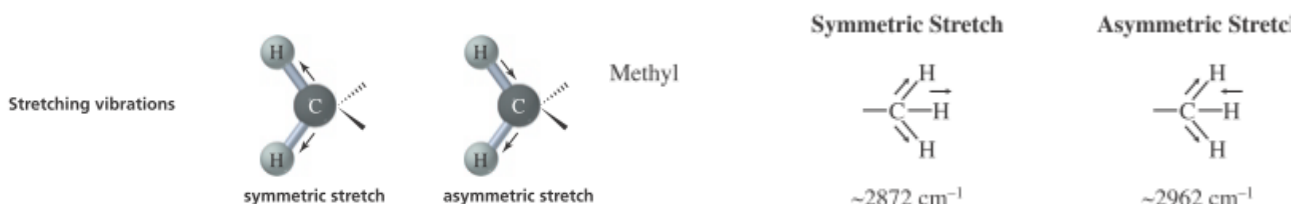


## Factors influencing vibration frequencies

The difference between calculated and experimental value of vibration frequencies arises from the fact that the exact position of the absorption band depends on other structural features of the molecule, such as electron delocalization, the electronic effect of neighboring substituents, bond angles, and hydrogen bonding. Following are some of the factors responsible for shifting the vibrational frequencies from their normal value:

### 1: Coupling vibration and Fermi resonance:

In any group of three or more atoms, at least two of which are identical ( $AX_2$ ), they appear as a doublet, two modes of vibration symmetry and asymmetry, e.g. coupling interaction between fundamental bands:



Other examples:  $\text{NH}_2$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ , anhydride...

In amides, the  $\text{C}=\text{O}$  band partially overlaps the  $\text{N}-\text{H}$  bending band which appears in the range  $1640\text{--}1620 \text{ cm}^{-1}$ , making the  $\text{C}=\text{O}$  band appear as a doublet.

**Fermi resonance:** This phenomenon was first observed by **Enrico Fermi**, is other type of coupling vibrations, it happens when the energy of an overtone level coincides with the fundamental mode of different vibration thus the molecule transfer its energy from fundamental to overtone and back again or (resonance). This type of resonance gives rise to a pair of transitions of equal intensities. Example: The  $\text{C}-\text{H}$  str. absorption of aldehyde appears as a doublet at ( $\sim 2820$  and  $2720 \text{ cm}^{-1}$ ) due the coupling interaction between  $\text{C}-\text{H}$  str. (fundamental) and the overtone of  $\text{C}-\text{H}$  bending (non-fundamental).

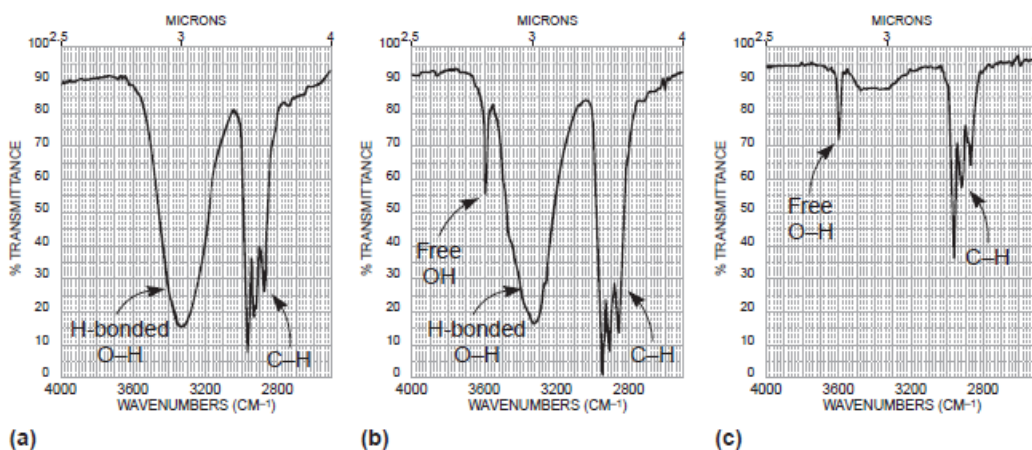
n-butyl vinyl ether gives two bands at  $1640$  &  $1630 \text{ cm}^{-1}$  due to the mixing of overtone of fundamental band at  $810 \text{ cm}^{-1}$  with fundamental at  $1640 \text{ cm}^{-1}$ .

