

IR spectroscopy

The most frequent spectroscopic technique used by organic and inorganic chemists is infrared (IR) spectroscopy. It deals with the absorption of radiation in the infrared region of the electromagnetic spectrum. IR spectrum gives sufficient information about the structure (identification of functional groups) of a compound and can also be used as an analytical tool to assess the purity of a compound. The absorption of infrared radiation by a molecule causes changes in their vibrational and rotational energy levels and hence IR-spectroscopy is also known as vibrational-rotational spectroscopy. Unlike UV-spectroscopy which has very few peaks in their spectrum, IR spectroscopy provides spectrum with a large number of absorption bands and hence provide plenty of information about the structure of a compound. Different bands present in the spectra correspond to various functional groups and bonds present in the molecule.

The infrared spectrum can be divided into three type of main regions: the far infrared ($<400\text{ cm}^{-1}$), the mid-infrared ($4000\text{--}400\text{ cm}^{-1}$) and the near-infrared ($13000\text{--}4000\text{ cm}^{-1}$). The mid IR region is of greatest practical use to the organic chemist, but the near- and far-infrared regions also provide important information about many compounds.

Mid IR region: The mid-infrared spectrum extends from 4000 to 400 cm^{-1} and results from vibrational and rotational transitions. This region is most useful for the organic chemist since most of the organic molecules absorb in this region. The mid-infrared can be divided into two regions viz functional group region ($4000\text{--}1300\text{ cm}^{-1}$) and finger print region ($1300\text{--}600\text{ cm}^{-1}$).

Functional group region ($4000\text{--}1300\text{ cm}^{-1}$): Most of the functional groups present in organic molecules exhibits absorption bands in the region $4000\text{--}1300\text{ cm}^{-1}$, hence this is known as functional group region. In this region, each band can be assigned to a particular deformation of the molecule, the movement of a group of atoms, or the bending or stretching of a particular bond.

Near-infrared region ($12500\text{--}4000\text{ cm}^{-1}$): The absorptions observed in the near-infrared region ($12500\text{--}4000\text{ cm}^{-1}$) are overtones or combinations of the fundamental stretching bands. Bands in the near infrared are usually weak in intensity. They are often overlapped and hence are less useful than the bands in mid-infrared region.

NIR shows some similarities to UV-visible spectrophotometry and some to mid-IR spectrometry. Indeed the spectrometers used in this region are often combined UV-visible-NIR ones.

NIR is generally used for quantitative organic functional-group analysis. The NIR region has also been used for qualitative analyses and studies of hydrogen bonding, solute-solvent interactions, organometallic compounds and inorganic compounds

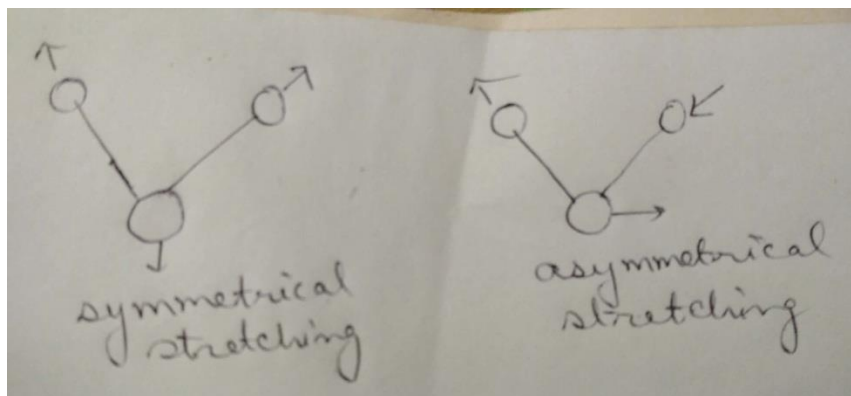
Far-infrared region ($600\text{--}100\text{ cm}^{-1}$): The far-infrared spectrum extends from 600 to 100 cm^{-1} . Organometallic and inorganic molecules contain heavy atoms and have weak bonds, therefore the fundamental vibrations of these molecules fall in this region. Lattice vibrations of crystalline materials occur in this region.

