| Subject | Chemistry |
|---|---|
| **Paper No and Title** | **Paper 12: Organic Spectroscopy** |
| **Module No and Title** | **Module 10: Application of IR spectroscopy and interpretation of IR spectrum** |
| **Module Tag** | **CHE_P12_M10_e-Text** |

| **Principal Investigator** | | **Co- Principal Investigator and Technical Coordinator** |
|---|---|---|
| **Prof A.K.Bakhshi**<br>Sir Shankar Lal Professor,<br>Department of Chemistry<br>University of Delhi | | **Dr Vimal Rarh**<br>Deputy Director, Centre for e-Learning and Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi<br>*Specialised in : e-Learning and Educational Technologies* |
| **Paper Coordinator** | **Content Writer** | **Reviewer** |
| **Prof Diwan S Rawat**<br>Department of Chemistry<br>University of Delhi | **Prof Diwan S Rawat**<br>Department of Chemistry<br>University of Delhi<br>**Dr. Deepak Kumar**<br>Assistant Professor<br>Department of Chemistry<br>University of Delhi | **Prof MSM Rawat**<br>Department of Chemistry<br>Hemwati Nandan Bahuguna Garhwal University |
| **Anchor Institute : SGTB Khalsa College, University of Delhi** | | |

## TABLE OF CONTENTS

## 1. Learning Outcomes

After studying this module, you shall be able to

- To understand the position, intensity and shape of an absorption band
- To understand the effect of bond strength on absorption frequency
- To understand how H-bonding affect the absorption band
- To know about the possible modes of vibration in aliphatic and aromatic hydrocarbons and their frequency values

## 2. Introduction

Infrared spectroscopy is a simple and reliable technique widely used in both organic and inorganic chemistry. It is also used in quality control analysis in industrial, scientific, and medical applications. It is employed in forensic analysis in civil and criminal analysis also. IR spectroscopy is used in dynamic measurement, quality control and monitoring applications. Some examples are the long-term unattended measurement of $CO_2$ concentrations in greenhouses and growth chambers by infrared gas analysers.

## 3. Detection of functional groups

The IR region is divided into group frequency region and fingerprint region. Range of group frequency is 4000-1500 $cm^{-1}$ while that of finger print region is 1500-400 $cm^{-1}$. Each functional group has their characteristic fundamental vibration which gives rise to absorption at a certain frequency range in the spectrum. Thus the presence or absence of absorptions at a certain frequency in the infrared spectrum can be interpreted in terms of the presence or absence of certain structural features in the compounds. For example, the oxygen in a compound containing carbon, hydrogen and oxygen can only be present as O-H, C=O, or C-O-C or a combination of these such as ester, carboxylic acid or anhydride. The presence or absence of absorption in the carbonyl region (1870-1650 $cm^{-1}$) or hydroxyl region (3700-3200 $cm^{-1}$) can serve to ascertain some of these possibilities. It is, thus possible to establish a co-relation between infrared absorptions and functional groups.

## 4. Identification of substances

Another important application of infrared spectroscopy is the identification of a compound with a reference infrared spectrum. If all the peaks of the unknown compound match with the reference, the compound can be identified. In an IR spectrum, a large number of absorption bands are observed and there is no chance to have the exact same IR spectrum for any two compounds. So if two compounds have identical IR spectra then both of them must be same structurally. IR spectra of two enantiomeric compounds are identical therefore IR spectroscopy fails to distinguish between enantiomers.

For example, consider the IR spectrum of benzaldehyde is observed as follows.

| | |
|---|---|
| C-H stretching of aromatic ring | 3080 $cm^{-1}$ |
| C-H stretching of aldehyde | 2860 $cm^{-1}$ and 2775 $cm^{-1}$ |

| | |
|---|---|
| C=O stretching of an aromatic aldehyde | 1700 $cm^{-1}$ |
| C=C stretching of an aromatic ring | 1595 $cm^{-1}$ |
| C-H bending | 745 $cm^{-1}$ and 685 $cm^{-1}$ |

No other compound then benzaldehyde produces same IR spectra as shown above.

