

Home Assignment

Write answers in your own hand writing in your Chemistry notes copy. Draw labelled diagram, cite examples, etc. where required.

Submit PDF file at our Google Classroom.

ACR1C2 Chemistry and Environmental Science

Unit-4 Instrumental Techniques in Material Characterization

Q.1 a) Draw and explain basic block diagram of Instrumental techniques used in material testing.

b) Classify Instrumental methods used in material testing with examples.

c) What are advantages and limitations of instrumental techniques over older methods?

Q.2 Derive and Explain Beer-Lamberts law and its applications. Calculate the molar absorptivity of a 3×10^{-4} M solution, which has an absorbance of 0.30, when path length is 1 cm.

Q.3 Explain construction, working and applications of Colorimeter.

Q.4 Define and classify Spectroscopic techniques. What is the basis (principle) of qualitative and quantitative analysis by spectroscopic method?

Q.5 Define and classify Chromatography. What is the role of stationary phase and mobile phase in column chromatography?

Q.6 Which spectroscopic method is best suitable for identification of functional groups present in organic samples? Why this technique is often called “molecular finger prints”?

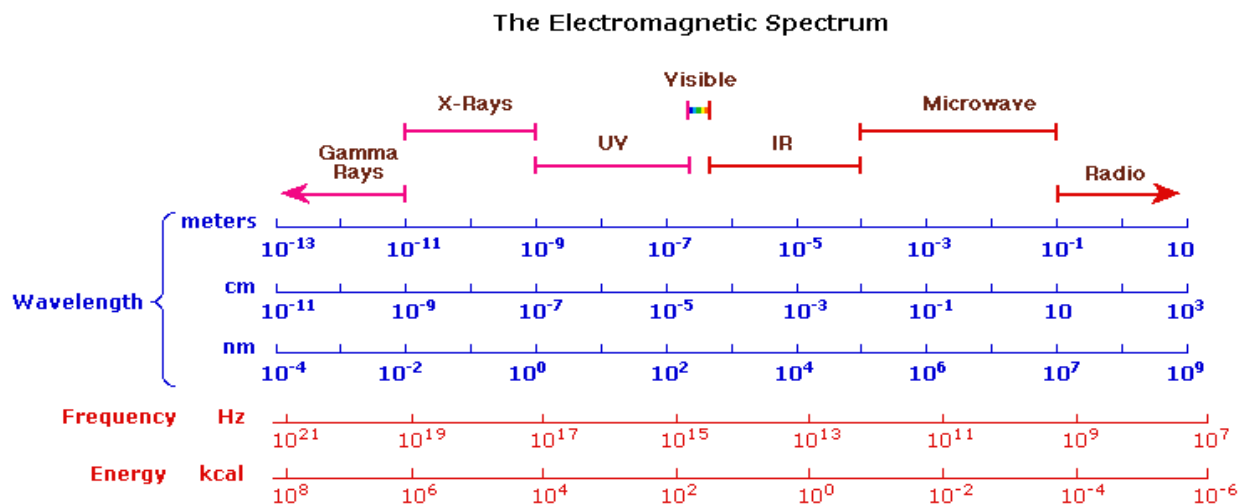
Q.7 Explain H^1 NMR spectroscopy. What informations are obtained by number of peaks, peak height, peaks splitting and position of peaks in the spectrum of sample?

INSTRUMENTAL TECHNIQUES IN CHEMICAL ANALYSIS

Spectroscopy:

Spectroscopy is a method of analysis based on the interaction of electromagnetic radiation and matter in other words spectroscopy is the study of interaction of light with matter. Modern experimental chemistry uses many spectroscopic techniques viz. ultraviolet and visible spectroscopy, infrared spectroscopy, nuclear magnetic resonance spectroscopy, and electron spin resonance spectroscopy. All depend in some manner on the absorption of energy by a collection of molecules, the energy involved being in different regions of the electromagnetic spectrum.

The visible spectrum constitutes a small part of the total radiation spectrum. Most of the radiation that surrounds us cannot be seen, but can be detected by dedicated sensing instruments. This **electromagnetic spectrum** ranges from very short wavelengths (including gamma and x-rays) to very long wavelengths (including microwaves and broadcast radio waves). The following chart displays many of the important regions of this spectrum, and demonstrates the inverse relationship between wavelength and frequency.



Advantages of analytical/spectroscopic techniques

- Fast determination
- Measurements obtained are more accurate
- Reliable
- Reproducible results
- Techniques are more sensitive
- Small amount of sample is required
- Recovery of sample is possible because most of the techniques are non destructive
- Easy handling
- Independent of atmospheric conditions
- No side reaction/product formation
- Chemicals/reagents are not required
- Methods are clean
- Complex sample can be handled easily
- Process can be made automatic

TRANSMITTANCE: The transmittance of a sample is the ratio of the intensity of the light that has passed through the sample to the intensity of the light when it entered the sample ($T = I_{\text{out}} / I_{\text{in}}$) or the ratio of transmitted light to the incident radiation i.e.

$$T = \frac{I_t}{I_0}$$

It is expressed in terms of % T i.e. $T \times 100$ or

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

ABSORBANCE: Absorbance is the measure of the quantity of light that a sample neither transmits nor reflects and is proportional to the concentration of a substance in a solution or a measure of the light-absorbing ability of an object, expressed as the logarithm to base 10 of the reciprocal of the transmittance or Negative log of transmittance

$$A = -\log T = -\log \frac{I_t}{I_0}$$

LAMBERT'S LAW: The statement of Lambert's law is "When a monochromatic light passes through a transparent medium the decrease in the intensity of light with respect to the thickness of the medium is proportional to the intensity of incident light."

$$-\frac{dI}{dx} \propto I, \text{ or } -\frac{dI}{dx} = k \cdot I \quad \text{or} \quad \frac{dI}{I} = -k \cdot dx \quad \text{after integration}$$

$$\int_{I_0}^{I_t} \frac{dI}{I} = -k \cdot \int_{x=0}^{x=x} dx$$

$$[\ln I]_{I_0}^{I_t} = -k \cdot x$$

$$\ln \frac{I_t}{I_0} = -k \cdot x$$

$$2.303 \cdot \log \frac{I_t}{I_0} = -k \cdot x \quad \text{or} \quad -\log \frac{I_t}{I_0} = k \cdot x$$

$$\frac{I_t}{I_0} = e^{-k \cdot x} \quad \text{or} \quad I_t = I_0 \cdot e^{-k \cdot x}$$

$$A = k' \cdot x \quad \text{or} \quad A \propto x$$

BEER'S LAW: The statement of Beer's law is "When a light of monochromatic radiation passes through a transparent medium the intensity of the radiation decreases exponentially as the concentration of absorbing medium increases arithmetically."

$$\frac{I_t}{I_0} = e^{-k \cdot c} \quad \text{or} \quad I_t = I_0 \cdot e^{-k \cdot c}$$

In other words

$$2.303 \cdot \log \frac{I_t}{I_0} = -k \cdot c$$

$$-\log \frac{I_t}{I_0} = k \cdot c$$

$$A = k' \cdot c \quad \text{or} \quad A \propto c$$

COMBINED BEER'S-LAMBERT'S LAW

From Lambert's law: $A \propto x$ and

From Beer's law: $A \propto c$

Combining these two results

$$A \propto x.c \quad \text{or} \quad A = \epsilon.x.c$$

Where c = Concentration of solute in Mole/liter,

x = The length of cell in cm and

ϵ = A constant characteristic of the solute called molar extinction coefficient or molar absorptivity. The unit of ϵ (molar extinction coefficient) is $L \text{ mole}^{-1} \text{ cm}^{-1}$.

Colorimetry

Colorimetry concerns with the measurement of visible light absorbed by a colored sample. Colorimetry is method of determining the concentration of a substance by measuring the relative absorption of light (usually visible) with respect to a known concentration of the substance. The most important idea in colorimetry is that color intensity is proportional to the concentration (at lower concentration). The instrument by which these measurements are made is called a colorimeter.

Colorimeter: A colorimeter is a device by which absorption measurements are made in colorimetry. In scientific fields the word generally refers to the device that measures the absorbance of particular wavelengths of light by a specific solution. This device is most commonly used to determine the concentration of a known solute in a given solution by the application of the Beer-Lambert law.

The essential parts of a colorimeter are:

- A light source (often an ordinary low-voltage filament lamp or Light Emitting Diodes (LED's))
- An adjustable aperture
- A set of colored filters
- A cuvette with a fixed path length, to hold the working solution
- A detector (usually a photo-resistor) to measure the transmitted light
- A meter to display the output from the detector

In addition, there may be a voltage regulator, to protect the instrument from fluctuations in mains voltage.

Light source: A colorimeter requires a light source. In most of the colorimeters, the light source uses tungsten bulb or Light Emitting Diodes (LED's) in more advance colorimeters. The advantage of using LED's is longer battery life and its temperature stability which does not shift wavelength with changes in temperature.

Filters: The filter removes all light except the wavelengths used for the analysis. Changeable optics filters are used in the colorimeter to select the wavelength of light which the solute absorbs the most, in order to maximize accuracy. The usual wavelength range is from 400 to 700 nanometers (nm).

Detector: The detector determines how much light was transmitted through the sample for correlation to concentration. Most commonly used detector is photo-cell.

Output: The output from a colorimeter may be displayed by a galvanometer or digital meter and may be shown as transmittance (a linear scale from 0-100%) or as absorbance (a logarithmic scale from zero to infinity).

Working of colorimeter: Light from a suitable source is passed through a light filter to select the most appropriate wavelength of light, some of which is then absorbed by the solution held in a special glass cuvette (a sort of 'test tube'). The amount of light transmitted by the sample is recorded and converted into absorbance which is a function of the coloured solute concentration. The absorbance and transmittance are related by the following formula-

$$A = -\log T \quad \text{or} \quad A = 2 - \log \%T$$

Determination of concentration of unknown sample

1. Calibration-curve method or Trend-line method:

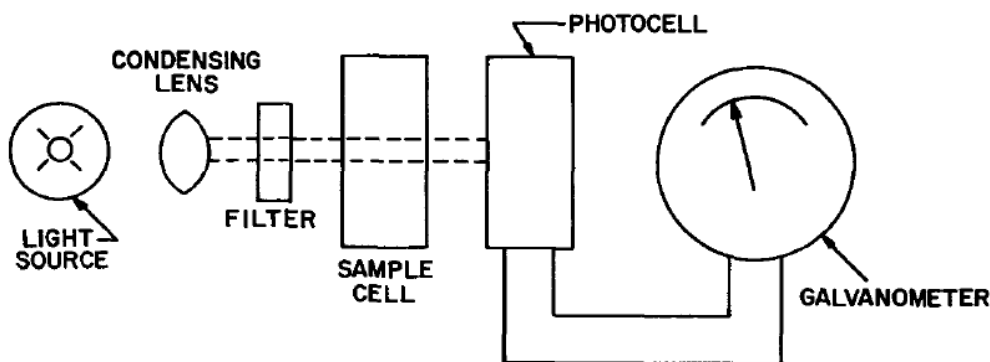
2. **Standard sample method:** For the determination of concentration of unknown sample one known sample is prepared. The absorbance of both, the known and unknown sample is recorded and the unknown concentration is determined using the following formula:

$$\frac{A_1}{A_2} = \frac{c_1}{c_2}$$

Where A_1 = Absorbance of known sample,
 c_1 = Concentration of known sample,

A_2 = Absorbance of unknown sample
 c_2 = Concentration of unknown sample

Schematic diagram of apparatus:



Most of the species in water do not have any color, meaning that the species do not absorb light in the visible region. To measure the absorbance of the colorless molecules, a reaction must be found which will produce a color that can be measured. Many approaches are available, and the most used are:

- React the species with a reagent to produce a new compound which has one or more chromophores
- Chelate the species to form a complex with a different color than either the species or the original chelant.
- Use a colored compound which is bleached by the species being analyzed.
- Form an intermediate compound that can be oxidized or reduced afterwards to give a colored compound.

Ultra-Violet Spectroscopy

Ultraviolet spectroscopy is primarily used to measure the multiple bond or aromatic conjugation by measurement of energy absorbed when electrons are promoted to higher energy level. On passing electromagnetic radiation in the UV and Vis region through a compound with multiple bonds; a portion of the radiation is normally absorbed by the compound. The amount of absorption depends on the wavelength of the radiation and the structure of the compound. The absorption of radiation is due to the subtraction of energy from the radiation beam when electrons in orbitals of lower energy are excited into orbitals of higher energy. The ultraviolet spectrum is simply a plot of wavelength of light absorbed versus the absorption intensity (absorbance or transmittance) and is conveniently recorded by plotting molar absorptivity (ϵ) against wavelength (nm). Since (ϵ) values range, in practice from as low as 10 to as high as 10,000, it is convenient to use $\log \epsilon$ as the abscissa of UV spectrum.

A molecule contains electronic, vibrational and rotational energy levels. Each electronic level, within a molecule, is associated with a number of vibrational levels with less energy separation and each vibrational level in turn is associated with a set of rotational levels with even less energy separation. Due to the relatively larger amounts of energy associated with the ultraviolet radiation, they are capable of electronic excitations and induce transition in the electronic, vibrational and rotational energy levels of a molecule. Thus, the ultraviolet spectrum of a molecule results from transition between electronic energy levels accompanied by changes both in vibrational and rotational states.

The strength of absorption i.e. molar absorptivity or ϵ_{\max} is defined by combined Beer's- Lambert's law-

$$\text{Log } (I_0/I) = \epsilon.C.l = A$$

The principal characteristics of an absorption band are its position and intensity. The position of absorption corresponds to the wavelength of radiation whose energy is equal to that required for an electronic transition. The intensity of absorption is largely dependent on two factors:

1. The probability of interaction between the radiation energy and the electronic system
2. the difference between the ground state and excited state

The molar absorptivity ϵ is a constant for an organic compound at a given wavelength, and is reported as ϵ_{\max} (molar absorptivity at an absorption maximum). It may be mentioned that ϵ is not dimensionless, but is correctly expressed in unit of $10^{-2} \text{ m}^2 \text{ mol}^{-1}$ but the unit is by convention never expressed. The intensity of absorption is directly proportional to the transition probability. A fully allowed transition will have ϵ value greater than 10000 and it is called high intensity absorption. The transition with low transition probability and the ϵ value less than 100 are called low intensity transitions. Transitions with low intensity are due to forbidden transitions.

Some important terms

Chromophore: a covalently unsaturated group responsible for electronic absorptions or any group of atoms that absorbs light whether or not a color is thereby produced. For example C=C, C=O, NO₂ etc. A compound containing chromophore is called chromogen. There are two types of chromophore

1. **Independent chromophore:** single chromophore is sufficient to impart color to the compound eg. Azo group .
2. **Dependent chromophore:** When more than one chromophore is required to produce color. eg acetone having one ketone group is colorless whereas diacetyl having two ketone groups is yellow.

Auxochrome: a saturated group with nonbonded electrons which, when attached to a chromophore, alters both the wavelength and the intensity of the absorption or a group which extends the conjugation of a chromophore by sharing of nonbonding electrons e.g. -OH, -NH₂, -Cl etc..

Bathochromic group: The group which deepens the colour of chromophore is called bathochromic group. e.g. primary, secondary and tertiary amino groups.

