

# STRUCTURE DETERMINATION BY IR – TECHNIQUES AND FTIR

*Alex Shinu Scaria*

# Infrared (IR) Spectroscopy

- IR deals with the interaction of infrared radiation with matter. The IR spectrum of a compound can provide important information about its chemical nature and molecular structure.
- Most commonly, the spectrum is obtained by measuring the *absorption* of IR radiation, although infrared emission and reflection are also used.
- Widely applied in the analysis of organic materials, also useful for polyatomic inorganic molecules and for organometallic compounds.

# Theory of Infrared Absorption Spectroscopy

- For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule. The alternating electrical field of the radiation (remember that electromagnetic radiation consists of an oscillating electrical field and an oscillating magnetic field, perpendicular to each other) interacts with fluctuations in the dipole moment of the molecule.
- If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of molecular vibration.

# Vibrational-Rotational Transitions

- In general, a molecule which is in an excited vibrational state will have rotational energy and can lose energy in a transition which alters both the vibrational and rotational energy content of the molecule.
- The total energy content of the molecule is given by the **sum** of the vibrational and rotational energies. For a molecule in a specific vibrational and rotational state, we can write its energy as:

$$E(v, J) = E_{\text{vib}}(v) + E_{\text{rot}}(J)$$

# VIBRATIONAL SPECTRUM

Consists of two major regions

- Group frequency region
- Finger print region (400 - 1300  $\text{cm}^{-1}$ )

# Group frequencies

With certain functional or structural groups, it has been found that their vibrational frequencies are nearly independent of the rest of the molecule – group frequencies.

*Carbonyl group* 1650 to 1740  $\text{cm}^{-1}$       *various aldehydes and ketones*

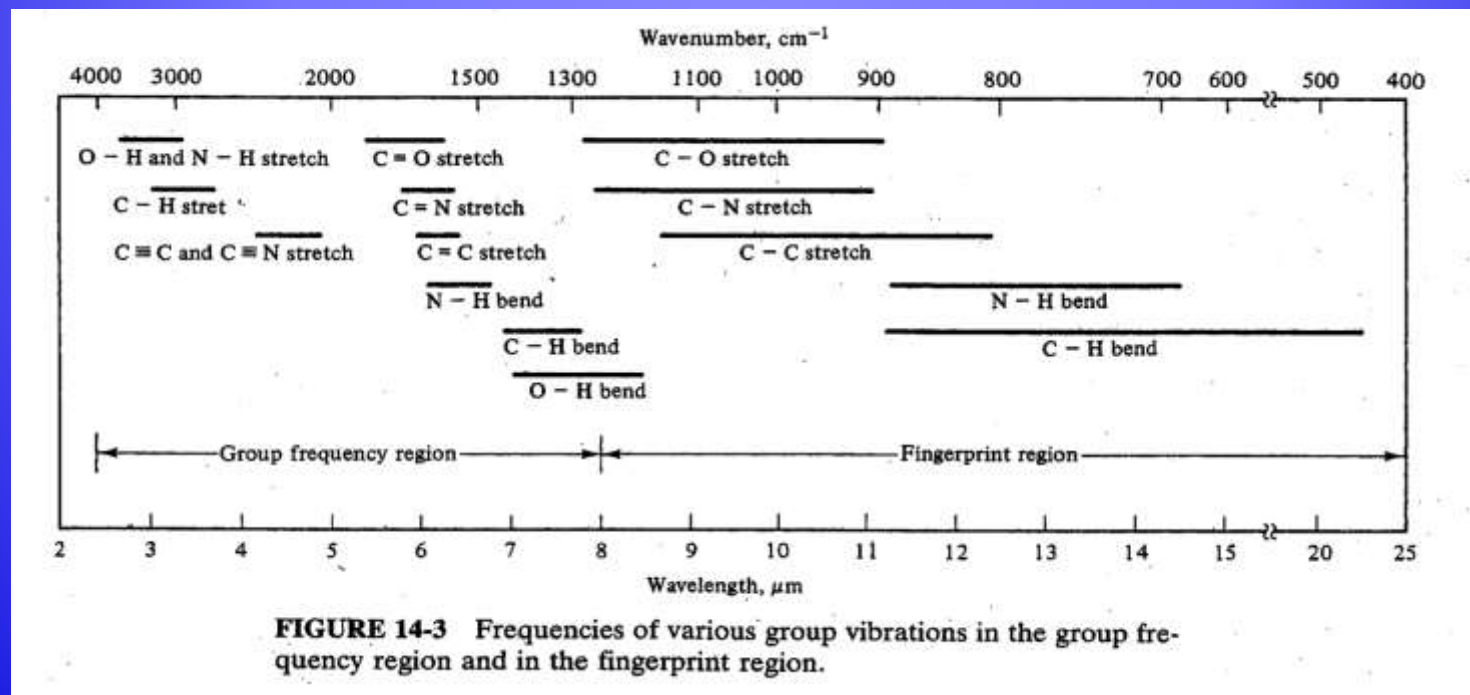
Calculations show that for most groups of interest, characteristic frequencies of stretching vibrations should lie in the region 4000 to 1000  $\text{cm}^{-1}$ . In practical, the region from 4000 to 1300  $\text{cm}^{-1}$  is often called the **group frequency region**.

