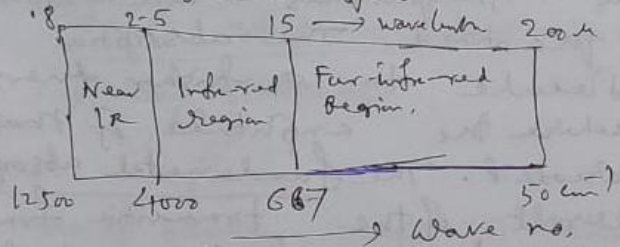


Topic: "Infrared spectroscopy"

SEM-4 (1) (M.S.)

By: Dr. Malay Kumar Bhattacharya.

Infrared spectrum is an ~~is~~ important record which gives sufficient information about the structure of a compound. The absorption of IR radiations (quantised) causes the various bands in a molecule to stretch and bend with respect to one another. The most important region for an organic chemist is 2.5  $\mu$  to 15  $\mu$  ( $1 \mu = 10^{-4} \text{ cm}$ ) in which molecular vibrations can be detected and measured in an infra-red spectrum and in a Raman spectrum.



Mostly infrared spectra of organic compounds are plotted as percentage transmittance against wave number.

$$\text{wave number} = \frac{1}{\text{wavelength in cm}}$$

Band intensity is either expressed in absorbance (A) or Transmittance (T).

$$A = \log_{10} (I/T)$$

In terms of wave no., the ordinary infrared region covers 4000  $\text{cm}^{-1}$  to 667  $\text{cm}^{-1}$ . The technique can be employed to establish the identity of two compounds or to determine the structure of a new compound. In order to determine the structure of a new compound, it is quite useful to predict the presence of certain functional groups which absorb at definite frequencies. For example, the -OH group in a compound absorbs at 3600-3200  $\text{cm}^{-1}$ ;  $\text{C}=\text{O}$  of ketones shows band at 1710  $\text{cm}^{-1}$ . The shift in absorption position helps in predicting the factors which cause this shift.

(H.B) (2) (14)

Some of the factors which shift the absorption band for a particular group from its characteristic frequency (or wave number) are inductive effect, conjugation, angle of strain, hydrogen bonding etc. It is, thus, a very reliable technique for disclosing the identity of a compound.

Describe the molecular processes that occur when IR radiation is absorbed by a molecule.

Ans: When IR light impinges on a molecule, only certain frequencies — those corresponding to vibrational frequencies — are absorbed; the process is quantized. The absorption excites the molecule to a higher energy vibrational state where the amplitude of that vibration is increased. The fundamental absorption peak is a result of the transition from the ground state to the first excited state. Radiation in the energy range of 2-11 kcal/mole corresponding to the range encompassing ~~the~~ stretching and bending frequencies in most covalent molecules.

What are the two fundamental vibrations for molecules?

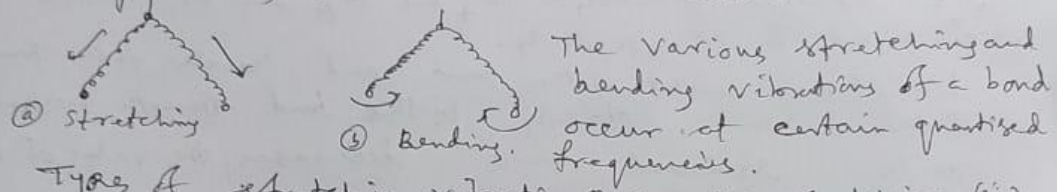
Ans: It may be noted that the atoms in a molecule are not held rigidly. The molecule may be visualized as consisting of balls of different sizes tied with springs of varying strengths. Here balls and springs correspond to atoms and chemical bonds respectively. When Infra-red light is passed through the sample, the vibrational and the rotational energies of the molecules are increased. Two kinds of fundamental vibrations are:

(a) Stretching: In this type of vibration, distance between the two atoms increases but the atoms remain in the same bond axis.