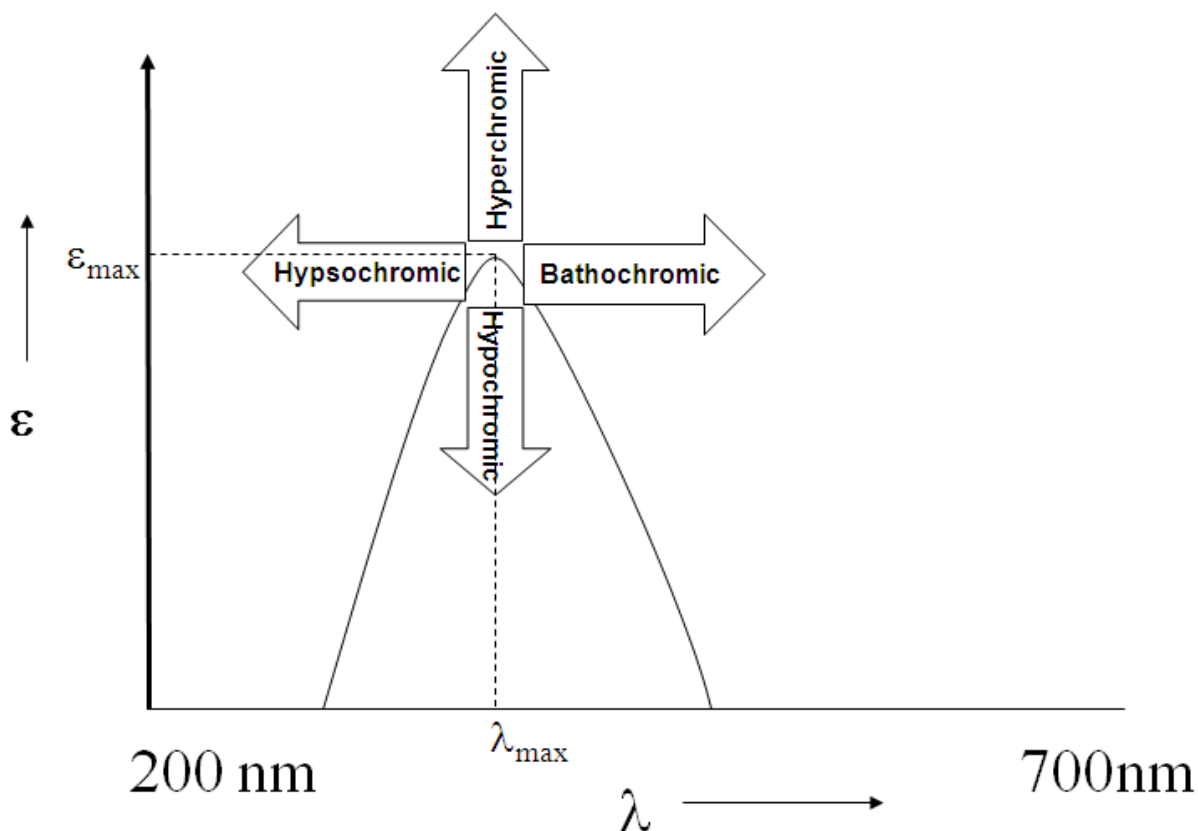
Bathochromic shift: the shift of absorption to a longer wavelength due to substitution or solvent effect is termed as bathochromic shift. This is also known as red shift.

Hypsochromic shift: the shift of absorption to a shorter wavelength is termed as hypsochromic shift. This is also known as blue shift.

Hyperchromic shift: an increase in absorption intensity

Hypochromic shift: an decrease in absorption intensity

Ultraviolet-visible spectrum: An ultraviolet-visible spectrum is essentially a [graph](#) of light absorbance versus wavelength in a range of ultraviolet or visible regions. Such a spectrum can often be produced by a more sophisticated spectrophotometer. Wavelength is often represented by the symbol λ . Similarly, for a given substance, a standard graph of extinction coefficient ϵ vs. wavelength λ may be made or used if one is already available. For the given substance, the wavelength at which maximum absorption in the spectrum occurs is called λ_{\max} , pronounced "Lambda-max".



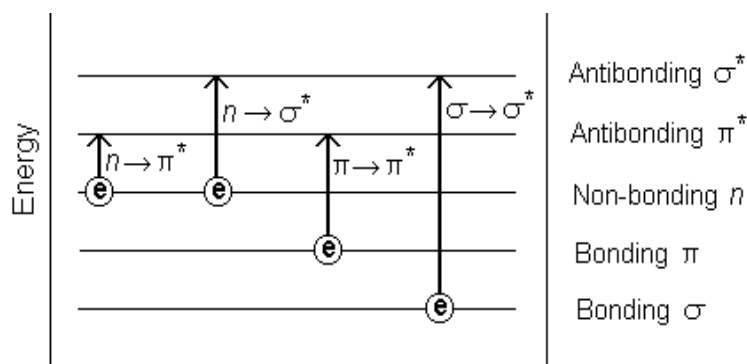
UV-visible spectroscopy investigates the interactions between ultraviolet or visible electromagnetic **radiation** and **matter**. UV-visible spectroscopic measurements provide precise information about atomic and **molecular structure**. The foundation of UV-visible spectroscopy was laid by English physicist and mathematician Sir **Isaac Newton** who, by diffracting white **light** through a prism, showed that it consisted of light of several colors ranging from violet to red. This is now termed the UV-visible **electromagnetic spectrum**. The red end of the spectrum corresponds to electromagnetic radiation of longer wavelengths (780 nm) and lower frequencies, while the violet end is associated with shorter wavelengths (380 nm) and higher frequencies. An understanding of the dual nature of light, however, which consists of particles called photons that also behave like **waves**, and of its interaction with matter, waited for the advent of **quantum theory**. German physicist Maxwell Planck (1858-1947) first postulated that the **energy** of the electromagnetic spectrum was not continuous, but consisted of small, discrete packets which he called **quanta**, and whose energy, E , was directly proportional to the **frequency** of the light as expressed in the fundamental equation of spectroscopy, i.e. $E = h\nu$ where h is a proportionality constant called **Planck's constant**. The direct relationship between energy and frequency shows that light of lower frequency will carry fewer energetic photons than light of a higher frequency.

Spectral lines observed in the UV-visible region correspond to the energy difference between two well-defined electronic energy levels of the absorbing **atom** or molecule. When an atom or molecule absorbs energy in that region, its electrons are promoted from a state of lowest energy, i.e. the ground state, to states, or **orbitals**, of higher energy.

Electronic transitions in organic molecules

Absorption of ultraviolet radiation by organic molecule leads to electronic excitation among various energy levels within the molecule. The transition generally occurs in between a bonding or lone pair orbital (occupied) and unoccupied anti-bonding orbitals. The energy difference between various energy levels in most organic molecules varies from 30-150 kcal/mole. In an organic molecule many electronic transitions are possible. Only four transitions are characterized as allowed transitions. These transitions are divided into two groups.

- A. Transitions from bonding to anti-bonding orbitals
($\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ Transitions)
- B. Transitions from non-bonding to anti-bonding orbitals
($n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ Transitions)



A. Transitions from bonding to anti-bonding orbitals

(1) $\sigma \rightarrow \sigma^*$ Transitions

$\sigma \rightarrow \sigma^*$ Transitions is observed when an electron in a bonding σ orbital is excited to the corresponding anti-bonding orbital. The energy required for this transition is large. These transitions are observed in vacuum ultraviolet region (below 200 nm). In saturated hydrocarbons this is the only possible transition. For example, methane (which has only C-H bonds, and can only undergo $\sigma \rightarrow \sigma^*$ transitions) shows an absorbance maximum at 125 nm. Absorption maxima due to $\sigma \rightarrow \sigma^*$ transitions are not seen in typical UV-Vis. spectra (200 - 700 nm).

(2) $\pi \rightarrow \pi^*$ Transitions

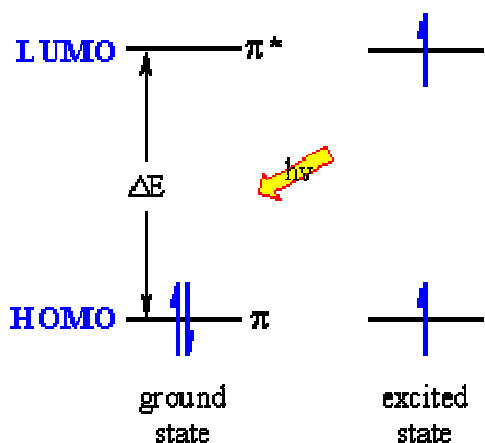
Most absorption spectroscopy of organic compounds is based on transitions of n or π electrons to the π^* excited state. $\pi \rightarrow \pi^*$ Transitions are the characteristic transitions of unsaturated compounds. To show this transition molecule must have at least one double bond. This is the most probable and lower energy transition. these transitions fall in the region from 200 nm to 700 nm of the spectrum. $\pi \rightarrow \pi^*$ transitions normally give molar absorptivities between 1000 and 10,000 $\text{L mol}^{-1} \text{cm}^{-1}$.

B. Transitions from non-bonding to anti-bonding orbitals**(3) $n \rightarrow \sigma^*$ Transitions**

Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of $n \rightarrow \sigma^*$ transitions. These transitions usually need less energy than $\sigma \rightarrow \sigma^*$ transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in the UV region is small.

(4) $n \rightarrow \pi^*$ Transitions

The absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm). These transitions need an hetero atom with pi bonds. Unsaturated groups in the molecule provide vacant anti-bonding pi orbitals and hetero atoms provide non bonding electrons. Molar absorptivities from $n \rightarrow \pi^*$ transitions are relatively low, and range from 10 to 100 $\text{L mol}^{-1} \text{cm}^{-1}$.

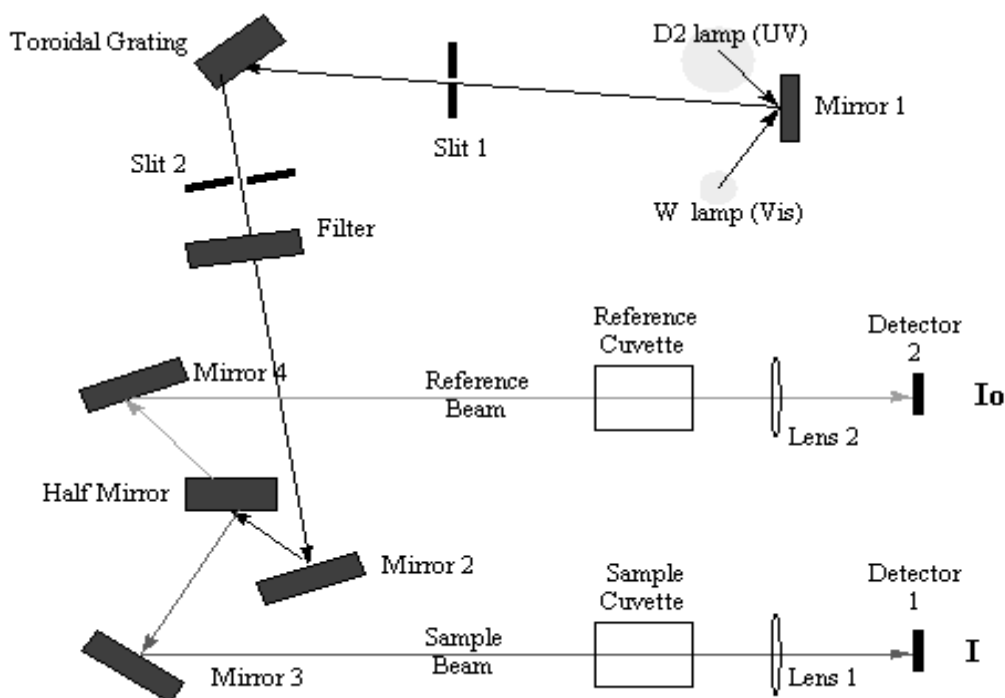


The lowest energy transition is that between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the ground state. The absorption of the Electromagnetic radiation excites an electron to the LUMO and creates an excited state. The more highly conjugated the system, the smaller the HOMO-LUMO gap, ΔE , and therefore the lower the frequency and longer the wavelength, λ . The colours we see in inks, dyes, flowers *etc.* are typically due to highly conjugated organic molecules. The unit of the molecule that is responsible for the absorption is called the chromophore, of which the most common are $\text{C}=\text{C}$ (π to π^*) and $\text{C}=\text{O}$ (n to π^*) systems.

The solvent in which the absorbing species is dissolved also has an effect on the spectrum of the species. Peaks resulting from $n \rightarrow \pi^*$ transitions are shifted to shorter wavelengths (*blue shift*) with increasing solvent polarity. This arises from increased solvation of the lone pair, which lowers the energy of the n orbital. Often (but *not* always), the reverse (i.e. *red shift*) is seen for $\pi \rightarrow \pi^*$ transitions. This is caused by attractive polarisation forces between the solvent and the absorber, which lower the energy levels of both the excited and unexcited states. This effect is greater for the excited state, and so the energy difference between the excited and unexcited states is slightly reduced - resulting in a small red shift. This effect also influences $n \rightarrow \pi^*$ transitions but is overshadowed by the blue shift resulting from solvation of lone pairs.

Ultraviolet-visible spectrophotometer:

The instrument used in Ultraviolet-visible spectroscopy is called a ultraviolet-visible **spectrophotometer**. The UV-Visible spectrophotometer uses two light sources, a deuterium (D_2) lamp for ultraviolet light and a tungsten (W) lamp for visible light. After bouncing off a mirror (mirror 1), the light beam passes through a slit and hits a diffraction grating. The grating can be rotated allowing for a specific wavelength to be selected. At any specific orientation of the grating, only monochromatic (single wavelength) successfully passes through a slit. A filter is used to remove unwanted higher orders of diffraction. (Recall the experiment you did last semester on Atomic Spectra) The light beam hits a second mirror before it gets split by a half mirror (half of the light is reflected, the other half passes through). One of the beams is allowed to pass through a reference cuvette (which contains the solvent only), the other passes through the sample cuvette. The intensities of the light beams are then measured at the end.

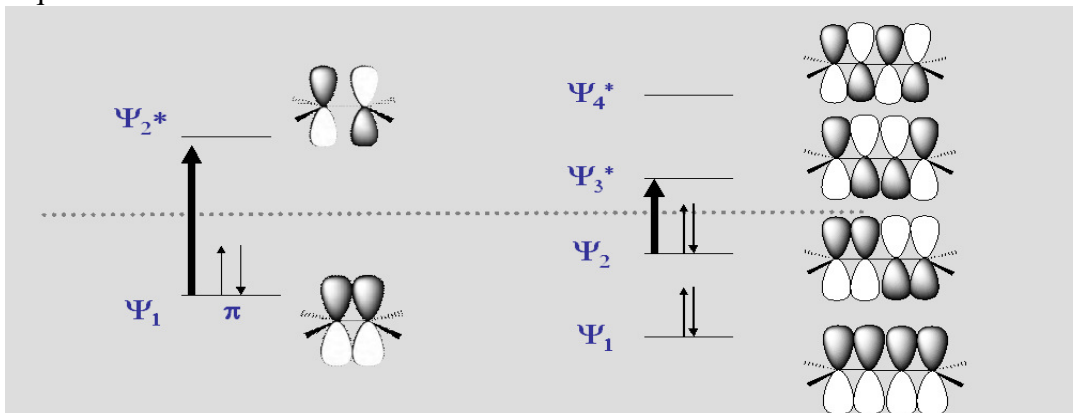


To obtain absorption information, a sample is placed in the spectrophotometer and ultraviolet or visible light at a certain wavelength, or range of wavelengths, is transmitted through the sample. The spectrophotometer measures how much of the light is absorbed by the sample. The intensity of light before going into a certain sample is symbolized by I_0 . The intensity of light remaining after it has gone through the sample is symbolized by I . The fraction of light transmittance is (I / I_0) , which is usually expressed as a percent Transmittance (%T). From this information, the absorbance of the sample is determined for that wavelength or as a function for a range of wavelengths. Sophisticated UV/Vis spectrophotometers often do this automatically.

Although the samples could be solid, or even gaseous, they are usually liquid. A transparent cell, often called a **cuvette**, is used to hold a liquid sample in the spectrophotometer. The path length L through the sample is then the width of the cell through which the light passes through. Simple, economical spectrophotometers may use cuvettes shaped like cylindrical test tubes, but more sophisticated ones use rectangular cuvettes, commonly 1 cm in width. For just visible spectroscopy, ordinary glass cuvettes may be used, but ultraviolet spectroscopy requires special cuvettes made of a ultraviolet-transparent material such as quartz.

