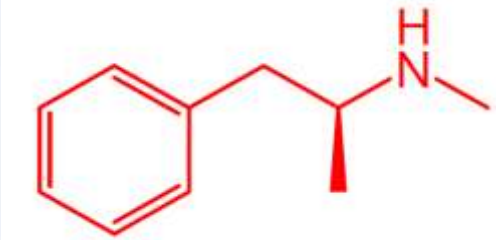
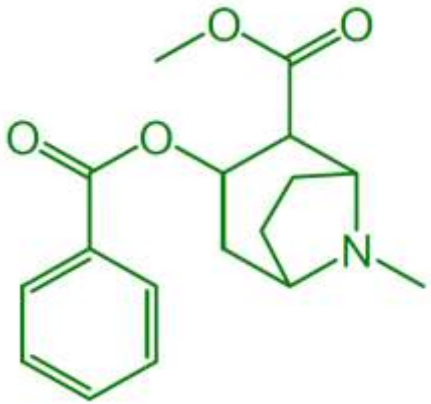
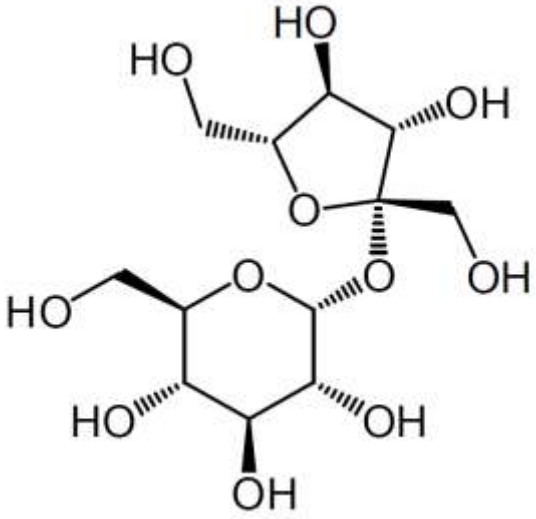
Analytical chemistry

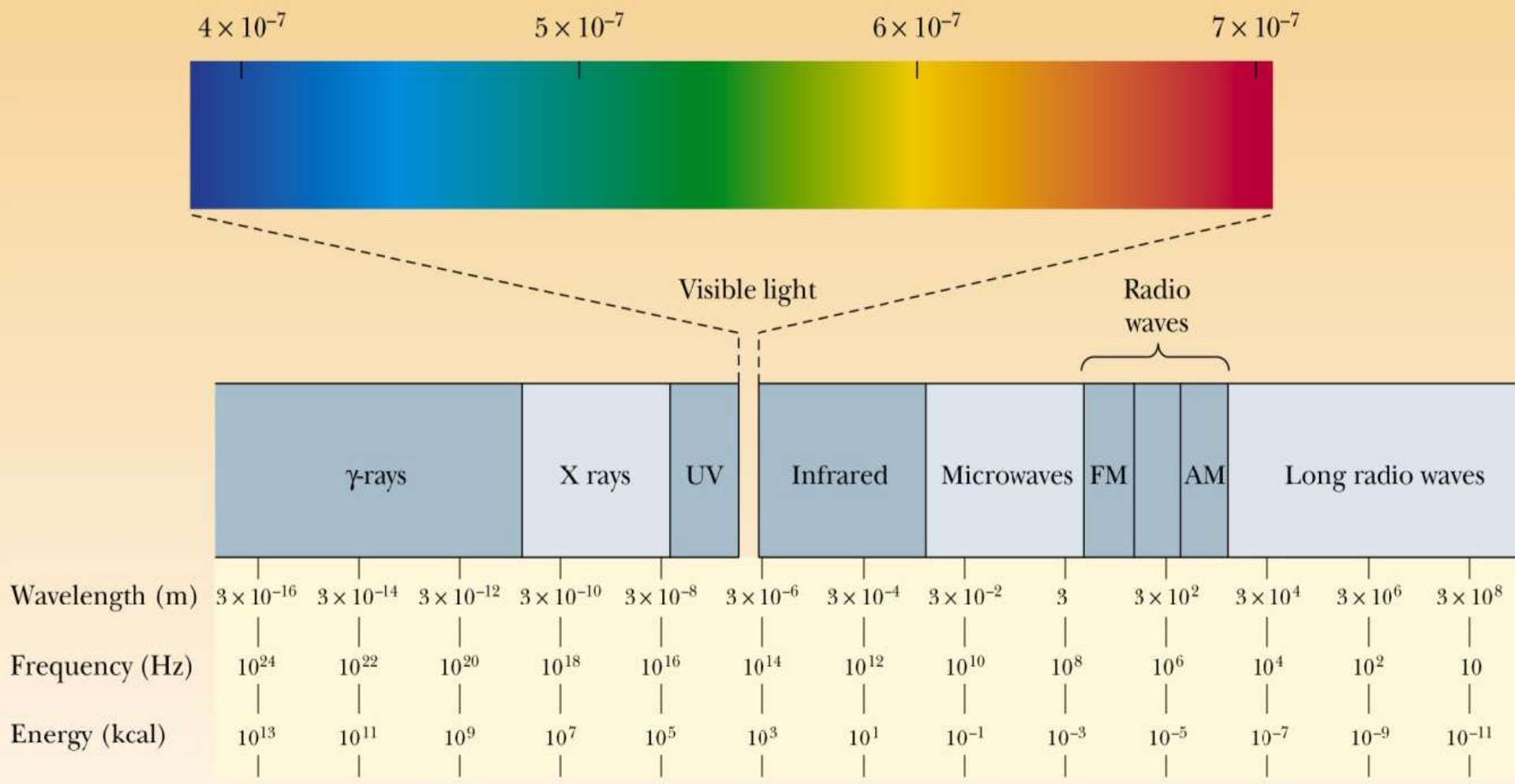
Lecture №27

Absorption spectroscopy
Part II









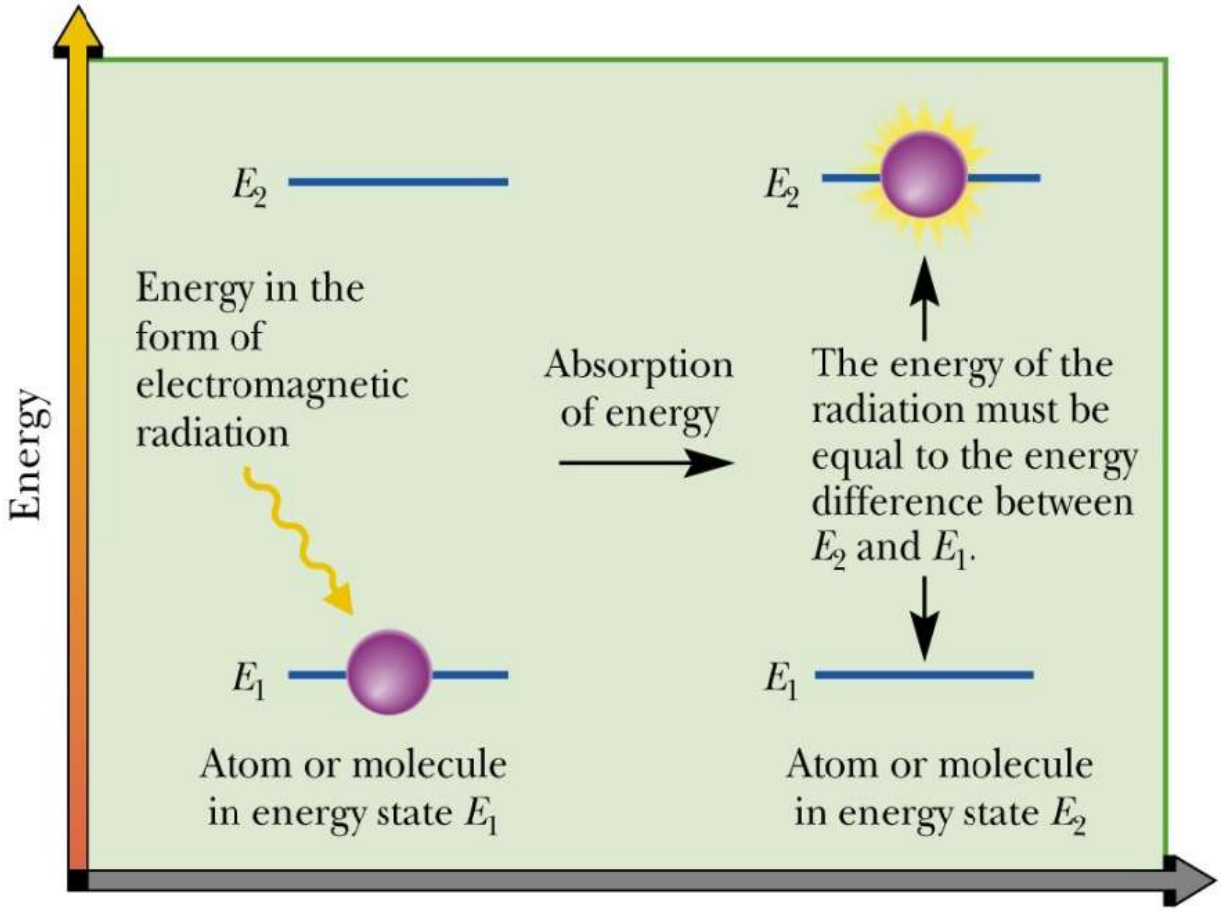
Not all molecules can absorb in the infrared region. The molecule must undergo a change in **dipole moment *(polarity)*** in order to absorb infrared radiation.

The alternating electrical field of the radiation (electromagnetic radiation consists of an oscillating electrical field and an oscillating magnetic field, perpendicular to each other) interacts with fluctuations in the dipole moment of the molecule. If the frequency of the radiation matches the vibrational frequency of the molecule, then radiation will be absorbed, causing a change in the amplitude of molecular vibration.

• **IR light** corresponds to an energy of about 5 – 50 kJ mol^{-1}. This compares very well to the energy differences of various conformations, suggesting that the absorption of IR results in conformational changes.

• However, the energy of IR that is absorbed must correspond to exactly that of the conformational change. This is because energy is quantized; there are discrete energy levels between ground and excited states.

• A molecule will absorb light of wavelength λ_1 only if λ_1 has an energy that is equal to ΔE.



