment ions at m/z=49 & 51amu, clearly incorporating a single chlorine atom. Fluorine and iodine, by contrast, are monoisotopic, having masses of 19 amu and 127 amu respectively. It should be noted that the presence of halogen atoms in a molecule or fragment ion does not change the odd-even mass rules given above.

Two other common elements having useful isotope signatures are carbon, ^{13}C is 1.1% natural abundance, and sulfur, ^{33}S and ^{34}S are 0.76% and 4.22% natural abundance respectively. For example, the small m/z=99 amu peak in the spectrum of 4-methyl-3-pentene-2-one (above) is due to the presence of a single ^{13}C atom in the molecular ion. Although less important in this respect, ^{15}N and ^{18}O also make small contributions to higher mass satellites of molecular ions incorporating these elements.

The calculator on the right may be used to calculate the isotope contributions to ion abundances 1 and 2 amu greater than the molecular ion (M). Simply enter an appropriate subscript number to the right of each symbol, leaving those elements not present blank, and press the "Calculate" button. The numbers displayed in the M+1 and M+2 boxes are relative to M being set at 100%.

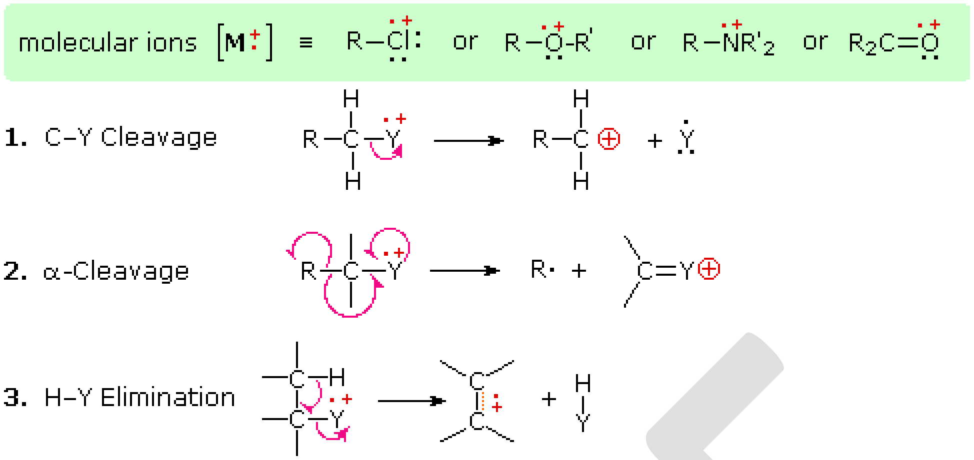


4.FragmentationPatterns

The fragmentation of molecular ions into an assortment of fragment ions is a mixed blessing. The nature of the fragments often provides a clue to the molecular structure, but if the molecular ion has a lifetime of less than a few microseconds it will not survive long enough to be observed. Without a molecular ion peak as a reference, the difficulty of interpreting a mass spectrum increases markedly. Fortunately, most organic compounds give mass spectra that include a molecular ion, and those that do not often respond successfully to the use of milder ionization conditions. Among simple organic compounds, the most stable molecular ions are those from aromatic rings, other conjugated pi-electron systems and cycloalkanes. Alcohols, ethers and highly branched alkanes generally show the greatest tendency toward fragmentation.

The mass spectrum of dodecane on the right illustrates the behavior of an unbranched alkane. Since there are no heteroatoms in this molecule, there are no non-bonding valence shell electrons. Consequently, the radical cation character of the molecular ion (m/z = 170) is delocalized over all the covalent bonds. Fragmentation of C-C bonds occurs because they are usually weaker than C-H bonds, and this produces a mixture of alkyl radicals and alkyl carbocations. The positive charge commonly resides on the smaller fragment, so we see a homologous series of hexyl (m/z = 85), pentyl (m/z = 71), butyl (m/z = 57), propyl (m/z = 43), ethyl (m/z = 29) and methyl (m/z = 15) cations. These are accompanied by a set of corresponding alkenyl carbocations (e.g. m/z = 55, 41 &27) formed by loss of 2 H. All of the significant fragment ions in this spectrum are even-electron ions. In most alkane spectra the propyl and butyl ions are the most abundant.

The presence of a functional group, particularly one having a heteroatom Y with non-bonding valence electrons (Y = N, O, S, X etc.), can dramatically alter the fragmentation pattern of a compound. This influence is thought to occur because of a "localization" of the radical cation component of the molecular ion on the heteroatom. After all, it is easier to remove (ionize) a non-bonding electron than one that is part of a covalent bond. By localizing the reactive moiety, certain fragmentation processes will be favored. These are summarized in the following diagram, where the green shaded box at the top displays examples of such "localized" molecular ions. The first two fragmentation paths lead to even-electron ions, and the elimination (path #3) gives an odd-electron ion. Note the use of different curved arrows to show single electron shifts compared with electron pair shifts.



The charge distributions shown above are common, but for each cleavage process the charge may sometimes be carried by the other (neutral) species, and both fragment ions are observed. Of the three cleavage reactions described here, the alpha-cleavage is generally favored for nitrogen, oxygen and sulfur compounds. Indeed, in the previously displayed spectra of 4-methyl-3-pentene-2-one and N,N-diethylmethylamine the major fragment ions come from alpha-cleavages. Further examples of functional group influence on fragmentation are provided by a selection of compounds that may be examined by clicking the left button below. Useful tables of common fragment ions and neutral species may be viewed by clicking the right button.

Nitrogen rule

The **nitrogen rule** states that organic compounds containing exclusively hydrogen, carbon, nitrogen, oxygen, silicon, phosphorus, sulfur, and the halogens either have 1) an *odd nominal mass* that indicates an *odd number* of nitrogen atoms are present or 2) an *even nominal mass* that indicates an *even number* of nitrogen atoms are present in the molecular ion. The nitrogen rule is not a rule, *per se*, as much as a general principle which may prove useful when attempting to solve organic mass spectrometry structures.

Formulation of the rule

This rule is derived from the fact that, perhaps coincidentally, for the most common chemical elements in neutral organic compounds (hydrogen, carbon, nitrogen, oxygen, silicon, phosphorus, sulfur, and the halogens), elements with even numbered nominal masses form even numbers of covalent bonds, while elements with odd numbered nominal masses form odd numbers of covalent bonds, with the exception of nitrogen, which has a nominal (or integer) mass of 14, but has a valency of 3.

The nitrogen rule is only true for neutral structures in which all of the atoms in the molecule have a number of covalent bonds equal to their standard valency (counting each sigma bond and pi bond as a separate covalent bond for the purposes of the calculation). Therefore, the rule is typically only applied to the molecular ion signal in the mass spectrum.

Mass spectrometry generally operates by measuring the mass of ions. If the measured ion is generated by creating or breaking a single covalent bond (such as protonating an amine to form an ammonium center or removing a hydride from a molecule to leave a positively charged ion) then the nitrogen rule becomes reversed (odd numbered masses indicate even numbers of nitrogens and vice versa). However, for each consecutive covalent bond that is broken or formed, the nitrogen rule again reverses.

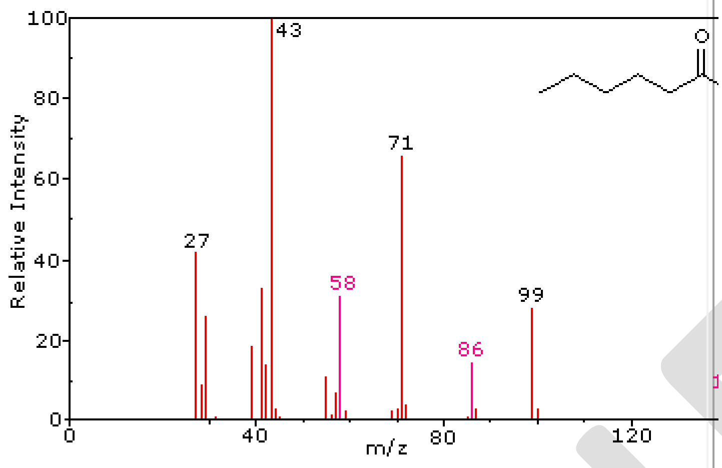
Therefore, a more rigorous definition of the nitrogen rule for organic compounds containing exclusively hydrogen, carbon, nitrogen, oxygen, silicon, phosphorus, sulfur, and the halogens would be as follows:

An even nominal mass indicates that a net even number of covalent bonds have been broken or formed and an even number of nitrogen atoms are present, or that a net odd number of covalent bonds have been broken or formed and an odd number of nitrogen atoms are present. An odd nominal mass indicates that a net even number of covalent bonds have been broken or formed and an odd number of nitrogen atoms are present, or that a net odd number of covalent bonds have been broken or formed and an even number of nitrogen atoms are present.

Inorganic molecules do not necessarily follow the rule. For example, the nitrogen oxides NO and NO_2 have an odd number of nitrogens but even masses of 30 and 46, respectively.

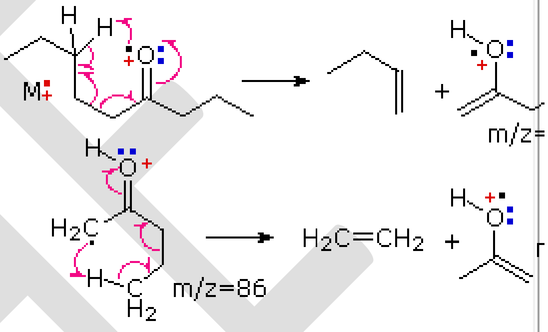
Rearangement Mechanisms in Fragmentation

4-nonanone

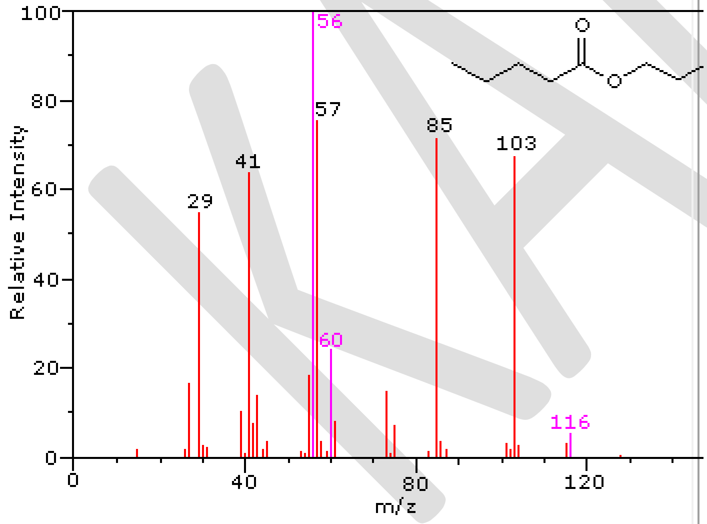


The odd-electron fragment ions at m/z = 86 and 58 are the result of a McLafferty rearrangement, involving the larger alkyl chain, and a subsequent loss of ethene (the "double-McLafferty" rearrangement).

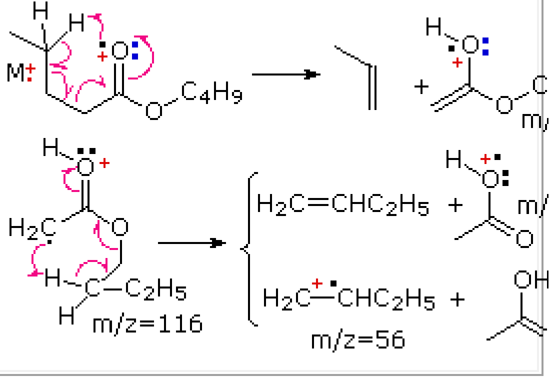
Alpha-cleavage leads to the m/z = 99, 71 and 43 ions. The charge is apparently distributed over both fragments.



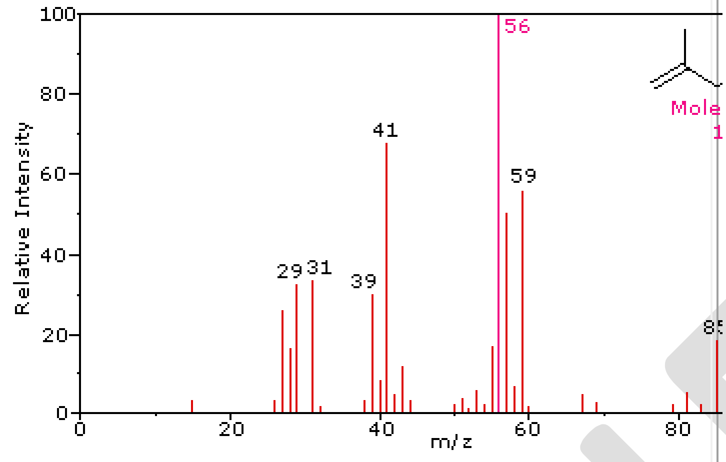
butylpentanoate



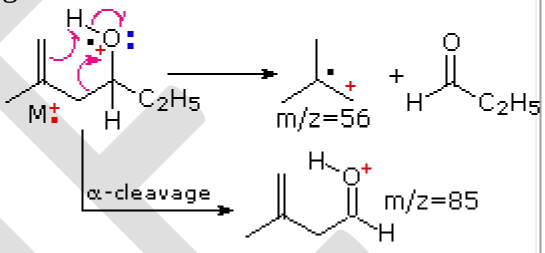
Alpha-cleavage gives ions at m/z=57 & 85 amu. The McLafferty rearrangement on the acid side generates a m/z=116 ion. Subsequent rearrangement on the alcohol side generates m/z=60 and 56 ions. The m/z=103 ion is probably $C_4H_9CO_2H_2^{(+)}$.



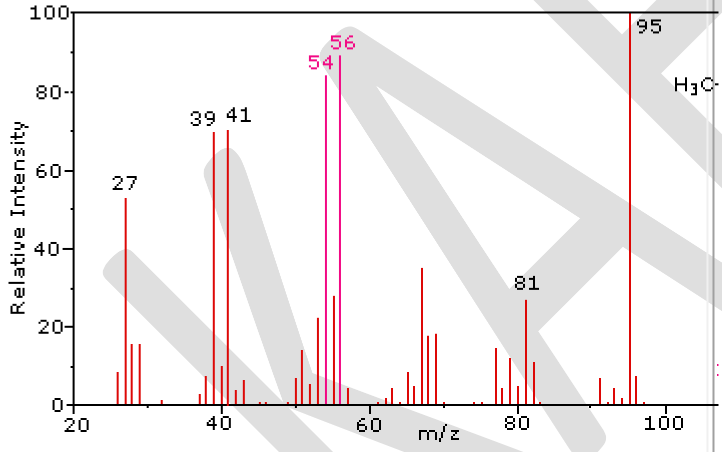
5-methyl-5-hexen-3-ol



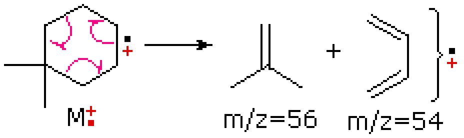
The molecular ion (m/z=114 amu) is not observed under electron impact ionization conditions. The highest mass ion (m/z=85) is due to an alpha-cleavage of ethyl; the other alpha-cleavage generates m/z=59. The rearrangement cleavage shown here generates the m/z=56 ion.



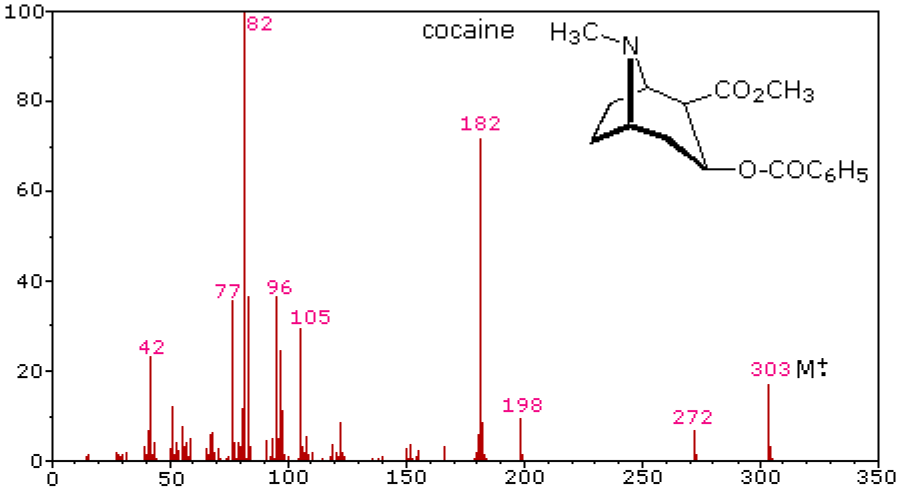
4,4-dimethylcyclohexene



The loss of a methyl radical generates the base peak at m/z=95 amu. The m/z=81 & 67 ions are smaller homologues of this ion (14 mass units less). Cyclohexene compounds undergo a retro-Diel-Alder rearrangement to give diene and alkene fragments. The charge may reside on either fragment, with the larger usually predominating. In this case both ions are relatively strong (m/z=54 & 56).



The complexity of fragmentation patterns has led to mass spectra being used as "fingerprints" for identifying compounds. Environmental pollutants, pesticide residues on food, and controlled substance identification are but a few examples of this application. Extremely small samples of an unknown substance (a microgram or less) are sufficient for such analysis. The following mass spectrum of cocaine demonstrates how a forensic laboratory might determine the nature of an unknown street drug. Even though extensive fragmentation has occurred, many of the more abundant ions (identified by magenta numbers) can be rationalized by the three mechanisms shown above. Plausible assignments may be seen by clicking on the spectrum, and it should be noted that all are even-electron ions. The m/z = 42 ion might be any or all of the following: C_3H_6, C_2H_2O or C_2H_4N. A precise assignment could be made from a high-resolution m/z value (next section).