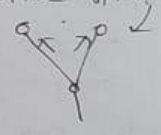
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(b) Bending: In this type of vibrations, the positions of the atoms change with respect to the original bond axis. We know that more energy is required to stretch a spring than that required to bend it. Thus, we can safely say that stretching absorptions of a bond appear at high frequencies (higher energy) as compared to the bending absorptions of the same bond.

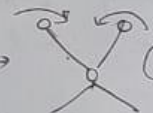


Types of stretching vibrations (i) Symmetric stretching (ii)

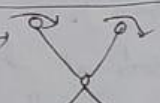
Asymmetric stretching



Types of bending vibrations: (i) Scissoring

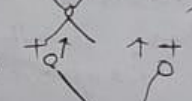


(ii) Rocking



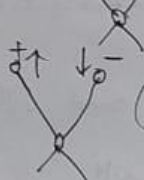
(The movement of the atoms takes place in the same direction) (Two atoms opposite each other)

(iii) Wagging



(Two atoms move up and below the plane with respect to the central atom. Same direction)

(iv) Twisting



(Bending in the opposite direction)

(iii) and (iv) out of plane bending

Stretching and bending (scissoring and rocking) → In plane bend  
What condition must be met for absorption of IR radiation by a molecule?

(a) In order to absorb IR radiation a molecule must undergo a net change in its dipole moment, due to its vibrational motion. (b) Stretching in homodiatonic molecules, e.g.,  $N_2$ ,  $O_2$ ,  $H_2$ , will not change the dipole moment and so these IR inactive molecules do not absorb. Heterodiatonic molecules whose atoms do not have

The same electronegativities, e.g., HCl and CBr, are IR active and absorb.

Q1) Write the equation that relates the fundamental stretching frequency of a covalent bond, A-B, to the force constant, k, of the bond and the masses of atoms A and B.

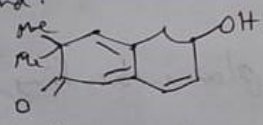
By:  $\frac{v}{c} = \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$   $\left[ \mu = \frac{m_A m_B}{m_A + m_B} \right]$  {Application of Hooke's Law}

$\mu$  = reduced mass;  $m_A$  and  $m_B$  are the masses of A and B, respectively.  
 $k$  = force constant of the bond and relates to the strength of the bond. Clearly, if the bond strength increases or the reduced mass decreases, the value of the vibrational frequency increases.

As for example: C=C stretching is expected to absorb at higher frequency than C-C stretching (for higher bond strength i.e. value of k) of the double bond.  
 Similarly, O-H stretching absorbs at higher frequency compared to C-H bond (Due to smaller value of reduced mass for O-H compared to C-H bond).

We can expect O-H to absorb at higher frequency as compared to F-H. But this is not true. Actually, F-H absorbs at the higher frequency. This can be explained due to the higher electronegativity of fluorine compared to that of oxygen.

Q2: Predict the expected UV and IR spectra of the following compound.



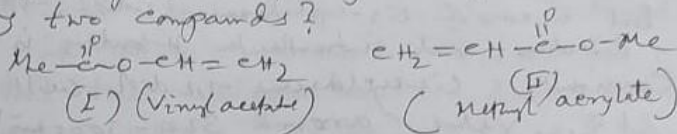
By: In case of the given compound, UV absorption peak ( $\lambda_{max}$ ) can be predicted on the basis of Woodward-Fieser's rule. This is shown below;

- $\lambda$  value in nm:
- 1) 215 nm for  $\alpha, \beta$  unsaturated six-membered ring ketone.
  - 2) 30 nm for one extend conjugation
  - 3) 39 nm for a homocyclic conjugated diene system.
  - 4) 12 nm for one  $\beta$ -ring residue.
  - 5) 17 nm for one  $\gamma$ -ring residue.
  - 6) 17 nm for two exocyclic double bonds
- Therefore,  $\lambda_{max}$  value for the compound to be 324 nm



The IR spectrum of the compound will show two very distinguished absorption peaks. One is around  $\bar{\nu}_{max}$  1640  $cm^{-1}$  for  $C=O$  stretching for  $\alpha-\beta$  unsaturated six-membered carbonylic ketone and another around  $\bar{\nu}_{max}$  3650  $cm^{-1}$  for free O-H stretching.

