INTRODUCTION TO SPECTROSCOPY
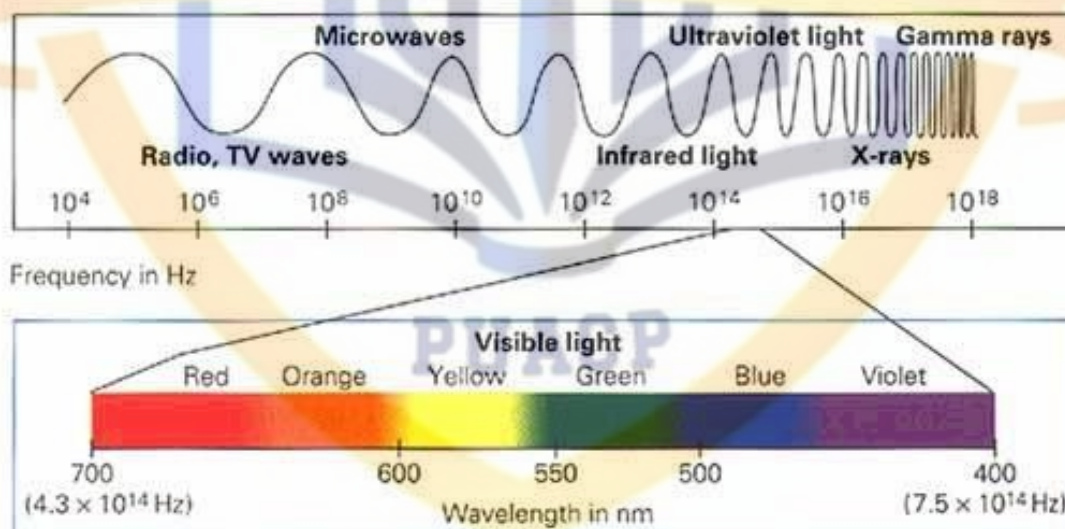
I   Spectroscopy and the Electromagnetic Spectrum

Spectroscopy is the study of the interaction of matter and electromagnetic radiation.

Electromagnetic radiation is radiant energy having the properties of both particles and waves. An electromagnetic spectrum consists of a range of all different types of electromagnetic radiation—each type associated with a particular energy range.

The arrangement of all types of electromagnetic radiations in order of their wavelength or frequencies is known as electromagnetic spectrum.

Visible light is the type of electromagnetic radiation with which we are most familiar, but it represents only a fraction of the range of the entire electromagnetic spectrum. X-rays and radio waves are other types of familiar electromagnetic radiation.

The electromagnetic spectrum is made up of the following components: (High energy (Frequency) to low energy (Frequency).

• ***Cosmic rays,*** which consist of radiation discharged by the sun, have the highest energy, the highest frequencies, and the shortest wavelengths.

• **(gamma rays)** are emitted from the nuclei of certain radioactive elements and, because of their high energy, can severely damage biological organisms.

• **X-rays**, somewhat lower in energy than are less harmful, except in high doses. Low-dose X-rays are used to examine the internal structure of organisms. The denser the tissue, the more it blocks X-rays.

• **Ultraviolet (UV)** light is responsible for sunburns, and repeated exposure can cause skin cancer by damaging DNA molecules in skin cells.

• **Visible light** is the electromagnetic radiation we see.

• **Infra Red (IR).** We feel infrared radiation as heat.

• **Micro waves.** We cook with microwaves and use them in radar.

• **Radio waves** have the lowest energy (lowest frequency). We use them for radio and television communication, digital imaging, remote controls, and wireless linkages for laptop computers. Radio waves are also used in NMR spectroscopy and in magnetic resonance imaging (MRI)

II   Both Particle and Wave nature: A particle of electromagnetic radiation is called a photon. We may think of electromagnetic radiation as photons traveling at the speed of light. Because electromagnetic radiation has both particle-like and wave-like properties, it can be characterized by either its frequency or its wavelength

III   Frequency: Frequency is defined as the number of wave crests that pass by a given point in one second. Frequency has units of hertz (Hz).

IV   Wavelength: Wavelength is the distance between two successive crusts or troughs. Wavelength is generally measured in micrometers or nanometers. One micrometer is 10^{-6} of a meter; one nanometer (nm) is 10^{-9} of a meter.

The frequency of electromagnetic radiation, therefore, is equal to the speed of light (c) divided by the radiation's wavelength:

$$\upsilon(Neu) = C/\lambda$$

So **wavelength has invers relation with frequency and energy**. Short wavelengths have high frequencies and high energy, and long wavelengths have low frequencies and low energy.

The relationship between the energy (E) of a photon and the frequency (or the wavelength) of the electromagnetic radiation is described by the equation

$$E = h\nu = hc/\lambda$$

where h is the proportionality constant called Planck's constant, named after the German physicist who discovered the relationship.

V   Wavenumber is another way to describe the frequency of electromagnetic radiation, and the one most often used in infrared spectroscopy. *It is the number of waves in one centimeter, so it has units of reciprocal centimeters.* Scientists use wavenumbers in preference to wavelengths because, *unlike wavelengths, wavenumbers are directly proportional to energy.* The relationship between wavenumber and wavelength is given by the equation:

$$\bar{\nu} \quad (cm^{-1}) = 1/\lambda$$

So high frequencies, large wavenumbers, and short wavelengths are associated with high energy.

**VI   Absorption and Emission Spectra**

VIA   Absorption Spectra:

When electromagnetic radiations are passed through an organic compound, these induce electronic, vibrational and rotational transitions in the molecule. The energy required for each of these transitions is quantized.

Thus only the radiation supplying the required quantum (Photon) of energy is absorbed and the remaining portion of the incident radiation is transmitted. The wavelength or the frequencies of the absorbed radiations are measured with the help of spectrophotometer. Generally a spectrometer records an absorption spectrum as a plot of intensity versus their wave length or frequency. Such spectra which are obtained by absorption of electromagnetic radiations are called as absorption spectra. UV, Visible, IR and NMR all are examples of absorption spectra. Absorption band in absorption spectrum can be characterized by the wave length at which max absorption occurs.

VIB   Emission spectra

The spectra which are obtained by the emission of electromagnetic radiations from the excited substances are known as **Emission spectra**
, like atomic emission spectra. The excitation is caused by heating the substance to a high temperature either thermally or electrically. The excited substance emits certain radiations when it comes to the ground state and a spectrometer records these radiations as an emission spectrum.
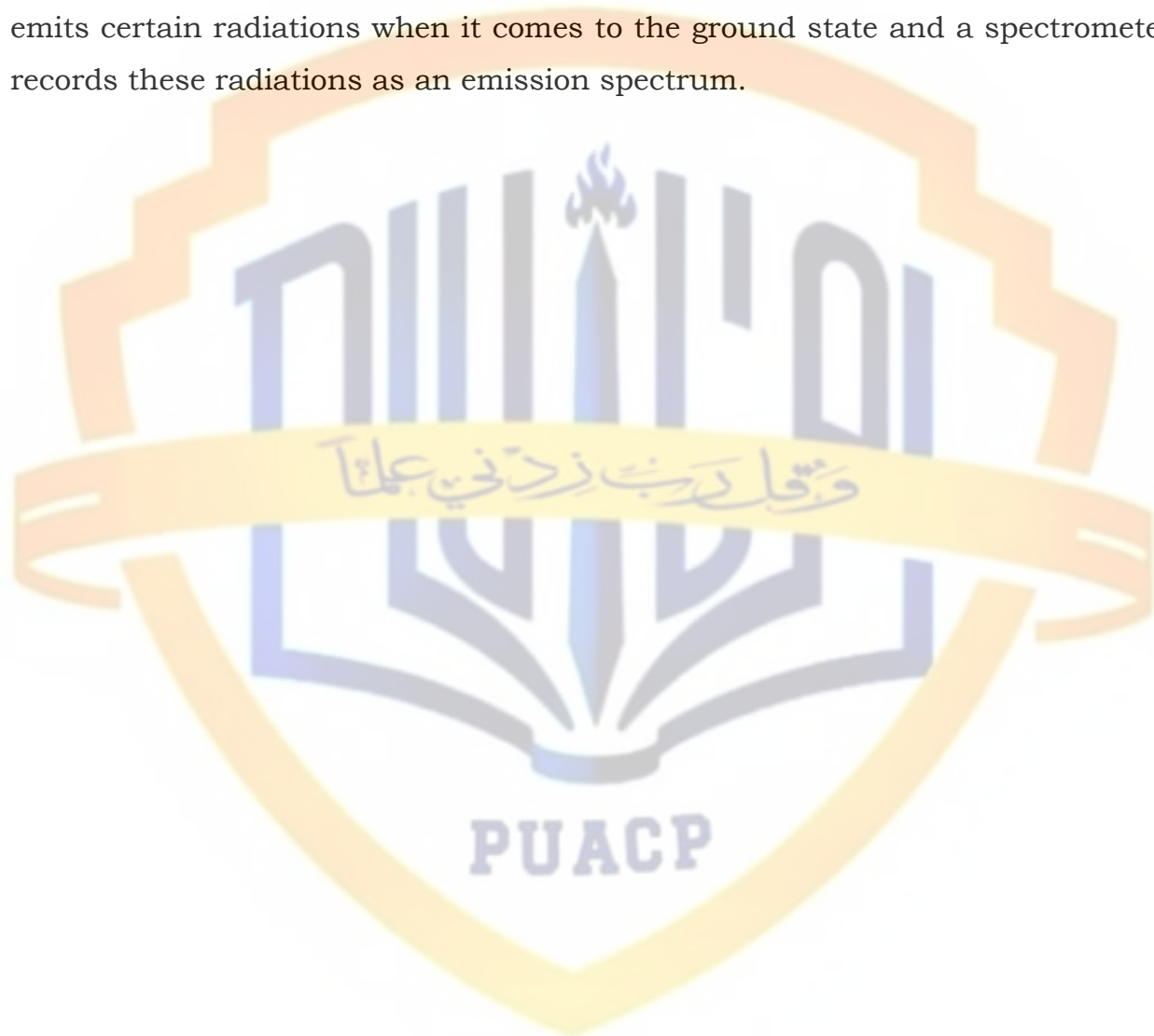
CHAPTER NO. 2 INFRARED SPECTROSCOPY