Molecular Vibrations

The atoms in a molecule do not remain fixed at certain positions. The two nuclei can vibrate backwards and forwards or towards and away from each other around an average position. There

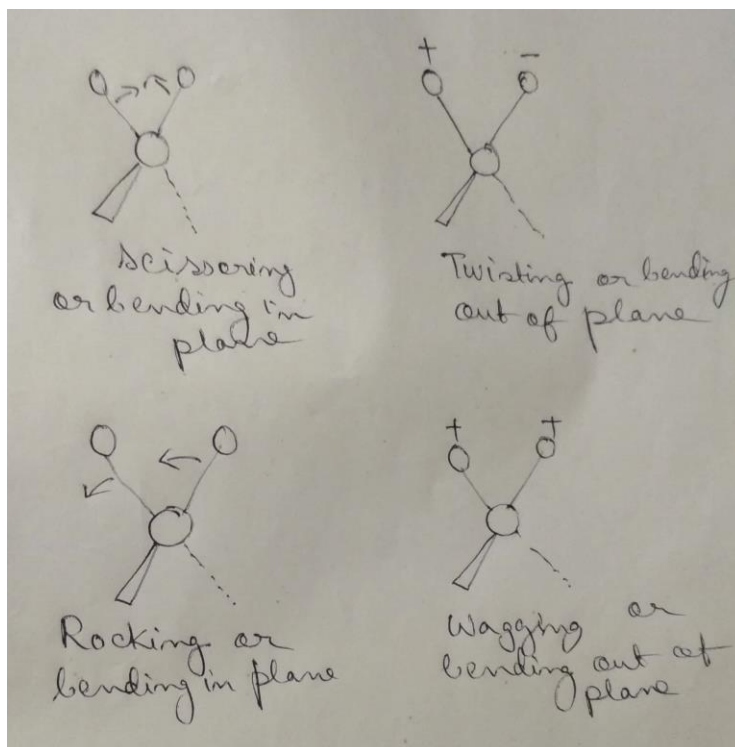
are two types of fundamental molecular vibrations *viz.*, stretching (change in bond length) and bending (change in bond angle).

Stretching vibrations: It involves a rhythmic movement along a bond axis with a subsequent increase and decrease in bond length. Stretching vibrations are of two types *viz.*, symmetrical stretching and asymmetrical stretching.



Bending vibrations: It involves a change in bond angle or movement of a group of atoms with respect to the rest of the molecule. Bending vibrations are of four types.

- i.) rocking
- ii.) Scissoring
- iii.) Wagging
- iv.) Twisting



All the bonds in a molecule are not capable of absorbing infrared radiation but only those bonds which are accompanied by a change in the dipole moment will absorb in the infra-red region. Thus, vibrations which are associated with the change in the dipole moment of the molecule are called infra-red active transitions otherwise the vibration is said to be IR-inactive and do not show any absorption band in the IR-spectrum. Generally, larger the change in the dipole moment, the higher is the intensity of absorption. Hence the vibrational absorption bands in simple hydrocarbons are weak while bands associated with bonds connecting atoms with considerable electronegativity difference give strong bands.

The position of an IR absorption band

The amount of energy required to stretch a bond depends on the strength of the bond and the masses of the bonded atoms. The stronger the bond, the greater the energy required to stretch it. The frequency of the vibration is inversely proportional to the mass of the atoms, so heavier atoms vibrate at lower frequencies.

The approximate vibration frequency of a bond can be calculated from the following equation derived from Hooke's law.

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

Where μ is the reduced mass

And $\mu = m_1 \times m_2 / m_1 + m_2$

m_1 and m_2 are the masses of the two atoms

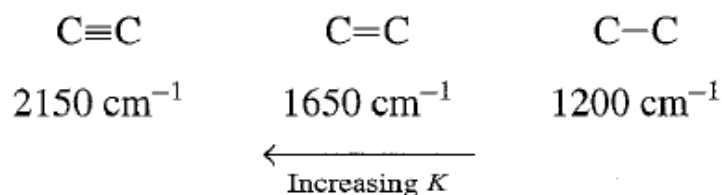
c is the velocity of light (2.998×10^{10} cms⁻¹)

K = force constant of the bond

[For a single C-C bond, it is approximately 5×10^5 gs⁻² and it doubles and triples for double and triple bond respectively.]