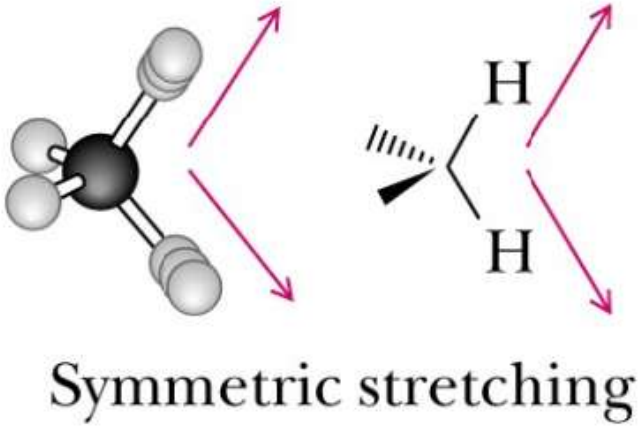
In fact, **infrared absorption spectra** are due to changes in vibrational energy accompanied by changes in rotational energy. Broadly speaking, the range in the electromagnetic spectrum that extends from 0.8 to 200 μ is referred to as the infrared region. In usual practice, however, either the wavelength (μ) or the wave number (cm^{-1}) is employed to measure the position of a given infrared absorption. More precisely, the infrared regions may be categorized into three distinct zones based on their respective wave numbers and wavelengths as stated below:

Region	Wave Number (cm^{-1})	Wavelength (μ)
Ordinary Infrared	4000-667	2.5-15
Near Infrared	12,500-4,000	0.8-2.5
Far Infrared	667-50	15-200

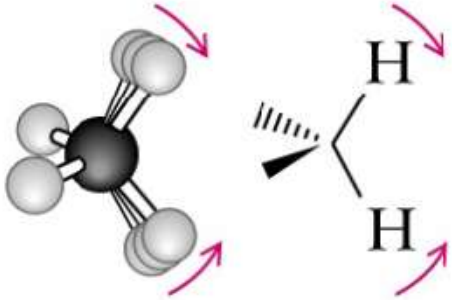
Absorption in the 6- to 15-*μm region is very dependent on the* molecular environment, and this is called the **fingerprint region.** A molecule can be identified by a comparison of its unique absorption in this region with cataloged known spectra.

Infrared radiation generally is not energetic enough to cause electronic transitions, but it can induce transitions in the vibrational and rotational states associated with the ground electronic state of the molecule.

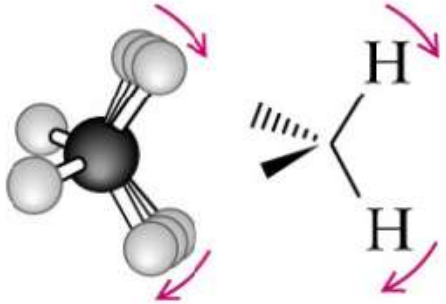
• Why do molecules absorb IR? At room temp, atoms within molecules are constantly vibrating about their equilibrium positions at specific frequencies.



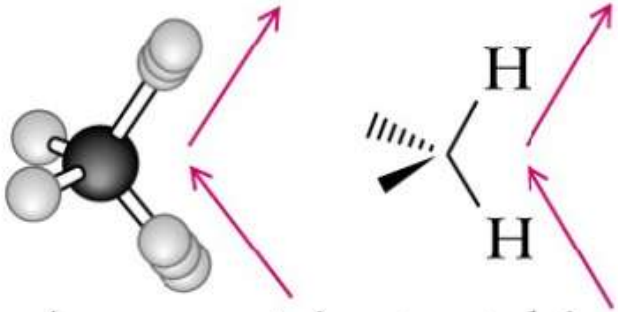
Symmetric stretching



Scissoring

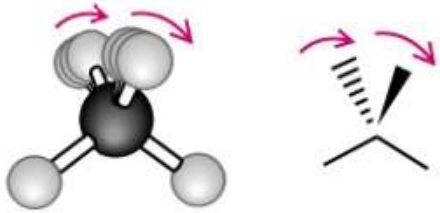


Rocking

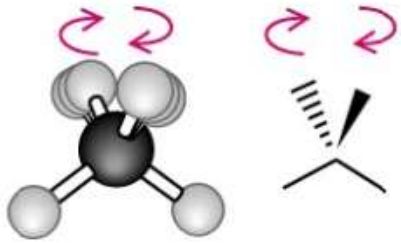


Asymmetric stretching

Stretching vibrations



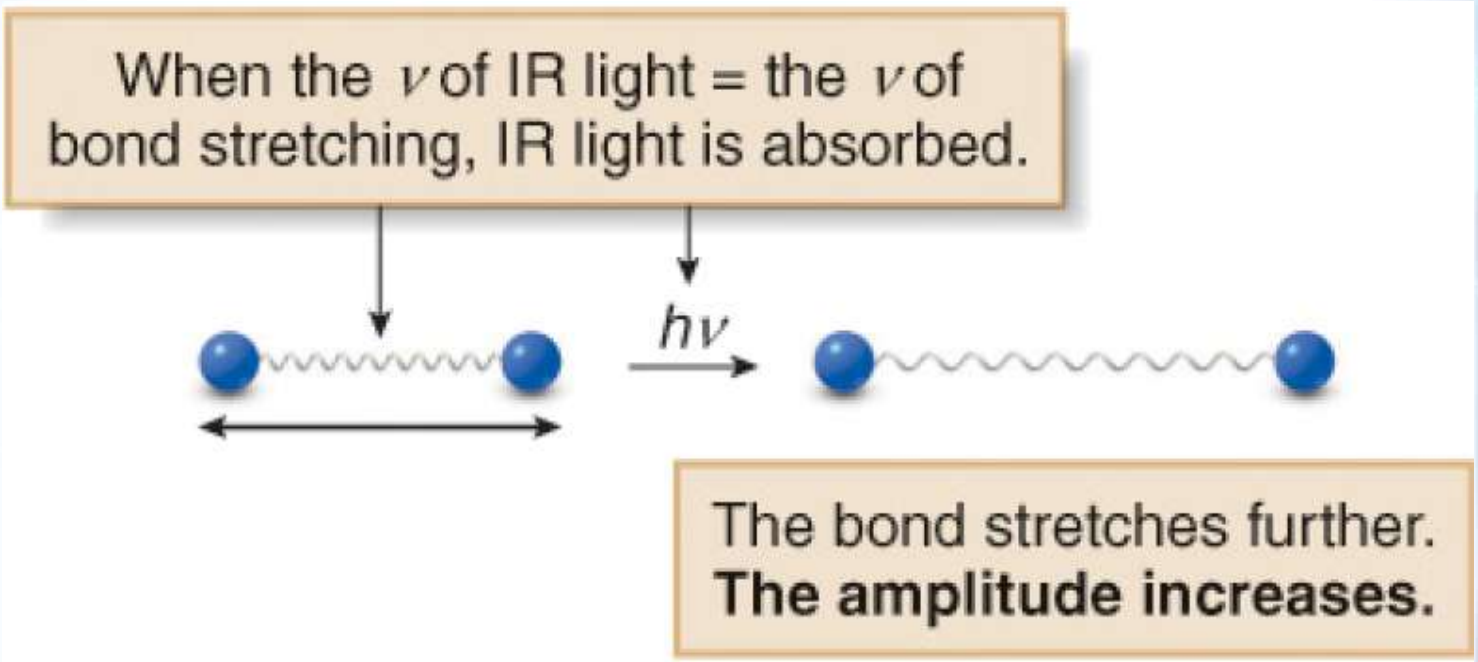
Wagging



Twisting

Bending vibrations

• If the frequency of the IR light matches the frequency of the vibration (stretching or bending), the bond will absorb the energy and vibrate to a greater extent.



• An important concept about IR spectroscopy is that different types of bonds, hence different functional groups, have different IR absorption frequencies.

• Thus, by measuring the different wavelengths that are absorbed by a molecule, we can learn about its structure. An infrared spectrometer measures IR absorption.

INFORMATION OBTAINED FROM IR SPECTRA

• IR is most useful in providing information about the presence or absence of specific **functional groups.**

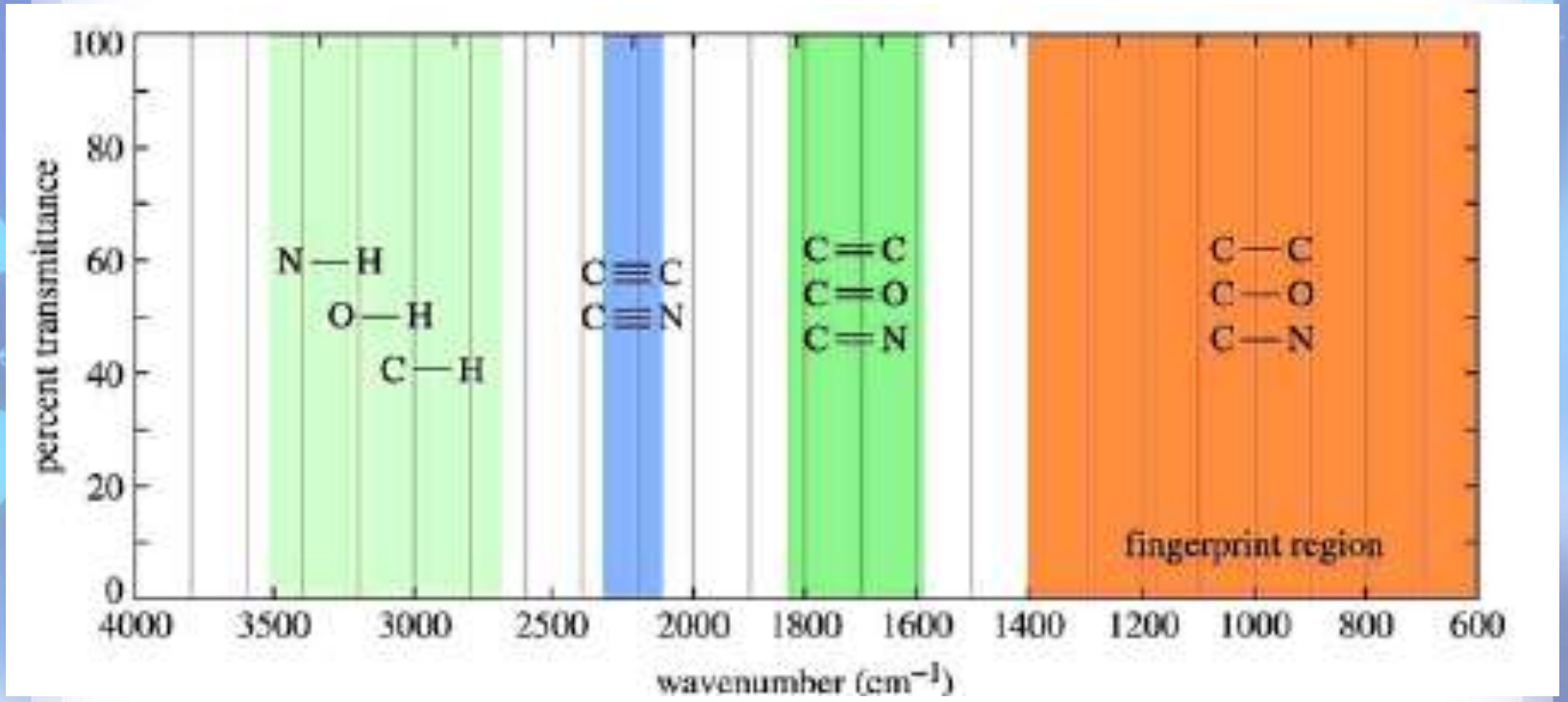
• IR can provide a **molecular fingerprint that** can be used when comparing samples. If two pure samples display the same IR spectrum it can be argued that they are the same compound.

• IR does not provide detailed information or proof of molecular formula or structure. It provides information on molecular fragments, specifically functional groups.

• Therefore it is very limited in scope, and must be used in conjunction with other techniques to provide a more complete picture of the molecular structure.

IR ABSORPTION RANGE

The typical IR absorption range for covalent bonds is **600 - 4000 cm^{-1}.** For example a sharp band around 2200-2400 cm^{-1} would indicate the possible presence of a C-N or a C-C triple bond.