Q6: Fermi resonance of cyclopentanone occurs at  $1746$  &  $1750 \text{ cm}^{-1}$ ?

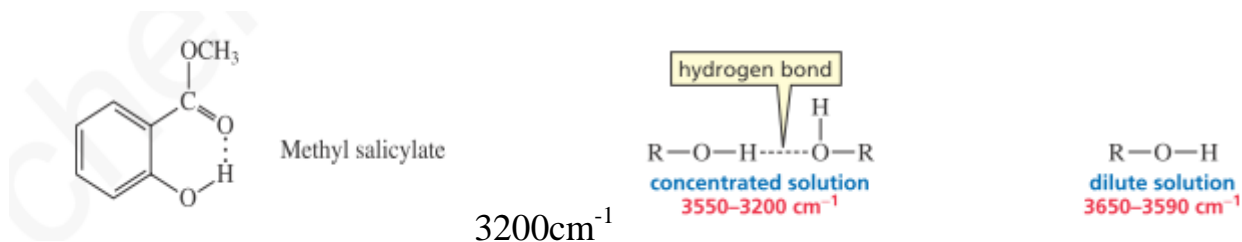
## 2: Hydrogen bonding:

**O-H** absorption bands are easy to detect. Polar bonds show intense absorption bands and the bands are quite broad. The **position** and the **breadth** of an absorption band 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 a bond if it is hydrogen bonded, because the hydrogen is attracted to the oxygen of a neighboring molecule. Therefore, the stretch of a concentrated (hydrogen bonded) solution of an alcohol occurs at  $3550$  to  $3200\text{cm}^{-1}$ , whereas the O-H stretch of a dilute solution (with little or no hydrogen bonding) occurs at  $3650$  to  $3590\text{cm}^{-1}$ .

Hydrogen-bonded OH groups have broader absorption band than non-hydrogen-bonded OH groups.



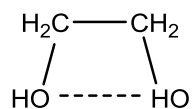
Intra-molecular hydrogen bonding, present in ortho carbonyl substituted phenols, usually shifts the broad O-H band to a lower frequency. For example, the O-H band is centered at about  $3200\text{cm}^{-1}$  in the neat spectrum of methyl salicylate, while O-H bands from normal phenols are centered at about  $3350\text{cm}^{-1}$ .



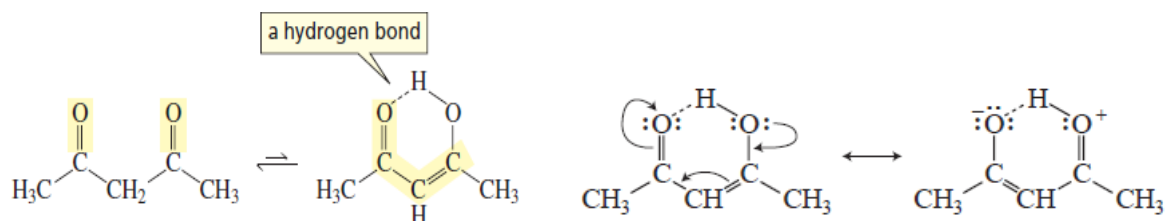
The intra-molecular hydrogen-bonded band does not change its position significantly even at high dilution because the internal bonding is not altered by a change of concentration. Although phenols have broader O-H bands than alcohols, it is difficult to assign a structure based on this absorption; use the aromatic C=C region and the C-O stretching vibration to assign a phenolic structure. Finally, the OH stretching vibrations in carboxylic acids also occur in this region. They may easily be distinguished from alcohols and phenols by the presence of a very broad band extending from 3400 to 2400  $\text{cm}^{-1}$  and the presence of carbonyl absorption.

