Infrared Spectroscopy

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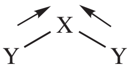
The energy of most of the molecular vibrations falls into the infrared region (4000 - 400 cm^{-1}) of the electromagnetic spectrum. Infrared (IR) or vibrational spectroscopy is used by organic chemists to: (i) identify functional groups in solid, liquid, or gaseous forms, (ii) differentiate inter- and intra-molecular hydrogen-bonding, and (iii) investigate chemical reactions. Recent developments in Fourier Transform Infrared (FT-IR) spectroscopy extended its applications to atmospheric, archaeological, pharmaceutical, food and biological fields, and also to analyze compounds/materials qualitatively and quantitatively.

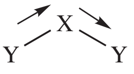
IR spectrometer measures the interaction of infrared radiation with matter by means of absorption/ transmittance. When molecules absorb energy, they get excited to higher vibrational/rotational energy levels, which causes constant movements in each covalent bond with respect to other atoms present in the molecule. These movements are called fundamental vibrational modes (FVM).

Fundamental vibrational modes

There are two main FVM: stretching and bending. **Stretching** modes are of two types: *e.g.*, symmetric and asymmetric.



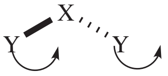
Symmetric



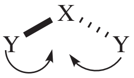
Asymmetric

Bending modes are of two types: *e.g.*, (i) in- plane (rocking and scissoring) and (ii) out of plane (twisting and wagging).

In plane bending

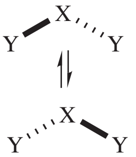


Rocking

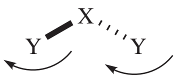


Scissoring

Out of plane bending



Twisting



Wagging

The number of **vibrational mode**s (degrees of freedom) for a **linear** molecule is equal to 3N-5 while that for **non-linear** molecule is 3N-6, where N = number of atoms in the molecule. For example, the number of modes in HCl and CO_2 are 1 and 4, respectively. The non-linear molecule, benzene has 30 modes.

Infrared spectra

An infrared spectrum is a graph of percentage transmittance (%T) on the vertical axis versus wavenumber ($\bar{\upsilon}$) in cm^{-1} on the horizontal axis (Fig. 1).

$$\%T = \frac{\text{transmitted intensity x 100}}{\text{original intensity}}$$

If the molecule does not absorb radiation, then %T is 100% and no peaks appear in the spectrum. When a molecule absorbs energy the %T decreases. The wavenumber range is related to the bond type and the **functional group (FG)** present in the molecule. Not all covalent bonds display IR bands; only the polar bonds are **IR active**. The **intensity** of the band depends on the magnitude of the **dipolar moment**. For example, polar bonds such as carbonyl (C=O) groups produce **strong** (s) bands; asymmetric stretching of bonds display **medium** (m) bands while symmetric stretching of bonds show **weak** (w) bands. Overlapping of a weak band on a side of a strong band gives rise to a **shoulder** (sh). The vibrational frequency of a bond (ν or $\bar{\upsilon}$) can be calculated using Hooke's law,

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} \quad \text{or} \quad \bar{\upsilon} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

K = force constant, c = velocity of light, reduced mass = $\mu = (m_1m_2)/(m_1+m_2)$, m_1 and m_2 are masses of atoms, strong bonds show higher frequencies, $\nu = c\bar{\upsilon}$, c = speed of light.

The IR spectrum is divided into two parts:

- Functional group region (4000-1400 cm^{-1})
- Finger print region (1400-400 cm^{-1}) which is specific to a molecule (see Fig. 1)

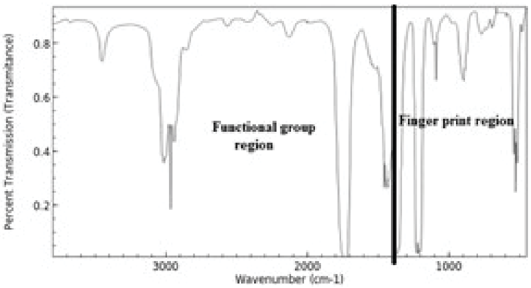


Figure1: Two regions of an IR spectrum

Characteristic IR frequencies of FGs

Even a simple organic molecule can have a large number of vibrational modes, *e.g.*, C-H, C-C, C-O, O-H, N-H, C=O, C=N *etc*. Bending and stretching frequencies of organic molecules are given in Table 1. The following bands are suggested by comparing the values obtained for a large number of molecules. RNH_2 and $RCONH_2$ show two strong bands at ~3340 & 3300; R_2NH gives only one band. The ν(C=O) values (1870-1650 cm^{-1}, see Table 1) depend on the inductive and resonance effects exerted by the atoms/groups attached to the C=O group.

