

## Solutions of the Tutorial Sheet: Infra-Red (IR) Spectroscopy

**Q.1. What do you understand by force constant? How is the force constant of a molecule related to its vibrational frequency?**

**Ans.** Force constant indicates the stiffness or the strength of a chemical bond in response to a force that causes deformation. The force constant of a molecule is related to its vibrational frequency as:

$\nu = (1/2\pi)\sqrt{(k/\mu)}$ ; where,  $\nu$ : vibrational frequency of a molecule,  $k$ : force constant, and  $\mu$ : reduced mass of a molecule

**Q.2. Calculate the approximate frequency of C-H stretching from the following data:  $k = 500 \text{ Nm}^{-1}$ ,  $m_C = 20 \times 10^{-24} \text{ g}$ ,  $m_H = 1.6 \times 10^{-24} \text{ g}$**

**Ans.**  $m_C = 20 \times 10^{-24} \text{ g} = 20 \times 10^{-27} \text{ kg}$ ;  $m_H = 1.6 \times 10^{-24} \text{ g} = 1.6 \times 10^{-27} \text{ kg}$ ;  $k = 500 \text{ Nm}^{-1}$

Reduced mass ( $\mu$ ) =  $(m_C \times m_H) / (m_C + m_H) = (20 \times 1.6 \times 10^{-54} \text{ kg}^2) / (20 + 1.6) \times 10^{-27} \text{ kg}$   
 $= 32 \times 10^{-27} \text{ kg} / 21.6 = 1.48 \times 10^{-27} \text{ kg}$ .

We know that,  $\nu = (1/2\pi)\sqrt{(k/\mu)}$

$\therefore$  Substituting all the values,  $\nu = (1/2 \times 3.14)\sqrt{500/(1.48 \times 10^{-27})} = (1/6.28)\sqrt{337.83 \times 10^{27} \text{ Hz}}$   
or,  $\nu = 0.16 \times \sqrt{33.783 \times 10^{28} \text{ Hz}} = 0.16 \times 5.81 \times 10^{14} \text{ Hz} = 0.93 \times 10^{14} \text{ Hz}$ .

**For conversion from Hz to wavenumber i.e.  $\text{cm}^{-1}$ :**

$\nu(\text{bar}) = \nu / c$  where  $c$  (speed of light):  $3 \times 10^{10} \text{ cm/s}$

$\therefore \nu(\text{bar}) = 0.93 \times 10^{14} \text{ Hz} / 3 \times 10^{10} \text{ cm/s} = 0.31 \times 10^4 \text{ cm}^{-1} \sim 3100 \text{ cm}^{-1}$  (C-H stretch)

**Q.3.  $^1\text{H}^{35}\text{Cl}$  has a force constant ( $k$ ) value of  $480 \text{ N/m}$ . Calculate the fundamental frequency and its wavenumber.**

**Ans.** Given molecule:  $^1\text{H}^{35}\text{Cl}$ , Force constant ( $k$ ):  $480 \text{ N/m}$ .

As we know,  $1 \text{ a.m.u.} = 1.67 \times 10^{-27} \text{ kg}$ ; therefore, conversion of the masses of H and Cl gives:

$m_H = 1 \times 1.67 \times 10^{-27} \text{ kg} = 1.67 \times 10^{-27} \text{ kg}$ ;  $m_{\text{Cl}} = 35 \times 1.67 \times 10^{-27} \text{ kg} = 58.45 \times 10^{-27} \text{ kg}$

Reduced mass ( $\mu$ ) =  $(m_H \times m_{\text{Cl}}) / (m_H + m_{\text{Cl}}) = (1.67 \times 58.45 \times 10^{-54} \text{ kg}^2) / (1.67 + 58.45) \times 10^{-27} \text{ kg}$   
 $= 97.61 \times 10^{-27} \text{ kg} / 60.12 = 1.62 \times 10^{-27} \text{ kg}$ .