The spectrum of glycol in dilute  $\text{CCl}_4$  shows two O-H bands at **3644 and 3612  $\text{cm}^{-1}$**  for free OH and O-H hydrogen bonded respectively. The shift **32  $\text{cm}^{-1}$**  is small indicating intra-molecular H.B not intermolecular H.B. But at higher conc., the IR spectra show a

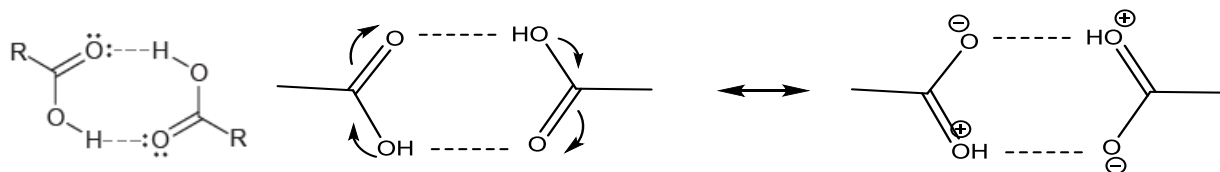
third strong and broad band at 3477  $\text{cm}^{-1}$  why?



Notes: In enols and chelates the H.B. is exceptionally strong and the O-H band appears at lower value, at low conc. Free O-H band may not be seen due the stabilization by resonance, e.g. acetyl acetone.



Carboxylic acids form dimer and bridge which stabilized by resonance, C=O appear at 1700 and O-H broad at 3000-2500 $\text{cm}^{-1}$ . While in vapor phase C=O appear at 1770  $\text{cm}^{-1}$  why?

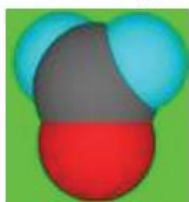


**Hydrogen bonds** in amines are weaker than alcohols? N-H str. appears at 3500 $\text{cm}^{-1}$  in dilute solution and 3300 $\text{cm}^{-1}$  in conc.

### 3: Electronic effect: The frequency shifts due to the electronic effects are include:

**3A:** Electronic effect include inductive (+I, -I), **3B:** mesomeric (resonance) (+M,-M) and **3C:** field effects. These effects cannot be isolated from one another and the contribution of one of them can only be estimated approximately. Under the influence of these effects, the force constant or the bond strength changes and its absorption frequency shifts from the normal value. The introduction of alkyl group causes + I effect which results in the lengthening or the weakening of the bond and hence the force constant is lowered and wave number of absorption decreases. Let us compare the wave numbers of (C=O) absorptions for the following compounds:

- |   |                       |
|---|-----------------------|
| (i) Formaldehyde (HCHO)                       | 1750 $\text{cm}^{-1}$ |
| (ii) Acetaldehyde ( $\text{CH}_3\text{CHO}$ ) | 1745 $\text{cm}^{-1}$ |
| (iii) Acetone ( $\text{CH}_3\text{COCH}_3$ )  | 1715 $\text{cm}^{-1}$ |



Formaldehyde



Acetaldehyde



Acetone

**Note.** Aldehydes absorb at higher wave number than ketones.

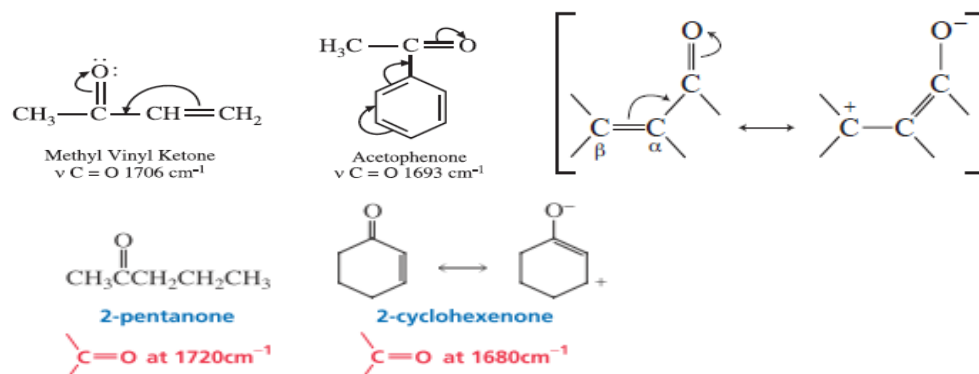
The introduction of an electronegative atom or group causes (-I effect) which results in the bond order to increase. Thus, the force constant increases and hence the wave number of absorption rises. Now, let us consider the wave numbers of absorptions in the following compounds:

- (i) Acetone ( $\text{CH}_3\text{COCH}_3$ ) 1715  $\text{cm}^{-1}$
- (ii) Chloroacetone ( $\text{CH}_3\text{COCH}_2\text{Cl}$ ) 1725  $\text{cm}^{-1}$
- (iii) Dichloroacetone ( $\text{CH}_3\text{COCHCl}_2$ ) 1740  $\text{cm}^{-1}$
- (iv) Tetrachloroacetone ( $\text{Cl}_2\text{CH}-\text{CO}-\text{CHCl}_2$ ) 1750, 1778  $\text{cm}^{-1}$

In most of the cases, mesomeric effect works along with inductive effect and cannot be ignored. Conjugation lowers the absorption frequency of C=O stretching whether the conjugation is due to  $\alpha$ ,  $\beta$ -unsaturation or due to an aromatic ring. In some cases, inductive effect dominates over mesomeric effect while reverse holds for other cases.

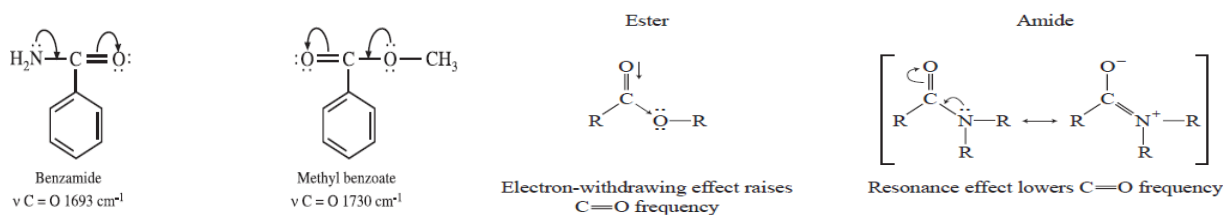
*Mesomeric effect* causes lengthening or the weakening of a bond leading in the lowering of absorption frequency. Consider the following compounds:

In these two cases, (–I effect) is dominated by mesomeric effect and thus, the absorption frequency falls.



In some cases, where the lone pair of electrons present on an atom is in conjugation with the double bond of a group, say carbonyl group, the mobility of the lone pair of electrons matters. This conjugation increases the single bond character of the C = O and C = C bonds in the resonance hybrid and hence lowers their force constants, resulting in a lowering of the frequencies of carbonyl and double-bond absorption. Conjugation with triple bonds also shows this effect.

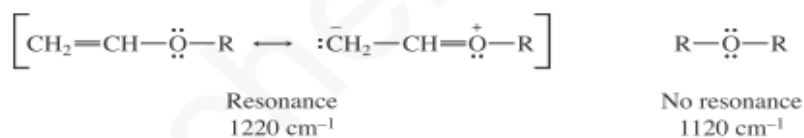
Let us compare the absorption frequencies of  $\nu$  (C=O) stretching in amides and esters.



