INFRARED SPECTROSCOPY

In contrast to ultraviolet spectroscopy, the infrared spectrum provides a rich array of absorption bands which can provide a wealth of structural information about a molecule. It provides methods for studying materials in all three physical states i.e gas, liquid or solid. Analytically useful IR spectrum covers the following range of the electromagnetic range.

Near IR	**15000 cm^{-1} to 3000 cm^{-1}**	**0.67 µm – 3.33 µm**
Mid IR	**4000 cm^{-1} to 400 cm^{-1}**	**2.5 µm – 25 µm**
Far IR	**200 cm^{-1} to 10 cm^{-1}**	**50 µm – 1000 µm**
Most used	**4000 cm^{-1} to 670 cm^{-1}**	**2.5 µm – 15 µm**

Microns or micrometers (μ or μm) were extensively used as the units of wavelength in the past but nowadays wave number (cm^{-1}) are the accepted units. A simple reciprocal relationship exists between wavelength (λ) and wave number i.e ν (cm^{-1}) = 10000 / λ (μm). The wave number is directly proportional to the absorbed energy (K = E/hc) where as wavelength is inversely proportional to the absorbed energy.

The information contained in an IR spectrum originates from molecular vibrations. These are either fundamental modes that are associated with the vibrations of specific functional groups, complex modes of the total molecule, vibrational overtones or summational modes of fundamental vibrations. IR analysis may simply involve the characterization of a material with respect to the presence or absence of a specific group frequency associated with one or more fundamental modes of vibration or by a complex pattern recognition or by a computer search- match algorithm when an unknown spectrum is compared to an existing reference database. The spectral data is also used to measure one or more compounds in a simple or complex mixture.

A nonlinear molecule containing n atoms has 3n – 6 possible vibrational modes through which infra red radiation may be absorbed. For example methane has 9 and benzene has 30 possible fundamental absorption bands respectively. In order that a particular vibration results in an absorption band, the vibration must cause a change in the dipole moment of the molecule. Thus molecules containing certain symmetry groups will display somewhat simplified spectra. The C=C stretching of ethylene and C-H stretching of methane do not result in an absorption band. Further if absorption occurs outside the IR region or too close for resolution or too weak in intensity, the observed number of absorption bands will be less than the predicted number .

Additional absorption bands may occur because of the overtones (at 1/2, 1/3 wavelengths with greatly reduced intensity), combination bands (sum of two or more different wave numbers), difference bands (the difference of two or more wave numbers) etc.

MOLECULAR VIBRATIONS

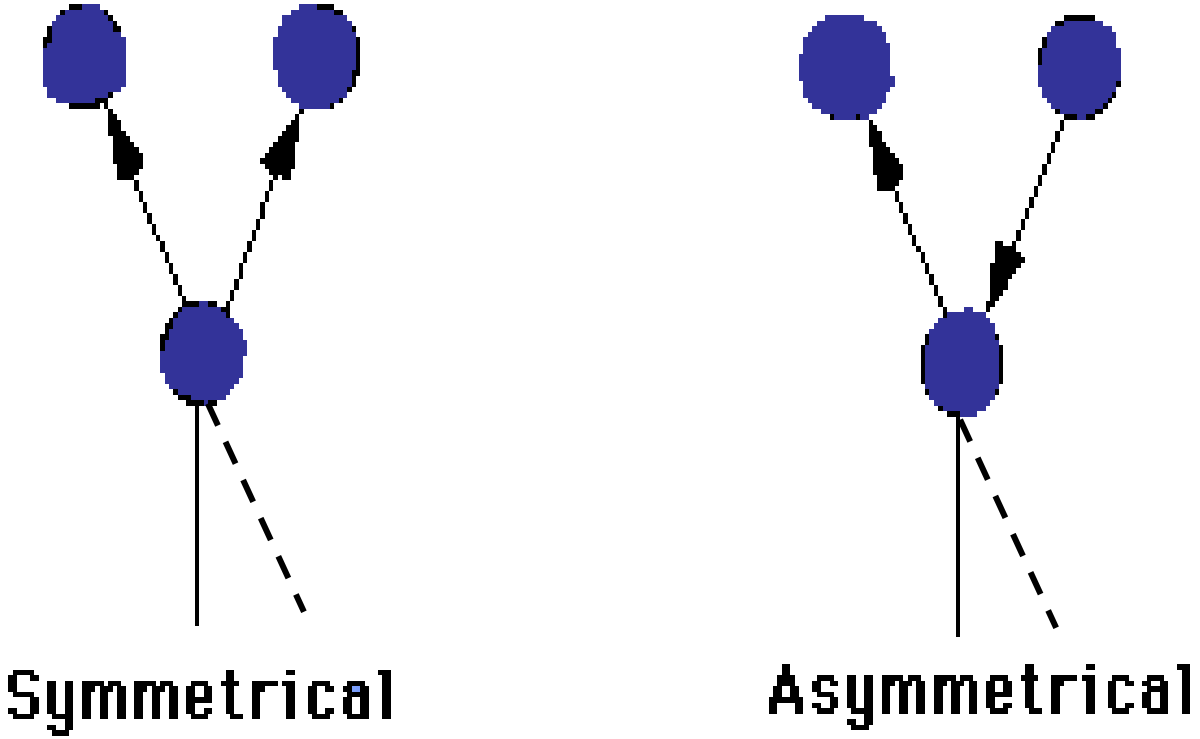
A molecule essentially resembles a system of balls of varying masses corresponding to the atoms of a molecule and springs of varying lengths corresponding to various chemical bonds. There are two kinds of fundamental vibrations of molecules.

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

ii) **Bending – in which the position of the atom changes relative to the bond axis.**

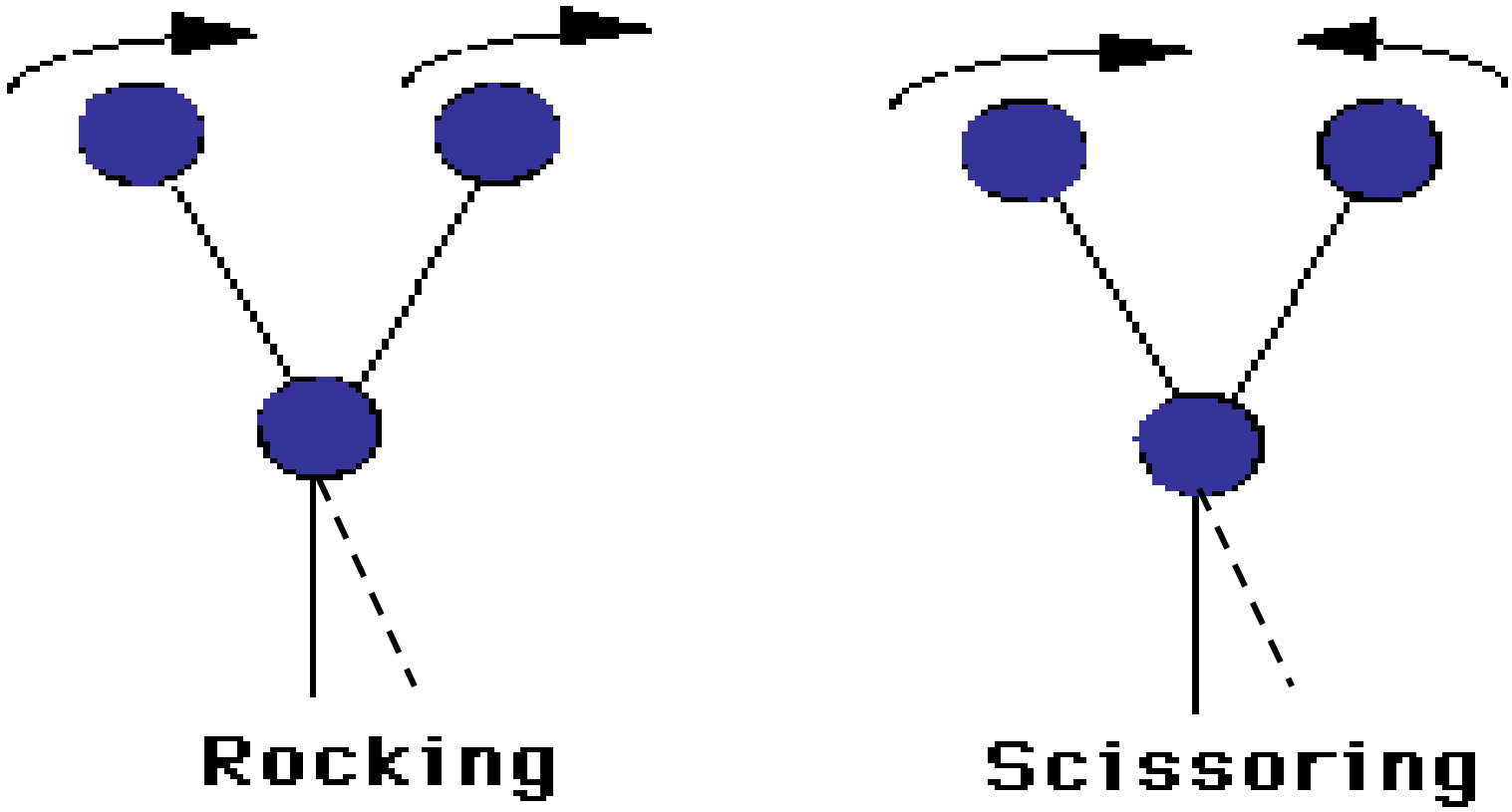
The various stretching and bending vibrations occur at certain quantized frequencies. When infra red radiation of the same frequency is incident on the molecule, energy is absorbed and the amplitude of that vibration increases correspondingly. When the molecule reverts to the ground state the absorbed energy is released as heat.

MOLECULAR VIBRATIONS



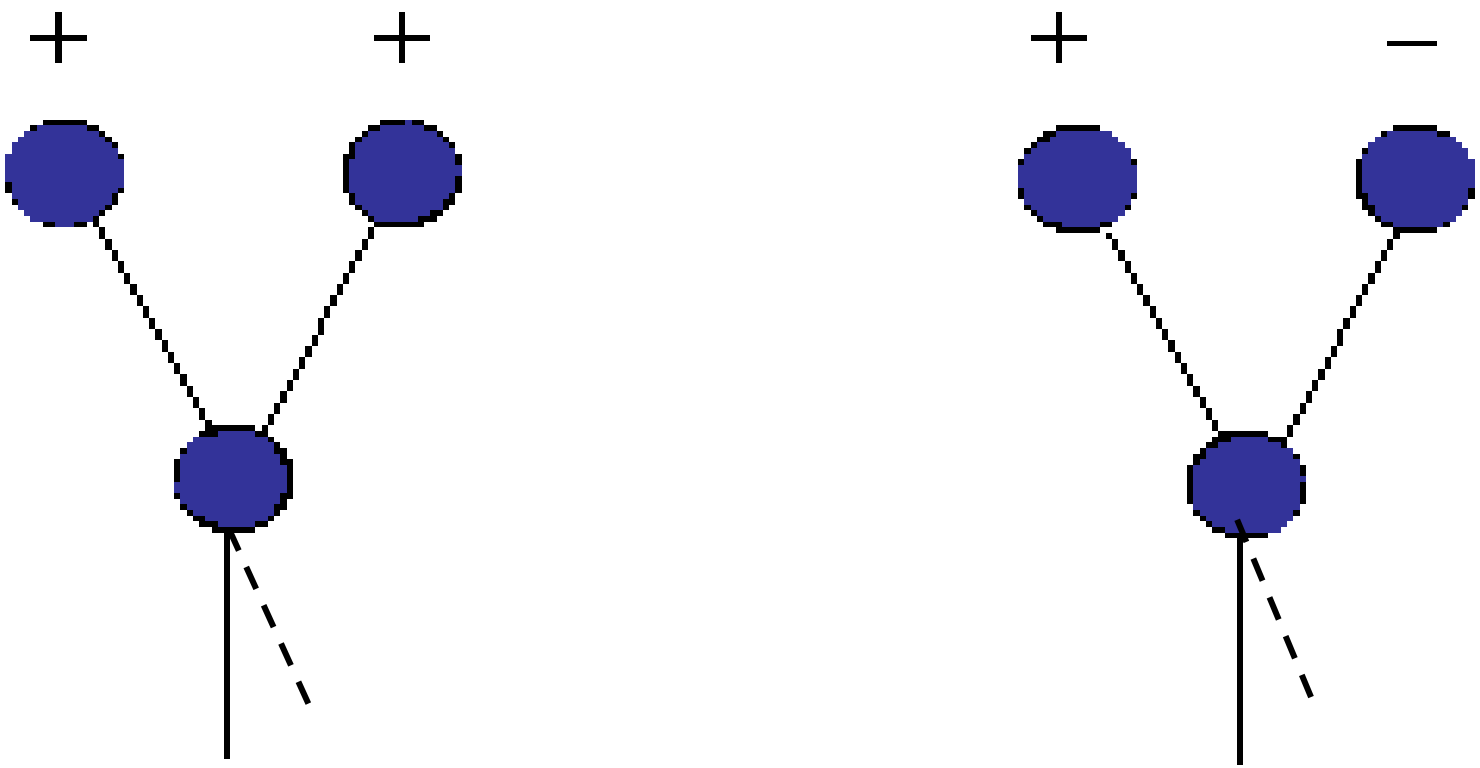
Stretching

MOLECULAR VIBRATIONS- BENDING



In-plane deformations

MOLECULAR VIBRATIONS-BENDING



Out-of-plane deformations

Bending vibrations generally require less energy and occur at longer wavelengths (lower cm^{-1}) than stretching vibrations. Stretching vibrations are found to occur in the order of their band strengths. Thus,

C≡C	2300 – 2000 cm^{-1}	4.4 – 50 μ
C=C	1900 – 1500 cm^{-1}	5.3 - 6.7 μ
C – C C – N C – O	1300 – 800 cm^{-1}	7.7 – 12.5 μ
N – H C – H O – H	3700 – 2630 cm^{-1}	2.7 – 3.8 μ
O – D	2630 cm^{-1}	3.8 μ
O – H	3570 cm^{-1}	2.8 μ

An approximate value of the stretching frequency in ν (cm^{-1}) of a bond can be calculated by the relationship,

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{\mathrm{k}}{\mathrm{M_X}M_Y / \ \mathrm{M_X} + M_Y}}$$

where k is a force constant (≃ 5,10,15 x 10^5 dynes/cm for single, double and triple bonds), M_X and M_Y are the masses of the atoms in grams.

INSTRUMENTATION

Modern commercial infrared instruments fall into three categories: Grating dispersive, filter dispersive and Fourier Transform (FT) infrared spectrometers. Essentially the infrared instruments consists of the following components:

i) The main optical system
ii) The source
iii) Sample compartment
iv) The detector and
v) The electronics and data handling

Whatever the mode of operation, spectrometer or the spectrophotometer forms the heart of the instrument. It takes the broad band infrared radiation and splits it into ultimate discrete frequencies or wavelengths with a given spectral resolution. This may be performed directly with a monochromator in a dispersive instrument or indirectly by a Fourier Transform instrument. In Fourier Transform, an interferometer assembly known as 'modulator' produces an output in the form of a modulated infrared beam which is decoded to produce the final infrared spectrum.

MONOCHROMATOR INSTRUMENTS

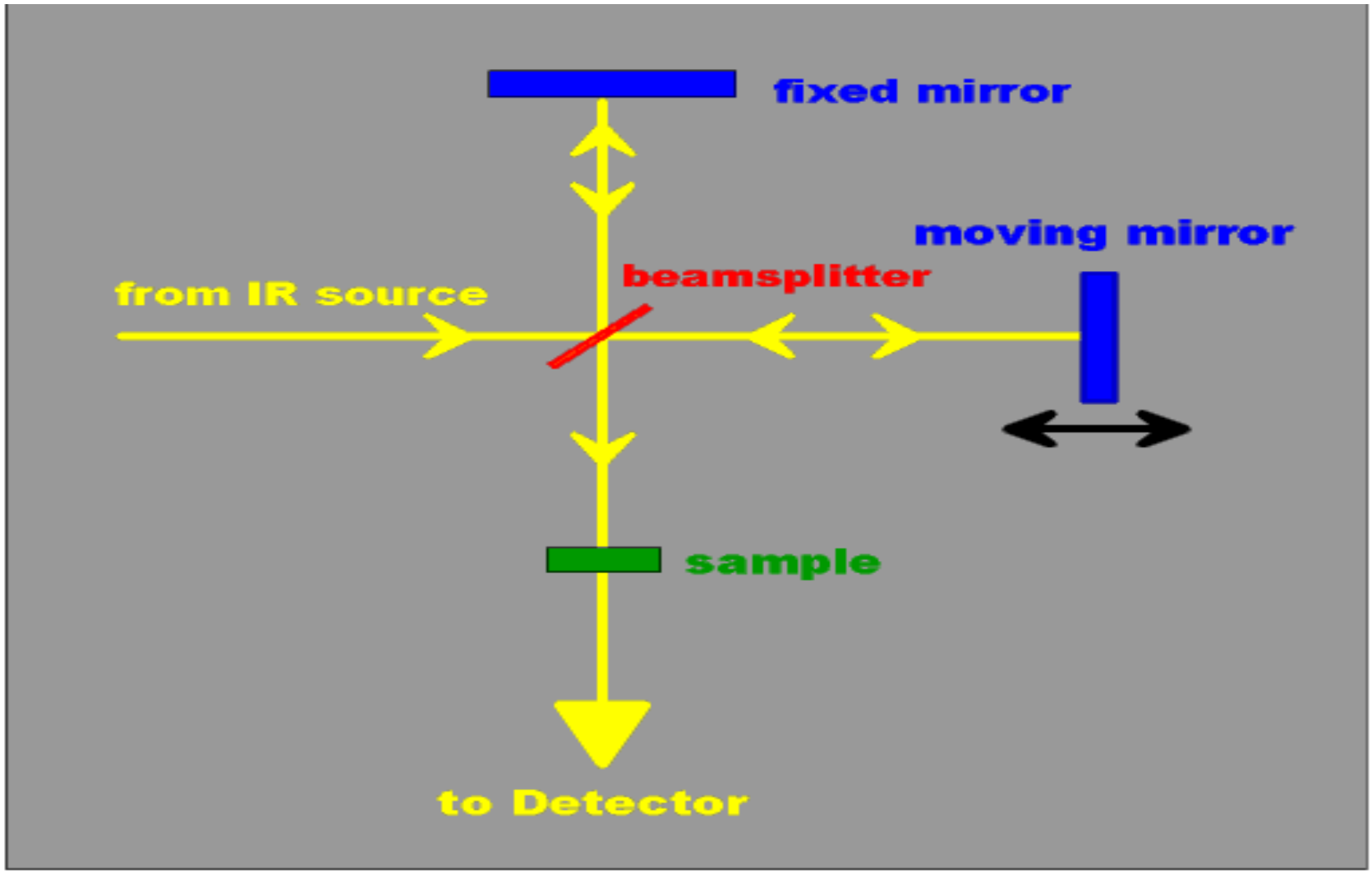
Monochromators range from simple filter based instruments to high resolution, double prism/grating /grating systems. Both Littrow and Czerney- Turner mountings are useful although the former is most useful. Earlier instruments were mostly prism based which provided a simple wavelength scan in micrometers. Nowadays littrow designs with one or more diffraction gratings are used. The gratings are driven by a stepping motor which is programmed into non linear fashion to produce a linear output in wave numbers.

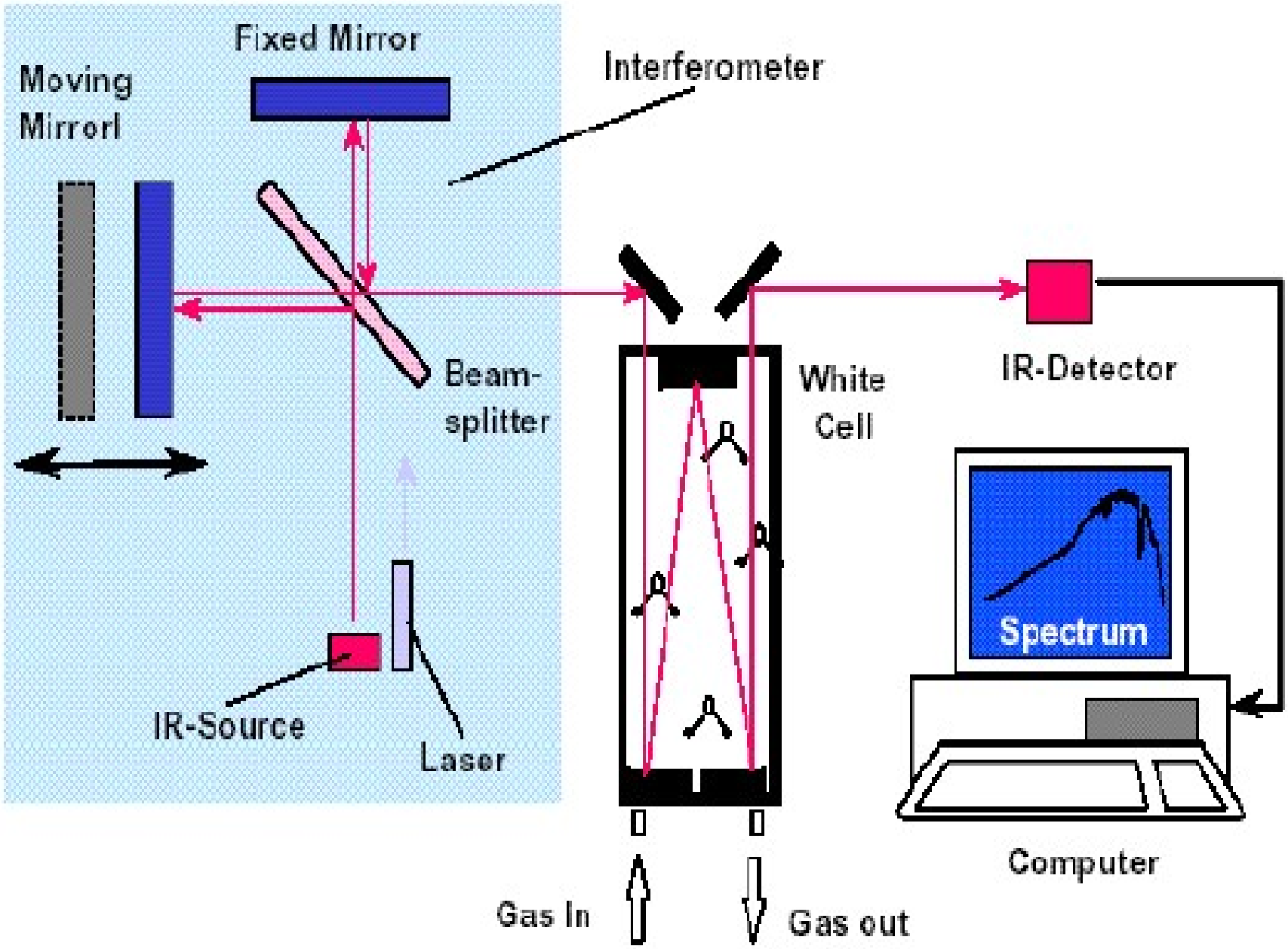
The full range of a grating spectrometer may be 4000 – 600 cm^{-1} or 5000 – 200 cm^{-1}. Gratings are normally operated in second or third order. Usually spectrums in the 4000 – 2000 cm^{-1} range is operated in second order and 2000 – 400 cm^{-1} range is obtained in the first order. A series of cut off and bandpass filters are placed between the monochromator and the detector to ensure the correct order of the grating. This is achieved by synchronizing with the scanning of the grating. In more expensive instruments only first order grating is used for all the gratings to provide optimum performance which is maximum over all the output range.

A grating blazed at two angles performs as two gratings in one. The drive is reproducible by 0.01 cm^{-1} but it can also be precalibrated against a spectroscopic standard. Modern monochromators are directly driven by a stepper motor and microprocessor controlled to provide high level of accuracy. This also provides a slit programming mechanism to give near constant energy.

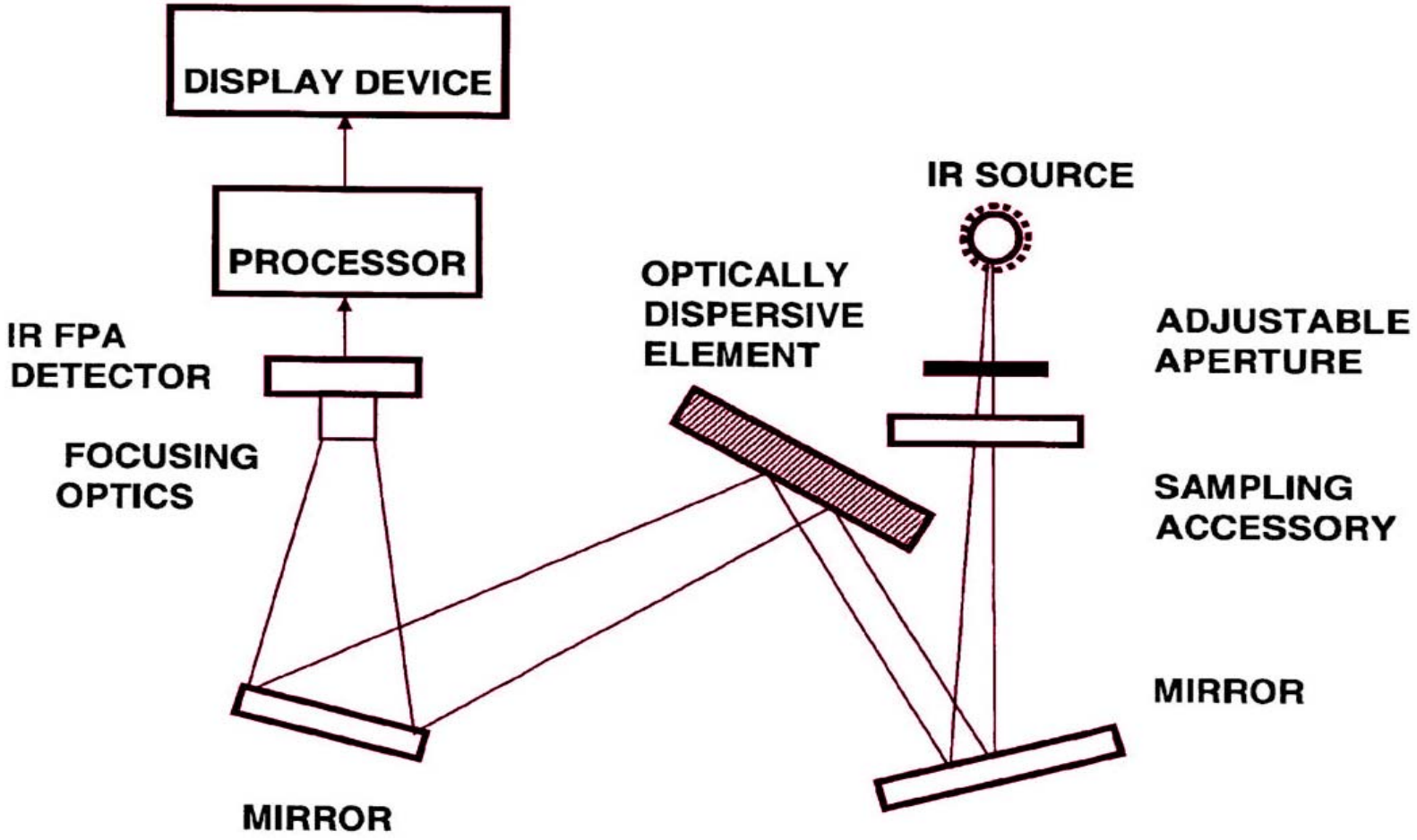
Single beam photometers posses the capacity for accurate measurement in quantitative analysis.