1.   Infrared Spectroscopy

IR spectroscopy is a very useful for the detection of different functional groups through their absorption of infrared light. All the bonds in a molecule are constantly vibrating. When these bonds absorb radiation in the IR region, their amplitude of vibration increases which is called vibrational excitement. IR spectroscopy measures this vibrational excitation of atoms around the bonds that connect them. The positions of the absorption lines associated with this excitation depend on the types of functional groups present, and the IR spectrum as a whole displays a pattern unique for each individual substance.

2.1   Stretching and Bending Vibrations

The covalent bonds in molecules are constantly vibrating. The bond between two atoms behaves like a vibrating spring.

There are two types of vibrating motions of covalent bonds.

1) Stretching vibration   2) Bending vibration

2.1   *A stretch is a vibration that occurs along the line of the bond and changes the bond length.*
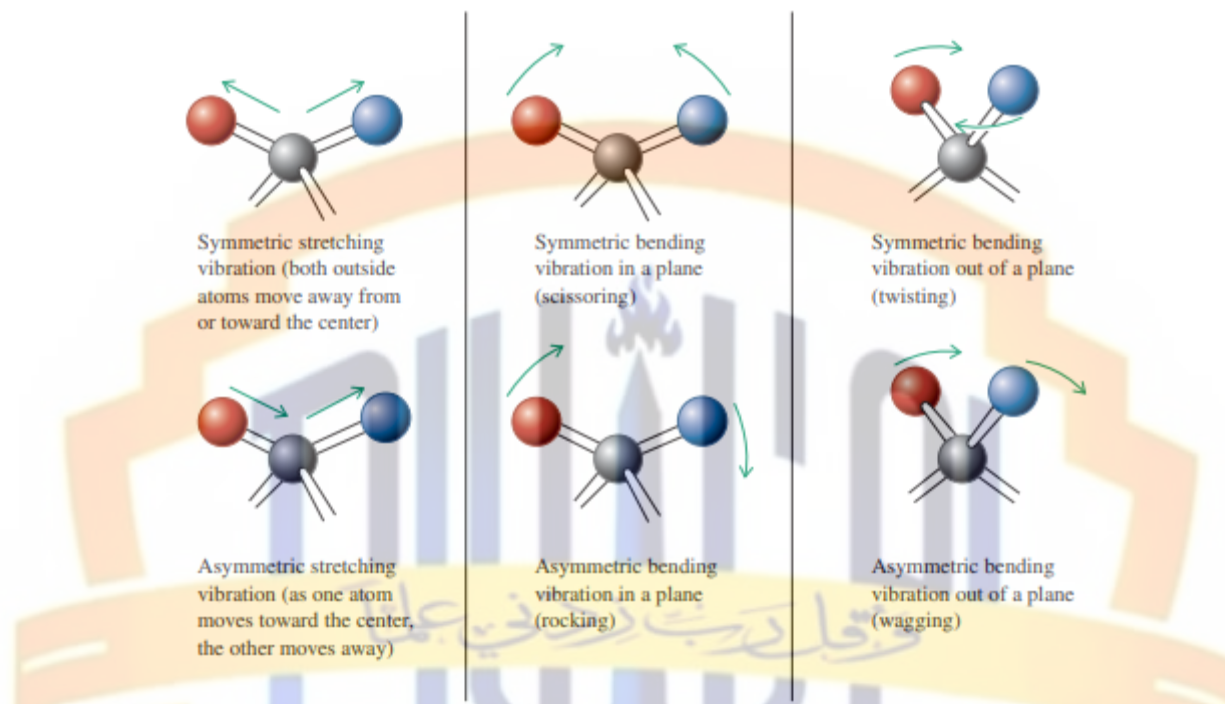
2.2   *A bend is a vibration that does not occur along the line of the bond, but changes the bond angle.*

 In general, **stretching vibrations occur at higher frequencies than bending vibrations**. Also **asymmetric stretching vibrations occur at higher frequencies than symmetric stretching vibration**.

A diatomic molecule such as H-Cl can undergo only a stretching vibration since it has no bond angles.

The vibrations of a molecule containing three or more atoms are more complex. Such molecules can have two types of stretching vibrations, symmetric and asymmetric.

Their bending vibrations can be either **in-plane** or **out-of-plane**. Bending vibrations can be divided into for main types **rocking, scissoring (in plane), wagging, and twisting (out of plane).**

Symmetric stretching vibration (both outside atoms move away from or toward the center)

Symmetric bending vibration in a plane (scissoring)

Symmetric bending vibration out of a plane (twisting)

Asymmetric stretching vibration (as one atom moves toward the center, the other moves away)

Asymmetric bending vibration in a plane (rocking)

Asymmetric bending vibration out of a plane (wagging)

2.2   Absorption of IR Radiations:

Each stretching and bending vibration of a bond in a molecule occurs with a characteristic frequency. When a compound is bombarded with radiation of a frequency that exactly matches the frequency of one of its vibrations, the molecule will absorb energy. This allows the bonds to stretch and bend a bit more. Thus, **the absorption of energy increases the amplitude of the vibration, but does not change its frequency**. By experimentally determining the wavenumbers of the energy absorbed by a particular compound, we can determine the type of bonds it has. For example, **the stretching vibration of a C=O bond absorbs energy of wavenumber 1700 cm^{-1}** whereas the **stretching vibration of an O-H bond absorbs energy of wavenumber 3450 cm^{-1}.**

C=O ~1700 cm^{-1} O-H ~3450 cm^{-1}

The amount of energy needed for stretching and bending individual bonds, corresponds to rather shorter wavelengths. These wavelengths lay in the infrared, that is, heat radiation just to the long wavelength side of visible light.

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When the carbon skeleton of a molecule vibrates, all the bonds stretch and relax in combination and these absorptions are unhelpful. However some bonds stretch essentially independently of the rest of the molecule. This occurs if the bond is either:

• much stronger or weaker than others nearby, or

• between atoms that are much heavier or lighter than their neighbors.

2.2.1 The Position of Absorption Bands

In IR Spectroscopy, it is very important to know the exact vibrational absorption of different functional groups. According to **Hooke's law for a simple harmonic oscillator**, there is a relationship between the frequency of the bond vibration, the mass of the atoms, and the strength of the bond.

The natural frequency of vibration of a bond is given by the equation

$$v = \frac{1}{2\pi c}\sqrt{K/\mu}$$

which is derived from Hooke's Law for vibrating springs. μ is called as the reduced mass m of the system which is given as

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

In above equation, K is a constant that varies from one bond to another and it is directly proportional to the vibrating frequency. But the reduces mass is inversely proportional to the vibrating frequency.

