CH 2252 Instrumental Methods of Analysis

Unit – I

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Infra Red Spectroscopy

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Contents

- Instrumentation (Source, Optical parts and Detectors)

Introduction

- **Applications:**
  - Suited for both qualitative and quantitative determination, particularly of inorganic compounds
  - Its use in the applications to inorganic compounds is limited, because of the strong absorption of IR radiation by water. This necessitates the study of inorganic materials in the solid state (else needs D_2O)

- **Wavelength region:**
  - IR spectrum extends from 0.8 to 200 μm in the electromagnetic spectrum. However, most of the commercial instruments are available in the region from 0.8 to 50 μm.
  - The region of IR spectrum which is of great interest to organic chemists is the wavelength range 2.5 to 15μm. In practice, wave number (cm^{-1}) rather than wavelength is commonly used. (4000 to 600 cm^{-1})

Introduction (contd.)

- IR spectroscopy deals with transitions between vibrational energy levels in molecules, and is therefore also called vibrational spectroscopy

- **IR spectrum**: It is a plot of the energy of the infrared radiation expressed in wavelength (μm) or wave number(cm^{-1}) versus the percentage of light transmitted by the compound

- IR spectroscopy is applicable to solids, liquids, and gases. It is fast and requires small sample sizes

Various Regions of the Infrared Range of Spectrum

Region	Wavelength range (μm)	Wave number range (cm^{-1})
Near	0.78 – 2.5	12800 – 4000
Middle	**2.5 – 50**	**4000 – 200**
Far	50 – 1000	200 – 10