Odd-electron fragment ions are often formed by characteristic rearrangements in which stable neutral fragments are lost. Mechanisms for some of these rearrangements have been identified by following the course of isotopically labeled molecular ions. A few examples of these rearrangement mechanisms may be seen by clicking the following button.

5. High Resolution Mass Spectrometry

In assigning mass values to atoms and molecules, we have assumed integral values for isotopic masses. However, accurate measurements show that this is not strictly true. Because the strong nuclear forces that bind the components of an atomic nucleus together vary, the actual mass of a given isotope deviates from its nominal integer by a small but characteristic amount (remember $E = mc^2$). Thus, relative to ^{12}C at 12.0000, the isotopic mass of ^{16}O is 15.9949 amu (not 16) and ^{14}N is 14.0031 amu (not 14).

Formula	C_6H_{12}	C_5H_8O	$C_4H_8N_2$
Mass	84.0939	84.0575	84.0688

By designing mass spectrometers that can determine m/z values accurately to four decimal places, it is possible to distinguish different formulas having the same nominal mass. The table on the right illustrates this important feature, and a double-focusing high-resolution mass spectrometer easily distinguishes ions having these compositions. Mass spectrometry therefore not only provides a specific molecular mass value, but it may also establish the molecular formula of an unknown compound. Tables of precise mass values for any molecule or ion are available in libraries; however, the mass calculator provided below serves the same purpose. Since a given nominal mass may correspond to several molecular formulas, lists of such possibilities are especially useful when evaluating the spectrum of an unknown compound. Composition tables are available for this purpose, and a particularly useful program for calculating all possible combinations of H, C, N & O that give a specific nominal mass has been written by Jef Rozenski.

Molecular formula determination

Nitrogen rule

The nitrogen rule states that organic molecules that contain hydrogen, carbon, nitrogen, oxygen, silicon, phosphorus, sulfur, and the halogens have an odd nominal mass if they have an odd number of nitrogen atoms or an even mass if they have an even number of nitrogen atoms are present. The nitrogen rule is true for structures in which all of the atoms in the molecule have a number of covalent bonds equal to their standard valency, counting each sigma bond and pi bond as a separate covalent bond.

Rings plus double bonds

From degree of unsaturation principles, molecules containing only carbon, hydrogen, halogens, nitrogen, and oxygen follow the formula

$$\text{Rings} + \pi \text{ bonds} = \mu = C - H/2 - X/2 + N/2 + 1$$

where C is the number of carbons, H is the number of hydrogens, X is the number of halogens, and N is the number of nitrogen.

Even electron rule

The **even electron rule** states that ions with an even number of electrons (cations but not radical ions) tend to form even-electron fragment ions and odd-electron ions (radical ions) form odd-electron ions or even-electron ions. Even-electron species tend to fragment to another even-electron cation and a neutral molecule rather than two odd-electron species.

$$OE^{+\bullet} \rightarrow EE^{+} + R^{\bullet},\ OE^{+\bullet} \rightarrow OE^{+\bullet} + N$$

Stevenson's rules

The more stable the product cation ion, the more abundant the corresponding decomposition process . Several theories can be utilized to predict the fragmentation process, such as the electron octet rule, the resonance stabilization and hyperconjugation and so on.

Rule of 13

The **Rule of 13** is a simple procedure for tabulating possible chemical formula for a given molecular mass. The first step in applying the rule is to assume that only carbon and hydrogen are present in the molecule and that the molecule comprises some number of CH "units" each of which has a nominal mass of 13. If the molecular weight of the molecule in question is *M*, the number of possible CH units is *n* and

$$M/13 = n + r/13$$

where r is the remainder. The base formula for the molecule is

$$C_n\ H_{n+r}$$

and the degree of unsaturation is

$$\mu = n - r + 2 \quad / \ 2$$

A negative value of *u* indicates the presence of heteroatoms in the molecule and a half-integer value of *u* indicates the presence of an odd number of nitrogen atoms. On addition of heteroatoms, the molecular formula is adjusted by the equivalent mass of carbon and hydrogen. For example, adding N requires removing CH_2 and adding O requires removing CH_4.

Isotope effects

Isotope peaks within a spectrum can help in structure elucidation. Compounds containing halogens (especially chlorine and bromine) can produce very distinct isotope peaks. The mass spectrum of methylbromide has two prominent peaks of equal intensity at *m/z* 94 (M) and 96 (M+2) and then two more at 79 and 81 belonging to the bromine fragment.

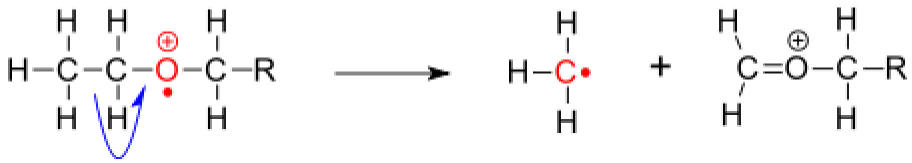
Even when compounds only contain elements with less intense isotope peaks (carbon or oxygen), the distribution of these peaks can be used to assign the spectrum to the correct compound. For example, two compounds with identical mass of 150 Da, $C_8H_{12}N_3^+$ and $C_9H_{10}O_2^+$, will have two different M+2 intensities which makes it possible to distinguish between them.

Fragmentation

The fragmentation pattern of the spectra beside the determination of the molar weight of an unknown compound also suitable to give structural information, especially in combination with the calculation of the degree of unsaturation from the molecular formula (when available). Neutral fragments frequently lost are carbon monoxide, ethylene, water, ammonia, and hydrogen sulfide. There are several fragmentation processes, as follows.

α - cleavage

Fragmentation arises from a homolysis processes.This cleavage results from the tendency of the unpaired electron from the radical site to pair up with an electron from another bond to an atom adjacent to the charge site, as illustrated below. This reaction is defined as a homolytic cleavage since only a single electron is transferred. The driving forces for such reaction is the electron donating abilities of the radical sites: N > S, O,π > Cl, Br > H. An example is the cleavage of carbon-carbon bonds next to a heteroatom.In this depiction, single-electron movements are indicated by a single-headed arrow.



Sigma bond cleavage

The ionization of alkanes weakens the C-C bond, ultimately resulting in the decomposition. As bond breaks, A charged, even electron species (R+) and a neutral radical species (R•) are generated. Highly substituted carbocations are more stable than the nonsubstituted ones. An example is depicted as below.

Sigma bond cleavage example

Inductive cleavage

This reaction results from the inductive effect of the radical sites, as depicted below.This reaction is defined as a heterolytic cleavage since a pair of electrons is transferred. The driving forces for such reaction are the electronegativities of the radical sites: halogens > O, S >> N, C. this reaction is less favored than radical-site reactions.

McLafferty rearrangement

The McLafferty rearrangement can occur in a molecule containing a keto-group and involves β-cleavage, with the gain of the γ-hydrogen atom. Ion-neutral complex formation involves bond homolysis or bond heterolysis, in which the fragments do not have enough kinetic energy to separate and, instead, reaction with one another like an ion-molecule reaction.

An example of the McLafferty rearrangement

Hydrogen rearrangement to a saturated heteroatom

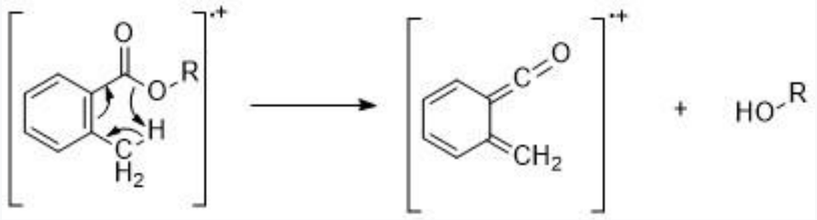
The “1,5 ” hydrogen shift cause transfer of one γ- hydrogen to a radical site on a saturated heteroatom. The same requirements for McLafferty rearrangement apply to hydrogen rearrangement to a saturated heteroatom. Such rearrangement initiates charge-site reaction, resulting in the formation of an odd electron ion and a small neutral molecule (water, or acid and so on). For alcohols, this heterolytic cleavage releases a water molecule. Since the charge-site reactions are dominant in the less bulky alcohols, this reaction is favored for alcohols as primary > secondary > tertiary.

Double-hydrogen rearrangement

The “1,5 ” hydrogen shift cause transfer of two γ- hydrogen to two radical sites on two different unsaturated atoms. The same requirements for McLafferty rearrangement apply to double-hydrogen rearrangement. This reaction is observed for three unsaturated functional groups, namely thioesters, esters and amides.

Ortho rearrangement

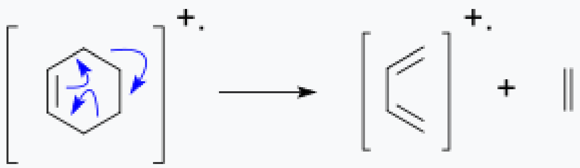
The “1,5 ” hydrogen shift cause transfer of two γ- hydrogen to two radical sites on two different unsaturated atoms. The same requirements for The “1,5 ” hydrogen shift occur between proper substituents in the ortho positions of the aromatic rings. The same requirements for McLafferty rearrangement apply to ortho rearrangement except for the strong α,β carbon-carbon double bond. Such rearrangement initiates charge-site reaction, resulting in the formation of an odd electron ion and a small neutral molecule (water, or HCl and so on). This reaction can be utilized to differentiate ortho from para and meta isomersMcLafferty rearrangement apply to double-hydrogen rearrangement. This reaction is observed for three unsaturated functional groups, namely thioesters, esters and amides.[11]



Ortho Rearrangement

Retro-Diels-Alder reaction

This reaction occurs mainly in cyclohexene and it's derivatives. Upon ionization, the pi electrons are excited and generate a charge site and a radical site. Following this, two successive α cleavages yield a butadiene radical and a neutral ethene since ethene has a higher ionisation energy than butadiene (Stevenson's rules).



Retro Diels-Alder reaction producing neutral ethylene

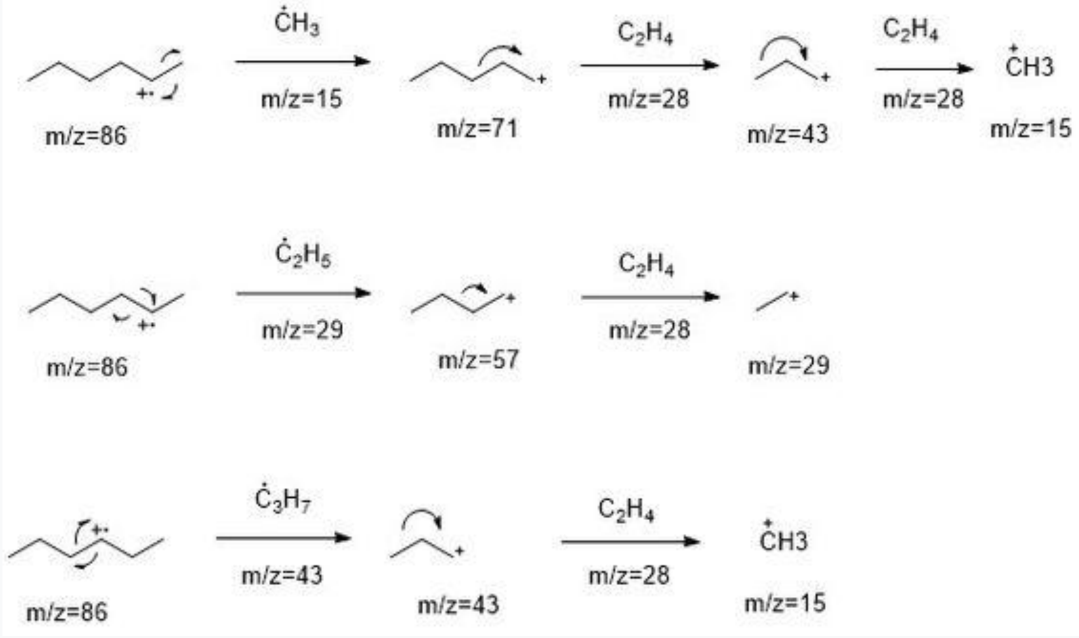
Cycloreversion reaction

This reaction occurs mainly in four-membered cyclic molecules. Once ionized, it produces a distonic ion and then further fragments to yield an ethene radical ion and a neutral ethene molecule.

Fragmentation patterns of specific compound classes

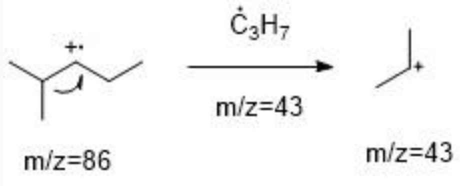
Alkanes

For linear alkanes, molecular ion peaks are often observed. However, for long chain compounds, the intensity of the molecular ion peaks are often weak. Linear fragments often differ by 14 Da (CH_2 = 14). For example, hexane fragmentation patterns. The m/z=57 butyl cation is the base peak, and other most abudant peaks in the spectrum are alkyl carbocations at m/z=15, 29, 43 Da.



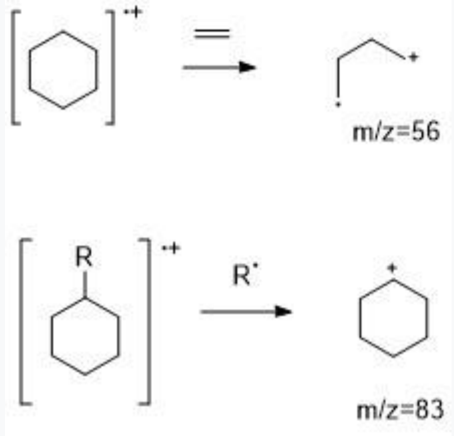
The possible mechanisms for EI ionization spectra of hexane

Branched alkanes have somewhat weaker molecular ion peaks in the spectra.They tend to fragment at the branched point. For the 2,3-dimethylbutane, an isopropyl cation peak (m/z=43) is very strong.



Branched alkane

Cycloalkanes have relatively intense molecular ion peaks (two bonds have to break). Alkene fragmentation peaks are often most significant mode. Loss of “CH_2CH_2“ (= 28) is common, if present. However, for the substituted cycloalkanes, they prefer to form the cycloalkyl cations by cleavage at the branched points.

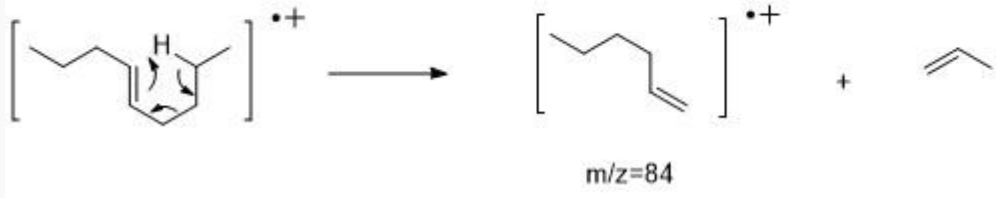


Alkenes

Alkenes often produce stronger molecular ion peaks than alkanes due to the lower ionization energy of a pi electron than a σ electron. After the ionization, double bonds can migrate easily, resulting in almost impossible determination of isomers. Allylic cleavage is most significant fragmentation mode due to resonance stabilization.

Most possible ionization mechanism of acyclic alkenes

McLafferty-like rearrangements are possible (similar to carbonyl pi bonds). Again, bond migration is possible.

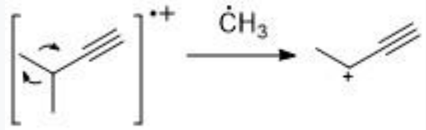


McLafferty-like rearragements of alkenes

Cyclohexenes often undergo retro Diels-Alder reactions.

Alkynes

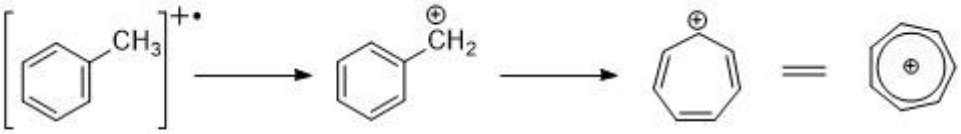
Similar to alkenes, alkynes often show strong molecular ion peak. Propargylic cleavage is a most significant fragmentation mode.



Most possible ionization mechanism of alkyne

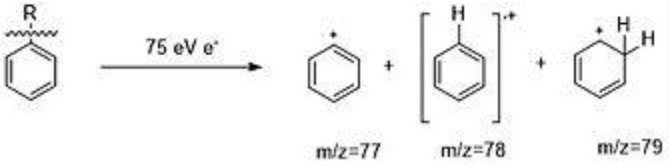
Aromatic hydrocarbons

Aromatic hydrocarbons show distinct molecular ion peak.benzylic cleavage is pretty common.When alkyl groups are attached to the ring, a favorable mode of cleavage is to lose a H-radical to form the tropylium cation (m/z 91).



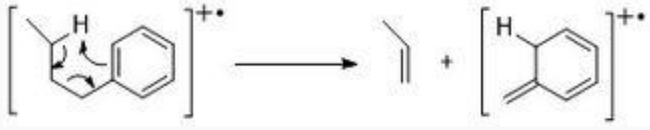
Benzylic cleavage

Alkyl substituted benzenes can fragment via the kinetic controlled process to form $C_6H_5^+$, $C_6H_6^+$ ions.