Two things should be noticeable immediately.

One is that stronger bonds have a larger force constant K and vibrate at higher frequencies than weaker bonds. In general, triple bonds are stronger than double or single bonds between the same two atoms and have higher frequencies of vibration (higher wavenumbers).

Given Values chiefly affected by bond strength (stronger bond, higher frequency)
C≡ O, C=O, C–O, 2143 cm^{-1}, 1715 cm^{-1}, 1100 cm^{-1}.

The second is that bonds between atoms of higher masses (larger reduced mass, m) vibrate at lower frequencies than bonds between lighter atoms.

e.g., As the atom bonded to carbon increases in mass, the reduced mass (m) increases, and the frequency of vibration decreases (wavenumbers get smaller). For example, these values chiefly affected by mass of atoms: (lighter atom, higher frequency) C–H, C–D, C–O, C–Cl, 3000 cm–1, 2200 cm^{-1}, 1100 cm^{-1}, 700 cm^{-1}.

2.2.2 The Intensity of Absorption Bands

Dipole moment

The intensity of an absorption band depends on the size of the change in dipole moment associated with the vibration: **The greater the change in dipole moment, the more intense the absorption.**

As we know the dipole moment of a bond is equal to the magnitude of the charge on one of the bonded atoms, multiplied by the distance between the two charges. **When the bond stretches, the increasing distance between the atoms increases the dipole moment**. The stretching vibration of an O-H bond will be associated with a greater change in dipole moment than that of an N-H bond because the O-H bond is more polar. Consequently, the stretching vibration of the bond will be more intense. Likewise, the stretching vibration of an N-H bond is more intense than that of a C-H bond because the N-H bond is more polar.

No. of bonds

The intensity of an absorption band also depends on the number of bonds responsible for the absorption. For example, the absorption band for the C-H stretch will be more intense for a compound such as octyl iodide, which has 17 C-H bonds, than for methyl iodide, which has only three C-H bonds.

Concentration of Sample

The concentration of the sample used to obtain an IR spectrum also affects the intensity of the absorption bands. Concentrated samples have greater numbers of absorbing molecules and, therefore, more intense absorption bands. Intensities can be strong (s), medium (m), weak (w), broad, and sharp.

2.3   Fundamental vibrations and overtones

The vibrations we have been discussing are called fundamental absorptions. They arise from excitation from the ground state to the lowest-energy excited

state. Usually, the spectrum is complicated because of the presence of weak **overtone, combination, and difference** bands.

2.3.1 Overtones: This result from excitation from the ground state to higher energy states, which correspond to integral multiples of the frequency of the fundamental (υ). For example, you might observe weak overtone bands at 2υ, 3 υ, ... An absorption in the infrared at 500 cm−1 may well have an accompanying peak of lower intensity at 1000 cm^{-1} an overtone.

2.3.2 Combination Bands: When two vibrational frequencies (n-1 and n-2) in a molecule couple to give rise to a vibration of a new frequency within the molecule, and when such a vibration is infrared active, it is called a **combination band**. This band is the sum of the two interacting bands ($υ_{comb}$ = υ-1 + υ-2). Not all possible **combinations** occur.

2.3.3 Difference Bands: There are similar to **combination bands**. The observed frequency in this case results from the difference between the two interacting bands (n_{diff} = $υ_1$- $υ_2$).

2.3.4 Fermi Resonance: When a fundamental vibration couples with an overtone or combination band, the coupled vibration is called **Fermi resonance**. Again, only certain combinations are allowed. Fermi resonance is often observed in carbonyl compounds.

Although rotational frequencies of the whole molecule are not infrared active, they often couple with the stretching and bending vibrations in the molecule to give additional fine structure to these absorptions, thus further complicating the spectrum. One of the reasons a band is broad rather than sharp in the infrared spectrum is rotational coupling, which may lead to a considerable amount of unresolved fine structure.

## 2.4 The infrared spectrophotometer

The instrument that determines the absorption spectrum for a compound is called an infrared spectrometer or, more precisely, a spectrophotometer. Two types of infrared spectrometers are in common use in the organic laboratory: dispersive and Fourier transform (FT) instruments. Both of these types of

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instruments provide spectra of compounds in the common range of 4000 to 400 cm^{-1}. Although the two provide nearly identical spectra for a given compound, FT infrared spectrometers provide the infrared spectrum much more rapidly than the dispersive instruments.

2.4.1 Dispersive Infrared Spectrometers

Figure below schematically illustrates the components of a simple dispersive infrared spectrometer.

1. IR source: The instrument produces a beam of infrared radiation from a hot wire and, by means of mirrors, divides it into two parallel beams of equal-intensity
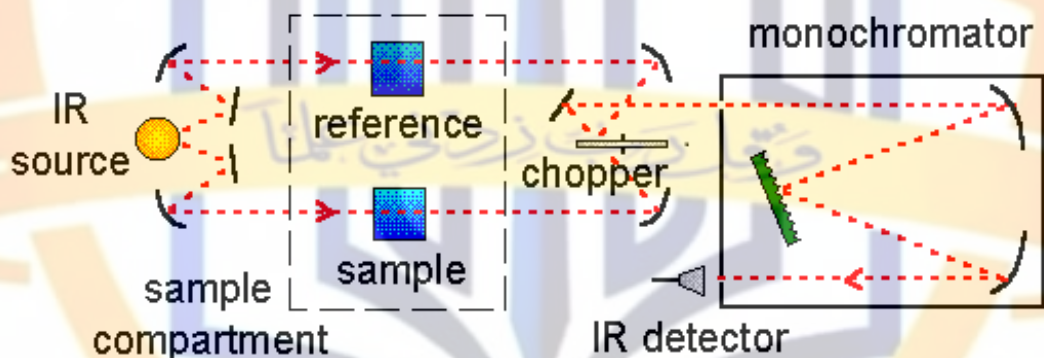
radiation. The sample is placed in one beam, and the other beam is used as a reference.

2.Monocharomator: The beams then pass into the monochromator, which disperses each into a continuous spectrum of frequencies of infrared light. The monochromator consists of a rapidly rotating sector (beam chopper) that passes the two beams alternately to a diffraction grating (a prism in older instruments). The slowly rotating diffraction grating varies the frequency or wavelength of radiation reaching the thermocouple detector.

3. Detector: The detector senses the ratio between the intensities of the reference and sample beams. In this way, the detector determines which frequencies have been absorbed by the sample and which frequencies are unaffected by the light passing through the sample.

4.Amplifier & Recorder: After the signal from the detector is amplified, the recorder draws the resulting spectrum of the sample on a chart. It is important to realize that the spectrum is recorded as the frequency of infrared radiation changes by rotation of the diffraction grating. ***Dispersive instruments are said to record a spectrum in the frequency domain.***

5. IR Graph: A detector generates a plot of ***percent transmission of radiation versus the wavenumber (or wavelength) of the radiation transmitted***. At 100% transmission, all the energy of the radiation passes through the molecule. Lower values of percent transmission mean that some of the energy is being absorbed by the compound. Each downward spike in the IR spectrum represents absorption of energy. **The spikes are called absorption bands**. Most chemists report the location of absorption bands using wavenumbers.

2.4.2 Fourier Transform Infrared (FT-IR) Spectrophotometers

A newer type of IR spectrometer, called a Fourier transform IR (FT-IR) spectrometer, has several **advantages.**

1-Its sensitivity is better because With this, a spectrum with a better signal-to-noise ratio can be plotted.

2-It is very fast. Instead of scanning through the frequencies one by one, it measures all frequencies simultaneously. With a conventional IR spectrometer, it can take 2 to 10 minutes to scan through all the frequencies. In contrast, FT-IR spectra can be taken in 1 to 2 seconds.

