

From the above equation it is clear that if the number of molecules in the ground state (population) is 1000 then only 8 molecules are present in the excited state. Therefore, in anharmonic vibrator only transitions $\Delta v = +1, +2, +3$ (absorptions from $v = 0$) are considered. The values for these three transitions can be calculated as given in equation (x), (xi) and (xii) below:

Transition I: $\Delta v = +1; v = 0 \longrightarrow v = 1$ [high intensity (fundamental) transition]

$$w_1 - w_0 = \left(\frac{3}{2}\right) w_e - \left(\frac{3}{2}\right)^2 w_e x_e - \left(\frac{1}{2}\right) w_e + \left(\frac{1}{4}\right) w_e x_e$$

$$w_1 - w_0 = w_e(1 - 2x_e) \quad (x)$$

Transition II: $\Delta v = +2; v = 0 \longrightarrow v = 2$ [low intensity (1st overtone) transition]

$$w_2 - w_0 = \left(\frac{5}{2}\right) w_e - \left(\frac{25}{4}\right) w_e x_e - \left(\frac{1}{2}\right) w_e + \left(\frac{1}{4}\right) w_e x_e$$

$$w_2 - w_0 = 2w_e(1 - 3x_e) \quad (xi)$$

Transition III: $\Delta v = +3; v = 0 \longrightarrow v = 3$ [negligible intensity (2nd overtone) transition]

$$w_3 - w_0 = \left(\frac{7}{2}\right) w_e - \left(\frac{49}{4}\right) w_e x_e - \left(\frac{1}{2}\right) w_e + \left(\frac{1}{4}\right) w_e x_e$$

$$w_3 - w_0 = 3w_e(1 - 4x_e) \quad (xii)$$

The data generated from the fundamental and overtone bands in IR spectrum is used to calculate the values of w_e and x_e .

Some general trends about vibrational frequency are given below:

- i) Stretching frequencies are higher than corresponding bending frequencies. (It is easier to bend a bond than to stretch or compress it).
- ii) Bonds to hydrogen have higher stretching frequencies than those to heavier atoms.
- iii) Triple bonds have higher stretching frequencies than corresponding double bonds, which in turn have higher frequencies than single bonds. (Except for bonds to hydrogen).

The complexity of infrared spectra in the 1450–600 cm⁻¹ regions makes it difficult to assign all the absorption bands, and because of the unique patterns found there, it is often called the *fingerprint region*. Absorption bands in the 4000–1450 cm⁻¹ region are usually due to stretching vibrations of diatomic units, and this is sometimes called the *group frequency region*.

Detailed information about the infrared absorptions observed for various bonded atoms and functional groups is given in Table 10.10. Since most organic compounds have C-H bonds, a useful rule is that absorption in the 2850 to 3000 cm⁻¹ is due to sp³ C-H stretching; whereas, absorption above 3000 cm⁻¹ is from sp² C-H stretching or sp C-H stretching if it is near 3300 cm⁻¹.

Infrared absorption data for some other functional groups not listed in the *Table 10.11* is given below in *Table 10.11*. Most of the absorptions cited are associated with stretching vibrations.