Effect of conjugation on absorption maximum

As the conjugation increases the energy difference between HOMO to LUMO also decreases. As a result the energy required for transition decreases and absorption shifted towards longer wavelength side. From molecular orbital (MO) theory two atomic p orbitals, ϕ_1 and ϕ_2 from two sp^2 hybrid carbons, combine to form two MOs ψ_1 and ψ_2^* in ethylene. The favorable transition in ethylene is ψ_1 (HOMO) to ψ_2^* (LUMO) as shown in the following figure. When we consider butadiene, we are now mixing 4 p orbitals giving 4 MOs of an energetically symmetrical distribution compared to ethylene. These MOs are ψ_1 , ψ_2 , ψ_3^* , and ψ_4^* . In butadiene the favorable transition is ψ_2 (HOMO) to ψ_3^* (LUMO) as shown in the figure. From the MOs description it is clear that for π to π^* transition in butadiene less energy is needed as compare to ethylene. The observed shifts from conjugation imply that an increase in conjugation decreases the energy required for electronic excitation.



Applications of UV-Vis spectroscopy

1. UV-Vis spectroscopy is routinely used in the quantitative determination of highly conjugated organic compounds. Organic molecules, especially those with a high degree of conjugation also absorb light in the UV or visible regions of the electromagnetic spectrum.
2. UV-Vis spectroscopy is also used in the quantitative determination of solutions of transition metals. It is possible to do so because transition metals are often colored because of the possibility of d-d electronic transitions within the metal atoms.
3. UV-Vis spectra can be used to identify an unknown compound by a comparative analysis. One can compare the UV or Visible spectra of the unknown with the spectra of known suspects.
4. UV and Visible spectra can also be used to determine the concentration of a chromophore compound in a mixture using the Beer Lambert Law.

- Usually 3-5 standard sample of the chromophore are prepared, and the absorbance of each standard is measured. The Absorbance can be plotted against the concentration and a standard curve can be generated. By measuring the absorbance of the unknown mixture, one can locate the absorbance on the "y" axis of the standard curve, drawing a perpendicular over till it intersects the standard curve and then a perpendicular down until it intersects the "x" axis. At the point of intersection on the "x" axis, the concentration of the chromophore can be determined.
- One can also use a proportional method where the Absorbance of a known concentration sample is measured and the Absorbance of the unknown can be measured.

Merits of UV/vis absorption for quantitative work:

- A. **Widely applicable:** many analytes absorb or can otherwise be detected by absorbing species
- B. **“High” sensitivity:** detection limits of 10^{-4} to 10^{-5} M typical, 10^{-6} - 10^{-7} M in optimal cases
- C. **Moderate to high specificity:** via wavelength dependence of absorption
- D. **Good accuracy:** 1-5% relative errors are typical
- E. Relatively simple, inexpensive, widely accessible

Woodward-Fieser rules:

Woodward-Fieser rules are a set of empirical observations which can be used to predict λ_{\max} , the wavelength of the most intense UV/Vis absorption, for conjugated organic compounds such as dienes and ketones.

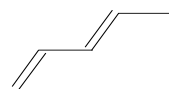
Woodward-Fieser's Rule for Predicting λ_{\max} Values for Conjugated Diene Systems.

Parent Value

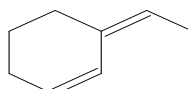
1. Parent Acyclic Diene	217 nm
2. Parent Heteroannular Diene	214 nm
3. Parent Homoannular Diene	253 nm

Increments for substituents

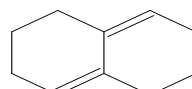
Alkyl Group / Ring Residue	+5
Exocyclic Double Bond	+5
Each Extending Double Bond	+30
Halogen (-Cl,-Br)	+5
Alkoxy (-OR)	+6
Acetoxy (-OCOR)	+0
Thio Alcohol/ Ether (-SR)	+30
Ammine (-NRR')	+60



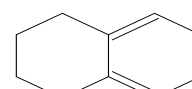
Acyclic



Acyclic



Heteroannular



Homoannular

Woodward-Fieser's Rule for Predicting λ_{\max} Values for α, β Unsaturated Carbonyl Systems.

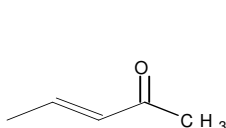
Parent Value (PV)

1. Parent Acyclic ketone	215 nm
2. Six and Higher membered ring ketone	215 nm
3. Five membered ring ketone	202 nm
α, β Unsaturated aldehyde	207
α, β Unsaturated acid and esters	197

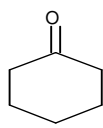
Increments

Homodiene component	+39
Exocyclic Double Bond (Exo DB)	+5
Each Extending Double Bond (EDB)	+30

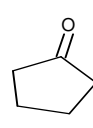
	α	β	γ	δ
Alkyl Group(-R) / Ring Residue (RR)	+10	+12	+18	+18
Alcohol (-OH)	+35	+30	+30	+50
Alkoxy (-OR)	+35	+30	+17	+31
Acetoxy (-OCOR)	+6	+6	+6	-
Chloro (-Cl)	+15	+12	-	-
Bromo (-Br)	+25	+30	-	-



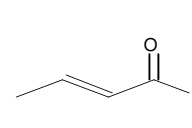
Acyclic



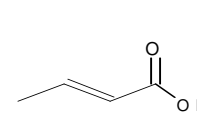
Six memb. and



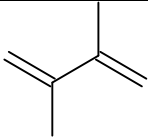
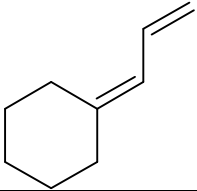
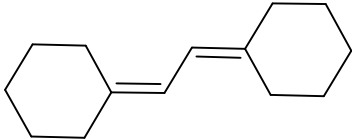
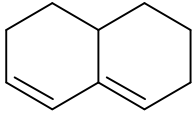
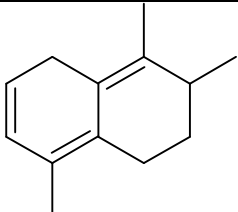
Five memb. ring ketone

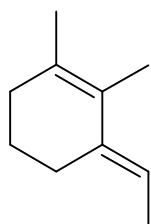


aldehyde

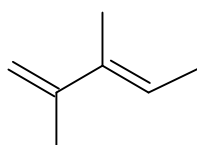


acid

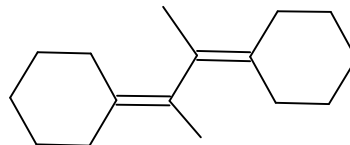
Example	Structure	λ_{\max} (Calculated)
1.		PV = 217 2xR = 10 λ_{\max} = 227 nm
2.		PV = 217 2xR = 10 EDB = 5 λ_{\max} = 232 nm
3.		PV = 217 4xR/RR = 20 Exo DB = 10 λ_{\max} = 247 nm
4.		PV = 214 3xR/RR = 15 Exo DB = 5 λ_{\max} = 234 nm
5.		PV = 253 Extra DB = 30 6xR/RR = 30 2Exo DB = 10 λ_{\max} = 323 nm



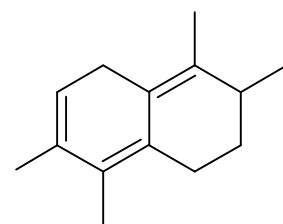
6



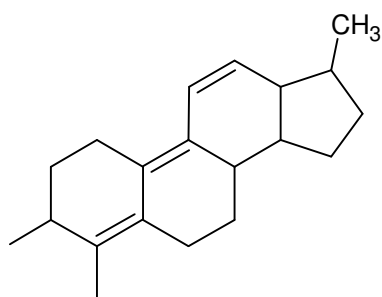
7



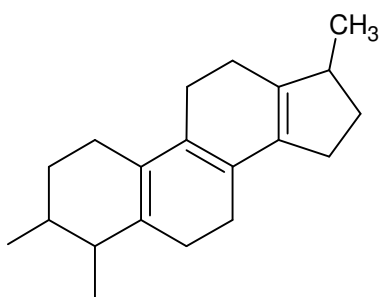
8



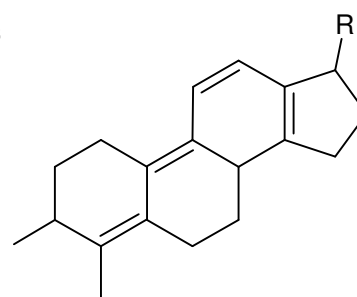
9



10



11



12

Infrared Spectroscopy

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Hence it is used to identify chemical compounds or monitor changes occurring in the course of a chemical reaction. For example, the spectra of two related molecules, 1-propanol (an alcohol), and propanoic acid (a carboxylic acid) are given below. Their spectra are considerably different and tell about important features of a molecule. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification.

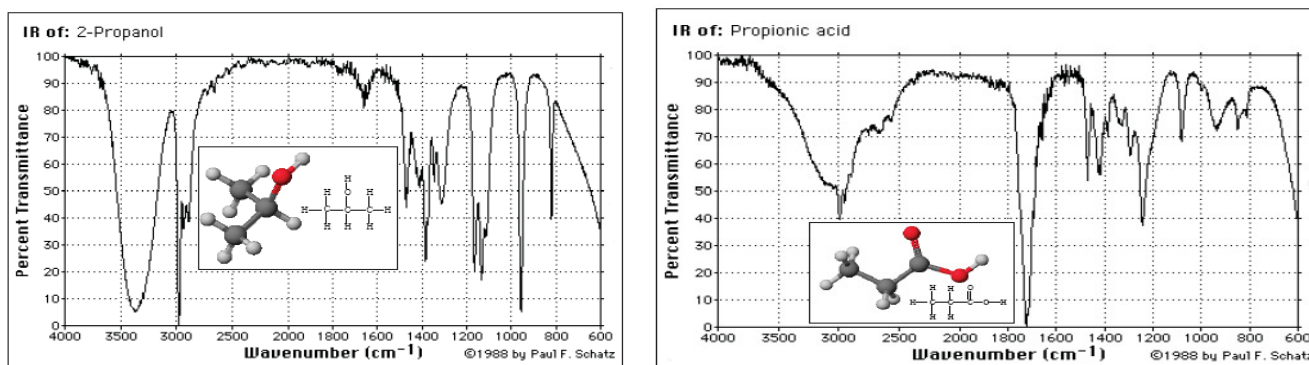


Figure 1. IR spectra of 1-propanol (an alcohol), and propanoic acid

Infrared refers to that part of the electromagnetic spectrum between the visible and microwave regions. Electromagnetic spectrum refers to the seemingly diverse collection of radiant energy, from cosmic rays to X-rays to visible light to microwaves, each of which can be considered as a wave or particle traveling at the speed of light. These waves differ from each other in the length and frequency as shown below-

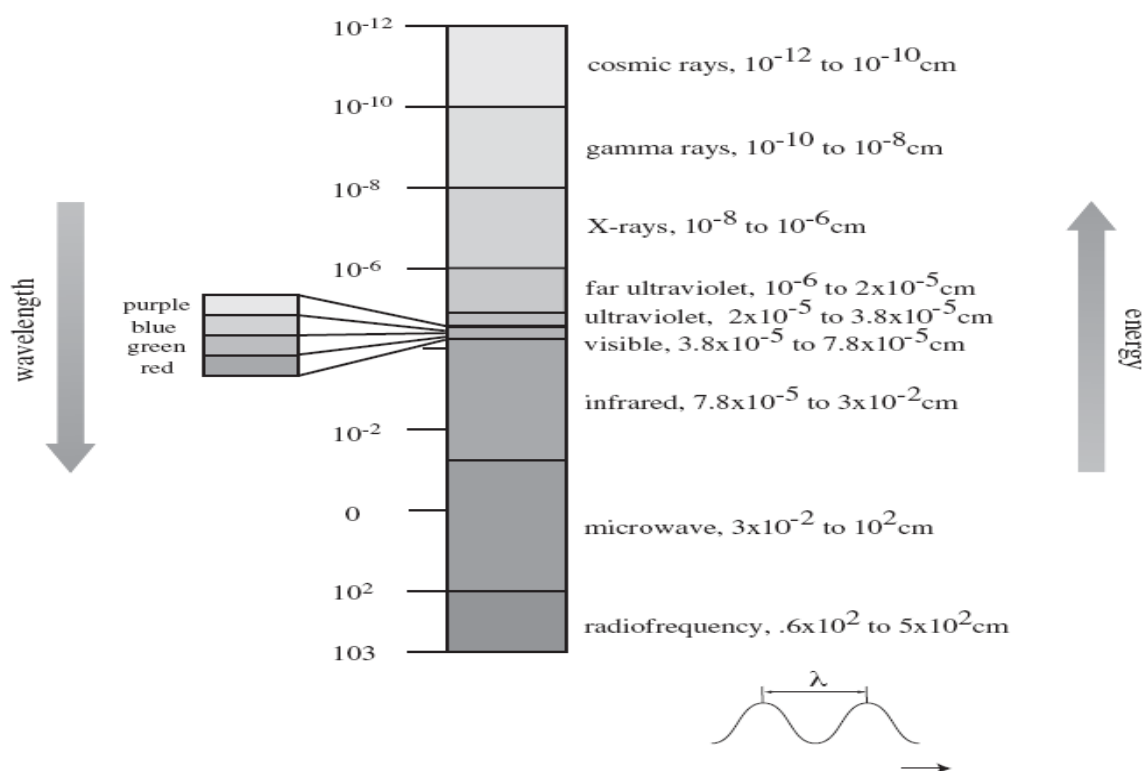


Figure 2. The electromagnetic spectrum

Infrared radiation spans a section of the electromagnetic spectrum having wave numbers from roughly $13,000$ to 10 cm^{-1} , or wavelengths from 0.78 to $1000\text{ }\mu\text{m}$. It is bound by the red end of the visible region at high frequencies and the microwave region at low frequencies.

Of greatest practical use to the organic chemist is the limited portion of this region, the mid IR range $4000\text{--}400\text{ cm}^{-1}$. An increase in wave number corresponds to an increase in energy. This is a convenient relationship for the organic chemist.

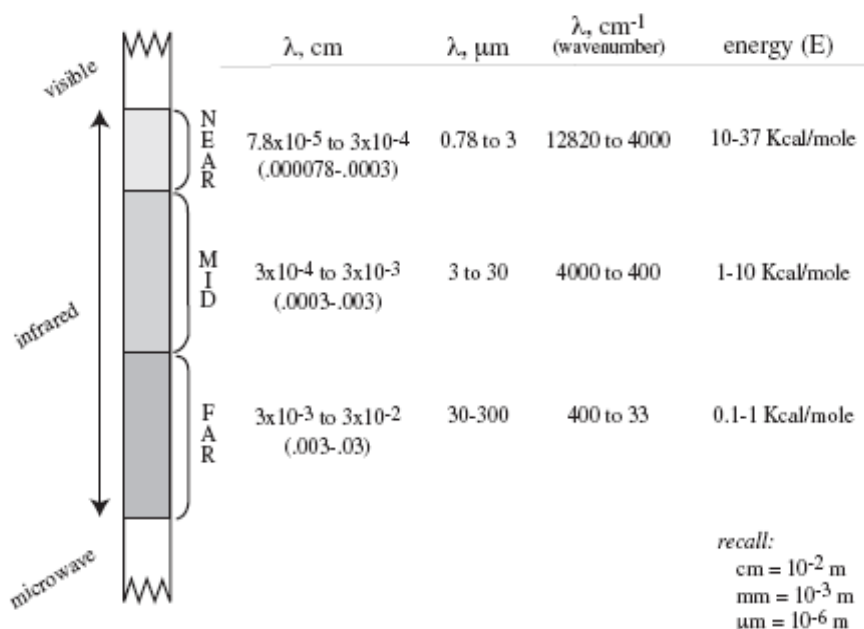


Figure 3. The IR regions of the electromagnetic spectrum

Infrared radiation in the range from about $10000\text{--}100\text{ cm}^{-1}$ is absorbed by organic molecules and converted into energy of molecular vibration. This absorption is quantized but vibrational spectra appear as bands rather than as lines because a single vibrational energy change is accompanied by a number of rotational energy changes. It is with these vibrational-rotational bands, particularly those occurring between $4000\text{--}400\text{ cm}^{-1}$ that an organic chemist is concerned. In IR spectroscopy, an organic molecule is exposed to infrared radiation. When the radiant energy matches the energy of a specific molecular vibration, absorption occurs. The frequency of absorption depends on the-

1. Relative masses of atoms
2. Force constants of the bonds and
3. Geometry of the molecule

In a typical IR spectrum the band positions are presented as wave numbers. The wave number, plotted on the X-axis, is proportional to energy; therefore, the highest energy vibrations are on the left. Band intensities can be expressed either as transmittance (T) or absorbance (A). Transmittance, T , is the ratio of radiant power transmitted by the sample (I) to the radiant power incident on the sample (I_0). Absorbance (A) is the logarithm to the base 10 of the reciprocal of the transmittance (T). The percent transmittance (%T) is plotted on the Y-axis. Absorption of radiant energy is therefore represented by a "trough" in the curve. Zero transmittance corresponds to 100% absorption of light at that wavelength. Organic chemists usually report intensity in semi-quantitative terms (s = strong, m = medium, w = weak).