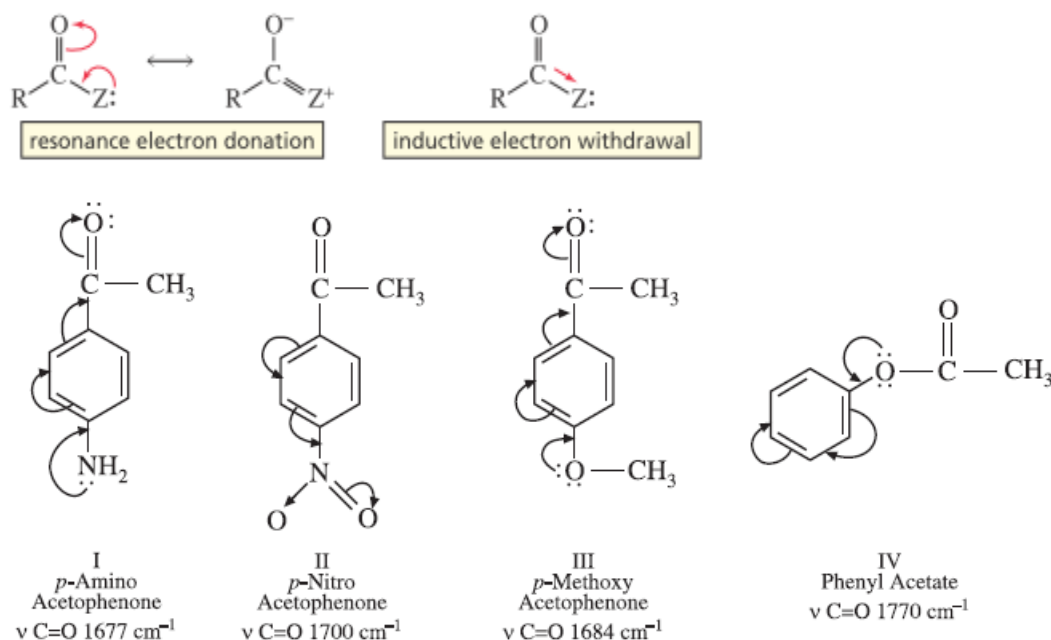
As nitrogen atom is less electronegative than oxygen atom, the electron pair on nitrogen atom in amide is more labile and participates more in conjugation. Due to this greater degree of conjugation, the C=O absorption frequency is much less in amides as compared to that in esters.

The C-O in vinyl alkyl ether is shifted to higher frequencies at ( $1220\text{cm}^{-1}$ ) because of increase double bond character. In dialkyl ethers the absorption occurs at  $1120\text{ cm}^{-1}$ . In addition, because resonance increases the polar character of the C = C double

bond, the band at about  $1640\text{ cm}^{-1}$  is considerably stronger than in normal C=C absorption.



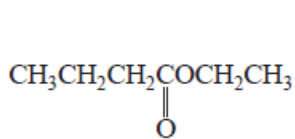
Putting an atom other than carbon next to the carbonyl group also causes the position of the carbonyl absorption band to shift. Whether it shifts to a lower or to a higher frequency depends on whether the predominant effect of the atom is to donate electrons by resonance or to withdraw electrons inductively.



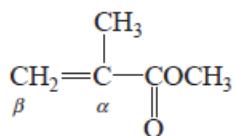
Due to the low electronegativity of nitrogen atom, the lone pair of electrons participates more in conjugation in compound I as compared to that in compound III. Thus, in compound I,  $\nu(\text{C=O})$  absorption occurs at lower wave number compared to that in compound III. In compounds II and IV, inductive effect dominates over mesomeric effect and hence absorption takes place at comparatively higher frequencies.

**It is important to note that only inductive effect is considered when the compound is meta substituted.**

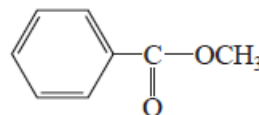
In para substitution, both inductive and mesomeric effects become important and the domination of one over the other will decide the wave number of absorption.



Ethyl butyrate  
1738  $\text{cm}^{-1}$



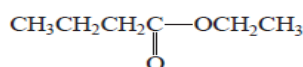
Methyl methacrylate  
1725  $\text{cm}^{-1}$



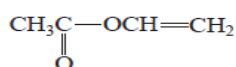
Methyl benzoate  
1724  $\text{cm}^{-1}$

Conjugation with a carbonyl group ( $\alpha,\beta$ - Unsaturation or Aryl Substitution). The  $\text{C}=\text{O}$  stretching vibrations are shifted by about 15 to 25  $\text{cm}^{-1}$  to lower frequencies with  $\alpha,\beta$ -unsaturation or aryl substitution. The spectra of both methyl methacrylate and methyl benzoate show the  $\text{C}=\text{O}$  absorption shift from the position in a normal ester, ethyl butyrate.