Benzene derivatives' fragmentation process

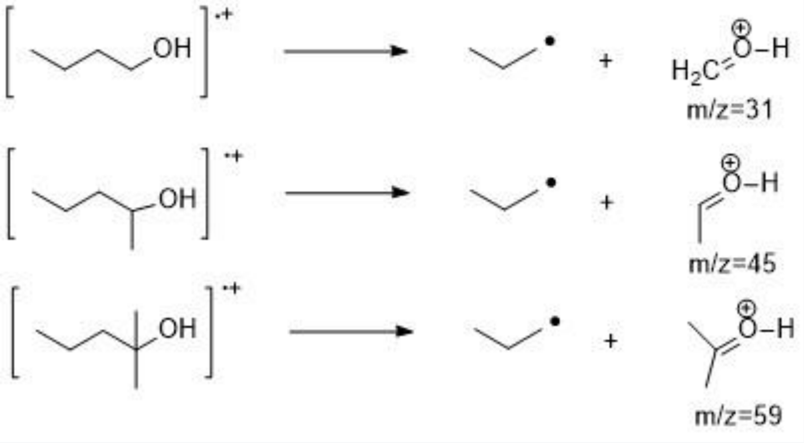
Another common mode of fragmentation is the McLafferty rearrangement, which requires the alkyl chain lengh to be at least longer than 3 carbons.



McLafferty rearrangement of aromatics

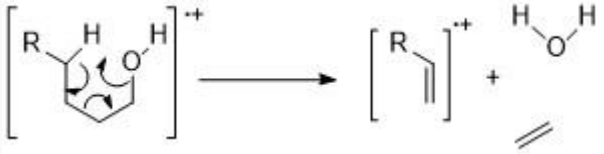
Alcohols

Alcohols generally have weak molecular ion peaks due to the strong electronegativity of oxygen. “Alpha” cleavage is common due to the resonance stabilization. The largest alkyl group will be lost.



α-cleavage fragmentation mechanism of alcohols

Another common fragmentation mode is dehydration (M-18). For longer chain alcohols, a McLafferty type rearrangement can produce water and ethylene (M -46).

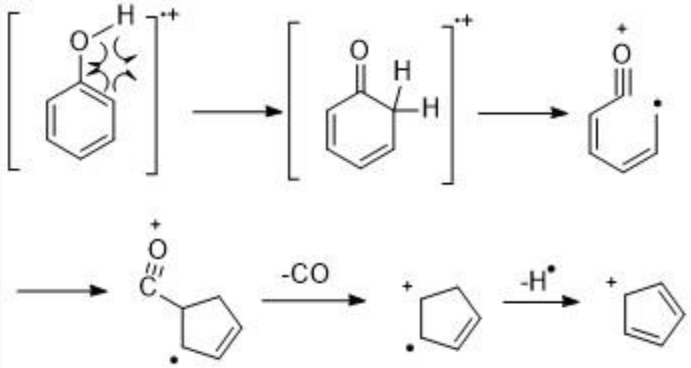


McLafferty type rearrangement for long chain alcohols

Cyclic alcohols tend to show stronger M+ peaks than linear chains. And they follow similar fragmentation pathways: Alfa cleavage and dehydration.

Phenol

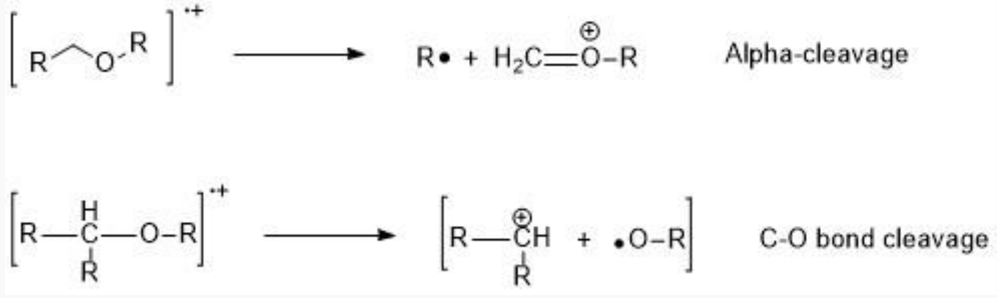
Phenol exhibit a strong molecular ion peak. Loss of H· is observed (M – 1), CO (M – 28) and formyl radical (HCO·, M – 29) is common observed.



Possible fragmentation mechanism of phenols

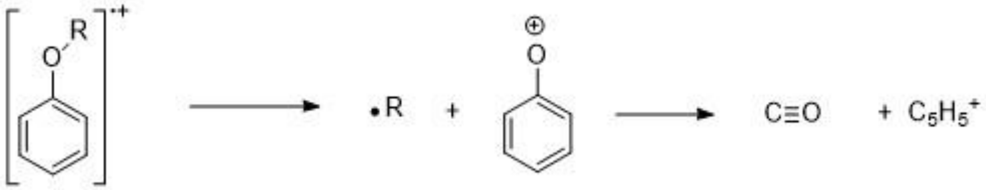
Ether

Ethers produce slightly more intense molecular ion peaks compared to the corresponding alcohols or alkanes. There are two common cleavage modes. α-cleavage and C-O bond cleavage.



Fragmentation modes of aliphatic ethers

Aromatic ethers can generate the C6H5O+ ion by loss of the alkyl group rather than H; this can expel CO as in the phenolic degradation.

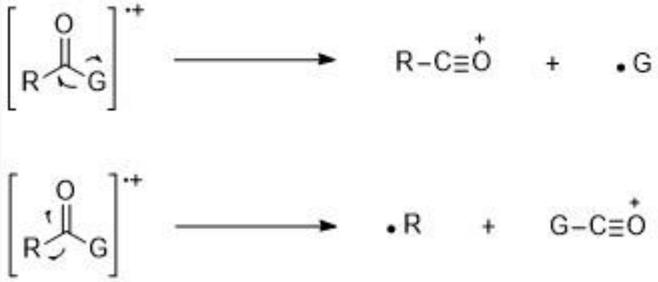


Fragmentation mechanism of aromatic ethers

Carbonyl compounds

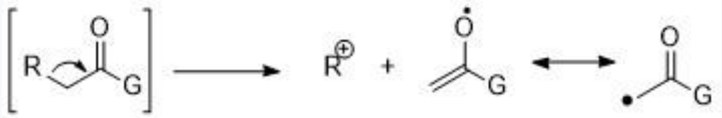
There are five types of carbonyl compounds, including aldehydes, ketones, carboxylic acids and esters. The principal fragmentation modes are described as follows:

Alpha-cleavage can occur on either side of the carbonyl functional group since an oxygen lone pair can stabilize the positive charge.



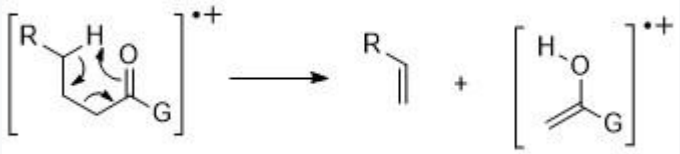
Alpha cleavage of carbonyl compounds

β-cleavage is a characteristic mode of carbonyl compounds' fragmentation due to the resonance stabilization.



Beta cleavage of carbonyl compounds

For longer chain carbonyl compounds (carbon number is bigger than 4), McLafferty rearrangements are dominant.

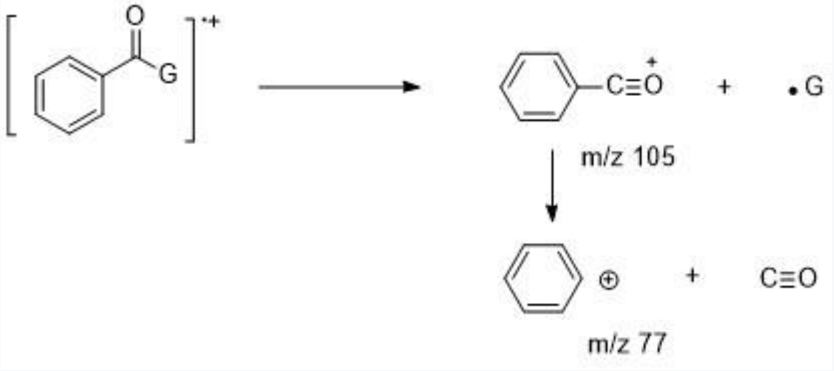


McLafferty rearrangement of carbonyl compounds

According to these fragmentation patterns, the characteristic peaks of carbonyl compounds are summarized in the following table.

		m/z of ion observed				
Fragmentation	Path	Aldehydes G = H	Ketones G=CH_3	Esters G=OCH_3	Acids G = OH	Amides G = NH2
Alpha-cleavage	Loss of R radical	29	43	59	45	44
Alpha-cleavage	Loss of G radical	M-1	M-15	M-59	M-45	M-44
Beta-cleavage		M-43	M-57	M-73	M-59	M-58
McLafferty rearrangement		44	58	74	60	59

For aromatic carbonyl compounds, Alpha-cleavages are favorable primarily to lose G· (M – 1,15, 29…) to form the C6H5CO+ ion (m/z=105), which can further lose CO (m/z= 77) and HCCH (m/z=51).



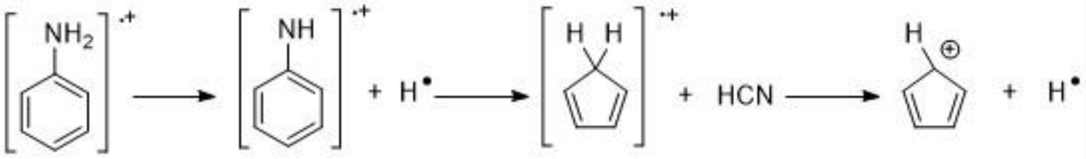
Aromatic carbonyl compound fragmentation mechanism

Amines

Amines follow nitrogen rule. Odd molecular ion mass to charge ratio suggests existence of odd numbers of nitrogens. Nonetheless, molecular ion peaks are weak in aliphatic amines due to the ease of fragmentation next to amines. Alpha-cleavage reactions are the most important fragmentation mode for amines; for 1° n-aliphatic amines, there is an intense peak at m/z 30.

Alpha cleavage of amines

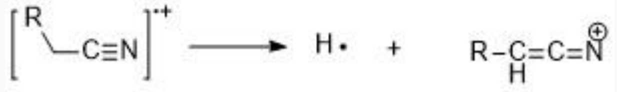
Aromatic amines have intense molecular ion peaks. For anilines, they prefer to lose a hydrogen atom before the expulsion of HCN.



Aniline fragmentation mechanism

Nitriles

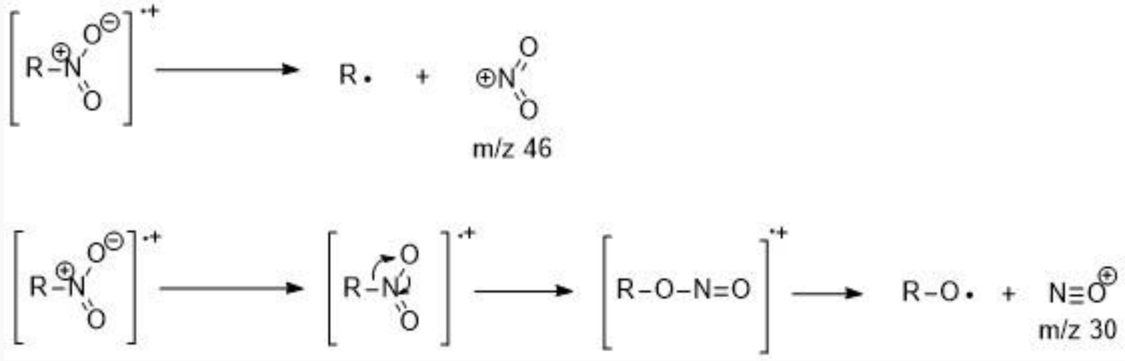
The principle fragmentation mode is the loss of an H-atom (M – 1) from the carbon next to the CN group due to the resonance stabilization. McLafferty rearrangement can be observed when they have longer chain lengths.



Nitrile fragmentation

Nitro compounds

The aliphatic nitro compounds normally show weak molecular ion peaks while the aromatic nitro compounds give a strong peak.Common degradation mode is loss of NO^+ and NO^{2+} .



Nitro compound fragmentation

Electrospray and atmospheric pressure chemical ionization

Electrospray and atmospheric pressure chemical ionization have different rules for spectrum interpretation due the different ionization mechanisms.

SUGGESTED READINGS:

Text Books:

1. Jag Mohan. (2007). *Organic Spectroscopy: Principles and Applications* (II Edition). New Delhi: Narose Publishing House.
2. Sharma, Y. R. (2007). Elementary Organic Spectroscopy: Principles and Chemical Applications (V Edition). New Delhi: S. Chand & Company Limited.

POSSIBLE QUESTIONS

MULTIPLE CHOICE QUESTIONS

(EACH QUESTION CARRY ONE MARK)

1. In Mass spectroscopy, molecules are bombarded with a beam of energetic

a) Neutrons b) Positrons c) E**lectrons** d) Nucleons

2. The intensity of the base peak is taken as

a) 80 b) **100** c) 87 d) 57

3. The energy required for removing one electron from the neutral parent molecule is usually

a) **10ev** b) 30ev c) 70ev d) 25ev

4. The energy required for the fragmentation of parent ion is

a) 40ev b) 100ev c) 80ev d) **70ev**

5. Position at metastable peak m* due to the reaction $M_1^{+-------}m_1^*$ is such that

a)$m^*=m_1^2/M_1$ b)$M_1=m_1^2/m^*$ c)$m^*=m_1^2M$ d)**$m_1^*M=m_1^2$**

6. The relative abundance of the metastable peak m*is often of the order or less compared to the abundance of parent ion

a) **10^{-2}** b)10^{-1} c)10^{-3} d)10^{-5}

7. Conjugated olefins show ------intense molecular ion peak as compared to the corresponding non-conjugated olefins

a) **less** b)more c)same d)poor

8. Double focusing mass spectrometers are capable of attaining much-------resolving power than single focusing instruments

a) higher b)**lower** c)same d)poor

9. In aliphatic acids carboxyl group is directly eliminated by

a) **β-cleavage** b) α-cleavage c) γ-cleavage d) δ-cleavage

10. Primary amides gives a strong peak at m/e=44 due to

a) H_2N b) $\mathbf{NH_3}$ c) NH_4 d) H_2N-C=O

11. For primary amines, the base peak is formed at m/e 30 due to $CH_2=N^+$ H2 by

a) α-cleavage b) β- cleavage c) γ- cleavage d) **δ- cleavage**

12. The Position of metastable peak m* is for $m_1=108$, $m_1=123$

a) **100** b) 70 c) 94.8 d) 90

13. In aromatic primary amines, a parent ion is formed by the loss of -------- electron from the lone pair present on the nitrogen atom

a) 1 b) 2 c) 3 d) **4**

14. A very weak parent ion peak and a prominent (M^+-18) peak would probably indicate

a) **Alcohol** b) Ketone

c) Aldehyde d) Presence of isotope of Oxygen

15. The compound whose mass spectrum shows m/e values at 156 (M+, base peak), 127 and 29 is

a) ethyl bromide b) methyl iodide

c) methyl bromide d) **ethyl iodide**

16. For mass spectrum of n-propyl benzene, the m/e value of tropiliun ion is

a) **91** b)85 c) 41 d)51

17. The molecular ion peak in phenol is--

a) **Intense** b) less abundance c) more abundance d) significant

18. In catechol the molecular ion peak is---

a) **Intense** b) less abundance c) more abundance d) significant

19. In aliphatic aldehydes and ketones the major fragmentation processes are

a) alpha cleavage b) beta cleavage

c) gamma cleavage d) **alpha and beta cleavage**

20. The intensity of molecular ion peak ---as the alkyl chain length---

a) **decreases, increases** b) increases, increases

c) decreases, decreases d) increases, decreases

PART-B

EACH QUESTION CARRY SIX MARK

1. Explain the following rearrangements in the mass spectra

(i) McLafferty rearrangement
(ii) Retero – Diels Alder's rearrangement

2. What is Mossbauer Effect? Explain the principle and theory of Mossbauer Spectroscopy

3. (i).What are the factors that influencing the fragmentation process?

(ii).What are the factors that governing the reaction pathways in mass spectroscopy. Explain any two.

4. (i). Write brief notes on isotropic and anisotropic system

(ii). Explain the factors affecting the magnitude of the g-value.

5. Write notes on

(i). Metastable peaks

(ii). Molecular ion peaks

(iii). Relative abundance of the parent and the fragment ions

6. (i). What is DPPH? Explain the importance of DPPH?

(ii) Write notes on hyperfine splitting

7. Explain the effect of external field on the energy states for an electron in hyperfine splitting.

8. What are the applications of mass spectroscopy?

9. (i).Explain the Biochemical applications in mossbauer spectroscopy?

(ii). what do you mean by isomer shift? Explain the Isomer shift for iron and tin

Compounds in different states of oxidation?