Except at very, very low temperatures, all molecules are in motion in some manner. Molecules *translate* (move from place to place), they *rotate* in space, and, importantly for this experiment, they *vibrate*. At temperatures above absolute zero, all the atoms in molecules are in continuous vibration with respect to each other. When the frequency of a specific vibration is equal to the frequency of the IR radiation directed on the molecule, the molecule absorbs the radiation.

You may have come to think of a molecule as having rigid bond lengths and bond angles, this is not the actual case, since bond lengths and angles represent the *average* positions about which atoms vibrate. A molecule is not a rigid assemblage of atoms. A molecule can be said to resemble a system of balls of varying masses corresponding to atoms and springs of varying strengths (force constants) corresponding to the chemical bonds of a molecule.

There are two types of molecular vibrations, stretching and bending. A stretching vibration is a rhythmical movement along the bond axis such that the inter-atomic distance is increasing or decreasing. A bending vibration may consist of a change in bond angle between bonds with a common atom or the movement of a group of atoms with respect to the remainder of the molecule without movement of the atom in the group with respect to one another.

Only those vibrations that result in a rhythmical change in the dipole moment of the molecule are observed in the IR. Various stretching and bending vibration of a molecule occur at certain quantized frequencies. When IR light of that same frequency is incident on the molecule, energy is absorbed and the amplitude of that vibration is increased. The frequency of the vibration remains unchanged. When the molecule reverts from the excited state to ground state the absorbed energy released as heat.

Each atom has three degrees of freedom, corresponding to motions along any of the three cartesian coordinate axes (x, y, z). A polyatomic molecule of n atoms has $3n$ total degrees of freedom. However, 3 degrees of freedom are required to describe translation, the motion of the entire molecule through space. Additionally, 3 degrees of freedom correspond to rotation of the entire molecule. Therefore, the remaining $3n - 6$ degrees of freedom are true, fundamental vibrations for nonlinear molecules. Linear molecules possess $3n - 5$ fundamental vibrational modes because only 2 degrees of freedom are sufficient to describe rotation.

The net number of fundamental vibrations for nonlinear and linear molecules is therefore:

molecule	degrees of freedom
nonlinear	$3n - 6$
linear	$3n - 5$

Fundamental vibrations involved no change in the center of gravity of the molecule. Among the $3n - 6$ (or $3n - 5$) fundamental vibrations (also known as normal modes of vibration), those that produce a net change in the dipole moment may result in an IR activity and those that give polarizability changes may give rise to Raman activity. Naturally, some vibrations can be both IR- and Raman-active.

Calculation reveals that a simple molecule such as propane, C_3H_8 , has 27 fundamental vibrations, and therefore, you might predict 27 bands in an IR spectrum! (The actual number is sometimes different as discussed in part later.) The fundamental vibrations for water, H_2O , are given in Figure 4. Water, which is nonlinear, has three fundamental vibrations.

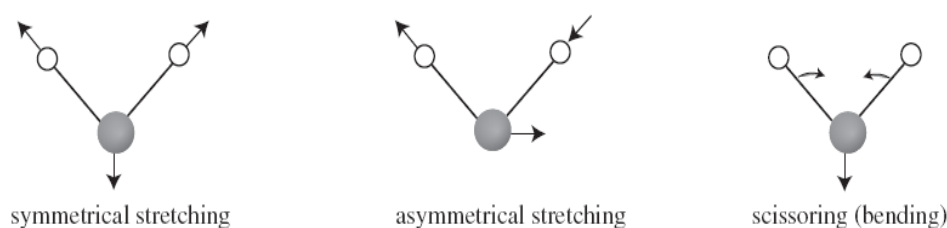
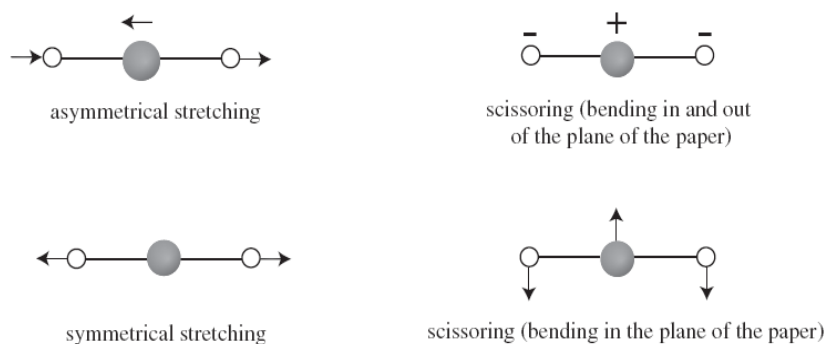
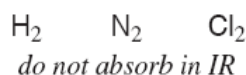
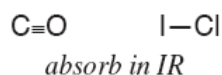


Figure 4. Vibrational modes for H_2O

Carbon dioxide, CO_2 , is linear and hence has four fundamental vibrations (Figure 5). The symmetrical stretch of CO_2 gives a strong band in the IR at 2350 cm^{-1} . You may notice this band in samples which you run on the instruments in the teaching labs, since CO_2 is present in the atmosphere. The two scissoring or bending vibrations are equivalent and therefore, have the same frequency and are said to be *degenerate*, appearing in an IR spectrum at 666 cm^{-1} .

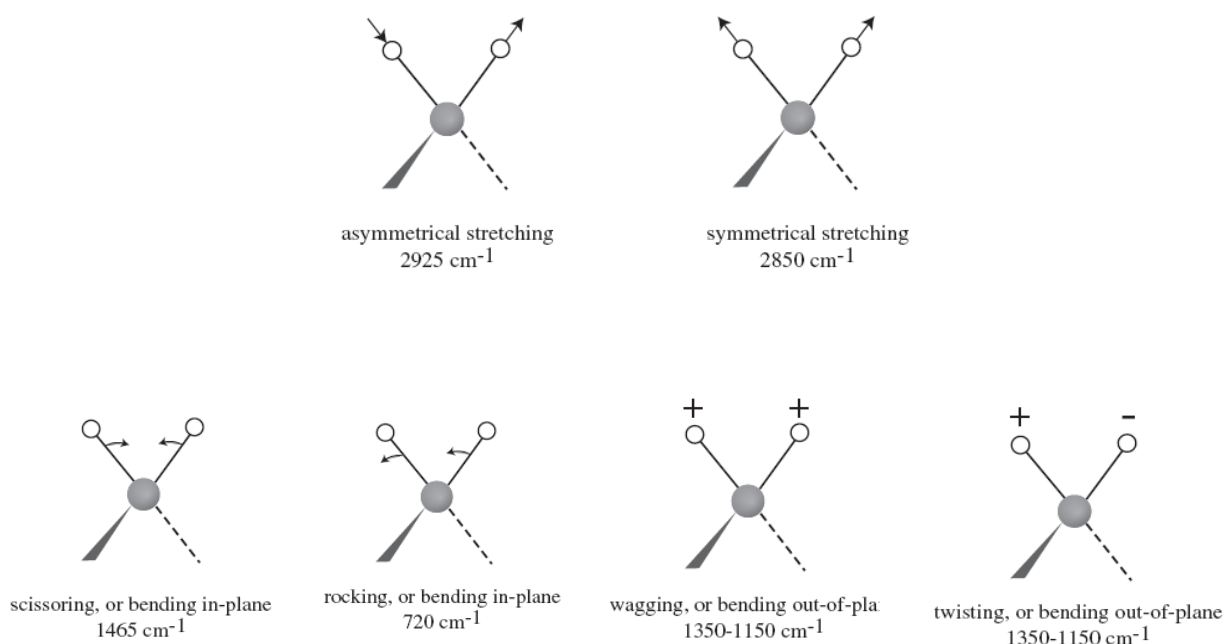
Figure 5. Vibrational modes for CO₂

The symmetrical stretch of CO₂ is inactive in the IR because this vibration produces no change in the dipole moment of the molecule. In order to be IR active, a vibration must cause a change in the dipole moment of the molecule. (The reason for this involves the mechanism by which the photon transfers its energy to the molecule, which is beyond the scope of this discussion.) Of the following linear molecules, carbon monoxide and iodine chloride absorb IR radiation, while hydrogen, nitrogen, and chlorine do not. In general, the larger the dipole change, the stronger the intensity of the band in an IR spectrum.



Only two IR bands (2350 and 666 cm⁻¹) are seen for carbon dioxide, instead of four corresponding to the four fundamental vibrations. Carbon dioxide is an example of why one does not always see as many bands as implied by our simple calculation. In the case of CO₂, two bands are degenerate, and one vibration does not cause a change in dipole moment..

The stretching and bending vibrations for the important organic group, -CH₂-, are illustrated in Figure 6. (The 3n-6 rule does not apply since the -CH₂- group represents only a portion of a molecule.) Note that bending vibrations occur at lower frequencies than corresponding stretching vibrations.

Figure 6. Stretching and bending vibrational modes for a CH₂ group

The theoretical number of fundamental vibrations will seldom be observed because of the following reasons –

1. The following phenomenon reduces the theoretical number of bands-
 - a. Overtones (multiple of a given frequency) and
 - b. Combination tones (sum of two different vibrations)

2. The following will reduce the theoretical number of bands
 - a. Fundamental frequencies that fall outside of the 400-4000 cm^{-1} region.
 - b. Fundamental bands that are too weak to be observed.
 - c. Fundamental vibrations that are too close to each other to be resolved on the instrument.
 - d. The occurrence of a degenerate band from several absorptions of the same frequency in highly symmetrical molecules.
 - e. The failure of certain fundamental vibrations to appear in the IR because of the lack of change in molecular dipole.

Stretching Vibrations

The stretching frequency of a bond can be approximated by Hooke's Law. In this approximation, two atoms and the connecting bond are treated as a simple harmonic oscillator composed of 2 masses (atoms) joined by a spring. The energy curve for a simple harmonic oscillator is illustrated in Figure 15.7. According to Hooke's law, the frequency of the vibration of the spring is related to the mass and the force constant of the spring, k , by the following formula:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

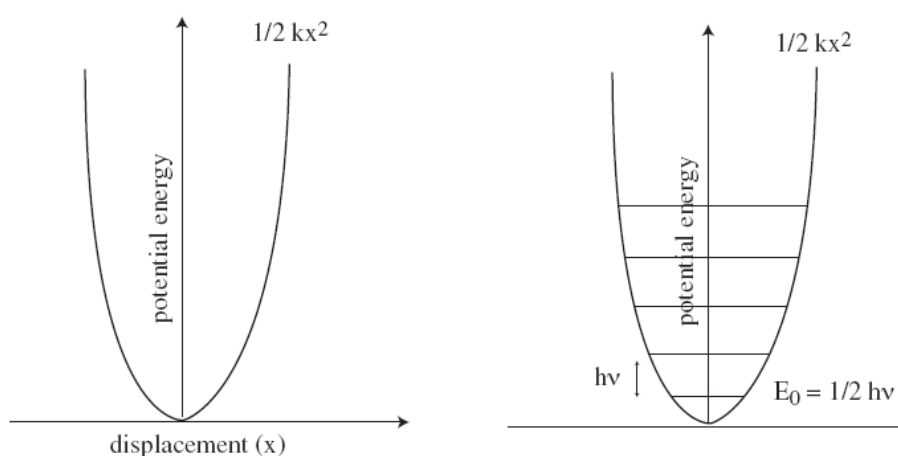
Where

k is the force constant

m is the mass

ν is the frequency of the vibration

In the classical harmonic oscillator, $E = 1/2kx^2 = h\nu$, where x is the displacement of the spring. Thus, the energy or frequency is dependent on how far one stretches or compresses the spring, which can be any value. If this simple model were true, a molecule could absorb energy of any wavelength.



However, vibrational motion is *quantized*: it must follow the rules of quantum mechanics, and the only transitions which are allowed fit the following formula-

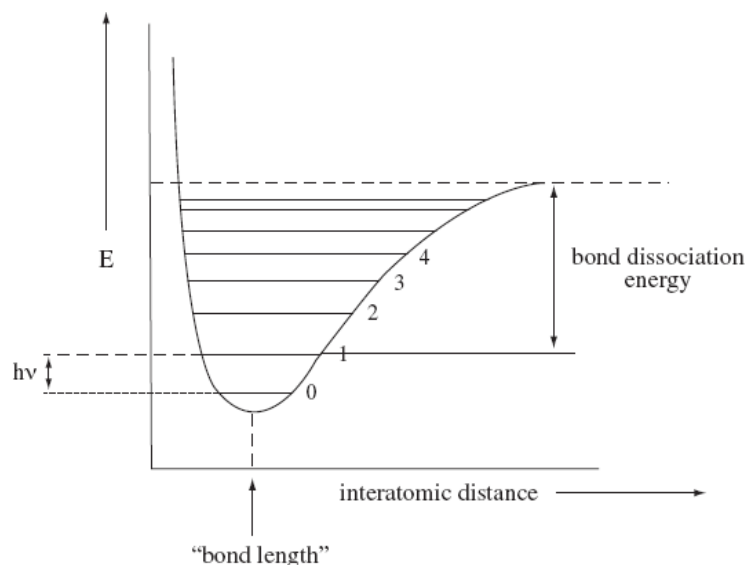
$$E = (n + 1/2) h\nu$$

Where

ν is the frequency of the vibration and n is the vibrational quantum number (0, 1, 2, 3, ...)

The lowest energy level is $E_0 = 1/2 h\nu$, the next highest is $E_1 = 3/2 h\nu$. According to the selection rule, only transitions to the next energy level ($\Delta n = \pm 1$) are allowed; therefore molecules will absorb an amount of energy equal to $(3/2)h\nu - (1/2) h\nu$ or $h\nu$. This rule is not inflexible, and occasionally transitions of $2h\nu$, $3h\nu$, or higher are observed. These correspond to bands called overtones in an IR spectrum. They are of lower intensity than the fundamental vibration bands.

A molecule is not just two atoms joined on a spring, of course. A bond can come apart, and it cannot be compressed beyond a certain point. A molecule is actually an *anharmonic* oscillator. As the interatomic distance increases, the energy reaches a maximum, as seen in Figure 8. Note how the energy levels become more closely spaced with increasing interatomic distance in the anharmonic oscillator. The allowed transitions, $h\nu$, become smaller in energy. Therefore, overtones can be lower in energy than predicted by the harmonic oscillator theory.



The following formula has been derived from Hooke's law. For the case of a diatomic molecule, (ν has been substituted for ν),

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

Where

k is the force constant

μ is the reduced mass [$1/\mu = (1/m_1 + 1/m_2)$]

ν is the frequency of the vibration and

c is the velocity of light (3×10^{10} cm/s)

Above equation shows the relationship of bond strength and atomic mass to the wave number at which a molecule will absorb IR radiation. As the force constant increases, the vibrational frequency (wavenumber) also increases. Approximate value of force constants for bonds are:

Single bond -	5×10^5 dyne/cm
Double bond -	10×10^5 dyne/cm
Triple bond-	15×10^5 dyne/cm

As the mass of the atoms increases, the vibration frequency decreases. Using the following mass values C, carbon $12/6.02 \times 10^{23}$ and H, hydrogen $1/6.02 \times 10^{23}$ ν for a C–H bond is calculated to be 3032 cm^{-1} . (Try this calculation!) The actual range for C–H absorptions is $2850\text{--}3000 \text{ cm}^{-1}$. The region of an IR spectrum where bond stretching vibrations are seen depends primarily on whether the bonds are single, double, or triple or bonds to hydrogen. The following table shows where absorption by single, double, and triple bonds are observed in an IR spectrum.