FOURIER TRANSFORM INTERFEROMETER




Fixed Mirror
Moving
Mirrorl
Interferometer
Beam-
splitter
White
Cell
IR-Detector
Spectrum
IR-Source
Laser
Computer
Gas In
Gas out

NON-INTERFEROMETRIC IR SPECTROSCOPY USING NO MOVING PARTS



Instead of using a monochromator, the IR radiation after passage through a sample can be analysed by means of a scanning Michelson interferometer. It consists of a moving mirror, a fixed mirror and a beam splitter. Radiation from the infrared source B is collimated by a mirror, split into two beams. One beam is passed through a fixed mirror and another to a moving mirror. After reflection the two beams are recombined at the beam splitter. The two beams interact at any particular wavelength constructively or destructively depending on the difference in the optical paths.

The intensity of the emerging radiation modulates in a sinusoidal manner. In the case of a broad band infrared source the emerging beam is a complex mixture of modulation frequencies, which after passing through the sample compartment is focused onto the detector.

The detector signal is sampled at very precise intervals during the mirror scan. Both the sampling rate and mirror velocity are controlled by a reference signal from the detector produced by the modulation of the beam from a He – Ne laser. The resulting signal is known as an interferogram which contains all the information required to reconstruct the spectrum using a mathematical process known as Fourier Transformation.

ADVANTAGES OF FTIR

i) Only one moving part is involved which is mounted on a frictionless air bearing.

ii) Slits and filters are not needed which saves energy especially in the far IR region.

iii) Near absolute frequency accuracy (better than 0.01 cm^{-1}).

iv) Same S/N ratio as in a dispersive spectrometer obtained in a fraction of time (Fellgets advantage).

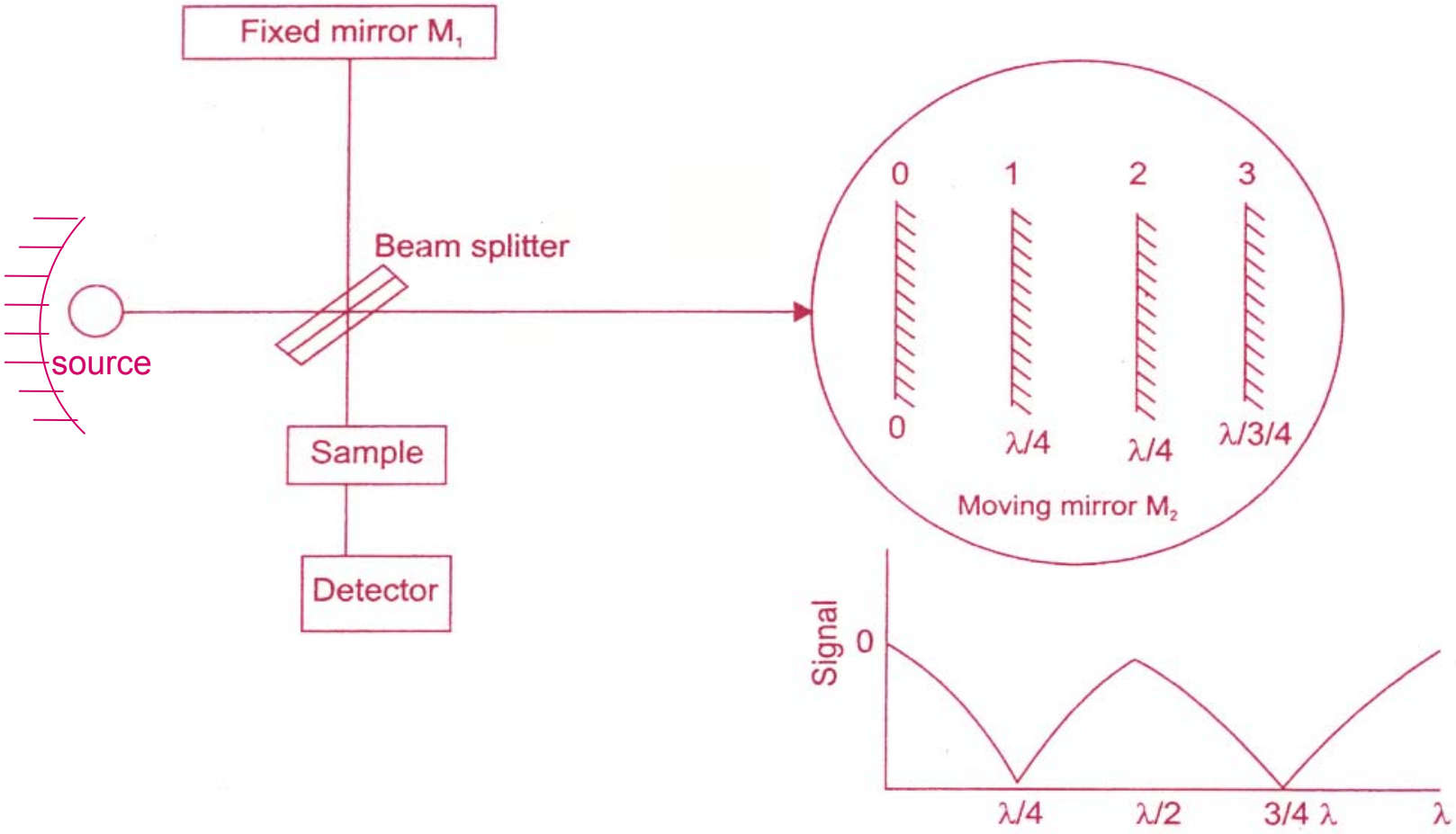
v) Saves time as many as 32 scans can be done per minute.

vi) Single beam spectrum is ratioed against stored background in the memory which gives the double beam accuracy.

To appreciate how the interferometer works and how it can be related to a spectroscopic measurement, let us see what happens with a single wavelength in an interferometer.

At position 1, the moving mirror and fixed mirror are equidistant from the beam splitter. In this situation both light beams travel the same distance and when they recombine at the beam splitter they are mutually in phase and constructive interference occurs. This is observed as a maximum signal being passed through to the detector. Let this signal be unity (zero path difference).

SCHEMATIC FTIR DIAGRAM



As the mirror moves away from ZPD (zero position displacement) to 1/4 λ, the signal reaches a minimum value or zero (out of phase). Further on, when it reaches 1/2 λ OPD (optical path difference), it again reaches a maximum value with constructive interference. This pattern continues where a series of maxima and minima are produced at λ /4 and λ /2 to yield an overall sine wave pattern or more accurately, a cosine wave.

If a second wavelength is selected now, a similar wave form is generated but the maxima and minima are separated by a distance equivalent to the new wavelength.

In this way a unique cosign wave is generated for each wavelength. The observed signal at the detector is a summation of all these cosign waves which gives a maximum at ZPD and rapidly decays to a complex overlapped signal which continues to decay with increasing distance from ZPD.

If the component cosign waves can be resolved then the contribution from individual wavelengths can be observed and a spectral output of the source could be constructed. This function is performed mathematically by a Fourier Transformation for frequency analysis.

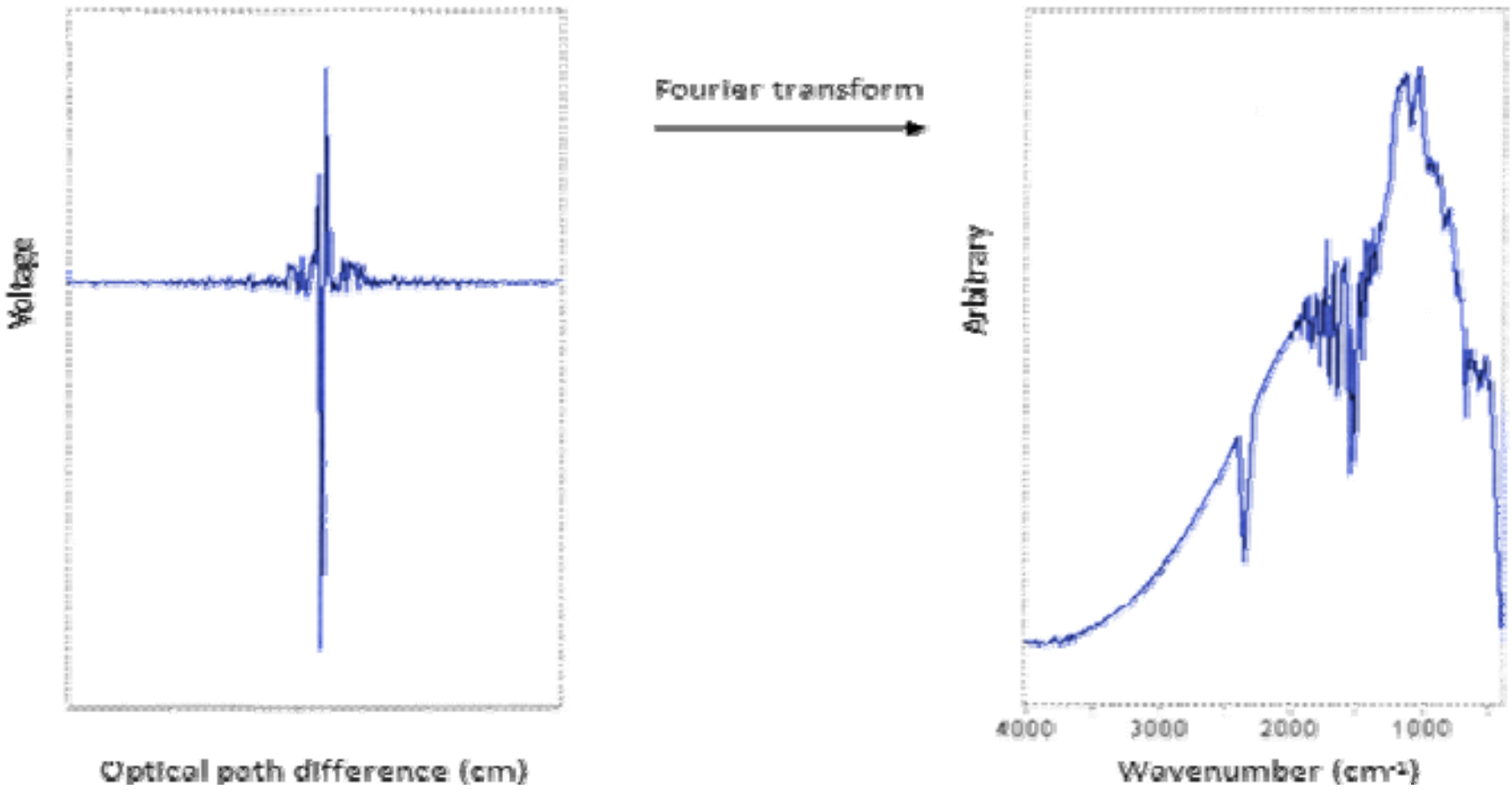
In mathematical terms, the Fourier relationship is defined as a pair of integrals.

$$\mathrm{I}(\delta) = \int_{-\infty}^{\infty} \mathrm{B}(\nu) \cos 2\pi\nu\delta \, \mathrm{d}\nu \quad \text{and}$$

$$\mathrm{B}(\nu) = \int_{-\infty}^{\infty} I(\delta) \cos 2\pi\nu\delta \, \mathrm{d}\delta$$

where I(δ) is the intensity of the interferogram as a function of retardation and B(ν) is the source intensity as a function of the wave number.

An idealized interferogram has a unique centre burst corresponding to ZPD with maximum intensity at the centre than on either side. As the sample is introduced, the distribution of information changes depending upon the natural line width of infrared spectrum of the sample and consequently more signal is observed in the wings of the interferogram.



INTERFEROGRAM **SINGLE BEAM SPECTRUM**

Spectral resolution of an IR instrument can be defined as the ability of the monochromator to separate two spectral features such as peaks or troughs or the ability to observe the separation of discrete wavelengths. This translates into the ability to define two cosine waves of different frequencies when they go out of phase and remain in phase at least once i.e 1/Δν cm, where

$$\Delta\nu = \nu_2 - \nu_1 \, (cm^{-1})$$

Maximum resolution of a spectra is approximately defined as 1/ Δ_{max}, where Δ_{max} is the distance of the moving mirror. Once data is obtained at a specific resolution, spectrum of lower resolutions can be artificially generated by using a subset of the data or by extrapolation.

Theoretically the information should be collected at infinite retardation but in practice the data is acquired at practical distances which results in the truncation of the interferogram at some stage and hence the separation will be always lower than the predicted value. This is known as apodization.

Thus an apodizing function needs to be applied to reduce the effect of premature truncation of the data. This acts like a weighting function. Two apodizing functions such as Hanning or Happ-Genzel are popular. This also reduces the noise since the noise is always uniformly distributed through out the interferogram.

The signal produced is also a phase dependent phenomenon. Optical components that can cause dispersion (mirrors) , beam splitter, detector etc., can also introduce phase errors in the final spectrum. Thus phase corrections are also normally applied to reduce the photometric errors.

SAMPLE HANDLING

Infrared instrumentation has reached a remarkable degree of standardization but sample handling itself presents a number of problems. No rugged window material for cuvettes exist that is transparent and inert over the entire infrared region.

Alkali halides such as NaCl are widely used since they are transparent up to 625 cm^{-1}. Cell windows are easily fogged by exposure to moisture and require frequent polishing. Glass and quartz absorb strongly in infrared region, so they can not be used as cell containers or optical prisms.

Almost invariably in all dispersive instruments, the sample compartment is positioned before the monochromator to conserve weak IR energy and reduce stray radiation and optical aberrations.

AgCl is often used for moist samples but it is not entirely satisfactory. It easily deforms, is too soft and darkens on exposure to light. For frequencies under 600 cm^{-1}, a polyethylene cell is useful. Characteristics of other useful window materials are shown in the next table.

Table1. IR TRANSMITTING MATERIALS

Window material	Useful frequency
NaCl	40000 – 625 cm^{-1}
KBr	40000 – 400 cm^{-1}
AgCl	25000 – 435 cm^{-1}
AgBr	20000 – 286 cm^{-1}
CaF_2	6670 – 1110 cm^{-1}
BaF_2	50000 – 870 cm^{-1}
CsBr	10000 – 270 cm^{-1}
ZnSe (Vacuum deposited)	10000 – 55 cm^{-1}
Polyethylene	625 – 33 cm^{-1}

Gases can be directly scanned in 10 cm pathlength cells. For trace analysis, cells of 1.5 – 120 meter are used. Such cells are constructed with folded light paths and gold surfaced mirrors.

Liquid samples are usually scanned in their neat form or in solution. The sample thickness should be 0.001 - 0.05 mm thickness which provides transmittance of 15 – 70%.

For solutions, a 10% carbon tetrachloride(CCl_4) is ideal for 4000-1333 cm^{-1} range. Carbon disulphide(CS_2) is useful for 13333 - 650 cm^{-1}. Methylene chloride, acetonitrile and acetone are the other useful solvents.

IR cells are constructed with sealed windows which are separated by thin gaskets copper and lead gaskets which are wetted with mercury. The whole assembly is securely clamped in a stainless steel holder. As the mercury penetrates a gasket it expands producing a tight seal.

FILMS

For polymers, resins and amorphous solids the sample is dissolved in a volatile solvent and a drop of the solution is placed on the window and sealed. As the solvent evaporates, a thin homogeneous film is deposited which can be scanned directly. For liquids and polymers a drop of the solution may be placed and squeezed between the windows.

MULLS

Powders can be examined as a thin paste or mull. About 5 mg of the sample is mixed with nujol (a high molecular weight liquid paraffin). Nujol has peaks around 3030 - 2860, ~ 1460 cm^{-1} and 1374 cm^{-1}. Therefore no useful information can be obtained in these regions. Hexachlorobutadine is another mulling agent. It has no CH bonds.

A solid sample can also be handled by mixing with KBr and pressing at 25000 psi into a small disc of 10 mm diameter and 2mm thickness. Quantitative analysis can be performed by the pellet technique .

RADIATION SOURCES

Most commercial instruments use an extended source close to that of a black body radiation around 1000-1500 K. Nicrome wire, the Nerst glower, the Opperman and Glober sources are commonly employed as sources of IR radiation.

Nichrome wire is either a simple coil or supported on a ceramic rod. Low and mid priced instruments use this. It is easy to maintain and replace. Prolonged use can lead to oxidation and thermal stresses deform the coil shape. Thus long term stability and output are affected.

Nernst glower is composed of a mixture of rare earth oxides that are heated by electric current. This has a negative coefficient of electrical resistance. Its electrical conductivity increases with increasing temperature. Therefore external heating is required to start the flow of electricity and it must be carefully regulated to control a 'run away' situation.

The Opperman consists of a ceramic rod filled with rare earth oxides with a coaxial metal wire located inside the centre. The wire is heated first which in turn heats the oxide mixture. This is self regulating and does not require external heating.

The Glober is essentially an electrically heated silicon carbide rod capable of being operated at high temperatures. In most cases external water cooling is essential to help stabilize the source and to reduce the heat dissipation to other components in the instrument.

Typical life spans are around 2 - 5 years. The most common failures are fractures or hot spots or loss of power by oxidation of electrical connections.

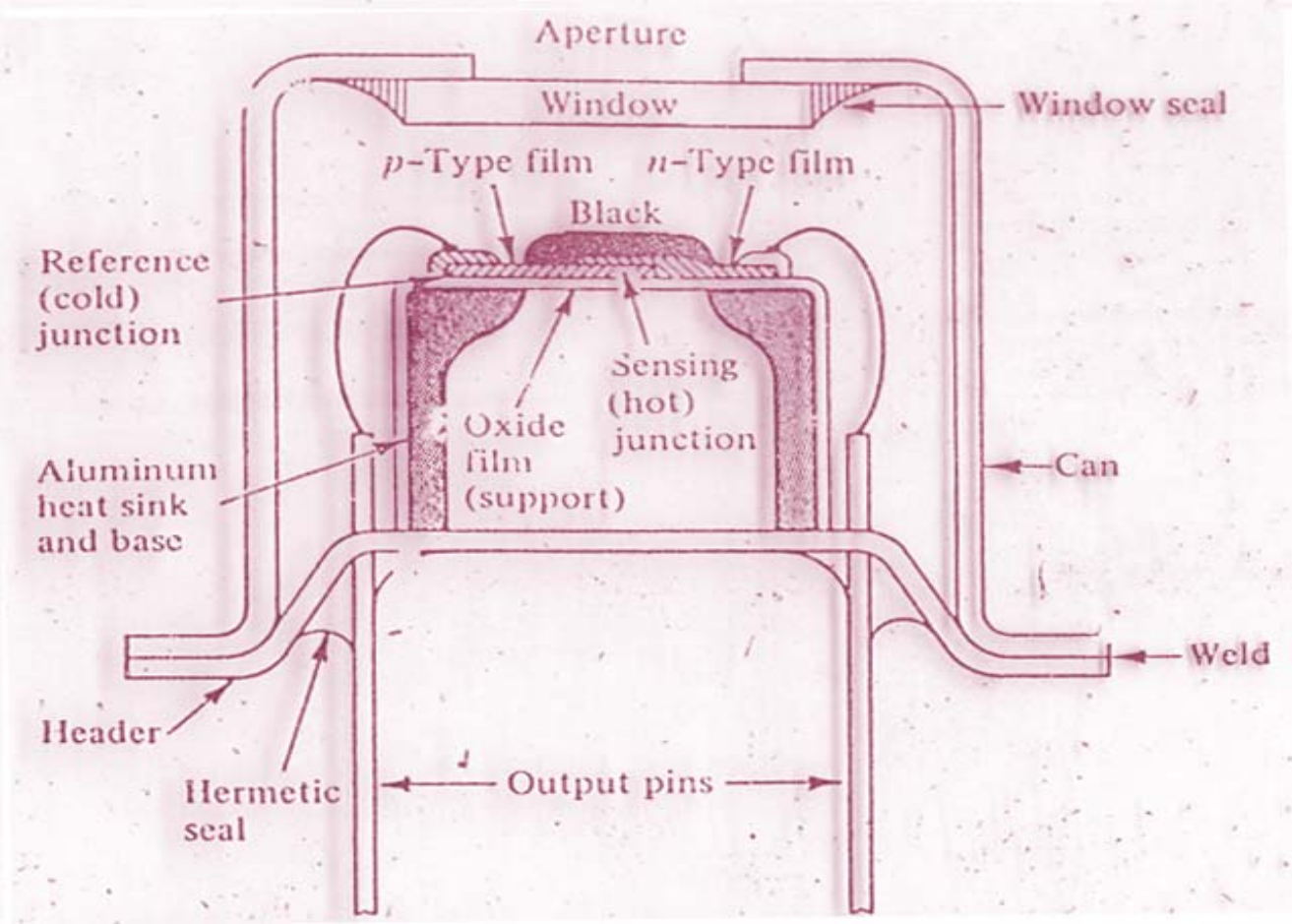
DETECTORS

Thermal detectors or photon sensitive (quantum) detectors are useful in IR. Thermal detectors sense temperature changes by a change in physical property such as generation of voltage or change in resistance. The speed of thermal detectors are influenced by the thermal or heat capacity of the detector element which is somewhat lower than photon counting detectors. But the response of thermal detector is independent of the wavelength of the incident radiations.

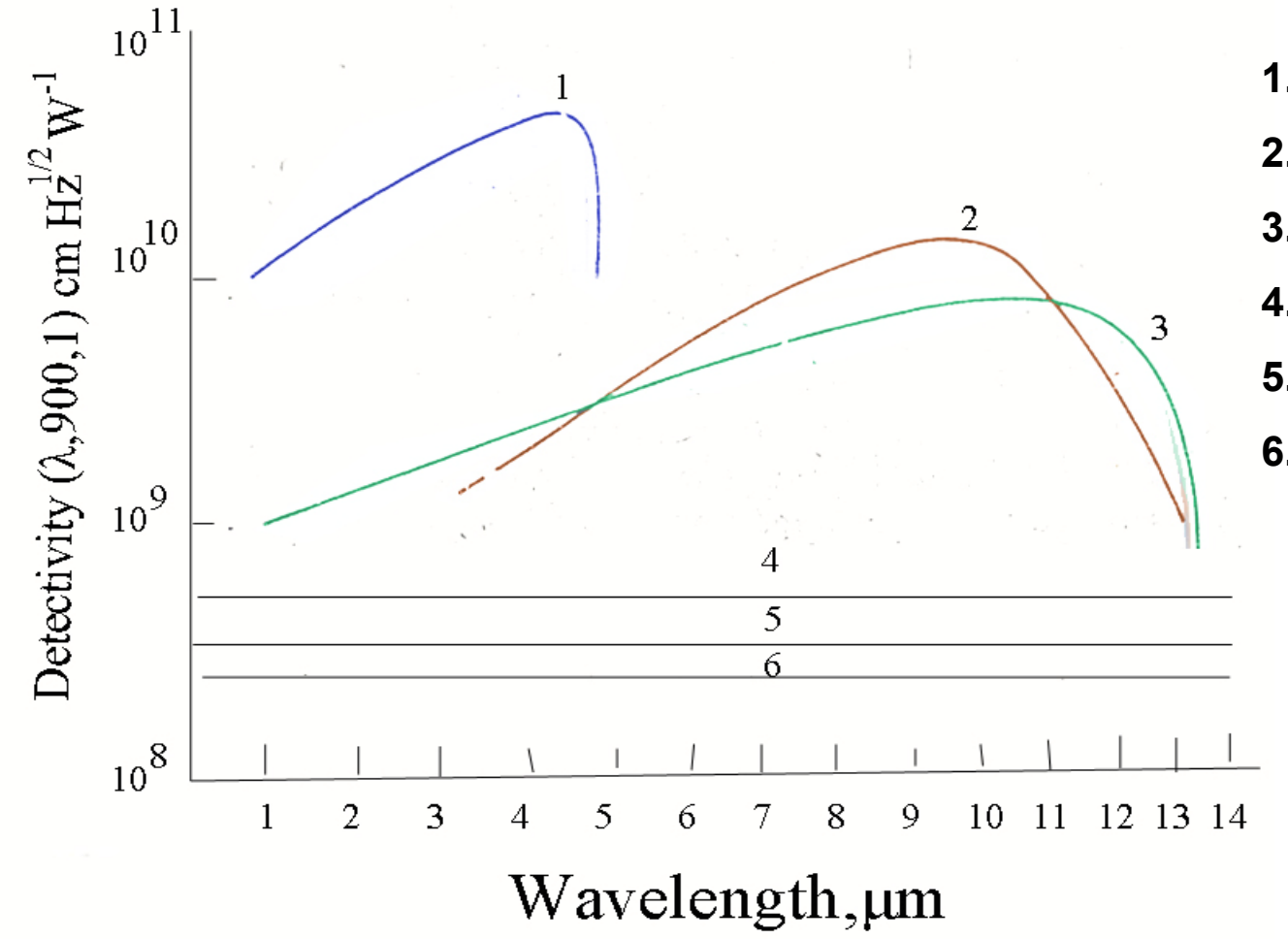
The thermocouple, the pneumatic or Golay detector and bolometer are of thermal detector type. IR response temperature changes are of the order of 10^{-3} to 10^{-2} K. These are used extensively in dispersive type instruments and bolometers are used in FT- IR instruments.