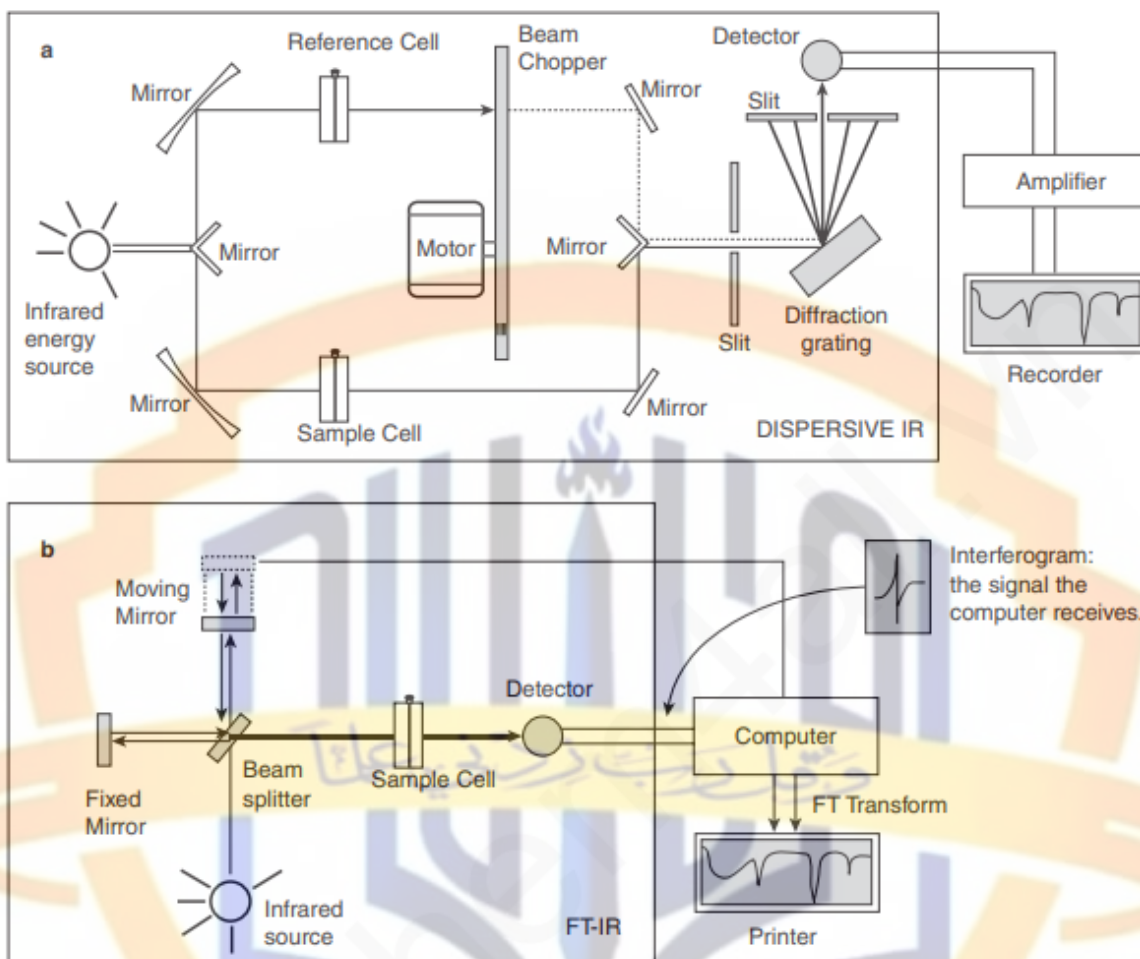3- The information is digitized and Fourier transformed by a computer to produce the FT-IR spectrum.

FIGURE 2.3 Schematic diagrams of (a) dispersive and (b) Fourier transform infrared spectrophotometers.

The most modern infrared spectrometers (spectrophotometers) operate on a different principle. The design of the optical pathway produces a pattern called an **interferogram**. The interferogram is a complex signal, but its wave-like pattern contains all the frequencies that make up the infrared spectrum. **An interferogram is essentially a plot of intensity versus time (a time-domain spectrum)**. However, a chemist is more interested in a spectrum that is a plot of intensity versus frequency (a frequency-domain spectrum). A mathematical operation known as a Fourier transform (FT) can separate the individual absorption frequencies from the interferogram, producing a spectrum virtually identical to that obtained with a dispersive spectrometer. This type of instrument is known as a Fourier transform infrared spectrometer, or FT-IR. The advantage

of an FT-IR instrument is that it acquires the interferogram in less than a second. It is thus possible to collect dozens of interferograms of the same sample and accumulate them in the memory of a computer. An FT-IR instrument is therefore capable of greater speed and greater sensitivity than a dispersion instrument.

A schematic diagram of an FT-IR is shown above.

1-The FT-IR uses an interferometer to process the energy sent to the sample. In the **interferometer**, the source energy passes through a beam splitter, a mirror placed at a 45° angle to the incoming radiation, which allows the incoming radiation to pass through but separates it into two perpendicular beams, one undeflected, the other oriented at a 90° angle. One beam, the one oriented at 90° in Figure above, goes to a stationary or "fixed" mirror and is returned to the beam splitter. The undeflected beam goes to a moving mirror and is also returned to the beam splitter. The motion of the mirror causes the path length that the second beam traverses to vary. When the two beams meet at the beam splitter, they recombine, but the path length differences (differing wavelength content) of the two beams cause both constructive and destructive interferences. **The combined beam containing these interference patterns is called the interferogram**. This interferogram contains all of the radiative energy coming from the source and has a wide range of wavelengths.

2-The interferogram generated by combining the two beams is oriented toward the sample by the beam splitter. As it passes through the sample, the sample simultaneously absorbs all of the wavelengths (frequencies) that are normally found in its infrared spectrum.

3-The modified interferogram signal that reaches the detector contains information about the amount of energy that was absorbed at every wavelength (frequency).

4-Detector: The computer compares the modified interferogram to a reference laser beam to have a standard of comparison. The final interferogram contains

all of the information in one time-domain signal, a signal that cannot be read by a human.

5-Fourier transformation: A mathematical process called a Fourier transform must be implemented by computer on interferogram. This method converts time domain spectra to frequency domain spectra which is similar to typivcal IR and can be understandable by humans.

To obtain a spectrum of a compound, the chemist first obtains an interferogram of the "background," which consists of the infrared-active atmospheric gases, carbon dioxide and water vapor (oxygen and nitrogen are not infrared active.

2.5   PREPARATION OF SAMPLES FOR INFRARED SPECTROSCOPY

To determine the infrared spectrum of a compound, one must place the compound in a sample holder, or cell. In infrared spectroscopy, this immediately poses a problem. **Glass and plastics absorb strongly throughout the infrared region of the spectrum**. Cells must be constructed of ionic substances—typically **sodium chloride or potassium bromide**. **Potassium bromide** plates are more expensive than sodium chloride plates but have the advantage of usefulness in the range of **4000 to 400 cm⁻¹**. **Sodium chloride plates** are used widely because of their relatively low cost. The practical range for their use in spectroscopy extends from **4000 to 650 cm⁻¹**. Sodium chloride begins to absorb at 650 cm⁻¹, and any bands with frequencies less than this value will not be observed. Since few important bands appear below 650 cm⁻¹, sodium chloride plates are in most common use for routine infrared spectroscopy.

2.5.1 Liquids

A drop of a liquid organic compound is placed between a pair of polished sodium chloride or potassium bromide plates, referred to as salt plates. When the plates are squeezed gently, a thin liquid film is formed between them. A spectrum determined by this method is referred to as a **neat spectrum** since no solvent is used. Salt plates break easily and are water soluble. Organic

compounds analyzed by this technique **must be free of water**. The pair of plates is inserted into a holder that fits into the spectrometer.

2.5.2 Solids

There are at least three common methods for preparing a solid sample for spectroscopy.

1-The first method involves mixing the finely ground solid sample with powdered potassium bromide and pressing the mixture under high pressure. Under pressure, the potassium bromide melts and seals the compound into a matrix. The result is a **KBr pellet** that can be inserted into a holder in the spectrometer. The main **disadvantage of this method is that potassium bromide absorbs water**, which may interfere with the spectrum that is obtained. If a good pellet is prepared, the spectrum obtained will have no interfering bands since potassium bromide is transparent down to 400 cm−1.

