

INFRARED SPECTROSCOPY

SEM-4, CC-8
PART-4, PPT-10

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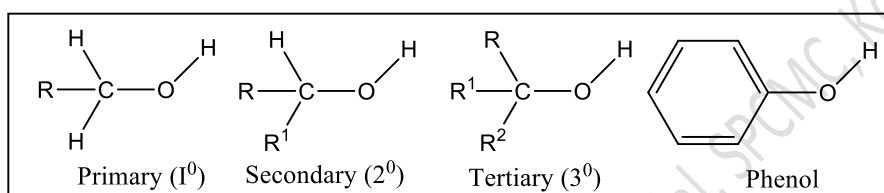
Kolkata

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INFRARED SPECTROSCOPY (PART-4, PPT-10)

Absorptions of Alcohols and Phenols (R-O-H)

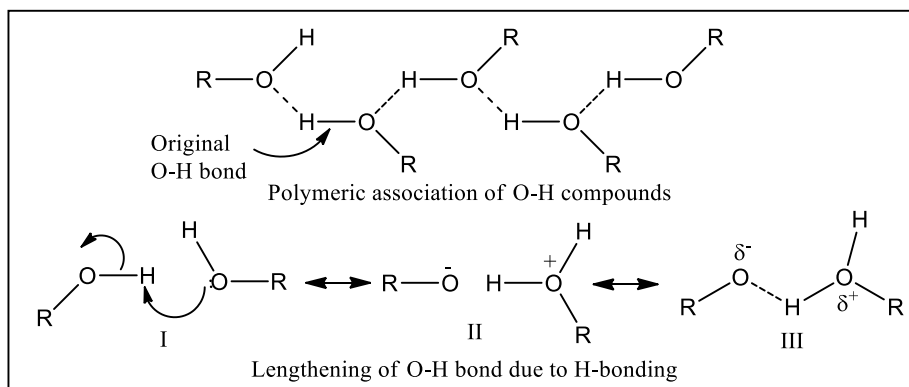
An alcohol is any molecule that contains a C-OH linkage. The -OH group is called a hydroxyl group, and the carbon atom attached to it is called the hydroxyl carbon. A phenol is any molecule with an -OH group directly bonded to an aromatic ring. The characteristic bands observed in the spectra of alcohols and phenols result from O-H stretching and C-O stretching. These vibrations are sensitive to hydrogen bonding. The C-O stretching and O-H bending modes are not independent vibrational modes because they couple with the vibrations of adjacent groups.



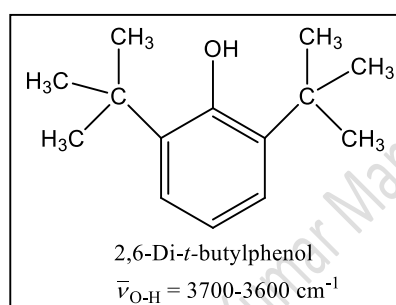
O-H Stretching Vibrations (R-O-H)

The unbonded or “free” hydroxyl group of alcohols and phenols absorbs strongly in the 3700-3584 cm^{-1} region (centred at 3623 cm^{-1}). These “sharp” hydroxyl bands are observed in the vapour phase, in very dilute solution in non-polar solvents or for hindered -OH group. Intermolecular H-bonding increases as the concentration of the solution increases, and additional bands start to appear at lower frequencies. Hydrogen bonding changes the position and shape of an IR absorption band. When the Hydrogen bonding is extensive, a wide band for the O-H stretching vibrations at lower frequency around 3550-3200 cm^{-1} (centred at 3333 cm^{-1}) is observed.

Hydrogen bonding lowers the absorption frequency as well as broaden the band. The band at 3623 cm^{-1} results from the monomer, whereas the broad absorption near 3333 cm^{-1} arises from “polymeric” structures. The hydrogen bond can be regarded as a resonance hybrid of I and II (approximating overall to III), so that hydrogen bonding involves a lengthening of the original O-H bond. This bond is consequently weakened (that is, its force constant is reduced), so the O-H stretching frequency is lowered. The stronger the H-bond, the longer is the original O-H bond, the lower is the vibration frequency and broader and more intense will be the absorption band.