PART-C(COMPULSORY QUESTION)

TEN MARK QUESTION

1. Determine the structure of compound which shows m/e peaks at 88, 70, 55, 42, 31 (much intense) and 29.

[19CHP104]

KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-641021

(For the candidates admitted on 2019 onwards)

DEPARTMENT OF CHEMISTRY

I - SEMESTER

ORGANIC CHEMISTRY

OBJECTIVE TYPE QUESTIONS(EACH QUESTION CARRY ONE MARK)

Unit-4 Mass Spectroscopy (19CHP104)

S.No	Questions	Option a	Option b	Option c	Option d	Answer
1	In Mass spectroscopy, molecules are bombarded with a beam of energetic	a.)neutrons	b)positrons	c)electrons	d)nucleons	c)electrons
2	The intensity of the base peak is taken as	a)80	b)100	c)87	d)57	b)100
3	The energy required for removing one electron from the neutral parent molecule is usually	a)10ev	b)30ev	c)70ev	d)25ev	a)10ev
4	The energy required for thle fragmentation of parent ion is	a)40ev	b)100ev	c)80ev	d)70ev	d)70ev
5	In Mass spectrometer the positive ions are separated according to their	a)m/e ratio	b)e/mratio	c)h/mratio	d)e/v ratio	a)m/e ratio
6	The molecular ion peak in aromatic compounds ia relatively much intense due to the presence of	a)σ-electron system	b)non-bonding electron system	c)π-electron sy;stem	d)unpaired electron system	c)π-electron sy;stem
7	In case of bromo compounds M^+ +2 and M^+ peaks are formed in the intensity ratio	a)1:2	b)3:1	c)1:1	d)3:4	c)1:1
8	Incase of choloro compounds M^+ and M^++2 peaks are formed in the intensity ratio	a)1:3	b)2:1	c)4:1	d)3:1	a)1:3

9	McLafferty rearrangement involves the	a)cleavage of a β-bond followed by a γ-hydrogen	b)cleavage of γ-bond followed by β-hydrogen transfer	c)cleavage of α-bond followed by γ-hydrogen	d)cleavage of δ-bond and followed by γ-hydrogen	a)cleavage of a β-bond followed by a γ-hydrogen tra;nsfer
10	InMcLafferty rearrangement ,mechanism involves a -------membered transition state	a)4	b)8	c)5	d)6	a)4
11	Position at metastable peak m* due to the reaction $M_1^{+-------}m_1$* is such that	a)$m^*=m_1^2/M_1$	b)$M_{1=}m_1^2/m^*$	c)$m^*=m_1^2M$	d)$m_1{}^*M=m_1^2$	d)$m_1{}^*M=m_1^2$
12	The relative abundance of the metastable peak m*is often of the order or lesscompared to the abundance of parent ion	a)10^{-2}	b)10^{-1}	c)10^{-3}	d)10^{-5}	a)10^{-2}
13	Conguated olefins show ------intense molecular ion peak as compared to the corresponding non-conjugated olefins	a)less	b)more	c)same	d)poor	a)less
14	Double foussing mass spectrometers are capable of attaining much-------resolving power than single focusing instruments	a)higher	b)lower	c)same	d)poor	b)lower
15	The Retro-Diels-Alder reaction is an example of a multicentered fragmentation mode which is characteristic of	a)olefins	b)alkanes	c)cyclicolefines	d)ketones	a)olefins
16	Nitogen containing compolyunds with an odd number of nitrlogen atoms in the molecule must have an---molecular weight	a)even	b)odd	c)fractional	d)decimal	c)fractional

17	An-----number of nitrogen atoms ,or no nitrogen at all,leads to an even molelcular weight according toNitrogen rule	a)even	b)whole	c)fractional	d)odd	b)whole
18	The metastable A+ions have the same mass as normal ,but simply have less	a)rotational energy	b)vibrational energy	c)translational energy	d)electronic energly	a)rotational energy
19	The first field fre region ,in double fouccing instr;ument,lilies between the	a)electrostatic and magnetic analyzer	b)ion source and the eletrostatic analyzer	c)recorder and ion soouorce	d)ion source and magnetic analyzer	c)recorder and ion soouorce
20	The second field freeanalyser region in a double focusing instrlu;ment lies between	a)electroatatilc and magnetic anallyser	b)ionsource and magnetic analyzer	c)ion source and electrostatic analyzer	d)detectoe and ion source	b)ionsource and magnetic analyzer
21	According toeven electron rule,an evenelectron species will not normally fragment to two	a)even electron species	b)odd electron species	c)even ,odd electron species	d)only neutral molecule	a)even electron species
22	In the homologous series of alkanes the relative height of the parent peak decreases with the-------of molecular mass	a)decrease	b) Increase	c) same value	d) Less value	b) Increase
23	The molelcular ion peak is not detected in	a)primary alcohol	b)secondary alcohol	c)tertiary alcohol	d)olefins	b)secondary alcohol
24	Primary alhols show M^+----18 peaks corresponding to the loss of	a)water	b)H^+ion	c)OH^-ion	d)O^{2-}ion	c)OH^-ion
25	The ----is the most significant peak in thespectra of primary alcohols	a)$CH_2=OH^+$	b)OH^-	c)CH_2^+	d)CH_3	a)$CH_2=OH^+$
26	In aliphatic ethers alkyl cation (or)an oxonium ion is formed by	a)α-cleavage	b)β-cleavage	c)γ-cleavage	d)δ-cleavage	a)α-cleavage
27	In aliphatic acids carboxyl group is directly eliminated by	a)β-cleavage	b)α-cleavage	c)γ-cleavage	d)δ-cleavage	a)β-cleavage
28	Primary amides gives a strong peak at m/e=44 due to	a)H_2N^-	b)NH_3	c)NH_4	d)$H_2N-C=O^-$	b)NH_3

29	For primary amines ,the base peak is formed at m/e 30 due to $CH_2=N^+$ H2 by	a)α-cleavage	b)β- cleavage	c)γ- cleavage	d)δ- cleavage	d)δ- cleavage
30	The Position of metastable peak m* is for m_1=108, m_1=123	a) 100	b) 70	c) 94.8	d) 90	a) 100
31	The substituent group like –OH,-OR,-NH_2 etc., which lower the ionization potential ----------- the relative abundance in aromatic compounds.	a) increase	b) decrease	c) Alter	d) influence	c) Alter
32	The substituent group like ------ etc., which increase the ionization potential, decrease the relative abundance of the aromatic compounds.	a)–NO_2 , -CN	b) –OH,-OR,-NH_2	c) R^+	d) H^+ ion	a)–NO_2 , -CN
33	In mass spectroscopy, the base peak is	a) Farthest to the right of the plot	b) Farthest to the left	c) Tallest peak	d) Peak preceding the isotope peaks	a) Farthest to the right of the plot
34	Mass Spectroscopy is a	a) Low pressure technique	b) High pressure technique	c) High pressure technique	d) Low temperature	c) High pressure technique
35	In mass spectroscopy, the compound containing Chlorine & Bromine show charecteristic ------ peak.	a) Base peak	b) Isotope peak	c) Both	d) None	a) Base peak
36	For primary amines the base peak is formed at -------- due to $CH_2=NH_2^+$	a) m/e=30	b) m/e=40	c) m/e= 50	d) m/e= 60	b) m/e=40
37	In the case a Cyclohexanol molecular ion peak appears at--------	a) m/e=100	b) m/e=108	c) m/e= 99	d) m/e= 101	a) m/e=100
38	A benzyl group will show a very important fragment at m/e values	a) 92	b) 78	c) 77	d) 91	a) 92

39	In aromatic primary amines , a parent ion is formed by the lose of ------- eletron from the lone pair present on the nitrogen atom	a) 1	b) 2	c) 3	d) 4	d) 4
40	A very weak parent ion peak and a prominent (M^+-18) peak would probably indicate	a) Alcohol	b) Ketone	c) Aldehyde	d) Presence of isotope of Oxygen	a) Alcohol
41	The compound whose mass spectrum shows m/e values at 156 (M+, base peak),127 and 29is	a.ethylbromide	b.methyliodide	c.methylbromide	d.ethyliodide	d.ethyliodide
42	For mass spectrum of n-propylbenzene, the m/e value of tropiliun ion is	a.91	b.85	c.41	d.51	a.91
43	Which of the following will not show ESR spectra?	a.O_2	b.C_2H_5	c. N_2	d.Cu^{2+}	c. N_2
44	Predict the number of lines in the ESR spectra of thefollowing systems respectively?1.CH_3CH_2 , 2. CH_3 3. $C_6H_6^-$	a. 4,7,6	b. 2,1,6	c. 5,3,6	d. 12,4,7	d. 12,4,7
45	In mass spectrum of ethylbenzene some of the prominent peaksappearat m/e=106, 91 and 65. Which of the species given below is not responsible for these peaks?	a. Ethyl benzene	b.Ethane	c.Tropiliuum ion	d.$C_5H_5^+$	b.Ethane
46	In mass spectrum the base peak is	a. lowest peak in themass spectrum	b. the largest peak in the mass spectrum	c.medium peak in the massspectrum	d.both lowest and highest peak in the	b. the largest peak in the mass
47	The largest mass spectrum is always the	a.Parent peak	b.first fragment ion peak	c.meclaffetry rearranged ion	d.base peak	d.base peak

48	In malaffetry rearrangent what type of hydrogen involes the cleavage of β bond	a.alpha	b.beta rays	c.gammarays	d.delta	c.gammarays
49	A molecule is fagmented with--- from an electron in mass	a. excessof energy	b. no energy	c.medium energy	d.higher energy	a. excessof energy
50	In the mass spectrum of cyclohexene, the peak at m/e--- is formed in the fairly high abundance	a.82	b.54	c.28	d.14	b.54
51	Mclaffetry rearrangement ion formed at m/e-- from pentene due to loss of ethylene molecule	a.42	b.15	c.28	d.14	a.42
52	The tropilium ion has the m/e value at	a.91	b.85	c.41	d.51	a.91
53	The molecular ion peak inphenol is--	a.intense	a.less abundane	c.more abundance	d.significant	a.intense
54	In catechol the molecular ion peak is---	a.intense	a.less abundane	c.more abundance	d.significant	a.intense
55	In aliphatic aldehydes and ketones the major fragmentation process are	a.alpha cleavage	b.beta cleavage	c.gammacleavage	d. alpha and beta cleavage	d. alpha and beta cleavage
56	The intensity of molecular ion peak ---as the alkyl chain length---	a. decreases,increase	b.increases,increases	c.decreases,decreases	d.increases,decreases	a. decreases,increases
57	In aldehydes and ketones containing--- atom	a)α-hydrogen	b)β- hydrogen	c)γ- hydrogen	d)δ- hydrogen	c)γ- hydrogen
58	In esters the molecular ion peak is	a. strong	b.less intense	c.more intense	d.weak	d.weak
59	The molecular ion abundance of a particular alkyl halide---as the electronegativity of the halogen substituent----	a. decreases,increases	b.increases,increases	c.decreases,decreases	d.increases,decreases	d.increases,decreases
60	The ion peak of aliphatic nitriles is	a. strong	b.less intense	c.more intense	d.weak	d.weak

LECTURE NOTES

UNIT-V

SYLLABUS

Mossbauer and Problems: *Mossbauer spectroscopy – principles - spectrometer - isomer shift - quadrapole interaction - nuclear zeeman splitting – applications.*

Problems involving UV, IR, NMR, Mass spectral data (for compounds not more than 10 carbon atoms).

Mössbauer Spectroscopy

Introduction to Mössbauer Spectroscopy

Mössbauer spectroscopy is a versatile technique that can be used to provide information in many areas of science such as Physics, Chemistry, Biology and Metallurgy. It can give very precise information about the chemical, structural, magnetic and time-dependent properties of a material. Key to the success of the technique is the discovery of recoilless gamma ray emission and absorption, now referred to as the 'Mössbauer Effect', after its discoverer Rudolph Mössbauer, who first observed the effect in 1957 and received the Nobel Prize in Physics in 1961 for his work.

This introduction to the theory and applications of Mössbauer spectroscopy is composed of four sections. First the theory behind the Mössbauer effect is explained. Next how the effect can be used to probe atoms within a system is shown. Then the principal factors of a Mössbauer spectrum are illustrated with spectra taken from research work. Finally a bibliography of books and web sites is given for further and more detailed information.

The Mössbauer Effect

Nuclei in atoms undergo a variety of energy level transitions, often associated with the emission or absorption of a gamma ray. These energy levels are influenced by their surrounding environment, both electronic and magnetic, which can change or split these energy levels. These changes in the energy levels can provide information about the atom's local environment within a system and ought to be observed using resonance-fluorescence. There are, however, two major obstacles in obtaining this information: the 'hyperfine' interactions between the nucleus and its environment are extremely small, and the recoil of the nucleus as the gamma-ray is emitted or absorbed prevents resonance.

In a free nucleus during emission or absorption of a gamma ray it recoils due to conservation of momentum, just like a gun recoils when firing a bullet, with a recoil energy E_R. This recoil is shown in Fig1. The emitted gamma ray has $E_R$less energy than the nuclear transition but to be resonantly absorbed it must be E_R *greater* than the transition energy due to the recoil of the absorbing nucleus. To achieve resonance the loss of the recoil energy must be overcome in some way.

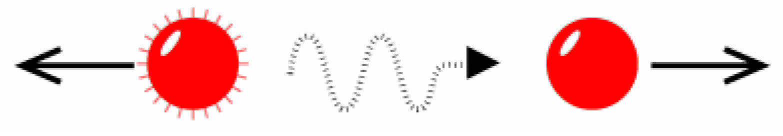


Fig1: Recoil of free nuclei in emission or absorption of a gamma-ray

As the atoms will be moving due to random thermal motion the gamma-ray energy has a spread of values E_D caused by the Doppler effect. This produces a gamma-ray energy profile as shown in Fig2. To produce a resonant signal the two energies need to overlap and this is shown in the red-shaded area. This area is shown exaggerated as in reality it is extremely small, a millionth or less of the gamma-rays are in this region, and impractical as a technique.

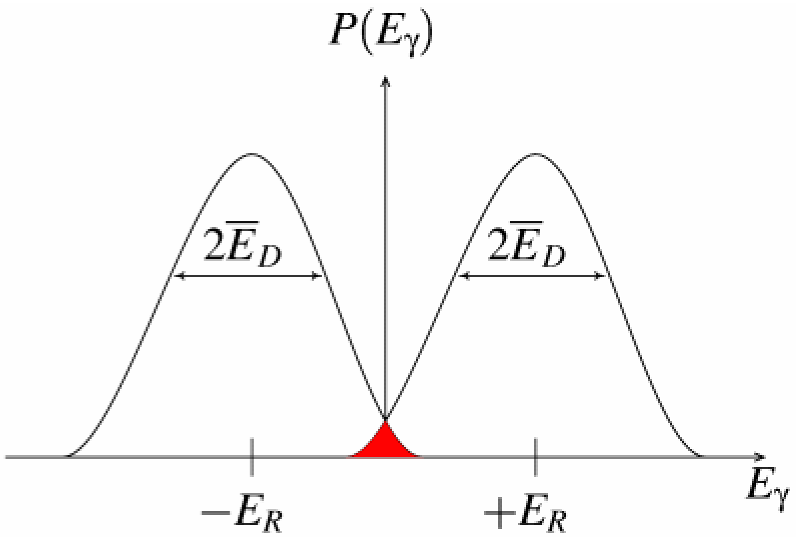


Fig2: Resonant overlap in free atoms. The overlap shown shaded is greatly exaggerated

What Mössbauer discovered is that when the atoms are within a solid matrix the effective mass of the nucleus is very much greater. The recoiling mass is now effectively the mass of the whole system, making E_R and E_D very small. If the gamma-ray energy is small enough the recoil of the nucleus is too low to be transmitted as a phonon (vibration in the crystal lattice) and so the whole system recoils, making the recoil energy practically zero: a recoil-free event. In this situation, as shown in Fig3, if the emitting and absorbing nuclei are in a solid matrix the emitted and absorbed gamma-ray is the same energy: resonance!

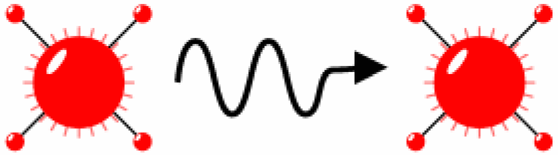


Fig3: Recoil-free emission or absorption of a gamma-ray when the nuclei are in a solid matrix such as a crystal lattice

If emitting and absorbing nuclei are in identical, cubic environments then the transition energies are identical and this produces a spectrum as shown in Fig4: a single absorption line.

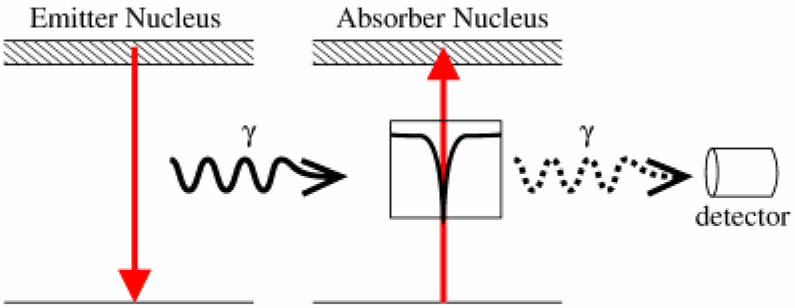


Fig4: Simple Mössbauer spectrum from identical source and absorber

Now that we can achieve resonant emission and absorption can we use it to probe the tiny hyperfine interactions between an atom's nucleus and its environment? The limiting resolution now that recoil and doppler broadening have been eliminated is the natural linewidth of the excited nuclear state. This is related to the average lifetime of the excited state before it decays by emitting the gamma-ray. For the most common Mössbauer isotope, ^{57}Fe, this linewidth is 5×10^{-9}ev. Compared to the Mössbauer gamma-ray energy of 14.4keV this gives a resolution of 1 in 10^{12}, or the equivalent of a small speck of dust on the back of an elephant or one sheet of paper in the distance between the Sun and the Earth. This exceptional resolution is of the order necessary to detect the hyperfine interactions in the nucleus.