THE FINGERPRINT REGION

Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the **600 - 1400 cm^{-1} range** is called **the fingerprint region.** This is normally a complex area showing many bands, frequently overlapping each other.

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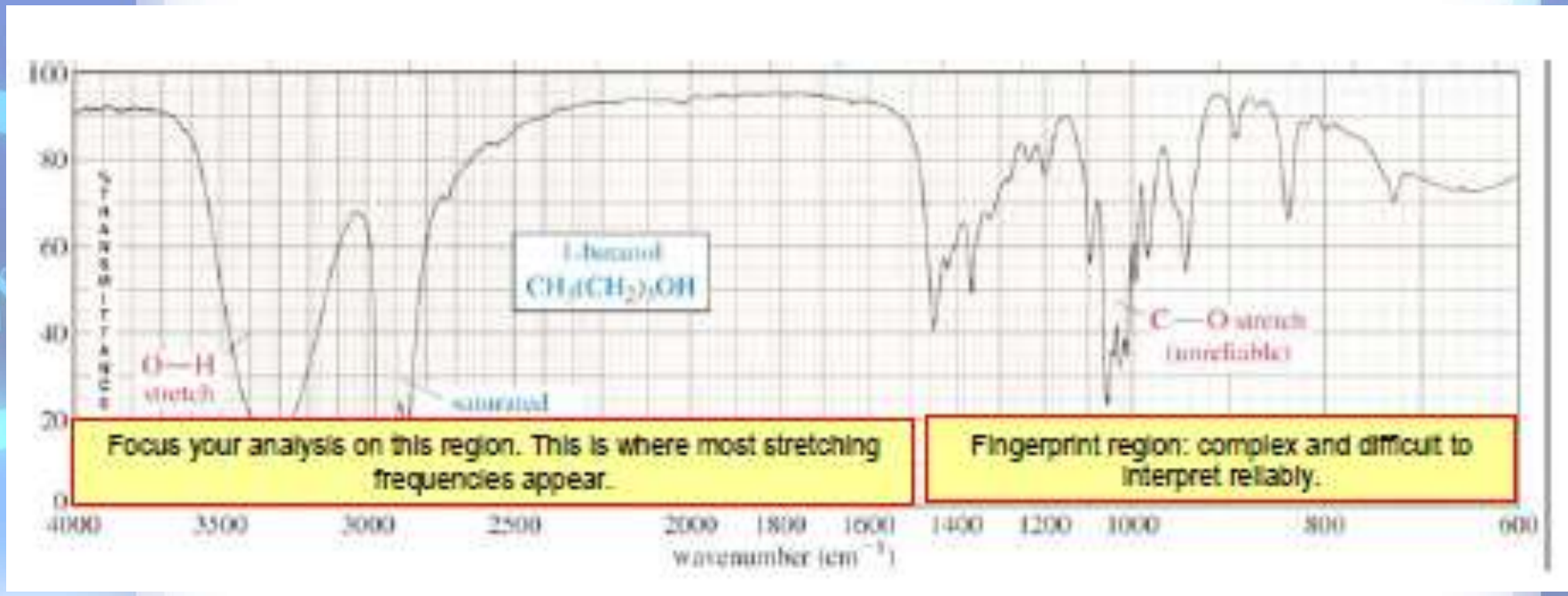
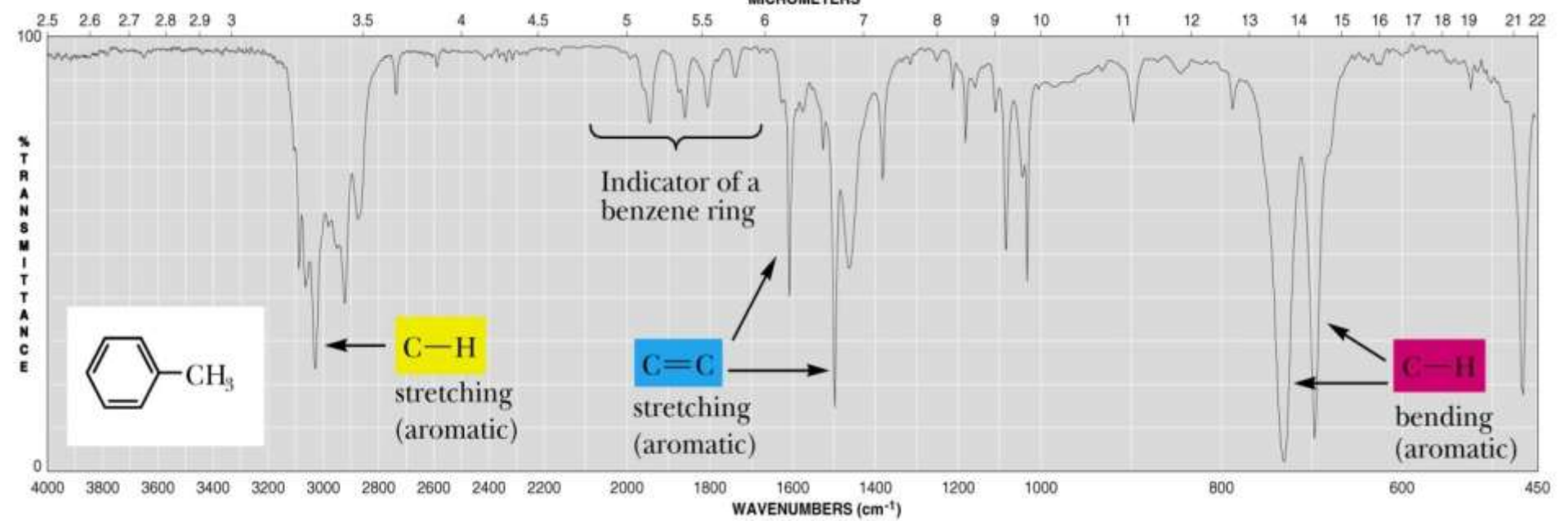
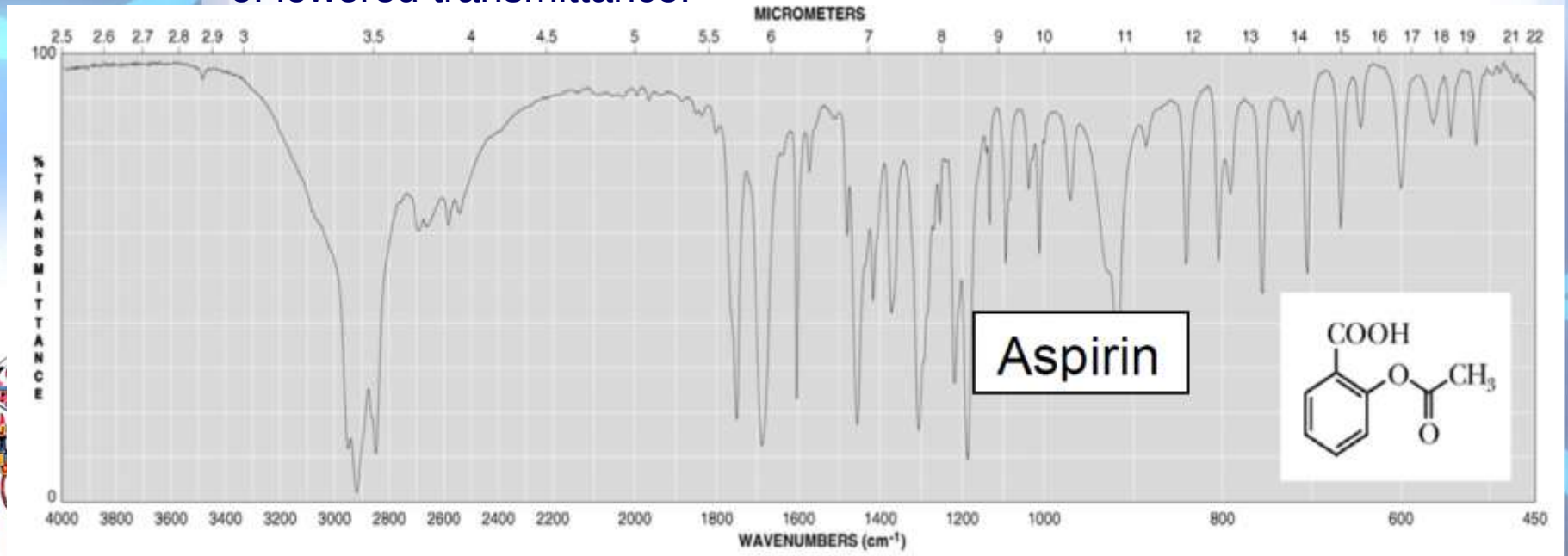


This complexity limits its use to that of a fingerprint, and should be ignored by beginners when analyzing the spectrum. As a student, you should focus your analysis on the rest of the spectrum, that is the region to the left of 1400 cm^{-1}.

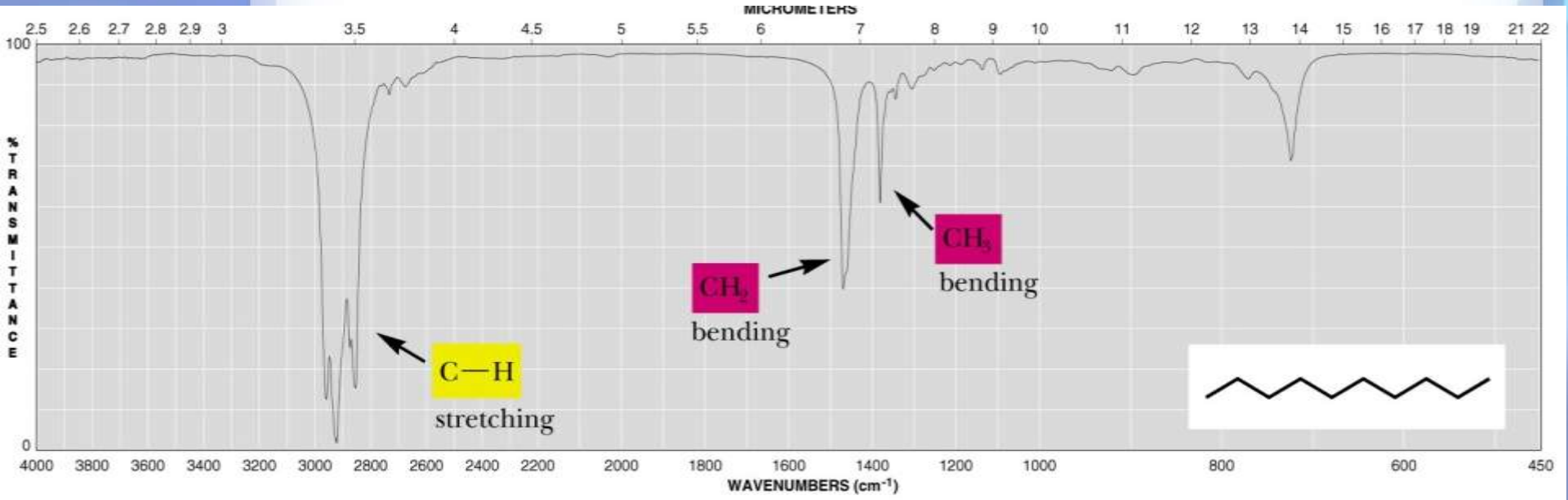


The instrument plots a chart % transmittance plotted against wavenumber (reciprocal of λ when in cm). Absorption appears as peaks of lowered transmittance.