Q.3: How can you spectroscopically distinguish between the following two compounds?

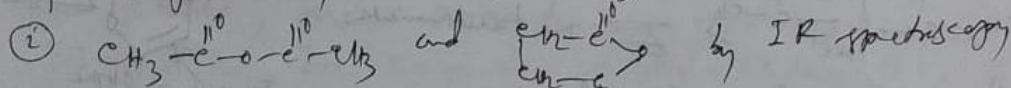


Ans: The compound (I) is Vinyl acetate and the compound (II) is methyl acrylate. Both are esters and give absorption peaks in IR for  $\pi-\pi^*$  and  $n-\pi^*$  electron transitions in their IR spectra. In case of (I), the ester carbonyl is not conjugated to the double bond but in case of (II), the double bond is conjugated to the ester  $C=O$  group. Consequently, Vinyl acetate would give absorption peaks at shorter wave length region with low  $\bar{\nu}_{max}$  values and methyl acrylate will do so at longer wave length (bathochromic shift) with higher  $\bar{\nu}_{max}$  values.

In case of IR spectra, methyl acrylate, being a  $\alpha-\beta$  unsaturated ester, will show absorption peak around  $\bar{\nu}_{max}$  1730-1715  $cm^{-1}$  for ester  $C=O$ . But vinyl acetate (I) is not a conjugated system and the ester  $C=O$  will give peak around  $\bar{\nu}_{max}$  1800-1750  $cm^{-1}$ .

Therefore, the above two compounds can be distinguished by both IR and UV spectroscopy.

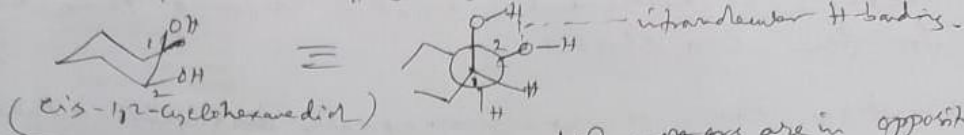
Q.4 How will you distinguish between the following pairs of compounds by the spectroscopic method mentioned.



(ii) cis-cyclohexane-1,2-diol and cis-cyclohexane-1,3-diol by IR spectroscopy

Ans:  $CH_3-\overset{O}{\parallel}C-O-\overset{O}{\parallel}C-CH_3 \rightarrow$  Peak at 1850  $cm^{-1}$  (s)  
 $CH_3-\overset{O}{\parallel}C-CH_2-\overset{O}{\parallel}C-CH_3 \rightarrow$  Peak at 1790-1740  $cm^{-1}$  (s)

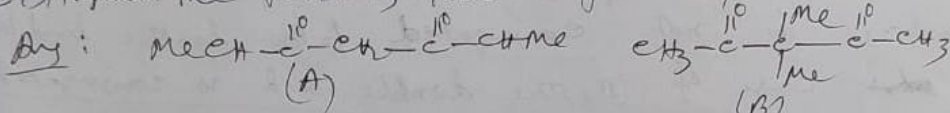
(ii) In case of cis-cyclohexane 1,2-diol, strong intramolecular H-bonding is possible because the dihedral angle between the two ~~groups~~ -OH groups are in opposite directions and intramolecular H-bonding is not possible.



But in case of cis-cyclohexane-1,3-diol, -OH groups are in opposite directions and intramolecular H-bonding is not possible.