The thermocouple is fabricated with two dissimilar metals such as bismuth and antimony which produce a small voltage proportional to the temperature of junction. Several thermocouples are connected in series for additional output. Half of the junctions are 'hot' containing the active element. Alternate junctions are 'cold' that are thermally bonded to the substrate and remain at a relatively lower temperature. Thin film techniques have miniaturized the thermocouples. The entire assembly is mounted on an evaluated enclosure with IR transmitting window. So that conductive heat losses are minimized. The response time is about 80μsec.

CROSS SECTION OF A THERMOCOUPLE DETECTOR



WAVELENGTH RESPONSE OF SOME IR DETECTORS

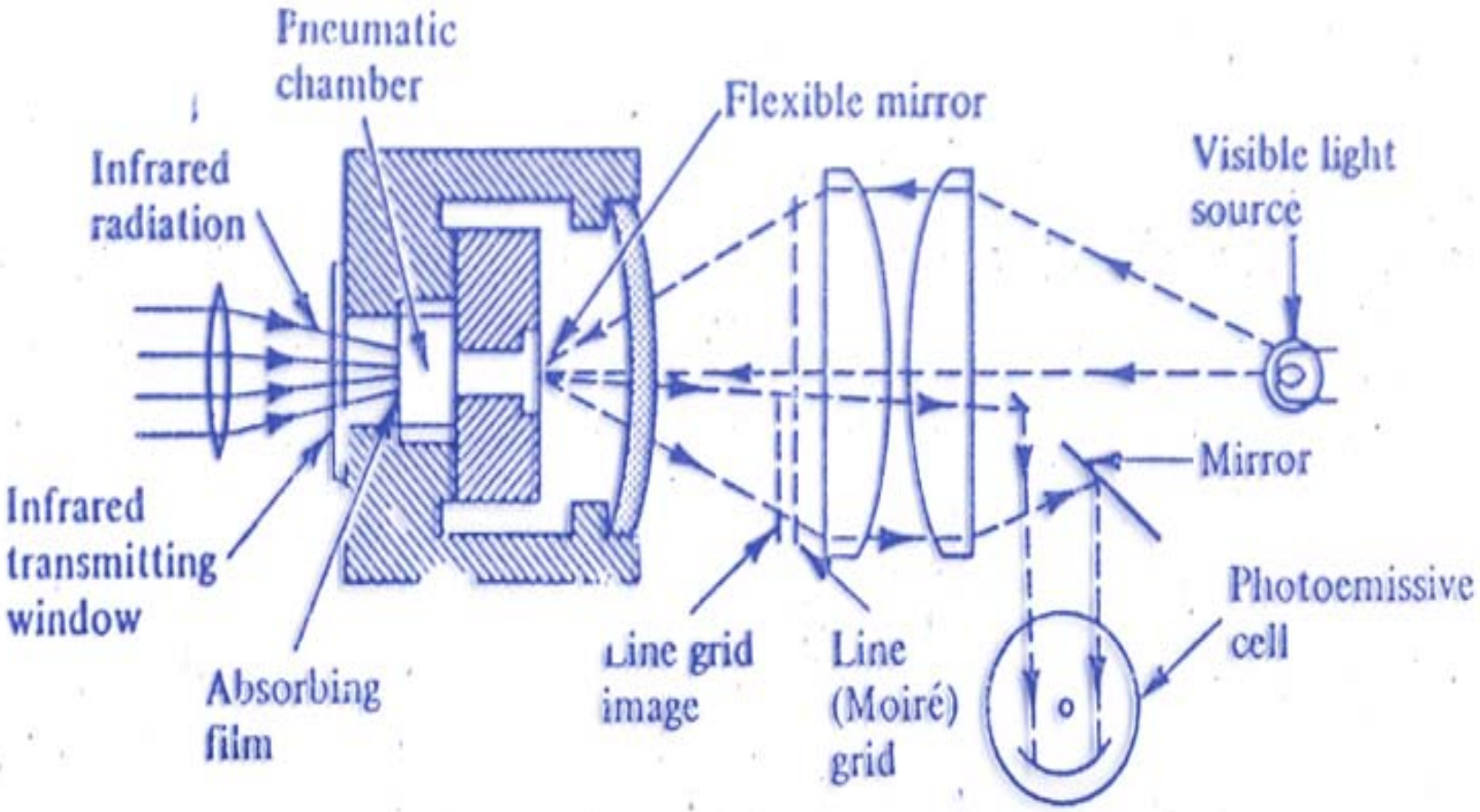


1. INSB at 77 K
2. PBSNTE at 77 K
3. PBSNTE at 42 K
4. Pyroelectirc at 300 K
5. Thermistor at 300 K
6. Thermopile at 300 K

A thermistor functions by changing resistance when illuminated with IR. These are made of sintered oxides of manganese , cobalt and nickel and have a high coefficient of resistance (4% / C^0). One of these is ‘active’, which is coated black and mounted to increase its IR absorption whereas reference is optically shielded to prevent IR exposure. Both are mounted on an insulating substrate placed on a heat sink. When connected with a bridge circuit, it compensates the ambient temperature drifts. The response times are a few milliseconds.

The Golay pneumatic detector uses the pneumatic expansion of a gas as the measuring device. The unit consists of a small metallic cylinder closed by a rigid blackened metal plate (2mm square) at one end and a flexible silver diaphram at the other end. The chamber is filled with xenon. The radiation absorbed by the blackened plate causes the gas to expand and deform the diaphragm which in turn obstructs the light path falling on a phototube. The distortion alters the plate separation and hence the capacity. Response time is 20 msec(similar to TC). It is best among the lot.

GOLAY PNEUMATIC INFRARED DETECTOR



PHOTON DETECTORS

These are more sensitive. Photons incident on a semiconductor produces electrons and holes (Internal photoeffect). A sufficiently energetic photon raises the electron to conduction band.

In a photoconducting detector, the presence of electrons in the conduction band will lower the chips resistance. Intrinsic hole-electron pairs are created by raising the electron to conduction band of the semiconductor. Extrinsic excitation refers to electrons raised from or to impurity doping levels within the forbidden band of the semiconductor. A bias current or voltage registers this change as output.

Photovoltaic detectors generate a small voltage in In-Sb p-n type junction in single crystals. The p type is laid as a thin layer over n type . The band gap is 0.23 ev at liquid nitrogen temperature.

Lead-tin-telluride detectors extend spectral sensitvity to considerably larger wavelenths than In-Sb .i.e. 5-13 μm and 6.6-18 μm. When used with a current mode amplifier response time is of the order to 20 nanoseconds.

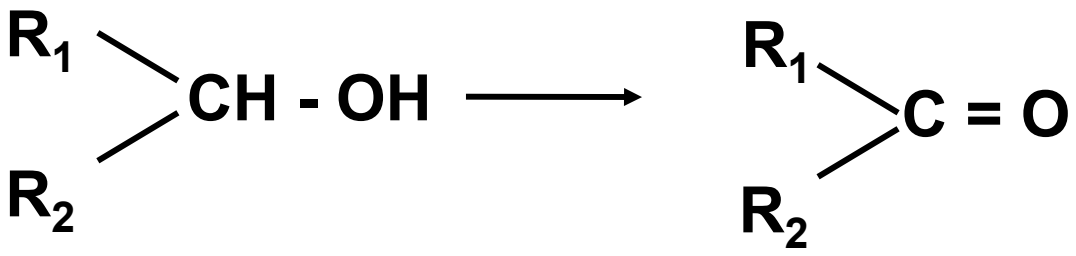
APPLICATIONS OF IR

1. In general IR peaks will occur at the same frequencies for specific groups except in molecules where steric or electrical effects are predominant. For example carbonyl (C=O) stretching vibration is same for acetone or di-n-hexylketone. But it is different for acetic acid (electrical effect) and for cyclobutane (steric effect).

   Also IR spectrum can not distinguish a pure sample from impure sample. Thus a crude product will show infrared peaks of all the reactants and side products. Even high molecular weight chemicals generally give poor spectra.

2. The progress of a chemical reaction can be followed by drawing an aliquot and checking the IR spectra for a specific functional group. Chemical separations also can be followed by the same principle.

Example :



OH frequency 3570 cm^{-1} decreases and C=O appears at 1725 cm^{-1}.

3. The most powerful function of IR is in establishing the identity of a sample by comparison using same medium. The region 1430 – 910 cm^{-1} contains many C – C , C – O, C – N stretching vibrations and bending vibrations. This is known as finger print region. Thus even if similar compounds show similar spectra, discernible differences can be identified in the finger print region.

Several compilations are available listing characteristic group absorptions which can be used to characterize an unknown material. Thus if a compound shows a peak at 1718 cm^{-1}, it certainly contains a C=O group. But it could be an aldehyde (CHO), a ketone (C=O), an amide (NHCO), an ester($RCOOR^{/}$) or an acid (COOH). Further analysis of IR spectra or classical techniques are required to identify the compound.

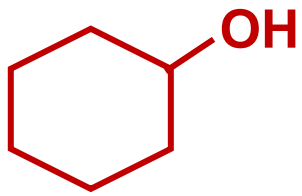
But if the IR spectrum does not contain (1850 – 1587 cm^{-1}) 1718 cm^{-1} peaks, it has no C=O group.

Given below are easily interpreted absorption bands of some common organic compounds. It is important to account for peaks that are not of the analyte e.g Nujol. This shows C-H stretching (2950, 2820 cm^{-1}) , $-CH_2$ bending (~ 1458 cm^{-1}), C - CH_3 bending (~ 1458, 1380 cm^{-1}) and $-(CH_2)-$ stretching (722 cm^{-1}). These peaks need to be discounted while interpreting the spectra.

1) $CH_3 - (CH_2)_{10} - CH_2OH \longrightarrow CH_3 - (CH_2)_2 - \overset{\overset{O}{\|}}{(CH_2)_{10}} - CH_3$

(O – H, 3448 cm^{-1}) 1758 cm-1 and 1110 cm^{-1}

C – O(st) 1053 cm^{-1} C – O (st)

2) 

in CCl_4 OH(st) 3788 cm^{-1}

OH 3571 cm^{-1}

In dilute CCl_4 , 3788 cm^{-1} peak is more prominent compared to 3571 cm^{-1}.

3) C = O ketones 1754 – 1667 cm^{-1}

cyclohexanones 1715 cm^{-1} – 1720 cm^{-1}

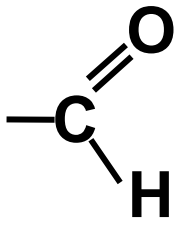
cyclopentenone 1745 cm^{-1}

pentanone 1751 cm^{-1}

4) The effects of ring size and conjugated unsaturation seem to be additive.

A halogen on C atom α to C=O raises the frequency by about 20 cm^{-1}.

5) C=O group in aldehydes also shifts to longer wavelength with C-H conjugation.

But in  **C-H (st) 2940 cm^{-1}**

Benzaldehyde – 2841 and 2762 cm^{-1} C-H stretching

3086 cm^{-1} for aromatic C-H stretching

6) Carboxylic acid anhydrides show two absorption bands in 1870 – 1740 cm^{-1}. Shorter wavelength is more intense.

7) AC_2O 1832 cm^{-1} and 1761 cm^{-1} C=O

1175 – 1050 cm^{-1} for C-O (stretching)

8) Amides 1786 – 1626 cm^{-1} C=O

1718 cm^{-1} C=O stretching (in vapour state)

1650 cm^{-1} in pure liquid

1701 cm^{-1} in chloroform

3570 – 312 cm^{-1} N - H stretching two peaks for 1^0 , one peak for 2^0 and no peak for 3^0 amines.

9) Amines	**3570 – 3333 cm^{-1}**	**N – H stretching**
	1658 – 1608 cm^{-1}	**N – H bending**

The molar extinction coefficients of functional groups can not be accurately determined since the path lengths can not be exactly measured. But average values can be calculated. For example, for the CO group the following molar extinction coefficients have been obtained.

500 (aldehyde)
800 (acid)
1300 (amide)

Thus for weak absorptions more quantity is required.

10) Alkenes **C=C** **1680 – 1620 cm^{-1} (weak)**

C-H **3135 cm^{-1} for C-H (stretching)**

Cis and trans forms can be identified by different bending vibrations.

11) Alkynes **C≡C** **2275 – 2085 cm^{-1} (weak)**

3333 C-H (stretching)

C≡N **In the same region but more intense.**

12) Aromatic compounds .

C-H stretching ~ 3030cm^{-1}, ~ 1600, 1580, 1500 and 1450 cm^{-1}
C=C in plane 1000 – 670 cm^{-1} CH bending

Monosubstituted aromatic rings show very characteristic IR peaks at 750 and 700 cm^{-1} .

Disubstituted aromatic rings show very characteristic IR peaks at 5730 cm^{-1} and 2000 – 1670 cm^{-1} which are overtone bands of low intensity.

Table 2: IR peaks for some characteristic functional groups

Group		Range μ	Intensity	Range cm^{-1}
A. Hydrocarbon chromophore				
1. C—H STRETCHING				
a. Alkane		3.38–3.51	(m–s)	2962–2853
b. Alkene, monosubstituted (vinyl)		3.29–3.32	(m)	3040–3010
	and	3.23–3.25	(m)	3095–3075
Alkene, disubstituted, *cis*		3.29–3.32	(m)	3040–3010
Alkene, disubstituted, *trans*		3.29–3.32	(m)	3040–3010
Alkene, disubstituted, *gem*		3.23–3.25	(m)	3095–3075
Alkene, trisubstituted		3.29–3.32	(m)	3040–3010
c. Alkyne		~3.03	(s)	~3300
d. Aromatic		~3.30	(v)	~3030
2. C—H BENDING				
a. Alkane, C—H		~7.46	(w)	~1340
Alkane, $—CH_2—$		6.74–6.92	(m)	1485–1445
Alkane, $—CH_3$		6.80–7.00	(m)	1470–1430
	and	7.25–7.30	(s)	1380–1370
Alkane, *gem*-dimethyl		7.22–7.25	(s)	1385–1380
	and	7.30–7.33	(s)	1370–1365
Alkane, *tert*-butyl		7.17–7.22	(m)	1395–1385
	and	~7.33	(s)	~1365
b. Alkene, monosubstituted (vinyl)		10.05–10.15	(s)	995–985
		10.93–11.05	(s)	915–905
	and	7.04–7.09	(s)	1420–1410

Table 2…

Alkene, disubstituted, *cis*	~14.5	(s)	~690
Alkene, disubstituted, *trans*	10.31–10.42	(s)	970–960
	and 7.64–7.72	(m)	1310–1295
Alkene, disubstituted, *gem*	11.17–11.30	(s)	895–885
	and 7.04–7.09	(s)	1420–1410
Alkene, trisubstituted	11.90–12.66	(s)	840–790
c. Alkyne	~15.9	(s)	~630
d. Aromatic, substitution type:‡			
five adjacent hydrogen atoms	~13.3	(v, s)	~750
	and ~14.3	(v, s)	~700
four adjacent hydrogen atoms	~13.3	(v, s)	~750
three adjacent hydrogen atoms	~12.2	(v, m)	~780
two adjacent hydrogen atoms	~12.0	(v, m)	~830
one hydrogen atom	~11.3	(v, w)	~880
3. C—C MULTIPLE BOND STRETCHING			
a. Alkene, nonconjugated	5.95–6.17	(v)	1680–1620
Alkene, monosubstituted (vinyl)	~6.08	(m)	~1645
Alkene, disubstituted, *cis*	~6.03	(m)	~1658
Alkene, disubstituted, *trans*	~5.97	(m)	~1675

† Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp, ~ = approximately

‡ Substituted benzenes also show weak bands in the region 5.0–6.0 μ (2000–1670 cm^{-1}) region that are characteristic of the substitution type. See Fig. 3-30.

Table 2 …

Group		Range μ	Intensity	Range cm⁻¹
Alkene, disubstituted, *gem*		~6.05	(m)	~1653
Alkene, trisubstituted		~5.99	(m)	~1669
Alkene, tetrasubstituted		~5.99	(w)	~1669
Diene		~6.06	(w)	~1650
	and	~6.25	(w)	~1600
b. Alkyne, monosubstituted		4.67–4.76	(m)	2140–2100
Alkyne, disubstituted		4.42–4.57	(v, w)	2260–2190
c. Allene		~5.1	(m)	~1960
	and	~9.4	(m)	~1060
d. Aromatic		~6.25	(v)	~1600
		~6.33	(v)	~1580
		~6.67	(m)	~1500
	and	~6.90	(m)	~1450
B. Carbonyl chromophore				
1. KETONE STRETCHING VIBRATIONS				
a. Saturated, acyclic		5.80–5.87	(s)	1725–1705
b. Saturated, cyclic:				
6-membered ring (and higher)		5.80–5.87	(s)	1725–1705
5-membered ring		5.71–5.75	(s)	1750–1740
4-membered ring		~5.63	(s)	~1775
c. α,β-Unsaturated, acyclic		5.94–6.01	(s)	1685–1665
d. α,β-Unsaturated, cyclic:				

Table 2…

6-membered ring (and higher)	5.94–6.01	(s)	1685–1665
5-membered ring	5.80–5.85	(s)	1725–1708
e. α,β,α′,β′-Unsaturated, acyclic	5.99–6.01	(s)	1670–1663
f. Aryl	5.88–5.95	(s)	1700–1680
g. Diaryl	5.99–6.02	(s)	1670–1660
h. α-Diketones	5.78–5.85	(s)	1730–1710
i. β-Diketones (enolic)	6.10–6.50	(s)	1640–1540
j. 1,4-Quinones	5.92–6.02	(s)	1690–1660
k. Ketenes	~4.65	(s)	~2150
2. ALDEHYDES			
a. Carbonyl stretching vibrations			
Saturated, aliphatic	5.75–5.81	(s)	1740–1720
α,β-Unsaturated, aliphatic	5.87–5.95	(s)	1705–1680
α,β,γ,δ-Unsaturated, aliphatic	5.95–6.02	(s)	1680–1660
Aryl	5.83–5.90	(s)	1715–1695
b. C—H Stretching vibrations, two bands	3.45–3.55	(w)	2900–2820
and	3.60–3.70	(w)	2775–2700
3. ESTER STRETCHING VIBRATIONS			
a. Saturated, acyclic	5.71–5.76	(s)	1750–1735
b. Saturated, cyclic:			
δ-lactones (and larger rings)	5.71–5.76	(s)	1750–1735
γ-lactones	5.62–5.68	(s)	1780–1760
β-lactones	~5.5	(s)	~1820

Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp, ~ = approximately

Table 2…

Group	Range μ	Intensity	Range cm^{-1}
Cyclic, γ-lactams, fused to another ring, dilute solution	5.71–5.88	(s)	1750–1700
Cyclic, β-lactams, dilute solution	5.68–5.78	(s)	1760–1730
Cyclic, β-lactams, fused to another ring, dilute solution	5.62–5.65	(s)	1780–1770
Ureas, acyclic	~6.02	(s)	~1660
Ureas, cyclic, 6-membered ring	~6.10	(s)	~1640
Ureas, cyclic, 5-membered ring	~5.81	(s)	~1720
Urethanes	5.75–5.92	(s)	1740–1690
Imides, acyclic	~5.85	(s)	~1710
	and ~5.88	(s)	~1700
Imides, cyclic, 6-membered ring	~5.85	(s)	~1710
	and ~5.88	(s)	~1700
Imides, cyclic, α,β-unsaturated, 6-membered ring	~5.78	(s)	~1730
	and ~5.99	(s)	~1670
Imides, cyclic, 5-membered ring	~5.65	(s)	~1770
	and ~5.88	(s)	~1700
Imides, cyclic, α,β-unsaturated, 5-membered ring	~5.59	(s)	~1790
	and ~5.85	(s)	~1710

Table 2…

b. N—H Stretching vibrations				
Primary, free; two bands		~2.86	(m)	~3500
	and	~2.94	(m)	~3400
Primary, bonded; two bands		~2.99	(m)	~3350
	and	~3.15	(m)	~3180
Secondary, free; one band		~2.92	(m)	~3430
Secondary, bonded; one band		3.0–3.2	(m)	3320–3140
c. N—H Bending vibrations				
Primary amides, dilute solution		6.17–6.29	(s)	1620–1590
Secondary amides, dilute solution		6.45–6.62	(s)	1550–1510
C. Miscellaneous chromophoric groups				
1. ALCOHOLS AND PHENOLS				
a. O—H Stretching vibrations				
Free O—H		2.74–2.79	(v, sh)	3650–3590
Intermolecularly hydrogen bonded (change on dilution)				
single bridge compounds		2.82–2.90	(v, sh)	3550–3450
polymeric association		2.94–3.13	(s, b)	3400–3200
Intramolecularly hydrogen bonded (no change on dilution)				
single bridge compounds		2.80–2.90	(v, sh)	3570–3450
chelate compounds		3.1–4.0	(w, b)	3200–2500

† Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp, ~ = approximately

Table 2…

Group		Range μ	Intensity	Range cm^{-1}
b. O—H Bending and C—O stretching vibrations				
Primary alcohols		~9.5	(s)	~1050
	and	7.4–7.9	(s)	1350–1260
Secondary alcohols		~9.1	(s)	~1100
	and	7.4–7.9	(s)	1350–1260
Tertiary alcohols		~8.7	(s)	~1150
	and	7.1–7.6	(s)	1410–1310
Phenols		~8.3	(s)	~1200
	and	7.1–7.6	(s)	1410–1310
2. AMINES				
a. N—H Stretching vibrations				
Primary, free; two bands		~2.86	(m)	~3500
	and	~2.94	(m)	~3400
Secondary, free; one band		2.86–3.02	(m)	3500–3310
Imines (=N—H); one band		2.94–3.03	(m)	3400–3300
Amine salts		3.2–3.3	(m)	3130–3030
b. N—H Bending vibrations				
Primary		6.06–6.29	(s–m)	1650–1590
Secondary		6.06–6.45	(w)	1650–1550
Amine salts		6.25–6.35	(s)	1600–1575
	and	~6.67	(s)	~1500

Table 2…

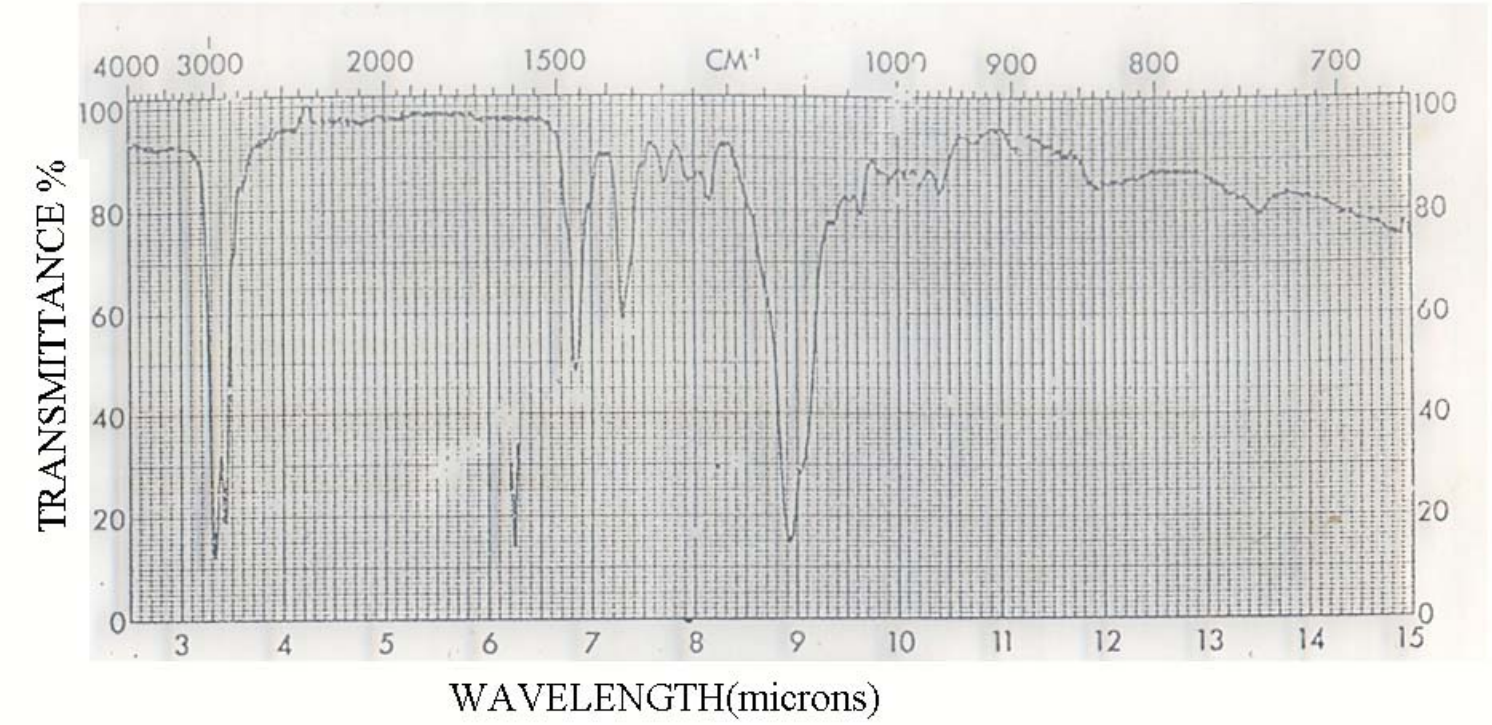
c. C—N Vibrations				
Aromatic, primary		7.46–8.00	(s)	1340–1250
Aromatic, secondary		7.41–7.81	(s)	1350–1280
Aromatic, tertiary		7.36–7.64	(s)	1360–1310
Aliphatic		8.2–9.8	(w)	1220–1020
	and	~7.1	w)	~1410
3. UNSATURATED NITROGEN COMPOUNDS				
a. C≡N Stretching vibrations				
Alkyl nitriles		4.42–4.46	(m)	2260–2240
α,β-Unsaturated alkyl nitriles		4.47–4.51	(m)	2235–2215
Aryl nitriles		4.46–4.50	(m)	2240–2220
Isocyanates		4.40–4.46	(m)	2275–2240
Isocyanides		4.50–4.83	(m)	2220–2070
b. C=N— Stretching vibrations (imines, oximes)				
Alkyl compounds		5.92–6.10	(v)	1690–1640
α,β-Unsaturated compounds		6.02–6.14	(v)	1660–1630
c. —N=N— Stretching vibrations, azo compounds		6.14–6.35	(v)	1630–1575
d. —N=C=N— Stretching vibrations, diimides		4.64–4.70	(s)	2155–2130
e. $-N_3$ Stretching vibrations, azides		4.63–4.72	(s)	2160–2120
	and	7.46–8.48	(w)	1340–1180