As resonance only occurs when the transition energy of the emitting and absorbing nucleus match exactly the effect is isotope specific. The relative number of recoil-free events (and hence the strength of the signal) is strongly dependent upon the gamma-ray energy and so the Mössbauer effect is only detected in isotopes with very low lying excited states. Similarly the resolution is dependent upon the lifetime of the excited state. These two factors limit the number of isotopes that can be used successfully for Mössbauer spectroscopy. The most used is ^{57}Fe, which has both a very low energy gamma-ray and long-lived excited state, matching both requirements well. Fig5 shows the isotopes in which the Mössbauer effect has been detected.

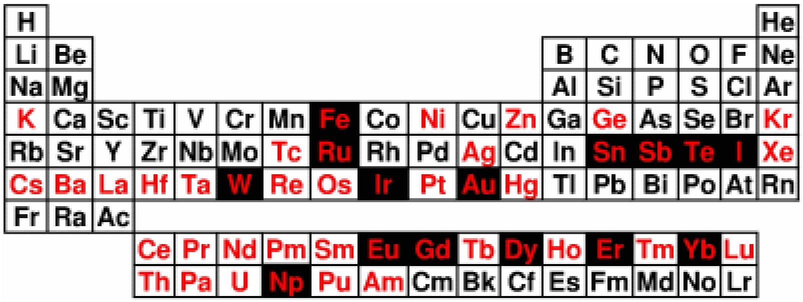


Fig5: Elements of the periodic table which have known Mössbauer isotopes (shown in red font).

So far we have seen one Mössbauer spectrum: a single line corresponding to the emitting and absorbing nuclei being in identical environments. As the environment of the nuclei in a system we want to study will almost certainly be different to our source the hyperfine interactions between the nucleus and the its environment will change the energy of the nuclear transition. To detect this we need to change the energy of our probing gamma-rays. This section will show how this is achieved and the three main ways in which the energy levels are changed and their effect on the spectrum.

Fundamentals of Mössbauer Spectroscopy

As shown previously the energy changes caused by the hyperfine interactions we will want to look at are very small, of the order of billionths of an electron volt. Such miniscule variations of the original gamma-ray are quite easy to achieve by the use of the doppler effect. In the same way that when an ambulance's siren is raised in pitch when it's moving towards you and lowered when moving away from you, our gamma-ray source can be moved towards and away from our absorber. This is most often achieved by oscillating a radioactive source with a velocity of a few mm/s and recording the spectrum in discrete velocity steps. Fractions of mm/s compared to the speed of light ($3x10^{11}$mm/s) gives the minute energy shifts necessary to observe the hyperfine interactions. For convenience the energy scale of a Mössbauer spectrum is thus quoted in terms of the source velocity, as shown in Fig1.

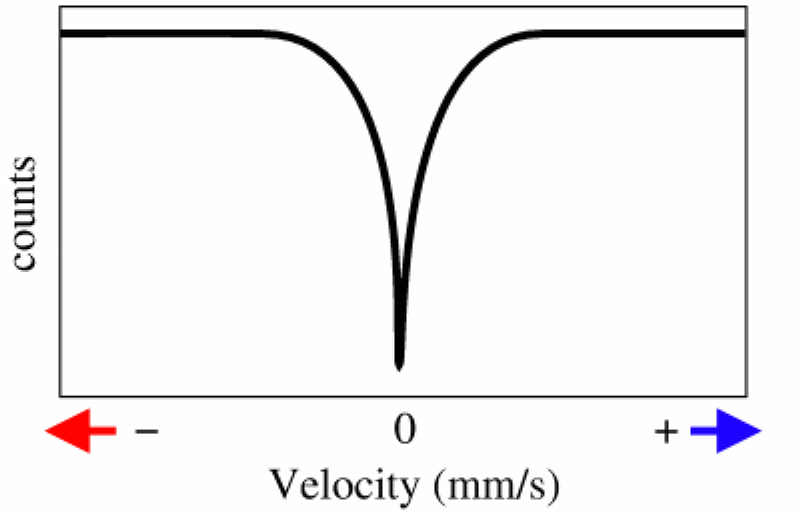


Fig1: Simple spectrum showing the velocity scale and motion of source relative to the absorber

With an oscillating source we can now modulate the energy of the gamma-ray in very small increments. Where the modulated gamma-ray energy matches precisely the energy of a nuclear transition in the absorber the gamma-rays are resonantly absorbed and we see a peak. As we're seeing this in the transmitted gamma-rays the sample must be sufficiently thin to allow the gamma-rays to pass through, the relatively low energy gamma-rays are easily attenuated.

In Fig1 the absorption peak occurs at 0mm/s, where source and absorber are identical. The energy levels in the absorbing nuclei can be modified by their environment in three main ways: by the Isomer Shift, Quadrupole Splitting and Magnetic Splitting.

Isomer Shift

The isomer shift arises due to the non-zero volume of the nucleus and the electron charge density due to s-electrons within it. This leads to a monopole (Coulomb) interaction, altering the nuclear energy levels. Any difference in the s-electron environment between the source and absorber thus produces a shift in the resonance energy of the transition. This shifts the whole spectrum positively or negatively depending upon the s-electron density, and sets the centroid of the spectrum.

As the shift cannot be measured directly it is quoted relative to a known absorber. For example ^{57}Fe Mössbauer spectra will often be quoted relative to alpha-iron at room temperature.

The isomer shift is useful for determining valency states, ligand bonding states, electron shielding and the electron-drawing power of electronegative groups. For example, the electron configurations for Fe^{2+} and Fe^{3+} are $(3d)^6$ and $(3d)^5$respectively. The ferrous ions have less s-electrons at the nucleus due to the greater screening of the d-electrons. Thus ferrous ions have larger positive isomer shifts than ferric ions.

Quadrupole Splitting

Nuclei in states with an angular momentum quantum number I>1/2 have a non-spherical charge distribution. This produces a nuclear quadrupole moment. In the presence of an asymmetrical electric field (produced by an asymmetric electronic charge distribution or ligand arrangement) this splits the nuclear energy levels. The charge distribution is characterised by a single quantity called the Electric Field Gradient (EFG).

In the case of an isotope with a I=3/2 excited state, such as ^{57}Fe or ^{119}Sn, the excited state is split into two substatesm_I=±1/2 and m_I=±3/2. This is shown in Fig2, giving a two line spectrum or 'doublet'.

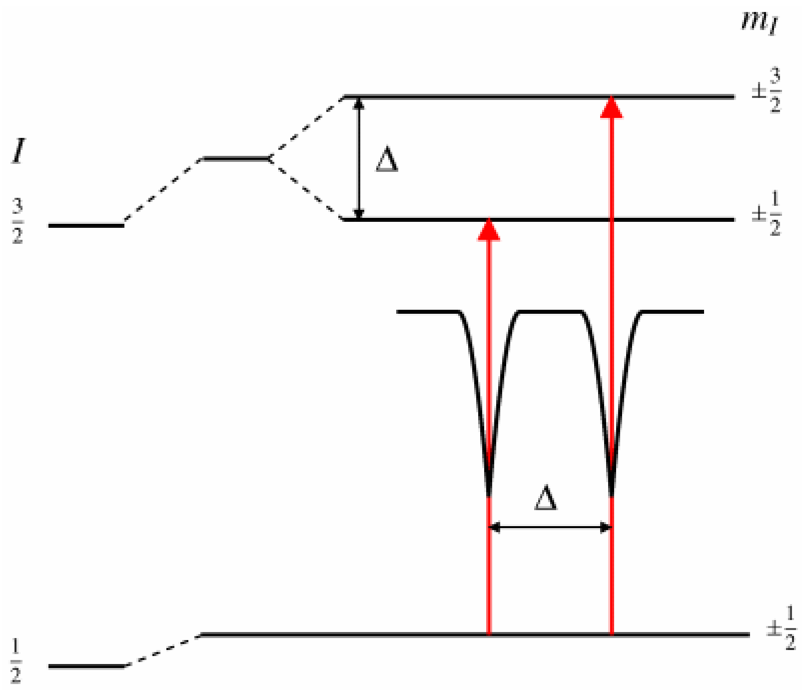


Fig2: Quadrupole splitting for a 3/2 to 1/2 transition. The magnitude of quadrupole splitting, Delta, is shown

The magnitude of splitting, Delta, is related to the nuclear quadrupole moment, Q, and the principle component of the EFG, V_{zz}, by the relation Delta=eQV_{zz}/2.

Magnetic Splitting

In the presence of a magnetic field the nuclear spin moment experiences a dipolar interaction with the magnetic field ie Zeeman splitting. There are many sources of magnetic fields that can be experienced by the nucleus. The total effective magnetic field at the nucleus, B_{eff} is given by:

$$B_{eff} = (B_{contact} + B_{orbital} + B_{dipolar}) + B_{applied}$$

the first three terms being due to the atom's own partially filled electron shells. $B_{contact}$ is due to the spin on those electrons polarising the spin density at the nucleus, $B_{orbital}$ is due to the orbital moment on those electrons, and $B_{dipolar}$ is the dipolar field due to the spin of those electrons.

This magnetic field splits nuclear levels with a spin of I into (2I+1) substates. This is shown in Fig3 for ^{57}Fe. Transitions between the excited state and ground state can only occur where m_I changes by 0 or 1. This gives six possible transitions for a 3/2 to 1/2 transition, giving a sextet as illustrated in Fig3, with the line spacing being proportional to B_{eff}.

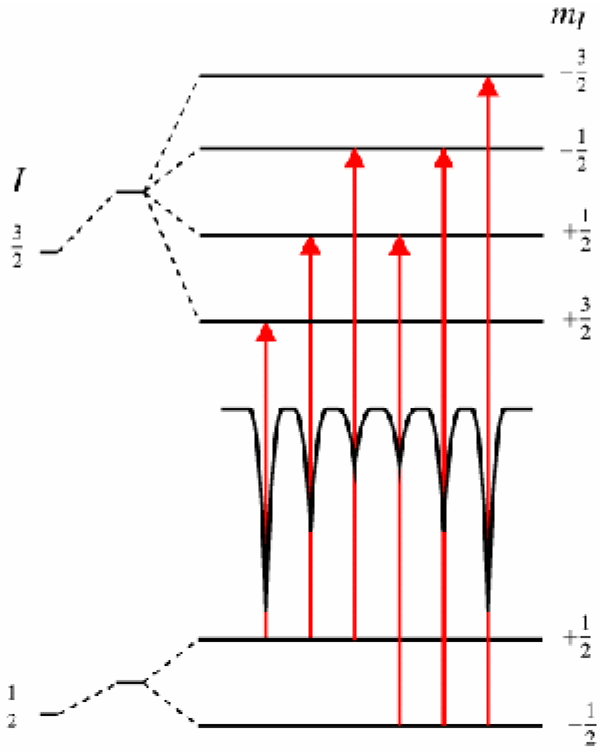


Fig3: Magnetic splitting of the nuclear energy levels

The line positions are related to the splitting of the energy levels, but the line *intensities* are related to the angle between the Mössbauer gamma-ray and the nuclear spin moment. The outer, middle and inner line intensities are related by:

3 : (4sin^{2}theta)/(1+cos^{2}theta) : 1

meaning the outer and inner lines are always in the same proportion but the middle lines can vary in relative intensity between 0 and 4 depending upon the angle the nuclear spin moments make to the gamma-ray. In polycrystalline samples with no applied field this value averages to 2 (as in Fig3) but in single crystals or under applied fields the relative line intensities can give information about moment orientation and magnetic ordering.

These interactions, Isomer Shift, Quadrupole Splitting and Magnetic Splitting, alone or in combination are the primary characteristics of many Mössbauer spectra. The next section will show some recorded spectra which illustrate how measuring these hyperfine interactions can provide valuable information about a system.

This section shows how Mössbauer spectroscopy can be a useful analytical tool for studying a variety of systems and phenomena. The spectra have been taken from active research projects and chosen to visually represent the hyperfine interactions presented in Part 2 and how they can be interpreted.

Example Spectra

Tin dioxide assisted antimony oxidation

Antimony-containing tin dioxide is an important catalyst for selective oxidation of olefins. Of particular importance in studying these systems to is to know the relative concentrations of the antimony charge states (3+ and 5+) during the catalytic process.

Fig1 shows three ^{121}Sb spectra taken at various stages during the catalytic process: 1) fresh Sb_2O_3, 2) Sb_2O_3 calcined at 1000C and 3) the calcined material after catalysis. Firstly the isotope-specificity of Mössbauer spectroscopy picks out only the antimony atoms from the Sn-Sb-O composite. Readily apparent from spectrum 1 is that practically all of the antimony is in a single state (the red component). Comparison with previous experiments shows that the isomer shift for this majority component matches that of Sb3+. The asymmetric shape is due to the quadrupole splitting in this isotope, which has 8 lines (it is a 7/2 to 5/2 transition).

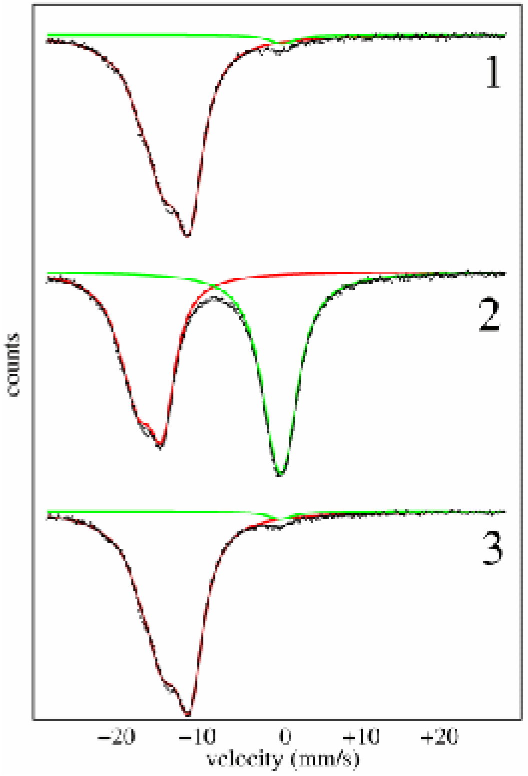


Fig1 shows three ^{121}*Sb spectra taken at various stages during the catalytic process: 1) fresh* Sb_2O_3*, 2)* Sb_2O_3 *calcined at 1000C and 3) the calcined material after catalysis. Firstly the isotope-specificity of Mössbauer spectroscopy picks out only the antimony atoms from the Sn-Sb-O composite. Readily apparent from spectrum 1 is that practically all of the antimony is in a single state (the red component). Comparison with previous experiments shows that the isomer shift for this majority component matches that of Sb3+. The asymmetric shape is due to the quadrupole splitting in this isotope, which has 8 lines (it is a 7/2 to 5/2 transition).*

After calcining the spectrum is now composed of two components of equal area. The second (green) component corresponds to the Sb5+ ion. The component areas give the relative proportion of each site within the compound, in this case 1:1 indicating either Sb_2O_4 or Sb_6O_{13}. After the catalysis in spectrum 3 we can see that the antimony is now all in the 3+ charge state again.

Tin spectra were also recorded, showing a single line spectrum of identical isomer shift during all parts of the process, indicating no change in the tin charge state.

In cases like this basic deductions can be made even without computer analysis: one can simply see one component appear and disappear and the differences in isomer shift are readily apparent. Unfortunately it isn't always quite this obvious!

Off-center tin atoms in PbSnTeSe

Off-center impurities are those which can be displaced from their regular positions in a crystal lattice. They can be considered as existing in an asymmetric double potential well. Such atoms can change their position as the temperature changes. Unfortunately there are often many other phenomena in such systems that can mask the off-centering effect.

Mössbauer spectroscopy provides a good tool for observing this effect. Firstly the movement of the off-center atom within the lattice will change the symmetry of the electric field it is in: hence changing the quadrupole splitting. Mössbauer spectroscopy is also isotope and site specific, meaning we can observe the off-center single component without any masking from other elements or effects.

A compound which was thought to exhibit off-centering is $Pb_{0.8}Sn_{0.2}Te_{0.8}Se_{0.2}$, with tin as an off-center atom. Spectra are shown in Fig2 from this sample at 200K and 20K. There are two components: one from an off-center site and one from a normal single-potential site. It can be seen in the highlighted region that the small green component develops from a single line to a (broad) doublet. The quadrupole splitting is increasing, indicating the electric field environment around these particular atoms is become more asymmetrical. This is consistent with an atom moving within an asymmetric potential well.

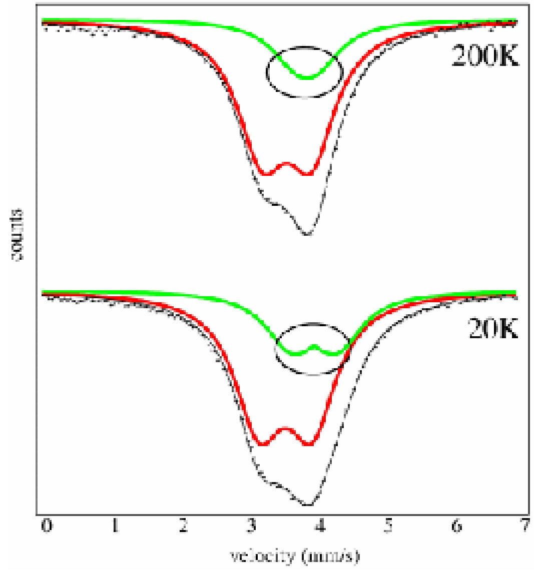


Fig2: ^{119}*Sn Mössbauer spectra showing the quadrupole splitting as an off-center atom changes position with a change in temperature*

The other component shows no variation in quadrupole splitting. A series of spectra were taken in a temperature cycle and a hysteresis was observed in the values of quadrupole splitting. These results show that tin is an off-center atom in this compound and that there are two tin sites within it: one normal and one off-center.