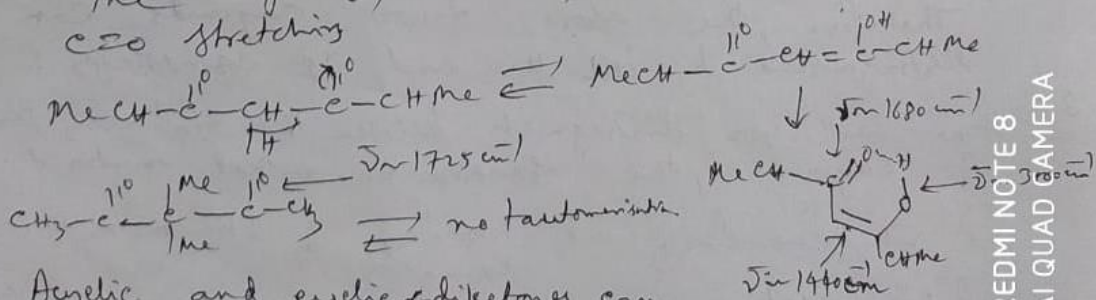
Consequently cis-cyclohexane-1,2-diol will give a shallow peak at  $\bar{\nu}_{max}$  value around  $3200-3000\text{ cm}^{-1}$  and the value will not show any change when diluted with inert solvents like  $\text{CCl}_4$  or  $\text{CHCl}_3$ . But cis-1,3-cyclohexanediol will show sharp peak at  $\bar{\nu}_{max}$  around  $3650-3590\text{ cm}^{-1}$ .

Q. Distinguish the following two compounds by IR spectroscopy.



Both the compounds (A) and (B) are structurally  $\beta$ -diketones. Compound (A), because of its active methylene group can tautomerise to give an enolic form which becomes stabilized by intramolecular H-bonding. The compd. (B) cannot do so because there are no hydrogen atom on the carbon atom flanked by two carbonyl groups. Thus the compd. (A) will exhibit a different IR spectrum comprises peaks of hydrogen bonded enolic -OH group, H-bonded  $\text{C}=\text{O}$  group and an olefinic  $\text{C}=\text{C}$  group.

The compd (B) will only give a strong peak for  $\text{C}=\text{O}$  stretching

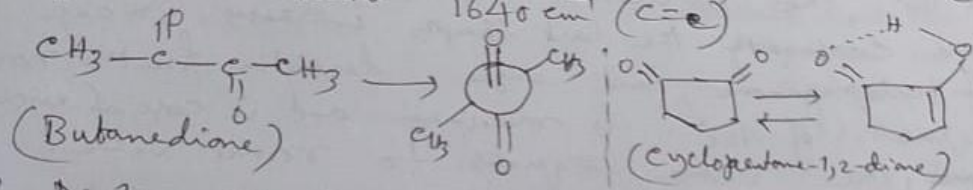


Q. Acyclic and cyclic  $\alpha$ -diketones can be distinguished by IR spectroscopy. Explain with an example.

Ans: Butanedione and cyclopentane-1,2-dione are

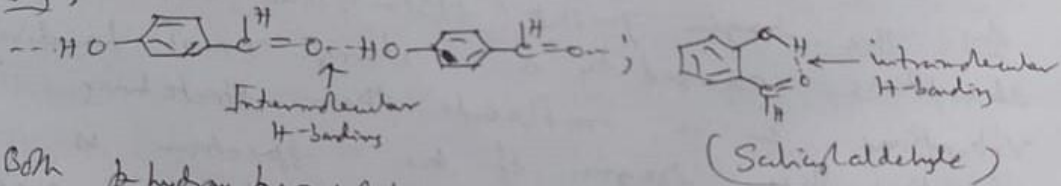


by IR spectroscopy. Butane dione mostly remains in trans conformation and does not form any end-form because it fails to become stabilized by intramolecular H-bonding. On the other hand, cyclopentane, being in a rigid cis form, tries to become stabilized by end-cis followed by intramolecular H-bonding. Therefore, butanedione will give IR peak around  $1720\text{ cm}^{-1}$  for C=O stretching. But the cyclopentane-1,2-dione will give peaks around  $1690\text{ cm}^{-1}$  (C=O),  $3300\text{ cm}^{-1}$  (H-bonded -OH) and around  $1640\text{ cm}^{-1}$  (C=C).