## 5. To study the progress of a chemical reaction

Progress of a chemical reaction can be determined by examining the small portion of the reaction mixture. As the reaction proceeds, some changes occur, such as the disappearance of a characteristic absorption band of the reactant group and/or the appearance of the characteristic absorption band of the product group due to formation of product. For example take an example of the reduction of a saturated aliphatic ketone to form secondary alcohol. Ketone forms a strong band at about 1710 $cm^{-1}$. When it is subjected to reduction, it forms butan-2-ol which absorbs at 3300 $cm^{-1}$ due to O-H stretching vibrations. The progress of reaction can be studied in this manner from time to time and the reduction will be complete when a strong band due to carbonyl group will be missing and only a band due to O-H group is present.

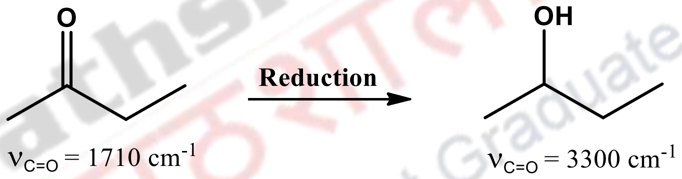

**Fig. 1: Monitoring the progress of a reaction using IR spectroscopy**

## 6. Detection of impurities

IR spectrum of the test sample to be determined is compared with the standard compound. If any additional peaks are observed in the IR spectrum, then it is due to impurities present in the compound being tested. Sometimes detecting impurities by IR techniques may be misleading because infrared bands are often not very intense and therefore small amounts of impurities remain undetected. However, the presence of impurities can be detected provided they absorb fairly strongly in that part of the spectrum where the main component does not. For example, the presence of cyclohexanone is readily detected as an impurity in cyclohexanol on account of its intense C=O absorption band. The “difference method” is sometimes useful in recording the actual spectrum of the impurities by placing the impure samples in the sample beam and the same thickness of the pure sample in the reference beam.

## 7. Study of keto-enol tautomerism

IR spectroscopy is useful in determining the keto-enol tautomerism. The β-diketones and β-ketoesters exist as a tautomeric mixtures and hence their IR spectra will show the absorptions due to both keto and enol forms. And also the absorption due to the C=O group will be lowered due to the intramolecular hydrogen bonding in such compounds. In addition, a broad O-H stretching frequency and a C=C stretching frequency will also be observed.

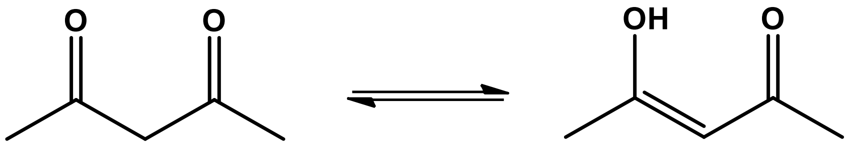

**Fig. 2: Determination of keto-enol tautomerism using IR spectroscopy**

## 8. Study of Geometrical Isomerism

As we know that only those vibrations are IR active which causes a change in dipole moment of the molecule and the intensity of the absorption depends upon the change in the dipole moment. By using this fact, we can distinguish between cis and trans isomers.

In cis isomers, there occurs a change in the dipole moment, whereas the trans isomer is non-polar with zero dipole moment. Generally, the configuration around a di-substituted double bond is easy to determine from the IR spectra. The trans configuration gives a characteristic band at 965 cm$^{-1}$, while the cis configuration gives a weak band at 1640 cm$^{-1}$ and a medium band at 3020 cm$^{-1}$.