Bond	Absorption region, (cm^{-1})
C–C, C–O, C–N	800–1300
C=C, C=O, C=N, N=O	1500–1900
C≡C, C≡N	2000–2300
C–H, N–H, O–H	2700–3800

Although a useful approximation, the motion of two atoms in a large molecule cannot be isolated from the motion of the rest of the atoms in the molecule. In a molecule, two oscillating bonds can share a common atom. When this happens, the vibrations of the two bonds are coupled. As one bond contracts, the other bond can either contract or expand, as in asymmetrical and symmetrical stretching. In general, when coupling occurs, bands at different frequencies are observed, instead of superimposed (or degenerate) bands as you might expect from two identical atoms in a bond vibrating with an identical force constant. In the case of the $-\text{CH}_2-$ group in Figure 6, you note there are two bands in the region for C—H bonds: 2926 cm^{-1} and 2853 cm^{-1} .

Table of Characteristic IR Absorptions

Frequency, cm^{-1}	Bond	Functional Group
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1° , 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	$-\text{C}\equiv\text{C}-\text{H}$: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	$=\text{C}-\text{H}$ stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	$\text{C}\equiv\text{N}$ stretch	nitriles
2260–2100 (w)	$-\text{C}\equiv\text{C}-$ stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch esters,	saturated aliphatic
1740–1720 (s)	C=O stretch aldehydes,	saturated aliphatic
1730–1715 (s)	C=O stretch	α , β -unsaturated esters
1715 (s)	C=O stretch ketones,	saturated aliphatic
1710–1665 (s)	C=O stretch	α , β -unsaturated aldehydes, ketones
1680–1640 (m)	$-\text{C}=\text{C}-$ stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch	(in–ring) aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag ($-\text{CH}_2\text{X}$)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	$=\text{C}-\text{H}$ bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1° , 2° amines
900–675 (s)	C–H	“oop” aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	$-\text{C}\equiv\text{C}-\text{H}$: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp

Examples

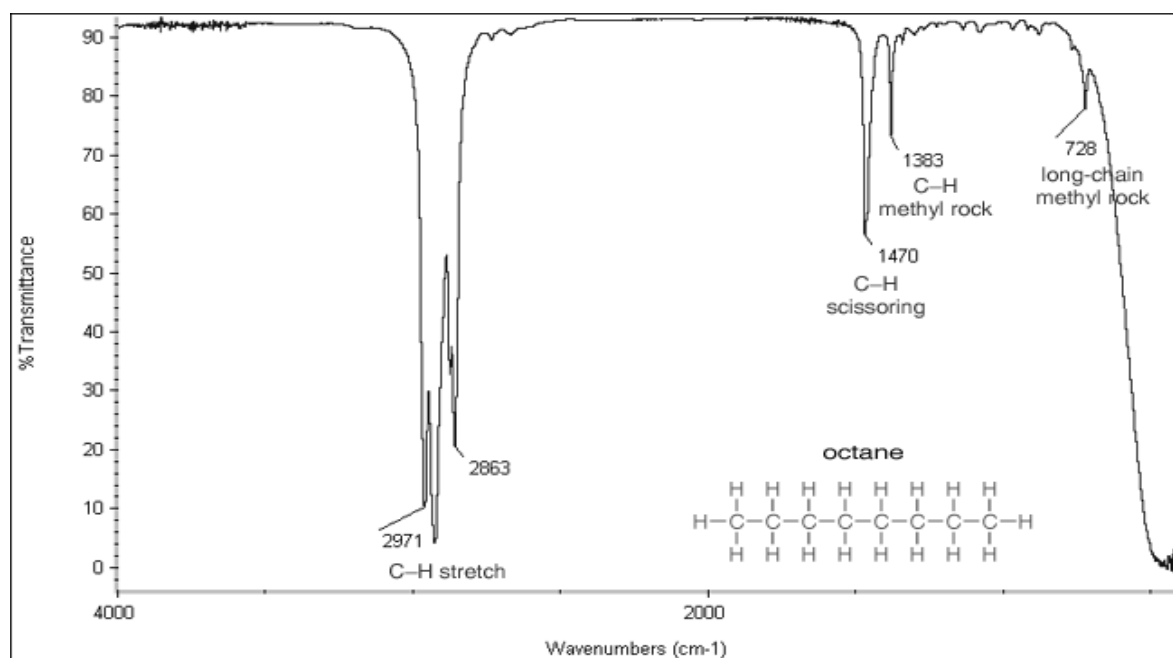
Alkanes

The spectra of simple alkanes are characterized by absorptions due to C–H stretching and bending (the C–C stretching and bending bands are either too weak or of too low a frequency to be detected in IR spectroscopy). In simple alkanes, which have very few bands, each band in the spectrum can be assigned.

- C–H stretch from 3000–2850 cm^{-1}
- C–H bend or scissoring from 1470–1450 cm^{-1}
- C–H rock, methyl from 1370–1350 cm^{-1}
- C–H rock, methyl, seen only in long chain alkanes, from 725–720 cm^{-1}

The IR spectrum of octane is shown below. Note the strong bands in the 3000–2850 cm^{-1} region due to C–H stretch. The C–H scissoring (1470), methyl rock (1383), and long-chain methyl rock (728) are noted on this spectrum. Since most organic compounds have these features, these C–H vibrations are usually not noted when interpreting a routine IR spectrum.

The region from about 1300–900 cm^{-1} is called the **fingerprint region**. The bands in this region originate in interacting vibrational modes resulting in a complex absorption pattern. Usually, this region is quite complex and often difficult to interpret; however, each organic compound has its own unique absorption pattern (or fingerprint) in this region and thus an IR spectrum be used to identify a compound by matching it with a sample of a known compound.

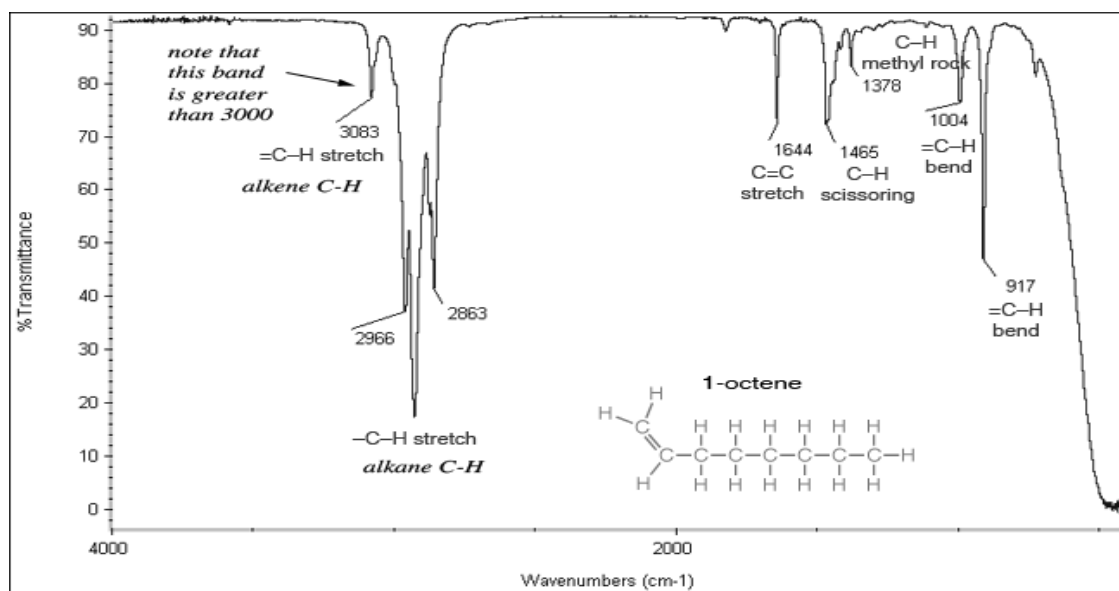


Alkenes

Alkenes are compounds that have a carbon-carbon double bond, $\text{C}=\text{C}$. The stretching vibration of the $\text{C}=\text{C}$ bond usually gives rise to a moderate band in the region 1680–1640 cm^{-1} . Stretching vibrations of the $\text{C}=\text{C}-\text{H}$ bond are of higher frequency (higher wavenumber) than those of the $\text{C}-\text{C}-\text{H}$ bond in alkanes. The strongest bands in the spectra of alkenes are those attributed to the carbon-hydrogen bending vibrations of the $=\text{C}-\text{H}$ group. These bands are in the region 1000–650 cm^{-1} (Note: this overlaps the fingerprint region).

- $\text{C}=\text{C}$ stretch from 1680–1640 cm^{-1}
- $=\text{C}-\text{H}$ stretch from 3100–3000 cm^{-1}
- $=\text{C}-\text{H}$ bend from 1000–650 cm^{-1}

The IR spectrum of 1-octene is shown below. Note the band greater than 3000 cm^{-1} for the $=\text{C}-\text{H}$ stretch and the several bands lower than 3000 cm^{-1} for $\text{C}-\text{H}$ stretch (alkanes). The $\text{C}=\text{C}$ stretch band is at 1644 cm^{-1} . Bands for C–H scissoring (1465) and methyl rock (1378) are marked on this spectrum; in routine IR analysis, these bands are not specific to an alkene and are generally not noted because they are present in almost all organic molecules (and they are in the fingerprint region).



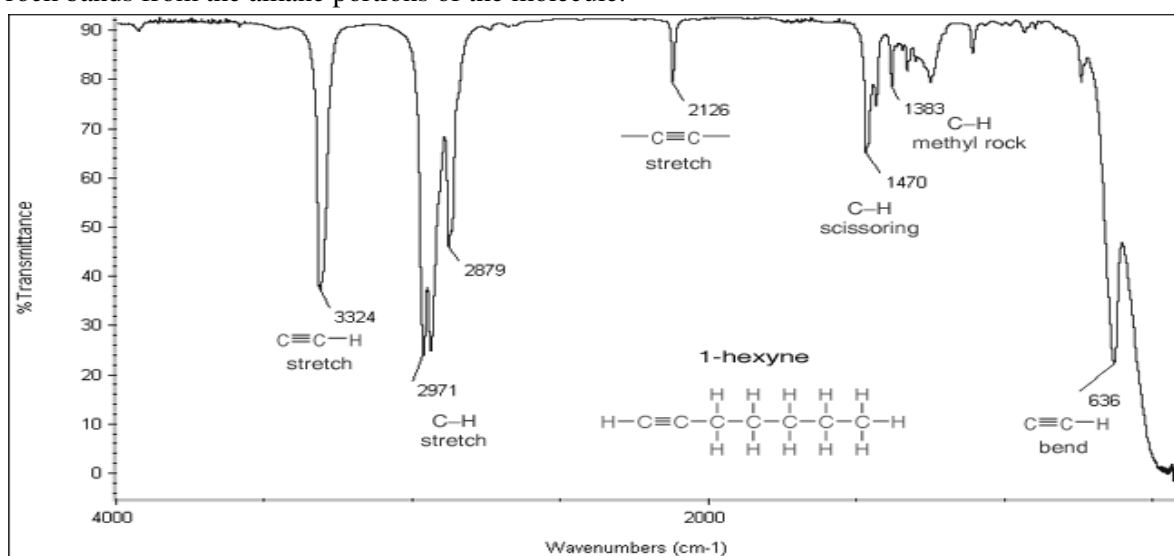
Note: Absorptions above 3000 cm^{-1} is a very useful tool for interpreting IR spectra: Only alkenes and aromatics show a C-H stretch slightly higher than 3000 cm^{-1} . Compounds that do not have a C=C bond show C-H stretches only below 3000 cm^{-1} .

Alkynes

Alkynes are compounds that have a carbon-carbon triple bond ($\text{-C}\equiv\text{C-}$). The $\text{-C}\equiv\text{C-}$ stretch appears as a weak band from $2260\text{-}2100\text{ cm}^{-1}$. This can be an important diagnostic tool because very few organic compounds show an absorption in this region. A terminal alkyne (but not an internal alkyne) will show a C-H stretch as a strong, narrow band in the range $3330\text{-}3270\text{ cm}^{-1}$. (Often this band is indistinguishable from bands resulting from other functional groups on the same molecule which absorb in this region, such as the O-H stretch.) A terminal alkyne will show a C-H bending vibration in the region $700\text{-}610\text{ cm}^{-1}$.

- $\text{-C}\equiv\text{C-}$ stretch from $2260\text{-}2100\text{ cm}^{-1}$
- $\text{-C}\equiv\text{C-H}$: C-H stretch from $3330\text{-}3270\text{ cm}^{-1}$
- $\text{-C}\equiv\text{C-H}$: C-H bend from $700\text{-}610\text{ cm}^{-1}$

The spectrum of 1-hexyne, a terminal alkyne, is shown below. Note the C-H stretch of the C-H bond adjacent to the carbon-carbon triple bond (3324), the carbon-carbon triple bond stretch (2126), and the C-H bend of the C-H bond adjacent to the carbon-carbon triple bond (636). The other bands noted are C-H stretch, scissoring, and methyl rock bands from the alkane portions of the molecule.

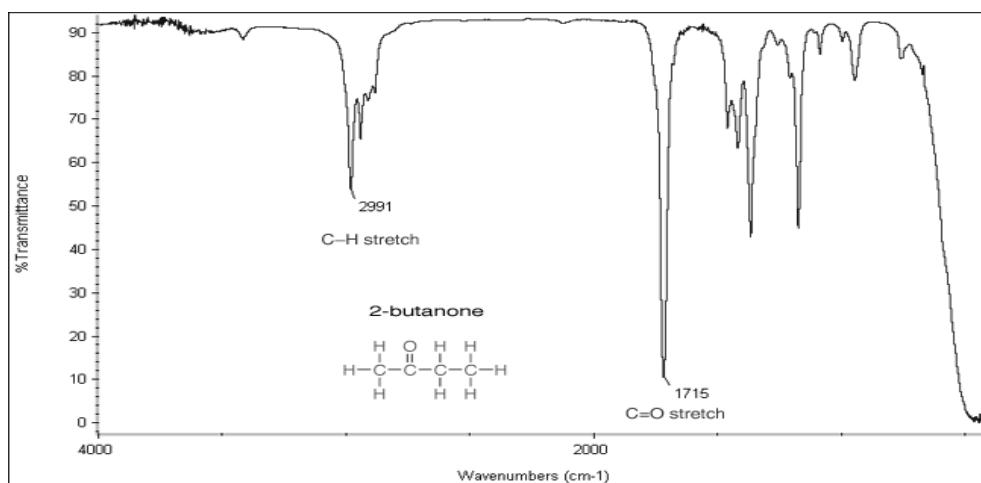


Ketones

The carbonyl stretching vibration band $\text{C}=\text{O}$ of saturated aliphatic ketones appears at 1715 cm^{-1} . Conjugation of the carbonyl group with carbon-carbon double bonds or phenyl groups, as in alpha, beta-unsaturated aldehydes and benzaldehyde, shifts this band to lower wavenumbers, $1685\text{-}1666\text{ cm}^{-1}$.

- $\text{C}=\text{O}$ stretch:
 - aliphatic ketones 1715 cm^{-1}
 - α, β -unsaturated ketones $1685\text{-}1666\text{ cm}^{-1}$

The spectrum of 2-butanone is shown below. This is a saturated ketone, and the $\text{C}=\text{O}$ band appears at 1715 . Note the $\text{C}-\text{H}$ stretches (around 2991) of alkyl groups. It's usually not necessary to mark any of the bands in the fingerprint region (less than 1500 cm^{-1}).

