

INFRARED (IR) SPECTROSCOPY

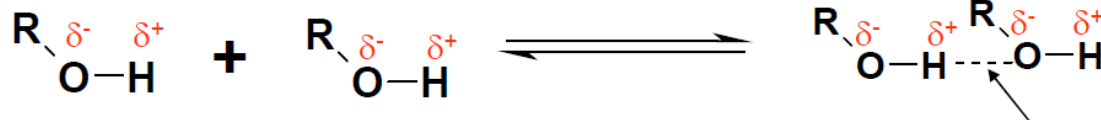
4) Hydrogen Bonding

- **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.**
- **Stronger the hydrogen bonding, greater is the absorption shift from the normal values.**

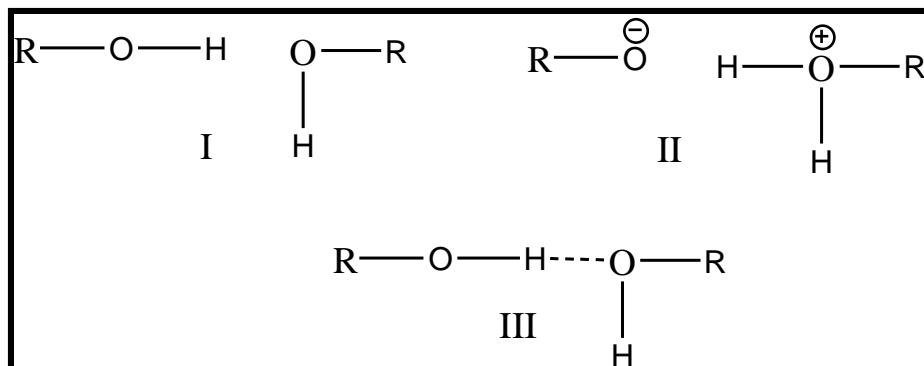
O-H stretching of alcohol affected by hydrogen bonding

- 'Free' hydroxyl groups absorb **between 3650-3585 cm⁻¹** (strong and sharp).
- Intermolecular H-bonding between -O-H groups causes **shift to 3550-3200cm⁻¹**

Reason:



Hydrogen bonding



Resonating structure of alcohols

Structure III is the hybrid of I & II which results in the lengthening of original O-H group

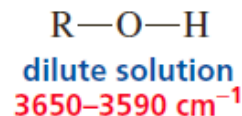
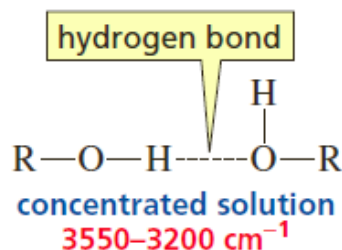
Reason:

The **stronger** the hydrogen-bonding

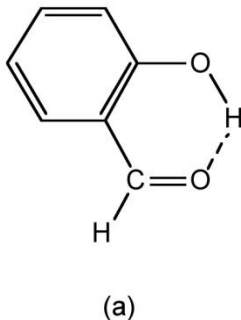
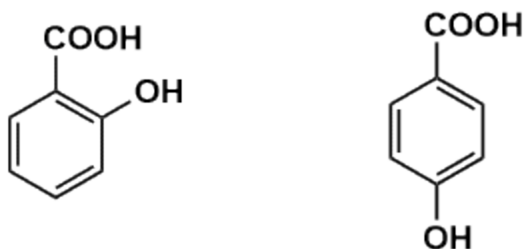
- the **longer the O-H bond** (more polarized)
- the lower the **force constant**
- the lower the **vibrational frequency**
- the **broader** the band (**H-bonding is not uniform throughout the sample**) and
- the more intense (**due to increased polarization** of the O-H bond) the absorption band.

The two types of hydrogen bonding (intramolecular and intermolecular) can be differentiated by the use of infrared spectroscopy.

