Chapter 4:
Infrared Spectrometry

1- Introduction:

Infrared radiation (IR) was discovered in 1800 by Friedrich Wilhelm Herschel. These radiations, located beyond the red wavelengths, are located between the visible spectrum and radio waves.

William Herschel , born Friedrich Wilhelm Herschel, is an astronomer German - British of German origin , born November 15, 1738 in Hanover and died August 25, 1822 in Slough . He was also a music composer.[1]

The infrared range used in typical spectra is between 400 and 4000 cm^{-1}, which corresponds to energies around 30 kj.mol^{-1} . Such energy remains insufficient to cause electronic transitions as in UV-Visible. This energy will act rather on the vibration and rotation of molecules.

The infrared range extends from 0.8 µm to 1000 µm. It is arbitrarily divided into three categories:

- Near infrared (0.8 → 2.5 µm).
- Mid-infrared (2.5 → 25 µm).
- Far infrared (25 → 100 µm)

This energy will act rather on the vibration and rotation of the molecules. Consequently, the functional groups give rise to infrared absorptions which are characteristic.

2- IR spectral range

The infrared spectral range can be divided into three main regions:

- Far infrared (<400 cm^{-1});
- Mid-infrared (4000 to 400 cm^{-1});
- Near infrared (13000-4000 cm^{-1}).

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[11] https://fr.wikipedia.org/wiki/William_Herschel

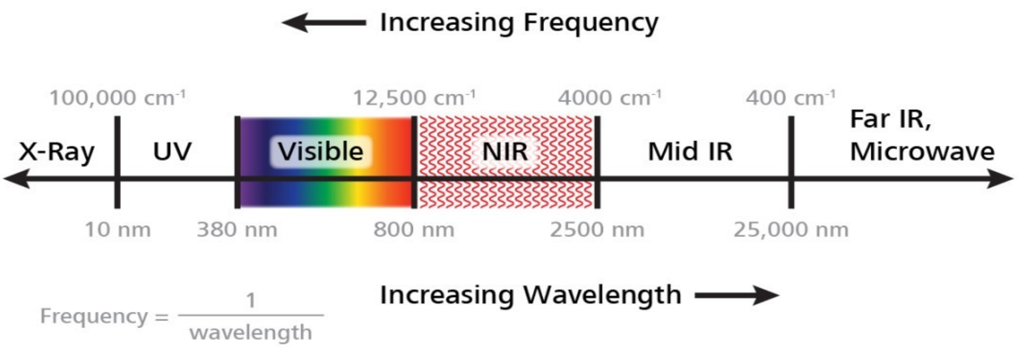


Fig.1: Infrared spectral bands

3. Principale

The atoms that make up molecules are hardly fixed. In fact, a covalent chemical bond, considered as a spring, can deform and elongate. Otherwise, the positions of the atoms are not fixed; they are vibrating incessantly. Each pair of atoms involved in a chemical bond vibrates with its own frequency (characteristic frequency). If such molecules are excited (irradiated) with photons (from the electromagnetic spectrum), having the same frequency as the natural (fundamental) vibrations of the target (irradiated) molecules, a quantity of energy from these photons will be absorbed and consequently the amplitude of the vibrations will increase and a decrease in the reflected or transmitted intensity will be recorded. In reality, the energy of the natural vibrations of atoms is compatible (order of magnitude) with the energy of photons from the infrared spectrum (mid-infrared).

If the variation of the dipole moment of a molecule and the oscillation of the electric field of electromagnetic radiation has the same frequency, there is resonance and under the action of the field, the molecule will vibrate intensely.

The strongest infrared absorptions are therefore often due to very polar groups such as: C=O or N=O (see Fig.2)

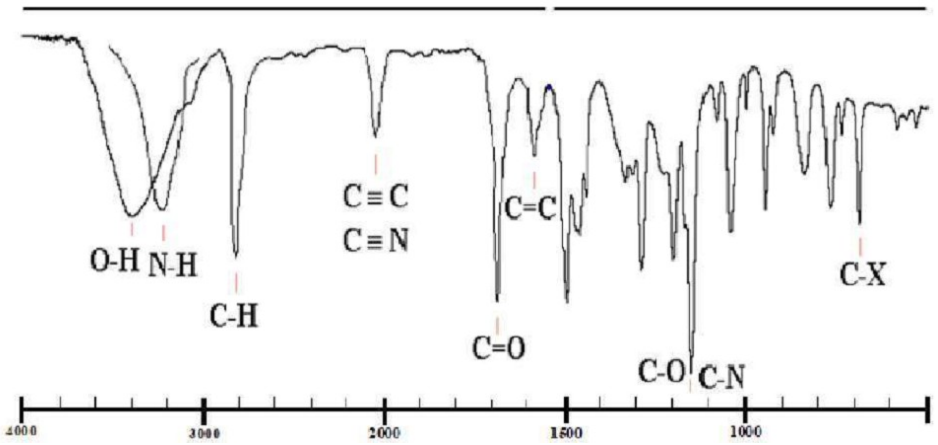


Fig.2 : Group IR Absorption

- Homo-nuclear molecules, such as H_2, O_2, have no dipole moment and regardless of the intermolecular distance, they do not interact with the oscillating electric field (**Fig.3**).

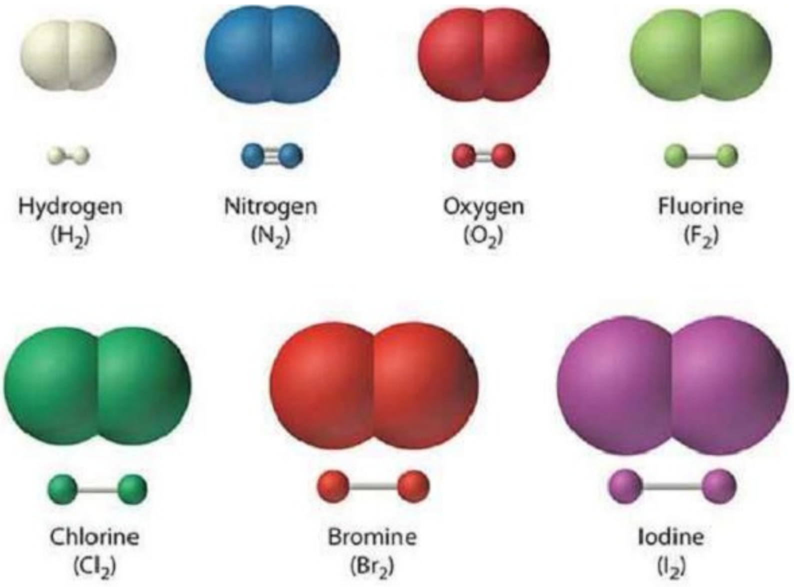


Fig .3: List of diatomic elements

4. Vibration frequency (harmonic oscillator model)

The vibration frequency of a simple (diatomic) molecule can be calculated theoretically and approximately using the harmonic oscillator model (application of Hooke's law) which takes into consideration the mass of the atoms involved in a chemical (covalent) bond as well as the strength of this bond (applies well for diatomic molecules). This is because the chemical system (atoms + bond) can be considered as a purely physical system by assimilating the atoms to point masses and the bond to a spring as shown in Fig. 4.