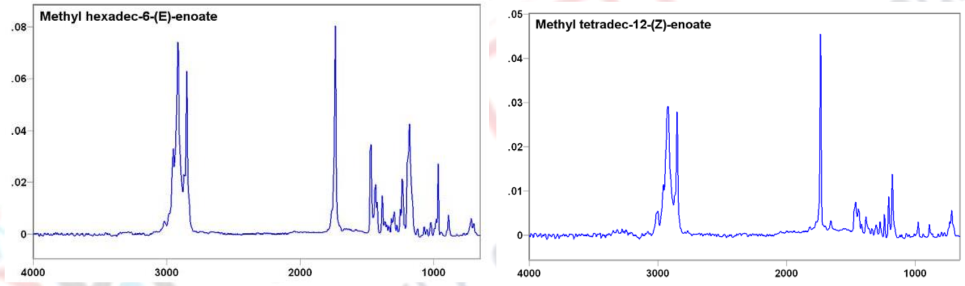

**Fig. 3: Differentiation between cis and trans isomers using IR spectroscopy**

Similarly the absorption peak due to C≡C stretching (IR active) is observed in $CH_3$-C≡CH, whereas it is absent in the IR spectrum of $CH_3$-C≡C-$CH_3$ (IR inactive).

## 9. Determination of orientation in aromatic compounds

The IR absorption bands in the region 675-900 cm$^{-1}$ due to out-of-plane bending vibrations gives information about the relative positions of substituents on the benzene ring. The position of these absorption bands in this region depends on the number of adjacent hydrogen atoms present in the ring. The o-substituted benzenes show a strong band in the region 735-770 cm$^{-1}$ but no band in the region 690-710 cm$^{-1}$. The m-disubstituted benzenes show two strong bands in the regions 680-725 cm$^{-1}$ and 750-810 cm$^{-1}$, whereas p-disubstituted benzenes exhibit only one band in the region 800-860 cm$^{-1}$.

## 10. Study of hydrogen bonding

IR spectroscopy is useful in detecting hydrogen bonding and in distinguishing inter-molecular and intra-molecular hydrogen bonding. Inter-molecular hydrogen bonding involves association of two or more molecules of the same or different compound, and it may result in dimer molecules as in carboxylic acids. Intra-molecular hydrogen bonds are formed when the proton donor and acceptor are present in a single molecule with a close proximity that allows the required overlapping of orbitals. The extent of both inter-molecular and intra-molecular hydrogen bonding depends upon the temperature. The inter-molecular hydrogen bonding move the X-H stretching bands to lower frequencies usually with increased intensity and band widening. Thus hydrogen bonding changes the position and shape of an infrared absorption band. Intramolecular hydrogen bonding however is not dependent on concentration and usually give sharp and well-defined bonds.

## 11. Identification of alcohol in breath analyzer

IR spectroscopy can be used in detecting alcohol level in the blood of a suspected drunk driver. The Intoxilyzer is the most current and accurate device for measuring blood alcohol levels. It is essentially an IR spectrometer that is specifically tuned to measure the intensity of the signals for the C-H bonds in ethanol. The diffusion of blood alcohol through the lung occurs into the blow of breath which is subjected to IR spectroscopy. For example, the Intoxilyzer 5000 measures the intensity of absorption at the five frequencies shown in the figure given below.

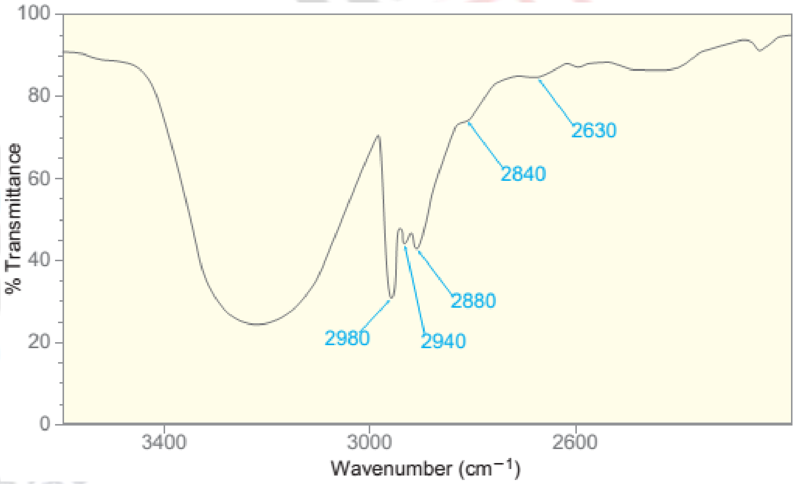

**Fig. 4: IR spectrum of a breath sample. The concentration of ethanol in the sample can be calculated based on the intensities of these signals.**