Table 1: Bending & stretching frequencies of common organic molecules in cm^{-1}

Type of molecules	Bond	Bending frequency	Stretching frequency
Alkane	C-H	1470-1450	3000-2840m
Alkene	C=C		1680-1620
	=C-H	1000-650s	3090-3010m
Alkyne	C≡C		2260-2100w
	≡C-H	700-600	3330-3270
Aromatic	C=C		1600-1585 1500-1400
	=C-H	900-690s	3100-3010m
Anhydride	C=O		1870-1800 I 1820-1770 II
RCOCl			1820-1770
Ester			1820-1770
RCO_2H			1725-1700
Aldehyde			1750-1720s
Ketone			1730-1705s
Amide			1690-1620
Alcohol	C-O		1260-1050
	O-H		3500-3200
H-bonded		1620-1590	3600-3200
Carboxylic acid		1440-1395 950-940	3400-2400
Amine 1^{ry}	N-H	1650-1580	3400-3300w 3330-3250w
Amine 2^{ry}	N-H		3350-3310w
	C-N		1360-1180s
Amide	N-H	1650-1560	3370 (asym) 3150 (sym)
Nitrile	C≡N		2280-2210m
Imine	C=N		1690-1640m
$R\text{-}NO_2$	N=O		1570-1500s 1385-1300s

Note that ν(asymmetric) > ν(symmetric).

Absorption bands for the C-X group of alkyl halides appear in the finger print region, e.g., ν(C-F) ~ 1200 cm^{-1}, ν(C-Cl) 850-550 cm^{-1}, ν(C-Br) 690-510 and ν(C-I) < 650 cm^{-1}.

The summary of absorption bands due to molecular vibrations is given is Fig, 2.

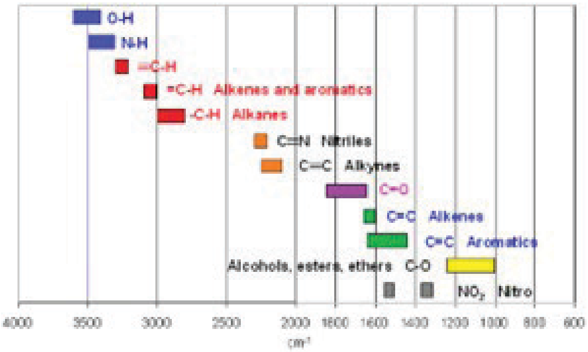


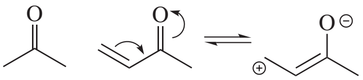
Figure 2: Summary of absorption bands due to molecular vibrations

Factors affecting the IR frequency

The main factors that affect the IR frequencies of a molecule are conjugation effect, resonance effect, inductive effect {electron donating (+I) and withdrawing (-I) effects}, hydrogen bonding, the ring size of the molecule, *etc*.

a) Conjugation and resonance effects

The resonance effect of the vinyl group attached to methylvinyl ketone increases the single bond character of the C=O group, thus, the ν(C=O) value is lowered to 1680 cm^{-1} (Fig. 3).



1715 **1680**

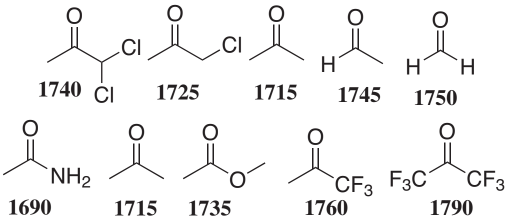
ν(**C=O**) / cm^{-1}

Figure 3: Resonance effect on the C=O group upon extended conjugation

Similarly, ν(C=O) shifts to lower values when an aryl group is conjugated to it, *e.g.*, the ν(C=O) values for PhCHO and $PhCO_2H$ are 1700 and 1680 cm^{-1}, respectively.

b) Inductive effect

The neighboring groups attached to the particular functional group strongly affect the IR frequency of that functional group. The trends in ν(C=O) for some carbonyl compounds are given in Fig. 4.



ν(C=O) / cm^{-1}

Figure 4: ν(C=O) values of C=O groups

In chloro-derivatives of acetone, the electron withdrawing effect of chlorine increases, thus, the bond order of the C=O group, ν(C=O), increases. The bond order of the C=O group in formaldehyde is higher than that of acetone. The donation of the lone-pair electrons on amino nitrogen weakens the C=O bond. The amino group can have a combination of inductive and resonance effects. Electron withdrawing effect of electronegative atoms such as oxygen and fluorine increases the bond order of the C=O group.

c) Hydrogen bonding

Inter- and intra-molecular H bonding (Fig. 5) lowers the frequency of the O-H bond. Neat phenol gives a broad band around 3350 cm^{-1} for the O-H bond which is H bonded. Upon dilution, the ν(O-H) value shifts towards a higher value, ~3600 cm^{-1}.