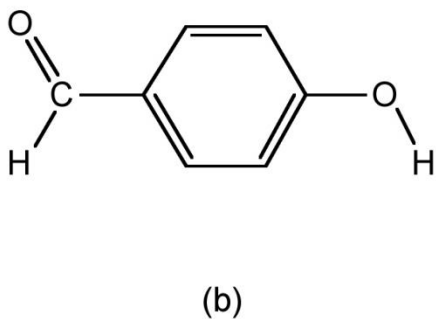
- Intermolecular hydrogen bonds give rise to broad bands whereas intra molecular hydrogen bonds give sharp well defined bands
- Intermolecular H-bonding increases as the **concentration of the solution increases and IR absorption band shifted to lower value..**
- In dilute solution or in presence of non-polar solvent **there is little or no hydrogen bonding therefore very little shift of -OH band position.**
- **On the other hand, the absorption band due to intramolecular hydrogen band remain unchanged by change in concentration of solvent.**
- **The absorption frequency difference between free and associated molecule is smaller in case of intramolecular hydrogen bonding than that in intermolecular hydrogen bonding.**



Can IR spectroscopy distinguish these isomers?

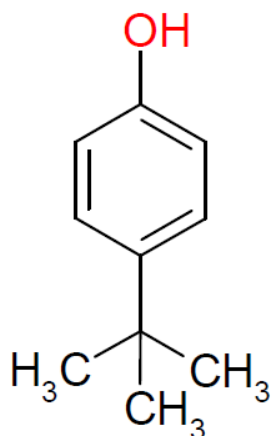


Intramolecular H-bonding
occurs in *O*-Hydroxy benzaldehyde
O-H absorption band at **3300 cm⁻¹** (lower frequency) (independent of concentration)

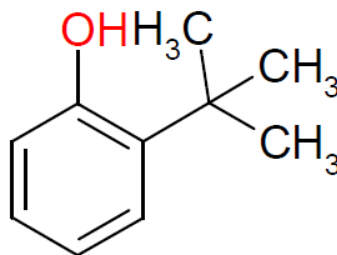


Association due to intermolecular H-bonding.
O-H absorption band at **3000 cm⁻¹** (broad) when run neat sample (high concentration).

Position of absorption raised as the solution is diluted by adding non aqueous solvent such as CCl₄

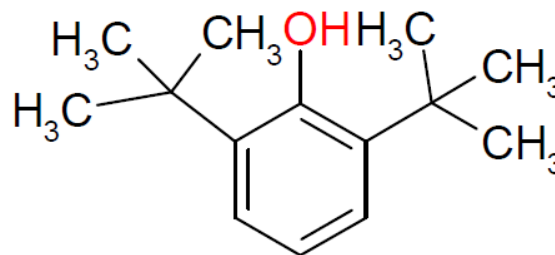
3105cm⁻¹

H-bonded OH

3105cm⁻¹3643cm⁻¹

partly

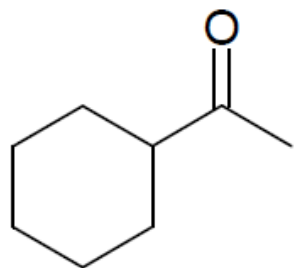
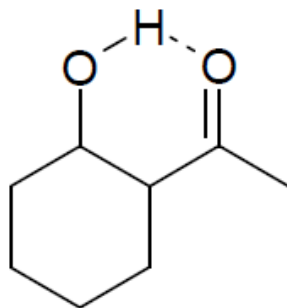
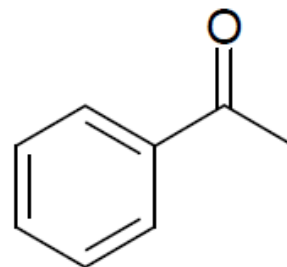
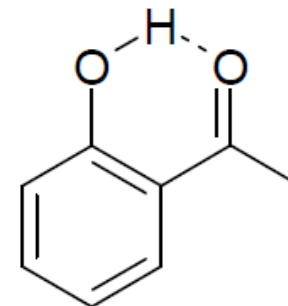
H-bonded OH