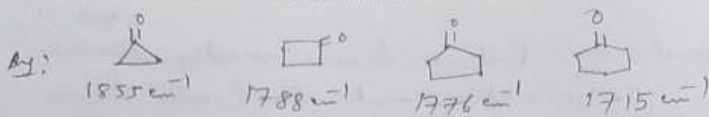
Q: Distinguish between p-hydroxybenzaldehyde and salicylaldehyde by IR spectroscopy.

Ans:



Both p-hydroxybenzaldehyde and salicylaldehyde give O-H stretching frequency around  $3200-3300\text{ cm}^{-1}$  and the signal is not sharp but broad. But dilution with non-hydroxy solvents like  $\text{CH}_2\text{Cl}_2$  does not rupture the strong intramolecular hydrogen bond in salicylaldehyde. Consequently, we have two types of species in the diluted solution i.e., free p-hydroxybenzaldehyde and hydrogen bonded p-hydroxybenzaldehyde and consequently, it will give two peaks, one around  $3600\text{ cm}^{-1}$  and another around  $3300\text{ cm}^{-1}$ . In case of, salicylaldehyde, there is no change in the nature and position of the peak, before and after dilution.

Q. Show how does C=O stretching frequency of ketones depends on the ring size of



In case of cyclic ketones,  $\nu_{C=O}$  ( $\text{cm}^{-1}$ ) value depends on the size of the ring. The  $\nu_{C=O}$  stretching values for the small monocyclic ketones are given below.

It is to be noted that as the size of the ring decreases, the  $\nu$  value for  $\nu_{C=O}$  ( $\text{cm}^{-1}$ ) increases. It is argued that when the value of  $C-C-O$  angle decreases from the normal value of  $120^\circ$ , the  $\sigma$ -character of the  $C=O$  bond increases and consequently the bond strength increases. In case of cyclopropanone, bond angle deviation from the normal value of  $120^\circ$  is maximum and in case of cyclohexanone, the value equals to normal value.

What is meant by 'fingerprint region' in an IR spectrum?

By: The region  $7-11 \mu$  ( $1430-910 \text{ cm}^{-1}$ ) contains many absorptions caused by a large no. of bending vibrations in a molecule than stretching vibrations, this region of the spectrum is particularly rich in absorption bands and shoulder peaks. For this reason, it is frequently called "Fingerprint region", because the patterns of absorption peaks in this region often give some idea regarding the nature of compds, particularly when IR spectra of complicated molecules of low nature are investigated. Some molecules containing the same functional group show similar absorptions above  $1500 \text{ cm}^{-1}$  but their spectra differ in fingerprint region. The identity of an unknown compound can also be revealed by comparing its IR spectrum with a set of spectra of known compds. under identical conditions. It is not possible to distinguish between two enantiomers even in their spectra are run with the same machine under exactly identical conditions such as scan speed etc.



Q: Arrange the following bonds in decreasing order of vibrational frequency: C-Br, C-C, C-Cl, C-O, C-H, C-I

Ans: As the atom bonded to carbon increases in mass the factor  $\mu$  (reduced mass) in the following equation increases and consequently, the frequency decreases.

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

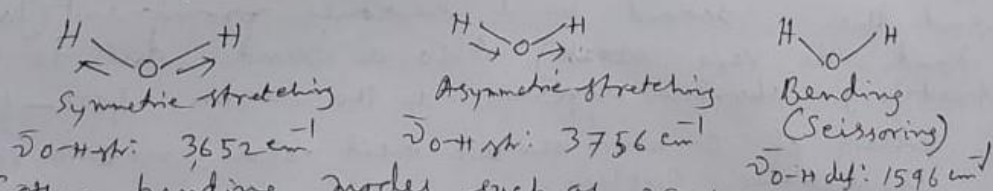
; Therefore, the decreasing order of vibrational frequency is: C-H > C-C > C-O > C-Cl > C-Br > C-I.