Most useful IR region

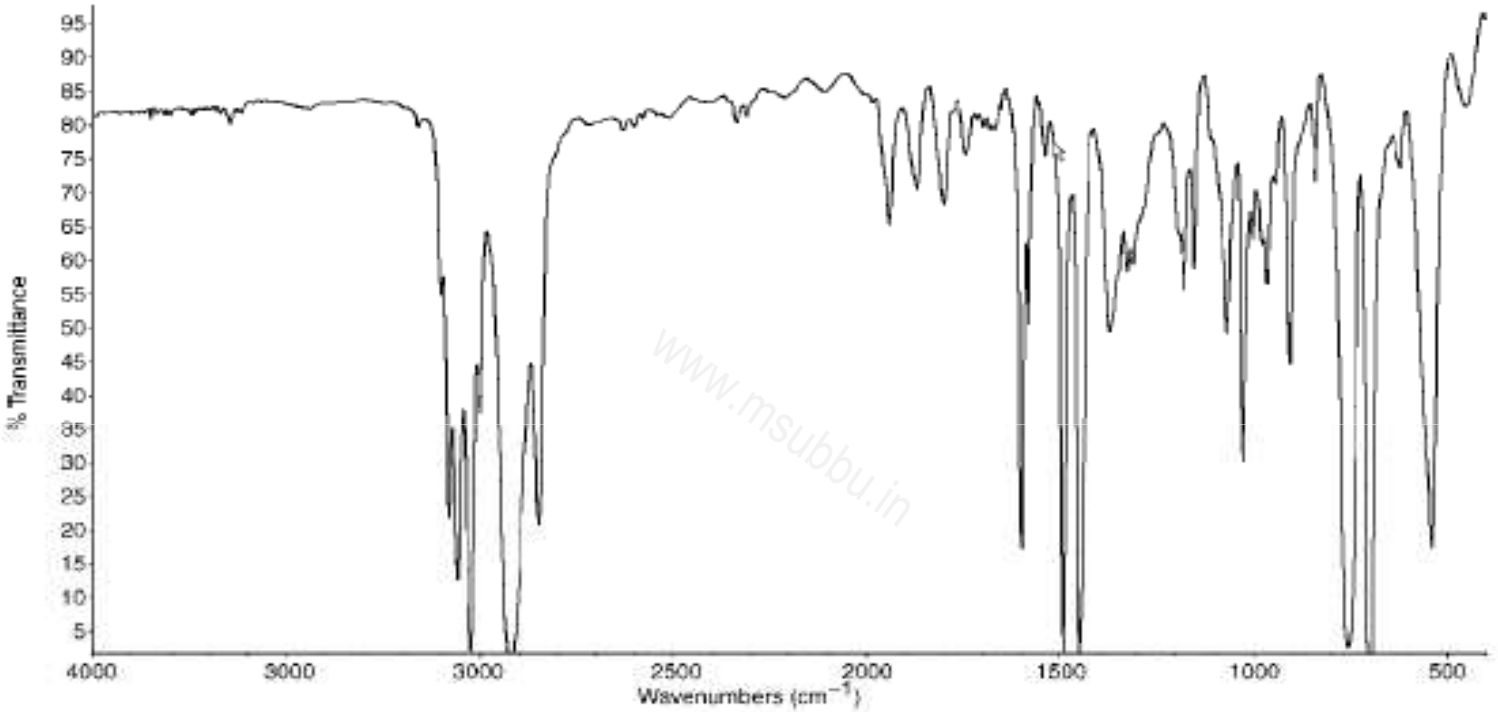


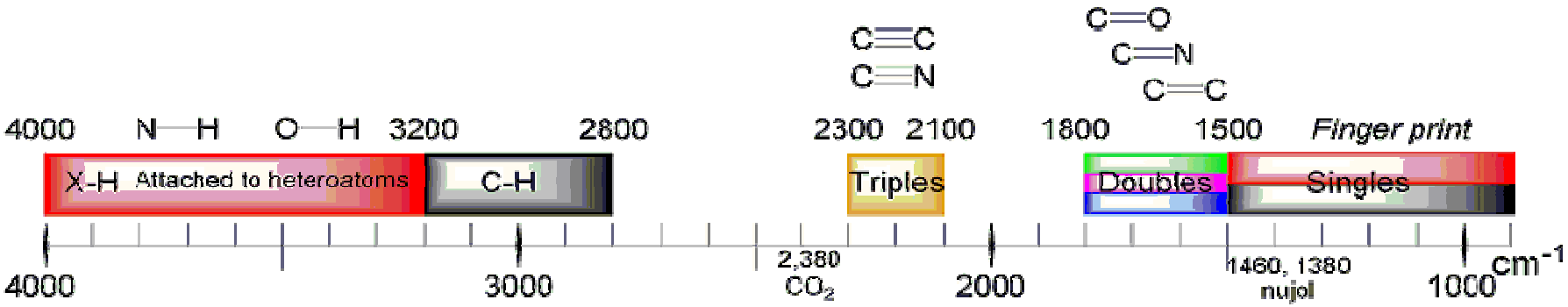
Figure 4.1 Fourier transform IR spectrum of a thin film of polystyrene. The *y* axis unit is %T, the *x* axis is in wavenumbers (cm^{-1}). Collected on a ThermoNicolet 6700 FTIR spectrometer with a DTGS detector. Courtesy of Thermo Electron Corp. (www.thermo.com).

Interpretation of Spectra

- IR rays produce vibrations and rotations in a molecule by the absorption of radiation
- The IR spectrum based on these absorption constitutes a powerful tool for the study of molecular structures and identification.
- Chemical identification is based on empirical correlations of vibrating groups, with specific absorption bands; and the quantitative determinations are dependent on the intensity measurements
- Interpretation of IR spectra is highly empirical and requires huge libraries of reference spectra; the interpretation of spectra is a skilled art.

IR Spectrum

Group	Bond	Wave number range (cm^{-1})
hydroxyl	O-H	3610-3640
amines	N-H	3300-3500
aromatic rings	C-H	3000-3100
alkenes	C-H	3020-3080
alkanes	C-H	2850-2960
nitriles	C≡N	2210-2260
carbonyl	C=O	1650-1750
amines	C=N	1180-1360



Since most organic molecules have single bonds, the region below 1500 cm-1 can become quite complex and is often referred to as the **fingerprint region**.

Infrared Spectrophotometer - Instrumentation

- Same basic elements as in UV-vis spectrophotometer

- **Radiation sources**: blackbody radiator
  - The optimum radiation source is an inert solid, heated electrically to temperatures between 1500 and 2000 K

- Practical infrared sources: Globar rod, Nernst filament, nichrome wire
  - Globar is a silicon carbide rod
  - Nernst filament is composed of fused rare earth oxides of zirconium and yttrium

- **Monochromators**: prism (for wavelengths less than 40μm), and gratings (for wavelengths higher than 40μm).

Sample Handling

- Solids, liquids, or gases can be handled
- Sample handling presents a number of problems, since no rugged window material for cell exists, which is transparent over the entire range and is also inert
- The most commonly used window material is NaCl, which transmits down to about 650 cm^{-1}. KBr transmits down to about 400 cm^{-1}, CaBr to about 250 cm^{-1} and CsI to about 200 cm^{-1}
  - Since these materials are all water soluble, the surfaces of the windows made from them are easily fogged by exposure to atmospheric water vapor or moist samples. Therefore, they require frequent policing when used under such conditions

Sample Handling (contd.)

- **Gas cells**: usually have a path length of 100 mm, since this thickness gives a reasonable absorbance level for the majority of gases and vapors at the normally encountered partial pressures

- **Liquid cells**: The extinction coefficient of most liquid hydrocarbons in the infrared region is such that a pure sample of thickness between 0.01 and 0.05 mm gives an absorption spectrum that is quite suitable for analysis. The transmittance lies between 15 and 70 percent Typical path length of cells: 0.02, 0.04, 0.06, 0.1, 0.16, 0.25, 0.4, 0.6 and 1.0 mm. The external cell diameter is 30 mm. About 100 μl sample volume per 0.1 mm path length is required

Sampling of Solids

- **Solids dissolved in solutions**:
  - there is no single solvent which is transparent through the entire infrared range
  - In order to cover the main spectral range between 4000 and 650 cm^{-1}, a combination of CCl_4 and CS_2 are employed

- **Pressed pellet technique**
  - Sample is finely ground and mixed with an alkali halide like KBr, and then pressed into the form of a disc for examination in the instrument

- **Mull technique**
  - Finely powdered solids are dispersed within a liquid medium to form a thick slurry. The liquid is so chosen that it has the same refractive index as the sample, so as to minimize scattering losses. The most commonly used liquid mulling agent is a mixture of liquid paraffins, known as Nujol.

Detectors

- Convert the thermal radiant energy into electrical energy
- Thermal detectors – thermopiles, bolometers, pneumatic detectors and pyroelectric detectors. Has low response speed and detectivity, operable at room temperature
- Quantum type detectors – photoconductive cells, and photo diodes. Has high detectivity and fast response speed, requires cooling