Uranium/Iron multilayers

Magnetic multilayers are very important in today's technology, particularly in the areas of data storage and retrieval. A recent development is the use of actinides, such as uranium. Uranium in the right environment displays very large orbital magnetic moments, crucial to engineering systems with strong magnetic anisotropy and for magneto-optical applications. As part of this research sputtered Uranium/Iron multilayers have been produced and Mössbauer spectroscopy has been used to investigate the state of the iron within them.

As these samples are sputtered onto a thick substrate we cannot use conventional Mössbauer spectroscopy in Transmission Mode (TM) as the substrate would block the gamma-rays and we would receive no signal at all. There is a technique known as Conversion Electron Mössbauer Spectroscopy or CEMS which records the conversion electrons emitted by the resonantly excited nuclei in the absorber. In TM mode we record the absorption peaks as the gamma-rays are resonantly absorbed and so see dips, whilst in CEMS we record the electrons emitted from those excited nuclei and so see emission peaks. As the electrons are strongly attenuated by the sample as they pass through it most of the signal only comes from the uppermost 1000Angstroms.

Fig3 shows ^{57}Fe CEMS spectra from three Uranium/Iron multilayers of varying layer thicknesses. They are composed of three components: two sextets and one doublet. The hyperfine parameters of the two sextets correspond to alpha-iron, the red component being fully crystalline and the green component being from diffuse and poorly crystalline alpha-iron. The magnetic splitting shows that the iron in these two components is magnetically ordered.

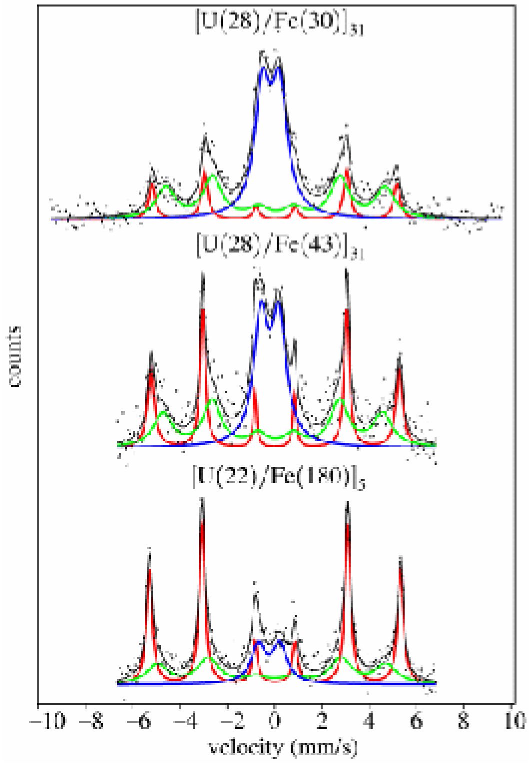


Fig3: ^{57}Fe CEMS spectra taken from U/Fe multilayers of varying layer thicknesses

The third component has an isomer shift and quadrupole splitting consistent with previous work on the UFe_2 intermetallic. This is paramagnetic at room temperature, as shown by the doublet. It is a doublet and not a sextet even though the intermetallic has a magnetic moment as the moment direction changes much faster in the paramagnetic state than the time it takes Mössbauer spectroscopy to record it and thus the experienced hyperfine field averages to zero.

As the iron layer thickness is increased to 43Angstroms the relative proportion of alpha-iron to UFe_2 increases and also the proportion of fully crystalline iron increases. As the iron layer is increased further to 180Angstroms this proportion becomes even greater. We can deduce from this that the thicker the iron layer the greater the *proportion* of crystalline iron, but more detailed analysis of the component areas compared to the layer thickness shows that the absolute thicknesses of the poorly crystalline iron and UFe_2 stay roughly constant.

Mössbauer spectroscopy has easily shown the existence of the three different iron sites within the sample and how their proportion has varied with layer thickness.

Superspin glass transition in $Al_{49}Fe_{30}Cu_{21}$

The magnetic properties of granular alloys and heterogeneous nanostructures built by ferromagnetic and non-magnetic components attract much attention due both to the fundamental interest of their rich phenomenology and to their potential applications, for instance in magnetoresistive devices and magnetic recording. Of particular interest are superspin glasses but their study is made difficult by the different possible sources for non-equilibrium magnetic behaviour and the mixtures of particle phases within the samples.

Mössbauer spectroscopy, as seen in the previous examples, is very good at distinguishing particular sites or phases within a sample. And as seen in the previous example can show the difference between magnetically ordered and paramagnetic sites. As the superspin glass phase reaches its freezing temperature the atoms become magnetically ordered and this will show up in the spectra as a sextet appearing.

A series of ^{57}Fe spectra were recorded from a ball-milled sample of $Al_{49}Fe_{30}Cu_{21}$ with decreasing temperature, shown in Fig4. At 40K, above the freezing temperature, there are two components of unequal proportion, both doublets. As the temperature is reduced the smaller component starts to spread outwards into a magnetic sextet. The peaks are broad and diffuse due to there being a distribution of grain sizes within the sample and hence a distribution of magnetic hyperfine fields. Plotting the recorded hyperfine field against temperature can then give the superspin glass transition temperature for this compound.

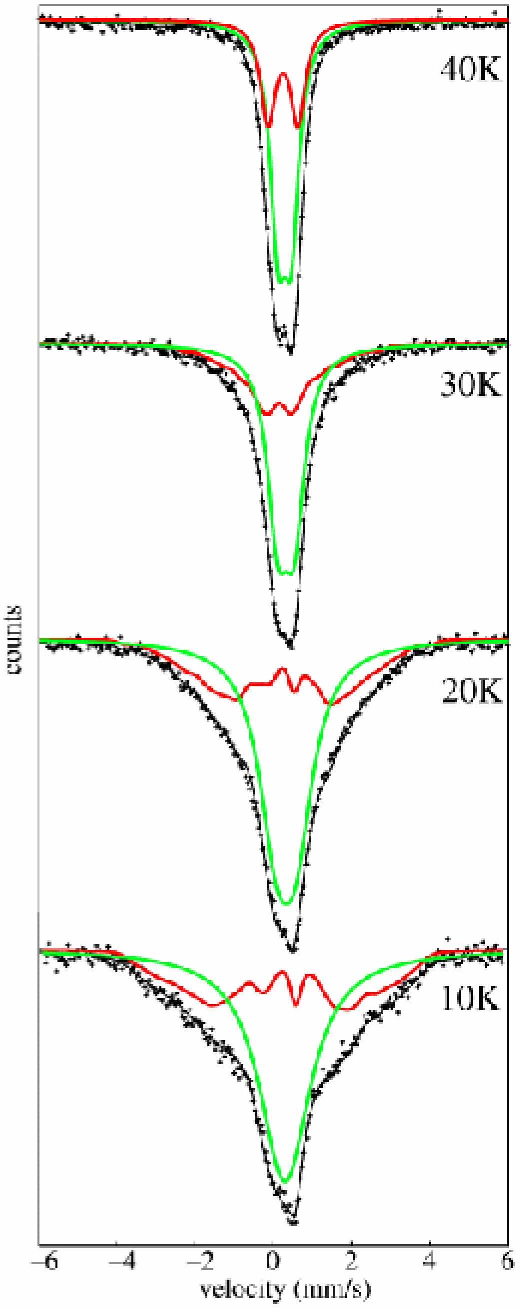


Fig4: Series of ^{57}*Fe Mössbauer spectra showing the superspin glass transition in nanogranular* $Al_{49}Fe_{30}Cu_{21}$

Mössbauer spectroscopy showed quite readily the onset of the superspin glass 'freezing' and the proportion of the magnetic particles and their surrounding non-magnetic matrix. Analysis of the hyperfine field distribution also proved consistent with that expected for a superspinglass.This section shows how Mössbauer spectroscopy can be a useful analytical tool for studying a variety of systems and phenomena. The spectra have been taken from active research projects and chosen to visually represent the hyperfine interactions presented in Part 2 and how they can be interpreted.

Ultraviolet-Visible (UV-Vis) Spectroscopy – Sample Problems Using Woodward-Fieser Rules

Introduction

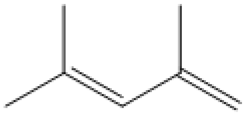
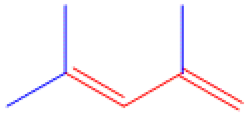
In this page we discuss a few examples of how we can utilize the Woodward-Fieser rules to determine the wavelength of maximum absorption for some molecules. We highly recommend that you read up the first two sections on the Woodward rules to calculate the λmax for conjugated dienes and the Woodward rules to calculate the λmax for unsaturated carbonyl compounds, before you read this page.

Note: Numerical values for Woodward-Fieser rules differ slightly from one textbook to another. We have tried to compile an extensive list of numerical values from online resources, textbooks and journal articles based on the popularity of the number. It is recommended that you learn on how to apply the values for the contributors and then follow the values given in a text book recommended by your teacher, or use our values. We believe that learning how to apply the rules is more essential than actually getting the exact answer. Other's opinions may vary.

In these sample problems you will be shown the structure, then the structure is highlighted to show you key features which would affect the λmax of the molecule. Then the table will show you the solutions on how to solve to get the wavelength of maximum absorption, with a final calculated λmax using the Woodward-Fieser rules. In some cases if we have an observed λmax for comparison, it may be given as well.

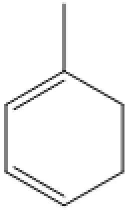
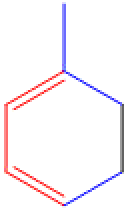
Note- If you have your own problems please write the IUPAC name in the comments section and I will attempt to solve it and add it to this list of examples.

Example/Sample Problem 1

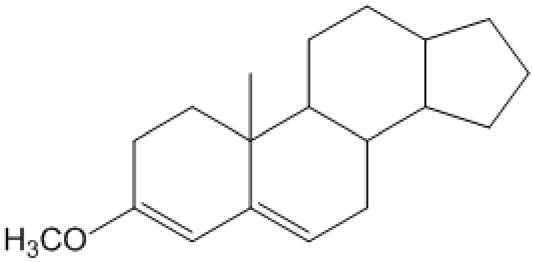
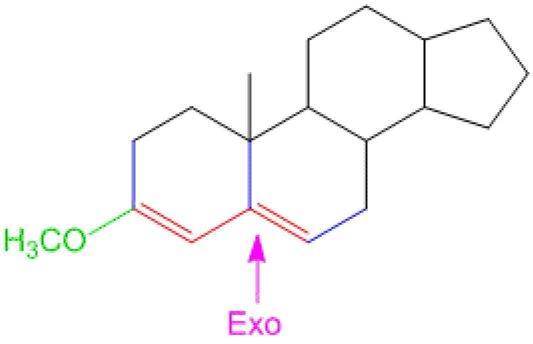
Name of Compound	2,4-dimethylpenta-1,3-diene
Woodward Component	**Contribution**
Core- Transoid/HeteroannularDiene	+ 215 nm
Substituents- 3 alkyl groups	3 x 5 = + 15 nm
Other Effects	0
Calculated λmax	**230 nm**
Observed λmax	234 nm

Example/Sample Problem 2

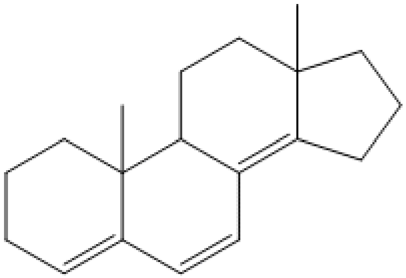
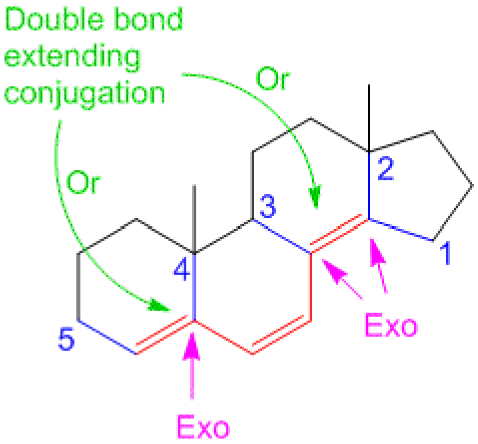
	
Name of Compound	1-methylcyclohexa-1,3-diene
Woodward Component	**Contribution**
Core- Cisoid/HomoannularDiene	+ 253 nm
Substituents- 3 alkyl groups	3 x 5 = + 15 nm
Other Effects	0
Calculated λmax	**268 nm**

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/HeteroannularDiene	+ 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

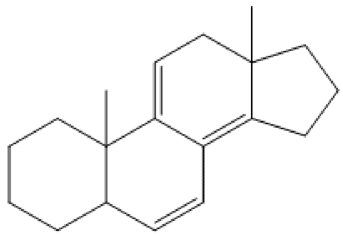
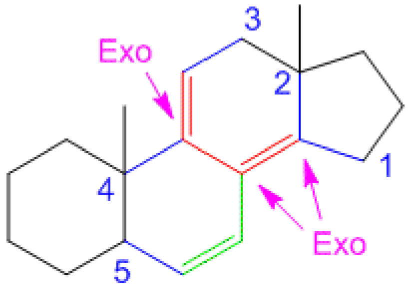
Example/Sample Problem 4

	
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

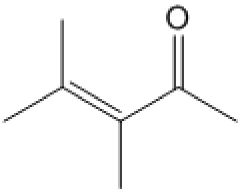
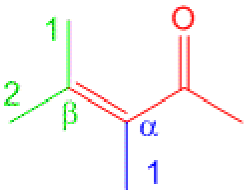
Example/Sample Problem 5

Note- In this example the molecule **contains both, a homoannulardiene system and a heteroannulardiene** system. In such a molecule the core chromophore is considered to be the homoannular system and accordingly the calculations are performed.

Homoannular system

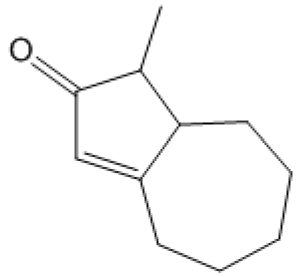
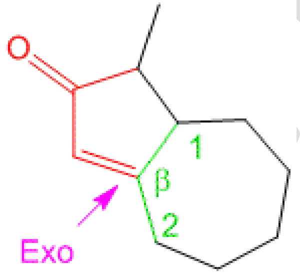
	
Component	**Contribution**
Core- Homoannular/Cisoiddiene	+ 253 nm
Substituents– 5 alkyl substituents Double bond extending conjugation	5 x 5 = + 25 nm + 30 nm
Other Effects- 3 Exocyclic double bonds	3 x 5 = + 15 nm
Calculated λ_{max}	**323 nm**
Observed λ_{max}	n/a

Example/Sample Problem 6

	
Name of Compound	3,4-dimethylpent-3-en-2-one
Component	**Contribution**

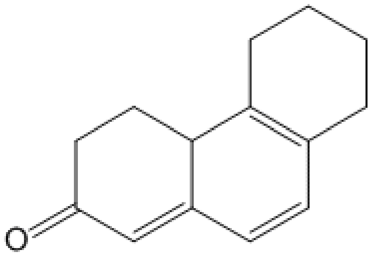
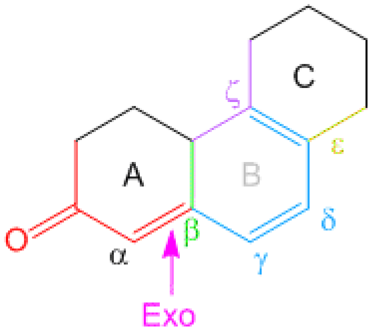
Core- α,β-unsaturated ketone	+ 215 nm
Substituents at α-position- 1 alkyl group	+ 10 nm
Substituents at β-position- 2 alkyl groups	2 x 12 = 24 nm
Other Effects	0
Calculated λ_{max}	**249 nm**
Observed λ_{max}	249 nm

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

HomoannularDiene system in ring B 1 Exocyclic double bond	+ 35 nm + 5 nm
Calculated λ_{max}	**381 nm**
Observed λ_{max}	388 nm

Note- If you have your own problems please write the IUPAC name in the comments section and I will attempt to solve it and add it to this list of examples.

IR Spectroscopy: Some Simple Practice Problems

By itself, Infrared (IR) spectroscopy isn't a great technique for solving the structure of an unknown molecule. However, we've seen that IR spectroscopy can a great technique for identifying *certain* functional groups in an unknown molecule – especially functional groups containing OH or C=O.

For instance, in an earlier post on the structure determination of deer tarsal gland pheromone, we saw how the authors of the study used IR spectroscopy to identify the presence of a lactone functional group (i.e. a cyclic ester) by its characteristic absorbance at 1775 cm^{-1}.

Additionally, if you've narrowed down a structure to several possibilities, it can be very helpful in ruling various possibilities *out.*

In this post we're going to go through four (simple) practice problems where you'll be provided with an IR spectrum and the molecular formula, and are then charged with the task of figuring out which molecule **best** fits the spectrum.