Q: Explain why methanol is a good solvent for URE but not for IR spectroscopy.

Ans: Methanol (CH<sub>3</sub>OH) does not absorb in URE region, i.e. it is transparent to above 2000 cm<sup>-1</sup>. But it absorbs strongly in the infrared region (4000 cm<sup>-1</sup> to 650 cm<sup>-1</sup>). It is for this reason methanol is a good solvent for URE but not for IR spectroscopy.

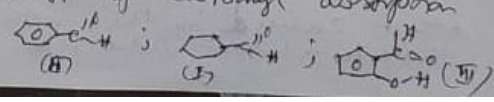
Q: How many types of vibrations are possible for H<sub>2</sub>O molecule? Explain with required figures.

Ans: The non linear H<sub>2</sub>O molecule have three vibrational degrees of freedom and they may be depicted as follows:



(Other bending modes such as rocking, wagging, and twisting are not considered because these do not change the shape of the molecule.)

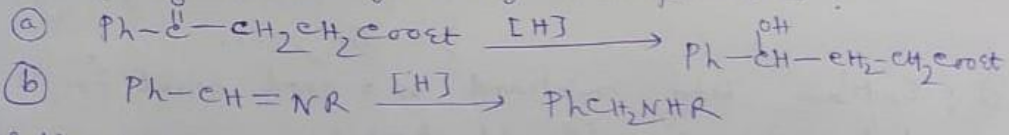
Q: Predict the frequency shift of carbonyl absorption in the following aldehydes:



Any cyclohexane carbaldehyde I, being saturated will absorb at about  $1730\text{ cm}^{-1}$ . In decanaldehyde II, the absorption will be shifted to lower frequency ( $1700\text{ cm}^{-1}$ ) due to conjugation. In salicylaldehyde III, intramolecular hydrogen bonding (chelation) causes a further large frequency shift to around  $1666\text{ cm}^{-1}$ .

(D. Redox Reactions)

Q. How IR spectroscopy can be used to study the progress of the following transformations?



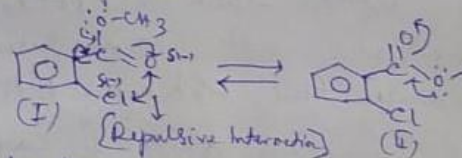
Solution: (a) In  $\text{PhCOCH}_2\text{CH}_2\text{COOEt}$ , the band due to  $\text{C}=\text{O}$  str. appears in the range  $1680-1700\text{ cm}^{-1}$  (because of conjugation with Ph). Reduction of this ketone produces a secondary alcohol which absorbs at  $3300\text{ cm}^{-1}$  due to  $\text{O}-\text{H}$  str. With progress of the reaction the  $\text{C}=\text{O}$  str. bond gradually disappears and the  $\text{O}-\text{H}$  str. band gradually appears. When the reaction is completed, the band due to  $\text{C}=\text{O}$  str. completely disappears and the only  $\text{O}-\text{H}$  str. band appears in the spectrum.

(b) With progress of the reaction the band due to  $\text{C}=\text{N}$  str. in the region  $1640-1690\text{ cm}^{-1}$  gradually disappears and the band due to  $\text{N}-\text{H}$  str. in the range  $3300-3500\text{ cm}^{-1}$  gradually appears. On completion of the reaction, the first band vanishes and the second band becomes prominent (but the band is very weak). Also, a band due to  $\text{C}-\text{N}$  stretching absorption appears in the region  $1000-1350\text{ cm}^{-1}$ .

No such effect observed in the reduction of  $\text{C}=\text{O}$  str. frequency.

Q. Esters of o-chlorobenzoic acid show two  $\text{C}=\text{O}$  str. frequencies. Explain.

Solution:



An ester of o-chlorobenzoic acid may exist in the two isomers (I) and (II). Due to the field effect of the ortho Cl atom, the  $\text{C}=\text{O}$  stretching frequency in (I) is higher than in (II).