Chapter-16
Infrared spectroscopy (Theory & Principle)
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Theory:

- **Infrared spectroscopy (IR spectroscopy or vibrational spectroscopy) involves the interaction of infrared radiation with matter.** It covers a range of techniques, mostly based on absorption spectroscopy. **As with all spectroscopic techniques, it can be used to identify and study chemical substances.** Samples may be solid, liquid, or gas. **The method or technique of infrared spectroscopy is conducted with an instrument called an infrared spectrometer (or spectrophotometer) to produce an infrared spectrum. An IR spectrum** can be visualized in a graph of infrared light **absorbance (or transmittance) on the vertical axis (y axis) vs. frequency or wavelength on the horizontal axis (x axis). Typical units of frequency used in IR spectra are reciprocal centimeters (sometimes called wave numbers), with the symbol cm^{-1}.** Units of IR wavelength are commonly given in micrometers (formerly called "microns"), symbol μm, which are related to wave numbers in a reciprocal way. **IR spectra used to identify bonds / functional groups.** It can only identify the exact molecule by comparison with library spectra.

IR Region:

- The infrared portion of the electromagnetic spectrum is usually **divided into three regions; the near-, mid- and far- infrared,** named for their relation to the visible spectrum. **The higher-energy near-IR, approximately 14000–4000 cm^{-1} (0.7–2.5 μm wavelength)** can excite **overtone** or harmonic molecular vibrations.

- **The mid-infrared, approximately 4000–400cm^{-1}** (2.5–25 μm) may be <u>**used to study the fundamental vibrations and associated rotational-vibrational structure**</u>**.**

- **The far-infrared, approximately 400–10 cm^{-1}** (25–1000 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy.

- **A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer.**

Experiment:

- Infrared radiation is passed simultaneously through the sample and a reference cell (Fig.1.).

- The reference ensures that peaks due to water or carbon dioxide in the air can be cancelled out.

- The frequencies of i.r. radiation absorbed are determined by passing through a rotating prism to focus one frequency at a time onto the detector.

- The spectrum shows the wave number (cm^{-1}) on the x axis (which is $1/\lambda$) and the absorbance or transmittance on the y-axis.
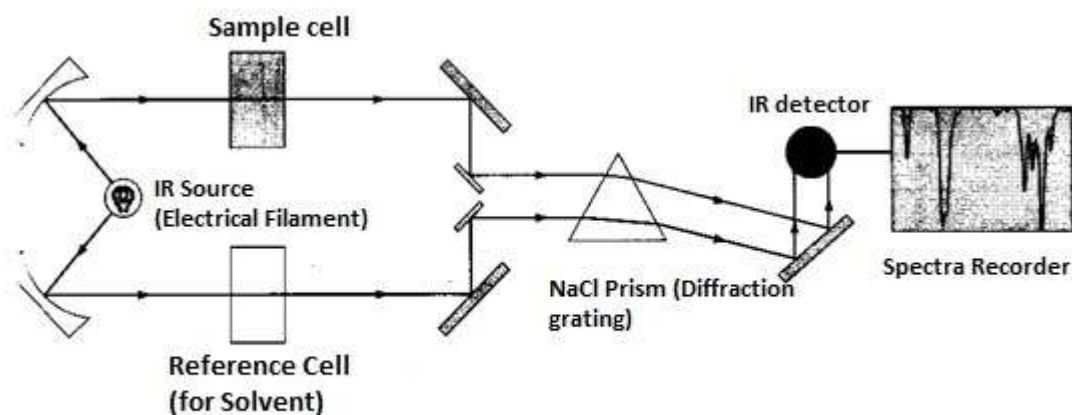

Fig.1.: Basic Parts of a double beam infrared spectrometer

Basic Principle of IR Spectra

Molecular Vibrations be the basic principle of the IR spectra. IR radiation corresponds to the **energy required to make chemical bonds vibrate more / move to a higher vibrational energy level**. Therefore, energy of certain wavelengths is absorbed by molecules. **The actual energy depends on the mass of the atoms and the strength of the bond,** so **different bonds will absorb at different frequencies**. **Stronger bonds (higher Electro negativity difference) need more energy to make them vibrate, so absorb a higher frequency of i.r. radiation (higher wave number) (Table-1&2).**

Table 1: Bond Enthalpies and infrared absorptions for the hydrogen halides

Compound	Electro negativity difference (END)	Bond enthalpy/KJ mol^{-1}	Infrared absorption / cm^{-1}
H-Cl	0.9	+432	2886
H-Br	0.7	+366	2559
H-I	0.4	+298	2230

Table 2 : Typical bond energies for X-F bonds.

Compound	Electro negativity difference (END)	Bond enthalpy/KJ mol^{-1}
P-F	1.9	490
C-F	1.5	486
N-F	1.0	272

Related Questions:

- Q.1. **Q. Draw the basic parts of a double beam infrared spectrometer.**

- **Q.2. Why reference cell used in the evaluation of i.r. peaks?**

- **Q.3. What wave number would appear on an i.r. spectrum if the frequency of radiation absorbed by a molecule was 2.5 x 10^{13} Hz?**

- **Q.4. Why HCl shows higher i.r. frequency over HBr and HI?**

Reference Books:

1. Fourier Transforms in NMR, Optical and Mass Spectroscopy, Alan G. Marshall, Francis R. Verdun, Elsevier, 1990.

2. Practical Fourier Transform Infrared Spectroscopy, John R. Ferraro, K. Krishnan, Academic Press, 1990

3. Infrared Spectroscopy: Fundamentals and Applications, Barbara H. Stuart, John Wiley & Sons, Ltd, 2004.

4. Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part A: Theory and Applications in Inorganic Chemistry, Sixth Edition, Kazuo Nakamoto, John Wiley & Sons, Ltd, 2008.

5. Infrared and Raman spectroscopy principles and spectral interpretation, Peter Larkin, Elsevier, 2011.