

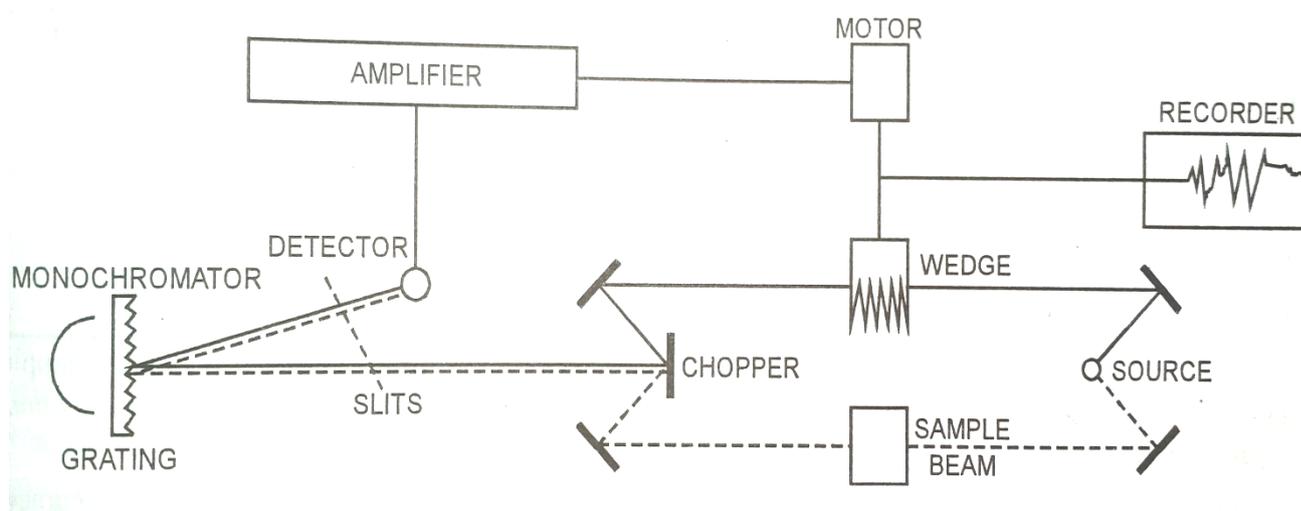
The modern double beam infra-red spectra consists of five main parts – radiation source, monochromator, detector, amplifier and a recorder. The flow-sheet diagram of a double beam IR spectrometer.

Radiation source .the most important infra red radiation is the Nernst glower which consists of asintered mixture of the oxides of Zr , y and Er(erbium).

Monochromator.To obtain monochromator radiations optical prisms are used.

Cell containers.the most common material for the cell containers of the prism is NaCl since it is transparent to infra red radiations down to 625cm^{-1}

Detectors .Most of the modern instruments use thermopile detectors..these work on the principle that if two different metal wires are joined head to tail then a difference in temperature between head and tail causes a current to flow in the wires.



MOLECULAR VIBRATIONS

There are two types of fundamental vibrations for molecules –stretching and bending .

In stretching vibrations ,the distance between the atoms remain in the same bond axis.on the other hand ,in bending vibrations ,the positions of the atoms change with respect to the original bond axis.these two types of vibrations are shown in fig 1.16 for an AX₂ system such as-NH₂-CH₃,-NO₂ etc.

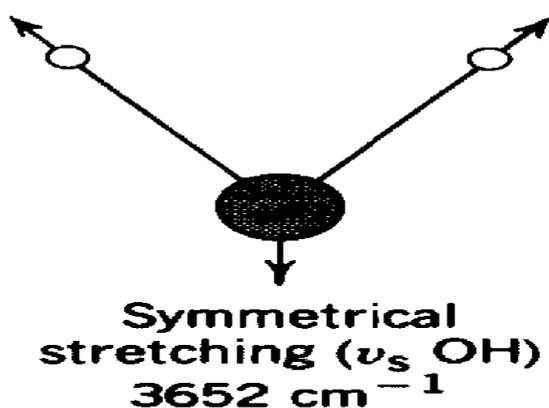
We know that more energy is required to stretch than to bend a spring .In a similar way, we can safely say that stretching vibrations require more energy than bending vibrations.in other words,stretching absorption of a bond will appear at higher energy i.e.higher wavenumber in

the infra-red spectrum than the bending vibrations of the same bond. Bending vibrations are also called deformation vibrations.