Now, substituting the values into the formula  $\nu = (1/2\pi)\sqrt{(k/\mu)}$ , we get:

$\nu = (1/2 \times 3.14)\sqrt{480/(1.62 \times 10^{-27})} = (1/6.28)\sqrt{296.29 \times 10^{27} \text{ Hz}} = 0.16 \times \sqrt{29.63 \times 10^{28} \text{ Hz}}$   
or,  $\nu = 0.16 \times 5.44 \times 10^{14} \text{ Hz} = 0.87 \times 10^{14} \text{ Hz}$

**For conversion from Hz to wavenumber i.e.  $\text{cm}^{-1}$ :**

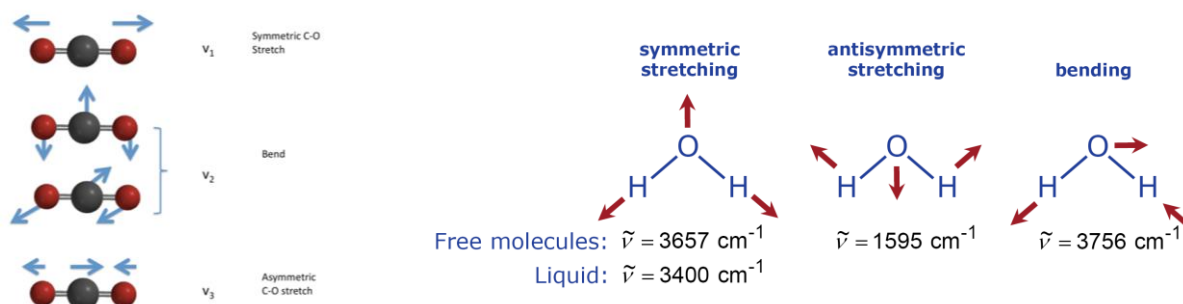
$\nu(\text{bar}) = \nu / c$  where  $c$  (speed of light):  $3 \times 10^{10} \text{ cm/s}$

$\therefore \nu(\text{bar}) = 0.87 \times 10^{14} \text{ Hz} / 3 \times 10^{10} \text{ cm/s} = 0.29 \times 10^4 \text{ cm}^{-1} \sim 2900 \text{ cm}^{-1}$

**Q.4. What is mode of vibration? Draw various vibrational modes of CO<sub>2</sub> and H<sub>2</sub>O. How many bands will appear in the IR spectra of these molecules?**

**Ans.** The mode of vibration represents different ways by which a molecule can vibrate. A diatomic molecule contains only 1 chemical bond which can either stretch or compress. On the other hand, a polyatomic molecule has more than 1 chemical bond which results in different vibrational motions such as bending, rocking, wagging, scissoring, etc. in addition to stretching. For a linear molecule,  $3N-5$  modes of vibrations are possible whereas, for a non-linear molecule,  $3N-6$  vibrational modes are possible. The “N” represents the total number of atoms in a molecule.

CO<sub>2</sub> is a linear molecule, hence, it will have a total no. of 4 vibrational modes ( $3N-5 = 3 \times 3 - 5 = 4$ ). These 4 vibrational modes are: (i) Symmetric stretch (ii) Anti-symmetric stretch (iii) Bending (2 types). Out of these, only 3 vibrational modes will be IR active viz. Anti-symmetric stretch and bending. And, we will see only 2 bands in the IR spectrum of CO<sub>2</sub> (1 for Anti-symmetric stretch and 1 for bending since both the bending vibrations occur at the same frequency).



H<sub>2</sub>O is a non-linear molecule, hence, it will have a total no. of 3 vibrational modes ( $3N-6 = 3 \times 3 - 6 = 3$ ). These 3 vibrational modes are: (i) Symmetric stretch (ii) Anti-symmetric stretch (iii) Bending. All of these vibrational modes will be IR active and all of them will appear in the IR spectrum as 3 bands.