3643cm⁻¹

No H-bonding

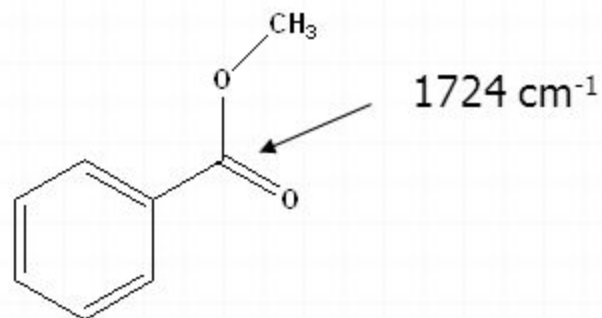
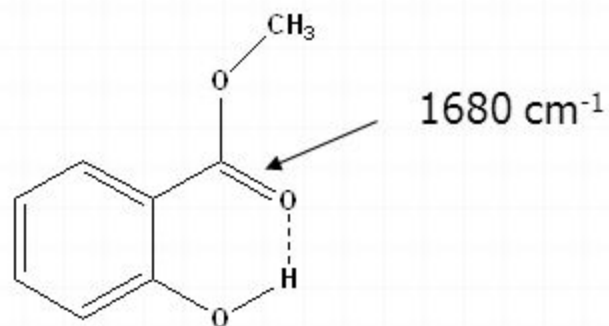
❖ Why the difference in absorption position?

*2,6-di-*t*-butylphenol* in which steric hindrance prevents hydrogen-bonding, No H-bonded hydroxyl band is observed, not even in spectra of neat samples.

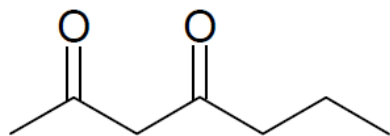
1715 cm^{-1} 1688 cm^{-1} 1685 cm^{-1} 1658 cm^{-1}

H-bonding reduces C=O stretching frequency. This is because the carbonyl bond order is reduced due to hydrogen bonding and the force constant falls..

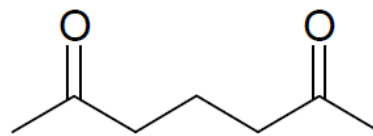
- Internal (intramolecular) H-bonding with carbonyl compounds can serve to lower the absorption frequency



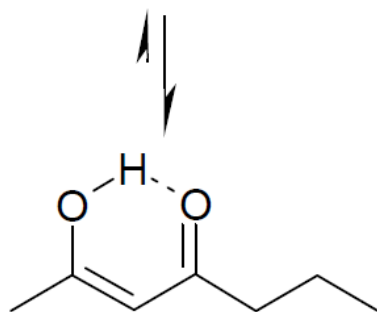
How can you distinguish the two isomers using IR?



Heptane-2,4-dione

36% 1725 cm⁻¹

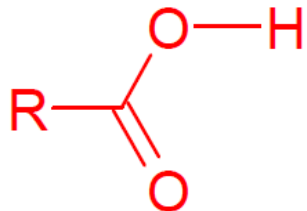
Heptane-2,6-dione

1715 cm⁻¹

64%

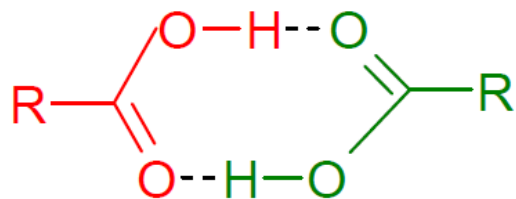
1613 cm⁻¹ 3077 cm⁻¹ for O-H stretching (H-bonded)

β -diketones exist as a mixture of ketonic and enolic form in equilibrium with each other. Enolic form is stabilised by resonance. For enolic form absorption band of C=O appear in 1613 cm⁻¹. The lowering effect is **due to exceptionally strong intramolecular hydrogen bonding**. Therefore two C=O absorption band appear, one for keto form (1725 cm⁻¹) and other for enol form (1613cm⁻¹). From the peak intensities percentage of keto and enol form can be obtained.



Monomers of saturated aliphatic
Carboxylic acids absorb at 1760 cm^{-1}

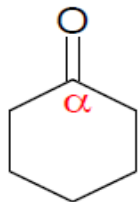
In liquid or solid state and in solutions ($>0.01\text{M}$),
carboxylic acids **exist as dimers**
due to **strong H-bonding**



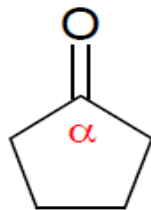
O-H stretching at 3000 cm^{-1}
(**very broad, intense**)

Dimerized saturated aliphatic
Carboxylic acids absorb at $1720\text{-}1706\text{ cm}^{-1}$

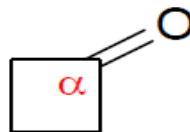
5) Ring Strain



Cyclohexanone

1715 cm⁻¹

Cyclopentanone

1751 cm⁻¹

Cyclobutanone

1775 cm⁻¹

Cyclopropanone

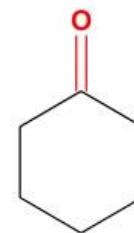
1815 cm⁻¹

The bond angle (α) influences the absorption frequency of C=O.