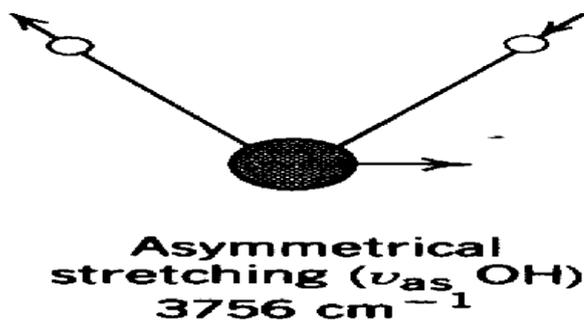
In nut shell absorption of infra red radiations correspond to energy changes of the order 1.90-11.44kcal mol⁻¹ and this amount of energy is sufficient to bring out the changes in the changes in the stretching and bending vibrational frequencies of colvant bonds in most of the organic compounds .

Types of stretching vibrations

- (a) Symmetric stretching. A stretching vibration is said to a symmetric if all the bonds are simultaneously stretched or compressed .It is denoted by V_{sym}



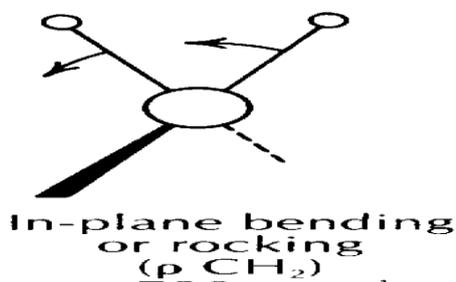
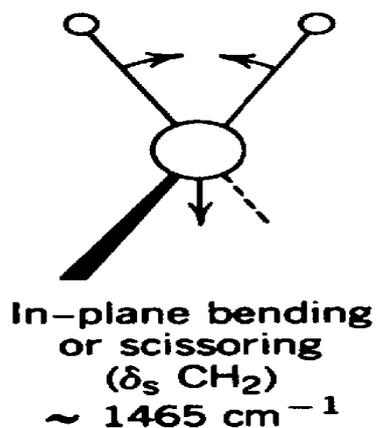
- (b) Asymmetric stretching. A stretching vibration is said to b a antisymmetric if one bond is being stretched ,while the other is being compressed .It is denoted by V_{asym} .



Types of bending vibrations

- (a) Symmetric stretching. In this type the movement of the atoms with respect to particular atom in a molecule is in the same direction

(b) Asymmetric vibration. In this type one atom approaches the central atom, while the other atom departs from it



Calculation of the vibrational frequency .

The frequency of the stretching vibration of any bond can be calculated fairly accurately by the application of the hooke's law.

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{m_1 m_2 (m_1 + m_2)}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\bar{\nu} = v/c = \frac{1}{2\pi c} \sqrt{\frac{k}{m_1 m_2 / (m_1 + m_2)}} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \dots(i)$$

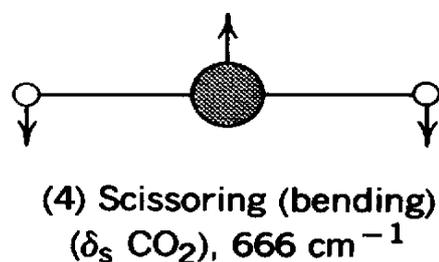
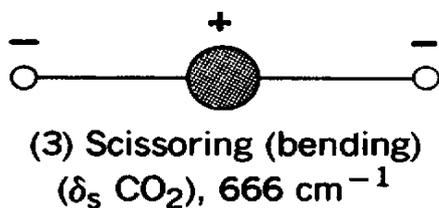
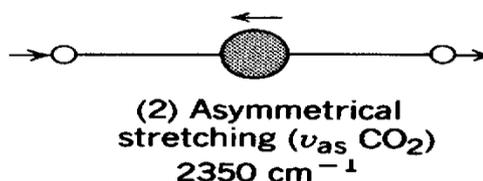
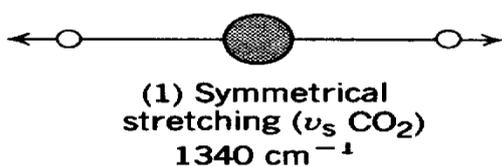
The value of k for single, double and triple bond are approx. 5, 10 and 15 x 10¹⁰ dynes/cm respectively. In the SI unit value of single, double and triple bond are approx. 500 Nm⁻¹, 1000 Nm⁻¹ and 1500 Nm⁻¹ respectively.