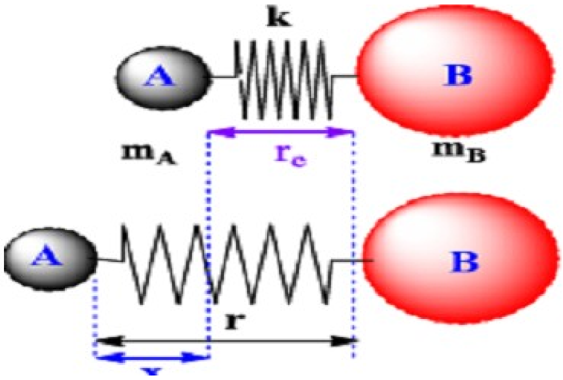


Fig. 4: Harmonic Oscillator Model

4.1. Vibrations in diatomic molecules:

Consider a diatomic molecule AB and denote by r the internuclear distance. The potential energy of the system is represented by the following curve (**Fig.4**), called the Morse curve, whose minimum corresponds to the equilibrium internuclear distance $\mathbf{r_0}$. This energy will act rather on the vibration and rotation of the molecules. To model these vibrations and rotations, we use the harmonic oscillator model: two masses connected by a spring:

Diatomic molecule (**AB**) is represented by a model consisting of 2 masses $\mathbf{m_A}$ and $\mathbf{m_B}$ connected by a spring of force constant **k** , length **r** and stretches and relaxes at a certain frequency **ν** .

- Hook's Law : $F = \pm k(r - r_e) = \pm k.x$ (1)
- Harmonic oscillation equation: $\frac{d^2x}{dt^2} + \frac{k}{m}x = 0$ (2)

$$F = m.\gamma = m.\frac{d^2x}{dt^2}$$

$$k.x = -m.\frac{d^2x}{dt^2}$$

The solution to the equation (2) gives: $x(t) = x_0 \cos(\varpi t + \phi)$

- x_0 : **The amplitude** of the oscillations
- $\varpi : \varpi = \sqrt{\frac{k}{m}}$
- ϕ : Phase at the origin, which depends on the initial conditions.

From where:

The vibration frequency is given by Hooke's law:

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad (3)$$

Where, m is the reduced mass of the system and m_A, m_B the masses of atoms A and B.

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B} \qquad (4)$$

The wave number:

$$\bar{\upsilon} = \frac{1}{\lambda} = \frac{\upsilon}{c}$$

- υ : Frequency
- c : Speed of light
- $\bar{\upsilon}$: Frequency of elongation vibration or valence vibration (stretching), it depends both on the mass of the atoms and on the strength of the bond (depends on k). the characteristic of the restoring force (spring stiffness constant *k*).

- *A bond with zero dipole moment will give no signal in IR.*
- ***Example:*** *O2 is not active in IR. Ethylene C2H4 gives signals in IR due to CH bonds. The C=C bond is inactive, its dipole moment is zero.*
- $1N = 10^5$ dynes

5. Types of fundamental vibrations

The absorption of IR radiation will cause the molecule to vibrate by changing the angles and lengths of the bonds. There are two modes of vibration: elongation vibrations and deformation vibrations.

5.1. Elongation vibration (stretching, valence, etc.) : *Stretching*

They occur when two atoms periodically move closer or further apart along their common axis. There are two possibilities for stretching vibration: symmetrical and asymmetrical

a) Symmetrical:

b) Asymmetric (antisymmetric) Asymmetric stretching vibrations generate stronger energy absorption bands than their symmetric counterparts.

5.2. Deformation vibration

Bending vibration These correspond to changes in the bond angle. Different types of vibration are possible: in-plane and out-of-plane.

Variation of the angle formed by two adjacent bonds. Deformation vibrations are characterized by:

- The corresponding absorption bands are less intense compared to the elongation;
- More numerous;
- More sensitive to their environment (steric gene);
- Either in-plan or out-of-plan;
- Are located in the region 1600 to 600 cm-1;
- Difficult to attribute;
- Allows to determine the position of a substituent in the ortho, meta or para position of an aromatic.

For a group formed of several identical bonds (three atoms), the following deformation modes can be considered:

• In the plan:

- Shearing (Scissoring)
- Rotation (rocking)