2-The second method, a **Nujol mull**, involves grinding the compound with mineral oil (Nujol) to create a suspension of the finely ground sample dispersed in the mineral oil. The thick suspension is placed between salt plates. **The main disadvantage of this method is that the mineral oil obscures bands that may be present in the analyzed compound**. Nujol bands appear at **2924, 1462, and 1377 cm^{-1}**.

cyanoacetamide
(spectrum taken as a Nujol mull)
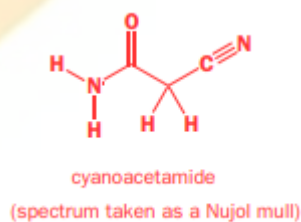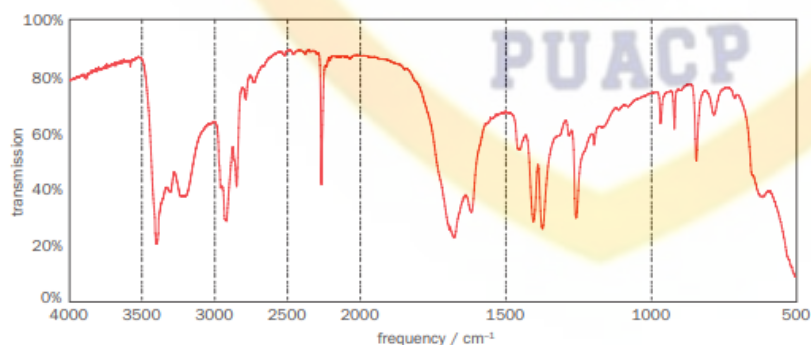
3- The third common method used with solids is to **dissolve the organic compound in a solvent, most commonly carbon tetrachloride (CCl4)**. Again, as was the case with mineral oil, some regions of the spectrum are obscured by

bands in the solvent. Although it is possible to cancel out the solvent from the spectrum by computer or instrumental techniques, the region around 785 cm^{-1} is often obscured by the strong CI-Cl stretch that occurs there.

2.6 Different Regions of IR spectra

An IR spectrum can be divided into two main areas.

1-The left-hand two-thirds of an IR spectrum is where most of the **functional groups** show absorption bands. This region is called the functional group region.

2-The right-hand one third of the IR spectrum is called the **fingerprint region** because it is characteristic of the compound as a whole, just as a fingerprint is characteristic of an individual. Even if two different molecules have the same functional groups, their IR spectra will not be identical, since the functional groups are not in exactly the same environment; this difference is reflected in the pattern of absorption bands in the finger print regions. **Each compound shows a unique pattern in this region**. For example, **2-pentanol and 3-pentanol** have the same functional groups, so they show similar absorption bands in the functional group region. Their fingerprint regions are different, however, because the compounds are different. **Thus a compound can be positively identified by comparing its fingerprint region with the fingerprint region of the spectrum of a known sample of the compound**. The useful information from this spectrum is the presence of the CN and C=O groups and the exact position of the C=O absorption.
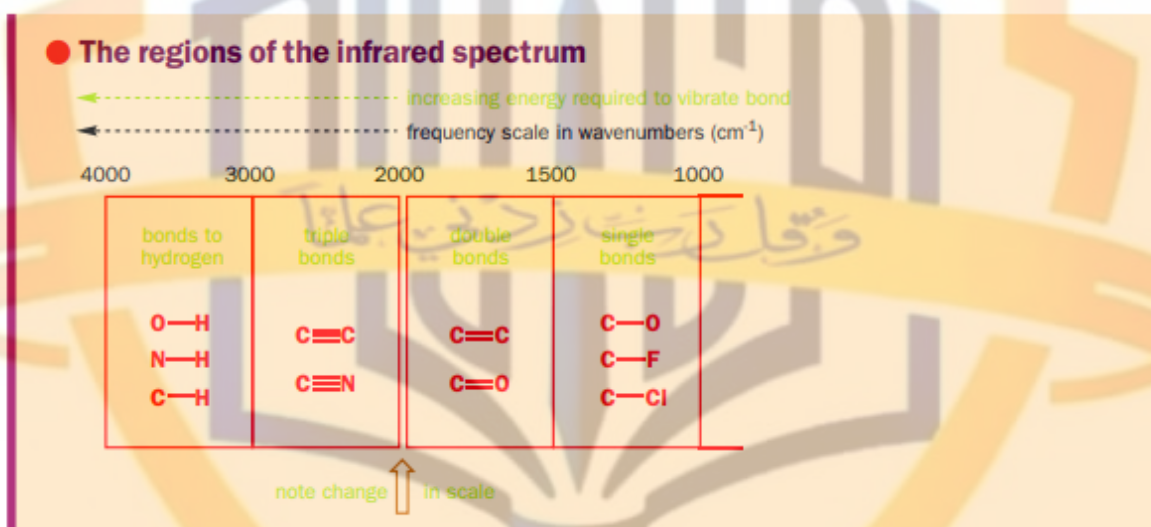
However, it is actually the left-hand half of the spectrum (Functional group region) that is more useful. It can be further divided into three regions.

A-X-H Region: The first region, from about 4000 to about 3000 cm^{-1} is the region for C–H, N–H, and O–H bond stretching. Most of the atoms in an organic molecule (C, N, O, for example) are about the same weight. Hydrogen is an order of magnitude lighter than any of these and so it dominates the stretching frequency by the large effect it has on the reduced mass. The reduced mass of a C–C bond is $(12 \times 12)/(12 + 12)$, i.e. $144/24 = 6.0$. If we change one of these atoms for H, the reduced mass changes to $(12 \times 1)/(12 + 1)$, i.e. $12/13 = 0.92$, but, if we

change it instead for F, the reduced mass changes to (12 × 19)/ (12 + 19), i.e. 228/31 = 7.35. **There is a small change when we increase the mass to 19 (F), but an enormous change when we decrease it to 1 (H).**

B-Even the strongest bonds—triple bonds such as C≡C or C≡N—absorb at slightly lower frequencies than bonds to hydrogen: these are in the next region from about 3000 to 2000 cm^{-1}. All regions of the spectrum follow in logical order of bond strength as the reduced masses are all about the same:

C-Third region consists of double bonds such as C=C and C=O from about 2000–1500 cm^{-1}. Single bonds are at the right- hand end of the spectrum (finger print region).

● **The regions of the infrared spectrum**

increasing energy required to vibrate bond

frequency scale in wavenumbers (cm^{-1})

4000	3000	2000	1500	1000
bonds to hydrogen	triple bonds	double bonds	single bonds	
O—H N—H C—H	C=C C≡N	C=C C=O	C—O C—F C—Cl	

note change in scale

2.6.1   The X–H IR stretches are very different in these four compounds.

The X–H region distinguishes C–H, N–H, and O–H bonds. The reduced masses of the C–H, N–H, and O–H combinations are all about the same. Any difference between the positions of the IR bands of these bonds must then be due to bond strength. In practice, **C–H stretches occur at around 3000 cm^{-1}** (though they are of little use as virtually all organic com- pounds have C–H bonds), **N–H stretches occur at about 3300 cm^{-1}**, and **O–H stretches higher still**. We can

immediately deduce that the O–H bond is stronger than N–H which is stronger than C–H. IR is a good way to measure such bond strengths.

Shapes of X-H groups: The IR peak of an NH group is different from that of an NH2 group. A group gives an independent vibration only if both bond strength and reduced mass are different from those of neighboring bonds. In the case of N–H, this is likely to be true and we usually get a sharp peak at about 3300 cm–1, whether the NH group is part of a simple amine (R_2NH) or an amide (RCONHR).

The NH2 group is also independent of the rest of the molecule, but the two NH bonds inside the NH2 group have identical force constants and reduced masses and so vibrate as a single unit. Two equally strong bands appear, one for the two N–H bonds vibrating in phase (symmetric) and one for the two N–H bonds vibrating in opposition (antisymmetric). The antisymmetric vibration requires more energy and is at slightly higher frequency.

The O–H bands occur at higher frequency, sometimes as a sharp absorption at about 3600 cm–1. However in most cases O-H bond forms hydrogen bonding so, you will see a **broad absorption at anywhere from 3500 to 2900 cm–1**. This is because OH groups form strong hydrogen bonds that vary in length and strength. **The sharp absorption at 3600 cm–1 is the non-hydrogen-bonded OH** and the lower the absorption the stronger the H bond.