SELECTION RULES

Infrared light is absorbed only when a change in dipole character of the molecule takes place. Complete symmetry about a bond eliminates some absorption bands. Clearly, some of the fundamental vibrations are Infra-red active and some are not. It is governed by the selection rules which are explained below:

- (a) If a molecule has a centre of symmetry, then the vibrations are centrosymmetric and are inactive in the Infra-red but are active in the Raman.
- (b) The vibrations which are not centrosymmetric are active in Infra-red but inactive in Raman.

Since in most of the organic compounds, the functional groups are not centrosymmetric, Infra-red spectroscopy is most informative. Consider various vibrations in case of CO_2 .



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The above vibrations are all fundamental vibrations of carbon dioxide. Since (i) does not give rise to any change in dipole-moment, it is infra-red inactive. Asymmetric stretching causes a net change in dipole-moment and thus is infra-red active and absorbs at 2350cm^{-1} . Vibrations (iii) and (iv) are said to be degenerate. The bending of bonds in the molecule are identical but occur in perpendicular planes and thus appear in the same position ($\nu = 667 \text{cm}^{-1}$) in the spectrum. Thus the spectrum of carbon dioxide consists of two bands (i) 2350cm^{-1} due to asymmetric stretching and (ii) 667cm^{-1} due to bending vibrations..

FINGERPRINT REGION.

One of the most important application of Infra-red spectroscopy is to determine the identity of two compounds. Two identical compounds have exactly the same spectra when run in the same medium under similar conditions. The region below 1500cm^{-1} is rich in many absorptions which are caused by bending vibrations and those resulting from the stretching vibrations of C-C, C-O and C-N. In a spectrum the number of bending vibrations is usually the number of stretching vibrations. The said region is usually rich in absorption bands and shoulders. It is called Finger print region. Some molecules containing the functional group show similar absorption above 1500cm^{-1} but their spectra differ in finger print region. Finger print region can be sub divided into three regions as follows

- (a) $1500-1350\text{cm}^{-1}$
- (b) $1350-1000\text{cm}^{-1}$
- (c) Below 1000cm^{-1}

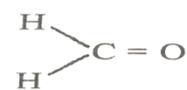
Factors affecting vibrational frequency

The frequency of absorption of a bond in its IR spectrum can be calculated with the help of Hooke's law. But the calculated for band is nearly in agreement with the actually observed value. The calculated value has never been found equal to experimental value. It is because of following factors.

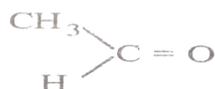
(1) Electronic effects (2) Hydrogen bonding (3) Vibrational coupling

(1) **Electronic effects.** On changing the substituents in the neighbourhood of a particular group the absorption of that group changes because of electronic effects such as inductive effect and resonance (or mesomeric effect). These electronic influence the C=O and C=C stretching vibrational to a considerable extent. These effects work together and cannot be isolated from one another.

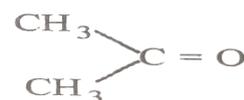
(a) **Inductive effect.** Introduction of increasing number of electron donating alkyl groups (+I effect) in the neighbourhood of the $>\text{C}=\text{O}$ bond, the bond length increases or decreases the bond strength. As a result the force constant decreases and the absorption shifts to lower wave numbers.



Formaldehyde
1740 cm^{-1}



Acetaldehyde
1725 cm^{-1}

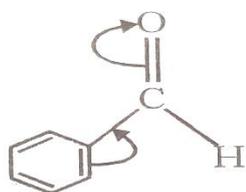


Acetone
1715 cm^{-1}

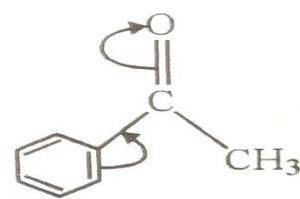
(b) **Resonance effect.** Conjugation decreases the absorption frequency or wave number of ethylenic double bond (C=C) in conjugation and the carbonyl group (C=O) in conjugation with ethylenic group aromatic ring. This is because of the that conjugation increases the bond length and decreases the bond strength of the group.