Off the Plan

- Wagging
- Twisting

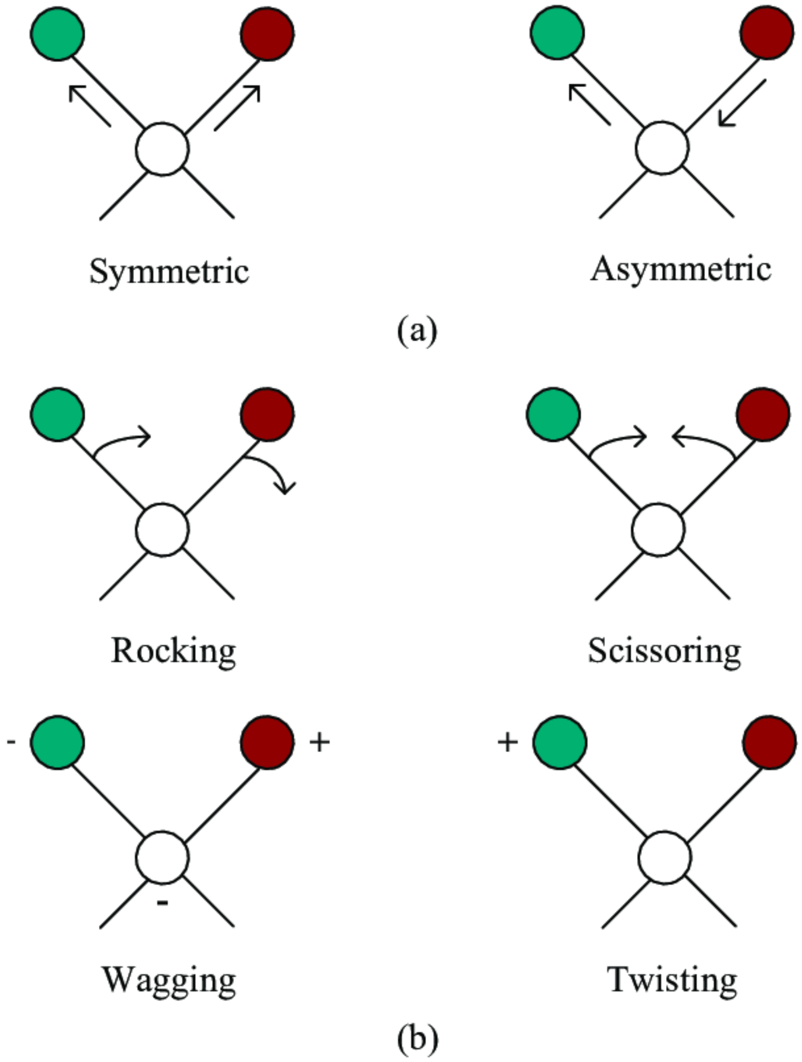


Fig. 5: Different types of vibrations

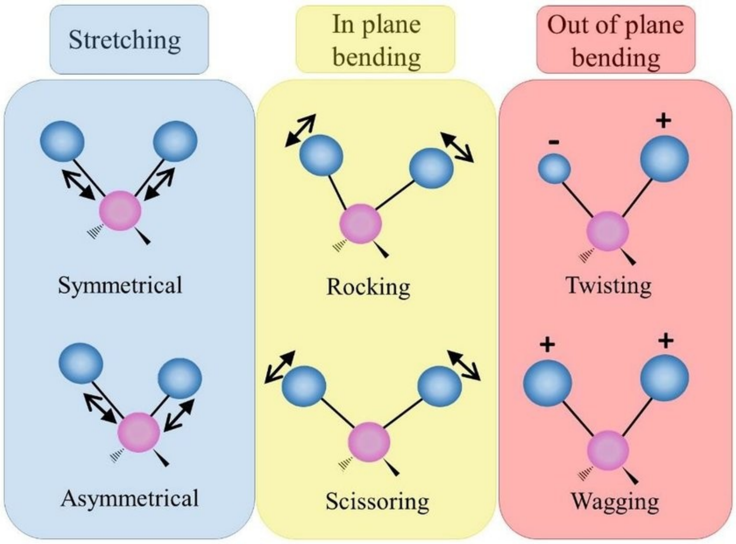


Fig. 6: Different types of vibrations

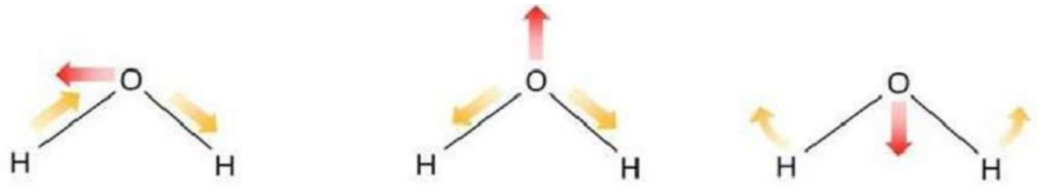
6. Number of vibration modes:

- A molecule composed of N atoms is defined by 3N coordinates, called degrees of freedom.
- The translational motion of the molecule is defined by three degrees of freedom.
- The remaining 3N-3 degrees of freedom are called internal degrees of freedom.
- It takes 3 degrees to define rotational motion.
- The internal vibrating motion number is therefore 3N-6
- So, 3N-6 absorption possible

Table 1: Number of vibration modes

N atoms	Degrees of freedom	translation	Rotation	Vibration
Linear molecule	3N	3	2	3N-5
Non-linear molecule	3N	3	3	3N-6

For a curved molecule like H_2O (n = 3): there will be 3 normal vibration modes or 3 possible vibration frequencies:



Antisymmetric elongation	Symmetrical elongation	Angular deformation
$\sigma = 3756\text{cm}^{-1}$, $\lambda = 2.66$ µm	$\sigma = 3652\text{cm}^{-1}$, $\lambda = 2.74$µm	$\sigma = 1595\text{cm}^{-1}$,$\lambda = 6.27$µm

Fig. 7: Diagrams of the vibration modes of H_2O

Noticed:

The types (modes) of vibrations depend on the number of degrees of freedom of the molecule; the larger the molecule, the more the types (modes) of vibration increase:

- Diatomic molecules: 1 stretching vibration;
- Linear molecules 3n-5 vibration modes (like CO_2);
- Nonlinear molecules 3n-6 vibration modes (n = number of atoms in a molecule).

Example

H_2O: 3n-6 =9-6= 3 types of vibrations: 1 symmetrical elongation, 1 asymmetrical elongation, 1 deformation.

:

7. Vibrational regions

We can consider four regions:

- Hydrogen stretching region;
- Carbon region sp hybridization ;
- Double bond region;
- Fingerprint region.

Table 1: Vibrational regions

$\bar{\upsilon}(\mathrm{cm}^{-1})$	4000 – 2500	2500 – 1900	1900 – 1500	1500 - 400
Region	XH	Sp	X=Y	ED
Examples	CH, NH ,0 - H, CH	C ≡C, C ≡N, X=C=Y (C,O,N,S)	C=C, C=0, C=N, N=N	Single bond C-Cl, CO, CN, CC, …… Polyatomic vibrations
Types of vibration	Elongation	Elongation	Elongation	Elongation Deformation

7.1 Remarks

(a). In general, the region 4000-1800 cm $^{-1}$ has few absorption bands; whereas the region from 1800 to 400 cm $^{-1}$ has many absorption bands. Sometimes the scale is modified so that the former is contracted and the latter is expanded to highlight certain absorption bands.

(b) The fingerprint region is used to differentiate two similar compounds

8. Characteristic frequencies of certain organic groups by family

8.1. Alkanes

(a) CH bond of the methyl group ($-CH_3$)

2970-2950 cm^{-1} ………………………asymmetric stretching vibration

2880-2860 cm^{-1} ………………………symmetrical stretching vibration

1470-1430 cm^{-1} ………………………symmetrical deformation vibration

1380-1370 cm^{-1} ………………………asymmetric deformation vibration

(b) CH bond of the methylene group ($> CH_2$)

2935-2915 cm^{-1} ………………………asymmetric elongation vibration

2865-2845 cm^{-1} ………………………symmetrical stretching vibration

1485-1445 cm^{-1} ………………………deformation vibration

(c) CH bond of the methine group ($> CH-$)

2900-2880 cm^{-1} ………………………elongation vibration

1350-1330 cm^{-1} ………………………deformation vibration

(d) CH bond of the specific methyl group ($-CH_3$)

2850-2815 cm^{-1} ………………stretching vibration of methoxy , methyl ether O- CH3

2820-2780 cm^{-1} ………………………stretching vibration of methylamino N- CH3

8.2. Aliphatic halogenated derivatives

1150-1000 cm^{-1} ……………………C - F stretching vibration

800-700 cm^{-1} ……………………C - Cl stretching vibration

700-600 cm^{-1} ……………………C - Br stretching vibration

600-500 cm^{-1} ……………………C - I stretching vibration

8.3. Alkenes

(a) C=C bond

1680-1640 cm^{-1} ……………………………...………elongation vibration (aliphatic)

1600, 1580, 1500, 1450 cm^{-1} ………………………elongation vibration (aromatics)

(b) CH (≡CH) bond

3095-3075 cm^{-1} ………………………elongation vibration

1420-1410 cm^{-1} ………………………in-plane deformation vibration

895-885 cm^{-1} …………………………..out-of-plane deformation vibration

8.4. Alkynes

(a) C≡C bond

2300-2100 cm^{-1} ……………………………...….elongation vibration

(b) CH bond (≡ C− H)

3320-3310 cm^{-1} ………………………elongation vibration

680-610 cm^{-1} ……………………….deformation vibration

8.5. Alcohols and phenols

(a) OH bond

3650-3600 cm^{-1} ……………………………...……….stretching vibration (free OH)

3400-3200 cm^{-1} ……………………………...……….stretching vibration (OH bound)

1350-1260 cm^{-1} ……………………………...……….in-plane deformation vibration

720-590 cm^{-1} ……………………………......……….out-of-plane deformation vibration

(b) CO bond

1260-1000 cm^{-1} ……………………………...……….stretching vibration (strong)

8.6. Aromatics

(a) C=CC bond

1615-1580 cm^{-1} ……………………….benzene ring stretching vibration

1510-1450 cm^{-1} ……………………….benzene ring stretching vibration

(b) CH bond (CH benzene ring)

3130-3070 cm^{-1} ……………………….elongation vibration

1225-950 cm^{-1} ………………………..in-plane deformation vibration (# bands)

900-670 cm^{-1} ……………………….. out-of-plane deformation vibration (# bands)

8.7. Carbonyls

Any compound (molecule) with a C=O group (ketones, aldehydes, carboxylic acids, esters, amides, etc.).