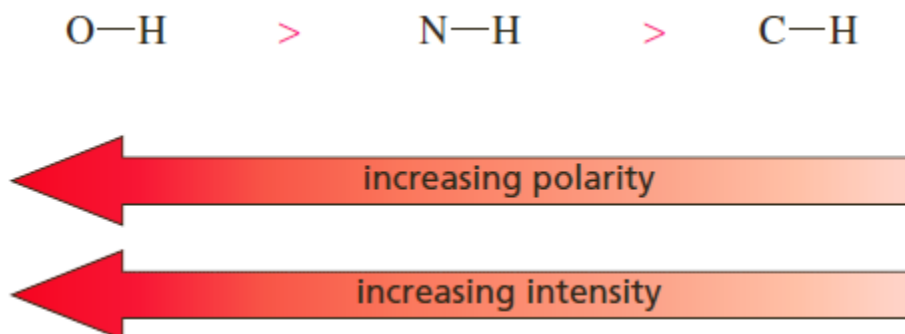
The force constant is a measure of the strength of a bond. Thus the value of stretching frequency of a bond increases with increasing the bond strength and decreasing the reduced mass of the bonded atoms.

The triple bonds are stronger than the double bonds followed by single bonds between the same two atoms and hence vibrational frequency is in the order of triple > double > single.



The Intensity of Absorption bands

The intensity of an absorption band depends on the change in the dipole moment of the bond associated with the vibration. The greater the change in dipole moment, the more intense is the absorption. 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. If we have two different atoms, there will be an electro-negativity difference and larger the electro-negativity difference, the more intense the absorption will be. 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 O-H bond is more polar. Consequently, the stretching vibration of the O-H 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.



The intensity of an absorption band also depends on the number of bonds responsible for the absorption. For example, if you compare the IR spectra of methane to that of octane, the octane molecule will have a much more intense C-H peak because it has many more C-H bonds than methane. 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.

Factors influencing vibrational frequency

The value of vibrational frequency of a bond calculated by Hooke's Law is not always equal to their observed value. The force constant is changed with the electronic and steric effects caused by other groups present in the surroundings. Following are some important factors affecting the vibrational frequency of a bond.

Effect of Bond Order

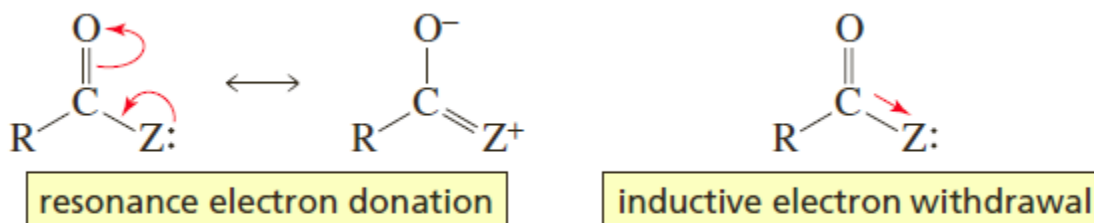
Bond order affects the position of absorption bands. Higher the bond order larger is the band frequency. A C-C triple bond is stronger than a C=C bond, so a C-C triple bond has higher stretching frequency than does a C=C bond. The C-C bonds show stretching vibrations in the region from 1200-800 cm⁻¹ but these vibrations are weak and of little value in identifying compounds. Similarly, a C=O bond stretches at a higher frequency than does a C-O bond and a C-N triple bond stretches at a higher frequency than does a C=N bond which in turn stretches at a higher frequency than does a C-N bond.

Resonance and Inductive Electronic Effects

Whenever we discuss about the IR band, a range of frequency for each stretch is usually assigned as the exact position of the absorption band depends on other structural features of the molecule, such as electron delocalization, the electronic effect of neighbouring substituents, and hydrogen bonding. Important details about the structure of a compound can be revealed by the exact position of the absorption band. For example, the IR bands for the carbonyl group in 2-pentanone, 2-cyclohexenone appears at different frequencies. The 2-Cyclohexenone absorbs at a lower frequency because the carbonyl group has less double-bond character due to electron delocalization.

If you put an atom other than hydrogen (aldehyde) or carbon (ketone) next to the carbonyl group, it also causes the shifting of the position of the carbonyl absorption band. Whether it shifts to a lower or to a higher frequency depends on the electronic effect (inductive and mesomeric effect) of the atom.