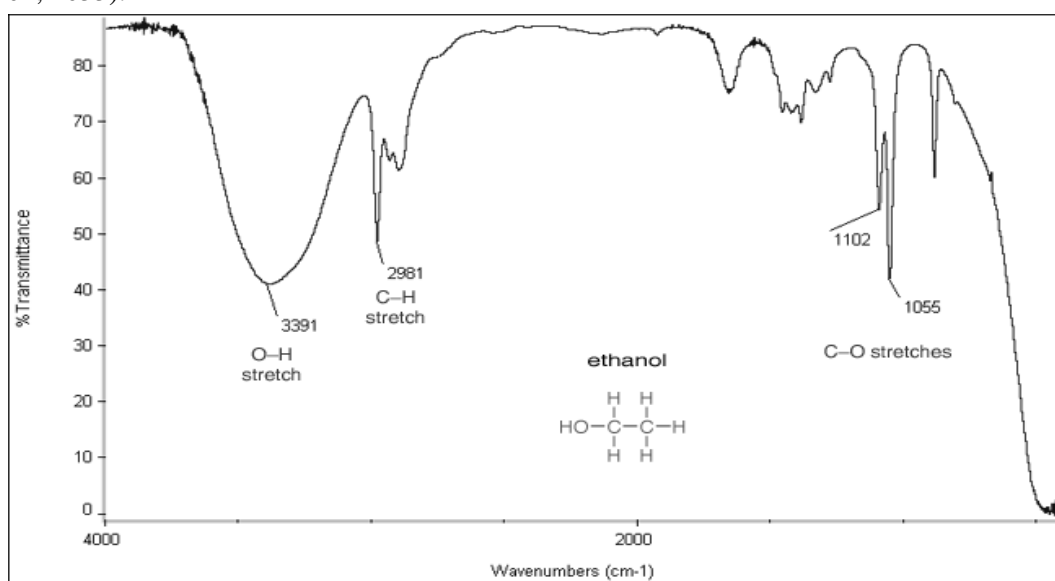


Alcohols

Alcohols have characteristic IR absorptions associated with both the $\text{O}-\text{H}$ and the $\text{C}-\text{O}$ stretching vibrations. When run as a thin liquid film, or "neat", the $\text{O}-\text{H}$ stretch of alcohols appears in the region $3500\text{-}3200\text{ cm}^{-1}$ and is a very intense, broad band. The $\text{C}-\text{O}$ stretch shows up in the region $1260\text{-}1050\text{ cm}^{-1}$.

- $\text{O}-\text{H}$ stretch, hydrogen bonded $3500\text{-}3200\text{ cm}^{-1}$
- $\text{C}-\text{O}$ stretch $1260\text{-}1050\text{ cm}^{-1}$ (s)

The spectrum of ethanol is shown below. Note the very broad, strong band of the $\text{O}-\text{H}$ stretch (3391) and the $\text{C}-\text{O}$ stretches ($1102, 1055$).



Aromatics

The =C–H stretch in aromatics is observed at 3100-3000 cm^{-1} . Note that this is at slightly higher frequency than is the –C–H stretch in alkanes. Aromatic hydrocarbons show absorptions in the regions 1600-1585 cm^{-1} and 1500-1400 cm^{-1} due to carbon-carbon stretching vibrations in the aromatic ring. Bands in the region 1250-1000 cm^{-1} are due to C–H in-plane bending, although these bands are too weak to be observed in most aromatic compounds. Besides the C–H stretch above 3000 cm^{-1} , two other regions of the infrared spectra of aromatics distinguish aromatics from organic compounds that do not have an aromatic ring:

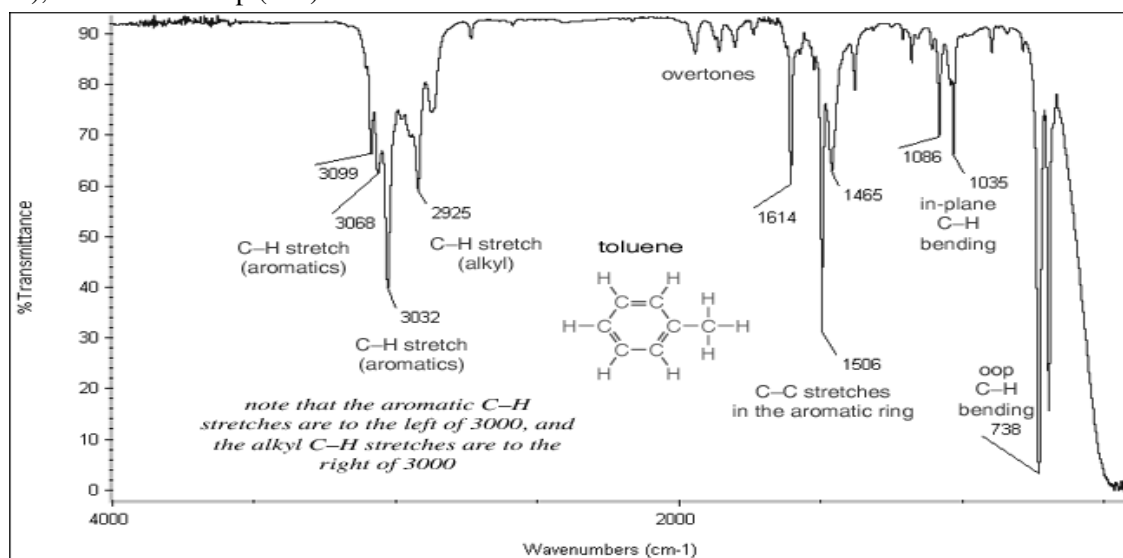
- 2000-1665 cm^{-1} (weak bands known as "overtones")
- 900-675 cm^{-1} (out-of-plane or "oop" bands)

Not only do these bands distinguish aromatics, but they can be useful if you want to determine the number and positions of substituents on the aromatic ring. The pattern of overtone bands in the region 2000-1665 cm^{-1} reflect the substitution pattern on the ring. The pattern of the oop C–H bending bands in the region 900-675 cm^{-1} are also characteristic of the aromatic substitution pattern. Details of the correlation between IR patterns in these two regions and ring substitution are available in the literature references linked in the left frame (especially the books by Shriner and Fuson, Silverstein et. al., and the *Aldrich Library of IR Spectra*).

In some instances, it is useful to remember that aromatics in general show a lot more bands than compounds that do not contain an aromatic ring. If you are presented with two spectra and told that one is aromatic and one is not, a quick glance at the sheer multitude of bands in one of the spectra can tell you that it is the aromatic compound.

- C–H stretch from 3100-3000 cm^{-1}
- overtones, weak, from 2000-1665 cm^{-1}
- C–C stretch (in-ring) from 1600-1585 cm^{-1}
- C–C stretch (in-ring) from 1500-1400 cm^{-1}
- C–H "oop" from 900-675 cm^{-1}

The spectrum of toluene is shown below. Note the =C–H stretches of aromatics (3099, 3068, 3032) and the –C–H stretches of the alkyl (methyl) group (2925 is the only one marked). The characteristic overtones are seen from about 2000-1665. Also note the carbon-carbon stretches in the aromatic ring (1614, 1506, 1465), the in-plane C–H bending (1086, 1035), and the C–H oop (738).

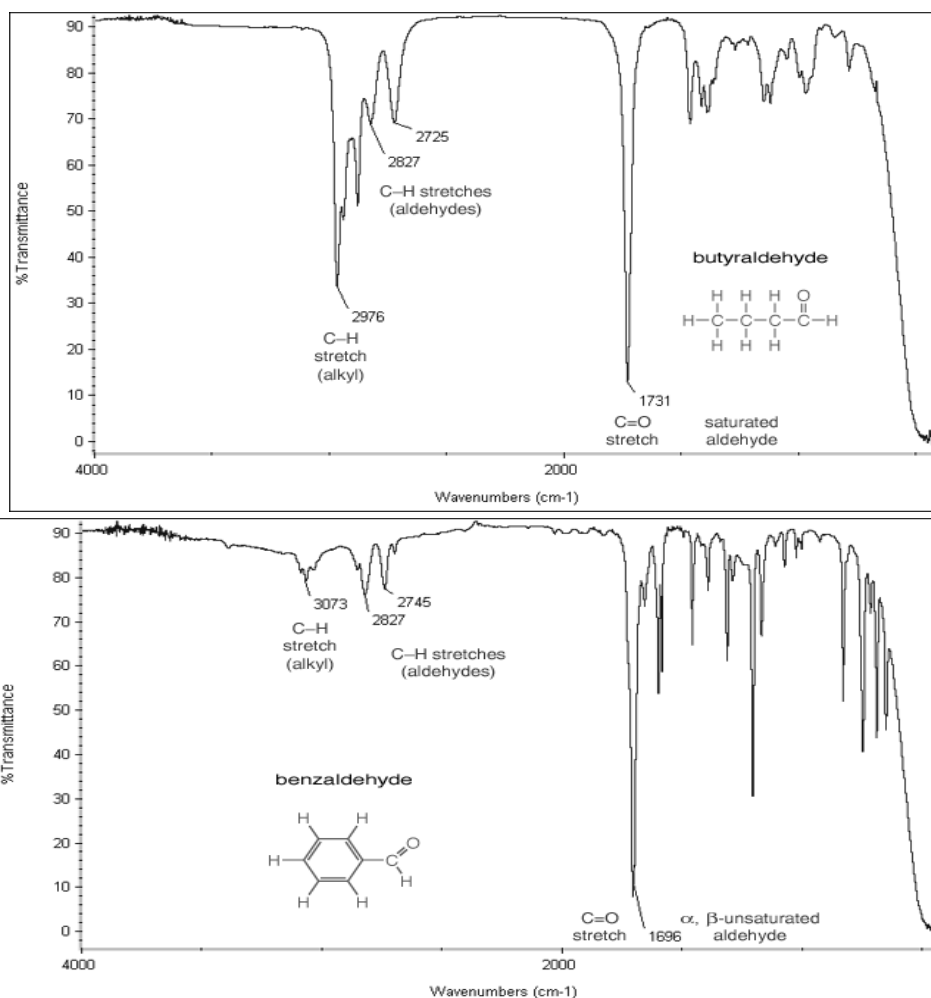


Aldehydes

The carbonyl stretch C=O of saturated aliphatic aldehydes appears from 1740-1720 cm^{-1} . As in ketones, if the carbons adjacent to the aldehyde group are unsaturated, this vibration is shifted to lower wave numbers, 1710-1685 cm^{-1} . Another useful diagnostic band for aldehydes is the O=C–H stretch. This band generally appears as one or two bands of moderate intensity in the region 2830-2695 cm^{-1} . Since the band near 2830 cm^{-1} is usually indistinguishable from other C–H stretching vibration bands (recall that the C–H stretches of alkanes appear from 3000-2850 cm^{-1}), the presence of a moderate band near 2720 cm^{-1} is more likely to be helpful in determining whether or not a compound is an aldehyde.

- $\text{H}-\text{C}=\text{O}$ stretch $2830\text{-}2695\text{ cm}^{-1}$
- $\text{C}=\text{O}$ stretch:
 - aliphatic aldehydes $1740\text{-}1720\text{ cm}^{-1}$
 - α , β -unsaturated aldehydes $1710\text{-}1685\text{ cm}^{-1}$

The spectra of benzaldehyde and butyraldehyde are shown below. Note that the $\text{O}=\text{C}$ stretch of the α , β -unsaturated compound -- benzaldehyde -- is at a lower wavenumber than that of the saturated butyraldehyde. Note the $\text{O}=\text{C}-\text{H}$ stretches in both aldehydes in the region $2830\text{-}2695\text{ cm}^{-1}$, especially the shoulder peak at 2725 cm^{-1} in butyraldehyde and 2745 cm^{-1} in benzaldehyde.



General Uses of IR spectroscopy:

- Identification of all types of organic and many types of inorganic compounds
- Determination of functional groups in organic materials
- Determination of the molecular composition of surfaces
- Identification of chromatographic effluents
- Quantitative determination of compounds in mixtures
- Nondestructive method
- Determination of molecular conformation (structural isomers) and stereochemistry (geometrical isomers)
- Determination of molecular orientation (polymers and solutions)

Common Applications:

- Identification of compounds by matching spectrum of unknown compound with reference spectrum (fingerprinting)
- Identification of functional groups in unknown substances

Nuclear Magnetic Resonance (NMR) spectroscopy

NUCLEAR MAGNETIC RESONANCE (NMR)

Nuclear Magnetic Resonance (NMR) is a spectroscopic technique that reveals information about the environment of magnetically active nuclei. Under proper conditions, such nuclei absorb electromagnetic radiation in the radio-frequency region at frequencies governed by their chemical environment. This environment is influenced by chemical bonds, molecular conformations, and dynamic processes. By measuring the frequencies at which these absorptions occur and their strengths, it is usually possible to deduce facts about the structure of the molecule being examined.

NMR is commonly used in organic chemistry to elucidate molecular structures and conformations by studying ^1H and ^{13}C nuclei. NMR is sensitive to many other nuclei, however, and is not restricted to these uses. The field of NMR continues to grow at a prodigious rate and applications of NMR can be found in virtually every field of chemistry. NMR has even led to the development of Magnetic Resonance Imaging (MRI), an important medical imaging technique.

SPIN

All nuclei have a property called spin. As moving charge produces electrical field as well as magnetic field and nucleus is considered as moving or spinning charge particle and hence produces magnetic field. Spin describes the nature of that nucleus' magnetic field. Spin is characterized by a spin number, I , which can be zero or some positive integer multiple of $1/2$ (e.g. $1/2$, $2/2$, $3/2$, etc.). Nuclei whose spin number, I , equals zero have no magnetic field, while nuclei with non-zero spin numbers do have magnetic fields. Higher values of spin number imply more complex magnetic fields.

Some common nuclei, such as ^{12}C and ^{16}O , have $I=0$ and have no magnetic field. This makes these nuclei invisible to NMR spectroscopy. Other elements such as ^1H , ^{13}C , ^{19}F and ^{31}P have $I=1/2$, while others have even higher spin numbers:

$I=1$ e.g. ^{14}N , ^2H

$I=3/2$ e.g. ^{11}B , ^{35}Cl , ^{37}Cl , ^{79}Br , ^{81}Br .

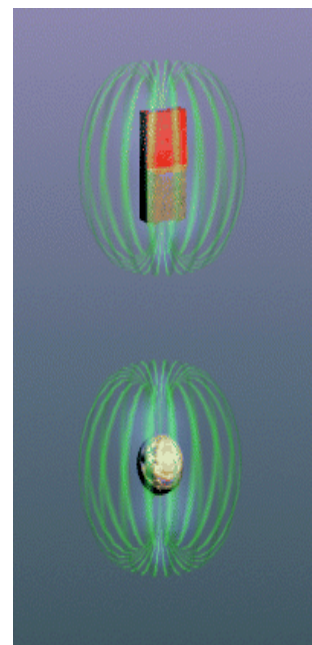
As the values for I increase, the shapes of the magnetic fields become progressively more and more complex.

While the shape of a nucleus' magnetic field is described by I , its strength is described by γ , the magnetogyric ratio. A nucleus with a large magnetogyric ratio has a stronger magnetic field than a nucleus with a small magnetogyric ratio. The strongest magnetic field is conveniently possessed by ^1H , the most common isotope of the most common element. These simple facts explain why hydrogen NMR (also called proton NMR) is the most popular form of NMR today. Carbon-13 and phosphorus-31 NMR are probably close seconds.

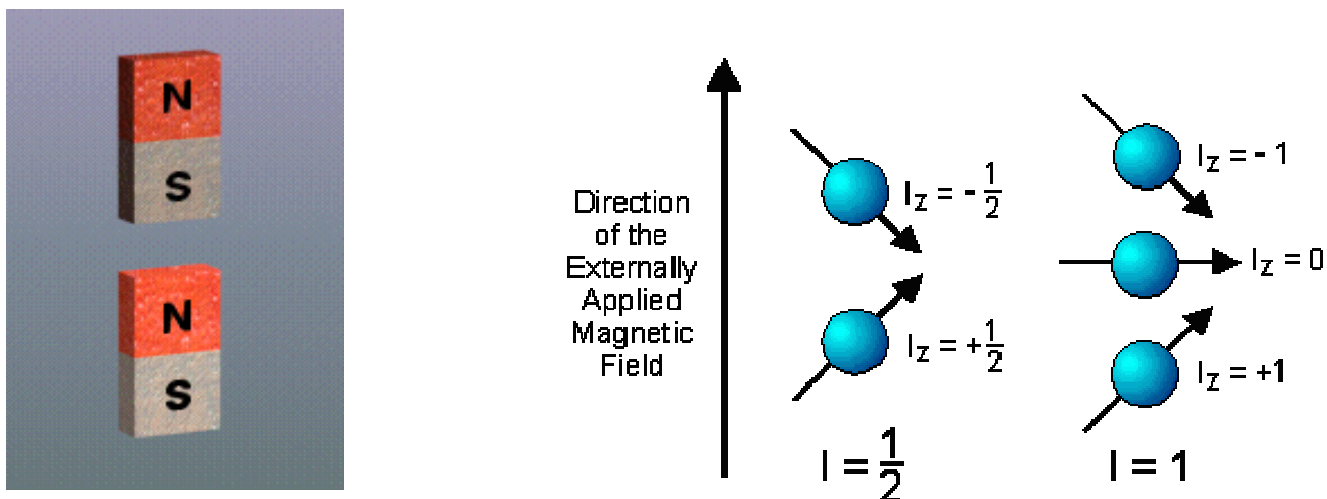
EFFECT OF EXTERNAL MAGNETIC FIELD

If two magnets are brought near each other they will exert a force on each other and will try to align themselves. For simple bar magnets, the favoured alignment is parallel (north pole of one magnet faces the south pole of the second).