Table 2…

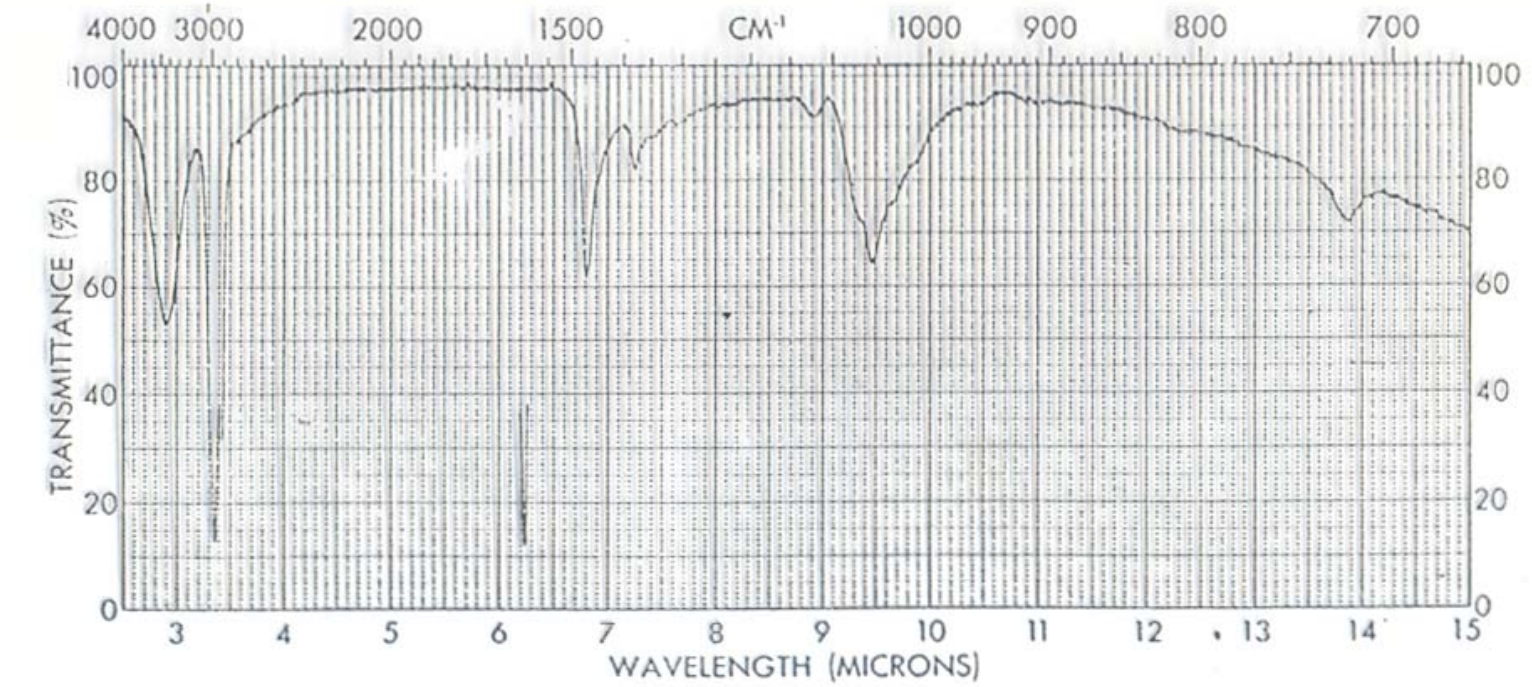
Group		Range μ	Intensity	Range cm^{-1}
f. C—NO_2, Nitro compounds:				
aromatic		6.37–6.67	(s)	1570–1500
	and	7.30–7.70	(s)	1370–1300
aliphatic		6.37–6.45	(s)	1570–1550
	and	7.25–7.30	(s)	1380–1370
g. O—NO_2, Nitrates		6.06–6.25	(s)	1650–1600
	and	7.70–8.00	(s)	1300–1250
h. C—NO, Nitroso compounds		6.25–6.67	(s)	1600–1500
i. O—NO, Nitrites		5.95–6.06	(s)	1680–1650
	and	6.15–6.21	(s)	1625–1610
4. HALOGEN COMPOUNDS, C—X STRETCHING VIBRATIONS				
a. C—F		7.1–10.0	(s)	1400–1000
b. C—Cl		12.5–16.6	(s)	800–600
c. C—Br		16.6–20.0	(s)	600–500
d. C—I		~20	(s)	~500
5. SULFUR COMPOUNDS				
a. S—H Stretching vibrations		3.85–3.92	(w)	2600–2550
b. C—S Stretching vibrations		8.33–9.52	(s)	1200–1050
c. S=O Stretching vibrations:				
sulfoxides		9.35–9.71	(s)	1070–1030
sulfones		8.62–8.77	(s)	1160–1140
	and	7.41–7.69	(s)	1350–1300
sulfites		8.13–8.70	(s)	1230–1150
	and	7.00–7.41	(s)	1430–1350
sulfonyl chlorides		8.44–8.59	(s)	1185–1165
	and	7.30–7.46	(s)	1370–1340
sulfonamides		8.48–8.77	(s)	1180–1140
	and	7.41–7.69	(s)	1350–1300
sulfonic acids		8.27–8.70	(s)	1210–1150
		9.43–9.71	(s)	1060–1030
	and	~15.4	(s)	~650

† Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp, ~ = approximately

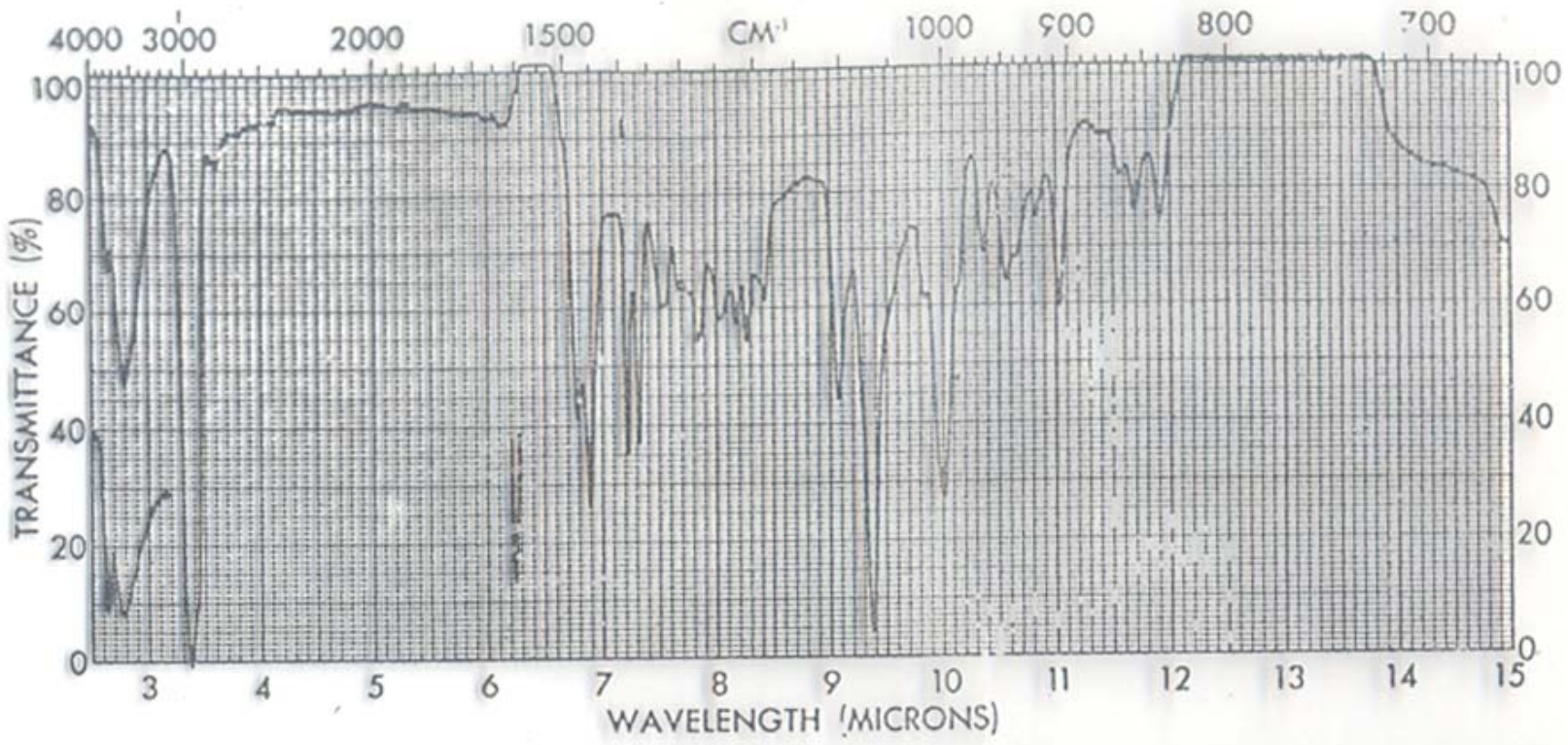
DI-N-BUTYL ETHER



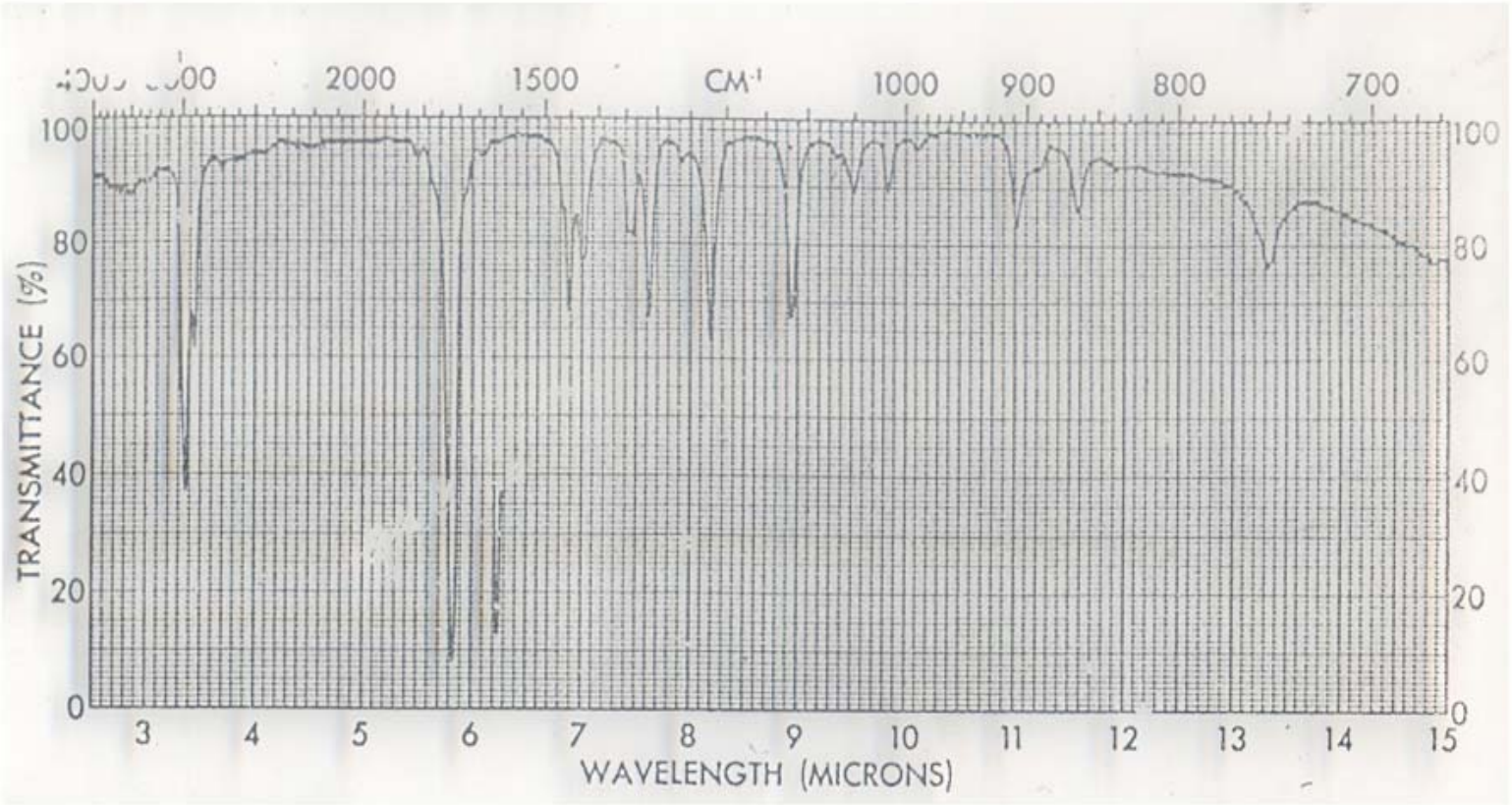
LAURYL ALCOHOL



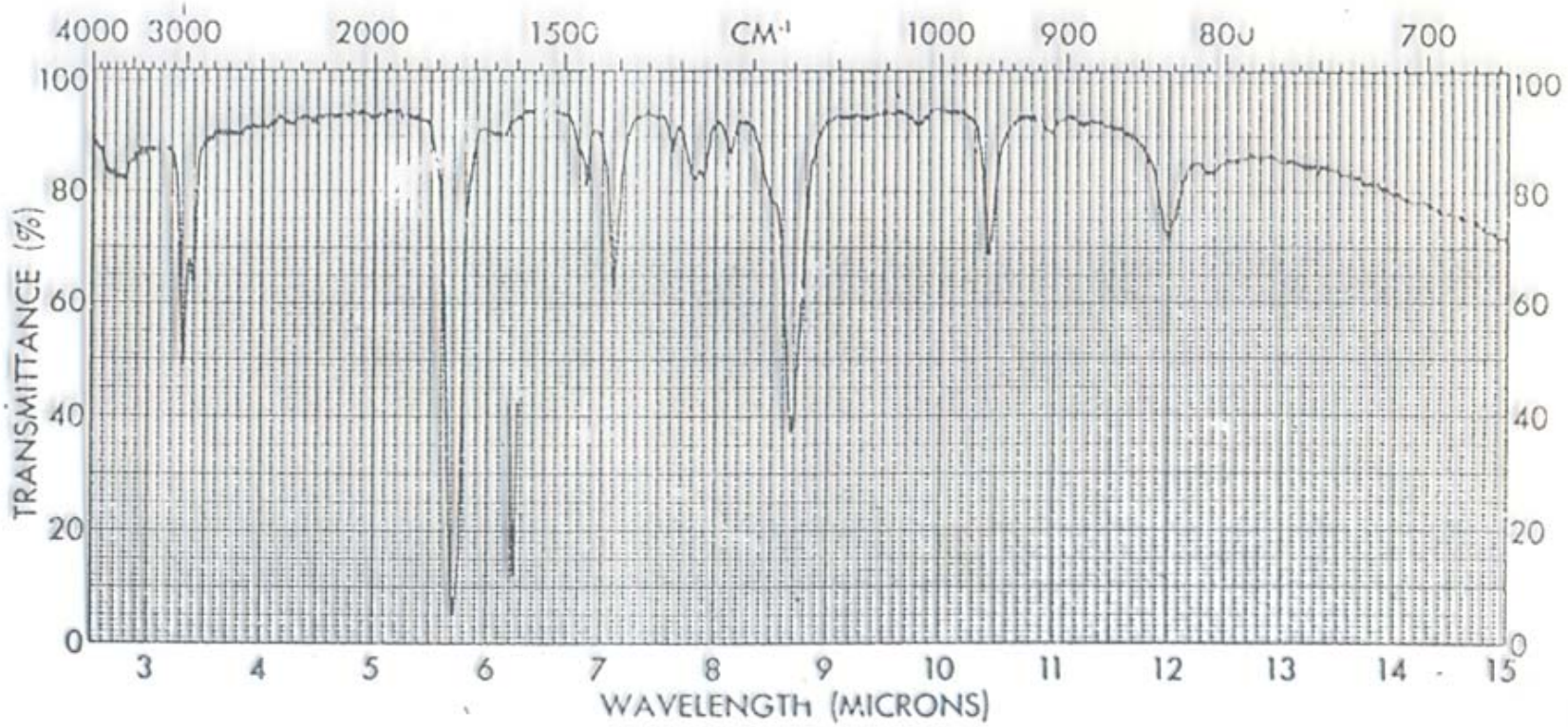
ISO BORNEOL IN CARBON TETRACHLORIDE



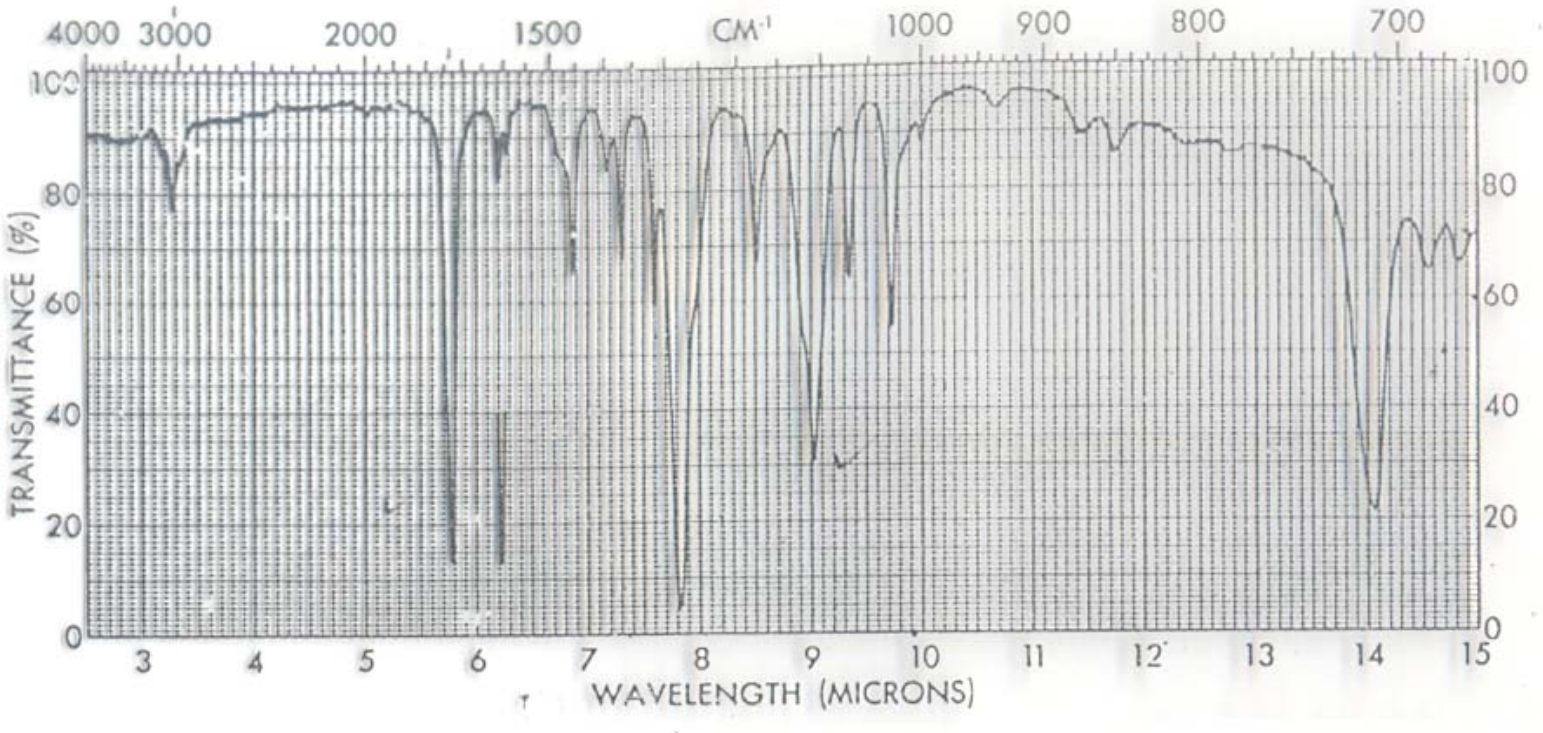
CYCLOHEXANONE



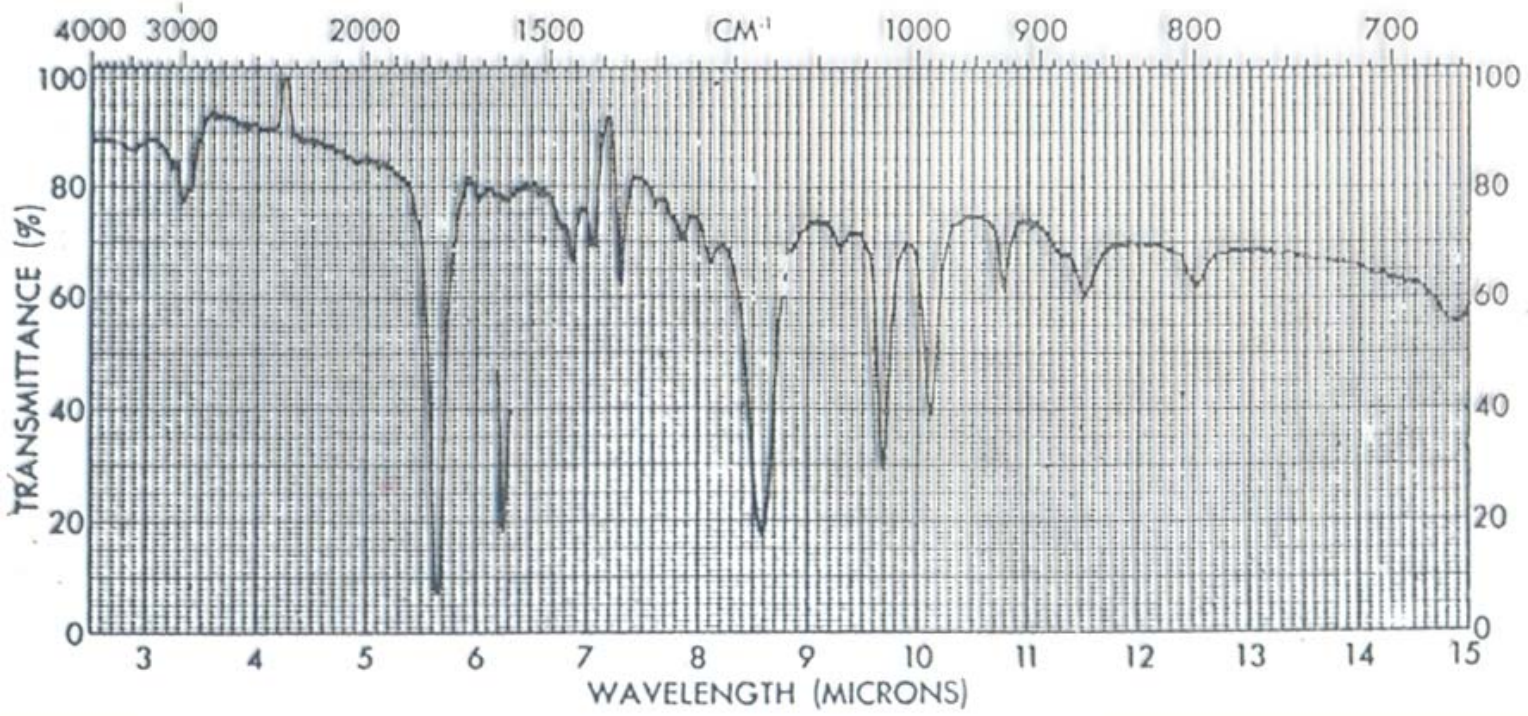
CYCLOPENTANONE



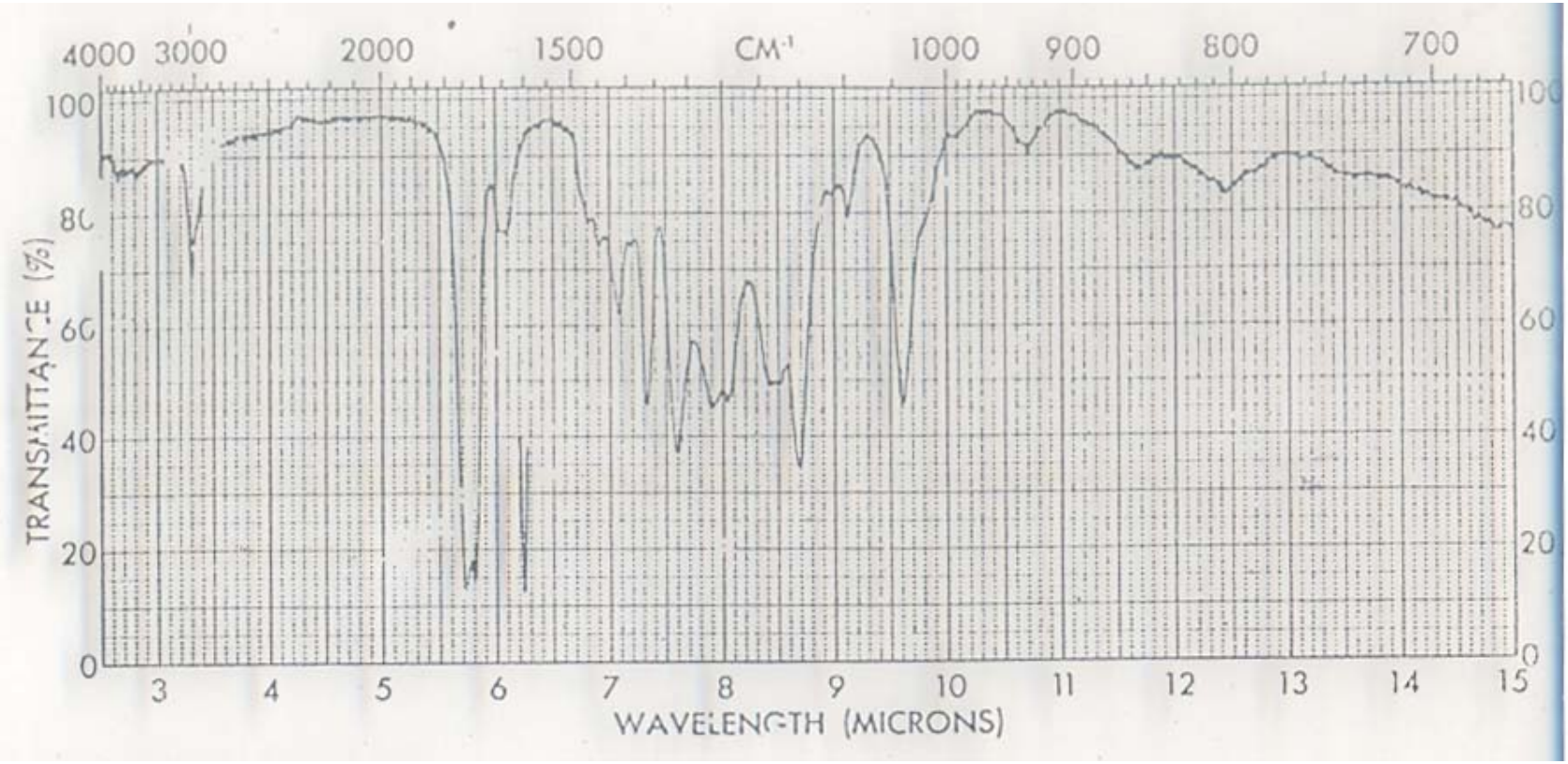
ETHYL BENZOATE



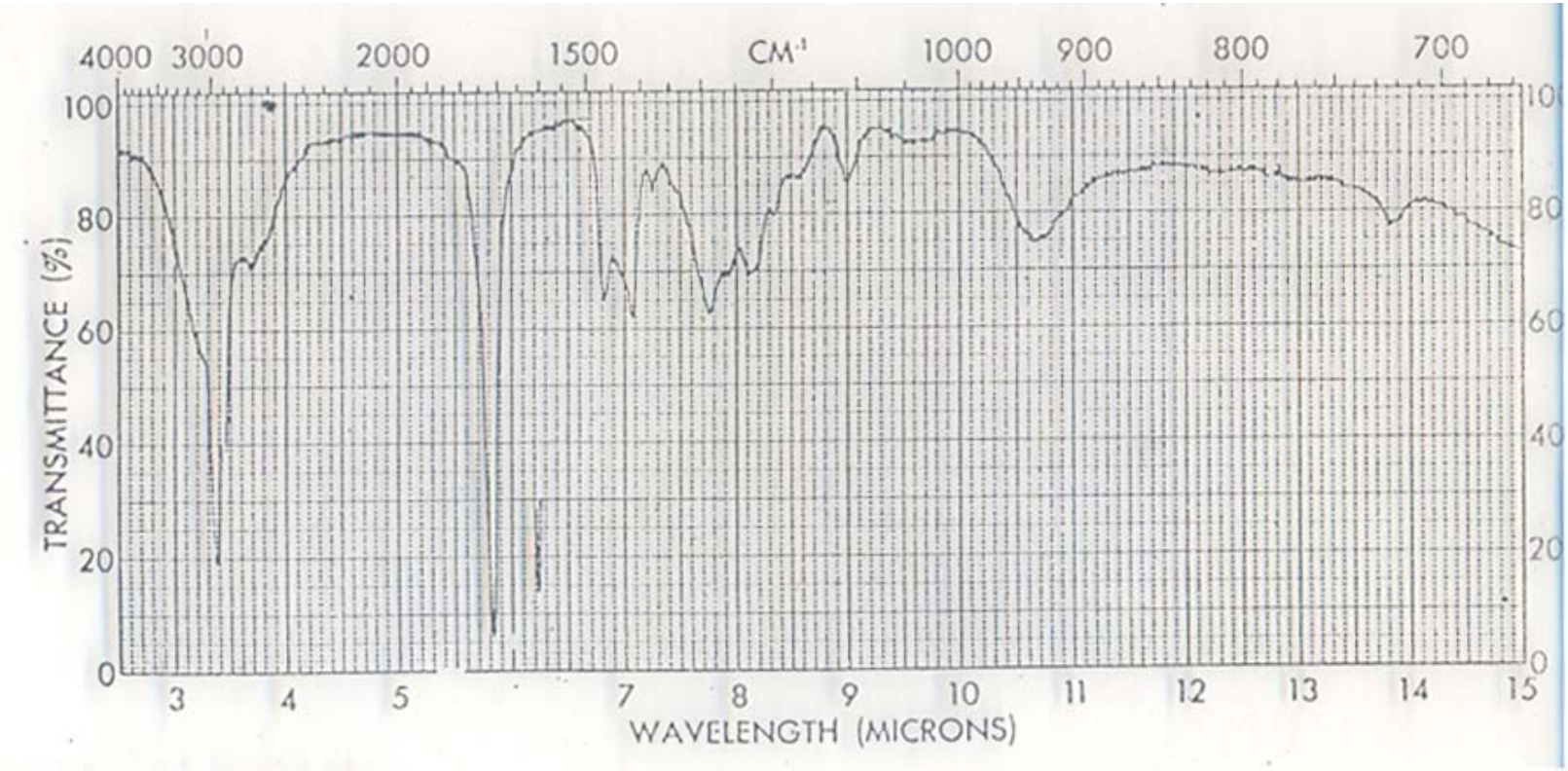
BUTYRO LACTONE



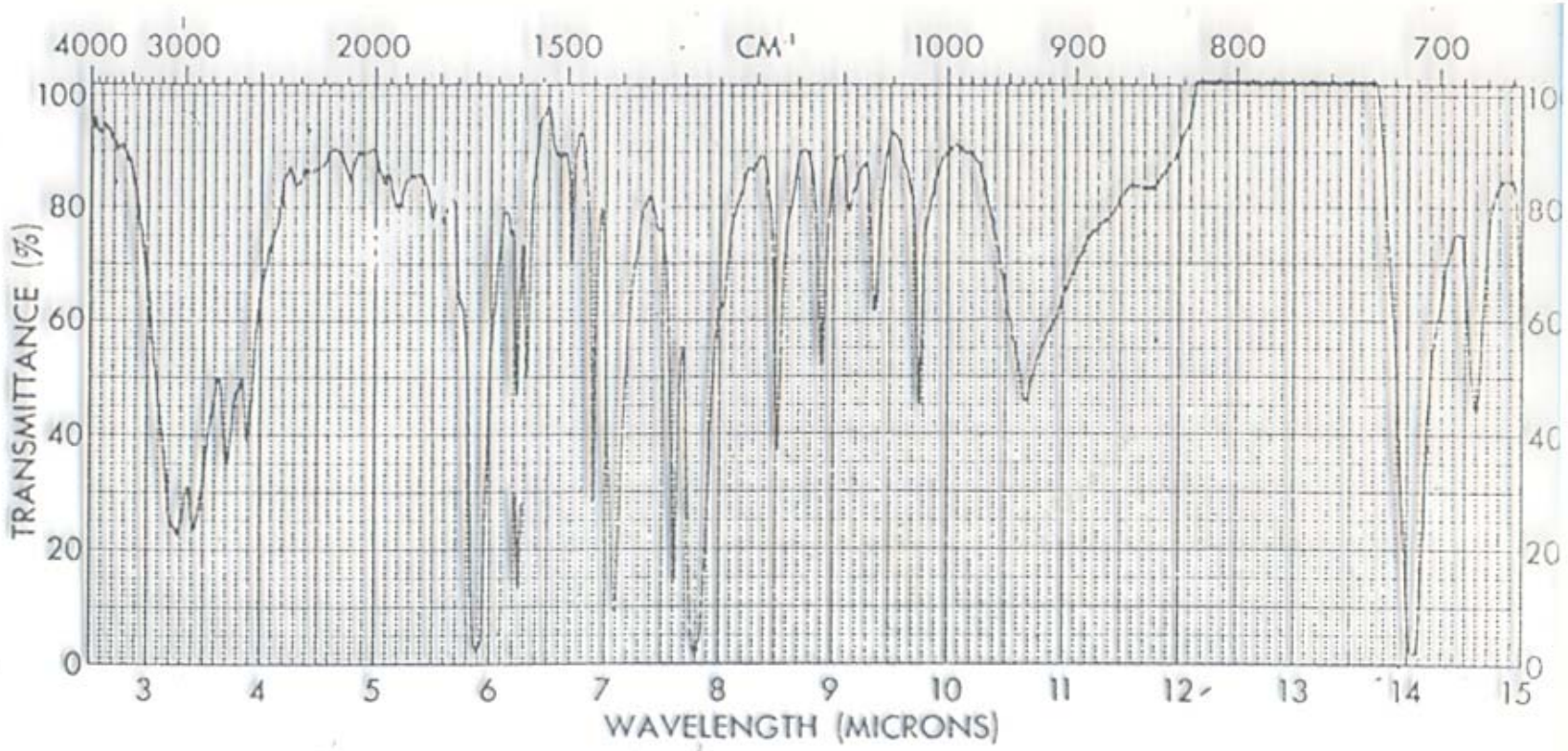
ETHYL ACETOACETATE



NONANOIC ACID

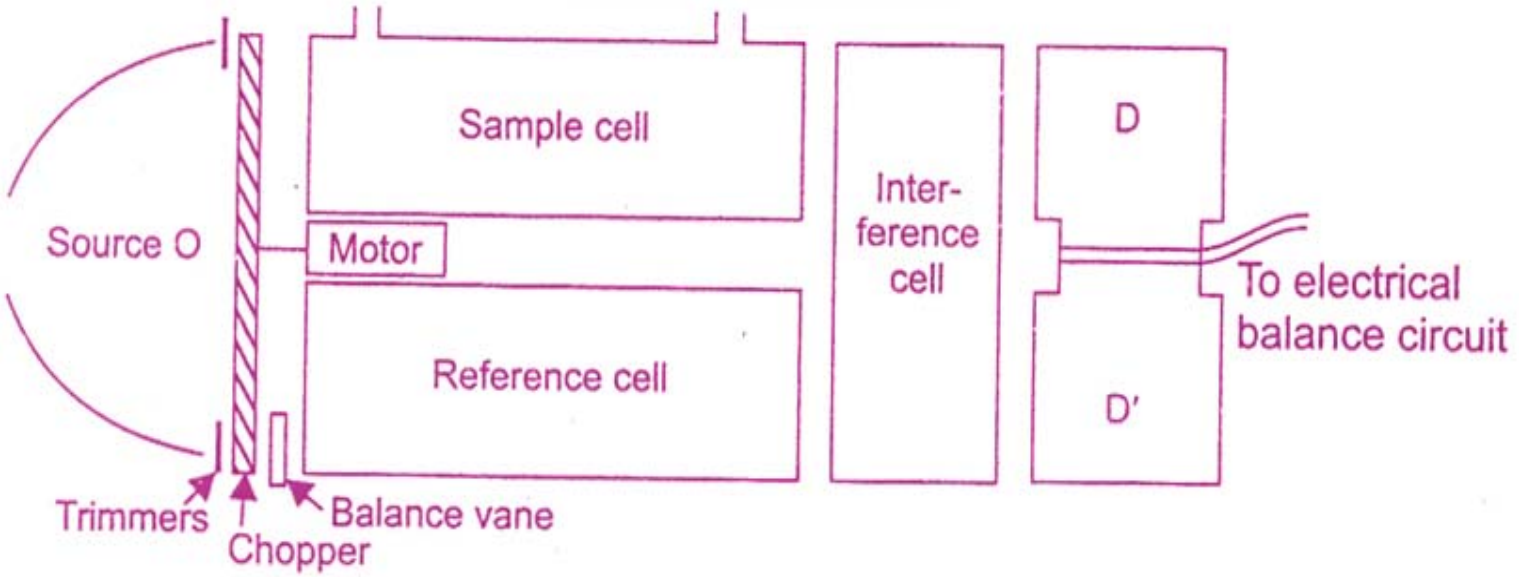


BENZOIC ACID



IR GAS ANALYSERS

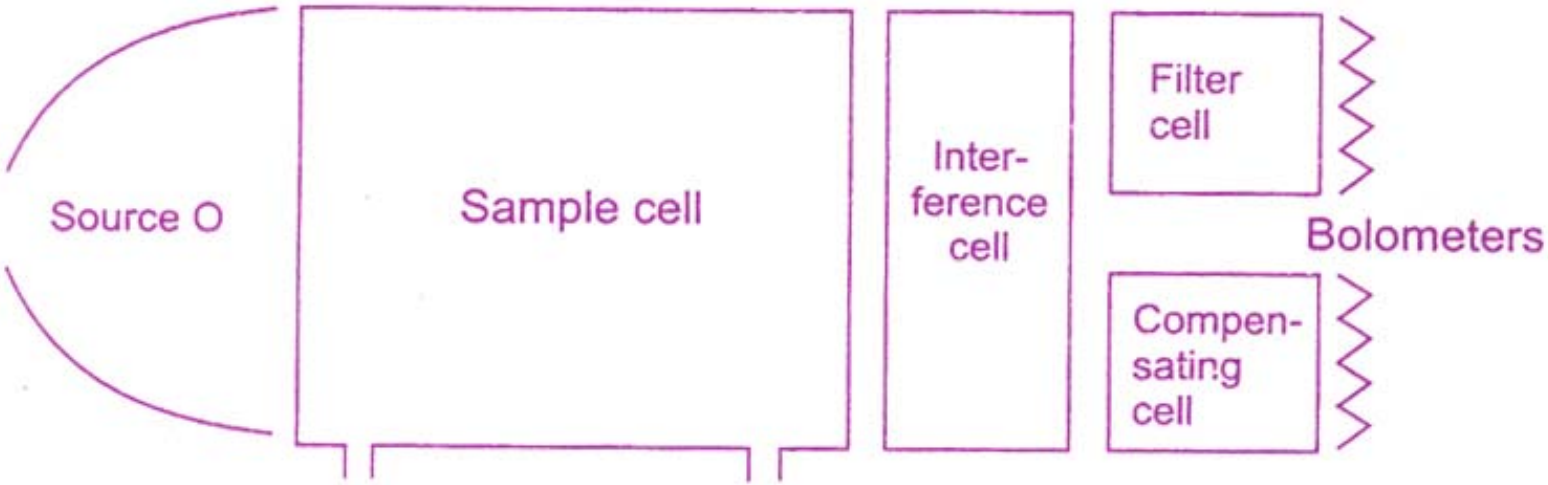
Analysis for single gas component can be carried out by using a simple IR filter photometer.



The energy is split into two beams directed towards bolometers wired in a balanced circuit. The sample gas flows through a cell that extends across both beams. One beam passes through a filter cell and the other one through a compensating cell. Filter cell contains pure gas being analysed and compensating cell contains a gas similar to that being analysed.

For example the analysis of ethylene, ethane and methane, three wavelengths can be selected in the IR region. If a filter cell is filled with ethylene, all IR absorbed by C_2H_2 will be completely eliminated from B_1 and also from the sample.

Similarly interference of methane is eliminated by placing pure methane in the interference cell which filters out from both beams the wavelengths absorbed by methane. Thus only ethylene is determined using this arrangement from 0 – 10% in a sample gas.



Another arrangement is shown here. Both D and D^{I} are identical containing a sample of the gas being determined. Usually dilution is carried out using argon to reduce specific heat. The vessels are separated by a diaphragm and one of them is pierced by a hole. The intact diaphragm is free to bend in response to variation in the pressure. This causes a change in the electrical capacitance between D and other pierced diaphragm D^{I} .

The pressure in D and D^{I} depends on temperature which is in turn dependent upon the IR absorbed. The reference cell is filled with dry nitrogen and sealed off. The two diaphragms of the detector constitute a capacitor which is incorporated in a high frequency electronic circuit which eventually energizes a small motor to drive a balancing vane across the reference beam till they match. The amount of compensation is recorded as a signal.

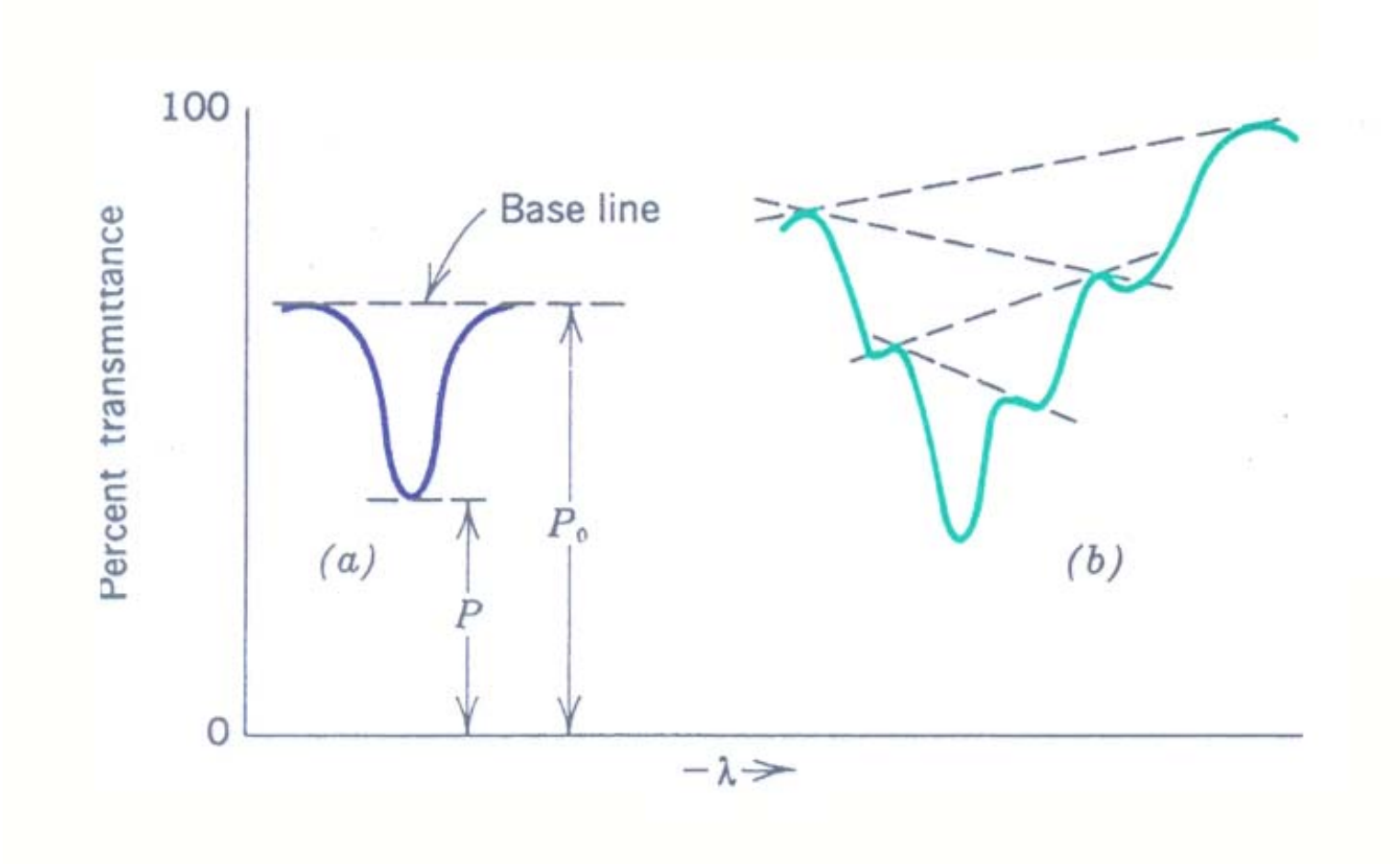
DETECTION LIMITS OF SOME GASES BY NON DISPERSIVE INFRARED SPECTROMETER

CO	1.0 mole%
CO_2	0.1
SO_2	0.1
NH_3	5.0
CH_4	1.0
C_2H_6	0.1
C_4H_{10}	0.1
C_2H_2	1.0
C_3H_6	0.05

QUANTITATIVE ANALYSIS

Quantitative IR analysis is based on Beer's law. Chemical and instrumental effects may cause apparent deviations and also high values of absorbances. Since the energy is quite small, it is necessary to use rather wide slit which introduces errors in the molar absorptivities. Hence it is only empirical. Usually base line method is employed for quantitative analysis.

BASE LINE MEASUREMENT TECHNIQUE



In this method a suitable IR band is selected. Incident radiant energy P_o is obtained by drawing a tangent to spectral absorption curve. The transmittance P is measured at the point of maximum absorption. The value of log P_o/P is plotted against concentration. Since the same cell is used for all determinations many possible errors are eliminated.

For solids, KBr pellets of known weights mixed with various quantities of the analyte are used. An internal standard of KSCN at 0.2% by weight of KBr is used and the ratio of SCN^- at 2125 cm^{-1} to a chosen band absorbance is plotted against concentration.

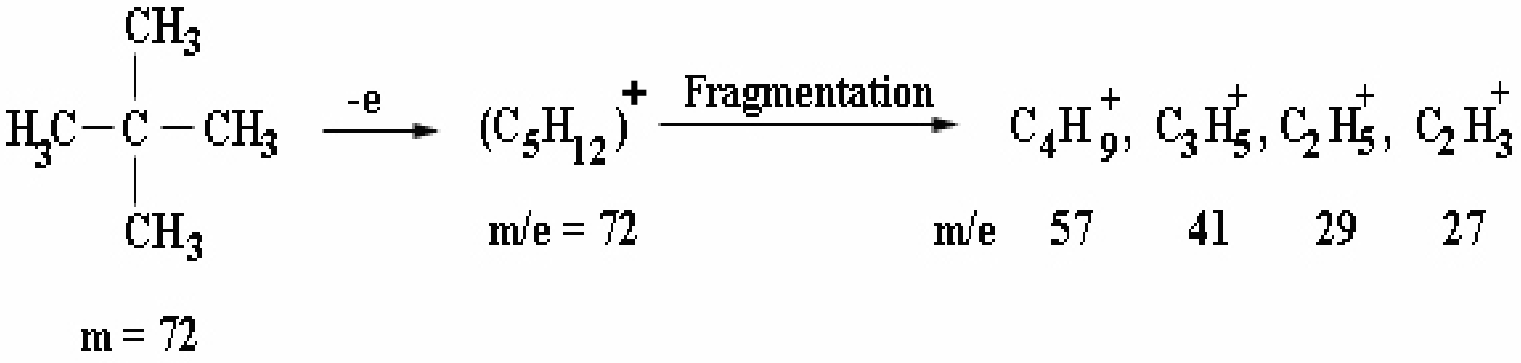
IR SPECTROPHOTOMETER

MASS SPECTROMETRY

Mass Spectrometry is the most accurate method for the determination of the mass of a molecule and its elemental and isotopic composition. Mass spectrometry is also extremely useful in the determination of the structure of molecules. In mass spectrometry molecules are converted into ions which are separated by electric and magnetic field gradients on the basis of their mass/charge ratios and detected.

When a molecule is bombarded with a beam of energetic electrons under controlled conditions it is converted largely into a single positively charged molecular ion. That is, one electron is knocked off from the molecule. The mass/charge ratio of this is simply the molecular mass of the ion.

Ex:



The molecular ion (M^+) breaks up into smaller units by a process known as fragmentation. The fragments which are positively charged are called daughter ions and the molecular ion is known as the parent ion. A signal is obtained for each m/e. The intensity of each signal represents the relative abundance of the ion producing the signal. The peak whose intensity is maximum in the spectrum is arbitrarily assigned a value of 100% and is labeled as the base peak. The intensities of other peaks are presented relative to the base peak. The base peak should not be confused with the molecular peak.