The presence of various group vibrations in the IR spectrum is of great assistance in identifying the absorbing molecule.

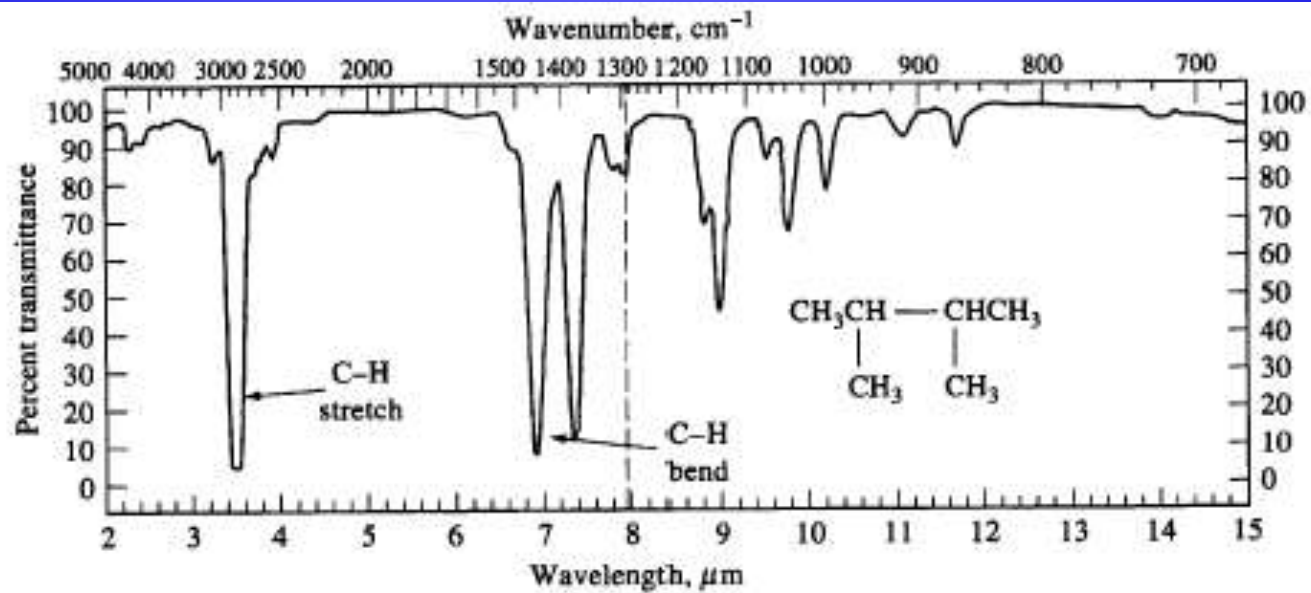
# Fingerprint region

In the region from  $\approx 1300$  to  $400\text{ cm}^{-1}$ , vibrational frequencies are affected by the entire molecule, as the broader ranges for group absorptions in the figure below – **fingerprint region**.