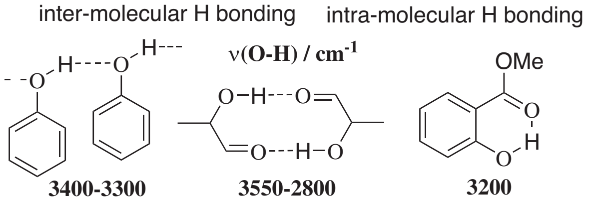


Figure 5: Inter- & intra-molecular H-bonding of O-H bonds

The IR spectrum of acetic acid (Fig. 6) showed a broad band between 3550-2800 cm^{-1} for the hydrogen bonded OH group.

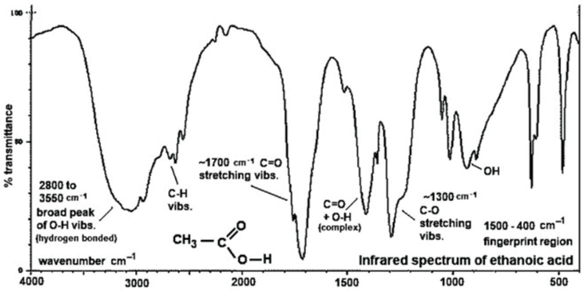


Figure 6: IR spectrum of acetic acid

Note that stretching frequencies ν(C=O) and ν(C-O) of the carboxylic group are around 1700 and 1300 cm^{-1}, respectively.

Hydrogen bonds are not present in the gas phase. The IR spectrum of the **gaseous** HCHO (Fig. 7) showed sharp bands at 2850 (asymmetric), 2750 (symmetric), 1485 (scissoring), 1250 (rocking) and 1165 (wagging) as the vibrational modes of the CH_2 group. The stretching frequency of ν(C=O) is 1750 cm^{-1}.

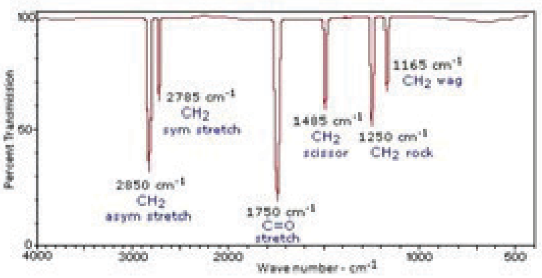


Figure 7: IR spectrum of HCHO vapor

d) Ring size effect

The ν(C=O) values given in Table 1 are normally for unstrained acyclic carbonyl compounds. The vibrational frequency of a C=O group in a strained ring system increases as shown in Fig. 8. Acyclic acetone and cyclohexanone have the same value of 1715 cm^{-1}. The ν(C=O) value gradually increases as the size of the ring decreases due to increase in the angle strain. Similar trend is observed for strained cyclic esters or lactones.

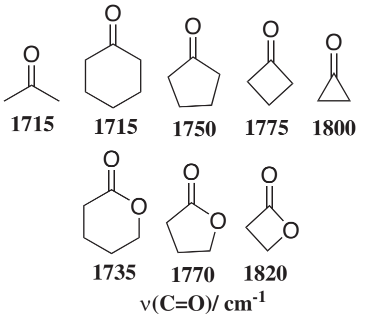


Figure 8: Ring size effect in cyclic ketones & lactones

Metal Carbonyls

IR spectroscopy is an important tool to study metal carbonyls because the C≡O stretching frequencies ν(C≡O) give rise to **strong** bands between 2150 and 1600 cm^{-1}. The free CO has a ν(C≡O) value of 2143 cm^{-1}.

IR spectra of metal carbonyls provide the following information:

1. *Bonding mode of CO* - whether it is terminal, doubly bridging or triply bridging.

   The ν(C≡O) for terminal and bridging carbonyls decreases in the following order:

   M-CO (2150-1900) > $M_2(\mu_2$-CO) (1900-1750) > $M_3(\mu_3$-CO) (1750-1600) in cm^{-1}.

2. *Geometry of the molecule* - the number of bands indicates the symmetry of the $M(CO)_n$ fragment.

   Metal carbonyls, $[Ni(CO)_4]$, $[M(CO)_6]$, *trans*-$[M(CO)_4L_2]$ (M = Cr, Mo, W), and $[M(CO)_3(L_{axial})_2]$ (M = Fe, Ru) show only **one** IR band whilst *fac*-$[M(CO)_3L_3]$ (M = W, Mo) shows **two** IR bands.

3. *Electron donor and withdrawing nature of other co-ligands* - electron donors lower the stretching frequency of C≡O.

Complex	ν(CO)/cm^{-1}
fac-$[Mo(CO)_3(PCl_3)_3]$	2040, 1991
fac-$[Mo(CO)_3(PEt_3)_3]$	1937, 1841

4. *Oxidation state of the metal or the charge on the complex ion* - anionic complexes show lower stretching frequencies.