Methyl vinyl ketone
1725 \rightarrow 1690 cm^{-1}



Benzaldehyde
1740 \rightarrow 1700 cm^{-1}

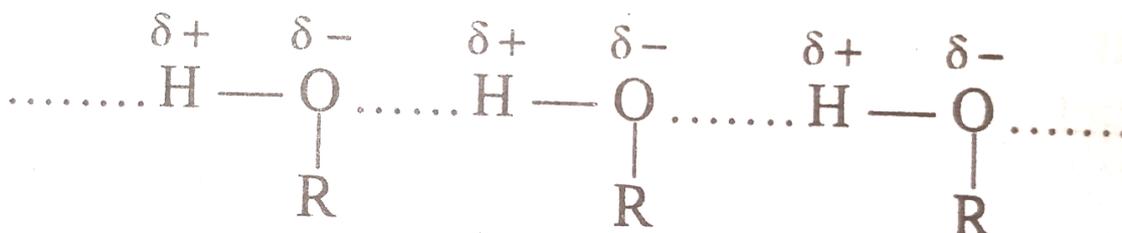


Acetophenone
1725 \rightarrow 1690 cm^{-1}

2. Hydrogen Bonding. Hydrogen bonding shifts the absorption frequencies of O-H bands of alcohols, phenols and carboxylic acid and of N-H bonds in amines. Explanation for this is offered below by taking the example of alcohols.

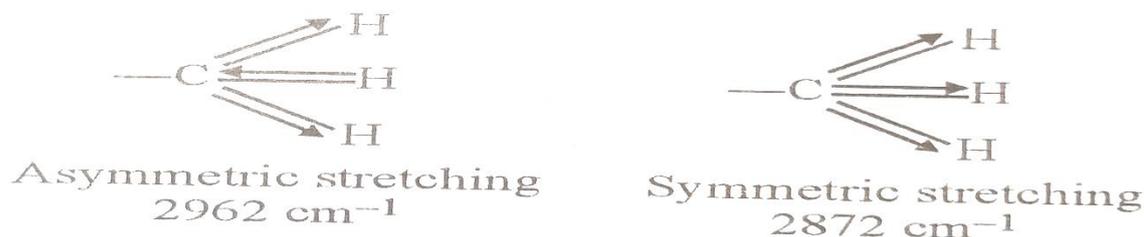
The hydrogen bonding in molecules of alcohol is represented as under.

Because of H-bonding the length of O-H bond increases. Consequently O-H bond weakens and hence the force constant decreases which moves the absorption frequency to lower wave numbers.



3. Vibrational coupling An isolated C-H bond has only one stretching frequency. However if two such C-H bonds share a common carbon atoms such as in a CH₂ group, then the two

C-H stretching vibrations interact mechanically to give rise to two coupled vibrations, each one of which occurs at a frequency from that of the isolated C-H. These are called symmetric and asymmetric vibrations.



HYDROCARBONS: ALKANES, ALKENES, AND ALKYNES

A. Alkanes

B. Alkanes show very few absorption bands in the infrared spectrum. They yield four or more C-H stretching peaks near 3000 cm⁻¹ plus CH₂ and CH₃ bending peaks in the range 1475–1365 cm⁻¹.

C.

B. Alkenes

Alkenes show many more peaks than alkanes. The principal peaks of diagnostic value are the C-H stretching peaks for the *sp*² carbon at values greater than 3000 cm⁻¹, along with C-H peaks for the *sp*³ carbon atoms appearing below that value. Also prominent are the out-of-plane bending peaks that appear in the range 1000–650 cm⁻¹. For unsymmetrical compounds, you should expect to see the C=C stretching peak near 1650 cm⁻¹.

C-H Stretch for *sp*² C-H occurs at values greater than 3000 cm⁻¹ (3095–3010 cm⁻¹).

C-H Out-of-plane (oop) bending occurs in the range 1000–650 cm⁻¹.

These bands can be used to determine the degree of substitution on the double bond (see discussion). C=C Stretch occurs at 1660–1600 cm⁻¹; conjugation moves C=C stretch to lower frequencies and increases the intensity. Symmetrically substituted bonds (e.g., 2,3-dimethyl-2-butene) do not absorb in the infrared (no dipole change). Symmetrically disubstituted (*trans*) double bonds are often vanishingly weak in absorption; *cis* are stronger

Alkynes

Terminal alkynes will show a prominent peak at about 3300 cm^{-1} for the *sp*-hybridized C-H. A $\text{C}\equiv\text{C}$ will also be a prominent feature in the spectrum for the terminal alkyne, appearing at about 2150 cm^{-1} . The alkyl chain will show C-H stretching frequencies for the *sp*³ carbon atoms. Other features include the bending bands for CH_2 and CH_3 groups. Nonterminal alkynes will not show the C-H band at 3300 cm^{-1} .