## 12. Identification of 1°, 2° and 3° amines

The primary (–$NH_2$), secondary (–NH) and tertiary (no hydrogen attached to N) amines may be differentiated by using infrared spectra. Primary amines, R-$NH_2$, show two N-H stretching bands in the range 3500-3300 $cm^{-1}$, whereas secondary amines, $R_2N$-H, show only one band in that region. Tertiary amines do not show any N-H stretch.

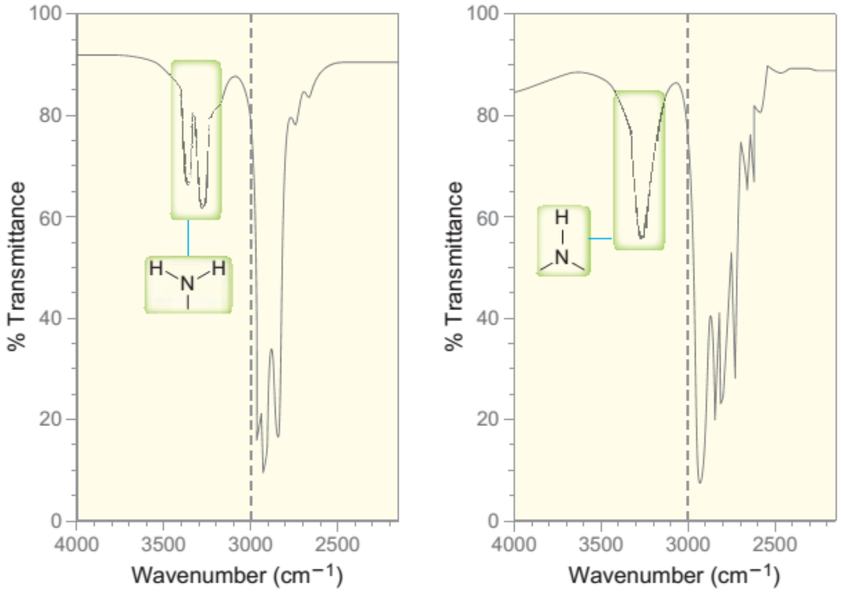

**Fig. 5: Difference in the shape of the signals for a primary and a secondary amine**

**Note:** One may consider that in primary amine, each N-H bond gives rise to a signal and hence two signals are observed but this is not true. In fact, both N-H bonds of a single molecule will together produce only one signal. The possible reason for the appearance of two signals can be explained by considering the two possible ways in which the $NH_2$ group can vibrate. The N-H bonds can be stretching in phase with each other, called symmetric stretching, or they can be stretching out of phase with each other, called asymmetric stretching. At any given time, approximately half of the molecules will be vibrating symmetrically, while the other half will be vibrating asymmetrically. The molecules vibrating symmetrically will absorb a particular frequency of IR radiation, while the molecules vibrating asymmetrically will absorb a different frequency. Thus two signals will be observed, one is produced by half of the molecules, and the other signal is produced by the other half of the molecules.

**Fig. 6: Stretching frequency values for a primary and a secondary amine**

## 13. Identification of *ortho*-, *meta*- and *para*- substitution in benzene rings

IR spectra of substituted benzene rings are quite messy, however some values are characteristic of the substitution pattern and are helpful in distinguishing between the substitution patterns in them.

Monosubstituted: Always gives a strong band at 690, but in a halocarbon solvent this may be obscured by a C-X stretch. A second strong band usually appears at 750.

Orthosubstituted: One strong band near 750.

Metasubstituted: One band near 690 and one near 780. A third band is often found at 880.

Parasubstituted: One strong band between 800 and 850.