In structures, such as 2,6-di-*t*-butylphenol, in which steric hindrance prevents hydrogen bonding, no bonded hydroxyl band is observed, not even in spectra of neat samples.

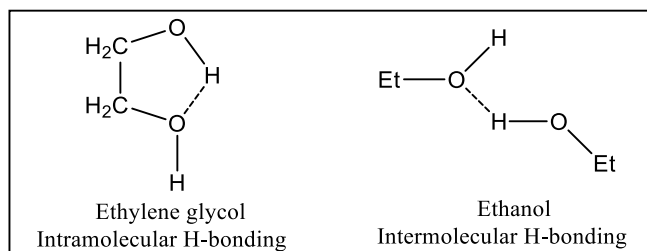


Distinction between intra- and intermolecular H-bonding

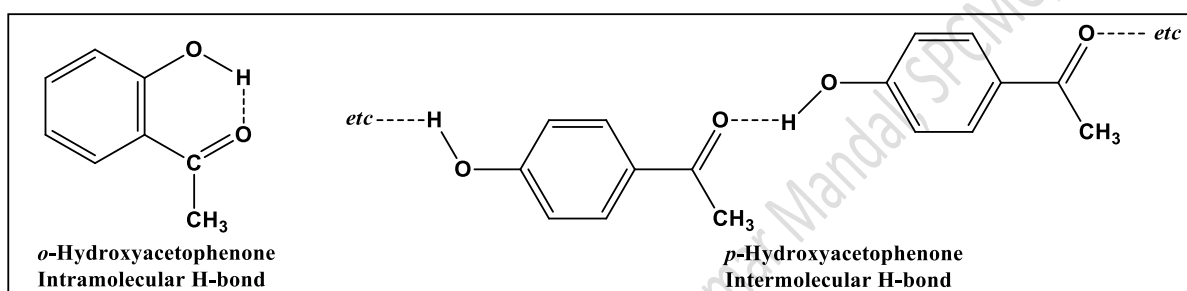
This can be made by the effect of dilution. Intermolecular hydrogen bonds are broken on dilution. This is because in a very dilute solution, the molecules are widely separated. As a result, there is an increase in the absorption frequency from bonded O-H absorption (broad band at around 3350 cm^{-1}) to an unbonded absorption for “free” OH group (sharp band at $\sim 3600 \text{ cm}^{-1}$). Intramolecular hydrogen bond remains unaffected on dilution and as a result the absorption band also remains unaffected.

Effect in O-H stretching of ethylene glycol and ethanol on dilution by carbon tetrachloride.

- ❖ IR spectrum of ethylene glycol is unaffected on dilution where as that of ethanol is shifted to a higher absorption frequency on dilution by CCl_4 . Ethylene glycol exists in the monomeric form at all concentrations due to the formation of intramolecular hydrogen bonding which is unaffected on dilution.
- ❖ Ethanol forms intermolecular hydrogen bond at higher concentration, but as the solution is diluted, the molecules get separated. As a result, intermolecular hydrogen bonds are broken. $\bar{\nu}_{\text{O-H}}$ shifts to a higher value.



Strong intramolecular hydrogen bonding occurs in *o*-hydroxyacetophenone. The resulting absorption at 3077 cm^{-1} is broad, and independent of concentration. In contrast, *p*-hydroxyacetophenone shows a sharp free hydroxyl peak at 3600 cm^{-1} in dilute CCl_4 solution as well as a broad, strong intermolecular peak at 3100 cm^{-1} in the spectrum of a neat sample.



C-O Stretching Vibrations (R-O-H)

In the spectra of alcohols and phenols have a strong band in the region $1260\text{-}1000\text{ cm}^{-1}$, which is designated as the “C-O stretching band”. In case of methanol this band appears at 1034 cm^{-1} whereas in the spectrum of ethanol it occurs at 1053 cm^{-1} . In ethanol, the C-O stretching mode is coupled with the adjacent C-C stretching vibration thereby producing an asymmetric C-C-O stretching vibration which appears at higher wavenumber.