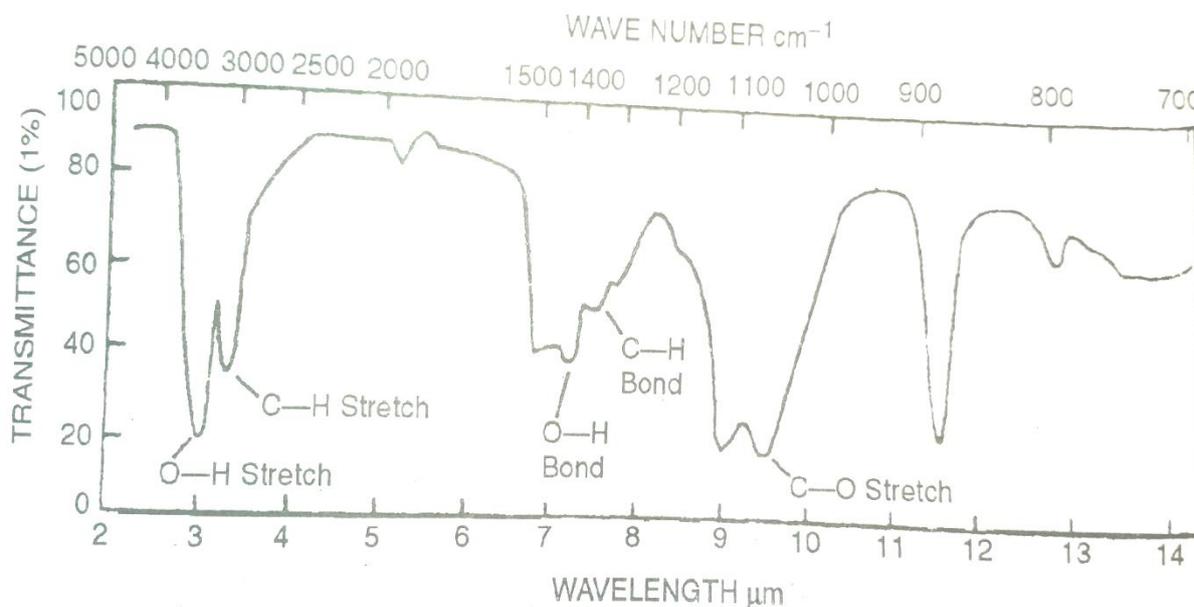
ALCOHOLS AND PHENOLS

Alcohols and phenols will show strong and broad hydrogen-bonded O-H stretching bands centered between 3400 and 3300 cm^{-1} . In solution, it will also be possible to observe a “free” O-H (non H-bonded) stretching band at about 3600 cm^{-1} (sharp and weaker) to the left of the hydrogen-bonded O-H peak. In addition, a C-O stretching band will appear in the spectrum at 1260 – 1000 cm^{-1} .

ALCOHOLS AND PHENOLS

O-H The free O-H stretch is a *sharp* peak at 3650 – 3600 cm^{-1} . This band appears in combination with the hydrogen-bonded O-H peak when the alcohol is dissolved in a solvent (see discussion).ⁿ The hydrogen-bonded O-H band is a *broad* peak at 3400 – 3300 cm^{-1} . This band is usually the only one present in an alcohol that has not been dissolved in a solvent (neat liquid). When the alcohol is dissolved in a solvent, the free O-H and hydrogen-bonded O-H bands are present together, with the relatively weak free O-H on the left (see discussion).ⁿ C-O-H Bending appears as a broad and weak peak at 1440 – 1220 cm^{-1} , often obscured by the CH_3 bendings.^m C-O Stretching vibration usually occurs in the range 1260 – 1000 cm^{-1} . This band can be used to assign a primary, secondary, or tertiary structure to an alcohol (see discussion).

Infra red spectrum of ethanol.