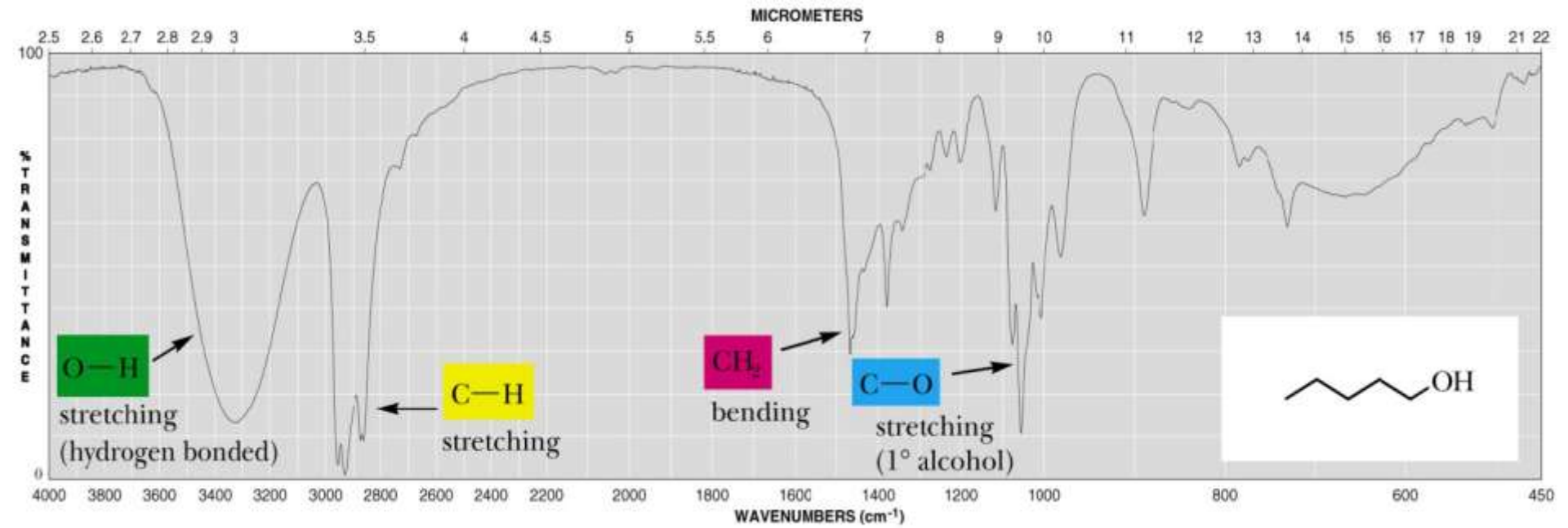


Functional groups have characteristic absorption peaks. These peaks (dips in the spectrum) are identified by their frequency (energy) in wavenumbers and intensity of the absorption (weak, medium, strong).

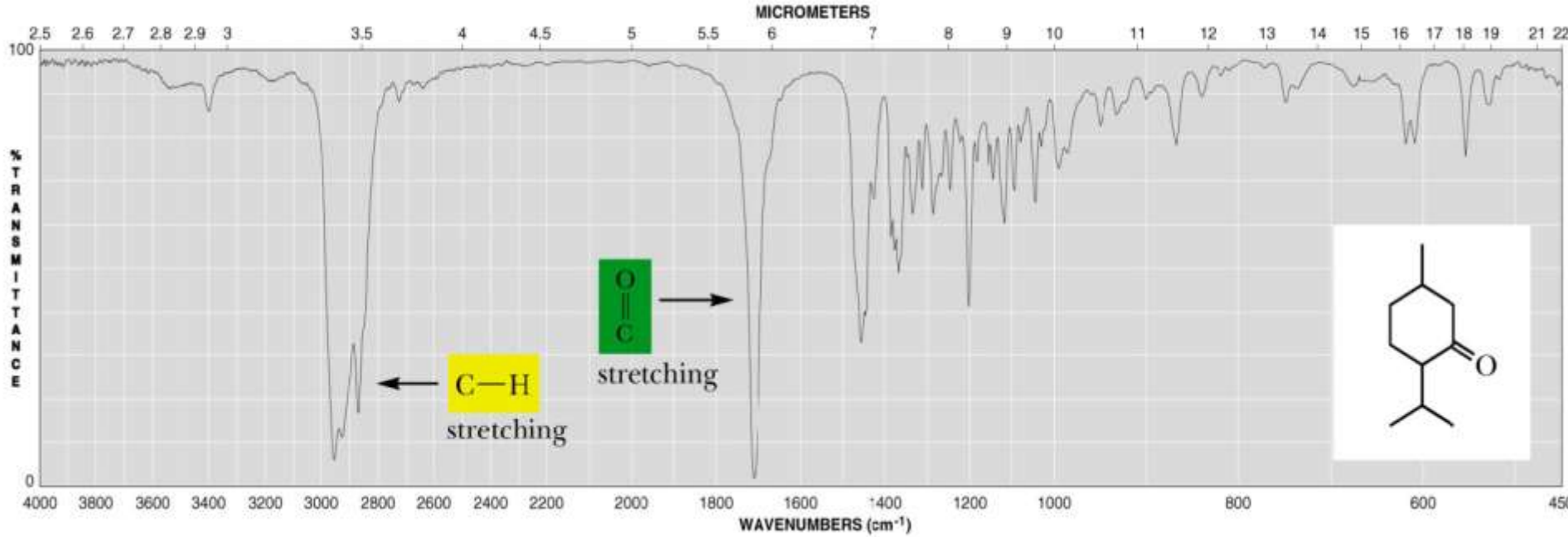
• Alkanes show CH signals from saturated carbons, but they're not very useful diagnostically, because most organic compounds contain alkyl groups.



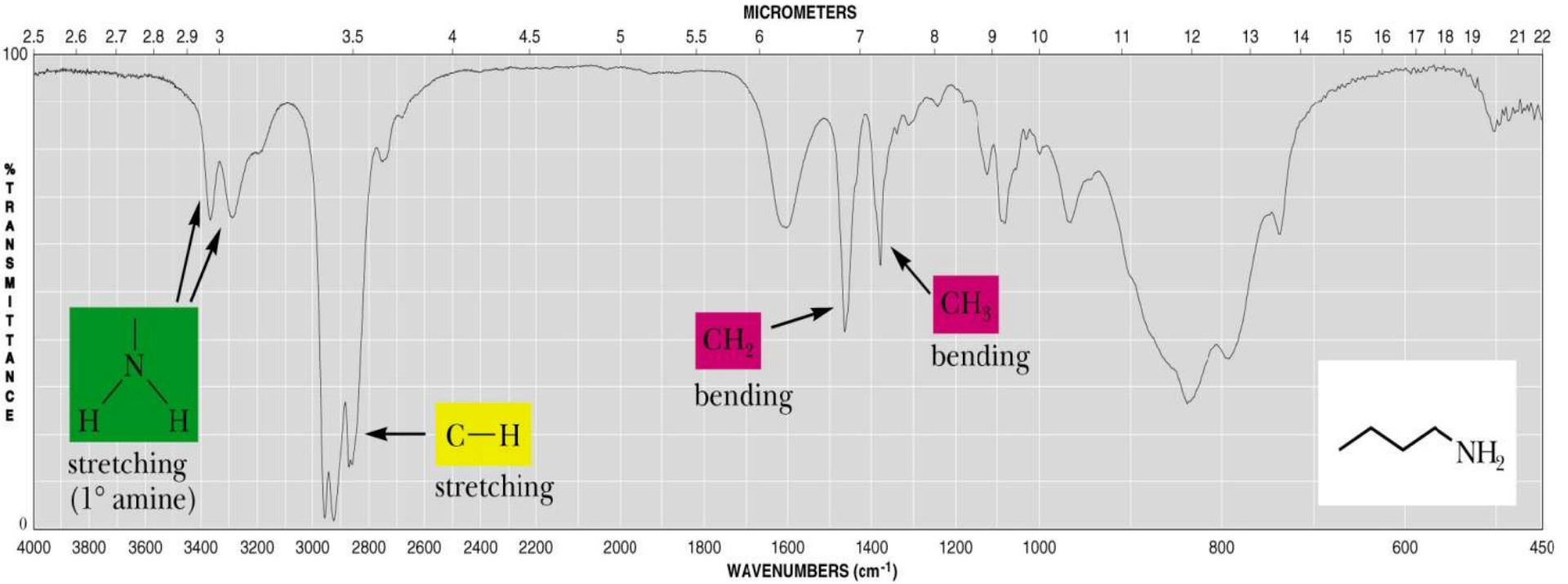
- Alcohols have a strong, broad OH stretch at 3200 – 3500 cm^{-1}, and a strong CO stretch at 1050 – 1250 cm^{-1}. The CH signals from the alkyl carbons are still present.



• Carbonyl groups (C=O) tend to absorb at 1600 – 1800 cm^{-1}, depending on the group (aldehyde, acid, ester, etc).



- Amines have N–H signals in the 3100 – 3500 cm^{-1} region. The number of signals depends on the number of H atoms connected to the N. Primary amines have two peaks, while secondary amines have one.
- Primary amine = one carbon connected to N (2 H)
- Secondary amine = two carbons connected to N (1 H)

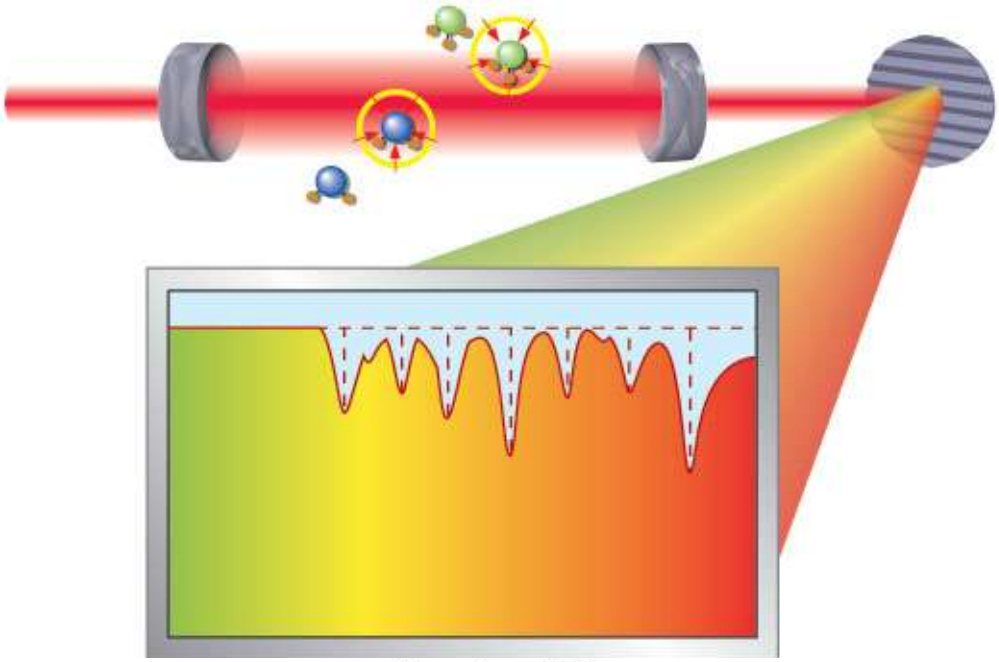


It is also possible to obtain structural information from an IR spectrum by noticing which absorptions are absent. For example, if an IR spectrum does not have a strong, sharp absorption near 1600 – 1800 cm^{-1}, then the compound does not have a C=O.