Alcohols form hydrogen bonds between the hydroxyl oxygen of one molecule and the hydroxyl hydrogen of another. These bonds are variable in length (though they are usually rather longer than normal covalent O–H bonds) and they slightly weaken the true covalent O–H bonds by varying amounts. When a bond varies in length and strength it will have a range of stretching frequencies distributed about a mean value. Alcohols typically give a rounded absorption at about 3300 cm–1 (contrast the sharp N–H stretch in the same region).
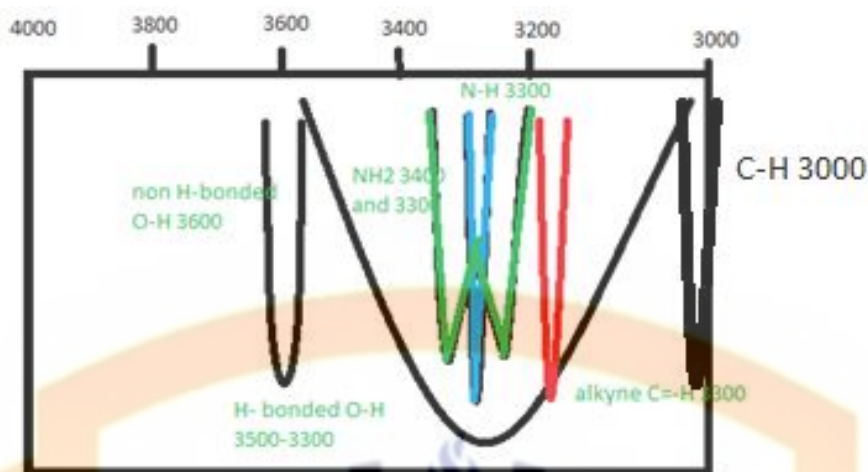
The X–H IR stretches are very different in these four compounds.
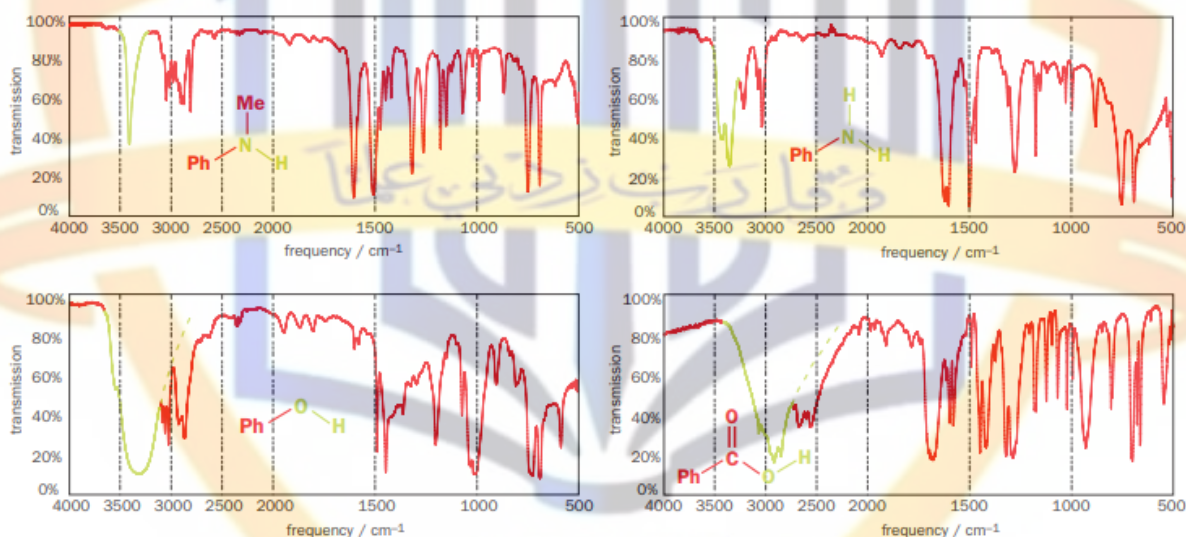
Carboxylic acids (RCO2H) form hydrogen-bonded dimers with two strong H bonds between the carbonyl oxygen atom of one molecule and the acidic hydrogen of the other. These also vary considerably in length and strength and usually give very broad V-shaped absorbances.

Good examples are **paracetamol and BHT**. Paracetamol has a typical sharp peak at 3330 cm^{-1} for the N–H stretch and then a rounded absorption for the hydrogen-bonded O–H stretch from 3300 down to 3000 cm^{-1} in the gap between the N–H and C–H stretches.
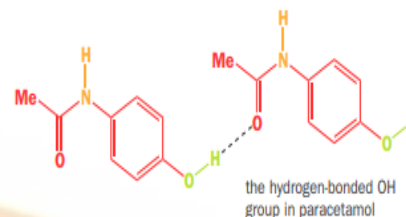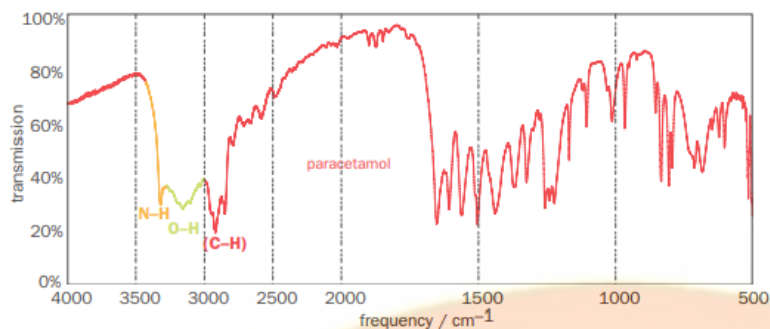
By contrast, BHT has a sharp absorption at 3600 cm⁻¹ as the two large and roughly spherical t-butyl groups prevent the normal H bond from forming.
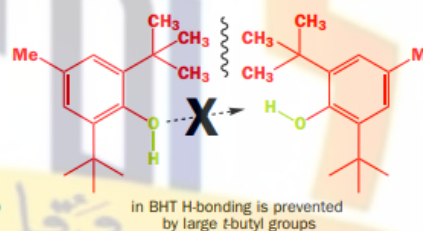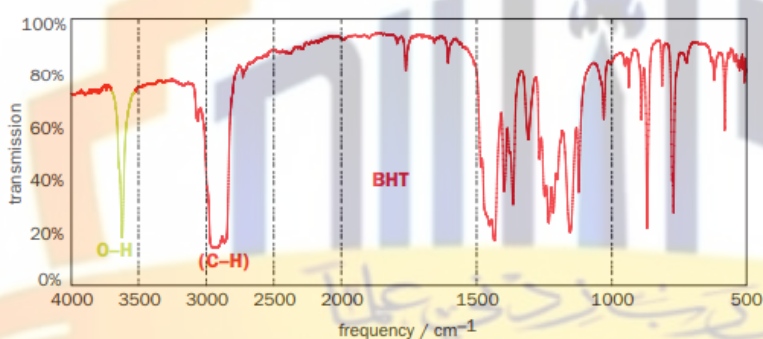

The IR spectrum of a terminal alkyne, R–C≡C–H, will show a strongish sharp peak at around 3300 cm–1 that looks just like an N–H stretch. The displacement of this peak from the usual C–H stretch at about 3000 cm–1 cannot be due to a change in the reduced mass, Actually it is due to a marked increase in bond strength. As R–C≡C–H has "sp" hybridized carbon as compared to sp₃ in alkane, so more "s" character is more near to nucleus and will be shorter and stronger than alkane C–H bonds.
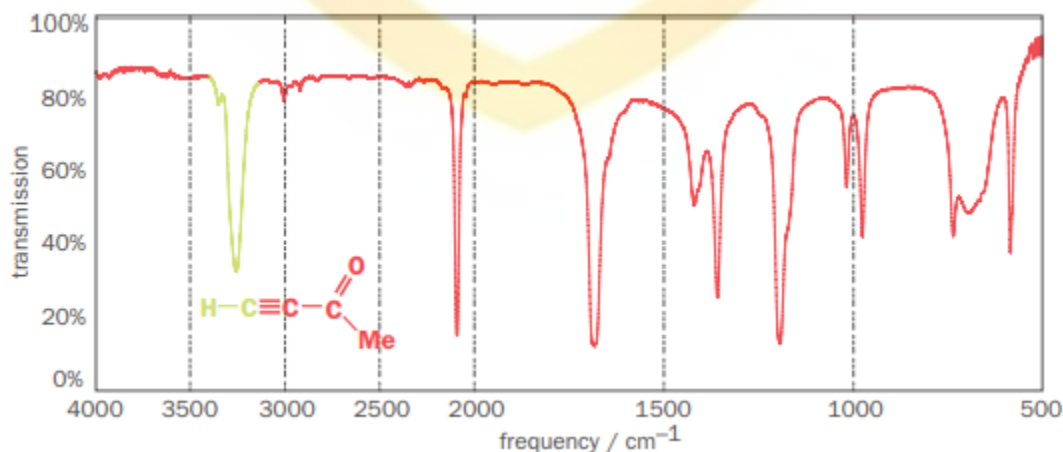
2.6.2 The double bond region is the most important in IR spectra