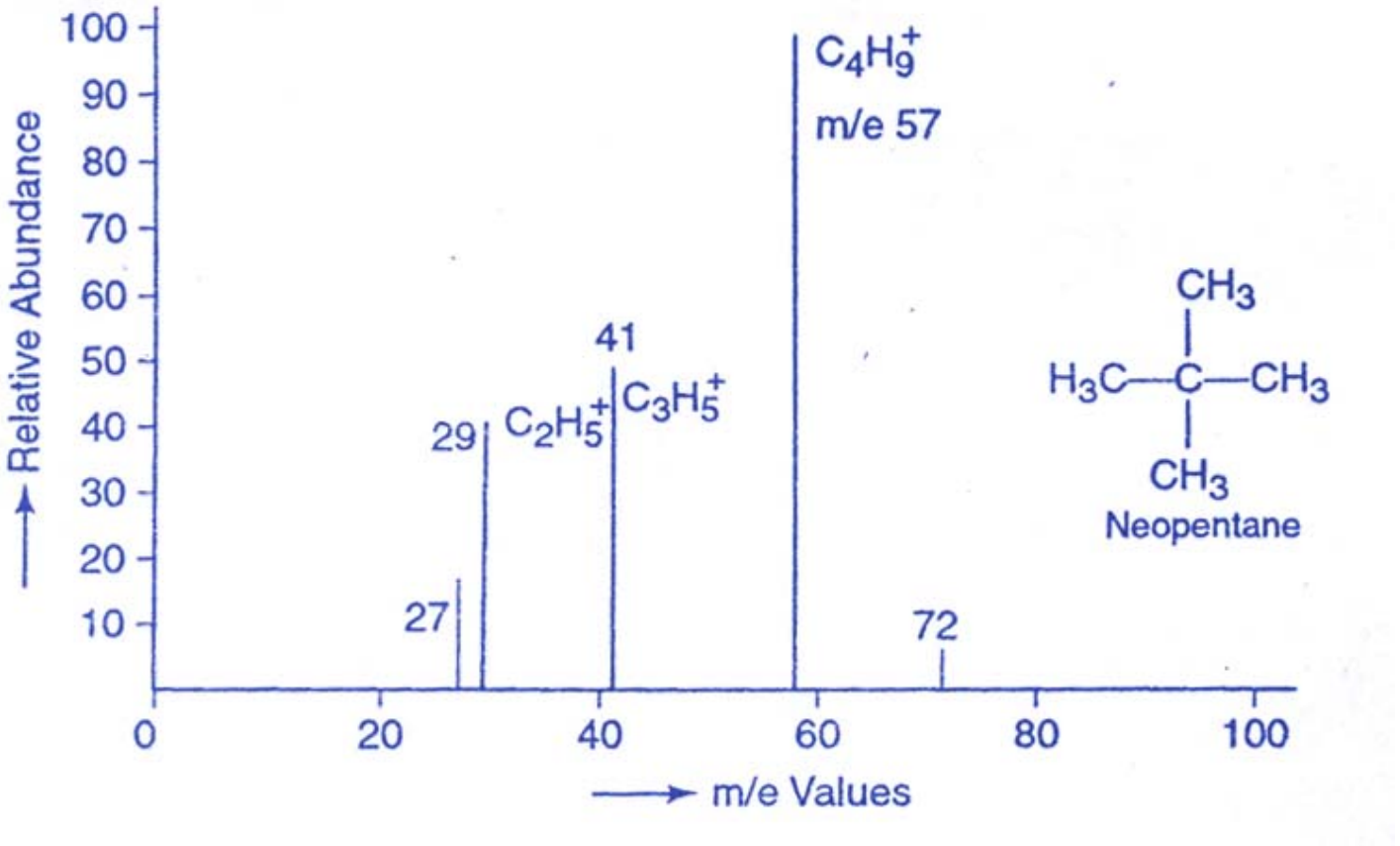
The mass spectrum is a graphic plot of the intensity versus m/e ratio. No two compounds can have exactly similar mass spectra. Therefore, the mass spectrum of a compound can be used as a finger print. Very small amounts of sample are required for mass spectrometric analysis. Mixtures can be analyzed easily. The method is accurate, highly sensitive and reproducible. It is also useful fro unraveling the reaction mechanisms and the identification of functional groups in organic compounds. It is used in stable isotope tracer techniques in research.

In a mass spectrometer a molecule M is bombarded with high energy electrons of the order of 70 ev (≈ 6688 k J $mole^{-1}$). This is the typical bond energy of organic molecules. When the energy of the bombarding electrons is equal to the ionization energy of the molecule, one electron is knocked off from the molecule to produce the molecular ion.

$$M + e^- \xrightarrow[\text{energy}]{\text{Ionization}} M^+ + 2e^-$$

If the energy of the bombarding electrons are much higher than the ionization energy of the molecule some bonds in the molecule will rupture forming a new ion N^+ and a fragment R. The minimum potential (used for accelerating the bombarding electrons) required to effect fragmentation is known as appearance potential of the fragment ion. Further increase in the potential may lead to more fragmentation into smaller ions and neutral fragments. For the parent ion m/e equals the molecular mass because mass of an electron is negligible.

The positively charged ions travel towards the detector and give rise to sharp lines at their respective m/e values. The detector is an electrometer with electric and magnetic focussing devices.

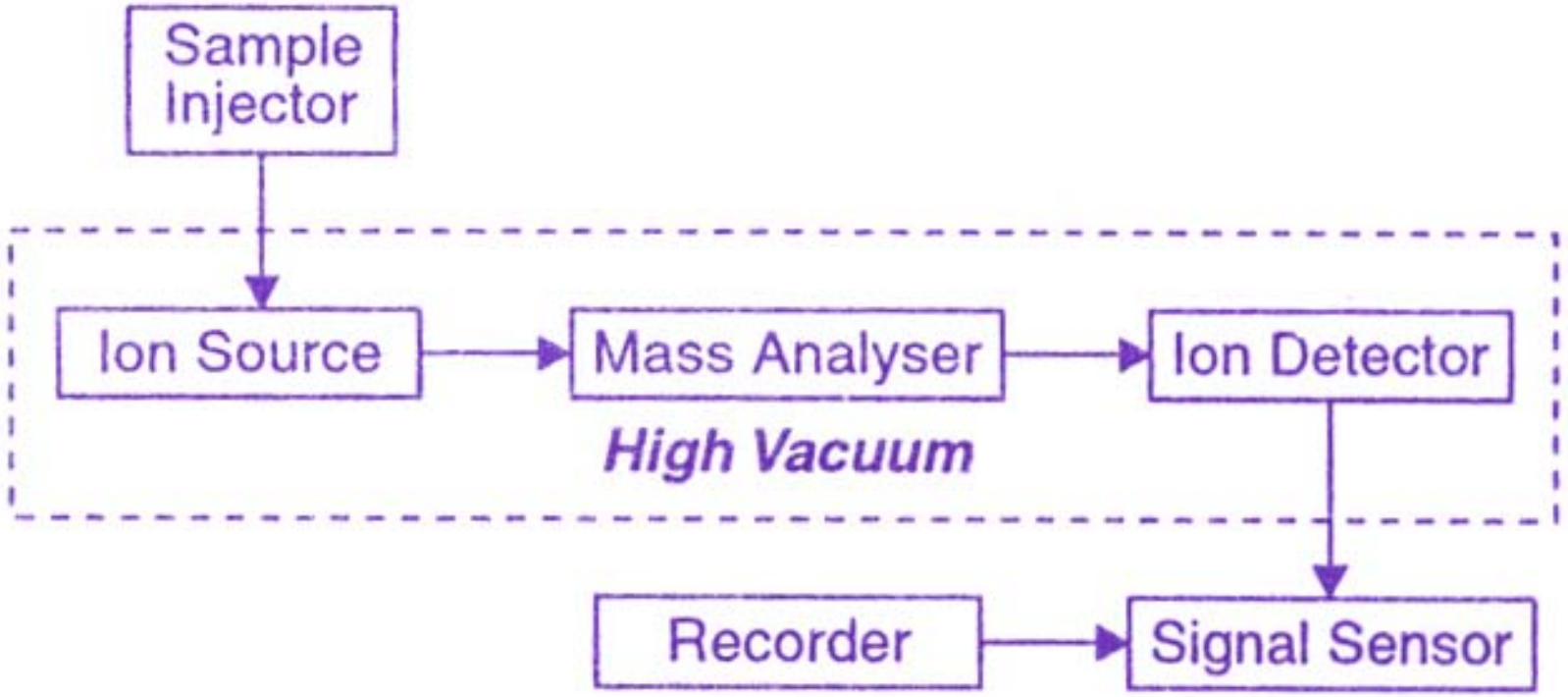


From the patterns obtained from pure compounds and that given by the sample, considerable information can be generated regarding the structure or composition of the sample. It is possible to obtain spectra of the negative ions but electrically neutral fragments can not be detected in a mass spectrometer.

The basic units of a mass spectrometer are:

- **A sample introduction system to produce a jet of vapour from the sample.**
- **An ion source to produce ions from the sample molecules.**
- **A mass analyzer to separate the ions according to their m/e ratios.**
- **An ion collector and amplifier to act as a detector.**
- **A recorder to record the spectrum.**
- **A high vacuum system from ion source to the detector.**

SCHEMATIC DIAGRAM OF A MASS SPECTROMETER



SAMPLE INTRODUCTION

Sample introduction can be achieved by any one of the following methods:

1. **The sample is converted into a spark electrode and kept in the ion source.**

2. **A small amount of sample is coated on a filament and heated within the ion source.**

3. **100 µg to 1 ng sample is directly introduced into the ion source (The sample must be sufficiently volatile for this).**

4. Gases can be introduced from a glass bulb, allowed to expand into a reservoir and the required quantity is allowed to flow into the ion chamber. Liquids can be introduced using micro pipettes or syringes. Solids having melting points below 200^0 C can be introduced in the same way because the reservoir is kept heated.

5. High melting inorganic materials can be placed in a furnace cell called 'Knudsen Cell' close to the ion source and the vapours may be allowed to pass into the ion chamber.

ION SOURCE

In the case of ion source, samples that are sufficiently volatile ions may be produced either by Electron Impact (EI) or by Chemical Ionization (CI).

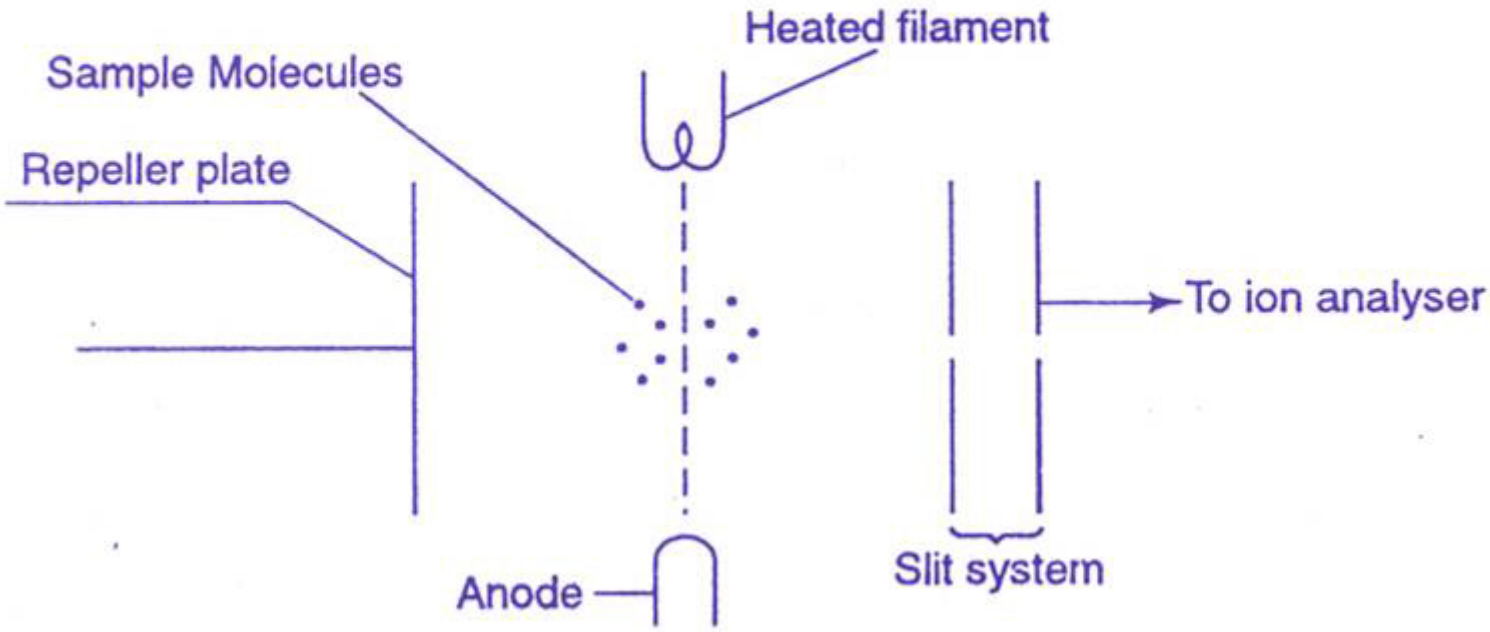
In electron impact technique a heated tungsten filament emitting electrons which are accelerated by applying a potential difference of 70 V. The kinetic energy of the electrons will be equal to 70 ev which is sufficient to ionize most organic molecules.

The most probable reaction is

$$M + e \rightarrow M^+ + 2e.$$

M^+ will then undergo extensive fragmentation reactions. Often the molecular ion line will be missing in the spectrum.

ELECTRON IMPACT SOURCE

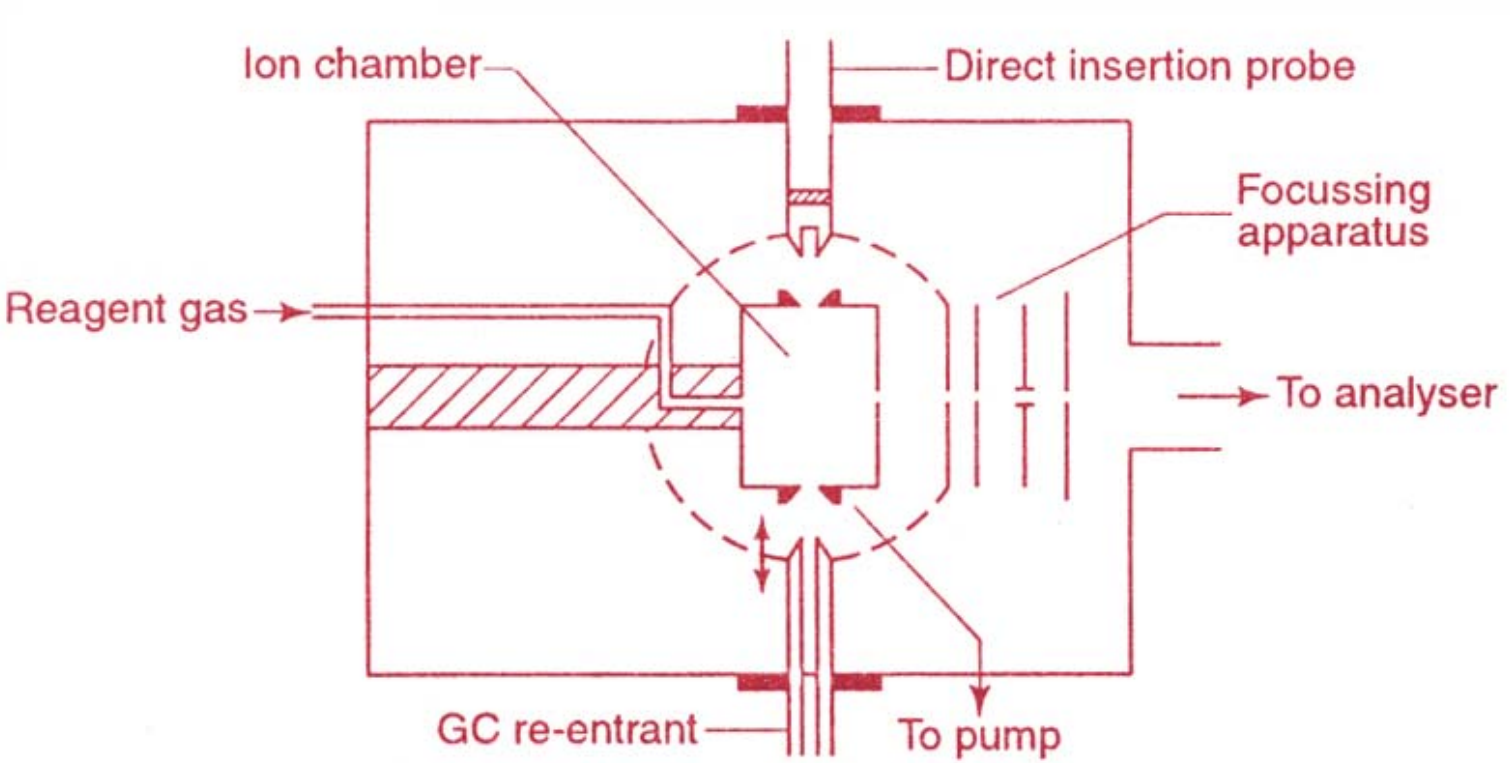


In chemical ionization technique, a reagent gas like isobutane, methane or ammonia is let into the ion chamber at a pressure of about 10^2 Nm^{-2} and ionized by bombarding with electrons having kinetic energies up to 300 ev. The sample molecules are volatilized into fragmented reagent ions which can also protonate the sample molecules.

$$M + CH_5^+ \rightarrow MH^+ + CH_4$$

The observed m/e will be one unit more than the molecular weight.

SCHEMATIC DIAGRAM OF C.I SOURCE



The internal energies of MH^+ ions decreases in the order

$$CH_5^+ > C_4H_9^+ > NH_4^+.$$

This means, when CH_5^+ transfers a proton to a molecule M to form MH^+, much energy is liberated because M has greater affinity for H^+ than CH_4. The liberated energy can cause fragmentation of MH^+. NH_4^+ has the least internal energy in the above. This is because NH_3 has great affinity for H^+. If at all it transfers H^+, there will be little excess energy to cause further fragmentation of the sample molecules.

Thus ammonia chemical ionization is an excellent method for determination of the molecular weights of unknown molecules. Negative ion spectra can be produced by chemical ionization method. Chemical ionization can be used for nonvolatile substances also.

For nonvolatile substance ionization methods include field desorption (F, D) fast atom bombardment (FAB), californium plasma desorption (CFPD), laser desorption (LD) and photon ionization (PI).

In field desorption method, a solution of the sample is smeared on a heated wire maintained at 8000 V. Electrons are transferred from the sample to the wire metal and positive ions (M^+) are desorbed by electrostatic repulsion. The ions may collide to form MH^+.

In laser desorption the (solid or the solution of the sample in a nonvolatile liquid) sample is irradiated with a laser beam. Energy absorbed by the sample volatizes and ionizes it.

In the fast atom bombardment method, the sample is dissolved in a solvent like a glycerol homologue and bombarded with a beam of fast xenon atoms. The fast Xe atoms are produced by accelerating Xe^+ to 6-9 kev and then neutralizing these by electron transfer.

$$\overrightarrow{Xe^+} + Xe \rightarrow \overrightarrow{Xe} + Xe^+$$

The sample is desorbed as an ion by momentum transfer.

In ^{252}Cf plasma desorption, ^{252}Cf undergoes spontaneous fission giving rise to $^{142}Ba^{18+}$ (79 Mev) and $^{106}Tc^{22}$ (104 Mev). These fast ions pass through the sample both M^+ and M^- are produced.

In a spark source electrodes are made out of the sample and a spark is generated to produce the ions. In a spark source electrodes are made out of the sample and a spark is generated to produce the ions.

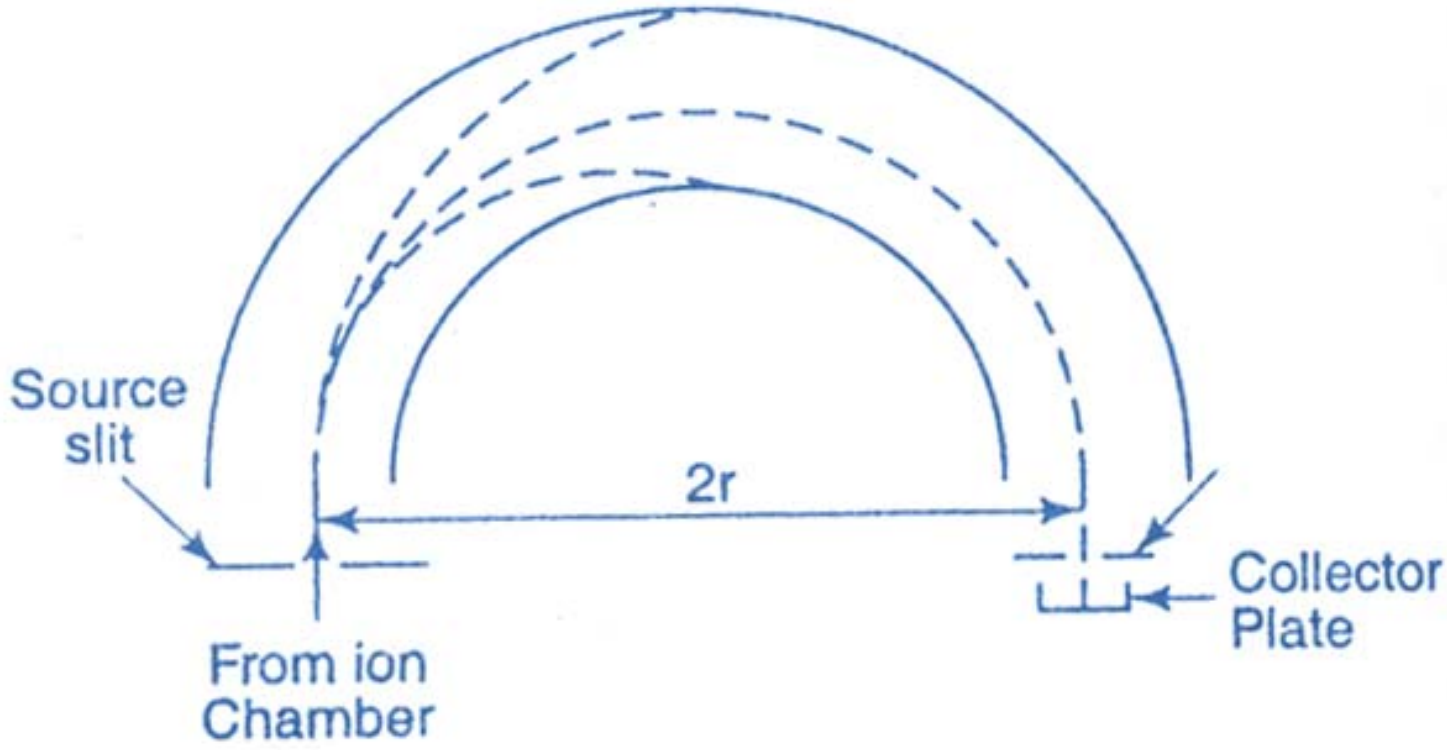
In a photo ionization source the sample is irradiated by intense light to produce ions.

MASS ANALYSER

The ions from the Mass analyzer ion source are repelled by repeller electrodes which are accelerated and injected into mass analyzer. Here, the ions are separated according to their (m/e). This principle is illustrated by Dempster's mass spectrometer.

In Dempster's mass spectrometer, positively charged ions entering from the ion source are accelerated by electrostatic field. A magnetic field H is applied in a perpendicular direction.

DEMPSTER'S MASS SPECTROMETER



Under the influence of this magnetic field, the ions travel in a circular path and fall on a collector after traveling 180^0. The kinetic energy of an ion of charge e accelerated by a voltage, is equal to V eV. That is,

$$1/2mv^2=eV$$

V = Velocity of the ions, m = mass, e = charge and v is the (voltage) potential applied.

In a magnetic field, the ions experience a force HeV such that it travels in a circular path of radius r.
By Newton's second law,

$F = ma$. Hence $a = F/m$

a is also equal to v^2/r. Hence,

$Hev/m = v^2/r$

$H^2e^2 = m^2v^2/r^2$

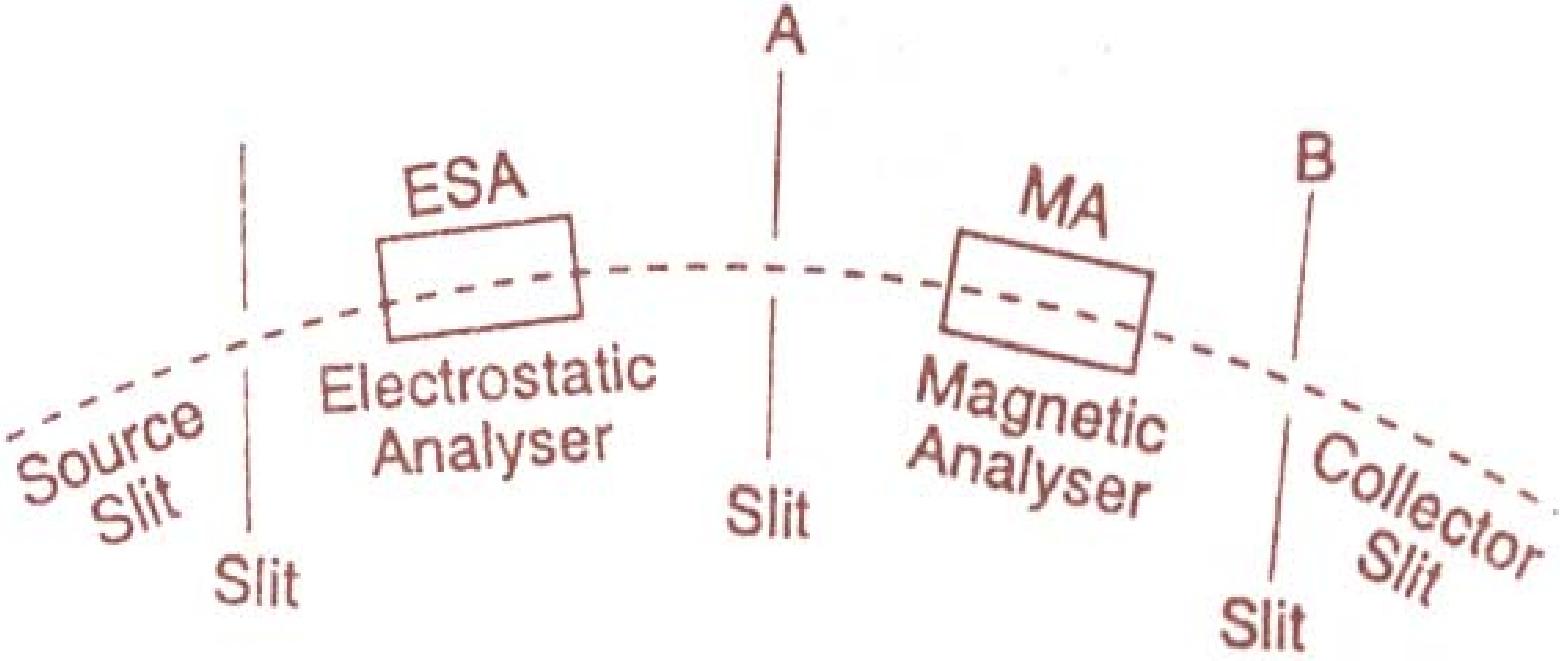
But $1/2mv^2 = eV$

Therefore $H^2e^2 = m^2eV/r^2$

$m/e = H^2r^2 / 2V$

If v is kept constant and H is varied (magnetic scanning) ions with different m/e will reach the collector at different values of H. If H is kept constant and V is varied, the process is called voltage scanning.