Table 10.10: Typical infrared absorption frequencies

Functional group	Stretching Vibrations			Bending Vibrations		
	Range (cm ⁻¹)	Intensity	Assignment	Range (cm ⁻¹)	Intensity	Assignment
Alkanes	2850-3000	str	CH ₃ , CH ₂ & CH 2 or 3 bands	1350-1470 1370-1390 720-725	med med wk	CH ₂ & CH ₃ deformation CH ₃ deformation CH ₂ rocking
Alkenes	3020-3100 1630-1680 1900-2000	med var str	=C-H & =CH ₂ (usually sharp) C=C (symmetry reduces intensity) C=C asymmetric stretch	880-995 780-850 675-730	str med med	=C-H & =CH ₂ (out-of-plane bending) cis-RCH=CHR
Alkynes	3300 2100-2250	str var	C-H (usually sharp) C≡C (symmetry reduces intensity)	600-700	str	C-H deformation
Arenes	3030 1600 & 1500	var med-wk	C-H (may be several bands) C=C (in ring) (2 bands) (3 if conjugated)	690-900	str- med	C-H bending & ring puckering
Alcohols & Phenols	3580-3650 3200-3550 970-1250	var str str	O-H (free), usually sharp O-H (H-bonded), usually broad C-O	1330-1430 650-770	med var- wk	O-H bending (in-plane) O-H bend (out-of-plane)
Amines	3400-3500 (dil. soln.) 3300-3400 (dil. soln.) 1000-1250	wk wk med	N-H (1°-amines), 2 bands N-H (2°-amines) C-N	1550-1650 660-900	med- str var	NH ₂ scissoring (1°-amines) NH ₂ & N-H wagging (shifts on H- bonding)
Carbonyl compounds	2690-2840 (2 bands) 1720-1740 1710-1720 1690 1675 1745 1780	med str str str str str str	C-H (aldehyde C-H) C=O (saturated aldehyde) C=O (saturated ketone) aryl ketone α, β-unsaturation cyclopentanone cyclobutanone	1350-1360 1400-1450 1100	str str med	α-CH ₃ bending α-CH ₂ bending C-C-C bending
Carboxylic acids & Derivatives	2500-3300 (acids) overlap C-H 1705-1720 (acids) 1210-1320 (acids) 1785-1815 (acyl halides) 1750 & 1820 (anhydrides) 1040-1100 1735-1750 (esters) 1000-1300 1630-1695	str str med-str str str str str str str	O-H (very broad) C=O (H-bonded) O-C (sometimes 2- peaks) C=O C=O (2-bands) O-C C=O O-C (2-bands) C=O (amide I band)	1395-1440 1590-1650 1500-1560	med med med	C-O-H bending N-H (1- amide) II band N-H (2- amide) II band

Standard abbreviations (str = strong, wk = weak, brd = broad & shp = sharp) are used to describe the absorption bands.

Table 10.11: Typical infrared absorption frequencies of other functional groups

Functional group	Characteristic Absorptions
Sulphur Functions	
S-H thiols	2550-2600 cm^{-1} (wk & shp)
S-OR esters	700-900 (str)
S-S disulfide	500-540 (wk)
C=S thiocarbonyl	1050-1200 (str)
S=O sulfoxide	1030-1060 (str)
sulfone	1325 \pm 25 (as) & 1140 \pm 20 (s) (both str)
sulfonic acid	1345 (str)
sulfonyl chloride	1365 \pm 5 (as) & 1180 \pm 10 (s) (both str)
sulfate	1350-1450 (str)
Phosphorous Functions	
P-H phosphine	2280-2440 cm^{-1} (med & shp)
	950-1250 (wk) P-H bending
(O=)PO-H phosphonic acid	2550-2700 (med)
P-OR esters	900-1050 (str)
P=O phosphine oxide	1100-1200 (str)
phosphonate	1230-1260 (str)
phosphate	1100-1200 (str)
phosphoramidate	1200-1275 (str)
Silicon Functions	
Si-H silane	2100-2360 cm^{-1} (str)
Si-OR	1000-11000 (str & brd)
Si-CH₃	1250 \pm 10 (str & shp)
Nitrogen Functions	
Nitriles = CN	2240-2260 (str & med),
= NOH oxime	
O-H (stretch)	3550-3600 cm^{-1} (str)
C=N	1665 \pm 15
N-O	945 \pm 15
Isocyanates (-N=C=O), Isothiocyanates (-N=C=S), Diimides (-N=C=N-), Azides (-N ₃) & Ketenes (C=C=O)	2100-2270 (str & med)
N-O amine oxide	
aliphatic	960 \pm 20
aromatic	1250 \pm 50
N=O nitroso	1550 \pm 50 (str)
nitro	1530 \pm 20 (as) & 1350 \pm 30 (s)
Standard abbreviations (str = strong, wk = weak, brd = broad & shp = sharp) are used to describe the absorption bands.	