C-O Stretching Vibrations in Alcohols and Phenols	
Compound	C-O Stretch (cm^{-1})
Primary Alcohols (Saturated)	~1050
Secondary Alcohols (Saturated)	~1100
Tertiary Alcohols (Saturated)	~1150
Phenols	~1220

O-H Bending Vibrations (R-O-H)

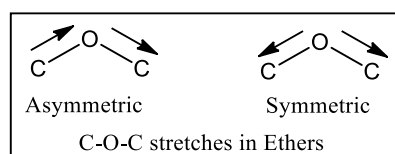
The O-H *in-plane* bending vibration occurs in the general region of $1420\text{-}1330\text{ cm}^{-1}$. In primary and secondary alcohols, the O-H *in-plane* bending couples with the C-H *wagging* vibrations to produce two C-O-H bending bands; the first appears near 1420 cm^{-1} , the second appears near 1330 cm^{-1} .

Tertiary alcohols, in which no C-H bond is directly attached to O-H bond, coupling cannot occur. Therefore, tertiary alcohols show a single O-H band in this region, the position depending on the degree of hydrogen bonding.

Absorptions of Ethers (R-O-R¹)

Like alcohols, ethers contain a C-O bond and have a strong C-O stretching band. The C-O stretch of an ether involves the C-O-C linkage.

C-O Stretching Vibrations: In ethers, C-C and C-O bonds couple to produce two stretching modes. These are C-O-C asymmetric, and C-O-C symmetric modes.



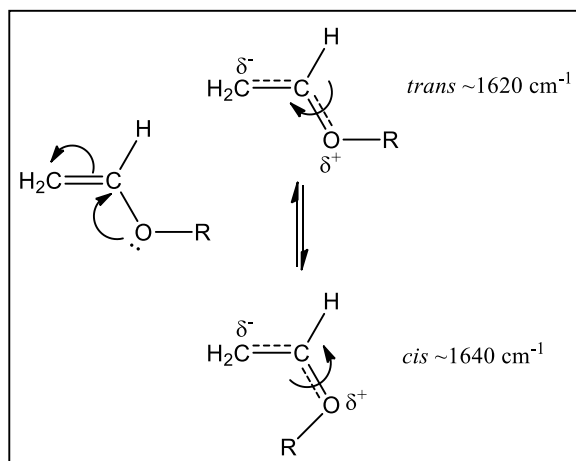
In the spectra of aliphatic ethers, the most characteristic absorption is an intense band in the 1150-1085 cm⁻¹ region because of asymmetrical C-O-C stretching. Since the C-O bond is quite polar, the dipole moment change for this vibration is large. The symmetric C-O-C absorption band is usually less intense than the asymmetrical stretch and is found in the 900-800 cm⁻¹ region.

The C-O-C group in a six-membered ring absorbs at the same frequency as in an acyclic ether. As the ring becomes smaller, the asymmetrical C-O-C stretching vibration moves progressively to lower wavenumbers, whereas the symmetrical stretching vibration moves to higher wavenumbers.

Spectra of an aryl ethers display an asymmetrical stretching band at 1275-1200 cm⁻¹ with symmetrical stretching near 1075-1020 cm⁻¹. Strong absorption due to asymmetrical C-O-C stretching in vinyl ethers occurs in the 1225-1200 cm⁻¹ region with a strong symmetrical band at 1075-1020 cm⁻¹. Resonance, which results in strengthening of the C-O bond, is responsible for the shift in the asymmetric absorption band of aryl alkyl and vinyl ethers.

The C=C stretching band of vinyl ethers occurs in the 1660-1610 cm⁻¹ region. This alkene band is characterized by its higher intensity compared with the C=C stretching band in alkenes. This band frequently appears as a doublet resulting from absorption of rotational isomers.

Coplanarity in the *trans* isomer allows maximum resonance, thus more effectively reducing the double bond character of the alkene linkage. Steric hindrance reduces resonance in the *cis* isomer.



Ethers can be distinguished from alcohols because of their lack of O-H stretching and bending bands.

Carbonyl Vibrations ($R^1R^2C=O$)

Ketones, aldehydes, carboxylic acids, carboxylic esters, lactones, acid halides, anhydrides, amides, and lactams show a strong C=O stretching absorption in the region of 1870-1540 cm^{-1} . C=O stretching frequency of a neat sample of a saturated aliphatic ketone is at 1715 cm^{-1} , as “normal”, e.g., acetone, cyclohexanone, etc. Changes in the environment of the carbonyl can either lower or raise the absorption frequency from this “normal” value. Because of its large change in dipole moment, the C=O stretching absorption is strong.