ETHERS

Ethers show at least one C-O –C band in the range 1300–1000 cm⁻¹. Simple aliphatic ethers can be distinguished from alkanes by the presence of the C-O-C band. In all other respects, the spectra of simple ethers look very similar to those of alkanes. Aromatic ethers, epoxides, and acetals are discussed in this section

CARBONYL COMPOUNDS

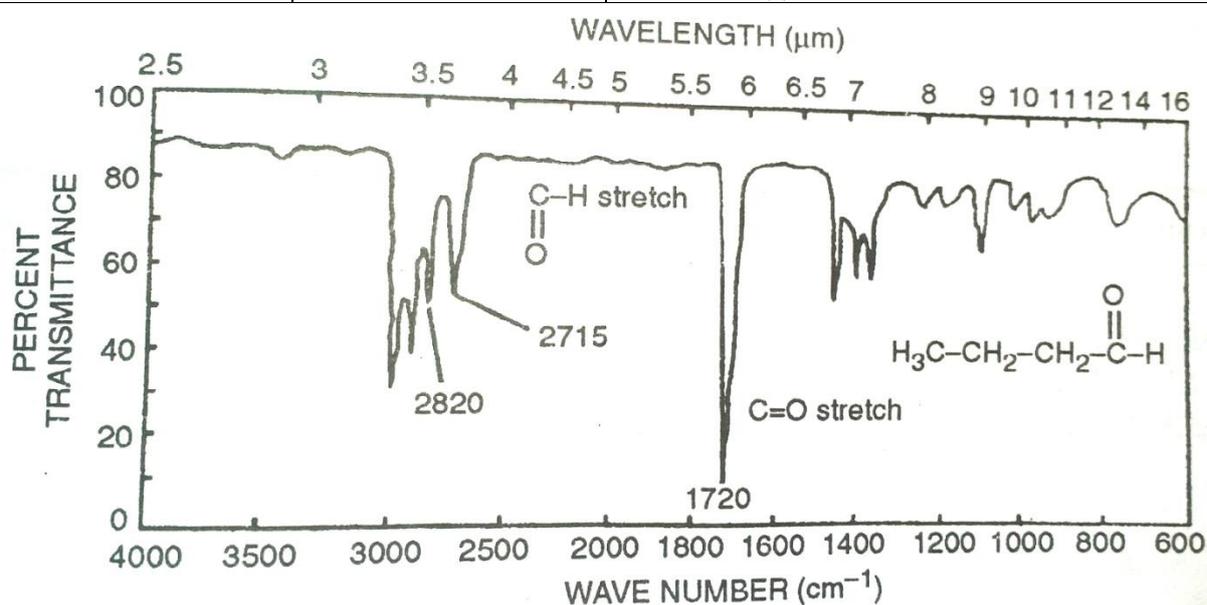
The carbonyl group is present in aldehydes, ketones, acids, esters, amides, acid chlorides, and anhydrides. This group absorbs strongly in the range from 1850 to 1650 cm⁻¹ because of its large change in dipole moment. Since the C=O stretching frequency is sensitive to attached atoms, the common functional groups already mentioned absorb at characteristic values. Figure 2.35 provides 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.

Aldehydes

Aldehydes show a very strong band for the carbonyl group (C=O) that appears in the range of 1740–1725 cm⁻¹ for simple aliphatic aldehydes. This band is shifted to lower frequencies with conjugation to a C=C or phenyl group. A very important doublet can be observed in the C-H stretch region for the aldehyde C-H near 2850 and 2750 cm⁻¹. The presence of this doublet allows aldehydes to be distinguished from other carbonyl-containing compounds

Compound	Type of vibration	Position of band (cm ⁻¹) and its intensity
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(i) saturated aliphatic aldehydes (R-C=O)	C=O stretching	1740-1720(s)
(ii) α , β -unsaturated aliphatic aldehydes (R-CH=CH-CH=O)	C=O stretching	1705-1680(s)
(iii) Aromatic aldehydes (Ar-CH=O)	C=O stretching	1715-1695
(iv) All aldehydes	C-H stretching	2860-2820(s) 2760-2720(s)



APPLICATIONS OF IR SPECTROSCOPY

1. Identification of an organic compound. If two substances have identical I.R spectra under similar conditions they must be same.
2. Structure determination. This technique helps to establish the structure of an unknown compound.
3. Checking the purity of compound. A pure compound gives clear I.R spectrum, where as an impure compound gives a blurred spectrum along with many bands which can not be interpreted.
4. The examination of the I.R spectrum can help in following the progress of the reaction.
5. Distinction between inter and intramolecular hydrogen bonding. The information about the nature of hydrogen bonding present in an organic compound is best obtained by the study of compound in dilute solutions using non-polar solvents.