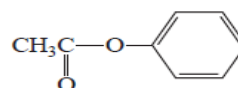
But the conjugation with the ester single-bonded oxygen shifts the  $\text{C}=\text{O}$  vibrations to higher frequencies. Apparently, the conjugation interferes with possible resonance with the carbonyl group, leading to an increase in the absorption frequency for the  $\text{C}=\text{O}$  band. The spectra of both vinyl acetate and phenyl acetate show the  $\text{C}=\text{O}$  absorption shift to higher frequencies 1762 and 1765 respectively.



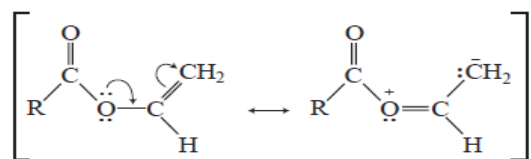
Ethyl butyrate  
1738  $\text{cm}^{-1}$



Vinyl acetate  
1762  $\text{cm}^{-1}$

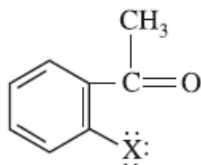


Phenyl acetate  
1765  $\text{cm}^{-1}$



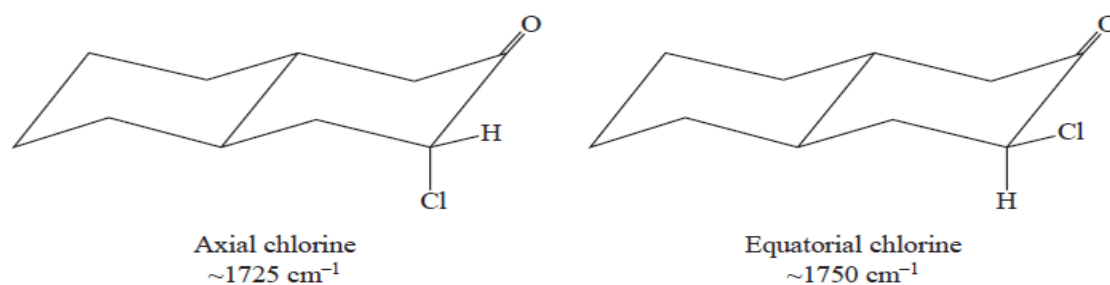
### 3C: Field effect:

In ortho substitution, inductive effect, mesomeric effect along with steric effect are considered. In ortho substituted compounds, the lone pairs of electrons on two atoms influence each other through space interactions and change the vibrational frequencies of both the groups. This effect is called **Field effect**. Consider ortho haloacetophenone.



The non-bonding electrons present on oxygen atom and halogen atom cause electrostatic repulsions. This causes a change in the state of hybridization of C=O group and also makes it to go out of the plane of the double bond. Thus, the conjugation is diminished and absorption occurs at a higher wave number. Thus, for such ortho substituted compounds, cis absorbs (field effect) at a higher frequency as compared to the trans isomer.

In ketones two bands, result from the substitution of an adjacent chlorine atom. One arises from the conformation in which the chlorine is rotated next to the carbonyl, and the other is due to the conformation in which the chlorine is away from the group. When the chlorine is next to the carbonyl, non-bonded electrons on the oxygen atom are repelled, resulting in a stronger bond and a higher absorption frequency. Information of this kind can be used to establish a structure in rigid ring systems such as in the following examples:

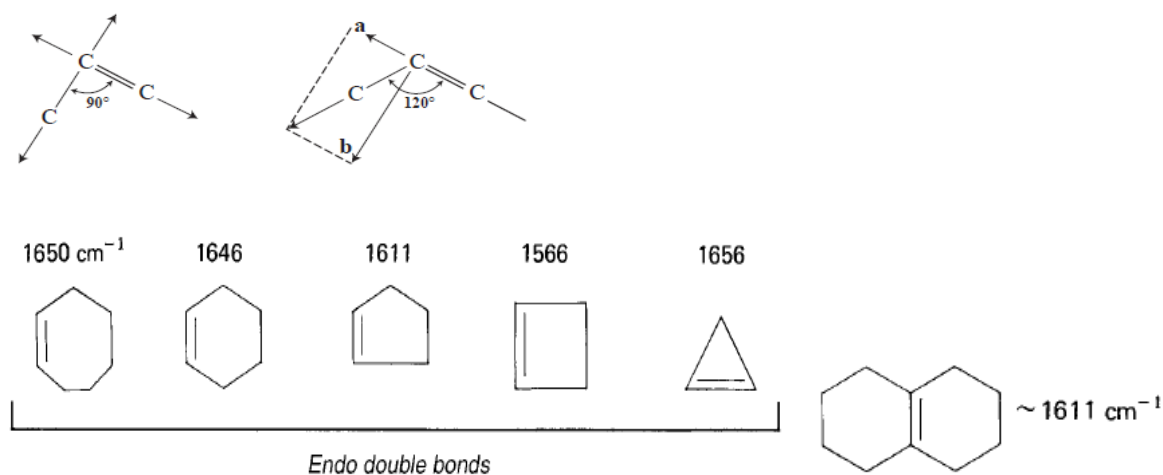


#### 4: Bond angle, ring size and ring strain:

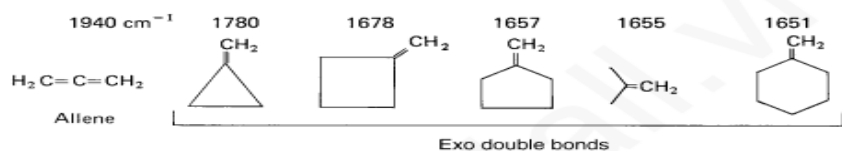
The absorption frequency of internal (endo) double bonds in cyclic compounds is very sensitive to ring size. As shown in e.g. the absorption frequency decreases as the internal angle decreases, until it reaches a minimum at  $90^\circ$  in cyclobutene. The frequency increases again for cyclopropene when the angle drops to  $60^\circ$ . This initially unexpected increase in frequency occurs because the C=C vibration in cyclopropene is strongly **coupled to** the attached C-C single-bond vibration. When the attached C-C



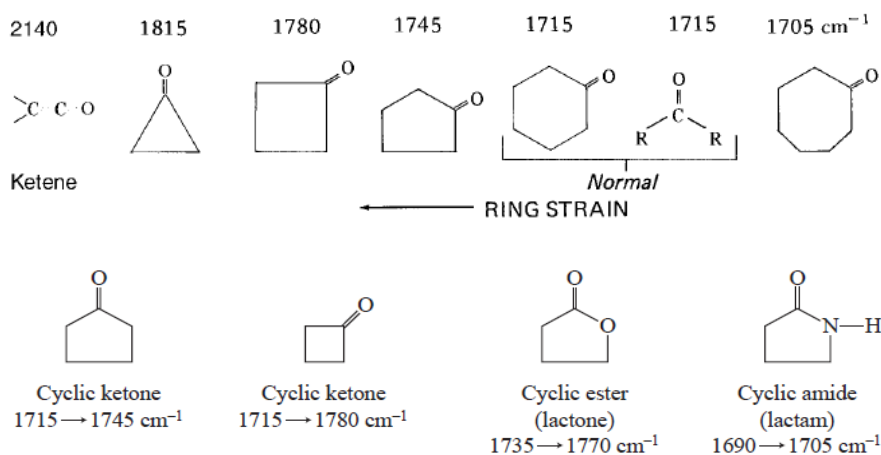
bonds are perpendicular ( $90^\circ$ ) to the C=C axis, as in cyclobutene, does not couple. When the angle less or greater than  $90^\circ$  the C-C will couple C=C tend to increase the C=C vibration frequencies.



External (exo) double bonds give an increase in absorption frequency with decreasing ring size, as shown in e.g. . Allene is included in the figure because it is an extreme example of an exo double-bond absorption. Smaller rings require the use of more p character to make the C - C bonds form the requisite small angles (recall the trend:  $sp = 180^\circ$  ,  $sp^2 = 120^\circ$  ,  $sp^3 = 109^\circ$  ,  $sp > 3 = < 109^\circ$  ). This removes p character from the sigma bond of the double bond but gives it more s-character, thus strengthening and stiffening the double bond.