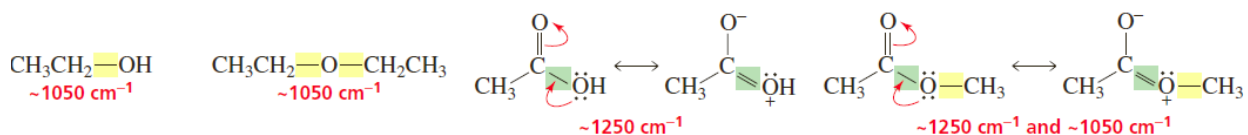
Different substituents on carbonyl carbon changes the electronegativity of carbonyl group due to the inductive effect arises due to the different electronegativities of the carbonyl carbon and of the substituent in compounds of the type RCOZ. It involves the electrons in the sigma bonds. The mesomeric effect involves the electrons in the pi and nonbonding orbitals and it operates in general opposite to the inductive effect. These effects cannot be isolated from one another and at a time only one of them can be applied to determine approximate results.



Electron releasing groups attached to the carbonyl group tend to favour the polar contribution by mesomeric effect and thus lower the bond order of the C=O bond (less double bond character) and hence resulting in a decrease of the carbonyl stretching frequency.

Electron withdrawing groups suppress the polar contribution with an effective increase in the double bond character and hence resulting in the increase of the frequency of absorption. The predominant effect of the nitrogen of an amide is electron donation by resonance. Therefore, the carbonyl group of an amide has less double bond character than the carbonyl group of a ketone and hence amide has low C=O bond IR frequency than the ketone. In contrast, the predominant effect of the oxygen of an ester is inductive electron withdrawal, therefore the

carbonyl group of an ester has more double bond character than the carbonyl group of a ketone, so the former appears at larger frequency value.



If we talk about the C-O stretching frequency it appears in the range of 1250-1050 cm^{-1} . If C-O bond is in an alcohol or in ether, the stretching frequency will be toward the lower end of the range. If this C-O bond is a part of a carboxylic group, the stretching frequency will occur at the higher end of the range. The position of the absorption varies because the bond in an alcohol is a pure single bond, whereas the bond in a carboxylic acid has partial double bond character that is due to resonance electron donation by OH group in acids. Esters show stretches at both ends of the range because esters have two single bonds, one that is a pure single bond and one that has partial double-bond character. In most of the cases, mesomeric effect works along with inductive effect and cannot be ignored. It is important to note that only inductive effect is considered when the compound is meta substituted. In para substitution, both inductive and mesomeric effects become important and the domination of one over the other will decide the wavenumber of the absorption.

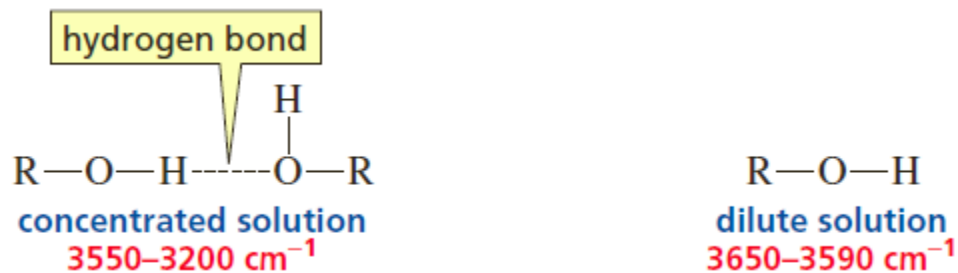
Hydrogen Bonding

The presence of hydrogen bonding changes the position and shape of an infrared absorption band.

Frequencies of both stretching as well as bending vibrations are changed because of hydrogen bonding. The X-H stretching bands move to lower frequency usually with increased intensity and band widening. The X-H bending vibration usually shifts to higher frequencies. Stronger the hydrogen bonding, greater is the absorption shift from the normal values. The two types of hydrogen bonding (intramolecular and intermolecular) can be differentiated by the use of infrared spectroscopy.

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 under special conditions that allow the required overlap of orbitals, e.g. formation of a 5 or 6 member rings. The extent of inter-molecular hydrogen bonding depends upon the concentration of the solution and hence the position and the shape of an absorption band also depend on the concentration of the solution. The more concentrated the solution, the more likely it is for the OH-containing molecules to form intermolecular hydrogen bonds. It is easier to stretch an O-H bond if it is hydrogen bonded, because the hydrogen is attracted to the oxygen of neighbouring molecule.

Therefore, the O-H stretching of a concentrated (hydrogen bonded) solution of an alcohol occurs at about 3550 cm^{-1} , whereas the O-H stretching band of a dilute solution (with little or no hydrogen bonding) appears at 3650 cm^{-1} . Additionally, hydrogen-bonded OH groups also have broader absorption bands whereas the absorption bands of non-hydrogen-bonded OH groups are sharper.