**Q.5. Distinguish between the following from their IR spectra: (a) Ethanol and dimethyl ether (b) Primary and secondary amines**

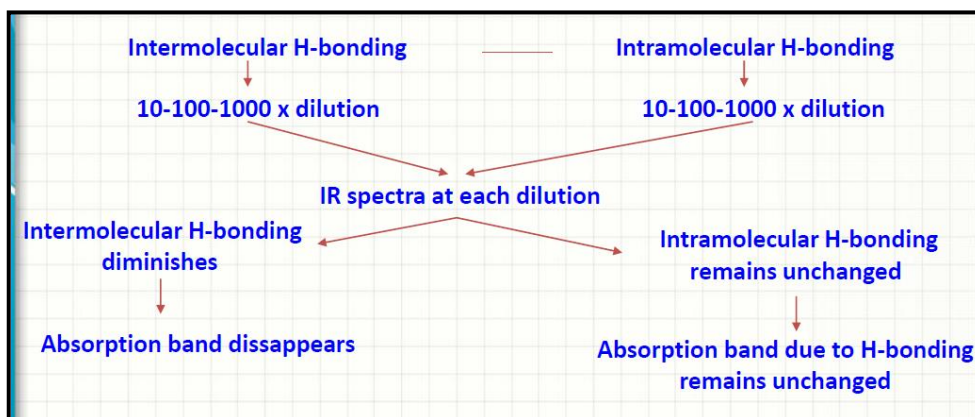
**Ans.** (a) Chemical formula of Ethanol is CH<sub>3</sub>CH<sub>2</sub>OH and that of dimethyl ether is CH<sub>3</sub>OCH<sub>3</sub>. These compounds can be distinguished based on the O-H group in ethanol which will show a broad band.

(b) Chemical formula of primary amine is R-NH<sub>2</sub> and that of secondary amine is R-NH-R'. “R” refers to an aliphatic group. These compounds can be distinguished based on the number of peaks in N-H group: primary amine will show 2 peaks whereas secondary amine will show only 1 peak.

**Q.6. How inter and intra hydrogen bonding can be distinguished from IR spectroscopy?**

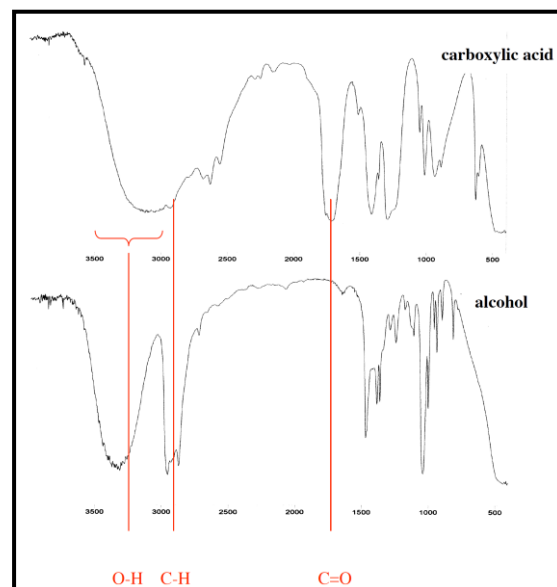
**Ans. Intermolecular hydrogen bonding** is formed between two molecules. Hence, it shows concentration dependence i.e. if we increase or decrease the concentration of the molecules, then the peak/band arising due to intermolecular hydrogen bonding will show a progressive shift from its position. Dilution experiment can be carried out for this purpose (see below). Typically, these bands are broad.

**Intramolecular hydrogen bonding** is formed within a single molecule and hence, it is concentration-independent. Consequently, the peak position will not shift or remain constant even if we change the concentration. Typically, these bands are sharp.



**Q.7. How does the O-H stretch in the IR spectrum of a carboxylic acid differ from the O-H stretch of an alcohol?**

**Ans.** Carboxylic acids show a strong, broad band for the O-H stretch in the region  $3300\text{--}2500\text{ cm}^{-1}$  because carboxylic acids usually form hydrogen-bonded dimers. This is in the same region as the C-H stretching bands of both alkyl and aromatic groups. Thus a carboxylic acid shows a somewhat "messy" absorption pattern in the region  $3300\text{--}2500\text{ cm}^{-1}$ , with the broad O-H band superimposed on the sharp C-H stretching bands. In case of alcohols, O-H stretch appears as broad band in the region of  $\sim 3650\text{--}3550\text{ cm}^{-1}$  (O-H free) and  $\sim 3550\text{--}3200\text{ cm}^{-1}$  (hydrogen bonding).