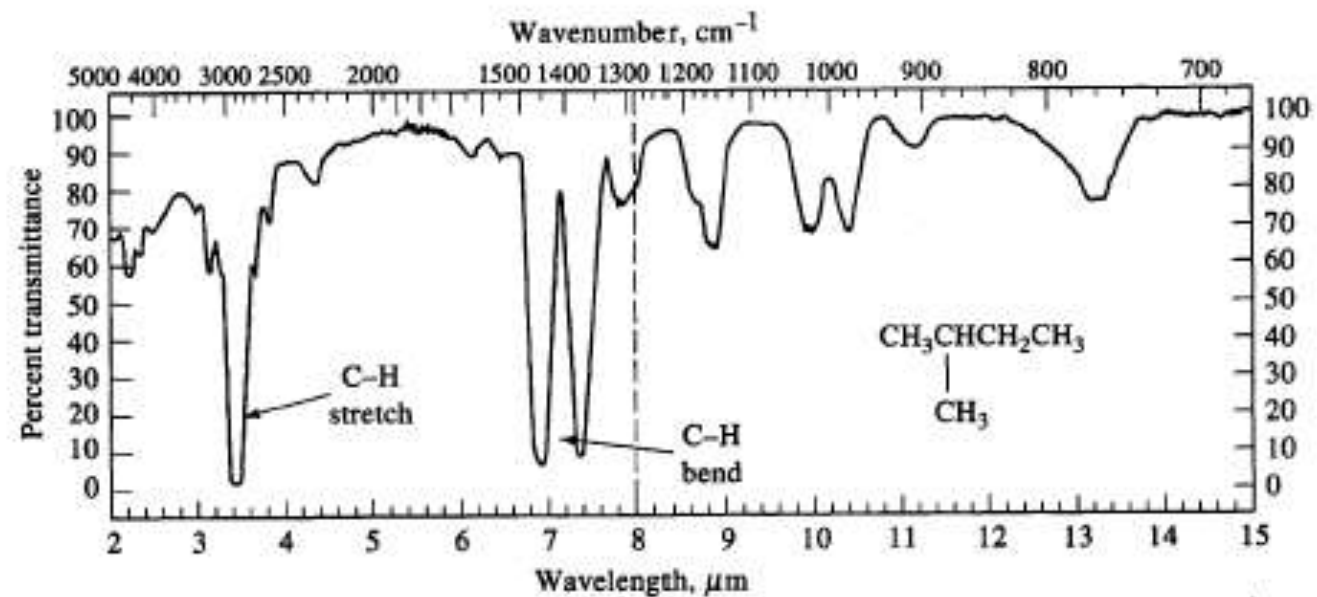
Absorption in this fingerprint region is characteristic of the molecule as a whole. This region finds widespread use for identification purpose by comparison with library spectra.



**FIGURE 14-3** Frequencies of various group vibrations in the group frequency region and in the fingerprint region.



(a)



← Group frequency region | Fingerprint region →

(b)