Due to variations in the kinetic energy of the ions entering the mass spectrometer from the ion source the resolution of Dempsters mass spectrometer is limited. To overcome this problem the ions are passed through an electric field prior to the magnetic field. The ions are focused and passed through a slit into the magnetic sector. This results in high resolution that can distinguish m/e differences of the order of 0.01.


A
ESA
MA
B
Source Slit
Electrostatic Analyser
Slit
Magnetic Analyser
Collector Slit
Slit
Slit

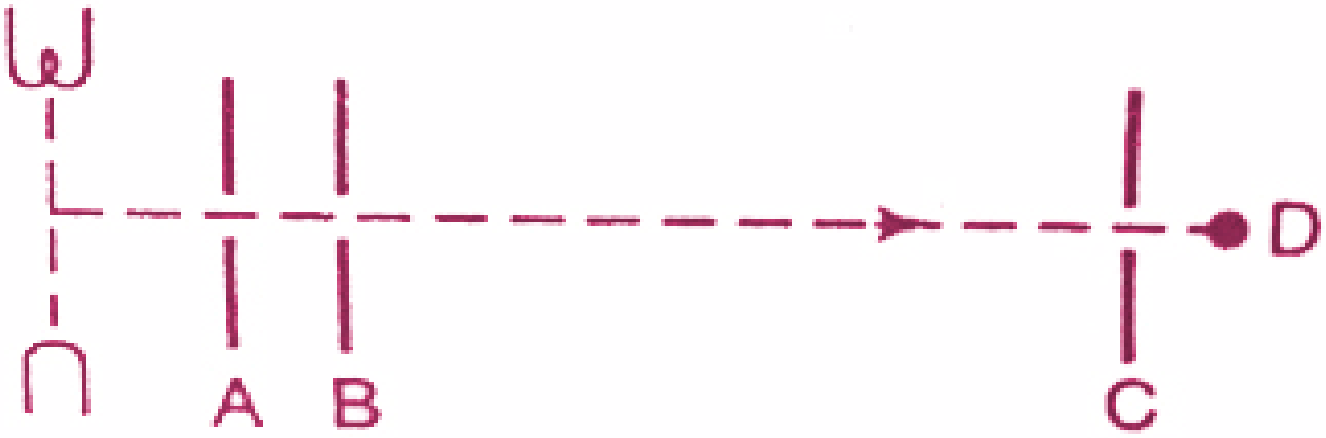
ION DETECTOR

The ion separated by the mass analyzer are measured by the currents of the order 10μA to 1aA they produce. The ions pass through the collecting slits and fall on the collector electrode. The latter is shielded thoroughly from stray ions. The recorder records peaks of all sizes and the scanned spectrum is recorded. It is possible to replace the collector electrode with a photographic plate, develop it and then measure the darkening at different positions which is proportional to intensity of the corresponding ions.

TIME OF FLIGHT MASS SPECTROMETERS

In a time of flight mass spectrometer all the ions emerge from the electro static field with the same energies. The ions with the largest mass will have the lowest velocity, so they take the longest time to cover a given distance. This is the principle of a time of flight mass spectrometer.

SCHEMATIC DIAGRAM OF TIME OF FLIGHT MASS SPECTROMETER



A voltage pulse on grid A extracts the ions from the source. The ions are accelerated by the potential difference between A and B and pass into a free flight tube where there is no field action on the ions. The ions are separated in time according to m/e ratios an collected at D. Time difference between successive peaks will be of the order of 0.1μ sec.

$$t \quad \alpha \quad \sqrt{m/e} \qquad\qquad t = k \sqrt{m/e}$$

k is a constant which depends on the length of free flight.

QUADRUPLE MASS SPECTROMETER:

In a quadruple mass spectrometer four electrode systems are used in which the opposite electrodes are connected together. A constant voltage, u and a radio frequency potential, V are applied between opposite pairs of four parallel rods. Ions are injected along x direction and the spectrum is scanned by varying v keeping the ratio u/v constant. These are relatively cheap instruments.

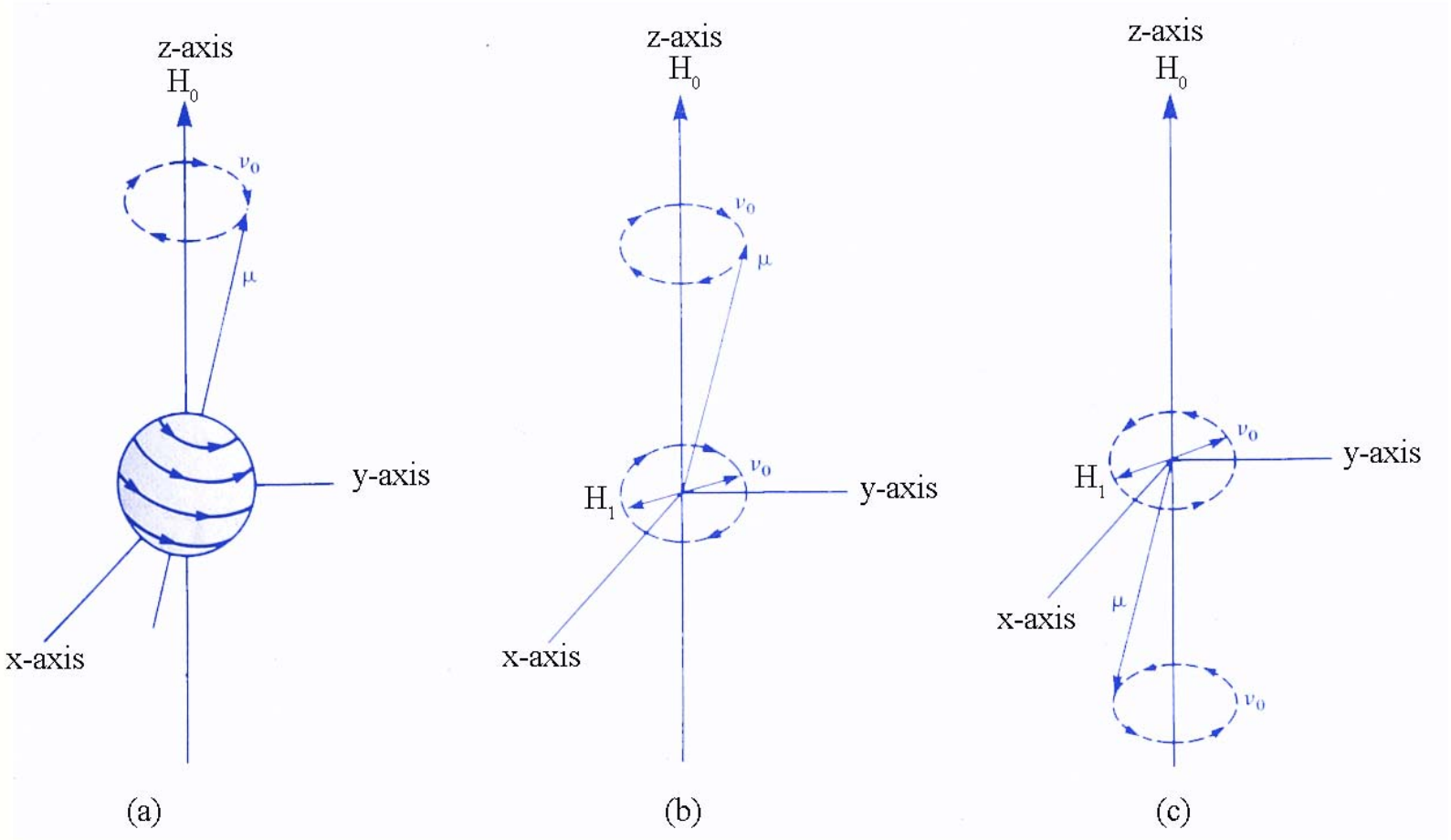
INTERPRETATION OF MASS SPECTRUM

Extensive libraries of mass spectrum are available and it is possible to make all the necessary conclusions by matching the spectrum of the unknown sample with the correct spectrum in the library with the help of a computer. Otherwise, interpretation of a mass spectrum depends on the though knowledge of the empirical facts relevant to the case. In otherwords interpretation of mass spectrum is a specialist's job.

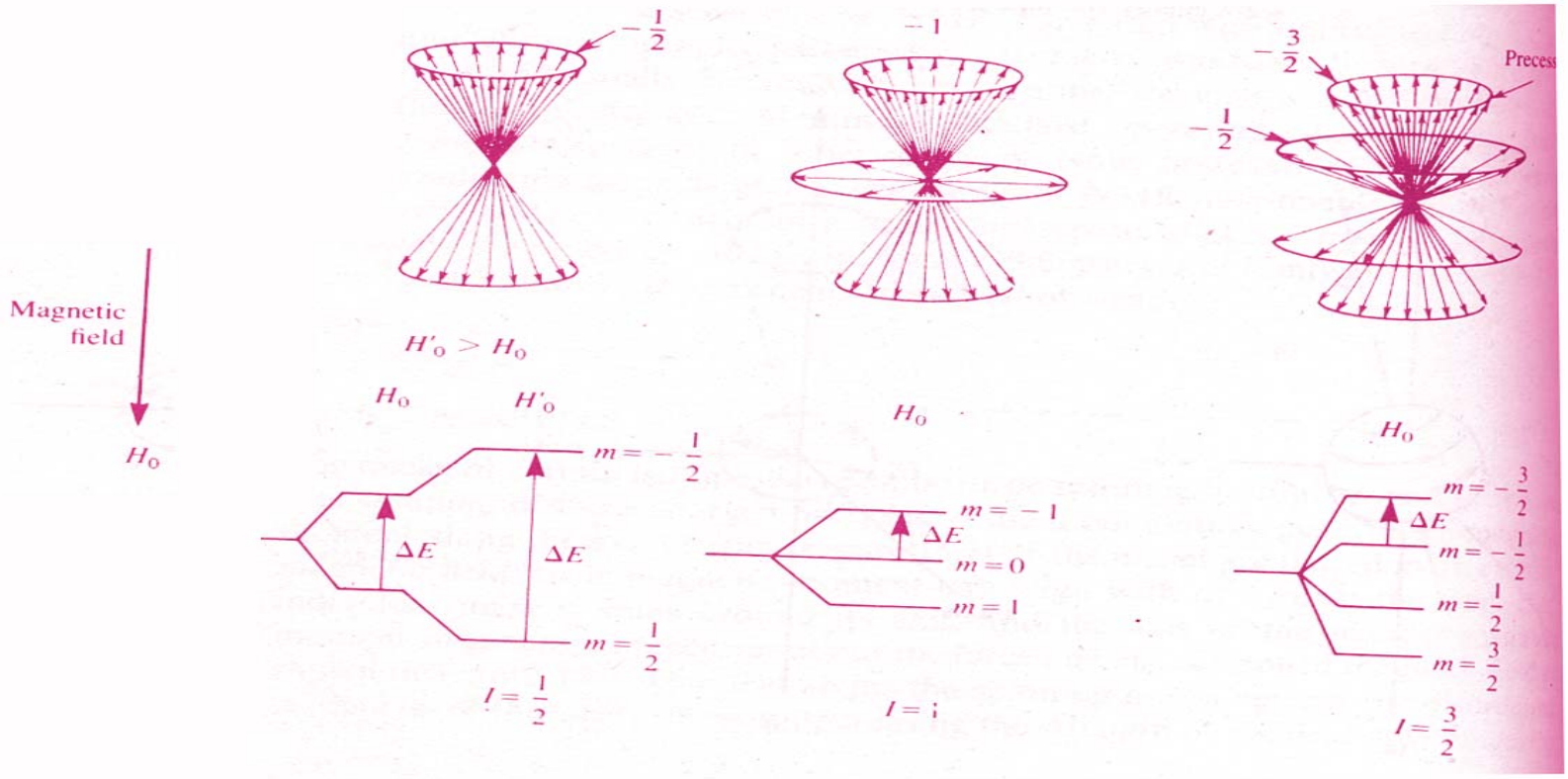
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance (NMR) spectroscopy is a technique for determining structure of molecules and ions and for their quantization based on transitions between the energy levels of the atomic nucleus under certain conditions. The energy involved is in the radio frequency range. Only those nuclei which have spin give signal in NMR. Even so, NMR is extremely useful because the signal given by a nucleus is influenced by its environment. In other words, the signal from a nucleus gives information about its neighbouring atoms, charge status etc. This often leads to determination of complete molecular structure.

The nuclei of certain isotopes have an intrinsic spinning motion around their axis. The spinning of a charged particle generates a magnetic moment along the axis of the spin.



If an external magnetic field is applied, their spin can align with or against the field. Each individual nucleus spins around its axis and the axis of the nuclear magnetic moment so generated precesses about the line of force of the applied magnetic field, like a top as shown here.



The spinning motion of a nucleus is quantized and is associated with a spin quantum number I. The relation between the mass atomic number and spin quantum number is shown in table below:

Mass number, (Protons + Neutrons)	Atomic number (no of Protons) Z	No of Neutrons	Spin Quantum no I	Examples
Even	Even	Even	0	^{12}C, ^{16}O, ^{32}S
Odd	Odd	Even	1/2 3/2	^{1}H, ^{19}F, ^{31}P ^{11}B, ^{79}Br
Odd	Even	Odd	1/2 3/2	^{13}C ^{127}I
Even	Odd	Odd	1	^{2}H, ^{14}N

Nuclei with both A and Z even have I = 0 and they do not give NMR signals.

For a nucleus to be magnetic it must possess spin angular momentum with a magnitude of $(h/2\pi)\sqrt{\mathrm{I}(\mathrm{I}+1)}$.

The maximum observable value of the spin angular momentum is $hI/2\pi$ **,where I is the spin quantum number of the nucleus and h is the Plank's constant. It generates a magnetic moment (μ) parallel to the axis of spin. Like spin moment, magnetic moment is also quantized. The magnetic quantum number(m), has the values -I, -I+1,…,0,..., I-1, I. The ratio of the magnetic moment to the angular moment,γ , is known as the gyromagnetic ratio. Different nuclei have different γ.The maximum observable component of magnetic moment, μ, has the value** $m\mu/I = \gamma h/2\pi\,\mathrm{I}$ **.**

Those nuclei with I = 1/2 behave like charged, spinning spheres and give well resolved spectra. Such nuclei include ^{1}H,^{13}C, ^{19}F and ^{31}P.

Among nuclei with I = 3/2, ^{7}Li, ^{11}B, ^{35}Cl are important. Nuclei with integral spins of I = 1 include ^{2}H and ^{14}N.Nuclei with spins greater than 1/2 behave like nonspherical charged rotating bodies and show line broadening in NMR spectra.

Many organic molecules contain only C,H and O. Since ^{12}C and ^{16}O do not have nuclear magnetic moments only the proton spectra are observed. ^{13}C has a low natural abundance of 1.1% and is not observed in ordinary NMR.

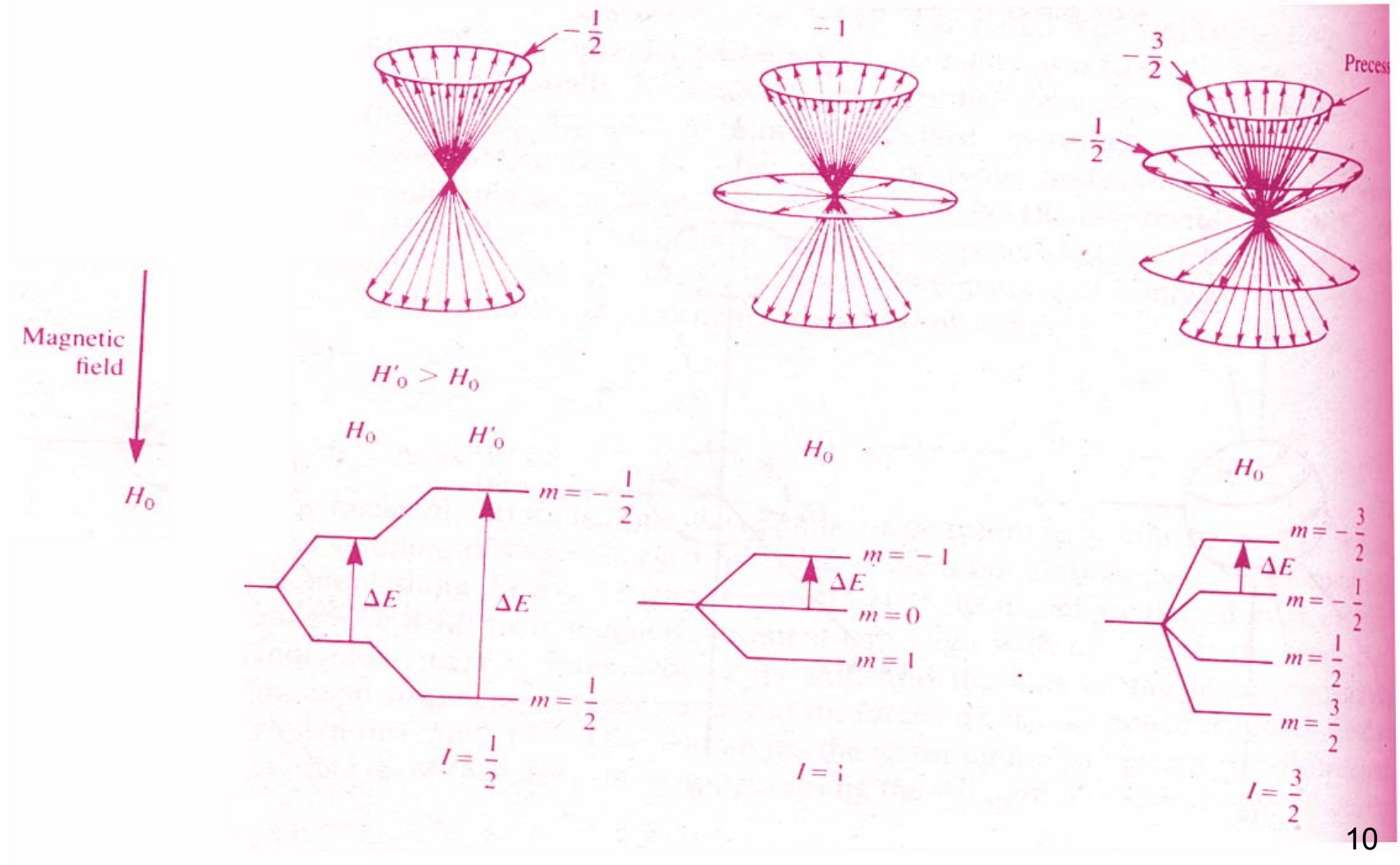
The magnetic moment of a spinning nucleus can assume 2I +1 orientations with respect to the external magnetic field leading to 2I+1 discrete energy levels. The energy levels can be calculated using the equation,

$$E = -m\,\mu / I\,H_0$$

where I = spin quantum number, m is the magnetic quantum number, μ is the magnetic moment of the nucleus, H_0 is the external (i.e., applied) magnetic field strength in gauss (G) and E is the energy corresponding to that orientation (in value).

The allowed values of m are I, (I-1), ….., 0, …..(-I+1), -I. Thus a nucleus with spin 1/2 has 2 orientations, with spin 1 has 3 orientations; and so on.

NUCLEAR ORIENTATION AND ENERGY LEVELS OF NUCLEI IN A MAGNETIC FIELD



Transitions between the energy levels produced by the application of a magnetic field can occur according to the selection rule Δm = ± 1. The resonance frequency, ν_0 that makes the transition possible is given by,

$$\Delta E = h\nu_0 = \frac{\mu H_0}{I}$$

Keeping the applied magnetic field H_0 constant, if an increasing radio frequency (rf) current is passed through a coil in the YZ plane, the rf frequency creates an alternating magnetic field(H_1), in the x direction. When H_1 equals the resonance frequency ν_0 , energy is absorbed by the spinning nucleus, flipping the spin direction such that its magnetic moment precesses against the applied field. This is known as Larmor frequency.

There is a linear relationship between the resonance frequency and the applied magnetic field H_0. Therefore, either H_0 can be kept constant and sweep radio frequency (rf) or keep a constant rf and vary the applied magnetic field H_0.

Magnetic field strength can be expressed in units of Gauss (G) or Tesla (T). 1T = 10,000 G

For a proton μ = 1.41 x 10^{-30} JG^{-1}or 2.7927 nuclear magnetons. If a magnetic field of 14092 G is applied,

$$\nu_0 = \frac{\Delta E}{h} = \frac{(1.41 \times 10^{-30}\ J\ G^{-1})(14{,}092\ G)}{(6.626 \times 10^{-34}\ J\ sec)\ \ (0.5)} \quad sec^{-1} = 60x10^{6}\ \ sec^{-1}$$

Thus, the resonance frequency of a proton in a magnetic field of 14,092 G would be 60 MHz.

In NMR the strength of the signal is approximately equal to the square of the magnetic field applied. Strong magnetic fields can be produced using super conductors.

MAGNETIC RESONANCE PROPERTIES OF SELECTED NUCLEI

Isotope	Magnetic moment, μ/μ_N*	Relative sensitivity at constant H_0†	*NMR frequency (MHz)*		
			At 14.09 kG	At 21.14 kG	At 23.49 kG
^{1}H	2.7927	100	60.000	90.000	100.000
^{2}H	0.8574	0.96	9.210	13.815	15.352
^{13}C	0.7024	1.59	15.086	22.629	25.147
^{19}F	2.6288	83.4	56.444	84.666	94.087
^{31}P	1.1317	6.64	24.288	36.432	40.485

* In multiples of the nuclear magneton, $eh/4\pi\ Mc$.

† Sensitivity relative to the proton, assuming equal numbers of nuclei and the same relaxation time ratio, T_2/T_1.

When there are two allowed energy levels the distribution of a population of nuclei at equilibrium follows Boltzmann equation:

$$\frac{n_{upper}}{n_{lower}} = e^{-\mu H_0/KT}$$

where K is the Boltzmann constant and T is the absolute temperature.

For a proton at 14.09 kG applied magnetic field $n_{upper} \approx n_{lower}$. Therefore it is easy to saturate the system. That is, after a very short time, there will be no signal because the number of nuclei absorbing rf energy will be equal to the number of nuclei releasing the same rf. Therefore, relaxation processes that allow nuclei in higher energy state to return to the lower state (by different ways) are important for the relaxation back to the lower energy state. Therefore a constant absorption signal can be observed.

Two types of relaxation processes occur. One, spin-lattice or longitudinal relaxation by which the nuclei with higher energy transfers its energy to other nuclei to increase their translational or rotational energy, for example. This process is associated with a time constant, T_1, which is the time required for (the Boltzmann distribution) the ratio n_{upper} / n_{lower} to reach 1/2 of its initial value in the presence of H_0.

The second type of relaxation is the spin-spin (or transverse) relaxation. In this process, the nuclei exchange spins with neighboring nuclei by interaction of their magnetic moments. Although no energy is lost by this mechanism, the precessing nuclei loose phase coherence. Some precess faster and some precess slower. The net magnetization in the XY plane falls towards zero. The time constant associated with this process is T_2.

For solids and viscous liquids T_1 is of the order of hours and for liquids and dilute solutions T_1 is in the range 0.01-100 sec. In general $T_2 \leq T_1$.

The width of the absorption line is related to T_1 by the equation,

$$\Delta \nu_{1,2} = \frac{1}{T_1}$$

where $\nu_{1,2}$ is the line width at half height in hertz. If T_1 is 1sec, the line width at half height in hertz would be 1.

The conventional NMR spectrometers scan the spectrum slowly to avoid passing very narrow lines too fast. Most of the time is spent on recording the background and only a small amount of time is utilized for recording the peaks which contain all the information one looks for. This leads to low efficiency and low sensitivity.

Time required for a scan by conventional method is given by Δ/r,

where Δ is the range of frequencies required to be scanned and r is the resolution desired.

For a ^{13}C NMR at 25 MHz and a typical Δ of 5 kHz and the line widths of about 1Hz, the scan rate has to be 1 Hz sec^{-1} and the total time required is 1 h 23 minutes.

If the spectrum is divided into a large number(N) of small frequency intervals and if all these frequencies are applied simultaneously the spectrum can be obtained much quickly. If N is equal to the bandwidth of the signal, S/N ratio improves by a factor of $(N)^{1/2}$. This is known as Felgett's advantage. This is achieved in Fourier Transform (FT) NMR. Felgett's advantage for a proton is about 30 and for ^{13}C, it is about 100.

In FTNMR a strong rf pulse is applied to the sample in a short time of 1-100 µsecs. This is applied by means of a coil placed parallel to X-axis of the spectrometer. The pulse contains a wide band of frequencies on either side of the center. Due to this all the magnetic nuclei are excited simultaneously. After the pulse, the precessing magnets revert back to their original state inducing a sinusoidal voltage in a coil surrounding the sample. This is the sum of all signals. After Fourier transformation, the spectrum appears similar to conventional spectrum.

Nuclear magnetic resonance frequencies are to a small degree dependent on the molecular environment of the nucleus. Since surrounding electrons shield the nucleus, the effective magnetic field experienced by the nucleus is slightly different from the applied field. Electronic shielding results from an induced circulation of electrons about the nucleus. These circulations are induced by the applied field and are in a direction perpendicular to the applied field. They produce a magnetic field opposing the applied field and proportional to the magnitude of the applied field.

The effective magnetic field, $H_{eff} = H_0 - \sigma H_0$.
where σH_0 is the induced magnetic field. The separations of resonance frequencies of nuclei in different structural environments from some arbitrary standard is known as chemical shift.

NMR spectra in which the width of the resonance line is as large as or larger than the resonance shifts caused by different chemical environments are known as wide-line NMR. These can give information regarding concentration and physical environment of nuclei but not their chemical environments. Wide line NMR provides a rapid and nondestructive method of quantitative analysis.

For example, proton contents of fats and oils can be measured. Moisture content in a variety of samples can be determined by wide-line NMR. Fluorine in fluorocarbons can be determined. The width of the absorption line is related to motional freedom of the nucleus in the lattice. This gives valuable information to polymer chemists and solid-state physicists.