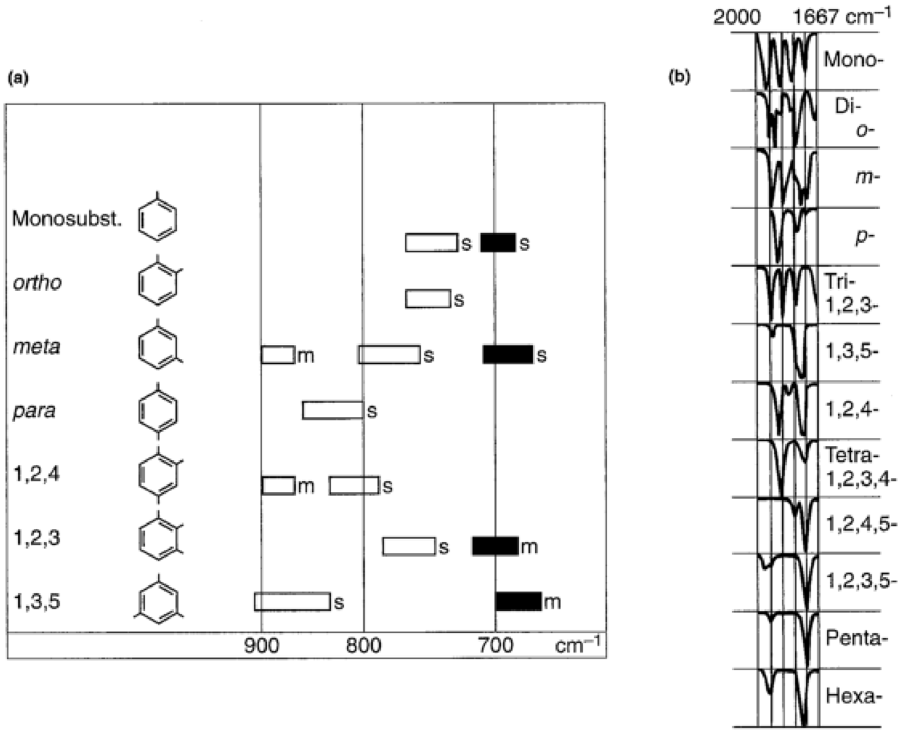

**Fig. 7: Stretching frequency values for substituted aromatic rings**

## 14. In detection of automobile pollutants

The exhaust from the poorly maintained automobiles contains carbon monoxide and hydrocarbons as two pollutants. These two pollutants are detected by remote sensing which consists of a source of IR radiation on side of the road for the intensity of absorption of CO (2170 cm$^{-1}$) and hydrocarbons (3000-2800 cm$^{-1}$). By placing a detector, calibrator and a computer the percent of pollutants and the vehicles owner can be detected and hence the extent of pollution can be checked.

## 15. Assessment of an Infrared Spectrum

IR Spectroscopy is an extremely effective method for determining a variety of functional groups present in a molecule. The best way to analyze an IR spectrum is to start looking from the high frequency end of the spectrum (typically 4000 cm$^{-1}$) and then move towards lower frequencies. Some of the most common, and distinctive absorptions are organized into several regions below.

**Absorptions in the region 3650–3250 cm$^{-1}$:** Hydroxy or amino groups mainly appear in this region, both giving rise to very characteristic band profiles. The position, intensity and shape of the band indicate whether the group is free or hydrogen bonded. One other characteristic vibration that is observed in this region is due to the C-H stretching of a terminal alkyne. This exhibits a relatively narrow absorption at 3300 cm$^{-1}$, and is associated with a second (C≡C) band at 2200 cm$^{-1}$. Now if in this region, a broad absorption band is observed that must be due to the presence of hydroxyl or amino group. The N-H absorption usually has one or two sharp absorption bands of lower intensity, whereas an O-H usually gives a broad absorption band, If there are some additional moderate to intense bands present the ranges 1600–1300 cm$^{-1}$, 1200–1000 cm$^{-1}$ and 800–600 cm$^{-1}$, the compound is more likely to be a simple hydroxyl compound. The simple hydrogen-bonded OH absorption of a hydroxyl (alcohol) function has a very characteristic shape. If the feature is relatively sharp and occurs between 3670 cm$^{-1}$ and 3550 cm$^{-1}$, the compound probably contains a non-hydrogen-bonded hydroxyl group, often an alcohol or phenol with a sterically hindered OH group.