(a) C=O bond

1725-1700 cm^{-1} ……………………….stretching vibration (carboxylic acid)

1725-1705 cm^{-1} ……………………….elongation vibration (ketone)

1740-1725 cm^{-1} ……………………….stretching vibration (aldehyde)

1750-1725 cm^{-1} ……………………….stretching vibration (ester)

1680-1630 cm^{-1} ……………………….stretching vibration (amide)

8.8. Amines

(a) NH bond

3400-3380 cm^{-1} ……………………….stretching vibration (primary amines)

3360-3310 cm^{-1} ……………………….stretching vibration (secondary amines)

1650-1590 cm^{-1} ……………………….deformation vibration (primary amines)

1650-1550 cm^{-1} ……………………….deformation vibration (secondary amines)

(b) CN Link

1090-1020 cm^{-1} ……………………….stretching vibration (primary amines)

1190-1130 cm^{-1} ……………deformation vibration (secondary amines).

9. Compliments:

For a better understanding and interpretation of IR spectra, it is desirable to keep in mind the six principles listed below.

9.1. Force constant (K) (

Weak bonds vibrate at low frequencies (ν is proportional to k).

Table 3: Order of carbon-carbon bond strength is given in the following table

Type of bond	Single bond (C ≡C)	Double bond (C=C)	Triple bond (CC)
$\bar{\upsilon}(cm^{-1})$	2100	1600	1200
K	$K(\equiv) < K(=) < K(-)$		

9.2 Type of hybridization

The vibrations of CH bonds also depend on the hybridization of the carbon atom carrying the hydrogen atom as shown in the following table:

Table 4: Order of strength according to hybridization

Type of connection	-CH	=CH	≡CH
Hybridization of C	Sp^3	Sp^2	sp
$\bar{\upsilon}(cm^{-1})$	2900	3100	3300

9.3. Reduced mass (μ)

Bonds formed by heavy atoms vibrate at low frequencies (ν is inversely proportional to μ).

If at least one of the masses (or both) changes, the vibration frequency changes as shown in the following table:

Table 5: Reduced mass

Atom	H	C	O	F	Cl	Br	I
Connection	CH	CC	CO	CF	C-Cl	C- Br	CI
$\bar{\upsilon}(cm^{-1})$	3030	1100	1050	1000	750	600	450

9.4. Dipole moment (electronegativity)

"Only vibrations accompanied by a change in the dipole moment are observable."

Examples

- The C=O bond is very polar because of the large difference in electronegativity between oxygen and carbon, which causes very intense absorption bands (always observed). CC or N=N stretching vibrations have weak absorption bands (due to the small variation in the dipole moment associated with their vibration).

- Simple gas molecules such as H_2 , Cl_2 and O_2 do not absorb in the infrared (no dipole moment).

- If the molecule is perfectly symmetrical such that the deformation of the molecule is not accompanied by a change in the dipole moment, there will be no absorption in this case and no band will be observed in the IR spectrum as shown in **Fig. 7.**

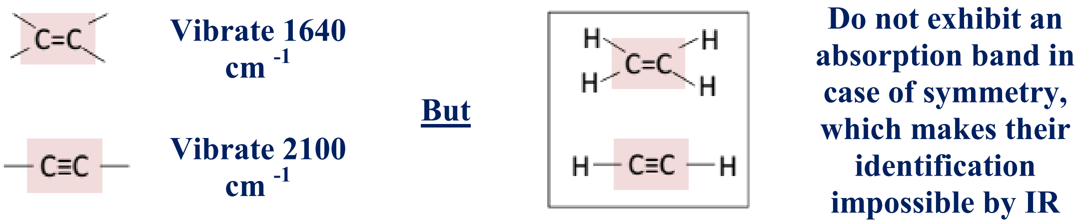


Fig.7: Influence of symmetry on the dipole moment

9.5. Type of vibration (elongation or deformation)

"Deformation vibrations tend to occur at lower frequencies than extension vibrations for the same connection." Is it easier to bend or stretch a spring?

In general, it is easier to bend a spring, so the deformation vibrations are of lower energy than the stretching vibrations for the same bond. The deformation vibrations generally have a lower absorption frequency and a lower intensity than the stretching vibrations, which brings the bands into the fingerprint region and makes their identification and analysis difficult. However, in the case of aromatic compounds, the out-of-plane deformation bands, located between 680 and 900 cm $^{-1}$, are intense and allow the determination of the different substitutions of the aromatic ring.

In practice, only deformations of XH-type bonds are observable.

Example

In an alkane, the stretching vibration of the CH bond absorbs at 2900-3000 cm $^{-1}$, while the straining vibration of the same bond absorbs at 1365-1485 cm $^{-1}$.

9.6. Vibration mode (symmetrical or asymmetrical)

The vibrations of two neighboring bonds (of the same type) within a given molecule can be coupled to symmetric or asymmetric vibration modes. An example is the vibration of $-CH_{2}$ group in an alkane (see application example below). For acetic anhydride, although the two C=O groups are identical by symmetry, two peaks are present in the C=O region of the IR spectrum (**Fig. 8**).

Symmetrical 1717cm $^{-1}$

Asymmetrical 1761cm $^{-1}$

Fig.8: Deformation vibration modes for acetic anhydride

9.7 Harmonics (harmonic absorption bands)

“Harmonics appear at frequencies that are multiples of the fundamental vibration.”

In practice, only three vibrational transitions are observable:

- Transition from v=0 to v=1 with relatively strong intensity;

- Transition from v=0 to v=2 with relatively low intensity;
- Transition from v=0 to v=3 with relatively negligible intensity.

The three corresponding spectral bands are approximately at frequencies ν (fundamental), 2ν (first harmonic), 3ν (second harmonic).

Noticed

If the normal vibrational frequency of a functional group coincides in frequency with a weak harmonic peak of a neighboring bond, the absorption peak will be observed as a Fermi doublet (combination bands). In the case of aliphatic aldehydes, the stretching vibration of the C - H group occurs at 2720 cm $^{-1}$, which coincides with the harmonic of the C - H deformation transition at 1380 cm $^{-1}$. This Fermi coupling also explains the observation of two peaks near 2300 cm $^{-1}$ in the spectrum of CO_2 .

This leads to the conclusion that symmetric vibrations are generally weaker in intensity and wavenumber than asymmetric vibrations, since the former are not accompanied by a change in the dipole moment.