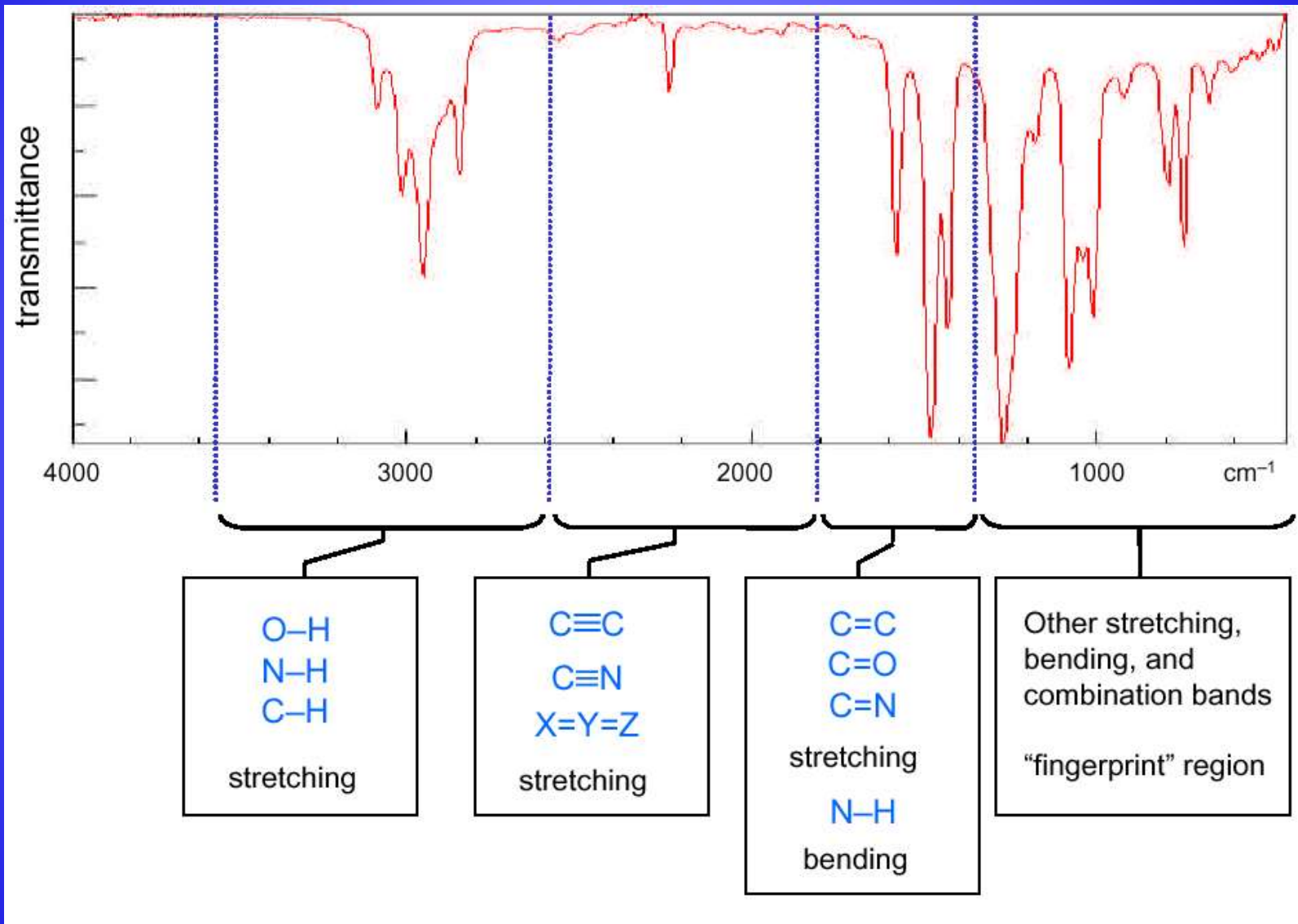
**TABLE 17-2** Abbreviated Table of Group Frequencies for Organic Groups