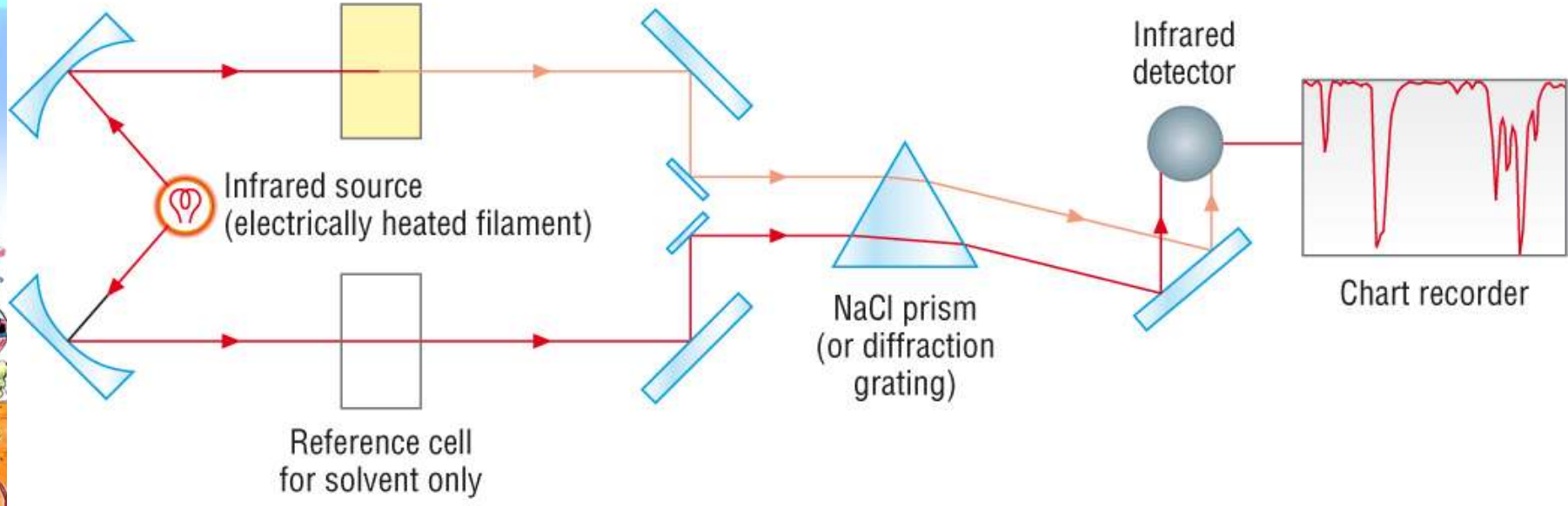
Two types of spectrometers are used in IR spectroscopy: the ***dispersive type*** and the ***Fourier transform*** variety.

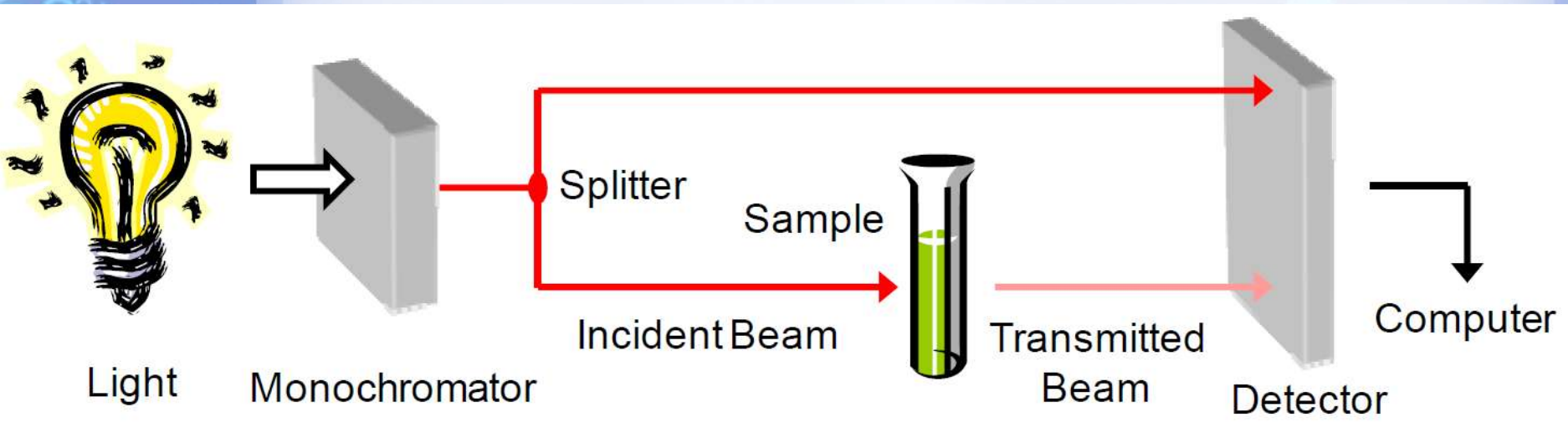
The older IR instruments were almost always ***dispersive*** double-beam designs. These were often of the double-beam-in-time variety shown in Figure except that the location of the cell compartment with respect to the monochromator was reversed. In most UV/visible instruments the cell is located between the monochromator and the detector in order to avoid photodecomposition of the sample, which may occur if samples are exposed to the full power of the source.

Infrared radiation, in contrast, is not sufficiently energetic to bring about photodecomposition. Also, most samples are good emitters of IR radiation. Because of these factors, the *cell compartment is usually located between the source and the monochromator* in an IR instrument. The components of IR instruments differ significantly from those in UV/visible instruments. Thus, IR sources are heated solids, and IR detectors respond to heat rather than to photons. Furthermore, the optical components of IR instruments are constructed from polished salts, such as sodium chloride or potassium bromide.



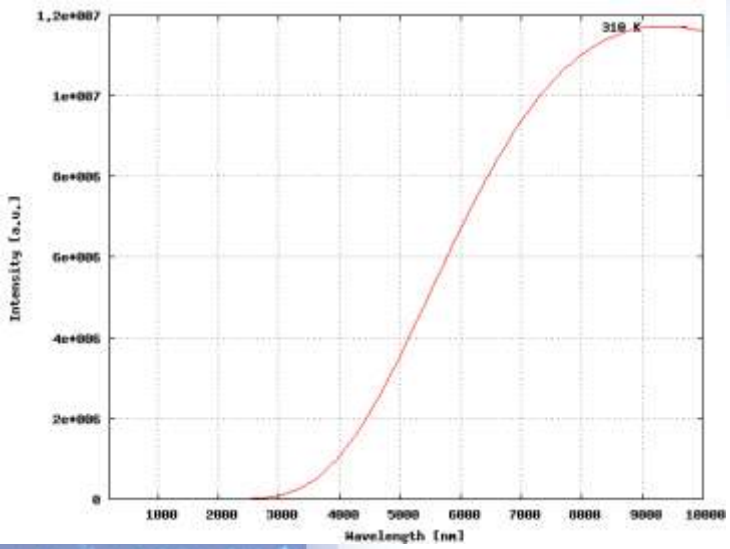
Sample cell for
solution of sample





• The detector compares the sample beam with the reference beam, and the difference is the amount absorbed.

INFRARED SOURCES

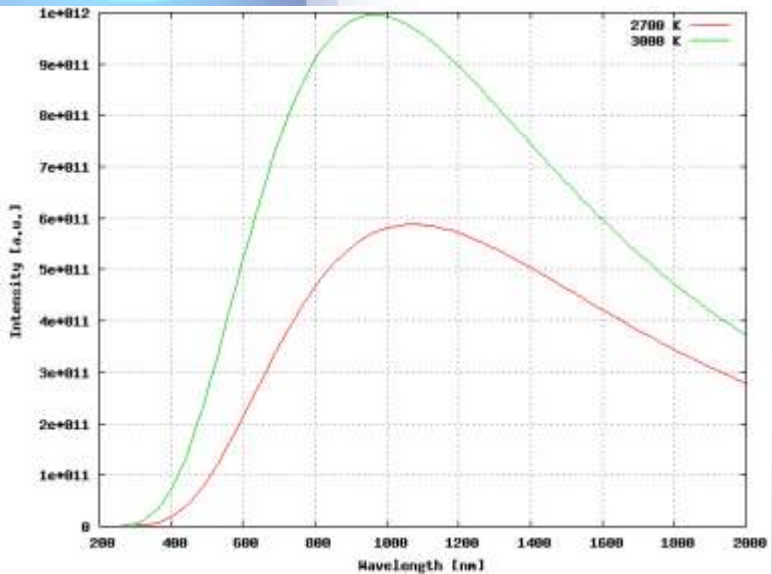


Ideally, a thermal IR source is a black body radiator that is in thermal equilibrium and produces unpolarized (non-coherent), continuous radiation. The most common type of IR source used in laboratories is a filament held at high temperature. Infrared radiation is essentially heat, and so hot wires, light bulbs, or glowing ceramics are used as sources.

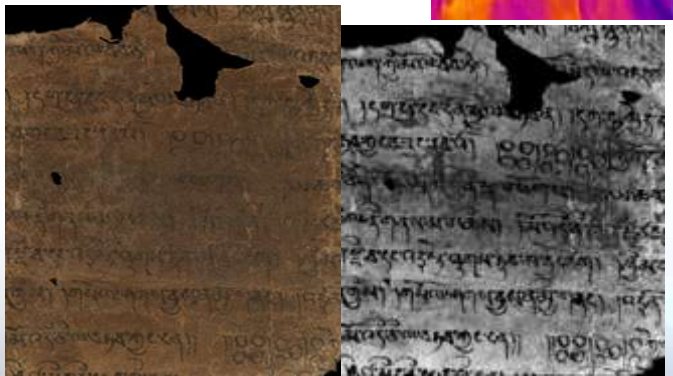
examples for black body radiators

- **Humans**

- **Incandescent lamps**



peak value = 1.1 μm
(T = 2700 K)
peak value = 966 μm
(T = 3000 K)



Parts of the Nernst Lamp

The elements of the Nernst Lamp are the glower, heater (made up of two or four *heater tubes*), ballast and cut-out. These are assembled in the lamp body and the holder.