10. Experimental aspect

There are several methods for recording the absorption spectrum of a substance. Optical spectrometers have the following features in common

10.1. Apparatus

The study of IR absorption requires the use of a device called **an IR spectrophotometer** . **Fig. 9** shows the schematic diagram of a Fourier transform IR absorption spectrophotometer (there are so-called scanning IR spectrometers: old model). It consists of an IR light source, *an interferometer (Michelson),* a sampling compartment, a detector and a recording system.

Fig.9: Infrared spectroscopy

Most IR spectrometers can be categorized into two classes: dispersive and Fourier Transform instruments.

(a) The basic design of a dispersive single beam instrument includes a source of infrared radiation, a monochromator, and the detector (**Fig.10**).

After interacting with the sample (or the blank), infrared radiation is dispersed by a monochromator into its individual frequency components and information on which frequencies were absorbed can be obtained using a photodiode array detector.

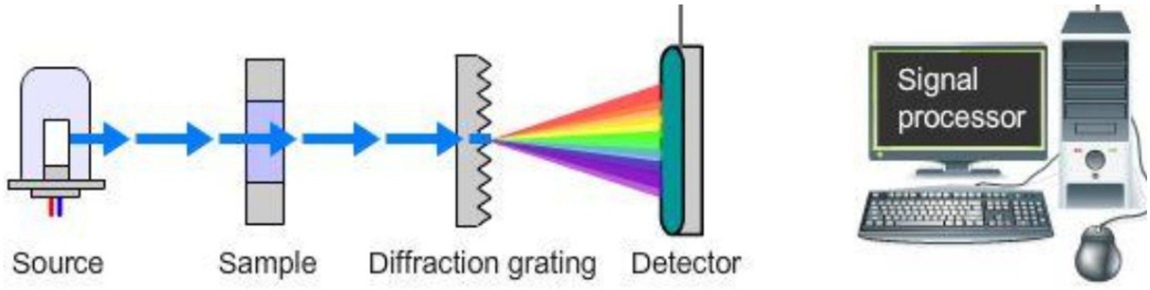


Fig.10: Basic concept of a single beam IR instrument

Sources and detectors for infrared radiation have limited stability; with light intensity and detector sensitivity changing over time, or with fluctuations in temperature etc. The blank (reference or background) and sample measurements should be made one after the other to ensure they are made under the same analytical conditions. This limitation is minimized by the use of double beam instruments which are capable of measuring the sample and reference simultaneously.

(b) Double beam instruments use 'choppers' to control the path of the radiation, alternating between the sample and the reference (**Fig.11**). These instruments use the known speed of rotation of the beam chopper to compare and resolve the information reaching the detector.

The use of an opaque surface provides the means for adjusting the 0% transmittance response of the detector.

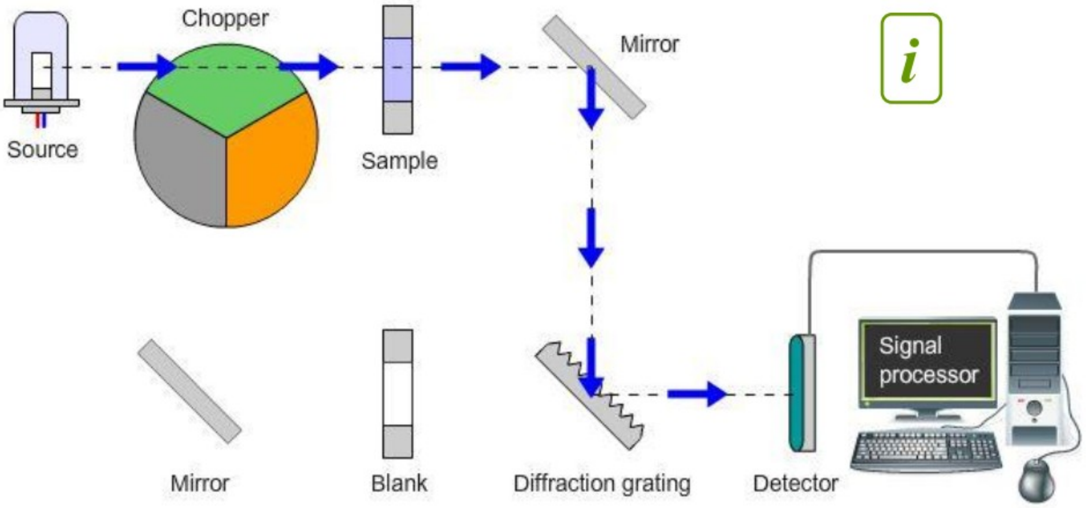


Fig.11: Double beam IR instrument

Finally, it is easier to correct for absorption of infrared radiation by carbon dioxide and water (present within the instrument background) with double beam instruments than with their single beam counterparts.

(c) FTIR Instruments

FTIR stands for Fourier Transform Infrared. FTIR spectrometers consist of an IR source, interferometer, sample cell or chamber, detector and a laser. A schematic of an FTIR instrument is shown below (Fig. 11).

- **IR source:**

IR radiation is emitted from a glowing black body source. IR radiation passes through an aperture which controls the amount of radiation that reaches the sample, and therefore, the detector.

Common IR sources are:

- Silicon carbide rods which are resistively heated and commonly known as a Globar. An electric current is passed through the rod which becomes very hot (1300 K) and emits large amounts of IR radiation. Previously, cooling with water was required to avoid damaging electrical components; however, advances in metal alloys have led to the production of Globars that do not require cooling by water.
- Nichrome and Kanthanl wire coils were once popular IR sources and did not require cooling as they ran at lower temperatures than Globars, however, this also resulted in lower amounts of IR radiation being emitted.
- Nernst Glowers are manufactured from a mixture of refractory oxides and are capable of reaching hotter temperatures than a Globar; however, they are not capable of producing IR radiation above 2000 cm^{-1}.

- **Interferometer**

The first interferometer was invented by Albert Abraham Michelson, who received a Nobel Prize for his work in 1907. Without this essential piece of optical equipment the modern day FTIR system would not exist. The interferometer consists of a beam splitter, a fixed mirror, and a moving mirror.

- **Beam Splitter**

The beam splitter is made of a special material which transmits half of the incident radiation and reflects the other half. IR radiation from the source strikes the beam splitter and is separated into two beams. One beam is transmitted through the beam splitter to the fixed mirror while the other beam is reflected from the beam splitter to the moving mirror. Both mirrors reflect the radiation back to the beam splitter where the two beams interfere to produce an interferogram.

- M**oving Mirror**

The moving mirror is a flat highly reflective surface mounted on air bearings that allow for high speed movement of the mirror (movements are made once every millisecond). The moving mirror only moves a few millimeters away from the beam splitter.

- **Fixed Mirror**

The fixed mirror is a flat highly reflective surface.

- **Laser** Many instruments employ a Helium-Neon laser as an internal wavelength calibration standard. It is imperative that the position of the moving mirror is known at any given moment. The moving mirror moves back and forth at a precise constant velocity that is timed using a very accurate laser wavelength. The intensity of the laser beam is measured at two points in the interferometer. As the mirror moves the intensity at these two points will rise and fall due to the enhancement and cancellation of the HeNe beam paths, producing a sine wave of intensity vs. mirror position. The number of “fringes” in the sine wave allows the instrument to know exactly how far the mirror has moved, and the relative phase of the sine wave tells the instrument in which direction the mirror is moving.