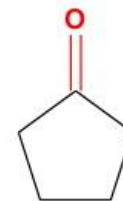
In non-cyclic ketones and in **cyclohexanone** $\alpha = 120^\circ$ (**normal**)

In strained rings in which $\alpha < 120^\circ$ (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 bonds.** Hence stretching frequency is increased.

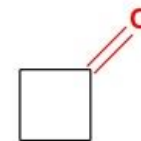
Therefore higher the ring strain, C=O stretching appear at higher frequency.

1715 cm⁻¹

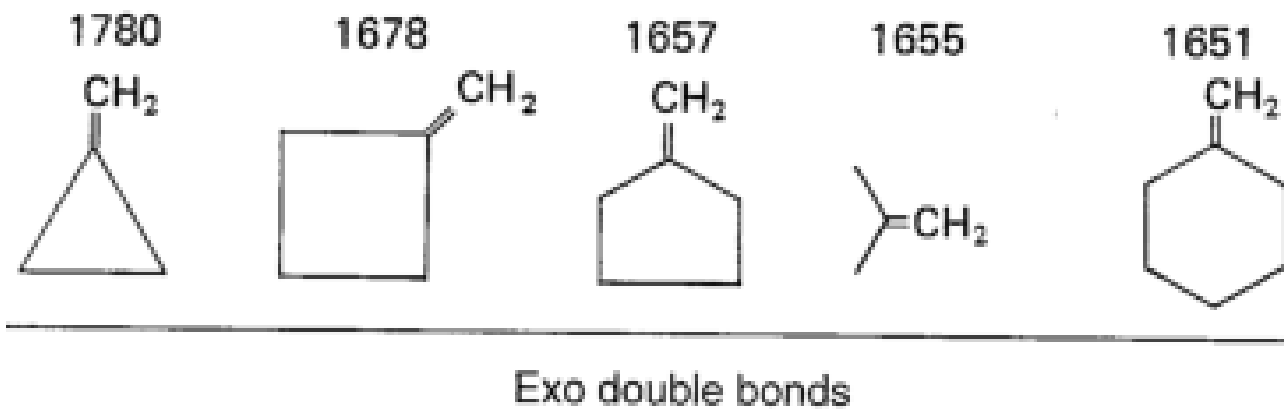
Angle ~ 120°

1751 cm⁻¹

< 120°

1775 cm⁻¹

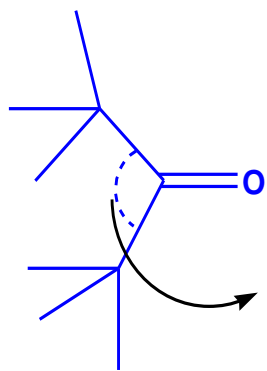
<< 120°



(a) Strain moves the peak to the left.

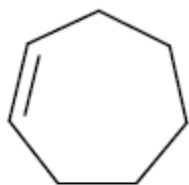
In case the bond angle $\alpha > 120^\circ$

Opposite effect operates i.e., C=O bond has less s-character than normal C=O bond.



Bond angle greater than normal sp^2 angle i.e., 120°
so more s character is used to form C-C bond and therefore C=O has more p-character.

$\nu_{C=O} = 1697 \text{ cm}^{-1}$ This causes weakening of C=O bond and lower the C=O stretching frequency.

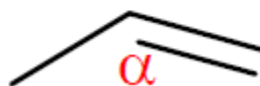
1650cm⁻¹1646cm⁻¹1611cm⁻¹1566cm⁻¹

Decreasing bond angle

Decreasing order of C=C stretching frequency

The C=C stretching vibration is **coupled** with **C-C stretching vibration** of the adjacent bonds.