Everything you need to know about IR in order to solve the problems below was presented in the previous post on how to do quick analyses of IR spectra, so go back and read that if you haven't done so already.

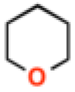
Let's begin.

(answers to each problem, along with analysis, are at the bottom of the post. **Don't peek until you've given each problem a thorough attempt**).

Problem #1: Unknown molecule with molecular formula $C_5H_{10}O$. Which of these five molecules is it most likely to be?

Which of these molecules best corresponds to the IR spectrum below?

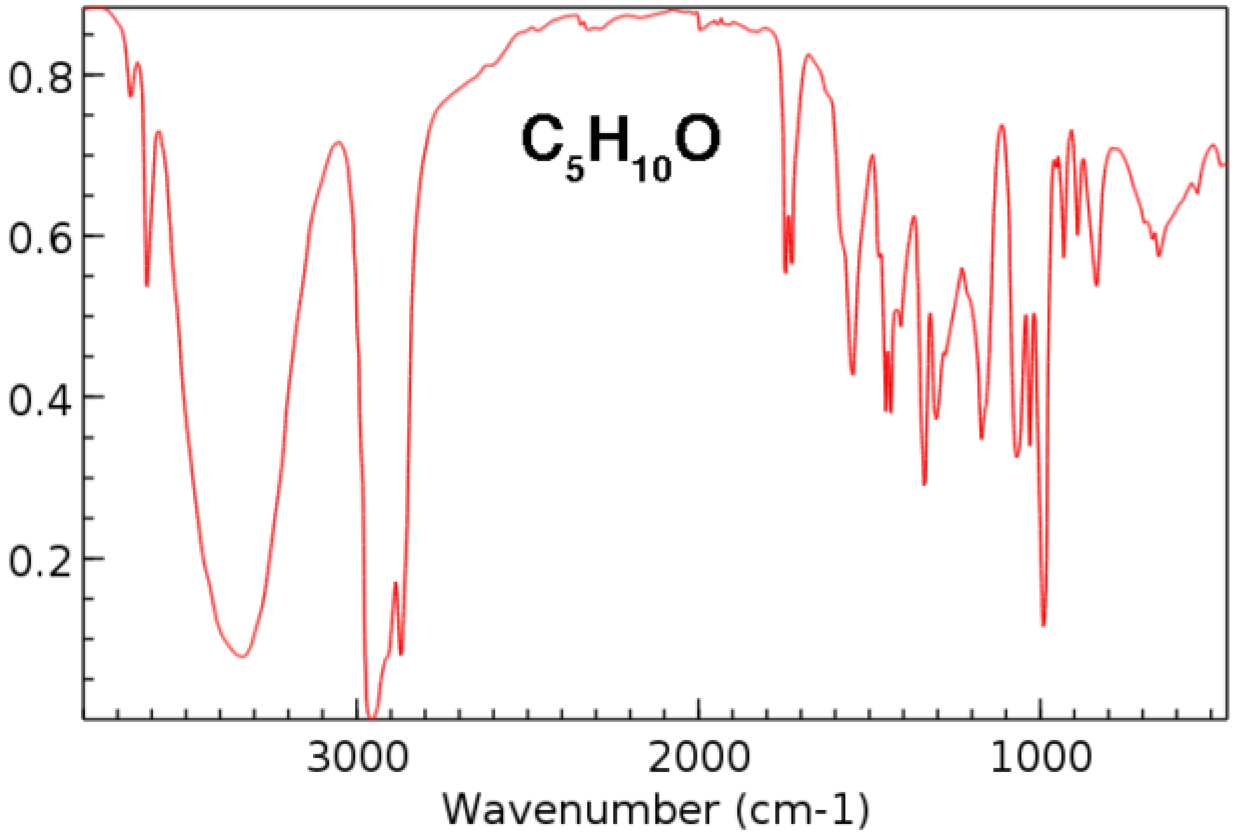
a)


b)


c)

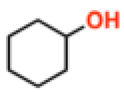

d)

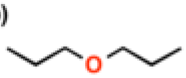

e)

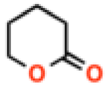



Problem #2: Unknown molecule with molecular formula $C_6H_{12}O$.

Which of these molecules best corresponds to the IR spectrum below?

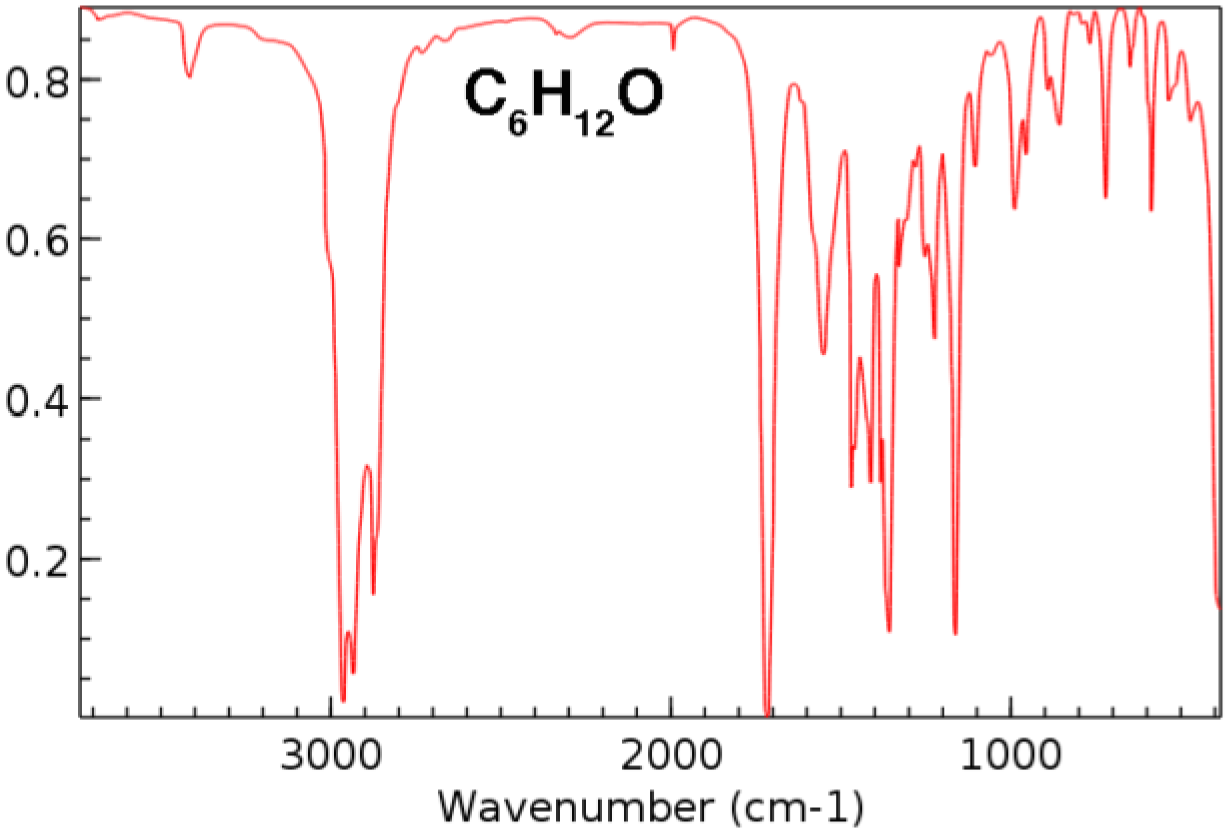
a)


b)


c)


d)


e)

Problem #3: Unknown molecule with molecular formula $C_6H_{14}O$.

Which of these molecules best corresponds to the IR spectrum below with molecular formula $C_6H_{14}O$?

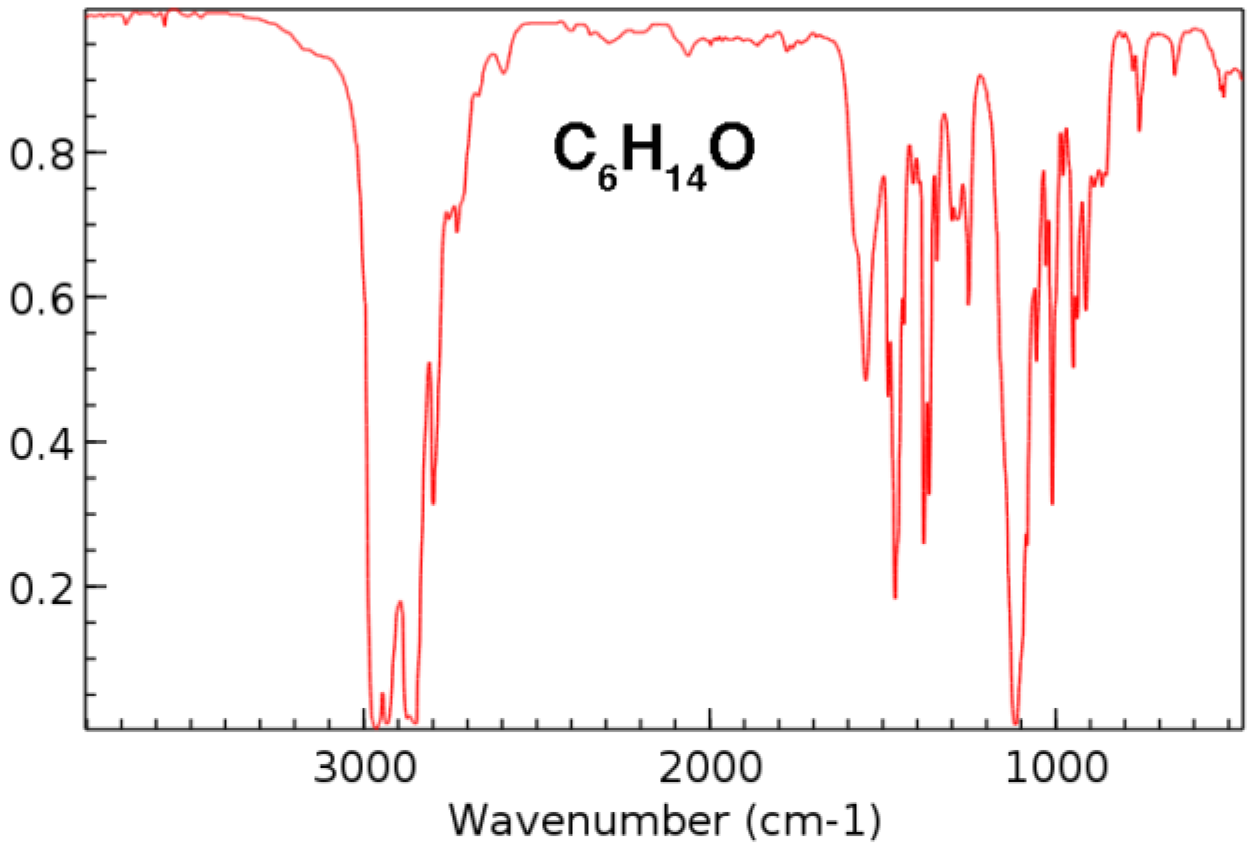
a)


b)


c)

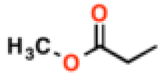

d)


e)

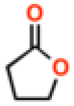



Problem #4: Unknown molecule with formula $C_4H_8O_2$ (Also, smells like vomit)

Which of these molecules best corresponds to the IR spectrum below?

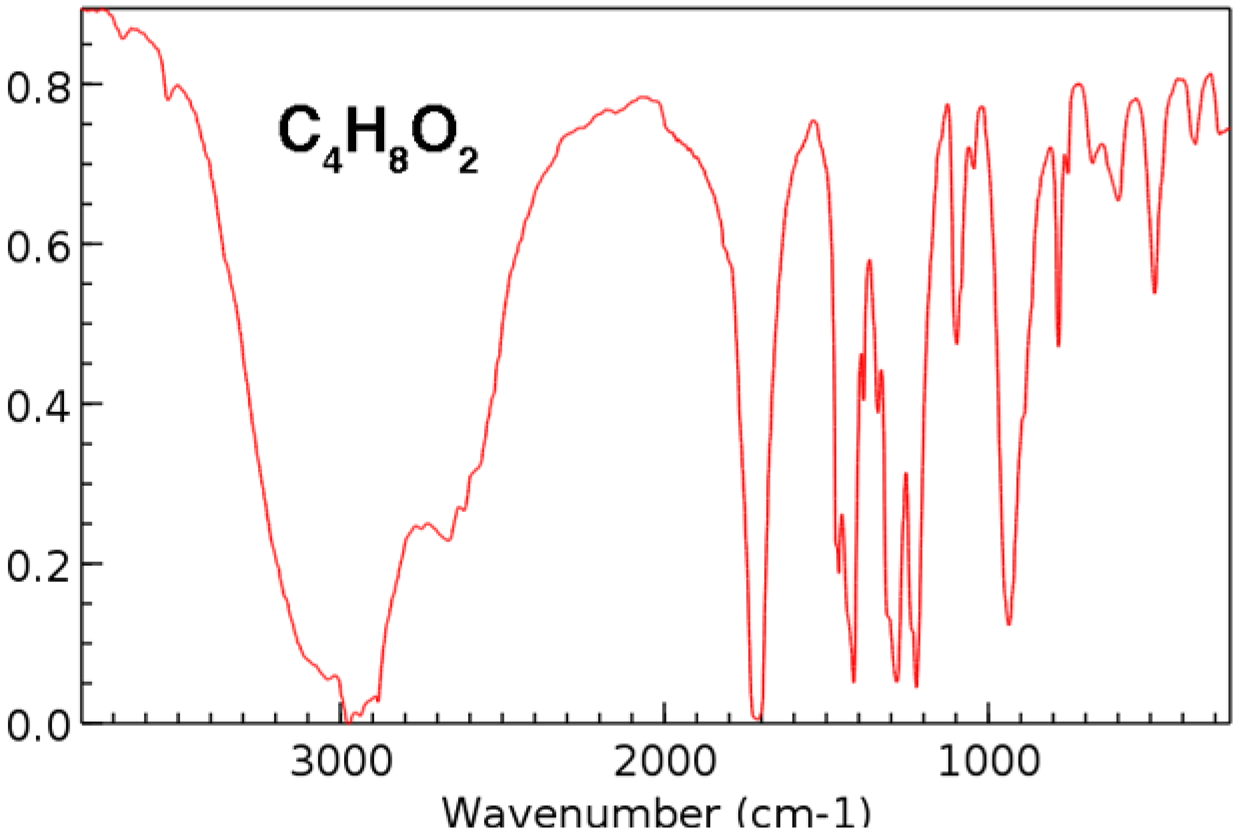
a) 

b) 

c) 

d) 

e) 



Answers

Problem 1:

- You're given the molecular formula, which is $C_5H_{10}O$. This corresponds to an index of hydrogen deficiency (IHD) of 1, so either a double bond or ring is present in the molecule. This immediately rules out **d)** whose IHD is zero and thus has a molecular formula of $C_5H_{12}O$.
- Looking at the spectrum we see a broad peak at 3300 cm^{-1} and no dominant peak around 1700 cm^{-1} (That peak halfway down around 1700 cm^{-1}? It's too weak to be a C=O.)
- That broad peak at 3300 tells us that we have an alcohol (OH group). The only option that makes sense is **e)** (cyclopentanol) since it has both an OH group and an IHD of 1. It can't be **b)** since that molecule lacks OH.
- **a)** and **c)** are further ruled out by the absence of C=O ; B is ruled out by the presence of the OH at 33oo

Problem 2:

- A molecular formula of C6H12O corresponds to an IHD of 1 so either a double bond or ring is present in the molecule.

- There is no strong OH peak around 3200-3400 cm^{-1} (that little blip around 3400 cm^{-1} is too weak to be an OH). We can immediately rule out **a)** and **e)** .
- However, we do see a peak a little above 1700 cm^{-1} that is one of the strongest peaks in the spectrum. This is a textbook C=O peak. We can safely rule out **b)** which lacks a carbonyl.
- The only option that makes sense is **d)** (2-hexanone) since **c)** doesn't match the molecular formula (two oxygens, five carbons).
- Note also that the C-H region shows all peaks below 3000 cm^{-1} which is what we would expect for a saturated ("aliphatic") ketone.

Problem 3:

- A molecular formula of $C_6H_{14}O$ corresponds to an IHD of zero. No double bonds or rings are present in the molecule.
- Using this we can immediately rule out **d)** and **e)** since their structures cannot correspond to molecular formula (they are both $C_6H_{12}O$)
- There is no OH peak visible around 3200-3400 cm^{-1}. We can rule out **a)** and **b)** .
- This leaves us with **c)** . It's an ether.
- Useful tip: ethers are "silent" in the prominent parts of the IR spectrum; this functional group is best identified through a process of deduction. Seeing an O in the formula but no OH or C=O peaks, the only logical selection is **c)** .
- Final note: **e)** is a cyclic ether called an "epoxide". The important clue to distinguish **c**) and **e)** was the fact that we were given the molecular formula. In the absence of that information it would have been difficult to tell the difference without a close consultation of an IR peak table.