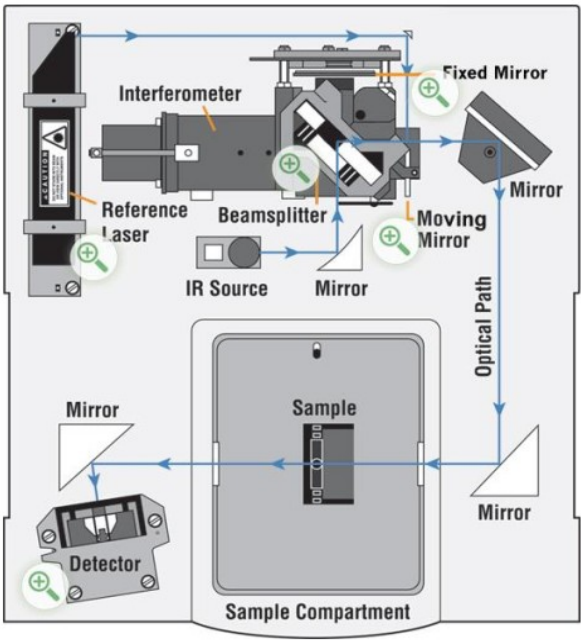


Fig.12: Operational Schematic of a Thermo Nicolet: TTIR instrument

- **Detector** There are two classes of infrared detectors; thermal and photonic detectors. Thermal detectors use the IR radiation as heat; whereas, quantum mechanical (photonic) detectors use the IR radiation as light which results in a more sensitive detector.

- **Thermal detectors**: detect changes in temperature of an absorbing material (lithium tantalate (LiTaO3), lead selenide (PbSe), germanium etc.). Many temperature dependent phenomena can be followed to measure the effects of the incident IR radiation. Bolometers and microbolometers use changes in resistance, while thermocouple and thermopiles use the thermoelectric effect. Golay cells monitor thermal expansion.

- **Photonic Detector:** exhibit faster response times and higher sensitivity in comparison to their thermal counterparts, therefore, they are much more prolific in FTIR instruments. The materials used in these detectors are semiconductors with narrow band gaps. The incident IR radiation causes electronic excitations between the ground and first excited states, which in photoconductive detectors result in a change in resistivity which is monitored.

10.2 FTIR Operation

Prior to the development of FTIR spectrometry, the limitation within IR was the slow scanning process. FTIR allows for all the infrared frequencies to be scanned simultaneously, allowing for data to be collected in a matter of seconds rather than several minutes. This is achieved through the use of an optical device called an interferometer which produces a signal which is made up of all of the infrared frequencies.

Most interferometers consist of a beam splitter which splits the incident infrared beam into two separate optical beams. One beam is reflected from a fixed mirror, while the other beam is reflected from a mirror that is constantly moving in the instrument. The moving mirror typically moves by only a few millimeters from the beam splitter (**Fig.12**).

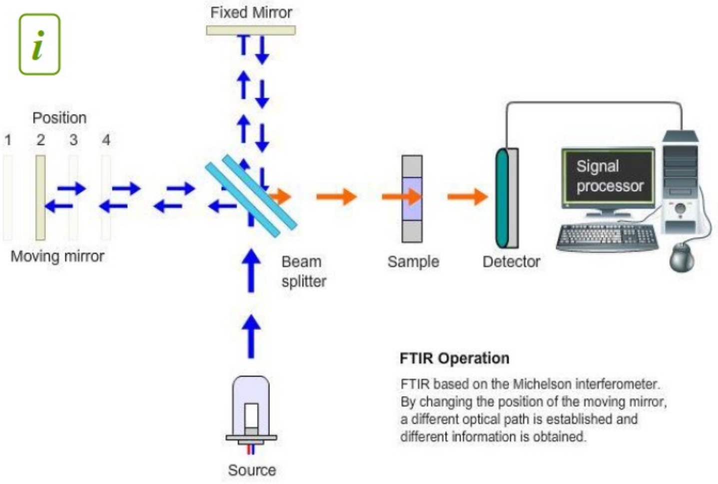


Fig.12: FTIR based on the Michelson interferometer. By changing the position of the moving mirror, a different optical path is established and different information is obtained.

The two beams are reflected from their respective mirrors and recombine at the beam splitter. The path length of the beam that is reflected from the fixed mirror remains constant, while the path length of the beam that is reflected from the moving mirror is constantly changing as the mirror moves. The signal that exits the interferometer is the result of these two beams interfering with each other, and is called an interferogram (**Fig.13**).

Fig.13: Interferogram

The interferogram is unique in that every data point, which is a function of the moving mirror position, has information about every infrared frequency emitted from the source. This allows for all frequencies to be measured simultaneously.

The interferogram is converted to a more familiar IR spectrum (wavenumber vs. % transmittance) using the well-known mathematical technique called Fourier transformation. The transformation of the interferogram is carried out by the instrument software.

IR spectra are presented on a relative scale (%T), therefore, a background spectrum must be measured. A background spectrum is taken with no sample in the beam and is then subtracted from the sample spectrum to remove artifacts generated by the instrument or air (i.e. water, carbon dioxide, etc.).

10.3 FTIR Advantages

FTIR instruments have several advantages over dispersive IR instruments including:

- **Speed:** All IR frequencies are measured simultaneously, resulting in measurements being taken in seconds rather than minutes. This is often referred to as the Felgett Advantage.

- **Sensitivity:** The detectors utilized in FTIR instruments are highly sensitive which results in lower signal to noise ratios. This is known as the Jacquinot Advantage.
- **Simplicity:** The only moving part in an FTIR instrument is the mirror in the interferometer; therefore, there is very little need for mechanical maintenance.

10.4 Internal calibration

The internal laser is used to self-calibrate the moving mirror in the FTIR instrument negating any need for timely or complicated external calibration. This is denoted as the Connes Advantage

11. Sample Preparation

Proper sample preparation is required to obtain meaningful spectra with sharp peaks, which have good intensity and resolution. Ideally the largest peaks should be attributable to the compound being analyzed opposed to the background or sample matrix (water, CO_2, solvent etc.) and should ideally have an intensity of 2-5 %T for the strongest peaks in the spectrum (**Fig.14**). A transmission of 5 % is equivalent to an absorbance (A) = 1.3 (i.e. the amount of light that is absorbed by the sample), which is the upper detection limit for most detectors.

$$A = 2 - \mathrm{Log}(\%T)$$

The equation above is worth remembering as it allows the absorbance of a sample to be calculated from the percentage transmittance data.

Peaks that are of higher intensity will be cut off and the sample will need to be prepared again.

Compounds can be analyzed in the vapor phase, as pure liquids, in solution, and as solids.