Bond	Type of Compound	Frequency Range, $\text{cm}^{-1}$	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes ( $\text{>C=C<H}$ )	3010–3095	Medium
		675–995	Strong
C—H	Alkynes ( $\text{—C}\equiv\text{C—H}$ )	3300	Strong
C—H	Aromatic rings	3010–3100	Medium
		690–900	Strong
O—H	Monomeric alcohols, phenols	3590–3650	Variable
	Hydrogen-bonded alcohols, phenols	3200–3600	Variable, sometimes broad
	Monomeric carboxylic acids	3500–3650	Medium
	Hydrogen-bonded carboxylic acids	2500–2700	Broad
N—H	Amines, amides	3300–3500	Medium
C=C	Alkenes	1610–1680	Variable
C=C	Aromatic rings	1500–1600	Variable
C≡C	Alkynes	2100–2260	Variable
C—N	Amines, amides	1180–1360	Strong
C≡N	Nitriles	2210–2280	Strong
C—O	Alcohols, ethers, carboxylic acids, esters	1050–1300	Strong
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760	Strong
NO <sub>2</sub>	Nitro compounds	1500–1570	Strong
		1300–1370	Strong

# Absorption Regions



Irtutord.exe



FOURIER TRANSFORM

INFRARED SPECTROSCOPY

# What is FTIR

- **Fourier-transform infrared spectroscopy is a vibrational spectroscopic technique, meaning it takes advantage of asymmetric molecular stretching, vibration, and rotation of chemical bonds as they are exposed to designated wavelengths of light.**
- **Fourier transform is to transform the signal from the time domain to its representation in the frequency domain**

# PRINCIPLE OF FTIR

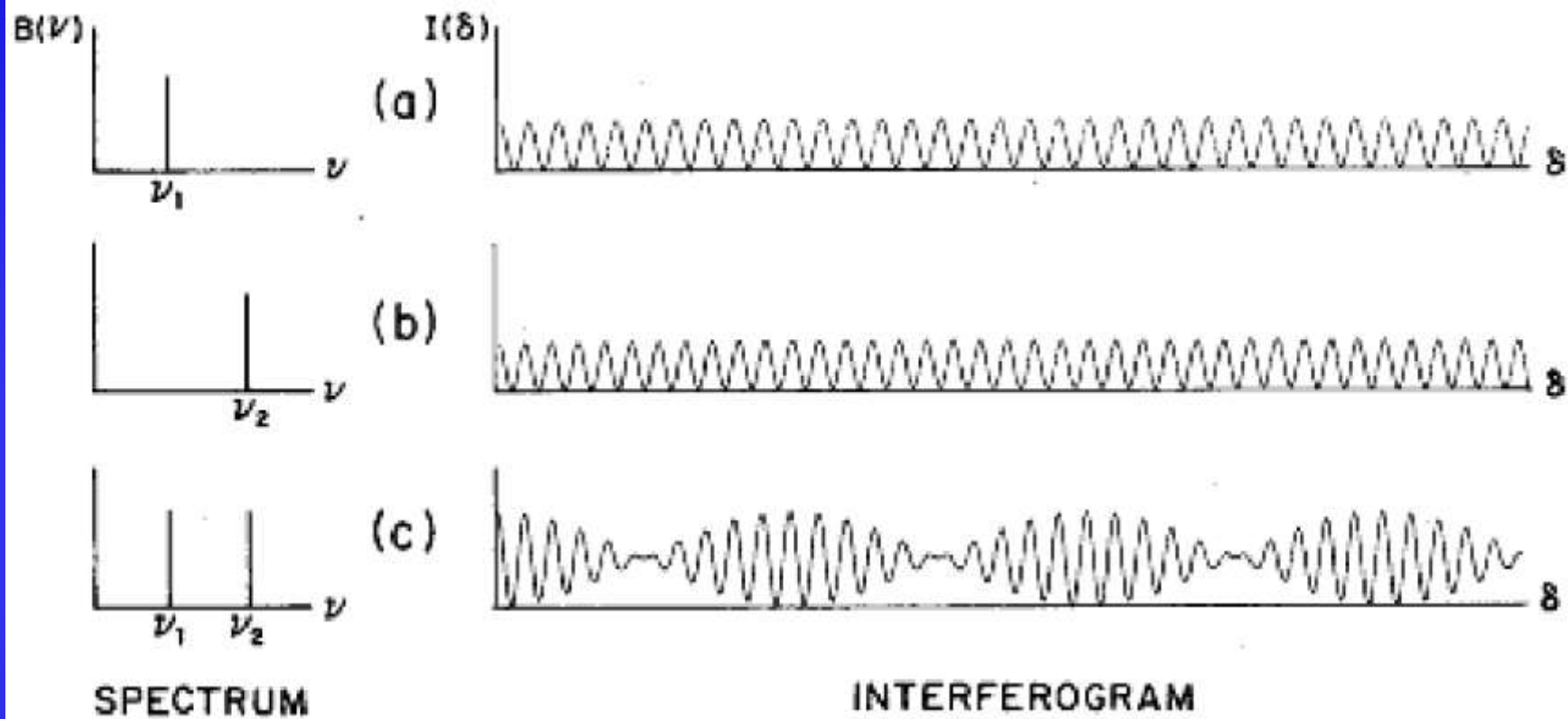
- Fourier transform of a function  $f(t)$  is