In the double bond region, there are three important absorptions, those of the carbonyl (C=O), alkene (C=C), and nitro (NO_2) groups. All give rise to sharp bands: C=O to one strong (i.e. intense) band anywhere between 1900 and 1500 cm^{-1}; C=C to one weak band at about 1640 cm^{-1}; and NO_2 to two strong (intense) bands in the mid-1500s and mid-1300s cm^{-1}. The number of bands is easily dealt with. Just as with OH and NH_2, it is a matter of how many identical bonds are present in the same functional group.
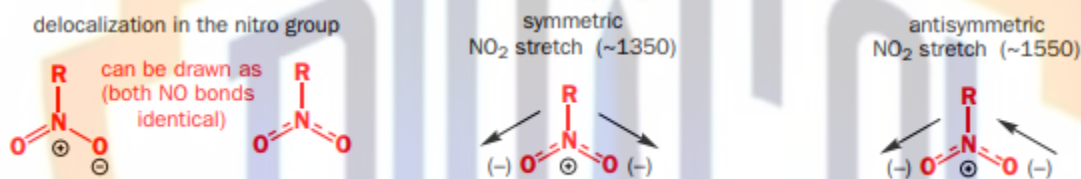
Carbonyl and alkene clearly have one double bond each. The nitro group at first appears to contain two different groups, N+–O– and N=O, but delocalization means they are identical and we see absorption for symmetrical and anti-symmetrical stretching vibrations. As with NH_2, more work is needed for the anti-symmetrical vibration which occurs at higher frequency (>1500 plus cm^{-1}).

2.6.2.1 Strength of IR absorption

The strength of an IR absorption depends on dipole moment. Now what about the variation in strength (i.e. intensity, the amount of energy absorbed)? The strength of an IR absorption varies with the change of dipole moment when the bond is stretched. If the bond is perfectly symmetrical, there is no change in dipole moment and there is no IR absorption. Obviously, the C=C bond is less polar than either C=O or N=O and is weaker in the IR. **Indeed, it may be absent altogether in a symmetrical alkene**. By contrast the carbonyl group is very polar and stretching it causes a large change in dipole moment and C=O stretches are usually the strongest peaks in the IR spectrum. You may also have noticed that O–H and N–H stretches are stronger than C–H stretches (even

though most organic molecules have many more C–H bonds than O–H or N–H bonds): the reason is the same.

This is a good point to remind you of the various deductions we have made so far about IR spectra.

● **Absorptions in IR spectra**

Position of band depends on →	reduced mass of atoms	**light** atoms give **high** frequency
	bond strength	**strong** bonds give **high** frequency
Strength of band depends on →	change in dipole moment	**large** dipole moment gives **strong** absorption
Width of band depends on →	hydrogen bonding	**strong H** bond gives **wide** peak

2.6.3   Single bond region

The single bond region is used as a molecular fingerprint. Single bond vibration occur below 1500 cm^{-1}. However individual bonds may not vibrate independently of the rest of the molecule. The atoms C, N, and O all have about the same atomic weight and C–C, C–N, and C–O single bonds all have about the same strength. In addition, C–C bonds are likely to be joined to other C–C bonds with virtually identical strength and reduced mass, and they have essentially no dipole moments. The only one of these single bonds of any value is **C–O** which is polar enough and different enough (Table 3.7) to show up as a strong absorption at about **1100 cm**$^{-1}$. Some other single bonds such as **C–Cl (weak and with a large reduced mass) are quite useful at about 700 cm–1.** Otherwise the single bond region is usually crowded with hundreds of absorptions from vibrations of all kinds used as a 'fingerprint' characteristic of the molecule but not really open to interpretation. Among the hundreds of peaks in the fingerprint region, there are some of a quite different kind. Stretching is not the only bond movement that leads to IR absorption. Bending of bonds, particularly C–H and N–H bonds, also leads to quite strong peaks. These are called deformations. Bending a bond is

easier than stretching it (which is easier, stretching or bending an iron bar?). Consequently, bending absorptions need less energy and come at lower frequencies than stretching absorptions for the same bonds. These bands may not often be useful in identifying molecules, but you will notice them as they are often strong (they are usually stronger than C=C stretches for example) and may wonder what they are.

Table 3.9 Useful absorptions in the fingerprint region

Frequency, cm^{-1}	Strength	Group	Comments
1440–1470	medium	CH_2	deformation (present in nujol)
~1380	medium	CH_3	deformation (present in nujol)
~1350	strong	NO_2	symmetrical N=O stretch
1250–1300	strong	P=O	double bond stretch
1310–1350	strong	SO_2	antisymmetrical S=O stretch
1120–1160	strong	SO_2	symmetrical S=O stretch
~1100	strong	C–O	single bond stretch
950–1000	strong	C=CH	*trans* alkene (out-of-plane deformation)
~690 *and* ~750	strong	Ar–H	five adjacent Ar–H (out-of-plane)
~750	strong	Ar–H	four adjacent Ar–H (out-of-plane)
~700	strong	C–Cl	single bond stretch

2.7 Carbonyl compounds IR absorption

The carbonyl group is present in aldehydes, ketones, acids, esters, amides, acid chlorides, and anhydrides. This group absorbs strongly in the range from **1850 to 1650 cm^{-1}** because of its large change in dipole moment. Since the C=O stretching frequency is sensitive to attached atoms, the common functional groups already mentioned absorb at characteristic values. Below we provide the normal base values for the C=O stretching vibrations of the various functional groups. The C=O frequency of a ketone, which is approximately in the middle of the range, is usually considered the reference point for comparisons of these values.

Anhydride (band 1) 1810---acid chloride 1800---- anhydride (Band 2) 1760-------- Ester 1735------ Aldehyde 1725-----ketone 1715-----Carboxylic acid (dimeric) 1710--------- amide 1690

1810	1800	1760	1735	1725	1715	1710	1690
Anhydride (band 1)	Acid chloride	Anhydride (band 2)	Ester	Aldehyde	Ketone	Carboxylic acid	Amide

F I G U R E 2 . 3 5 Normal base values for the C=O stretching vibrations for carbonyl groups.

The range of values given in Figure above may be explained through the use of electron-withdrawing effects **(inductive effects, resonance effects, and hydrogen bonding).** The first two effects operate in opposite ways to influence the C=O stretching frequency.

ESTERS: First, an electronegative element may tend to draw in the electrons between the carbon and oxygen atoms through its electron-withdrawing effect, so that the C=O bond becomes somewhat stronger. A higher-frequency (higher-energy) absorption result. Since **oxygen is more electronegative than carbon, this effect dominates in an ester to raise the C=O frequency above that of a ketone.**

AMIDE: Second, a **resonance effect** may be observed when the unpaired electrons on a nitrogen atom conjugate with the carbonyl group, resulting in increased single-bond character and a lowering of the C=O absorption frequency. **This second effect is observed in an amide.** Since nitrogen is less electronegative than an oxygen atom, it can more easily accommodate a positive charge. The resonance structure shown here introduces single-bond character into the C=O group and thereby lowers the absorption frequency below that of a ketone.

Electron-withdrawing effect raises C=O frequency

Resonance effect lowers C=O frequency
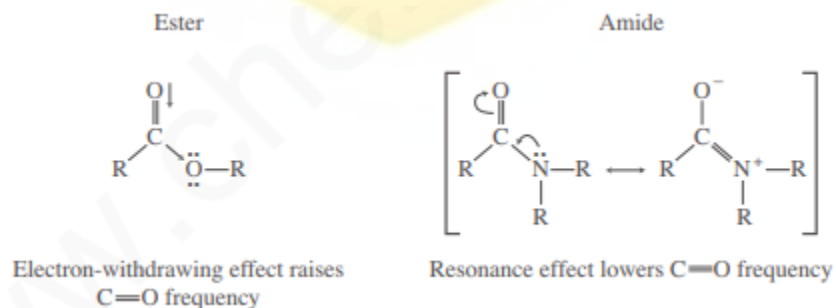
ACID CHLORIDES: In acid chlorides, the highly electronegative halogen atom strengthens the C=O bond through an enhanced inductive effect and shifts the frequency to values even higher than are found in esters.