Complex/ion	ν(CO)/cm^{-1}
$[Mn(CO)_6]^+$	2090
$[Cr(CO)_6]$	2000
$[V(CO)_6]^-$	1860

Metal hydrides

The IR absorption frequency of the M-H bond, ν(M-H), appears in the region of 1500-2200 cm^{-1}, but intensities are often **weak** to **medium** when compared to intensities of the carbonyl bands of metal carbonyls.

The presence of a M-H bond can be confirmed by converting it into a M-D bond with D_2O and recording the IR spectrum again. The absence of the M-H band and appearing of a new M-D band is observed according to the relationship, ν(M-D) = ν(M H) ÷√2.

Other metal complexes

It is important to have an idea of the values of stretching frequencies of metal complexes and neutral ligands, used in coordination and organometallic chemistry. Table 2 gives the ranges of stretching frequencies of some neutral ligands (L) when they are **bound** to a metal center or **unbound**, *i.e.*, the **free** ligand.

Table 2: Stretching frequencies of some neutral ligands (L) in cm^{-1}.

L	ν(free-L)	ν(bound-L)
C≡S	1270	1410-1160 (terminal) 1150-1020 (μ-CS)
N≡N	2330	2200-1800 (terminal) 2030-1700 $M_2(\mu-N_2)$
N≡O	1880	1830-1610 (linear) 1720-1520 (bent-NO)
N≡O$^+$	2250	1520-1490 M_2(μ-NO)
$CH_2=CH_2$	1623	1520-1450 M(η^2-L)
PhC≡CH	2110	2200-1900 (MC≡CPh)
MeN≡C	2170	2200-1900 (linear) 1870-1830 (bent) 1700-1600 M_2(μ-L)
H-H		2900-2300 M-(η^2-H_2)

Inorganic ions

Table 3: Stretching frequencies of common inorganic ions in cm^{-1}.

Ion	ν(ion)/cm^{-1}
NH_4^+	3300-3030, 1485-1390
CO_3^{2-}	1450-1410, 880-800
SO_4^{2-}	1130-1080, 680-610
NO_3^-	1380-1350, 860-800
NO_2^-	1250-1230
PO_4^{3-}	1100-1000
NC^-, NCS^-, SCN^-	2200-2000
SiO_4^{2-}	1100-900
MnO_4^-	920-890, 850-840

Student Corner

UV-visible Spectroscopy

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Molecules have different energy states: electronic, vibrational, rotational, and nuclear. Quantized energy is responsible for each transition (*e.g.*, rotational - microwaves, infrared - vibrational) within the molecule. UV-visible spectroscopy is one of the principle analytical tools used by chemists to find out absorption properties of molecules in ultraviolet (200 - 400 nm) and visible (400 - 700 nm) regions of the electromagnetic (EM) spectrum. The absorption of UV-*vis* radiation corresponds to electronic transitions of outer electrons.

An electron of a molecule in the ground state absorbs energy and moves to the excited state. **Energy gap** (ΔE) between these two states is related to the absorbed energy. The maximum wavelength (**λ_{max}**) is measured where, $\Delta E = h\nu = hc/\lambda$, h = Plank's constant ($6.626 \times 10^{-34}$ Js), ν = frequency, c = speed of light.

There are 3 types of **electrons** in organic molecules; **sigma** (σ), **pi** (π) and **lone-pair** (n), which are in **non-bonding** orbitals. Electrons in σ and π orbitals have lower energies. Anti-bonding orbitals (σ* and π* have higher energies and are usually empty. Main electron transitions (**T_1-T_4**) between these energy levels are shown in Fig. 1, which depend on the availability of σ, π and n-electrons (see Table 1).

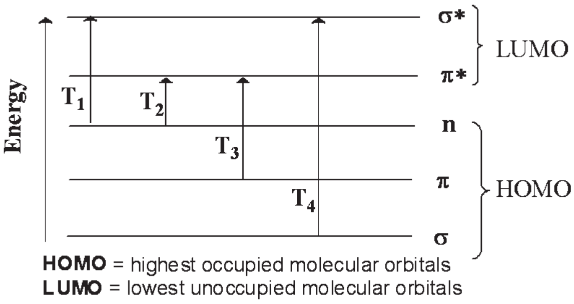

Figure 1: Main electronic transitions

HOMOs of propane, propene, acetone and ethanol are σ, π, n & n, respectively. LUMOs of propane, propene, acetone and ethanol are σ*, π*, π* & σ*, respectively. Table 1 gives some details with respect to transitions (T_1-T_4).

Table 1: Details of electronic transitions

	Transition	λ_{max}/nm	Compound
T_1	n → σ*	> 185	compounds with O, S, N, halogen
T_2	n → π*	> 275	carbonyls