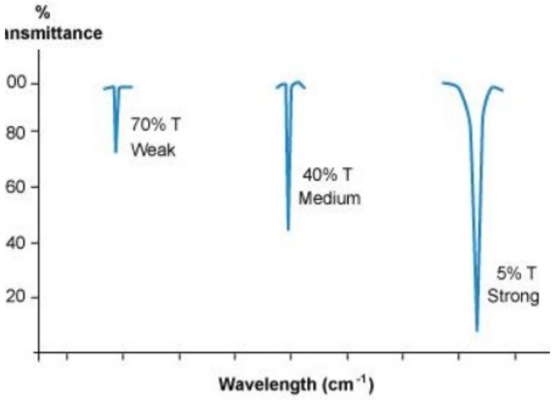


Fig. 14: Classifications of IR signals

11.1 As a Liquid

A drop of the liquid is squeezed between two sodium chloride (NaCl) plates, which are transparent in the 4000-625 cm^{-1} region (**Fig.15**).

The plates are then placed in a holder and a spectrum is taken.

If the peaks in the spectrum are too intense the liquid can be wiped from one plate, then the spectrum taken again.

Fig.15: Sodium chloride (NaCl) plates in various conditions

NaCl plates are very fragile and sensitive to water. Samples should never be dissolved in water and placed on a NaCl plate as it will fog up or dissolve. The plates should be held by the edges to avoid moisture from fingers damaging them. After a sample has been run, ethanol can be used to clean the plates. Moisture in the air can also damage NaCl plates; therefore, they should be stored in a desiccator. Cloudy or damaged plates (pitted, fingerprints etc.) will result in **poor spectra** with broad bands and spectra with less than optimum transmission (**Fig.16**). Cloudy plates can be restored by polishing.

Liquids can also be placed directly on an Attenuated Total Reflectance (ATR) plate which will be discussed later

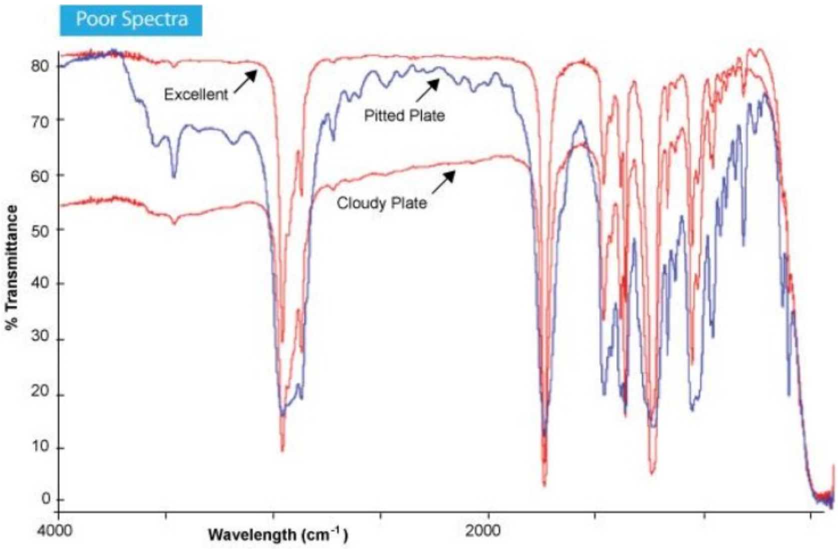


Fig.16: representative spectra obtained with sodium chloride plates in various conditions

11.2 As a Solution

Samples can be dissolved in an appropriate solvent to give a solution. The spectrum is then taken by placing a drop on a NaCl plate or by using a sodium chloride solution cell (**Fig.17**). Solvents should be free of water to avoid damaging the sodium chloride cell surfaces. A reference spectrum of the blank solvent should be obtained and subtracted from the sample spectrum.

When solvents absorb ~80**%** of the incident light, spectra cannot be obtained because insufficient light will be transmitted and detected. The regions in which common solvents absorb too strongly to give meaningful spectral information from a sample are shown in the table below.

If aqueous solvents must be used for solubility, special calcium fluoride cells can be used.

Fig.17: Sodium chloride solution cell

11.3 As a Nujol Mull

IR spectra of solid samples can be obtained using a Nujol mull. Nujol is a mineral oil which itself has an IR spectrum (**Fig.18**).

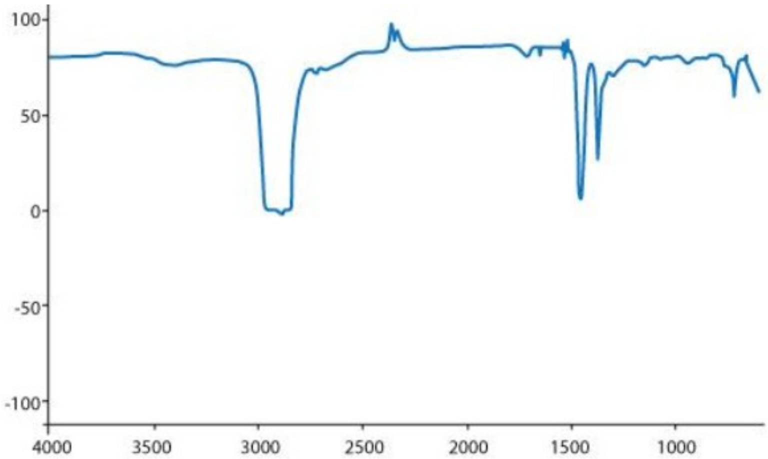


Fig. 18 : IR spectrum of pure Nujol

A small amount of sample is ground using a small agate mortar and pestle and a drop of Nujol (**Fig.19**). The mull is then pressed between two NaCl plates and the spectrum obtained. The mull should appear transparent and free of bubbles when properly prepared. If the peaks in the spectrum are too strong one plate can be wiped clean and the spectrum re-run.

Fig.19: Agte mortar and pestle

11.4 As a KBr Disc

A solid sample can be ground with 10-100 times its mass of pure potassium bromide (KBr). Solid samples should be finely ground before adding the KBr. This is then pressed into a disc using a special mold and a hydraulic press (**Fig.20**). The use of KBr eliminates any bands that may obscure analyte signals when using a Nujol mull. A band at 3450 cm^{-1} will often be present and is attributable to the OH group from traces of water. Water can be minimized by drying the KBr in an oven. Excessive grinding of the hygroscopic KBr can increase the water content.

Solid state spectra can differ greatly from solution state spectra due to intermolecular interactions between functional groups, i.e. hydrogen bonding. Conversely, solid state spectra will often exhibit a greater number of resolved bands which can aid in compound identification.

Table 6: Material used for obtaining solid state IR spectra. Note these materials can also be used to produce plates and solution cells for obtaining spectra with liquids and mulls

Material	Wavelength Range (µm)	Wave number Range (cm^{-1})	Refractive Index at 2 µm
NaCl	0.25-17	40,000-590	1.52
KBr	0.25-25	40,000-400	1.53
KCl	0.30-20	33,000-500	1.5

Fig. 20: KBr Press

11.5 Attenuated Total Reflectance (ATR)

As has been discussed previously, IR spectra can be obtained from samples as liquids, solids, or mulls; however, the primary drawback is the sample preparation that is required to obtain good quality spectra. IR instruments which utilize an attenuated total reflectance (ATR) stage negate the necessity for complex and timely sample preparation resulting in good quality, reproducible spectra.

With traditional means of IR spectroscopy the IR radiation is passed through the sample and the resulting radiation which is transmitted is measured. Attenuated total reflectance measure the changes which occur in a totally internally reflected IR beam when it is in contact with a sample (**Fig.21**).