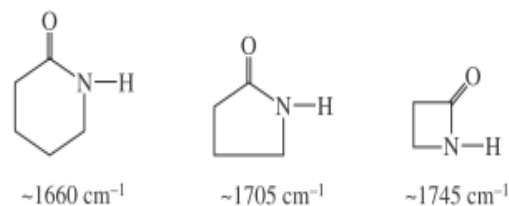


Decreasing the ring size increases the frequency of the C=O absorption as shown in C=C stretching vibrations and exocyclic double bonds. All of the functional groups which can form rings, give increased frequencies of absorption with increased angle strain. For ketones and esters, there is often a  $30\text{cm}^{-1}$  increase in frequency for each carbon removed from the unstrained six-membered ring value.

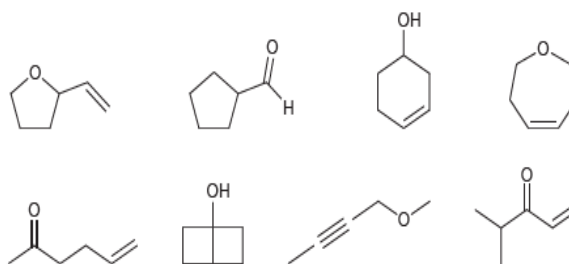
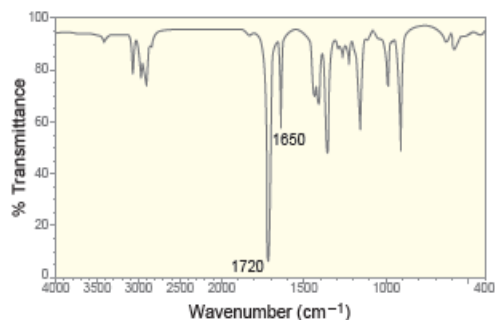


EFFECTS OF RING SIZE,  $\alpha,\beta$  UNSATURATION, AND CONJUGATION WITH OXYGEN ON THE C=O VIBRATIONS IN LACTONES

Ring-Size Effects ( $\text{cm}^{-1}$ )	$\alpha,\beta$ Conjugation ( $\text{cm}^{-1}$ )	Conjugation with Oxygen ( $\text{cm}^{-1}$ )
1735	1725	1760
1770	1750	1800
1820		



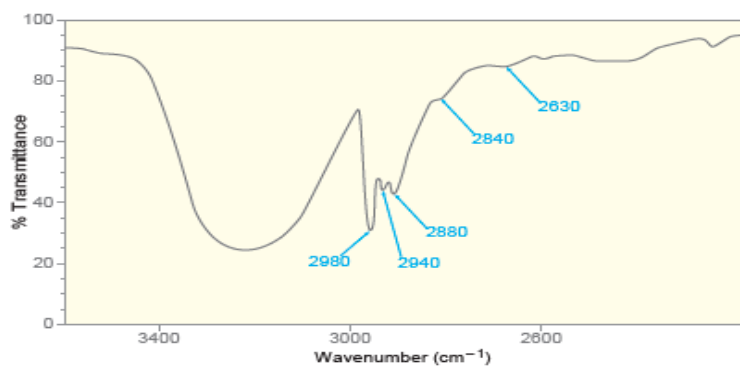
Q7/ A compound with molecular formula  $\text{C}_6\text{H}_{10}\text{O}$  gives the following IR spectrum. Identify the structure below that is most consistent with the spectrum:



## IR Spectroscopy for Testing Blood-Alcohol Levels

The intensity of the signal is dependent on the concentration of the sample being analyzed. This fact is used by **law enforcement officials** to measure blood alcohol levels accurately. 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. For example, the Intoxilyzer 5000 measures the intensity of absorption at the five frequencies illustrated. A breath sample is analyzed, and the device is able to calculate the concentration of ethanol in the sample based on the intensities of these signals.



Q8/ Choose the structure that best fits the infrared spectrum shown.