Similarly, when a magnetic nucleus ($I>0$) is placed between the poles of an external magnet, it too will try to align itself with respect to this externally applied magnetic field (H_0). In the macroscopic world, two magnets can be aligned in an infinite number of orientations. At the atomic level, these alignments are quantized. There are only a finite number of alignments a nucleus can take against an external magnetic field. This number depends on the shape of the nucleus' magnetic field and therefore depends on the value of its spin number I . Each possible alignment is assigned a value called I_z which ranges from $-I$ to $+I$ in steps of 1. These orientations are referred to as spin states. In general, a nucleus will have $(2I+1)$ orientations (spin states) with respect to the external magnetic field.



The diagram illustrates the possible spin states for a spin 1/2 and a spin 1 nucleus.

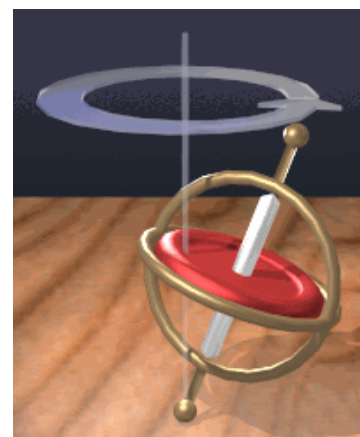


Nuclei with $I=1/2$ have a simple magnetic field and can align **With** ($I_z = 1/2$) or **Against** ($I_z = -1/2$) the external magnetic field yielding two spin states. Nuclei with $I=1$ have a more complex magnetic field and can have one of three orientations ($I_z = 1, 0, -1$).

PRECESSION

Classical magnets, when brought together, will align exactly parallel to each other and will maintain this alignment in a static fashion. Magnetic nuclei, due to restrictions described by quantum mechanics, do not align exactly parallel to or against the external magnetic field but rather, they align at an angle. This has an important consequence that can be illustrated by considering a gyroscope.

A gyroscope is first encountered by many people as a child's toy. A gyroscope is typically a spinning mass supported in a frame. A spinning gyroscope, when placed in a specific orientation, will tend to hold that orientation despite the effects of external forces like gravity.



In a vertical gravity field (gravity pulling straight down) a gyroscope placed vertically will maintain this orientation motionlessly. If the gyroscope is placed at an angle to the gravity field, it will rotate about an axis parallel to this field demonstrating something called **precession**. The frequency of this precession depends on two factors, the force exerted by the gravity field, and the force exerted by the gyroscope. This can be illustrated in two ways. A mass placed on the upper tip of a gyroscope will increase the force exerted by the gravity field and the precession frequency will increase. Increasing the speed or mass of the gyroscope's spinner will increase the force it exerts and, again, the precession frequency will increase.

A magnetic nucleus in an external magnetic field behaves very much like a gyroscope and precesses about the external magnetic field. The angular frequency at which this precession occurs is given by

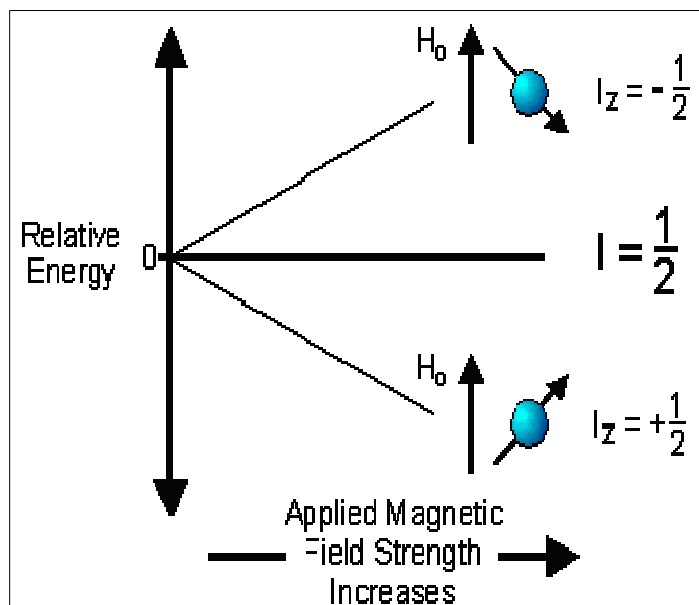
$$\nu = \frac{\gamma H}{2\pi} \text{ Hz}$$

and is called the **Larmor frequency**. The value, γ , is the magnetogyric ratio and is characteristic for each type of nucleus. It relates to the strength of the nucleus' magnetic field. H is the strength of the externally applied magnetic field. For example, a ^1H atom in a magnetic field $H=1.41$ Tesla has a Larmor frequency of 60 megahertz (MHz).

ENERGIES

The orientations a magnetic nucleus can take against an external magnetic are not of equal energy. Spin states which are oriented more nearly parallel to the external field are lower in energy than in the absence of an external field. In contrast, spin states whose orientations more nearly oppose the external field are higher in energy than in the absence of an external field.

Where an energy separation exists there is a possibility to induce a transition between the various spin states. By irradiating the nucleus with electromagnetic radiation of the correct energy (as determined by its frequency), a nucleus with a low energy orientation can be induced to "jump" to a higher energy orientation. The absorption of energy during this transition forms the basis of the NMR method.



When discussing NMR you will find that spin state energy separations are often characterized by the frequency required to induce a transition between the states. While frequency is not a measure of energy of these states, the simple relationship $E=h\nu$ (where E =energy, h =Planks constant, and ν =frequency) makes this substitution understandable. The statement "the transition (peak) shifted to higher frequencies" should be read as "the energy separation increased".

Comparison of various spectroscopic methods

NMR	~60x10 ⁶ to 600x10 ⁶ Hz	Probes nucleus' magnetic field
ESR	~1x10 ⁹ to 30x10 ⁹ Hz	Probes electron's magnetic field
Microwave	~1x10 ⁹ to 600x10 ⁹ Hz	Probes molecular rotation
Infrared	~6x10 ¹¹ to 4000x10 ¹¹ Hz	Probes bond vibrations and bending
Ultraviolet/Visible	~7.5x10 ¹⁴ to 300x10 ¹⁴ Hz	Probes outer core electron transitions
Mössbauer	~3x10 ¹⁶ to 300x10 ¹⁶ Hz	Probes inner core electron transitions Probes transitions within the nucleus

Population Distribution

In a given sample of a specific nucleus, the nuclei will be distributed throughout the various spin states available. Because the energy separation between these states is comparatively small, energy from thermal collisions is sufficient to place many nuclei into higher energy spin states. The numbers of nuclei in each spin state are described by the Boltzmann distribution

$$\frac{N_{\text{upper}}}{N_{\text{lower}}} = e^{-\gamma_N H h / kT}$$

where the N values are the numbers of nuclei in the respective spin states, γ is the magnetogyric ratio, h is Planck's constant, H is the external magnetic field strength, k is the Boltzmann constant, and T is the temperature. For example, given a sample of ^1H nuclei in an external magnetic field of 1.41 Tesla

$$\begin{aligned} \text{Ratio of populations} &= e^{((-2.67519 \times 10^8 \text{ rad.s}^{-1} \cdot \text{T}^{-1} * 1.41 \text{ T} * 6.626176 \times 10^{-34} \text{ J.s}) / (1.380662 \times 10^{-23} \text{ J.K}^{-1} * \text{K} 293))} \\ &= 0.9999382 \end{aligned}$$

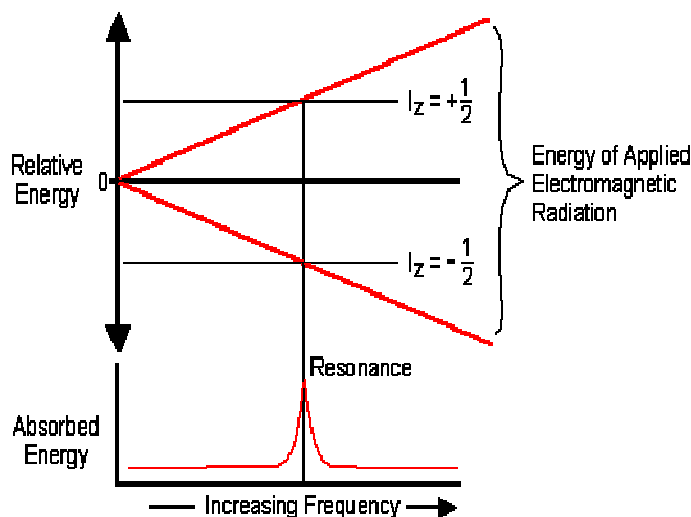
At room temperature, the ratio of the upper to lower energy populations is 0.9999382. In other words, the upper and lower energy spin states are almost equally populated with only a very small excess in the lower energy state.

When a system is irradiated with a frequency, whose energy matches that separating the levels, transitions will be induced not only from the lower energy level to the higher, but also in the reverse direction. Upward transitions absorb energy while downward transitions release energy.

NMR EXPERIMENT

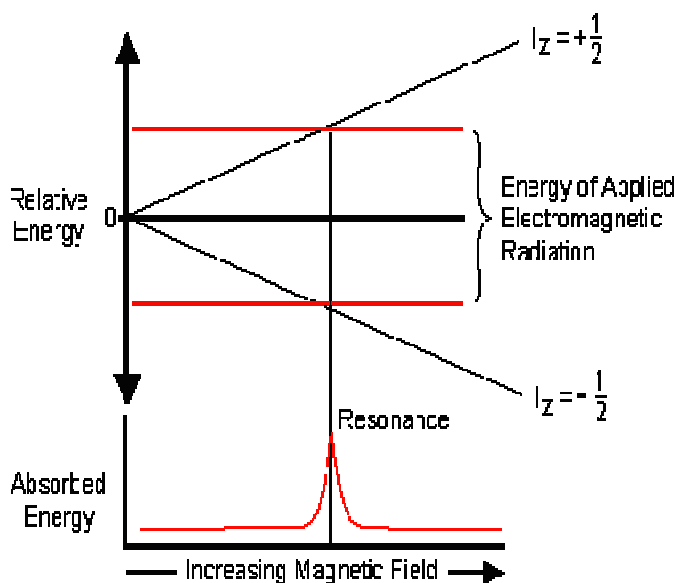
When a sample of magnetically active nuclei is placed into an external magnetic field, the magnetic fields of these nuclei align themselves with the external field into various orientations. Each of these spin-states will be nearly equally populated with a slight excess in lower energy levels. During the experiment, electromagnetic radiation is applied to the sample with energy exactly equivalent to the energy separation of two adjacent spin states. Some of the energy is absorbed and the alignment of one nucleus' magnetic field reorients from a lower energy to a higher energy alignment (spin transition). By sweeping the frequency, and hence the energy, of the applied electromagnetic radiation, a plot of frequency versus energy absorption can be generated. This is the NMR spectrum.

In a homogeneous system with only one kind of nucleus, the NMR spectrum will show only a single peak at a characteristic frequency. In real samples the nucleus is influenced by its environment. Some environments will increase the energy separation of the spin-states giving a spin transition at a higher frequency. Others will lower the separation consequently lowering the frequency at which the spin transition occurs. These changes in frequency are called the chemical shift of the nucleus and will be examined in more detail. By examining the exact frequencies (chemical shift) at which the spin transitions occur conclusions about the nature of the various environments can be made.



In a simply type of experiment, where the frequency is swept across a range, is known as a continuous wave (CW) experiment. One simple variation on this experiment is to hold the frequency of the electromagnetic radiation constant and to sweep the strength of the applied magnetic field instead. The energy separation of the spin states will increase as the external field becomes stronger. At some point, this energy separation matches the energy of the electromagnetic radiation and absorption occurs. Plotting energy absorption versus external magnetic field strength produces the identical NMR spectrum.

In fact, the NMR spectrum obtained by plotting magnetic field increasing to the right will be a mirror image of the spectrum where frequency is plotted increasing to the right. Low energy transitions (to the left) in a frequency swept experiment will not occur until very high magnetic fields (to the right) in a magnetic field swept experiment. Early NMR spectrometers swept the magnetic field since it was too difficult to build the very stable swept RF sources that NMR required. Even today where this is no longer required, NMR spectra are still plotted with magnetic field increasing to the right.



Technological advances have made the CW experiment obsolete and today virtually all NMR experiments are conducted using pulse methods. These methods are inherently much more sensitive and this explains part of their popularity.

THE NMR SPECTRUM - INTRODUCTORY COMMENTS

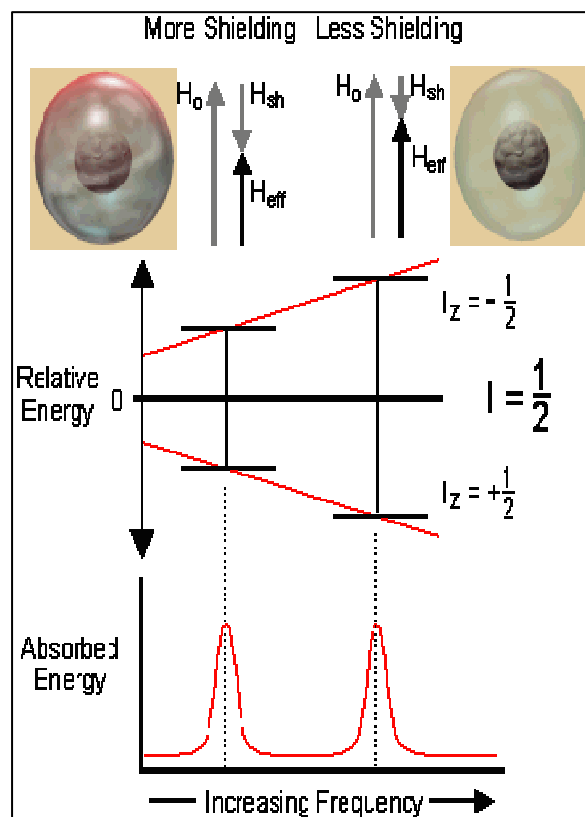
The magnetic nuclei are influenced by their chemical environments. In this section we will explore how the chemical environment influences the nuclei and what effects will be produced in the NMR spectrum. By understanding these effects, we will be able to interpret the features of an NMR spectrum and make predictions about the structure of the compound being examined.

SHIELDING AND DESHIELDING - CHEMICAL SHIFT

Electrons, like nuclei, have an inherent magnetic field (Electrons have spin = 1/2). The strength of this magnetic field is, however, several thousands of times stronger. Also, because the electron's charge is negative rather than positive, the polarity of the magnetic field generated by an electron is opposite that of the nucleus.

In a molecule, the nucleus is always surrounded by an electron cloud. As a result, the nucleus will experience an effective magnetic field (H_{eff}) which is a combination of the externally applied magnetic field and the magnetic field generated by the electron cloud surrounding the nucleus. Since the electron's magnetic field opposes the external magnetic field, the nucleus is "shielded" from the full force of the external magnetic field. H_{eff} is normally less than H_0 .

Within a molecule there are factors which can increase or decrease the electron density surrounding a nucleus. Factors which reduce the electron density are said to deshield the nucleus since H_{eff} at the nucleus increases. Similarly, factors which increase the electron density are said to "shield" the nucleus since H_{eff} will decrease.