Coupling is dependent on bond angle α



As the angle (α) becomes smaller the coupling interaction becomes less until it is minimum at 90° (the attached C-C bond is orthogonal to C=C bond)



1566cm⁻¹



1641cm⁻¹

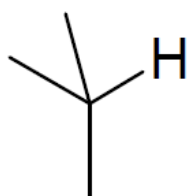
In cyclopropene, interaction becomes **again appreciable** (1641cm⁻¹)

The **C=C** vibration is **strongly coupled** to the attached **C-C** single bond vibration

6) Coupled Vibration and Fermi Resonance

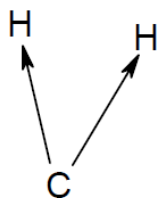
- An isolated C-H bond has only one stretching frequency, but the stretching vibrations of C-H bonds in CH₂ groups combine together to produce **two coupled vibrations of different frequencies** – **the antisymmetric, ν_{anti} , symmetric, ν_{sym}** .
- The C-H bonds in CH₃ groups also give rise to symmetric and antisymmetric vibrations, **these are of different frequencies from those of CH₂ group**.
- **Asymmetric vibration always takes place at high wave number compared with symmetric vibration.**

methine

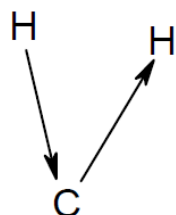


2890cm⁻¹

Methylene group



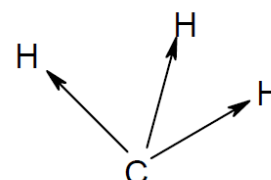
Symetrical
stretching (ν_s)
2870-2845cm⁻¹



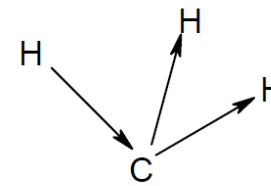
Asymetrical
stretching (ν_{as})
2940-2915cm⁻¹

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Methyl group



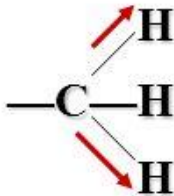
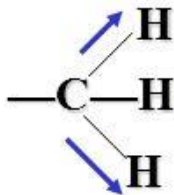
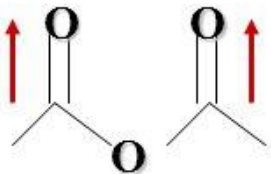
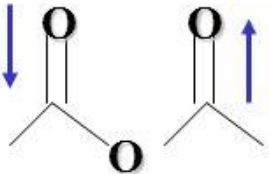
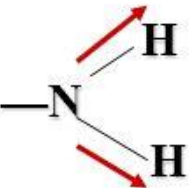
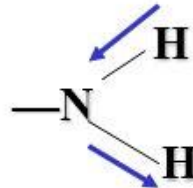
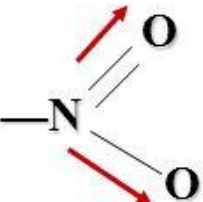
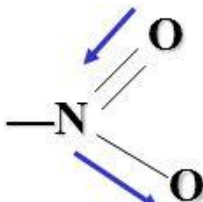
Symetrical
stretching (ν_s)
2885-2860cm⁻¹



Asymetrical
stretching (ν_{as})
2975-2950cm⁻¹

<

Symmetrical and asymmetrical stretch

	Symmetrical Stretch	Asymmetrical Stretch
Methyl	 $\rightarrow 2872 \text{ cm}^{-1}$	 $\rightarrow 2962 \text{ cm}^{-1}$
Anhydride	 1760 cm^{-1}	 1800 cm^{-1}
Amino	 3300 cm^{-1}	 3400 cm^{-1}
Nitro	 1350 cm^{-1}	 1550 cm^{-1}

Vibrational coupling takes place when

- Two bonds vibrating with similar frequency
- The bonds are reasonably close in molecules