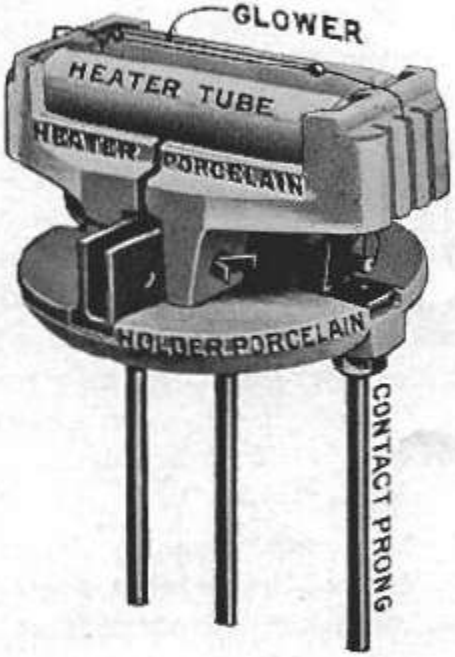


FIG. 3. NAMES OF PARTS OF THE NERNST LAMP HOLDER

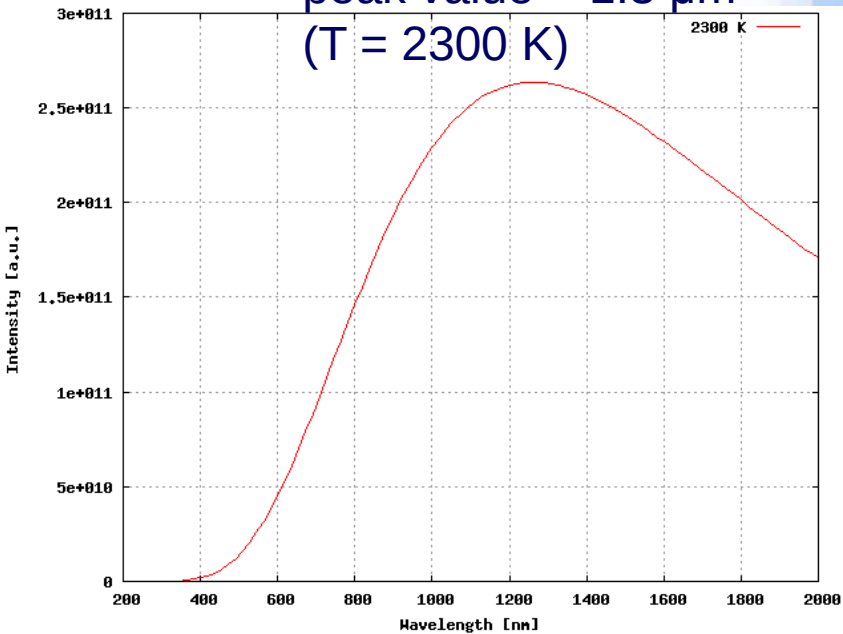
Glower The glower, or light giving element, is a white porcelain-like rod about $\frac{1}{32}$ inch in diameter by 1 inch long. It is fastened to the holder mechanically and electrically by means of terminal wires and small aluminum

- **Nernst glower**

A ***Nernst glower*** is a cylinder of zirconium and yttrium oxides that emits IR radiation when heated to a high temperature by an electric current. Electrically heated spirals of nichrome wire also serve as inexpensive IR sources.

composition:
Zirconium oxide ZrO_2 90% wt/wt
Yttrium oxide Y_2O_3 7% wt/wt
Erbium oxide Er_2O_3 3% wt/wt
operating temperature: 2300K
preheating necessary

peak value = 1.3 μm
(T = 2300 K)



A **Globar** source consists of a silicon carbide rod. Infrared radiation is emitted when the Globar is heated to about 1500°C by passing electricity through it.

composition
Silicon carbide
operating temperature: 1400K
no preheating necessary

peak value = 2.1 μm
(T = 1400 K)

The Globar is a less intense source than the Nernst glower, but it is more satisfactory for wavelengths longer than 15 *μm because its intensity decreases less rapidly.* IR sources have no protection from the atmosphere, as no satisfactory envelope material exists.

Continuum Sources for Optical Spectroscopy

Source	Wavelength Region, nm	Type of Spectroscopy
Xenon arc lamp	250–600	Molecular fluorescence
H_2 and D_2 lamps	160–380	UV molecular absorption
Tungsten/halogen lamp	240–2500	UV/visible/near-IR molecular absorption
Tungsten lamp	350–2200	Visible/near-IR molecular absorption
Nernst glower	400–20,000	IR molecular absorption
Nichrome wire	750–20,000	IR molecular absorption
Globar	1200–40,000	IR molecular absorption

IR Sources

- Nernst glower: a rod or cylinder made from several grams of rare earth oxides, heated to 1200-2200K by an electric current.
- Globar: similar to the Nernst glower but made from silicon carbide, electrically heated. Better performance at lower frequencies.
- Incandescent Wires: nichrome or rhodium, low intensity
- Mercury Arc: high-pressure mercury vapor tube, electric arc forms a plasma. Used for far-IR
- Tungsten filament: used for near-IR
- CO_2 Lasers (line source): high-intensity, tunable, used for quantitation of specific analytes.

Sample cells are made from materials, such as NaCl and KBr, that are transparent to infrared radiation. Gases are analyzed using a cell with a pathlength of approximately 10 cm. Longer pathlengths are obtained by using mirrors to pass the beam of radiation through the sample several times. A liquid samples may be analyzed using a variety of different sample cells. For non-volatile liquids a suitable sample can be prepared by placing a drop of the liquid between two NaCl plates, forming a thin film that typically is less than 0.01 mm thick. Volatile liquids must be placed in a sealed cell to prevent their evaporation. Gases may be analyzed by infrared spectrometry, and for this purpose a longpath cell is used, usually 10 cm in length.

(a) NaCl salts plates

(b) fixed pathlength (0.5 mm) sample cell with NaCl windows;

Most solid samples, however, are opaque, and must be dispersed in a more transparent medium before recording the IR spectrum. If a suitable solvent is available, then the solid can be analyzed by preparing a solution and analyzing as described above. When a suitable solvent is not available, solid samples may be analyzed by preparing a mull of the finely powdered sample with a suitable oil. Alternatively, the powdered sample can be mixed with KBr and pressed into an optically transparent pellet.

Properties of Infrared Materials

Material	Useful Range (cm^{-1})	General Properties
NaCl	40,000–625	Hygroscopic, water soluble, low cost, most commonly used material.
KCl	40,000–500	Hygroscopic, water soluble.
KBr	40,000–400	Hygroscopic, water soluble, slightly higher in cost than NaCl and more hygroscopic.
CsBr	40,000–250	Hygroscopic, water soluble.
CsI	40,000–200	Very hygroscopic, water soluble, good for lower wavenumber studies.
LiF	83,333–1425	Slightly soluble in water, good UV material.
CaF_2	77,000–1110	Insoluble in water, resists most acids and alkalis.
BaF_2	67,000–870	Insoluble in water, brittle, soluble in acids and NH_4Cl.
AgCl	10,000–400	Insoluble in water, corrosive to metals. Darkens upon exposure to short-wavelength visible light. Store in dark.
AgBr	22,000–333	Insoluble in water, corrosive to metals. Darkens upon exposure to short-wavelength visible light. Store in dark.
40% TlBr, 60%TlI (KRS-5)	16,600–285	Insoluble in water, highly toxic, soluble in bases, soft, good for ATR work.
ZnS	50,000–760	Insoluble in water, common acids and bases, brittle.
ZnSe	20,000–500	Insoluble in water, common acids and bases, brittle.
Ge	5000–560	Brittle, high index of refraction.
Si	83,333–1430 400–30	Insoluble in most acids and bases.
UV quartz	56,800–3700	Unaffected by water and most solvents.
IR quartz	40,000–3000	Unaffected by water and most solvents.
Polyethylene	625–10	Low-cost material for far-IR work.

Monochromators

Three types of substances are normally employed as monochromators, namely:

• ***Metal Halide Prisms:*** Various metal halide prisms, such as: KBr (12-25 μm), LiF (0.2-6 μm) and CeBr (15-38 μm) have been used earlier, but they have become more or less obsolescent nowadays.

• ***NaCl Prism (2-15 μm):*** Sodium chloride prism are of use for the whole of the region from 4000-650 cm^{-1}. First, it offers low resolution at 4000-2500 cm^{-1}, and secondly, because of its hygroscopic nature the optics have got to be protected at 20 °C above the ambient temperature.

• ***Gratings:*** In general, gratings are commonly employed in the design of the instruments and offer better resolution at higher frequency than the prisms. They offer much better resolution at low frequency, *viz.,* typical rulings are 240 lines per nm for the 4000-1500 cm^{-1} region and 120 lines per nm for the 1500-650 cm^{-1} region.

Detectors

There are ion all *three different types of detectors that are used in the infrared region:*

1) ***Thermocouples (or Thermopiles):*** The underlying principle of a thermocouple is that if two dissimilar metal wires are joined head to tail, then a difference in temperature between head and tail causes a current to flow in the wires. In the infrared spectrophotometer this current shall be directly proportional to the intensity of radiation falling on the thermocouple. Hence, the thermocouples are invariably employed in the infrared region, and to help in the complete absorption of 'available energy' the 'hot' junction or receiver is normally blackened.

2*)* ***Golay Detector:*** In this specific instance the absorption of infrared radiation affords expansion of an inert gas in a cell-chamber. One wall of the cell-chamber is provided with a flexible mirror and the resulting distortion alters the intensity of illumination falling on a photocell from a reflected beam of light. Thus, the current from the photocell is directly proportional to the incident radiation.

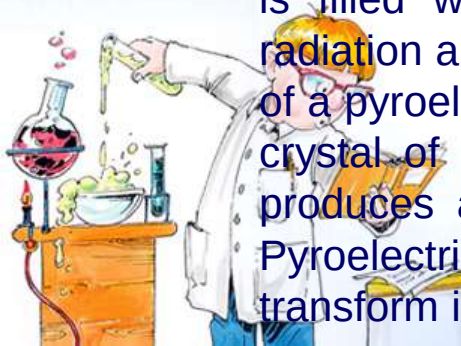
3*)* ***Bolometers:*** These are based on the principle that make use of the increase in resistance of a metal with increase in temperature. For instance, when the two platinum foils are appropriately incorporated into a Wheatstone bridge, and radiation is allowed to fall on the foil, a change in the resistance is observed ultimately. This causes an out-of-balance current that is directly proportional to the incidental radiation. Just like the thermocouples, they are used in the infrared region.

thermocouple	thermal	0.8–40 μm	voltage
thermistor	thermal	0.8–40 μm	change in resistance
pneumatic	thermal	0.8–1000 μm	membrane displacement
pyroelectric	thermal	0.3–1000 μm	current

The most widely used is a tiny thermocouple or a group of thermocouples called a **thermopile.** A thermopile consists of thermocouples connected in series, or less commonly, in parallel. A typical thermocouple may consist of a pair of antimony and bismuth wires connected at two points. When a temperature difference exists between the two points, a potential difference is developed, which can be measured. One of the junctions, then, is placed in the path of the light from the monochromator. A thermopile consists of up to six thermocouples in series, mounted in a vacuum to minimize heat loss by conduction. Half are sensing and half are bonded to a substrate. Thermopiles have response times of about 30 ms.