**Absorptions in the region 3200–3000 cm$^{-1}$:** Absorption bands due to =C-H stretching and aromatic C-H stretching appear in this region. These bands are of medium intensity.

**Absorptions in the region 3000-2700 cm$^{-1}$:** In this region, absorption bands are usually characteristics vibration of C-H bonds of saturated aliphatic groups. If the main absorptions bands are associated with the absorptions at 1470 and 720 cm$^{-1}$ then the compound probably contains a long linear aliphatic chain.

**Absorptions in the region 1850–1650 cm$^{-1}$:** A strong band in this region usually indicates the presence of a carbonyl group in the compound. If the absorption is at the high end of this range (≥1775 cm$^{-1}$), the compound probably contains a reactive carbonyl group such as an anhydride, acid halide or α-halogenated carbonyl, or a strained-ring carbonyl, such as a lactone, or an organic carbonate. If the absorption is in the middle range i.e. 1750–1700 cm$^{-1}$ then the compound is probably a simple carbonyl compound, such as a ketone, an aldehyde, an ester, or a carboxylic acid. If the absorption is at the lower end of the range i.e. <1700 cm$^{-1}$ then the compound is probably an amide or a carboxylate (carboxylic acid salt). It is important to note here that the conjugation with another carbonyl group, or a double bond or an aromatic ring, will lower the carbonyl absorption by 30–50 cm$^{-1}$. Therefore, conjugated aldehydes, ketones, esters, and carboxylic acids may fall into this lower end of this region.

**Absorption in the region 2300–1990 cm$^{-1}$:** Multiple bonded nitrogen compounds and cumulated multiple bond compounds, such as cyanides (nitriles), cyanates, isocyanates, thiocyanates, and diazo compounds exhibit characteristic absorptions in the region 2300–1990 cm$^{-1}$. Cyanide absorptions vary from weak to moderate to strong, depending on the nature of other substituents present in the molecule. Conjugation including substitution on an aromatic ring modifies the intensity of this absorption. If the absorption band is extremely strong, the group is more likely to be three-centre functionality such as cyanate, isocyanate or thiocyanate.

Acetylenes and alkyne substituents also exhibit weak to moderate absorption within the same spectral region. If the acetylenic function is internal (-C≡C-), then the absorption can be extremely weak. However, a terminal alkyne group (-C≡C-H) band may have moderate intensity, and this is supported by a characteristic C-H stretching absorption around 3310 cm$^{-1}$. A relatively low-frequency C-H bending vibration near 630 cm$^{-1}$ also confirms the terminal alkyne vibration.

**Absorptions in the region 1000–1600 cm$^{-1}$:** This region is useful for identification of nitro compounds and also for confirming the presence of ethers, esters, and primary, secondary and tertiary alcohols. For example, the appearance of strong band in the range 1000-1300 cm$^{-1}$ confirms the presence of an ester provided the band due to C=O is also present in the expected region (1700-1750 cm$^{-1}$).

## 15. Summary

- Infrared spectroscopy is a simple and reliable technique widely used to identifying the different organic and inorganic compounds. Each functional group has its characteristic IR absorption frequency.
- IR spectroscopy is also useful in determining the different types of isomerism such as cis-trans isomerism and keto-enol tautomerism.
- It can be used to study the progress of a chemical reaction by taking the IR spectrum of a small portion of the reaction mixture.
- The different substitution pattern i.e. *ortho*,- *meta*- or *para*- substitution on the benzene ring can be determined with the help of IR spectrum.
- It is used in studying the hydrogen bonding interaction and in distinguishing inter-molecular and intra-molecular hydrogen bonding.
- IR spectroscopy is useful in determining the alcohol level of motor drivers through their breath by traffic police at the road side.
- It is used to check the pollution level in the automobiles**.**