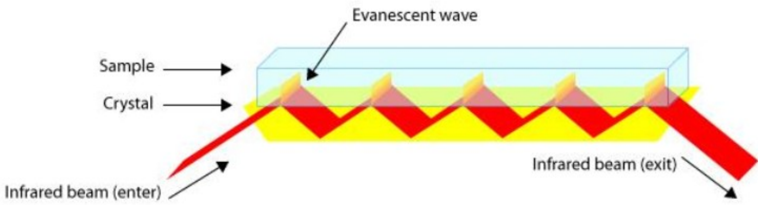


Fig.21: Evanescent wave

The infrared beam enters the crystal which is made of an optically dense material (i.e. it has a high refractive index) at a particular angle of incidence, the IR beam is internally reflected (usually between five and ten times), this internal reflectance results in the production of an evanescent wave which can extend beyond the crystal surface and into the sample itself. The wave will usually penetrate into the sample with a depth of 0.5-2 µm. The depth to which the wave penetrates is dependent on the angle of the incident IR beam and the refractive index of the crystal material and sample itself.

When a samples absorbs the infrared radiation there is a change in the evanescent wave; in other words the wave is attenuated. The attenuated energy from each of the evanescent waves is then transferred back to the IR beam which exits the crystal and is measured by the detector to produce an IR spectrum.

11.6 Typical ATR Crystal Materials

In ATR instruments the crystal is an optically dense material which has a refractive index that is greater than the sample. Common ATR crystal materials are listed in Table 4. The most common are zinc selenide (ZnSe) and Germanium (Ge).

Zinc selenide is applicable to the analysis of liquids and non-abrasive pastes. It has a working pH range of 5 – 9. Germanium is more robust with a working pH range of 1 – 14 and can be used to analyze weak acids and alkalis. For a greater initial cost, instruments which utilize diamond as the ATR crystal material exhibit greater durability and robustness, with the crystal having to be replaced less in comparison to ZnSe and Ge.

Materials such as ZeSe and Ge can scratch easily; therefore, care must be taken when cleaning the

crystal surface. It is recommended that crystal surfaces are cleaned with lint free tissues soaked with solvents such as water, methanol or isopropanol.

Table 7: Attenuated total reflectance (ATR) crystal materials.

Material	Wavenumber Range (cm^{-1})	Refractive Index
ZnSe	20,000-500	2.43
ZnS	22,000-750	2.25
Ge	5,000-600	4.01
Si	10,000-100	3.42
Diamond	45,000-10	2.40

11.7 ATR Instrument

In traditional ATR instruments the sample was clamped against the vertical face of the crystal. This design has now been replaced by horizontal ATR stages where the upper surface of the crystal is exposed (**Fig.22**). ATR accessory kits can be purchased which can be used to modify existing IR instruments.

Similarly to FT-IR instruments a background spectrum must be collected; this is taken from the clean ATR crystal. The background spectrum which is obtained can be a useful indication of the cleanliness of the ATR crystal; a line at 100% T should be obtained with no spectral features. In order for total internal reflectance to occur there must be good contact between the sample and crystal surface. Liquid samples can be placed directly onto the ATR crystal; the whole crystal must be covered. Similarly pastes or other viscous substances can be spread onto the crystal. In the case of solids, these are more readily analyzed on single reflection ATR instruments which are often made of diamond. High quality spectra can be obtained directly from powder samples placed on the ATR crystal. The amount of sample should entirely cover the crystal and does not need to be more than a few millimeters thick. In order to ensure that there is good contact with the crystal surface the instrument pressure arm is positioned over the sample and tightened; it may be necessary to apply greater pressure when analyzing high density polymers or coatings on metal surfaces, however, the user manual should always be consulted for optimum operating parameters.

The major advantages of ATR instruments are the lack of sample preparation, the ability to obtain high quality reproducible spectra, and due to their ease of use, the variation between users is minimized.

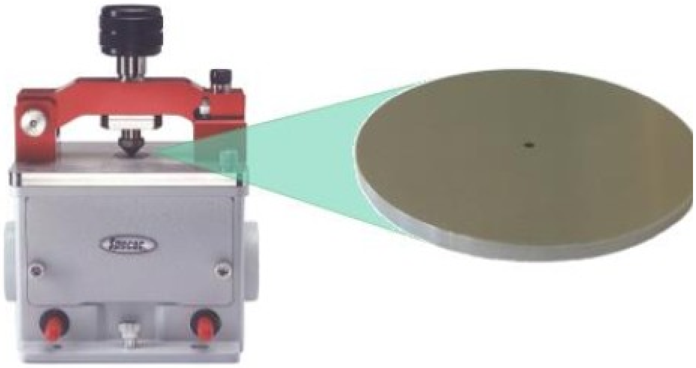


Fig.22: ATR Instrument

12. Applications of IR Spectroscopy

IR spectroscopy has primarily been used for structural elucidation and identification of unknowns (by comparison with a spectrum of a standard).

Modern advances have seen the development of 2D IR techniques which have been applied to a myriad of different applications including isotope labeling studies of biological species, the investigation of proteins, peptides, and hydrogen bond dynamics, and also the study of nanocrystalline thin films.

Other areas of note where IR spectroscopy is being utilized are in stem cell studies, materials science, catalysis, and reaction kinetics. Which demonstrates the applicability and flexibility of this analytical technique?

Sampling

The samples to be analyzed can be in solid, liquid or gaseous state, using appropriate techniques and specific sample holders.

a) Gas: Gases are measured in low-pressure long-path cells. The most common path length is 10 cm, although for specific purposes paths of several meters can be used! The gases are introduced into a tank of larger volume than that used for liquids.

b) Solids: A solid will be ground in the presence of potassium bromide, then compressed into a pellet by a hydraulic press. Another technique consists of dispersing the solid in a paraffin (nujol) and depositing the suspension on a sodium chloride pellet.

b) Liquids: A liquid will be deposited between two KBr or NaCl pellets, so as to obtain a thin film (caution: they must not be washed with water!).

Fig. 23: Pure KBr pellets

Solvent: It should be noted that all solvents have infrared absorption bands and that it is necessary to compensate these bands with a reference. Since compensation is not always perfect, the solvents used for solutions are chosen to avoid absorption bands in the particularly interesting areas of the spectrum. The most commonly used are carbon tetrachloride, chloroform and carbon disulfide. There is no solvent that is transparent across the entire IR range. These preparation steps generate reproducibility problems and greatly increase analysis time.

Cells: It excites several types of IR cells depending on the required range: NaCl, KBr, CsI, polyethylene…

10. Procedure and presentation of spectra

The sample to be analyzed is placed in a tank and subjected to IR radiation. The instrument then compares the two beams of respective intensities I t and I 0 and plots the IR spectrum A=f(λ). An infrared spectrum is a graph representing the position of the bands in the form of wavenumber (cm-1) on the abscissa and the intensity of these bands (the percentage of transmission) on the ordinate. Most commercial instruments present a spectrum with the wavenumber decreasing from left to right. The band intensities can be expressed either in transmittance (T) or in absorbance (A).

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