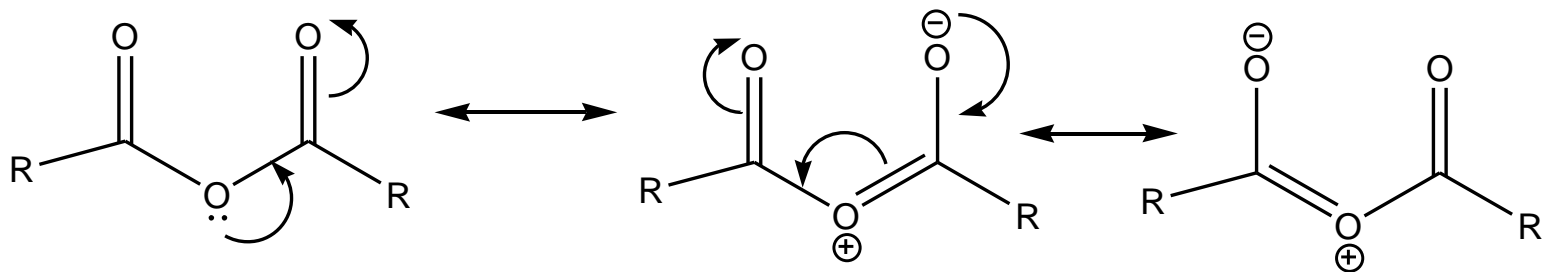
Different types of coupling:

1. Coupling vibrations may both be fundamental i.e., two vibrational level have same energy.

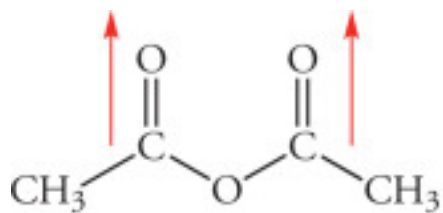
Such vibrations belongs to the same species (as in the case of AX_2 groups, such as $-CH_2-$, $-CH_3$ groups, NH_2 groups, $-NO_2$ groups). In this case a mutual perturbation of energy may occur, resulting in the shift of one towards lower frequency and other towards higher.

- ❖ **Carboxylic acid anhydrides give rise to two C=O str absorption vanti**, vsym around 1800-1900 cm⁻¹, with a separation of about 65 cm⁻¹

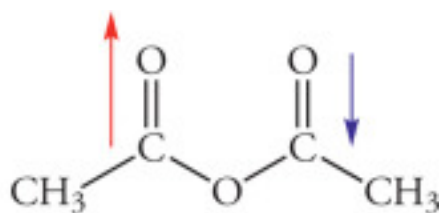
Here coupling occur between two carbonyl groups, which are indirectly linked through -O-. The interaction is encouraged because of the slight double bond character in the carbonyl - oxygen bonds due to resonance, since this will keep the system coplanar. The high-frequency band in this case is the symmetric C=O stretching.