$$G(\omega) = \frac{1}{2\pi} \int f(t) \exp(i\omega t) dt$$

- Inverse relation is

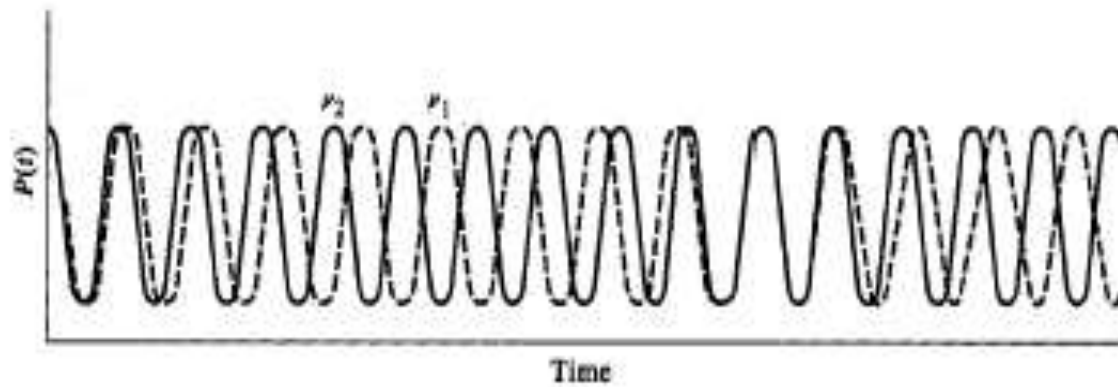
$$f(t) = \frac{1}{2\pi} \int G(\omega) \exp(-i\omega t) d\omega$$

These two relations are said to form a fourier transform pair



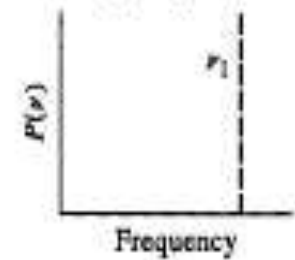
a) a sine wave b) sine wave of slightly different frequency c) sum of sine waves

Time domain

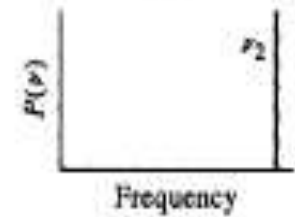


(a)