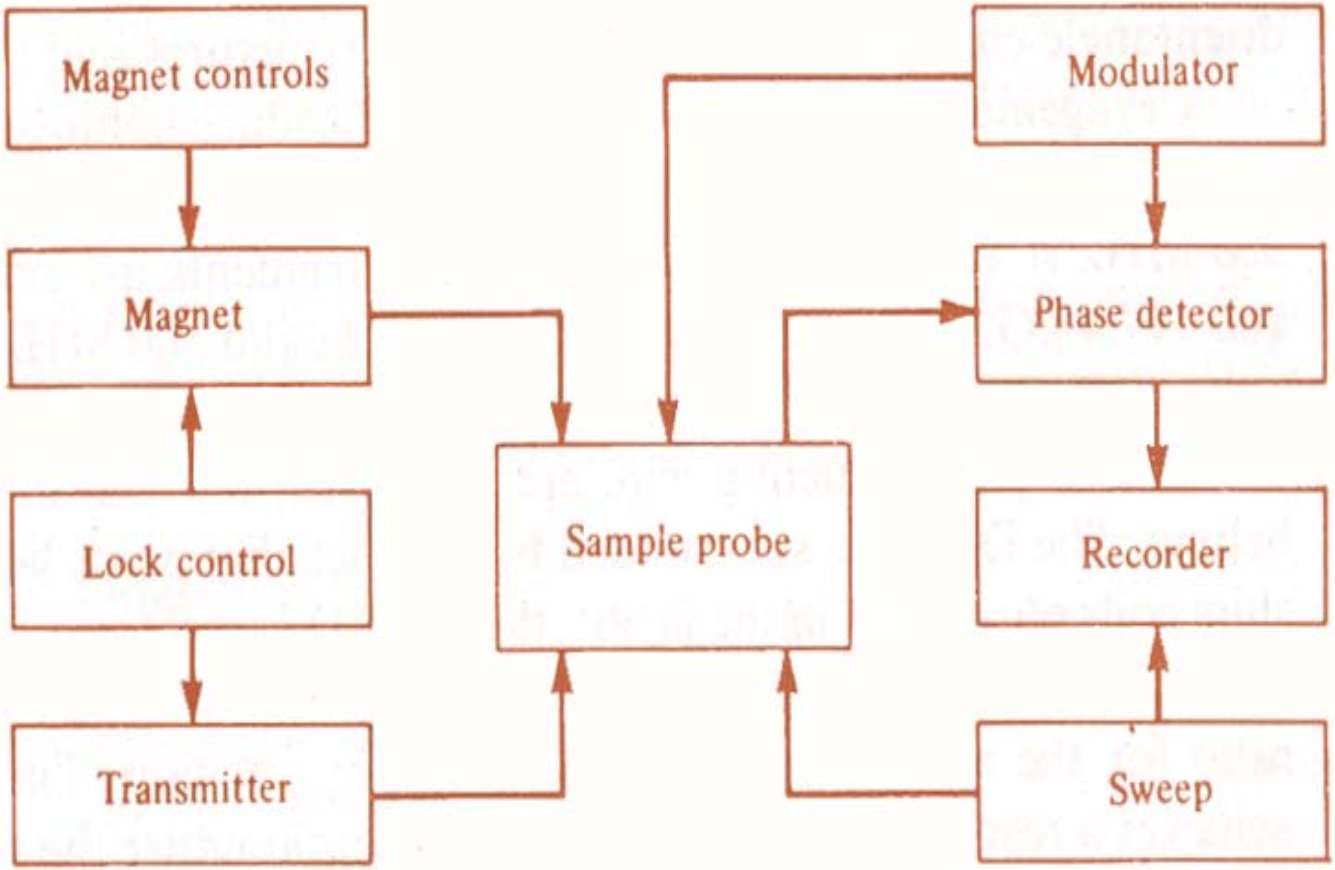
CONTINUOUS-WAVE NMR SPECTROMETERS

Continuous-wave NMR instruments consist of six basic units:

- **A powerful magnet.**
- **Two or more rf channels. One serves to stabilize the magnetic field or radio frequency and another provides irradiating energy. A third rf coil may be used for decoupling nuclei.**
- **A sample probe containing coils for coupling the sample with the rf field.**

- A detector to process the NMR signals.
- A sweep generator for either magnetic field or for radio frequency field.
- A recorder to display the spectrum.

SCHEMATICS OF CONTINUOUS-WAVE NMR SPECTROMETERS



The magnet should give a high field strength which is homogenous and stable. The stronger the field, the better the separation of the absorption lines. Also, multiplet overlapping decreases with increasing field strength.

In a stronger field the separation of energy levels of nuclei is greater and the Boltzmann distribution favours the lower level. Therefore sensitivity also increases. To ensure homogeneity of magnetic field two large pole pieces made of a homogenous metal are used.

The pole faces are polished. The gap between the poles is kept narrow. Slim coils are used for correcting any inhomogeneity. Permanent magnets are cheaper than electromagnets but require elaborate shielding and should be thermostated to $\pm 0.001^0$ C. Electromagnets require elaborate power supply and cooling systems but they can be operated at different field strengths. Commercial NMR spectrometers operate at 14.09, 21.14 or 23.49 kG. Using super conductivity technology 51.7, 70.5, 93.5 or 117.4 kG fields can be produced providing high resolution NMR.

THE PROBE UNIT

The probe unit is the sensing element of the spectrometer. It is inserted between the magnetic poles by an adjustable probe holder. The probe holder houses the sample holder, the rf transmitters, output attenuator, receiver and a phase-sensitive detector. The sample holder is a thin walled glass tube of 5mm outer diameter. To average minute inhomogeneities the sample holder is rotated at 1200 to 2400 rpm. The sample is filled to get a length / diameter ratio of 5.

A few micrograms to a few milligrams of the sample is dissolved in a solvent like CCl_4, CS_2 or a completely deuteriated chloroform, acetone or benzene. The solvent should not contain hydrogen. The magnetic resonance response of the deuterium nuclei is used to lock the ratio of the magnetic filed and frequency of the instrument over long periods of time. Single coil probes as well as dual coil probes are available. Tetra methyl silane (TMS) is traditionally used as an internal standard.

TYPES OF CONTINUOUS WAVE NMR SPECTROMETERS

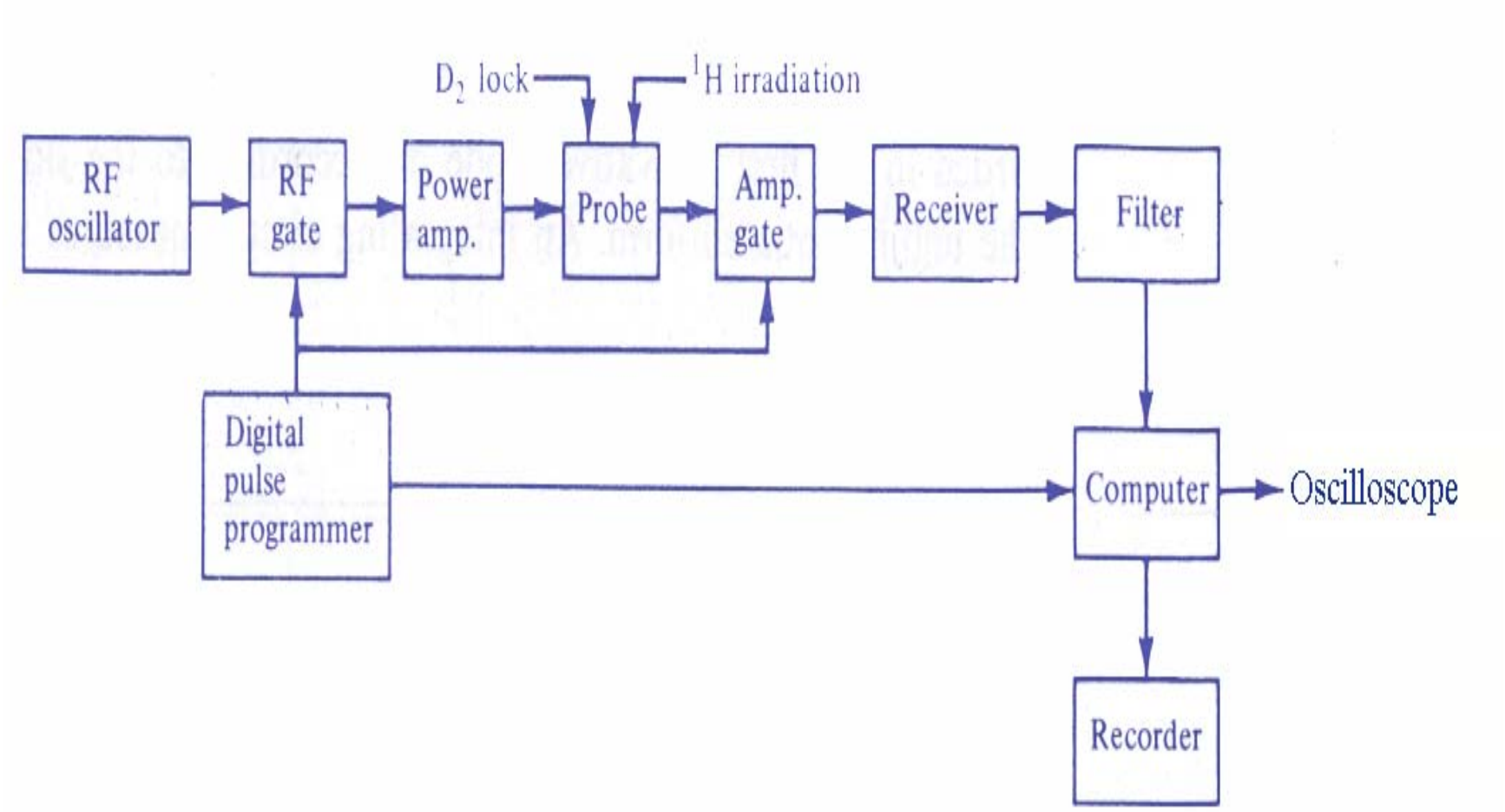
Minimal type NMR spectrometers are relatively cheap and suitable for proton NMR spectral measurements. Multipurpose NMR spectrometers are more sophisticated and versatile. They provide high precision and they are used in research.

Wide-line NMR instruments have a permanent or a light-weight electromagnet with large sample tubes (15 to 18mm outer diameter). The sample temperature can be varied from -170 to $+200^0$ C.

FOURIER TRANSFORM NMR SPECTROMETER

A Fourier transform NMR spectrometer is similar to the continuous wave NMR spectrometer except that it has a computer controlled pulse generator and a digital computer for signal processing and presentation of spectra. Operator skill requirements are much reduced.

SCHEMATICS OF FTNMR



MAGIC ANGLE SPINNING

In powdered solid samples, molecules are oriented in all possible directions. This results in a broadening of the NMR lines. The shielding of any particular nucleus depends upon the electronic environment and the orientation of the molecules in which it is present. This is known as Chemical Shift Anisotropy.

This can be overcome to a large extent by rotating the sample very rapidly (speeds > 2 kHz) about an axis oriented at an angle of approximately 54.7^0 , the magic angle, with respect to the applied magnetic field. The averaging that occurs is similar to tumbling in liquids. The angle is a property of the local fields that electrons exert on the nuclei.

Important parameters NMR spectra provide are chemical shifts, coupling constants, spin-lattice (T_1) and spin-spin (T_2) relaxation times.

The same type of nucleus in different chemical environments experience different shielding from the applied field depending on the distribution of electronic charge in its surroundings. If the external field H_0 is held constant, different shielding effects cause slightly different resonance frequencies.

The magnitude of effective field felt by each group of nuclei is given by,

$$H_{eff} = H_0 - \sigma H_0$$

where σ is a shielding constant which can be positive or negative. The more the field induced by the circulating electrons shielding the nucleus (opposes the applied field), the higher must be the applied field to achieve resonance.

The value of the shielding constant depends on several factors, among which are hybridization and electro negativity of the groups attached to the atom to which the nucleus belongs. Shielding effects rarely extends beyond one bond length.

To express the position of the resonances independent of the strength of the applied field the resonance of a reference compound is required. For proton spectra in nonaqueous media, the reference material is tetramethyl silane. TMS gives a single sharp signal due to 12 equivalent protons and this is taken as 0.0 on the chemical shift (σ) scale.

The magnitude of the chemical shift is expressed as parts per million:

$$\delta = \frac{H_{ref} - H_{sample}}{H_{reference}} \times 10^{-6} = \frac{\nu_{sample} - \nu_{reference}}{\nu_{reference}} \times 10^{6}$$

where H_{ref} and H_{sample} are the positions of the absorption lines for the reference and the sample, respectively expressed in Gauss and V ref and V sample are the corresponding frequencies expressed in hertz. A positive σ represents a greater degree of shielding than in the reference.

For other nuclei, recommended reference materials are:

CS_2 or TMS for ^{13}C

CCl_3F for ^{19}F

NH_3 liquid for ^{14}N and ^{15}N

TMS for ^{29}Si

85% Orthophosphoric acid for ^{31}P

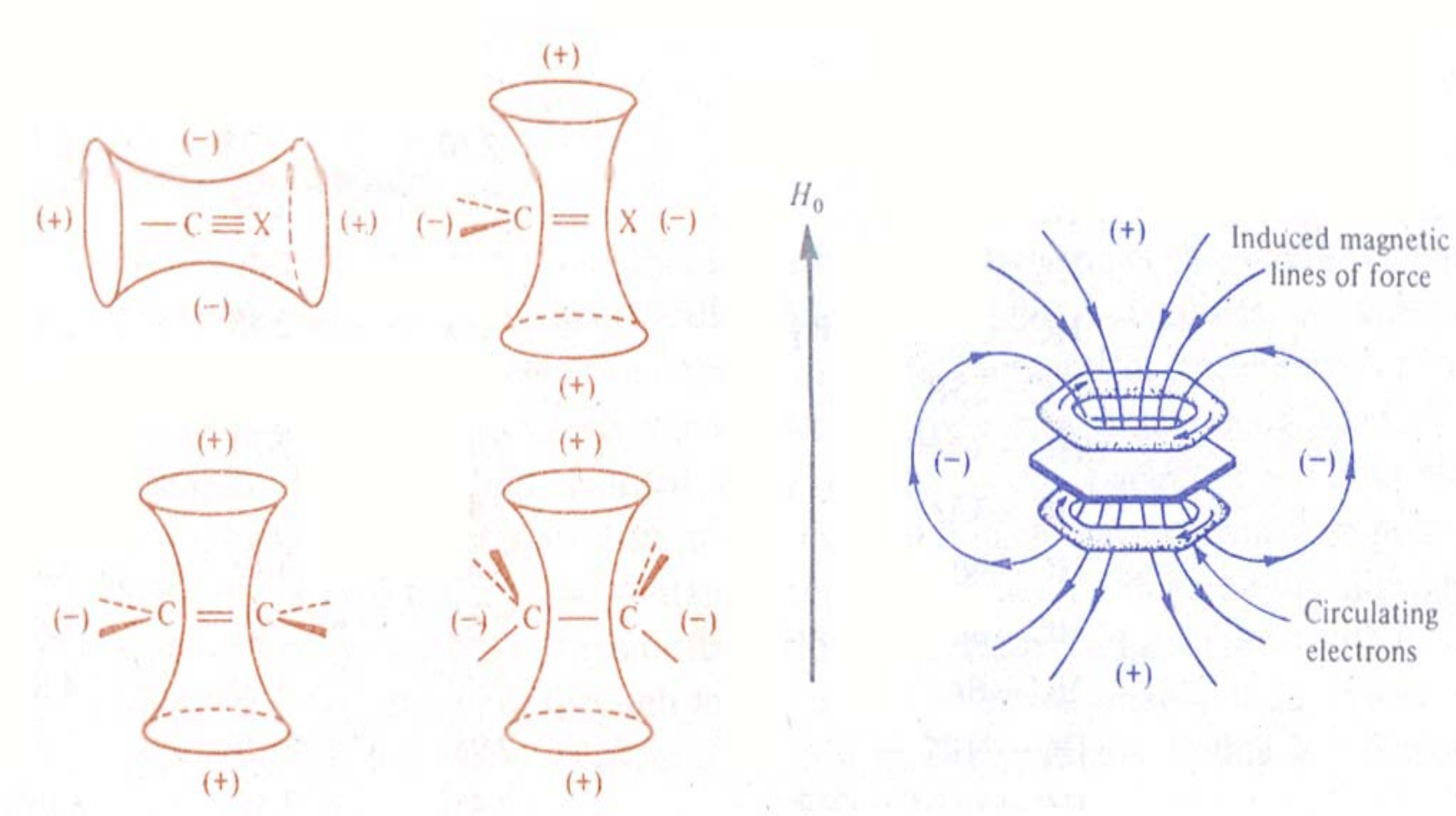
Proton resonances from C-H bonds are found in the range $\delta = 0.9$ to 1.5 when only aliphatic groups are substitutents.

CH_3 protons generally show up slightly down field in that order. If there is an adjacent unsaturated bond the CH_3 proton resonance shifts to $\delta = 1.6 - 2.7$.

An adjacent oxygen atom markedly shifts proton signals downfield to $\delta = 3.2$ to 3.4 for aliphatic entities and to $\delta = 3.6 - 3.9$ for aryl-O-CH entities.

When a double or a triple bond is present in a molecule the electrons in these bonds can circulate only in certain preferred directions. Figure shows shielding (+) and deshielding (-) zones in the neighborhood of triple, double and single bonds to carbon.

SHIELDING MECHANISMS



In C=C and C=O double bonds, the deshielding zone extends along the bond direction. C-C bonds also show some deshielding in this direction. The deshielding of a proton depends on the latter's distance from the bond and also on its orientation with respect to that bond, Aromatic rings have a strong anisotropic effect. The delocalized π electrons of an aromatic ring circulate in two doughnut-shaped orbits on each side of the ring under the influence of the applied magnetic field, H_0.

This circulation results in a magnetic field that opposes H_0 in a cone-shaped region of excess shielding that extends along the perpendicular to the ring plane but it reinforces H_0 in a zone of deshielding from the edge of the ring.Thus, in aromatic compounds, protons which are usually found in the deshielding zone appear at much lower fields (δ = 6 to 7) than olefinic protons (δ = 5 to 6).

In acetylenes, the electron current circulates in such a way that the shielding zone extends along the bond direction and acetylenic protons appear at higher fields (δ = 1.6 to 3.0).

CHEMICAL SHIFT OF SOME COMPOUNDS

Substituent group	Methyl protons (δ)	Methylene protons (δ)	Methine proton (δ)
HC—Cl	3.05	3.45	4.05
HC—OH and —OR	3.20	3.40	3.60
HC—NH_2	3.50	3.75	4.05
HC—O(C=O)R	3.65	4.10	4.95
HC—OAr	3.80	4.00	4.60
HC—O(C=O)Ar	3.80	4.20	5.05
HC—F	4.25	4.50	4.80
HC—NO_2	4.30	4.35	4.60
Cyclopropane		0.20	0.40
Cyclobutane		2.45	
Cyclopentane		1.65	
Cyclohexane		1.50	1.80
Cycloheptane		1.25	

Substituent group	Proton shift (δ)	Substituent group	Proton shift (δ)
HC≡CH	2.35	HO—C=O	10–12
HC≡CAr	2.90	HO—SO_2	11–12
HC≡C—C=C	2.75	HO—Ar	4.5–6.5
HAr	7.20	HO—R	0.5–4.5
HCO—O	8.1	HS—Ar	2.8–3.6
HCO—R	9.4–10.0	HS—R	1–2
HCO—Ar	9.7–10.5	HN—Ar	3–6
HO—N=C(oxime)	9–12	HN—R	0.5–5

SOURCE: J. A. Dean, ed., *Lange's Handbook of Chemistry*, 13th ed., McGraw-Hill, New York, 1985, in which additional proton chemical shifts may be found.
NOTE: Values are given on the officially approved δ scale. R = alkyl group; Ar = aryl group.

CHEMICAL SHIFT OF SOME COMPOUNDS…

Substituent group	Primary carbon	Secondary carbon	Tertiary carbon	Quaternary carbon
Alkanes				
C—C	−20 to 30	25 to 45	30 to 60	35 to 70
C—O	40 to 60	40 to 70	60 to 75	70 to 85
C—N	20 to 45	40 to 60	50 to 70	65 to 75
C—S	10 to 30	25 to 45	40 to 55	55 to 70
C—Halide	−37 to 35	−10 to 45	30 to 65	35 to 75
	(I) (Cl)	(I) (Cl)	(I) (Cl)	(I) (Cl)

Substituent group	δ	Substituent group	δ
Alkynes	70 to 100	Isocyanides	130 to 150
Alkenes	110 to 150	Carbonates	150 to 160
Aromatics	110 to 135	Oximes	155 to 165
C-substituted	125 to 145	Ureas	150 to 170
Heteroaromatics	115 to 140	Thioureas	165 to 185
C-α	135 to 155	Esters, anhydrides	150 to 175
Cyanates	105 to 120	Amides	160 to 180
Isocyanates	115 to 135	Acids, acyl chlorides	160 to 185
Thiocyanates	110 to 120	Aldehydes	175 to 205
Isothiocyanates	120 to 140	Ketones	175 to 225
Cyanides	110 to 130		

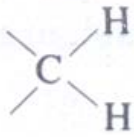
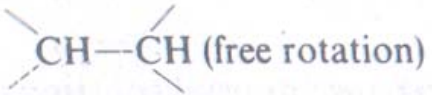
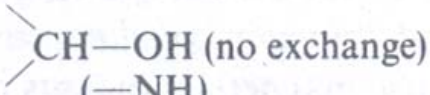
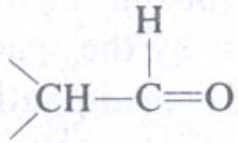
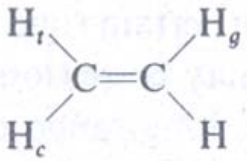
NOTE: Values are given on the δ scale, relative to TMS.

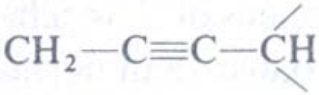
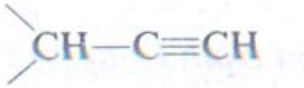
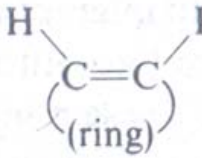
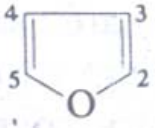
SPIN-SPIN COUPLING

Nuclei in proximity interact with each other causing a splitting of resonance lines into multiplets. This is called spin-spin coupling or J coupling. This is due to interaction of magnetic moments of the nuclei through the magnetic properties of the electrons in the intervening bonds. The strength of the coupling is denoted by J which is equal to the spacing of the multiplets in hertz. Proton – proton couplings in aliphatic organic compounds are normally transmitted through only two or three bonds.

PROTON SPIN-SPIN COUPLING CONSTANTS

PROTON SPIN COUPLING CONSTANTS

Structure	*J* (Hz)
	12–15
	6–8
	5
	1–3
 (*gem*)	0–3
(*cis*)	6–14
(*trans*)	11–18

Structure		*J* (Hz)
		0–3
		0–3
	(3-member)	0–2
	(4-member)	2–4
	(5-member)	5–7
	(6-member)	6–9
	(7-member)	10–13
	(2–3)	1.8
	(3–4)	3.5
	(2–4)	0–1
	(2–5)	1–2

In double bond straight chain systems coupling can be observed over several bond lengths. In aromatic rings, couplings of protons in ortho positions are 7- 9 Hz, meta 2-3 Hz and para 0.5-1.0 Hz.

Coupling also depends on geometry. Axial-axial protons are strongly coupled but axial - equatorial and equatorial-equatorial protons are coupled moderately. It has been shown that $\frac{J_{trans}}{J_{eis}} \approx 2$

The number of lines in a multiplet is given by 2n + 1 where n is the number of nuclei involved. For protons, this becomes n + 1 lines.

In a multiplet, the total intensity is proportional to the number of nuclei involved and the relative intensities of the individual peaks follow the coefficients of binomial expansion. Thus, one neighboring proton splits the observed resonance into a doublet (1:1), two produce a triplet (1:2:1), three a quartet (1:3:3:1), four a quintet (1:4:6:4:1) and so on.

The magnitude of J is independent of the field strength. Other nuclei with spin 1/2., i.e., ^{19}F and ^{31}P interact with protons and cause spin-spin splitting. J is usually larger than for proton-proton coupling. ^{13}C proton coupling can be noticed.

When a proton is coupled to a nucleus that has a quadrupole moment, spin-lattice relaxation becomes so efficient (T_1 is reduced) that the spin-spin interaction with proton is greatly or completely decoupled. Coupling of protons with chlorine, bromine or iodine is thus not observed. In case of ^{14}N, the decoupling is partial, so ^{14}N-^{1}H protons give a broad peak.

DOUBLE RESONANCE (SPIN DECOUPLING)

To remove the coupling of spins an additional rf field, ν_2, perpendicular to ν_1 is applied. ν_1 is the resonance frequency of the nuclei being observed and ν_2 is that for the nuclei causing spin-spin splitting. Then the multiplets collapse into a single peak of intensity equal to the total intensity of the multiplet. This increases the sensitivity of the measurement. It is a common practice to decouple protons for observing ^{13}C spectra because ^{13}C has a low abundance. Hence higher sensitivity is desirable.

NUCLEAR OVERHAUSER EFFECT (NOE)

The nuclear overhauser effect is observed when the signal of one nucleus (^{1}H) is saturated and that of another nucleus (^{13}C) is not spin coupled. Decoupling takes place due to intra-molecular dipole-dipole relaxation. The intensity of the signal (^{13}C) will be more than the total intensities of the multiplets that would have shown up if there was no decoupling. This additional gain in intensity is the overhauser effect. This arises because saturation of one nucleus (^{1}H) causes a change in the population of the nuclear energy levels of the other nucleus (^{13}C).

MAGNETIC RESONANCE IMAGING (MRI)

Proton rich soft tissues of the human body can be imaged using nuclear resonance to complement the x-ray images of the bones. Unlike x-ray there is no health risk in MRI because the energy involved is low. The image is produced by applying gradient magnetic field when protons in different locations resonate at different frequencies and then combining all the signals to reconstruct an image.