**Q.8. Why IR absorption due to C=O stretching occurs at higher frequencies than stretching of C=C bond?**

**Ans.** The bond strength of C=O bond is higher than that of the C=C bond. Since vibrational frequency of a molecule is directly proportional to the bond strength/stiffness of a molecule, C=O stretching occurs at higher frequencies compared to the C=C bond.

**Q.9. Distinguish between an ester and ketone on the basis of IR spectroscopy.**

**Ans.** The IR band of an ester appears at  $\sim 1735\text{--}1750\text{ cm}^{-1}$  whereas that of a ketone appears at  $\sim 1710\text{--}1720\text{ cm}^{-1}$ .

**Q.10. Rank the following bonds in order of increasing stretching frequency ( $\text{cm}^{-1}$ ) in IR spectroscopy: O-H,  $\text{C}\equiv\text{N}$ , C-N and C=O**

**Ans.** Following is the order:  $\text{C-N} < \text{C=O} < \text{C}\equiv\text{N} < \text{O-H}$

**Q.11. Write IR absorption frequencies ( $\text{cm}^{-1}$ ) for the following groups: (i) Alkane-C-H, C-C (ii) Alkene =CH, C=C (iii) alkyne  $\equiv\text{C-H}$ ,  $\text{C}\equiv\text{C}$  (iv) alcohols O-H (v) Ether C-O (vi) aldehyde, Ketone C=O (vii) Nitrile  $\text{C}\equiv\text{N}$  (viii) amine C-N**

**Ans.** Following are the IR frequencies of the given groups:

**(i) Alkane-C-H, C-C:** C-H:  $2900\text{--}3100\text{ cm}^{-1}$  (stretch),  $1350\text{--}1390\text{ cm}^{-1}$  (deformation),  $720\text{--}725\text{ cm}^{-1}$  (rocking). C-C:  $970\text{--}1040\text{ cm}^{-1}$  (stretch)

**(ii) Alkene =CH, C=C:** =C-H:  $3020\text{--}3100\text{ cm}^{-1}$  (stretch),  $880\text{--}995\text{ cm}^{-1}$  (bend). C=C:  $1630\text{--}1680\text{ cm}^{-1}$  (stretch)

**(iii) Alkyne  $\equiv\text{C-H}$ ,  $\text{C}\equiv\text{C}$ :**  $\equiv\text{C-H}$ :  $3300\text{ cm}^{-1}$  (stretch),  $600\text{--}700\text{ cm}^{-1}$  (deformation).  $\text{C}\equiv\text{C}$ :  $2100\text{--}2250\text{ cm}^{-1}$  (stretch)

**(iv) Alcohols O-H:** 3580 – 3650  $\text{cm}^{-1}$  (free O-H group), 3200 – 3550  $\text{cm}^{-1}$  (hydrogen bonded O-H).

**(v) Ether C-O:** 1000 – 1300  $\text{cm}^{-1}$  (stretch)

**(vi) Aldehyde & Ketone C=O:** 1720 – 1740  $\text{cm}^{-1}$  (stretch; Aldehyde), 1710 – 1720  $\text{cm}^{-1}$  (stretch; Ketone)

**(vii) Nitrile C $\equiv$ N:** 2210 – 2260  $\text{cm}^{-1}$  (stretch)

**(viii) Amine C-N:** 1080 – 1250  $\text{cm}^{-1}$  (stretch)

**Q.12. IR spectra are often characterized as molecular finger-prints. Comment on it.**

**Ans.** IR spectra are often characterized as molecular finger-prints because the IR bands arising from each molecule is unique in nature and hence, can be easily identified.

**Q.13. Why are inorganic materials useful as sample “windows” and matrix material for IR analysis?**

**Ans.** Inorganic materials such as KBr, NaCl are considered useful as sample “windows” and matrix material for IR analysis because they are ionic compounds and do not absorb any IR radiation (since, vibrational modes and transitions are absent due to lack of covalent bond) and hence, do not interfere with the IR spectrum of the sample/analyte.