Anhydrides- resonance form



symmetric stretch
1820 cm⁻¹



asymmetric stretch
1768 cm⁻¹

2. Fundamental vibration may couple with the overtone of some other vibration

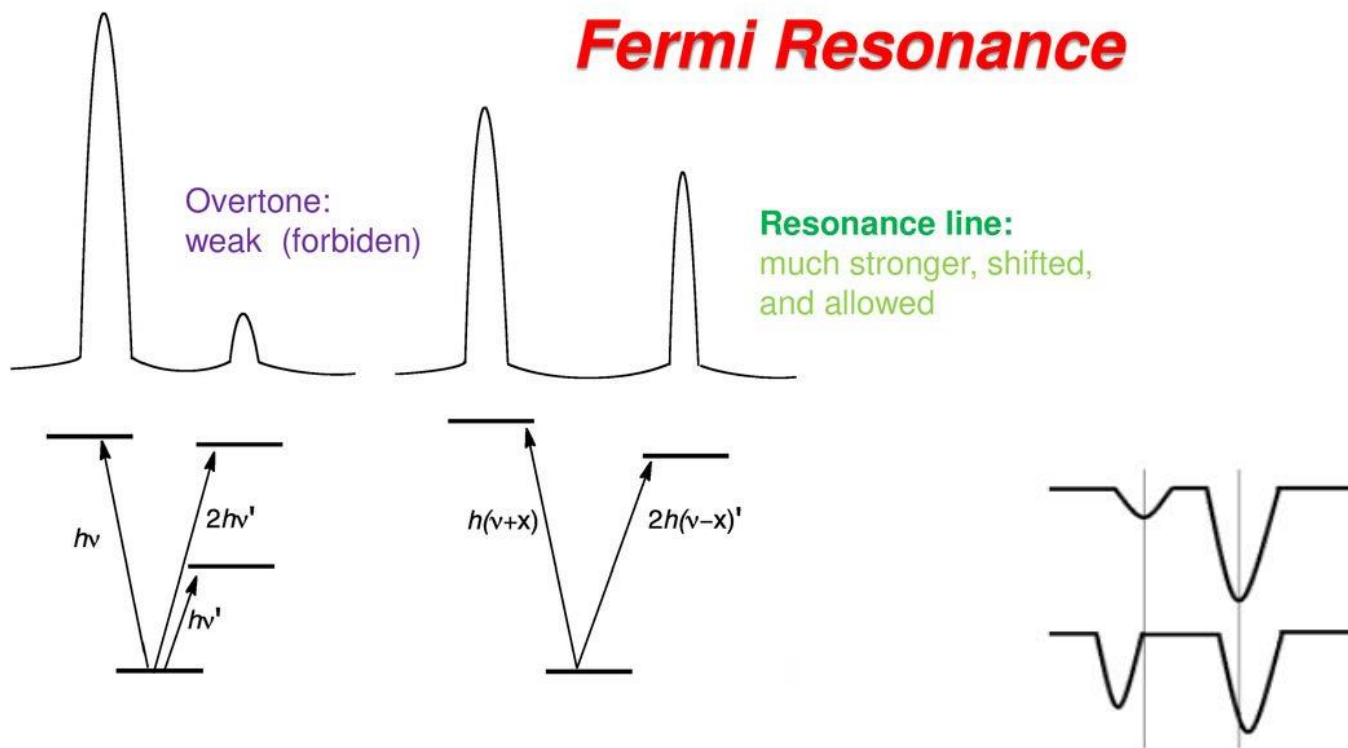
❖ It may happen that **the energy of an overtone level chances to coincide with the fundamental mode of different vibration**. A type of resonance occurs as in this case. This type of resonance is called **Fermi Resonance**, first described by Enrico Fermi.

Fermi resonance was first discovered in carbon dioxide by Fermi

In CO₂, for symmetric stretching, Raman spectrum shows a strong band at 1337 cm⁻¹. The two bending vibrations are at 667.3 cm⁻¹. **Now the first overtone of this bending vibration is at $667.3 \times 2 = 1334.6$ cm⁻¹ which is very close to fundamental vibration of symmetric stretching band 1337 cm⁻¹.** Thus **in this case coupling between two vibrational levels occurs and Fermi Resonance takes place resulting in the shift of first level towards higher frequency.**

The mutual perturbation of 1337 cm⁻¹ (fundamental) and 1334.6 cm⁻¹ (overtone) gives rise to two bands at 1285.5 cm⁻¹ and 1388.3 cm⁻¹ having intensity ratio of 1: 0.9.

Fermi Resonance



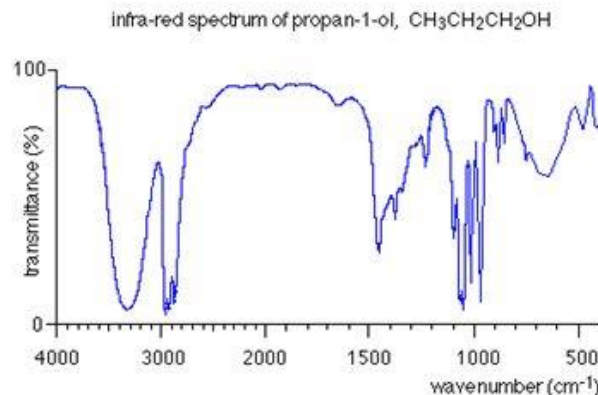
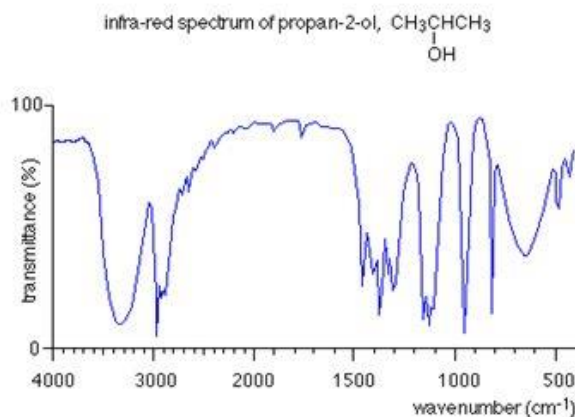
E.g.: CO₂

- It normally shows fundamental band at 1337 cm⁻¹ and overtone at 1334.6 cm⁻¹ .
- But due to the effect of Fermi resonance the first band shift towards higher frequency and give rise to two bands at 1285.5 cm⁻¹ and 1388.3 cm⁻¹ .