Hydrogen bonding interactions can also occur between functional groups of solvent and solute. Three classes of solvent exist which may lead to trouble when used for hydrogen-bonding studies in solution. First, compounds which contain hydrogen donor groups, e.g. halogenated compounds which contain a sufficient number of halogens to activate the hydrogens present, such as chloroform. Secondly, compounds which contain non-bonded electron pairs, such as ethers, aldehydes and tertiary amines.

In addition, there are compounds which contain both types of group, e.g. water and alcohols. There are only a few solvents that do not have the above characteristics, such as carbon tetrachloride (CCl_4) and carbon disulfide (CS_2). These still contain lone electron pairs, but being on S and Cl are less available, and any interactions will be extremely weak.

Apart from the concentration and solvent effects, temperature also affects the degree of hydrogen bonding in a compound. High temperature decreases the extent of hydrogen bonding.

Fermi Resonance

Fermi resonance is a phenomenon which was first explained by the Italian physicist Enrico Fermi to account for shifting of the energies and intensities of absorption bands in an infrared spectroscopy. Sometimes, it happens that two different vibrational levels have nearly the same energy. If such vibrations belong to the same species of molecules, then a mutual perturbation of energy may occur, resulting in the shift of one towards lower frequency and the other towards a higher frequency. It is also accompanied by a substantial increase in the intensity of the respective bands.

Fermi resonance was first discovered in carbon dioxide by Fermi and it is also found in the vibrational spectra of aldehydes, where the C-H bond in the CHO group interacts with the second harmonic level, derived from the fundamental frequency of the deformation vibration of the CHO group ($2 \times 1400 \text{ cm}^{-1}$). The result is a Fermi doublet with branches around 2830 cm^{-1} and 2730 cm^{-1} . It is important for Fermi resonance that the vibrations connected with the two interacting levels be localized in the same part of the molecule.

Bond angles

Smaller ring requires the use of more p-character to make the internal C-C bonds for the requisite small angles. This gives more s character to the C=O sigma bond which causes the strengthening and stiffening of the exocyclic double bond. The force constant K is then increased and the absorption frequency increases.

Cyclic ketones

The frequency of C=O group in cyclic ketones increases with decreasing the ring size. The ring strain shifts the absorption values to a higher frequency. Six-membered rings with carbonyl group e.g. cyclohexanone absorb at normal value i.e. 1715 cm^{-1} . Decrease in ring size increases the C=O stretching frequency. Smaller rings require the use of more p-character to make C-C bonds

for the requisite small angles. This gives more s character to the C=O sigma bond and thus results in strengthening of C=O double bond causing absorption at higher frequency (Figure 7).

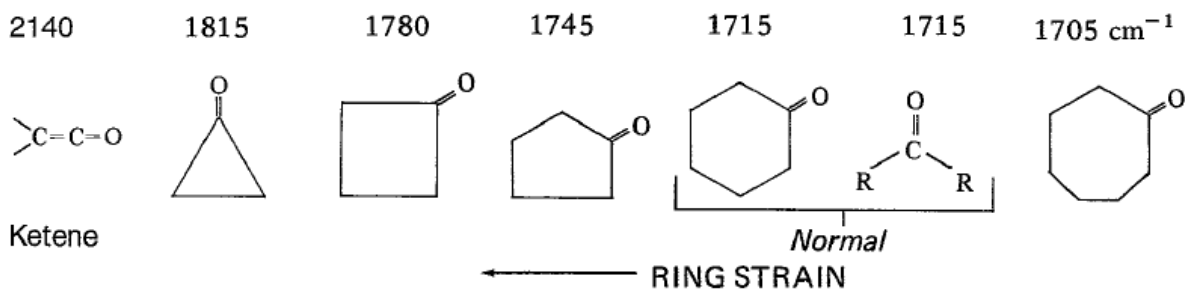


FIGURE 2.44 The C=O stretching vibrations for cyclic ketones and ketene.

Identification 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 fingerprint 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.

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.

Other applications are

1. Detection of impurities in a sample
 2. Study of Geometrical isomers
 3. Study of H-bonding
 4. Identification of alcohol in breath analyzer
 5. Identification of primary, secondary and tertiary amines
- Etc.