Previously we saw that the energy separation of a nucleus' spin states is proportional to the strength of the magnetic field that the nucleus is exposed to. If the magnetic field strength is reduced by shielding, the spin state energy separation decreases and a lower frequency of RF can induce a spin transition. Analogously, if the nucleus is de-shielded, the H_{eff} at the nucleus is larger, the spin state energy separation increases, and a higher frequency of RF is needed to induce a spin transition. This change in absorption frequency due to shielding is called the **Chemical Shift**.

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

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{reference}}}{\nu_0} \times 10^6 \text{ (ppm)}$$

$$\text{OR } \delta = \frac{H_{\text{sample}} - H_{\text{reference}}}{H_0} \times 10^6 \text{ (ppm)}$$

Consider ^1H NMR. On a spectrometer where the proton transition frequencies are nominally 60 MHz, the chemical shift frequency changes may be only hundreds of hertz; about a million times smaller than the resonance frequency. Because of how the electron shielding and deshielding effects arise, they are proportional in strength to that of the externally applied magnetic field. Because of this relationship, chemical shifts are typically reported as a fraction of the nominal resonance frequency. Due to their small size, parts-per-million (ppm) are used.

STANDARD FOR NMR SPECTROSCOPY

The following compounds are generally used as internal standard (reference materials) in NMR spectroscopy-

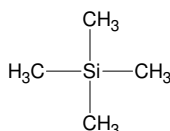
1. Tetramethylsilane (TMS)-

TMS is generally employed as internal standard for measuring the position of ^1H and ^{13}C in the NMR spectrum because of the following facts:

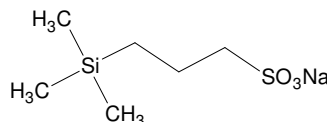
1. It gives single sharp line from twelve magnetically equivalent protons.
2. It is chemically inert and miscible with a large range of solvents.
3. It, being highly volatile, can easily be removed if the sample has to be recovered.
4. It does not involve in intermolecular association with the sample.
5. It has the added advantage that its resonance position is far removed from the absorptions due to protons in most organic molecules. Therefore, by arbitrarily assigning TMS = 0, it is possible to devise a scale in which most proton resonance will be of the same sign.

2. Sodium salt of 3-(trimethylsilyl)propane sulphate

This water soluble compound is commonly used as an internal standard for running the PMR spectra of water soluble materials in deuterium oxide solvents.



Tetramethylsilane (TMS)



Sodium salt of 3-(trimethylsilyl)propane sulphate

FACTORS AFFECTING THE VALUE OF CHEMICAL SHIFT –

1. Inductive effect (Electronegativity)
2. Anisotropic effects
3. van der Waal's deshielding
4. Hydrogen bonding
5. Hybridization

1. Inductive effect (Electronegativity)-

A nucleus is shielded or deshielded whenever it is influenced by the magnetic fields of nearby electrons. The closest electrons to a nucleus are those that bond the nucleus to its neighbouring atoms. Any factor that effects the distribution of these bonding electrons will also effect the degree of shielding the nucleus experiences. Electronegativity is one important factor that will alter the distribution of bonding electrons.

Electronegative atoms have an affinity for electrons. The more electronegative the atom is, the stronger this affinity. Consider the following two cases; an ^1H atom bonded to a carbon; an ^1H atom bonded to an oxygen. Carbon is less electronegative than oxygen. In an oxygen-hydrogen bond, the bonding electrons will be drawn towards the oxygen. The electron density around the hydrogen atom will be reduced in comparison to the same hydrogen bonded to a carbon atom. In the case of an O-H bond, hydrogen has a lower electron density surrounding it and is, therefore, less shielded. Electronegative atoms or electron withdrawing functional groups are considered to be deshielding. Electropositive atoms or electron donating functional groups are considered to be shielding.

As the electronegativity of atom increases the proton becomes more deshielded and the peak is shifted towards down field direction (left hand side away from TMS signal). The inductive effect decreases with distance and hence deshielding decreases as the distance increases.



2. Anisotropic effects (Pi-System Ring Currents)-

The magnetic fields associated with the electron circulations induced by applied magnetic field H_0 , in molecules containing pi bonds, are anisotropic, that is, they do not sum to zero in overall possible orientations of the molecule with respect to applied magnetic field H_0 . This phenomenon is, therefore, called anisotropic effect. The effect is particularly important in molecule containing pi bonds for example alkenes, alkynes, aromatic systems and carbonyl compounds.

The bonding electrons always produce a shielding effect. The strength of this effect will vary depending on the exact nature of the bonded atoms but the resulting H_{eff} will always be less than H_0 . There are, however, some effects which can actually produce a magnetic field that reinforces H_0 . One of these effects is a ring current.

The primary shielding effect comes from the electron's inherent magnetic field. We know from physics, however, that a moving charge (current) can also produce a magnetic field by virtue of its motion. Most organic compounds contain a carbon atom skeleton. When the atoms of this skeleton are sp^2 hybridized, there is a p-orbital available on each carbon. There is a strong tendency for p-orbitals on adjacent carbon atoms to align and when they do a π -system is produced. Organic compounds containing π -system permit this type of electron "motion". Because the benzene ring is the classic example of this type of system, this electron "motion" is termed a ring current.

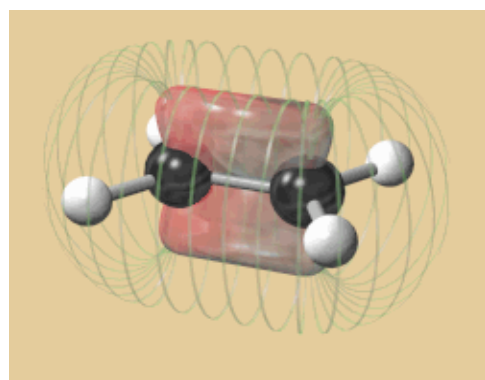
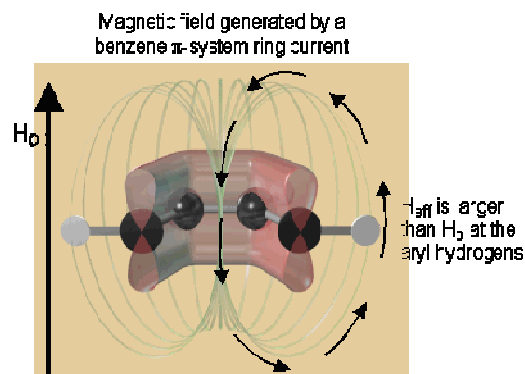
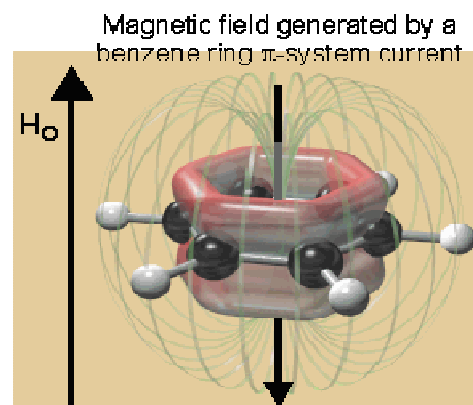
As in the case of an individual electron, the magnetic field generated by this ring current opposes the externally applied magnetic field, H_0 . The aryl hydrogens, however, are located in the "return" portion of the ring current magnetic field and experience a magnetic field which reinforces H_0 . Ring currents strongly deshield the aryl hydrogens. This can be seen more clearly in the cut-away view of the aryl π -system. The direction of the ring current magnetic field is shown by the black arrows.

The situation is exactly analogous for other π -system. The vinyl system is the other commonly encountered π -system. As seen below, the ring current generates exactly the same type of field and, again, the vinyl hydrogens are located in the "return" region of the magnetic field. These hydrogens are strongly deshielded although to a lesser extent when compared to aryl hydrogens.

In some rigid systems it is possible for hydrogens to be located directly above or below the π -system. Thus they will be shielded by the π -system's magnetic field. While these cases are uncommon, one should be aware of them as the effect can be pronounced.

3. van der Waal's deshielding-

In overcrowded molecule, when the molecular geometry constrains two groups of protons, in a rigid molecule, to approach more closely than the sum of their van der Waals radii, weak repulsive forces, called van der Waals forces operate between them. These force result in the decrease of electron density around the nucleus causing deshielding of the nucleus (downfield shift). Although the intramolecular van der Waals deshielding effects are small usually less than one ppm however valuable conformational information may be derived from such chemical shifts.



4. Hydrogen bonding-

Hydrogen bonding involves electron cloud transfer from hydrogen atom to neighbouring electronegative atoms. The electron withdrawal from a proton, involved in hydrogen bonding, thus causes deshielding of the proton. Greater is the degree of hydrogen bonding of a proton, the greater the downfield shift (higher delta value) of its resonance.

5. Hybridization-

As the s-character of hybrid orbital increases the electronegativity of carbon also increases and hence the electron cloud shifted towards carbon. This results in the downfield shift of peak in NMR spectrum.

SPIN- SPIN COUPLING

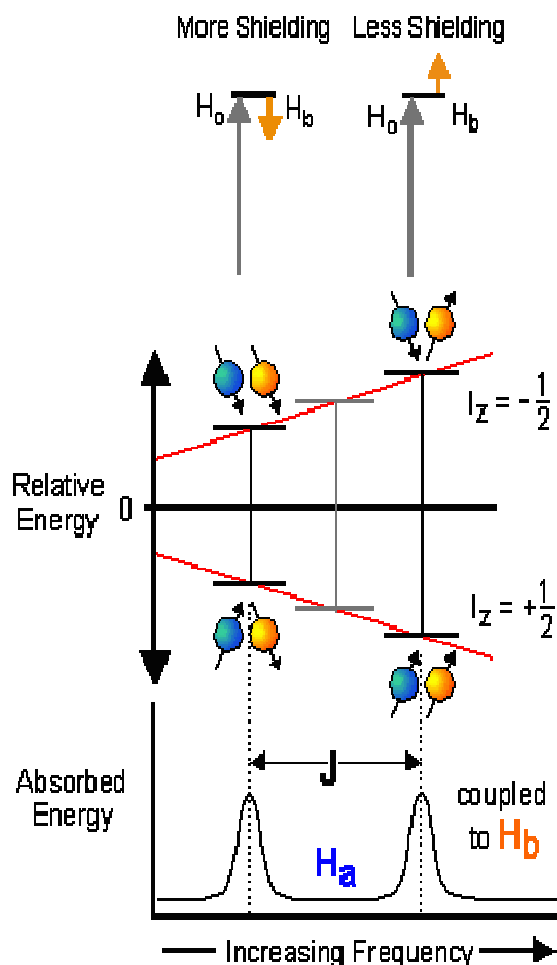
Spin-Spin coupling (splitting of NMR signals) arises due to interaction of magnetic moment of particular nuclei with magnetic moments of nearby nuclei. The H_{eff} that a nucleus experiences is primarily a combination of the externally applied magnetic field and the shielding and deshielding effects of bonding electrons & nearby ring currents. A smaller, but very important, effect is produced by the magnetic fields of neighbouring nuclei. While these fields are very small, they can produce an observable effect if the nuclei are brought close enough together. Typically, "close" means within 3 bonds.

To understand this effect, consider $\text{CH}_b\text{Cl}_2\text{CH}_a\text{Br}_2$ molecule having two types of suitably close hydrogen atoms, A and B, that have different chemical shifts. Hydrogen A has two spin states, $I_z = +1/2$ and $I_z = -1/2$. and in the absence of hydrogen B, it will give a single NMR peak. Its neighbour, hydrogen B, has a small magnetic field, however, which is either aligned with or against the external field. We know that the two orientations have about the same probability.

When hydrogen B's field is aligned with H_0 , hydrogen A will be deshielded and H_{eff} will become slightly larger. When hydrogen B's field is aligned against H_0 , hydrogen A will be shielded and H_{eff} will become slightly smaller.

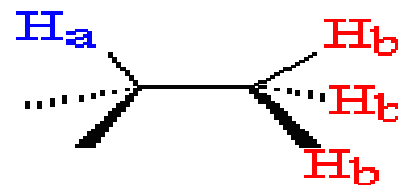
In our sample, half of the molecules will have hydrogen B's magnetic field aligned with H_0 . Hydrogen A in these molecules will resonate at a higher frequency. The other half of the molecules will have hydrogen B's magnetic field aligned against H_0 and hydrogen A will resonate at a lower frequency. The presence of hydrogen B, therefore, causes the single peak for hydrogen A to split into a doublet (two peaks).

The frequency separation between these two peaks is called **J**, the **dipolar coupling constant**, and typically is between 0 and 15 Hz. Whereas, the chemical shift is dependent on the strength of H_0 and is reported in ppm, the coupling constant is **independent** of H_0 and is reported in Hz. An important point to note is that if hydrogen B splits the peak for hydrogen A by J Hz, the reverse is true too. Hydrogen A will split the peak for hydrogen B by J Hz as well. This fact is very useful for identifying which hydrogens are coupled to each other.

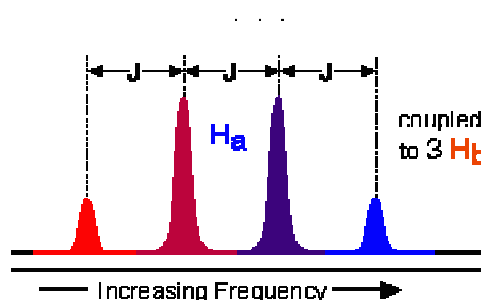
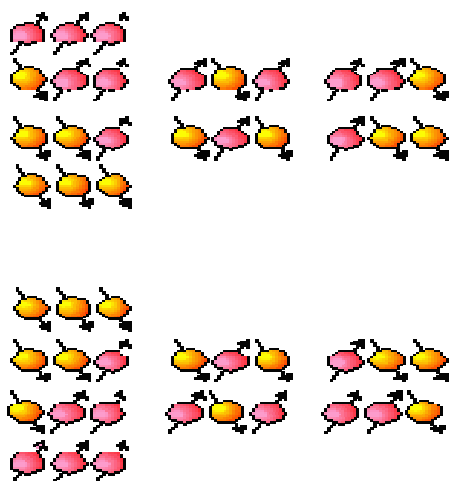


As the number of coupled hydrogens increases, the splitting pattern becomes more complicated. Consider a hydrogen (A) located adjacent to a methyl group.

The diagram, to the right, illustrates the possible alignments that the methyl hydrogen magnetic fields can have and the effect this has on hydrogen A's spin state energies. For three identical hydrogens there are eight possible combinations of Up/Down spin. The net shielding or deshielding experienced at hydrogen A depends on the sum of the three hydrogen's magnetic fields. The most shielding (lowest frequency) occurs when all three hydrogens oppose H_0 (**DDD**). The next most shielded case occurs when two of the three hydrogens oppose H_0 . There are three combinations of magnetic fields that can produce this effect (**DDU** **DUD** **UDD**).



All of the combinations have the same probability of occurring (1/8th). Since only one combination can produce the lowest frequency NMR peak compared to three combinations producing the next higher frequency peak, the relative intensities of these peaks will be 1 to 3. The situation is exactly analogous for the remaining two cases, one hydrogen opposing H_0 and no hydrogens opposing H_0 . Overall, the set of four NMR peaks have the intensity ratio of 1:3:3:1.



INTENSITIES OF MUTIPLATES:

Where a single coupled hydrogen produces a doublet, three identical coupled hydrogens produce a quartet. In general, N identical coupled nuclei will produce $(2N+1)$ lines. The intensities of the lines can be predicted (for N identical coupled spin 1/2 nuclei) by using **Pascal's triangle**.

SINGLET	1	no coupled nuclei
	/ \	
DOUBLET	1 1	1 coupled spin 1/2 nucleus
	/ \ / \	
TRIPLET	1 2 1	2 coupled spin 1/2 nuclei
	/ \ / \ / \	
QUARTET	1 3 3 1	3 coupled spin 1/2 nuclei
	/ \ / \ / \ / \	
QUINTET	1 4 6 4 1	4 coupled spin 1/2 nuclei

In Pascal's triangle, a number is always the sum of the two numbers in the preceding row that straddle it.