10.12 INFRARED SPECTROMETER

The most commonly used infrared spectrometer is double beam infrared spectrometer which mainly comprises radiation source, absorption cells, monochromator, detector, amplifier and recorder. The diagrammatic representation of the double beam infrared spectrometer is shown in *Figure 10.16*. The various parts of the spectrometer are discussed below:

(i) **Radiation source:** In double beam IR spectrometer the source of radiation is a ceramic rod heated electrically at 1100-1800°C. This rod is made either of silicon carbide or from Nernst filament (consisting of high resistance, brittle element made of a mixture of sintered oxides

of cerium, thorium and zirconium). The radiation source produces two beams, one acts as a reference beam and the other passes through the sample. These two beams are alternatively passed into a monochromator at very short intervals by using a rotating mirror.

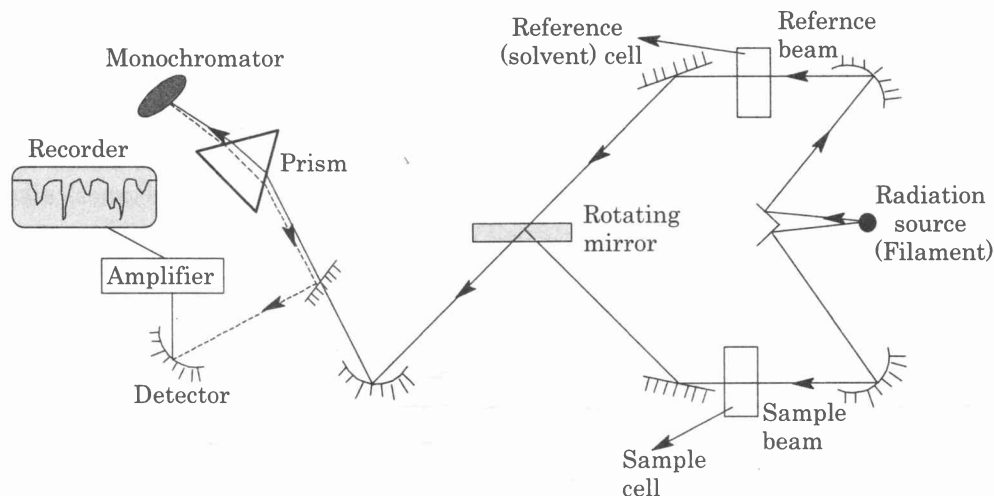


Figure 10.16: Double beam infrared spectrometer

(ii) **Monochromator:** The pulse beam enters the monochromator through a slit and is dispersed using a Littrowmount or grating prism. The resultant beams are separated into various wavelengths by NaCl prism which is transparent to IR radiation in the frequency range of $4000\text{--}650\text{ cm}^{-1}$. In the range of $4000\text{--}1000\text{ cm}^{-1}$, even LiF prism may also be used as it is not transparent below 1000 cm^{-1} . If the spectrum is to be recorded below 400 cm^{-1} or 200 cm^{-1} , the prisms made of KBr and CsI respectively are used. A filter may be used in case of high resolution instruments to remove unwanted radiation.

(iii) **Absorption cells:** The cells used for recording IR spectrum are made of KBr or rock salt. The compounds can be tested in the liquid or solid form. In case of solids, the compounds are either examined as a mull in nujol (white mineral oil) or as a KBr pellet made by hydraulic pressing. In the liquid form the compounds are examined in organic solvents. The most commonly used solvents are CCl_4 , CS_2 and CHCl_3 .

(iv) **Detector:** After dispersion of the beams through the prism, they are focused through monochromator at specific wavelength on to the detector using a mirror system. The detector is a sensitive fast thermocouple.

(v) **Amplifier and Recorder:** The signals from the detector are amplified electronically using a mechanical arrangement. The amplified signals are recorded on a graph paper mounted on a rotating drum. The IR spectrum is actually the difference between the intensities of the reference and the sample beams. The IR spectrum so formed is calibrated using the very sharp band at 1603 cm^{-1} for polystyrene immediately before or after the sample spectrum is recorded. On the basis of the position of this band, the corrections can be made in reading the band positions on the graph paper if required.