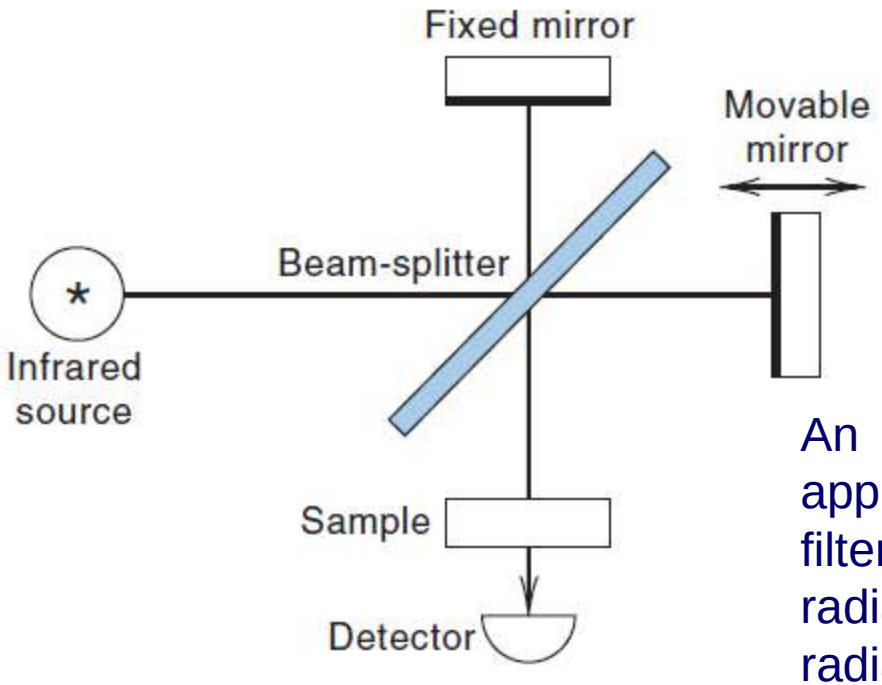
The base of each thermopile detector is formed by the so-called thermocouple. Due to thermal diffusion currents of two different metals, it generates an electrical voltage.

Bolometer consists of a conducting element whose electrical resistance changes as a function of temperature. A bolometer consists of a thin layer of an absorber, which acts as a resistance thermometer connected to a large capacity thermal reservoir at a constant temperature (often cooled to liquid nitrogen or even lower temperatures). A **pneumatic detector** consists of a small cylindrical chamber that is filled with xenon and contains a blackened membrane to absorb infrared radiation and heat the gas. **Pyroelectric detectors** are manufactured from crystals of a pyroelectric material, such as barium titanate or deuterated triglycine sulfate. A crystal of either of these compounds sandwiched between a pair of electrodes produces a temperature-dependent voltage when exposed to infrared radiation. Pyroelectric transducers are used in IR spectrometers, particularly the Fourier transform instruments.



Fourier Transform Infrared Spectrometers

Conventional infrared spectrometers are known as dispersive instruments. Rather than a grating monochromator, an FTIR instrument employs an ***interferometer*** to obtain a spectrum.



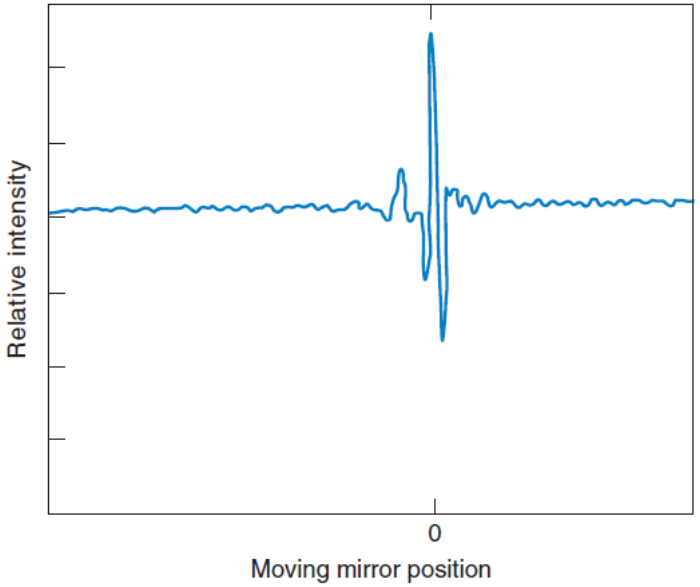
Schematic of interferometer for FTIR spectrometry.

Fourier-transform infrared (FTIR) spectroscopy is based on the idea of the interference of radiation between two beams to yield an ***interferogram***.

An interferometer provides an alternative approach for wavelength selection. Instead of filtering or dispersing the electromagnetic radiation, an interferometer allows source radiation of all wavelengths to reach the detector simultaneously.

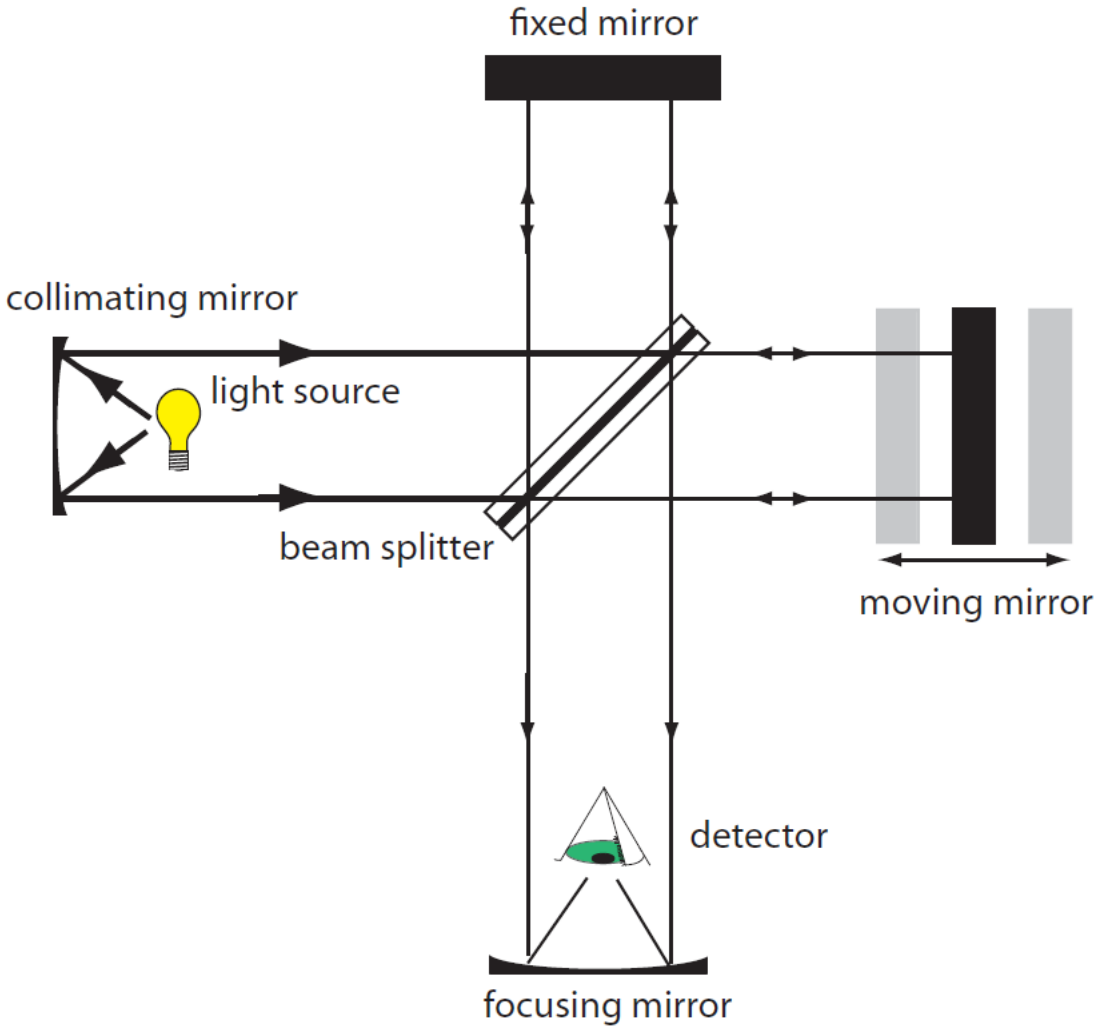
Because an FT-IR includes only a single optical path, it is necessary to collect a separate spectrum to compensate for the absorbance of atmospheric CO_2 and H_2O vapor. This is done by collecting a background spectrum without the sample and storing the result in the instrument's computer memory. The background spectrum is removed from the sample's spectrum by ratioing the two signals.

Albert Abraham Michelson (1852–1931) was one of the most gifted and inventive experimentalists of all time. He was a graduate of the United States Naval Academy and eventually became professor of physics at The University of Chicago. He studied the properties of light and performed several experiments that laid the foundation for our modern view of the universe. He invented the ***interferometer*** to determine the effect of the Earth's motion on the velocity of light. For his many inventions and their application to the study of light, Michelson won the 1907 Nobel Prize in Physics. At the time of his death, Michelson and his collaborators were attempting to measure the speed of light in a milelong vacuum tube located in what is now Irvine, California.