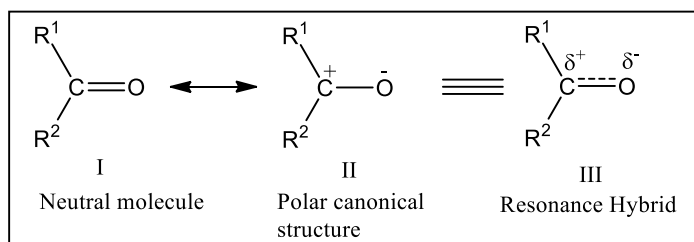
Factors Influencing the Position of the C=O Stretching Band

1. Physical State of measurement
2. Electronic and Mass effects of the neighbouring substituents
3. Conjugation
4. Hydrogen bonding
5. Ring strain/Steric Strain

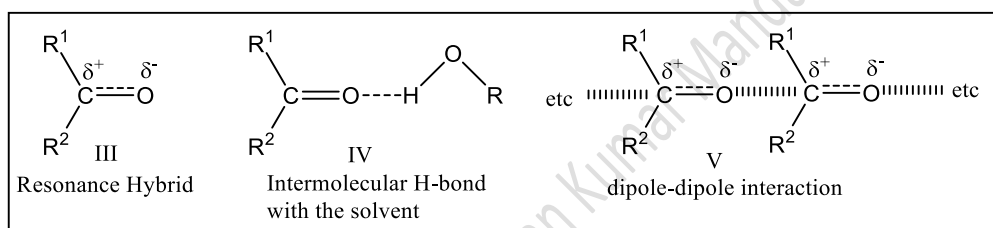
Physical State

C=O stretching frequency of a neat sample of a saturated aliphatic ketone is at 1715 cm^{-1} , as “normal”, e.g., acetone, cyclohexanone, di-*n*-hexyl ketone, etc. The absorption frequency observed for a neat sample is increased in non-polar solvents. In the pure liquid, these molecules are held together by the strong “dipole-dipole” interaction with a reduced C=O bond strength. In a solution of non-polar solvent, molecules are separated to each other.

Therefore, contribution of the neutral structure (I) to the “resonance hybrid” (III) increases. C=O bond strength increases and $\bar{\nu}_{\text{CO}}$ shifts to a higher wavenumber region.

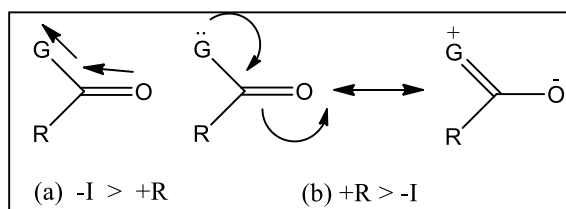


Polar solvents reduce the frequency of absorption. This is due to the increasing contribution of the polar canonical structure (II) to the “resonance hybrid” (III). C=O bond strength decreases and $\bar{\nu}_{\text{CO}}$ shifts to a lower wavenumber region. Hydroxylic solvents reduce the frequency of absorption. $\bar{\nu}_{\text{CO}}$ of acetone in 10% MeOH is 1706 cm^{-1} . This is due to the formation of intermolecular H-bonding with the solvent (IV), here, MeOH molecules. C=O bond strength decreases and $\bar{\nu}_{\text{CO}}$ shifts to a lower wavenumber region.