In these days, *Fourier-transform infrared (FT-IR) spectrophotometer* is being widely used for recording IR spectrum. In this type of instrument, one of the two beams from the

in plane and out of plane bending vibrations occur at 1625 and 675 cm^{-1} , respectively. The characteristic IR spectrum of *p*-toluidine is given in Figure 10.26. The spectrum shows sharp bands at 3360 and 3440 cm^{-1} assigned to symmetric and asymmetric N-H stretching vibrations due to amino group. The corresponding N-H in plane and out of plane bending vibrations are shown at 1625 and 675 cm^{-1} respectively. The weak absorption due to N-H stretching bonded vibration is shown at 3225 cm^{-1} . The band due to C-N stretching vibration is shown at 1270 cm^{-1} .

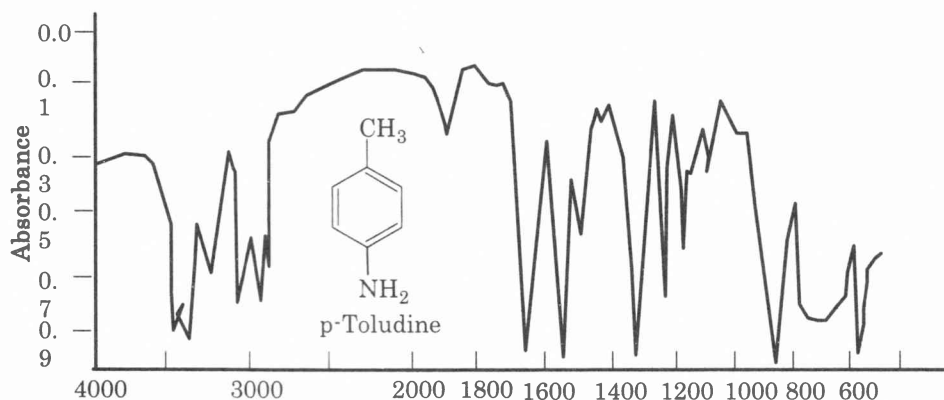


Figure 10.26: IR spectrum of *p*-Toluidine (Amines)

10.14 APPLICATIONS OF IR SPECTROSCOPY

(i) **Identification of functional groups:** As given in Table 10.10 and 10.11, the different organic compounds absorb at different characteristic frequencies in the IR spectrum, so on the basis of IR spectrum of an organic compound the possible functional groups present can be predicted.

(ii) **Identification of compounds:** By comparing the IR spectra of known compounds, the unknown compounds may be identified. It is because a particular functional group gives rise to characteristic absorption pattern giving a definite spectrum, for example, the presence of a strong band at or around 1700 cm^{-1} in IR spectrum indicates the presence of carbonyl functional group whereas the band at $2210\text{--}2260\text{ cm}^{-1}$ indicates the presence of nitrile functional group (carbon–nitrogen triple bond).

(iii) **Hydrogen bonding:** IR spectrum gives important information about the presence of intermolecular or intramolecular hydrogen bonding. This can be achieved by taking spectra at different concentrations of the sample solution. As the dilution increases, the absorption band due to intermolecular hydrogen bonding decreases while the absorption band due to intramolecular hydrogen bonding is not effected.

(iv) **Detection of impurities:** The IR spectra of an impure compound show few additional absorption bands. By comparing the IR spectrum of the pure compound, the presence of impurities can be detected in the given sample.

(v) **Quantitative analysis:** The IR spectrum can be used for quantitative analysis of a mixture of compounds. The most common use is in quantitative analysis of pollution causing compounds and milk analysis

(vi) **Other applications:** IR is used for important information regarding molecular symmetry, dipole moments, positional isomerism and bond length, etc.

10.15 PRACTICE ZONE

10.15.1 Solved Numerical Problems

SNP 1: Calculate the frequency of the radiation whose wavelength is 420 nm.