Another example of Fermi Resonance is given by aldehyde in which C-H stretching absorption usually appears as a doublet ($\sim 2820 \text{ cm}^{-1}$ and $\sim 2720 \text{ cm}^{-1}$) **due to the interaction between C-H stretching (Fundamental) and the overtone of C-H deformation (bending).**

Fingerprint region

The **fingerprint region** is found on the right hand side of an infrared spectrum from about 1500-500 cm^{-1} . It can be used to compare two similar compounds.



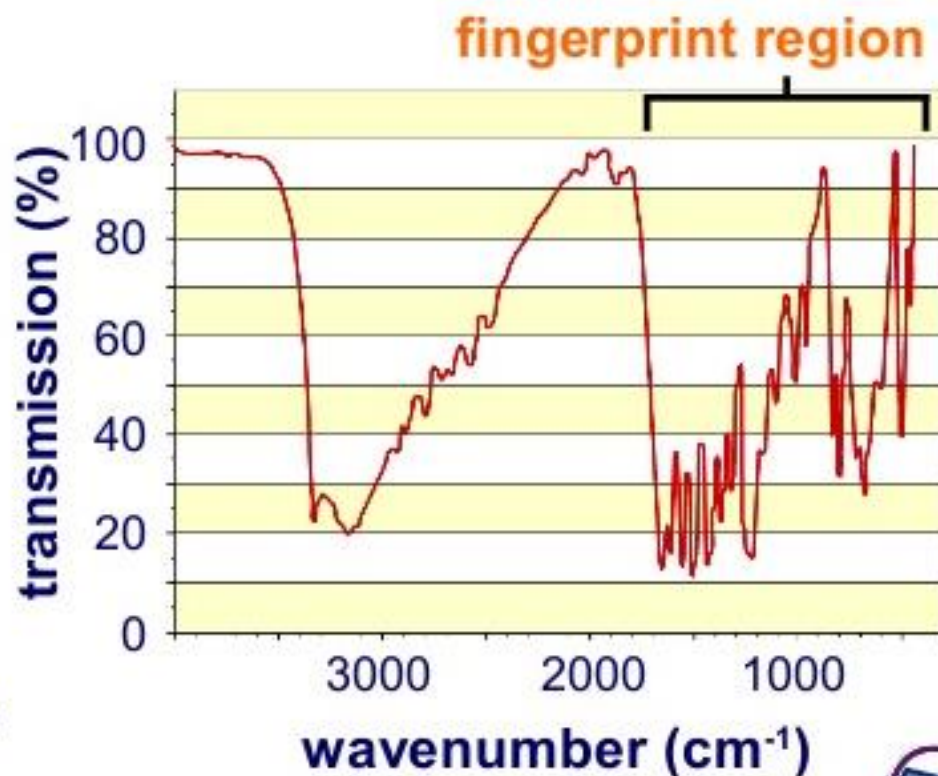
Above two molecules containing the same functional group show similar absorption above 1500 cm^{-1} but their spectra differ in finger print region.

Using finger print region

The region below 1500 cm^{-1} , usually called the **finger print region**, has many peaks that are difficult to assign. The pattern of these peaks is unique to a particular compound.

A substance may be identified by comparing the IR spectrum to a database of reference spectra.

An exact match in the fingerprint region identifies a compound.



2. Fingerprint region

- This region accounts for many absorption bands characteristic of functional group. Since numbers of sharp bands of varying intensities are encountered, close examination is needed.
- This region is useful for the identification of compounds since no two compounds can have identical IR spectra under identical conditions. (**Except enantiomers**)
- Regions present below 1500 cm^{-1} shows absorption bands due to bending vibrations and stretching vibrations of C-C, C-O and C-N bonds.
- Regions less than 1250 cm^{-1} consists of complex vibrational and rotational spectra of the complete molecule.