Electronic factors

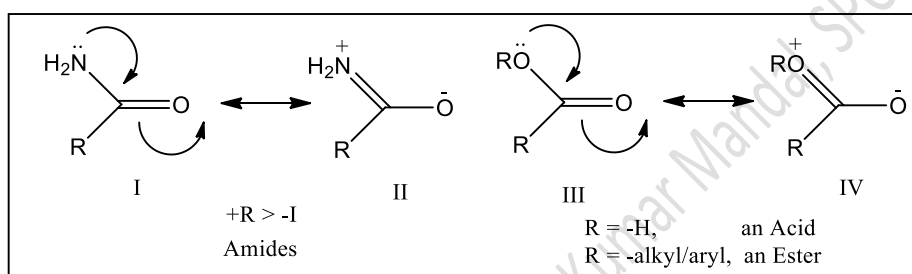
Replacement of an alkyl group of a saturated aliphatic ketone by a hetero atom (G) shifts the carbonyl absorption. The direction of the shift depends on whether the inductive effect (a) or resonance/mesomeric effect (b) predominates. The electron withdrawing inductive effect reduces the length of the C=O bond and thus increases its force constant and the frequency of absorption. The resonance effect increases the C=O bond length and reduces the frequency of absorption.



G Effect predominantly Inductive		G Effect predominantly Mesomeric/Resonance	
G	$\bar{\nu}_{\text{CO}} (\text{cm}^{-1})$	G	$\bar{\nu}_{\text{CO}} (\text{cm}^{-1})$
-OH (Monomer)	1760	-NH ₂	1695-1650
-OMe	1750-1735	-Ph	1700
-Cl	1815-1785	-CH=CH ₂	1700

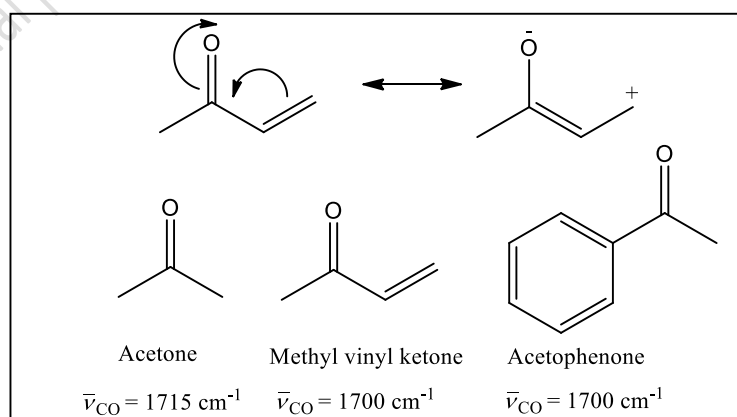
In amides, the mesomeric effect of the nitrogen lone pair is more important than the inductive effect of the nitrogen, and this leads to a decrease in the C=O bond strength due to electron delocalization from nitrogen atom. Consequently, frequency of carbonyl absorption decreases from 1715 cm^{-1} .

In acids (for monomers) and esters, the inductive effect of the oxygen (which is more electronegative than nitrogen) gains more importance to result in an increase in the frequency of carbonyl absorption. Both the structures, neutral (III) and the polar forms (IV), possess a C=O bond. Consequently, mesomeric electron delocalization does not produce an appreciable change in the C=O bond strength in both the structures. On the other hand, -OR group possesses an electron withdrawing inductive effect. C=O bond strength, thus, increases and $\bar{\nu}_{\text{CO}}$ appears at a higher wavenumber than 1715 cm^{-1} .



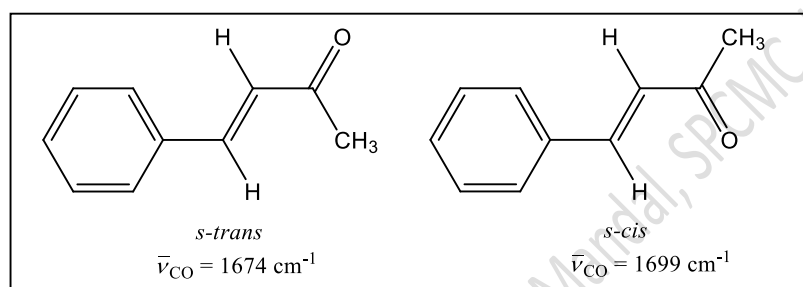
Conjugation

Conjugation lowers the C=O stretching. This is because, conjugation with a C=C results in delocalization of the π -electrons of both unsaturated groups. Delocalization of the π -electrons of the C=O group reduces the double-bond character of the C=O bond, which is consequently weakened. This decreases the force constant and lowers the carbonyl stretching vibration frequency than 1715 cm^{-1} .