Ans: Frequency, $\nu = c/\lambda$

$$= \frac{3 \times 10^8 \text{ ms}^{-1}}{420 \times 10^{-9} \text{ m}} = 7.14 \times 10^{14} \text{ s}^{-1}$$

SNP 2: The ionization energy for the reaction, $\text{Na}^+ (g) \longrightarrow \text{Na}^{2+} (g)$ is 47.3 eV. Calculate the wavelength of the radiation involved in the reaction.

Ans: The wavelength is related to the energy by the following expression

$$E = h\nu = hc/\lambda$$

$$E = 47.3 \text{ eV} = 47.3 \times 1.6022 \times 10^{-19} \text{ J} = 75.78 \times 10^{-19} \text{ J}$$

$$\nu = E/h = 75.78 \times 10^{-19} \text{ J} / 6.626 \times 10^{-34} \text{ Js}$$

$$= 11.437 \times 10^{15} \text{ s}^{-1}$$

$$\lambda = c/\nu = 3 \times 10^8 \text{ ms}^{-1} / 11.437 \times 10^{15} \text{ s}^{-1}$$

$$= 2.62 \times 10^{-8} \text{ m}$$

SNP 3: The intensities of the incident and transmitted light were observed to be 68 and 16 respectively on a linear scale using a 2 cm cuvette for a chromophoric compound having molar absorptivity $3100 \text{ L mole}^{-1} \text{ cm}^{-1}$ (at $\lambda = 510 \text{ nm}$). Calculate the concentration of the compound.

Ans: According to the Beer-Lambert law, the ratio of the intensity of incident radiation (I_0) and the transmitted radiation (I) is related to concentration as

$$\log(I_0/I) = \epsilon C l$$

where ϵ , C and l are molar absorptivity, concentration and path length respectively.

Substituting the values in the above equation

$$\log(68/16) = 3100 \times C \times 2$$

$$0.6284 = 3100 \times C \times 2$$

$$C = 0.6284 / 6200 = 1.013 \text{ M}$$

SNP 4: Calculate vibrational frequency for each of the following stretching vibrations using Hooke's law approximation: (i) $^{12}\text{C}-^1\text{H}$ (ii) $^{16}\text{O}-^1\text{H}$

Ans: The vibrational frequency of a bond is related to the masses of the vibrating atoms and force constant (k) of the vibrating bond by the following equation called as Hooke's law:

$$\nu = \frac{1}{2\pi c} \left[\frac{k (M_a + M_b)}{(M_a M_b)} \right]^{1/2}$$

$$(i) \quad \nu_{\text{C-H}} = \frac{1}{2\pi \times 3 \times 10^{10} \text{ cm/s}} \left[\frac{5 \times 10^5 \text{ gm/s}^2 [(12/6.023) + (1/6.023)] \times 10^{-23}}{[(12/6.023) (1/6.023)] \times 10^{-23}} \right]^{1/2} = 3032 \text{ cm}^{-1}$$

$$(ii) \quad \nu_{\text{O-H}} = \frac{1}{2\pi \times 3 \times 10^{10} \text{ cm/s}} \left[\frac{5 \times 10^5 \text{ gm/s}^2 [(16/6.023) + (1/6.023)] \times 10^{-23}}{[(16/6.023) (1/6.023)] \times 10^{-23}} \right]^{1/2} = 3000 \text{ cm}^{-1}$$

SNP 5: Acrolein ($\text{CH}_2=\text{CHCHO}$) absorbs at 217 nm ($\epsilon = 16000$). What is the weight concentration (gm/cc) required to observe an absorbance of 0.75 for a cell length of 10 mm?

Ans: $\ln I_0/I = 0.75 = \epsilon c l$

$$\epsilon = 16000; l = 1 \text{ cm}$$

$$c = 0.75 / 16000 \times 1 = 4.69 \times 10^{-5} \text{ moles/cc}$$

As the molecular weight of acrolein ($\text{CH}_2=\text{CHCHO}$) is 56, so concentration in gm/cc is

$$\text{Concentration (gm/cc)} = 56 \times 4.69 \times 10^{-5} = 262.64 \times 10^{-5} \text{ gm/cc}$$