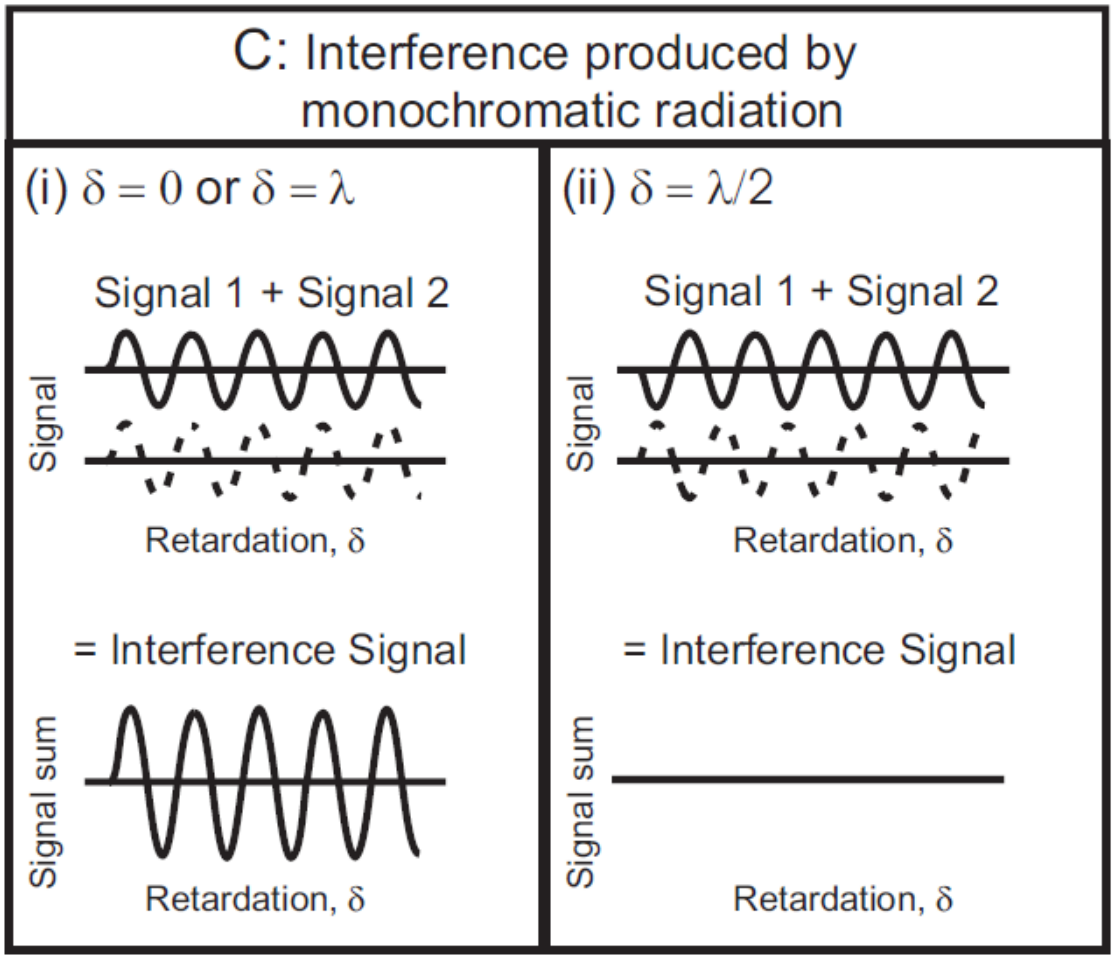


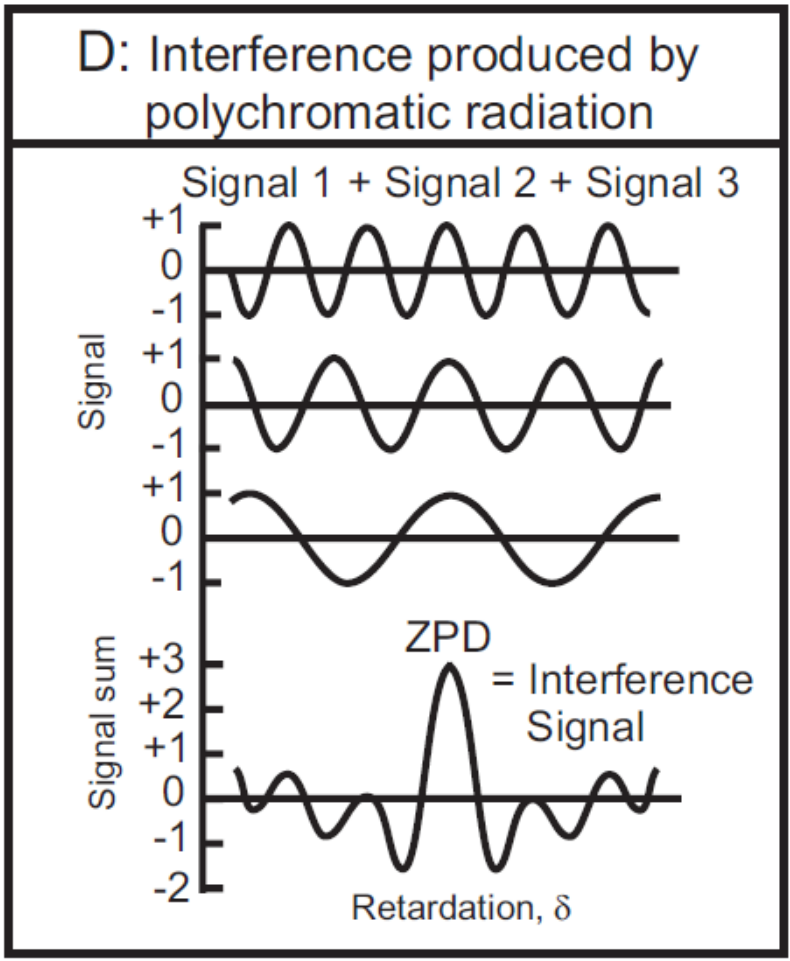
Typical interferogram. Point marked "0" is where both mirrors of the interferometer are the same distance from beam splitter.

Radiation from the source is focused on a beam splitter that reflects half of the radiation to a fixed mirror and transmits the other half to a movable mirror. The radiation recombines at the beam splitter, where constructive and destructive interference determines, for each wavelength, the intensity of light reaching the detector.



As the moving mirror changes position, the wavelengths of light experiencing maximum constructive interference and maximum destructive interference also changes. The signal at the detector shows intensity as a function of the moving mirror's position, expressed in units of distance or time. The result is called an ***interferogram***, or a time domain spectrum. The time domain spectrum is converted mathematically, by a process called a ***Fourier transform***, to a spectrum (also called a frequency domain spectrum) showing intensity as a function of the radiation's energy.

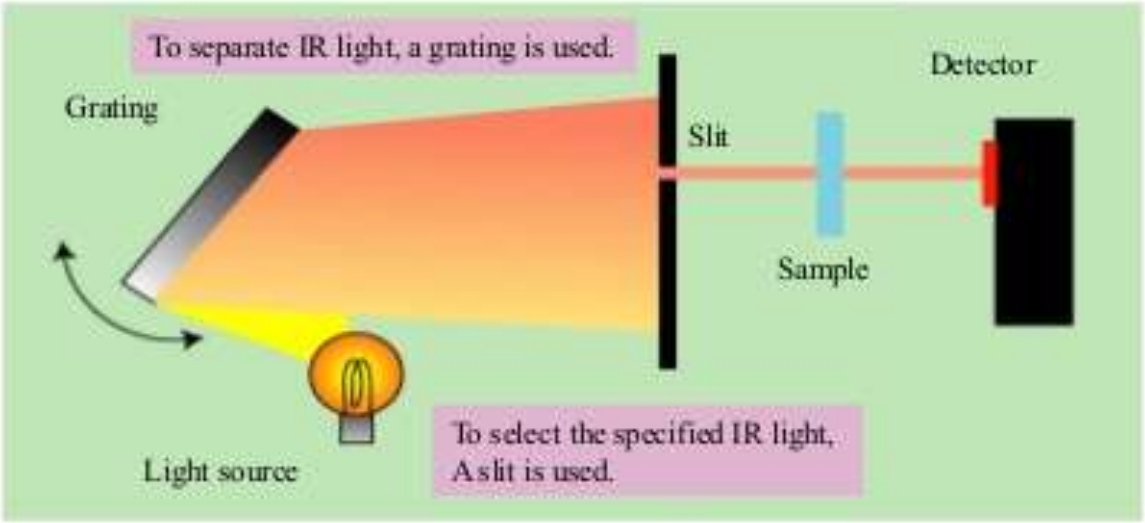




C: Schematic representation of the interference produced by adding monochromatic electromagnetic waves from the stationary mirror and movable mirror at different values of the optical path difference or retardation, δ. i) The optical path has a zero path difference (ZPD), δ = 0 or λ causing the waves to interact constructively; ii) The optical path difference is one half of a wavelength, δ = λ/2, causing the waves to interact destructively. Note that constructive interference occurs where the retardation is an integral number of wavelengths. **D:** Schematic diagram showing how an interferogram is the sum of a series of electromagnetic waves of different wavelength (polychromatic radiation). Note that at ZPD, δ = 0, the maximum signal is produced.

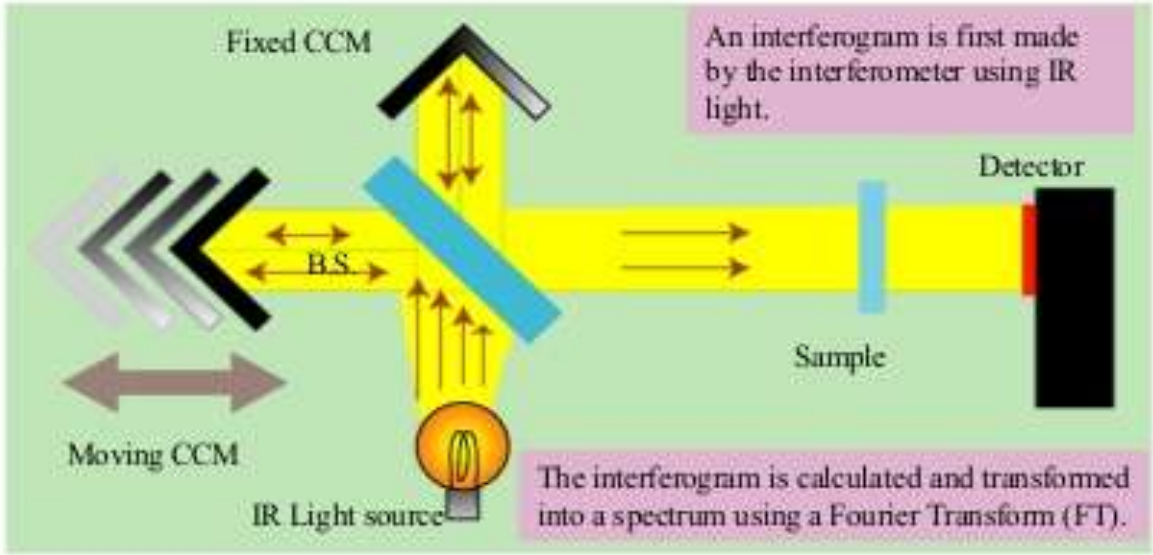
In comparison to a monochromator, an interferometer has two significant advantages. The first advantage, which is termed ***jacquinot's advantage***, is the higher throughput of source radiation. Because an interferometer does not use slits and has fewer optical components from which radiation can be scattered and lost, the throughput of radiation reaching the detector is 80–200× greater than that for a monochromator. The result is less noise. The second advantage, which is called ***fellgett's advantage***, is a savings in the time needed to obtain a spectrum. Because the detector monitors all frequencies simultaneously, an entire spectrum takes approximately one second to record, as compared to 10–15 minutes with a scanning monochromator.

Comparison Beetween Dispersion Spectrometer and FTIR



Dispersion Spectrometer

In order to measure an IR spectrum, the dispersion Spectrometer takes several minutes.
Also the detector receives only a few % of the energy of original light source.



FTIR

In order to measure an IR spectrum, FTIR takes only a few seconds.
Moreover, the detector receives up to 50% of the energy of original light source.
(much larger than the dispersion spectrometer.)

General Uses

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

Common Applications

• Identification of compounds by matching spectrum of unknown compound with reference spectrum (fingerprinting)
• Identification of functional groups in unknown substances
• Identification of reaction components and kinetic studies of reactions
• Identification of molecular orientation in polymer films
• Detection of molecular impurities or additives present in amounts of 1% and in some cases as low as 0.01%
• Identification of polymers, plastics, and resins
• Analysis of formulations such as insecticides and copolymers

Samples State

Almost any solid, liquid or gas sample can be analyzed. Many sampling accessories are available.

Amount

Solids 50 to 200 mg is desirable, but 10 µg ground with transparent matrix (such as KBr) is the minimum for qualitative determinations; 1 to 10 µg minimum is required if solid is soluble in suitable solvent.

Liquids 0.5 µL is needed if neat, less if pure. Gases 50 ppb is needed.

Preparation

Little or no preparation is required; may have to grind solid into KBr matrix or dissolve sample in a suitable solvent (CCl_4 and CS_2 are preferred). Many types of sample holders and cells are available. Water should be removed from sample if possible.

Analysis Time

Estimated time to obtain spectrum from a routine sample varies from 1 to 10 min depending on the type of instrument and the resolution required. Most samples can be prepared for infrared (IR) analysis in approximately 1 to 5 min.

Limitations

- Minimal elemental information is given for most samples.
- Background solvent or solid matrix must be relatively transparent in the spectral region of interest.
- Molecule must be active in the IR region. (When exposed to IR radiation, a minimum of one vibrational motion must alter the net dipole moment of the molecule in order for absorption to be observed.)

Accuracy

In analysis of mixtures under favorable conditions, accuracy is greater than 1%. In routine analyses, it is ± 5%.

Sensitivity and Detection Limits

Routine is 2%; under most favorable conditions and special techniques, it is 0.01%.