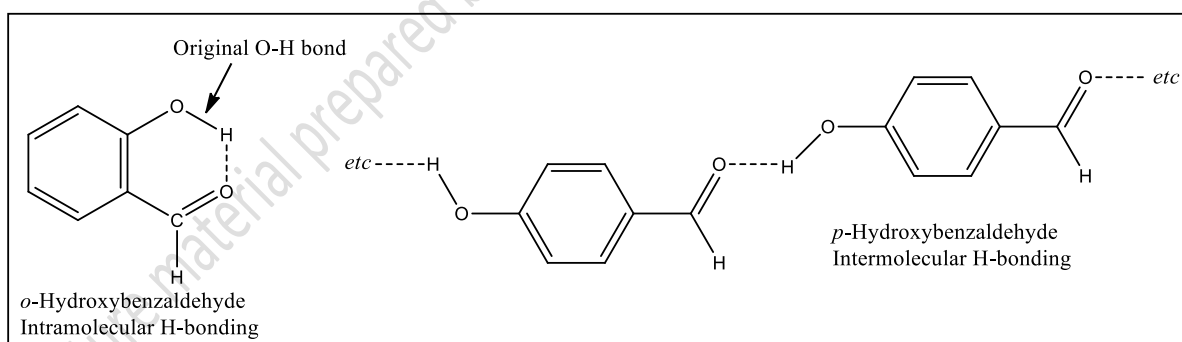
Conjugation versus Steric effect

Steric effects that reduce the coplanarity of the conjugated system reduce the effect of conjugation. In the absence of steric hindrance, a conjugated system will tend toward a planar conformation. Thus, α,β -unsaturated ketones may exist in *s-cis* and *s-trans* conformations. When both forms are present, absorption for each of the forms is observed. Both the *s-cis* and *s-trans* forms of benzalacetone are present at room temperature. The absorption of the alkene bond in conjugation with the carbonyl group occurs at a lower frequency than that of an isolated C=C bond.



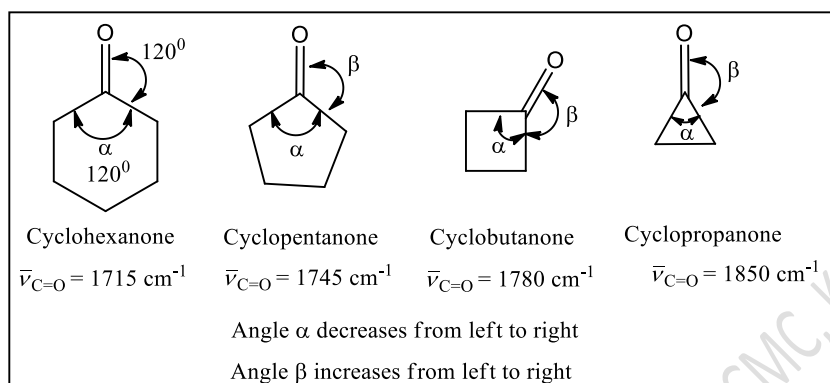
Hydrogen-Bonding

Hydrogen bonding (both intramolecular and intermolecular) reduces the O-H and C=O stretching frequencies to a lower wavenumber region. H-bonding increases the lengths of C=O and the original O-H bonds. These bonds are thus weakened (i.e., force constant reduced) and so carbonyl stretching frequencies are lowered from 1715 cm^{-1} .



Ring Strain

Ring strain in cyclic compounds causes a comparatively large shift of the C=O stretching to a higher frequency.



C-CO-C bond angle (α) is reduced below the normal ($\sim 120^\circ$ in acyclic and six-membered ring ketones) 120° in strained rings, consequently C-C-O bond angle (β) becomes greater than 120° . This leads to an increase in the *s*-character in the C=O bond, hence bond order is greater than that of cyclohexanone and consequently, C=O stretching frequency is increased from cyclohexanone to cyclopropanone.

Steric Strain

Branching at the α -carbon atoms leads to an increase in the C-CO-C bond angle (β) and consequent decrease in the C-C-O bond angle (γ) from the normal value ($\approx 120^\circ$). This leads to a decrease in the *s*-character in the C=O bond, hence bond order decreases, leading to a decrease in frequency of carbonyl absorption from the normal value (1715 cm^{-1}).