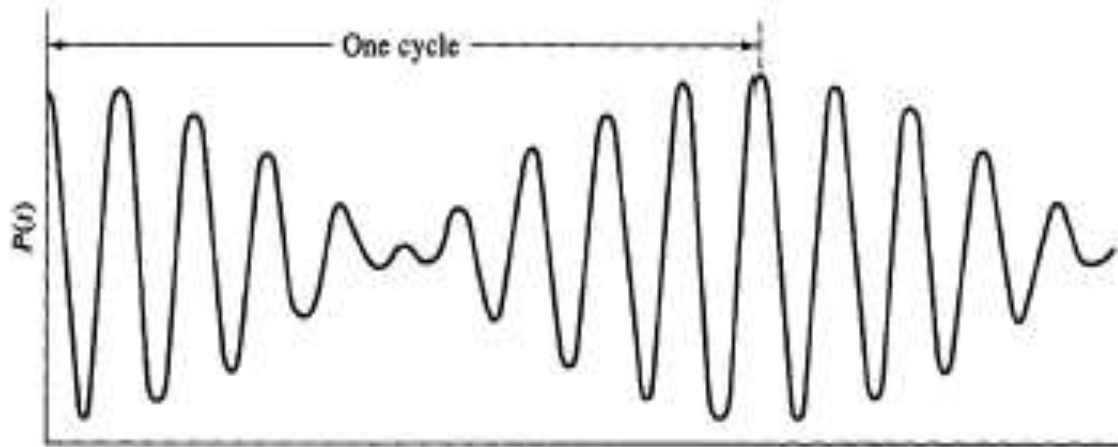
Frequency domain



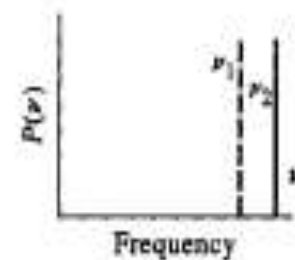
(c)



(d)