Problem 4:

- The immediate giveaway is the smell of puke. That's butyric acid for sure!
- More seriously: the formula of $C_4H_8O_2$ corresponds to an IHD of 1. We can immediately rule out **c)** .
- Looking at the IR spectrum we see a huge peak in the 3300-2600 cm^{-1} region that blots out everything else. This seems like a textbook "hairy beard" typical of a carboxylic acid, but let's look for more information before confirming it. We can at least rule out **a)** , which has no OH peaks.
- We also see a strong peak a little above 1700 cm^{-1} which is typical of a C=O. We can safely rule out **e)** which lacks carbonyl groups entirely.
- This leaves us with two reasonable choices: **b)** (the carboxylic acid) and **d)** the ketone / alcohol. *How to choose between the two?* The "hairy beard" is diagnostic. Alcohol OH peaks don't fill up 600 wavenumber units the way that carboxylic acid peaks do. [Go back and look at a few examples from the previous post if you'd like confirmation] A more subtle way to distinguish the two might be the position of the carbonyl peak, but carboxylic acids (1700-1725 cm^{-1}) show up largely in the same range as do ketones (1705-1725 cm^{-1}).

You might recognize that in each of these four examples we followed a simple procedure:

1. Since we were given the molecular formula, we calculated the **index of hydrogen deficiency.** This is a quick calculation and gives us useful information. We were able to use it to "rule out" a few answers which you might classify as "trick questions".
2. Next, we examined the **hydroxyl region** around 3200-3400 cm for *broad, rounded peaks* ("tongues") typical of OH groups . The most important question we want to answer is: "is there an OH present"?
3. Then, we looked at the **carbonyl region** from about 1650 – 1830 cm for *sharp, strong peaks* ("swords") typical of C=O groups. Here we want to quickly know if there are any C=O groups present.
4. Using these three pieces of information we could then rule out various options that were given to us, narrowing down the possible options. Granted, these were relatively simple examples (only C,H, and O), but the thought process is what's important.

Two final notes in conclusion:

- It's nice to be able to get a positive ID on a functional group, but **ruling things out can be valuable too.** The *absence* of an OH or C=O peak (or both) is still helpful information! We used this in Problem 3 to **infer** the existence of an ether by the absence of an OH or C=O.
- A related point: information you get about a molecule from various sources (e.g. molecular formula, UV-Vis, IR, mass spec, 13-C and 1H NMR) is self-consistent and should not contradict. I like to think of structure determination as being a bit like trying to infer the structure of a three-dimensional object by analyzing the shadows it casts from lights at various angles (or different *wavelengths*, to use a slightly more apt analogy) Through logic and deduction (and perhaps one or two intuitive leaps) we can use the varying layers of information to work backwards to the shape of the object that casts the shadow in the first place.

It's crucial to be able integrate each of these sources of information together. In this post we saw examples of using both index of unsaturation and IR together to draw conclusions about the functional groups present in the molecule. As we move towards increasingly complex spectral techniques, this skill of "integration" will become increasingly more important! As we'll see, solving the structure of an unknown is a bit like filling out one of those "logic squares" you've likely encountered in grade school.

	Red	Yellow	Green	Blue	12	15	18	21	Marmite	Honey	Marmalade	Jam
Peter						X						
Jane			X			X						
Simon					X	●	X	X				
Alice						X						
Marmite												
Honey												
Marmalade												
Jam												
12												
15												
18												
21												

SUGGESTED READINGS:

Text Books:

1. Jag Mohan. (2007). *Organic Spectroscopy: Principles and Applications* (II Edition). New Delhi: Narose Publishing House.
2. Kemp, W. (2004). *Organic Spectroscopy* (III Edition). New York: Palgrave Macmillan.
3. Sharma, Y. R. (2007). Elementary Organic Spectroscopy: Principles and Chemical Applications (V Edition). New Delhi: S. Chand & Company Limited.
4. Silverstein, R. M., Webster, F. X., & Kiemle, D. (2005). *Spectroscopy of Organic Compounds* (VI Edition). New York: John Wiley & Sons.

PART-A

POSSIBLE QUESTIONS

MULTIPLE CHOICE QUESTIONS

1. The energies of the emitted γ-ray is
a) 10 to 150 kev b) **10 to 100 kev** c)10 to 200 kev d)10 to 175 kev

2. The Mossbauer Effect is based on
a) Electromagnetic radiation b) Recoil momentum
c) R**ecoil energy of the nucleus**d) Radioactive source

3. Most commonly used isotopes in Mossbauer spectroscopy is
a)U^{235} b)**Sn^{119}** c)I^{131} d)Fe^{35}

4. Isomer shift is denoted by
a) **δ** b) γ c) λ d)η

5. Quadrupole interaction is related to
a)S-electron density b) nuclear energy level
c)**Symmetry of electron cloud** d)Selection rule

6. Isomer shift is related to
a)**S-electron density** b)nuclear energy level
c)symmetry of electron cloud d)Selection rule

7. Example for ferromagnetic and antiferro magnetic substance
a)Co and Cu b)**Mn and Cr** c)Ni and I d)K and Mn

8. The shift of the resonance curve from zero velocity is termed as
a)quadrupole interaction b)nuclear-Zeeman splitting
c)Doppler shift d) **Isomer shift**

9. Who have investigated the magnetic moments in metals by Mossbauereffect?
a) Johnson b)Lang and marshall c)**Hufner and steiner** d)Zavoisky

10.Mossbauer data for a large number of biochemical have actually been compiled by
a) Jhonson b) **Bhide** c) Hufner and Steiner d) Lang and marshall

11. Mossbauer data for a large number of biochemical have actually been compiled by bhide in………….

a) **1973** b) 1975 c) 1985 d)1978

12. The value of β is

a) **β =0.9723 x 10^{-20}** b) β=0.6723 x 10^{-22}
c) β =0.9723 x 10^{-22}d) β =0.6723 x 10^{-20}

13. Mossbauer effect is also related withresonance fluorescence of---

a)beta rays b) alpha rays c) **gamma rays** d) X-rays

14. Which one is not used as radioactive isotopes for Mossbauer Effect?

a) Fe^{57} b) Zn^{67} c) Sn^{119} d)**P^{31}**

15. Hufner and Steiner have investigated the magnetic moments in………. By MossbauerEffect

a) Metals b) rocks c) woods d) dust

16. Who have preparedspin orientation diagram in rare earth cubic compounds

a) Hufner and Steiner b) **Atzmony and Dariel**
c) Johnson d) Muir

17. In spectroscopy cm-1 is also known as

a)Candela b)**Kayser** c) Lux d)Lumen

18. The resonance gamma ray of 67Zn has a width at half height of only

a) **4.8 x 10^{-11}ev** b) 4.2x 10^{-12} ev c) 4.4 x 10^{-11} ev d) 4.6 x 10^{-11} ev

19. Who demonstrated the resonance absorption in iredium by a different system?

a) **R.L.Mossbauer** b) Moon c) Johnson d) Lang and marshall

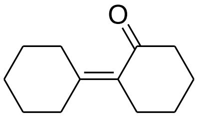
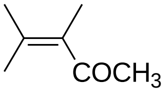
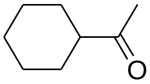
20. Benzene in proton NMR spectroscopy gives

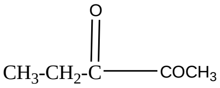
a) no signal b) **only one signal** c) 2 signal d) six signal

PART-B

EACH QUESTION CARRY SIX MARK

1. Calculate the λ_{max} of the following compounds?.

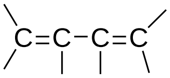
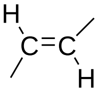
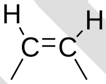
a. 
b. 
c. 

d. 

$CH_3\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{—}COCH_3$

2. Write notes on types of bands in UV?

3.How will you detect the following types of compounds by infra-red spectroscopy?

a. 
b. 
c. 

4. Discuss in detail the various factors that influence the vibrational frequency of a particular group. Give examples.

5. What are the applications of mass spectroscopy?

6. a. How would you distinguish between Ethylamine and triethylamine on the basis of mass spectroscopy?

7. Explain the instrumentation of Mossbauer spectroscopy.

8. (i) Give the probable ppm values to the various kinds of protons in the compound,

CH_2=CH-C=CH_2 with respect to TMS as the standard.

(ii). A hydrocarbon containing 90.9% carbon shows the following four signals:

1. Unsymmetrical multiplet = 2.82τ (5H)
2. Triplet 0.9ppm (2H)
3. Triplet 1.15ppm (2H)
4. Singlet 1.4ppm (3H)

What is the structure of the compound?

9. Illustrate Mossbauer effect and explain with suitable example?

10. Write a note on Moss Bauer spectroscopy principles, Isomer shift and Quadra pole Interaction.

PART-C(COMPULSORY QUESTION)

TEN MARK

1. (i) Give the probable chemical shift values to the various kinds of protons in the compound, $CH_2=CH-C=CH_2$ with respect to TMS as the standard.

(ii). A hydrocarbon containing 90.9% carbon shows the following four signals:

1. Unsymmetrical multiple = 2.82τ (5H)
2. Triplet 0.9 ppm (2H)
3. Triplet 1.15 ppm (2H)
4. Singlet 1.4 ppm (3H)

What is the structure of the compound?

(a) Explain the applications of Mossbauer spectroscopy.

[19CHP104]

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-641021
(For the candidates admitted on 2019 onwards)
DEPARTMENT OF CHEMISTRY
I - SEMESTER
ORGANIC CHEMISTRY

OBJECTIVE TYPE QUESTIONS(EACH QUESTION CARRY ONE MARK)

Unit-5 Mossbauer Spectroscopy and spectral problems (19CHP104)

S.No	Questions	Option a	Option b	Option c	Option d	Answer
1	The energies of the emitted γ-ray is	10 to 150 kev	10 to 100 kev	10 to 200 kev	10 to 175 kev	10 to 100 kev
2	The massbauer effect is based on	electromagnetic	recoil momentum	recoil energy of the	radioactive	recoil energy of the
3	The most commonly used isotopes in mossbauer spectroscopy is	U^{235}	Sn^{119}	I^{131}	Fe^{35}	Sn^{119}
4	Isomer shift is denoted by	δ	γ	λ	η	δ
5	Unit of isomer shift is	mms^{2}	$mm^{-1}s^{3}$	mms^{-1}	mms	mms^{-1}
6	Mossbouer effect increases as the temperature	decreases	increases	decreases with increases	remains constant	decreases
7	Which type of absorber used in Fe^{57}	Barium Stannate	sodium	potassium	Ferrous	sodium
8	Which type of absorber used in Sn^{119}	Barium Stannate	sodium	potassium	Ferrous	Barium Stannate
9	Quadrupole interaction is related to	S-electron	nuclear energy level	symmetry of electron	Selection rule	symmetry of
10	Isomer shift is related to	S-electron	nuclear energy level	symmetry of electron	Selection rule	S-electron density
11	Example for ferromagnetic and antiferro magnetic substance	Co and Cu	Mn and Cr	Ni and I	K and Mn	Mn and Cr
12	The shift of the resonance curve from zero velocity is termed as	quadrupole interaction	nuclear-zeeman splitting	Doppler shift	isomer shift	isomer shift
13	The quadrupole moment is denoted by	eQ	Eq	Ea	Qe	eQ
14	The field gradient is denoted by	S	q	r	e	q
15	The unit of quadrupole moment is	cm^{-1}	cm	cm^{2}	cm^{-2}	cm^{2}
16	Mossbauer work on biological molecule has also been carried out on	Iron sulphur proteins	Iron-phosporous proteins	iron manganees proptein	Iron magnesium protein	Iron sulphur proteins

17	Who made the first systematic study of biological molecules with these proteins using mossbauer effect?	Lang and marshall	Jhonson	Roberts	Shenoy	Lang and marshall
18	Who have used mossbauer effect in the study of iron-sulphur proteins?	Lang and marshall	Jhonson	Owen	Zavoisky	Jhonson
19	Who have investigated the magnetic moments in metals by mossbauer effect?	Jhonson	Lang and marshall	Hufner and steiner	Zavoisky	Hufner and steiner
20	Mossbauer data for a large number of biochemicals have actually been compiled by	Jhonson	Bhide	Hufner and steiner	Lang and marshall	Bhide
21	Mossbauer data for a large number of biochemicals have actually been compiled by bhide in…………	1973	1975	1985	1978	1973
22	The value of β is	$\beta = 0.9723 \times 10^{-}$	$\beta = 0.6723 \times 10^{-22}$	$\beta = 0.9723 \times 10^{-22}$	$\beta = 0.6723 \times 10^{-}$	$a\beta = 0.9723 \times 10^{-20}$
23	Unit of Bohr magneton is	erg/gauss^4	erg/gauss^2	erg/gauss	erg/gauss^3	erg/gauss
24	The first measurements of the mossbauer spectrum of 57Fe in haemin were reported by……….	Gnoser	Jhonson	Bhide	Lang and marshall	Gnoser
25	The first measurements of the mossbauer spectrum of 57Fe in haemin were reported by gnoser in……………..	1962	1965	1982	1972	1962
26	The recoilless fraction of gamma-rays emitted from a source imbedded in a solid lattice is called…………….	Lamb Mossbauer Factor	Chemical shift	Resonance	Crompton effect	Lamb Mossbauer Factor
27	The Debye temperature QD of the crystal structure is ----	Small	remains constant	high	medium	high
28	Isomer shift in the mossbauer spectra reflects differences in the ----------- density around the emitterand absorber nuclei.	s-electron	p-electron	d-electron	f-electron	s-electron

29	Isomer shift------as the s-electron densityandhence the oxidation state-----	decreases, increases	increases,increases	decreases,decreases	increases,decreases	decreases, increases
30	Unit of hyperfine coupling constant is	tesla	tesla^2	tesla^3	tesla^4	tesla
31	Who has studied various phase transitions through mossbauer effect	Shenoy	Roberts	Johnson	Greenwood	Shenoy
32	Mossbauer effect has been used to study the	effect of temperature	effect of pH	effect of concentration	effect of pressure	effect of temperature
33	The nitroxide molecules bound to macromolecules are called	spin free	spin resonance	spin tables	spin paired	spin tables
34	Commonly used nitroxide is	TEMPLO	TEMPOL	TEMMOL	TEPPOL	TEMPOL
35	The Droppler energy shift	V/c	V/e	C/V	e/V	V/c
36	In copper protein complex, copper is	monovalent	divalent	trivalent	tetravalent	divalent
37	In biologically active copper complex, copper is	trivalent	monovalent	divalent	tetravalent	monovalent
38	The temperature of the crystal source is	big	constant	small	high	small
39	ELDOR is	electron nuclear double resonance	electron double resonance	electron nuclear resonance	electron spin resonance	electron double resonance
40	ELDOR technique has been used to study the	free radical mechanism	spin pair mechanism	relaxation mechanism	proton mechanism	relaxation mechanism
41	Mossbauer effect is also related withresonance fluoresence of---	.beta rays	alpha rays	gammarays	X-rays	gammarays
42	Which one is not used as radioactiveisotopes for Massbauer effect?	Fe^{57}	. Zn^{67}	Sn^{119}	P^{31}	P^{31}
43	Hufner and Steiner have investigated the magnetic moments in………. By mossbauer effect	Metals	rocks	woods	dust	Metals
44	Who have preparedspin oreintation diagram in rare earth cubic compounds	Hufner and steiner	Atzmony and Dariel	Johnson	Muir	Atzmony and Dariel
45	Johnson have used mossbauer effect in the study of ---------	Iron sulphur proteins	Iron-phosporous proteins	iron manganees proptein	Iron magnesium protein	Iron sulphur proteins

46	Rubredoxins contain only -----iron sulphur group per molecule	one	two	three	four	one
47	Plant ferredoxins and hydroxylase proteins contain----------iron atoms per molecule	one	two	three	four	two
48	The source of radiationoperating in microwave region used in EPR spectrometer is	Klystron	.W.lamp	.hydrogen discharge tube	.Nernst filament	Klystron
49	In spectroscopy cm-1 is also known as	Candela	Kayser	Lux	Lumen	Kayser
50	The resonancegamma ray of 67Zn has a width at half height of only	4.8 x 10-11 ev	4.2x 10-12 ev	4.4 x 10-11 ev	4.6 x 10-11 ev	4.8 x 10-11 ev
51	Who demonstrated the resonance absorption in iredium by a different system	R.L.Mossbauer	Moon	Johnson	Lang and marshall	R.L.Mossbauer
52	Benzene in proton NMR spectroscopy gives	no signal	only one signal	2 signal	six signal	only one signal
53	An organic compound of molecular formula $C_4H_{10}O$, exhibits in its infra red spectrum a strong band around 1120cm^{-1}, but no absorption above 300 cm^{-1}. the most likely structure of the compound is	diethyl ether	1-butanol	. isopropyl alcohol	tertiary alcohol	.Diethyl ether
54	Which of the following is the value of λ max for alkenes?	175nm	170nm	.165nm	185nm	.175nm
55	In which of the following regio NMR spectra obtained	.microwave region	.Radio wave	.IR region	.UV visible	.Radio wave
56	The energy of the gamma radiationnshould be in the range	.10-200KeV	20-200KeV	100-200KeV	1000-2000KeV	10-200KeV
57	Lamb mossbauer factor (f) is given by	. f=exp(-E/hω$_{E)}$	.f=exp(+e/hω$_{E)}$	.f=exp(E/hω)	.f=exp(+E/hω$_{)}$	. f=exp(-E/hω$_{E)}$
58	Which of the compounds will have multiplets in their NMR spectra?	2-methyl propene	.2-chloropropene	Cyclohexane	Methyl chloride	.2-chloropropene

59	The quantum number involved in the tracition which gave the line at 169 cm-1 are---	9 and 10	10 and 11	.6 and7	8 and 9	9 and 10
60	The molecular formula of a compound is XY2. If thismolecule shows three IR bands, speculate the structure of the molecule-	bent	linear	.bent and linear	angle 120°	bent and linear