ANHYDRIDES: Anhydrides are likewise shifted to frequencies higher than are found in esters because of a concentration of electronegative oxygen atoms. In addition, anhydrides give two absorption bands that are due to symmetric and asymmetric stretching vibrations.

CARBOXYLIC ACID: A carboxylic acid exists in **monomeric form only in very dilute solution,** and it absorbs at about 1760 cm^{-1} because of the electron-withdrawing effect just discussed. However, acids in concentrated solution, in the form of neat liquid, or in the solid state (KBr pellet and Nujol) tend to dimerize via hydrogen bonding. This dimerization weakens the C=O bond and lowers the stretching force constant K, resulting in a lowering of the carbonyl frequency of saturated acids to about 1710 cm^{-1}.
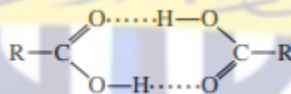

ALDEHYDES: Ketones absorb at a lower frequency than aldehydes because of their additional alkyl group, which is electron donating (compared to H) and supplies electrons to the C=O bond. This electron-releasing effect weakens the C=O bond in the ketone and lowers the force constant and the absorption frequency.

2.8 Factors that Effect C=O stretching vibration:

2.8.1 Conjugation Effects.

The introduction of a C=C bond adjacent to a carbonyl group results in delocalization of the p electrons in the C=O and C=C bonds. This conjugation increases the single-bond character of the C=O and C=C bonds in the resonance hybrid and hence lowers their force constants, resulting in a lowering of the frequencies of carbonyl and double-bond absorption. Conjugation with triple bonds also shows this effect.
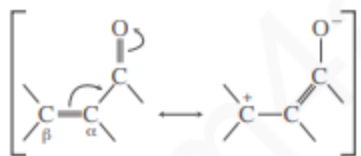
Generally, the introduction of an alpha, Beta double bond in a carbonyl compound results in a 25- to 45-cm^{-1} lowering of the C=O frequency from the base value given in Figure above. A similar lowering occurs when an adjacent aryl group is introduced. Further addition of unsaturation (gamma, delta) results in a further shift to lower frequency, but only by about 15 cm^{-1} more. In addition, the C=C absorption shifts from its "normal" value, about 1650 cm^{-1}, to a lower-frequency value of about 1640 cm^{-1}, and the C=C absorption is greatly intensified. Often, two closely spaced C=O absorption peaks are observed for these conjugated systems, resulting from two possible conformations, the s-cis and s-trans. The s-cis conformation absorbs at a frequency higher than the s-trans conformation. In some cases, the C=O absorption is broadened rather than split into the doublet.

The following examples show the effects of conjugation on the C=O frequency.

α ,β-unsaturated ketones--------1715-1690, Aryl substituted aldehyde---1725-1700, aryl susbstituted acids---1710-1680

Conjugation does not reduce the C=O frequency in amides. The introduction of a,b unsatu- ration causes an increase in frequency from the base value given in Figure 2.35. Apparently, the introduction of sp2-hybridized carbon atoms removes electron density from the carbonyl group and strengthens the bond instead of interacting by resonance as in other carbonyl examples. Since the parent amide group is already highly stabilized (see p. 53), the introduction of the C=C unsaturation does not overcome this resonance.

Ring-Size Effects.

Six-membered rings with carbonyl groups are unstrained and absorb at about the values given in Figure 2.35. Decreasing the ring size increases the frequency of the C=O absorption for the reasons discussed in Section 2.10 (C=C stretching vibrations and exocyclic double bonds; p. 41). All of the functional groups listed

in Figure 2.35, which can form rings, give increased frequencies of absorption with increased angle strain. For ketones and esters, there is often a 30-cm−1 increase in frequency for each carbon removed from the unstrained six-membered ring values. Some examples are

In ketones, larger rings have frequencies that range from nearly the same value as in cyclohexanone (1715 cm−1) to values slightly less than 1715 cm−1. For example, cycloheptanone absorbs at about 1705 cm−1.

a-Substitution Effects. When the carbon next to the carbonyl is substituted with a chlorine (or other halogen) atom, the carbonyl band shifts to a higher frequency. The electron-withdrawing effect removes electrons from the carbon of the C=O bond. This removal is compensated for by a tightening of the p bond (shortening), which increases the force constant and leads to an increase in the absorption frequency. This effect holds for all carbonyl compounds.

In ketones, two bands result from the substitution of an adjacent chlorine atom. One arises from the conformation in which the chlorine is rotated next to the carbonyl, and the other is due to the conformation in which the chlorine is away from the group. When the chlorine is next to the carbonyl, nonbonded electrons on the oxygen atom are repelled, resulting in a stronger bond and a higher absorption frequency. Information of this kind can be used to establish a structure in rigid ring systems, such as in the following examples:

Axial chlorine ~1725 cm−1

Equatorial chlorine ~1750 cm−1

Hydrogen-Bonding Effects. Hydrogen bonding to a carbonyl group lengthens the C=O bond and lowers the stretching force constant K, resulting in a lowering of the absorption frequency. Examples of this effect are the decrease in the C=O frequency of the carboxylic acid dimer (p. 53) and the lowering of the ester C=O frequency in methyl salicylate caused by intramolecular hydrogen bonding:

C OCH3 O H O • • • Methyl salicylate 1680 cm−1

HOW TO APPROACH THE ANALYSIS OF A SPECTRUM (OR WHAT YOU CAN TELL AT A GLANCE)

When analyzing the spectrum of an unknown, concentrate your first efforts on determining the presence (or absence) of a few major functional groups.

The C=O, O-H, N-H, C-O, C=C, C=-C, C=-N, and NO2 peaks are the most conspicuous and give immediate structural information if they are present. Do not try to make a detailed analysis of the C-H absorptions near 3000 cm-1; almost all compounds have these absorptions. Do not worry about subtleties of the exact environment in which the functional group is found. Following is a major checklist of the important gross features.

1. Is a carbonyl group present? The C=O group gives rise to a strong absorption in the region 1820–1660 cm-1. The peak is often the strongest in the spectrum and of medium width. You can't miss it.

2. If C=O is present, check the following types (if it is absent, go to step 3):

ACIDS Is O-H also present?

• Broad absorption near 3400–2400 cm-1 (usually overlaps C-H).

AMIDES Is N-H also present?

• Medium absorption near 3400 cm-1; sometimes a double peak with equivalent halves. ESTERS Is C-O also present?

• Strong-intensity absorptions near 1300–1000 cm-1.

ANHYDRIDES Two C=O absorptions near 1810 and 1760 cm-1.

ALDEHYDES Is aldehyde C-H present?

• Two weak absorptions near 2850 and 2750 cm-1 on right side of the aliphatic C-H absorptions.

KETONES The preceding five choices have been eliminated.

1. If C=O is absent:

   ALCOHOLS, PHENOLS Check for O-H.

   • Broad absorption near 3400–3300 cm-1.

   • Confirm this by finding C-O near 1300–1000 cm-1.

   AMINES Check for N-H.

   • Medium absorption(s) near 3400 cm-1.

ETHERS Check for C-O near 1300–1000 cm−1 (and absence of O-H near 3400 cm−1).

2. Double bonds and/or aromatic rings

•C=C is a weak absorption near 1650 cm.

• Medium-to-strong absorptions in the region 1600–1450 cm−1; these often imply an aromatic ring.

• Confirm the double bond or aromatic ring by consulting the C-H region; aromatic and vinyl C-H occur to the left of 3000 cm−1 (aliphatic C-H occurs to the right of this value).

5. Triple bonds

•C≡-N is a medium, sharp absorption near 2250 cm−1. •C≡-C is a weak, sharp absorption near 2150 cm−1. • Check also for acetylenic C≡-H near 3300 cm−1.

6. Nitro groups

• Two strong absorptions at 1600–1530 cm−1 and 1390–1300 cm−1.

7. Hydrocarbons

• None of the preceding is found. • Major absorptions are in C-H region near 3000−1. • Very simple spectrum; the only other absorptions appear near 1460 and 1375 cm−1.

The beginning student should resist the idea of trying to assign or interpret every peak in the spectrum. You simply will not be able to do it. Concentrate first on learning these major peaks and recognizing their presence or absence. This is best done by carefully studying the illustrative spectra in the sections that follow.