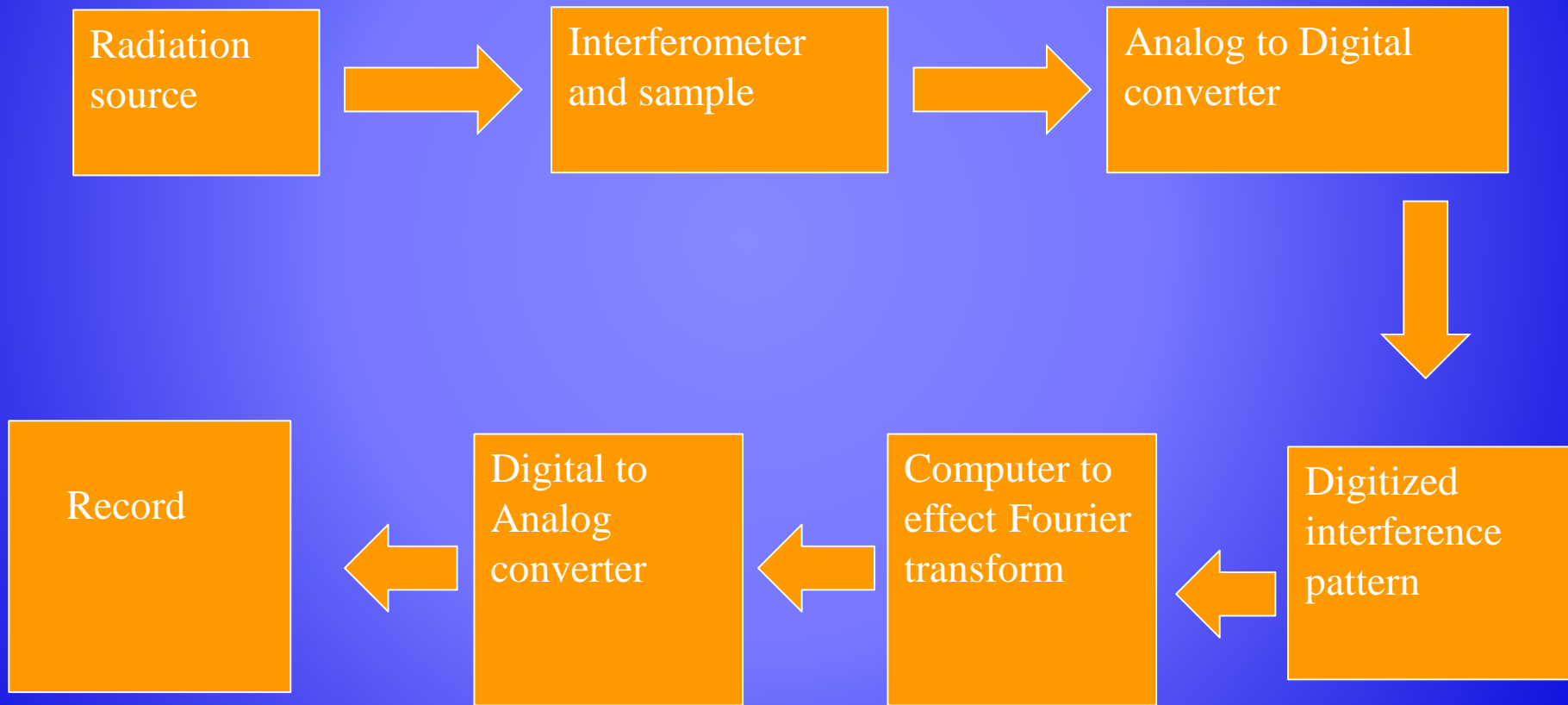


(b)



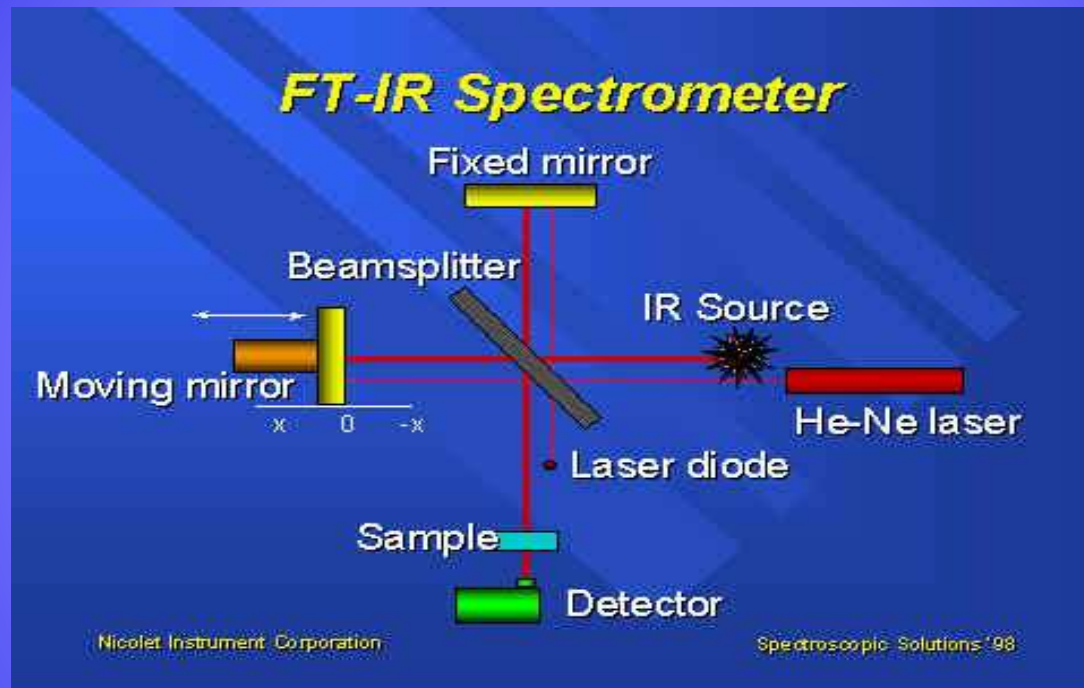
(e)

# FOURIER TRANSFORM SPECTROMETER



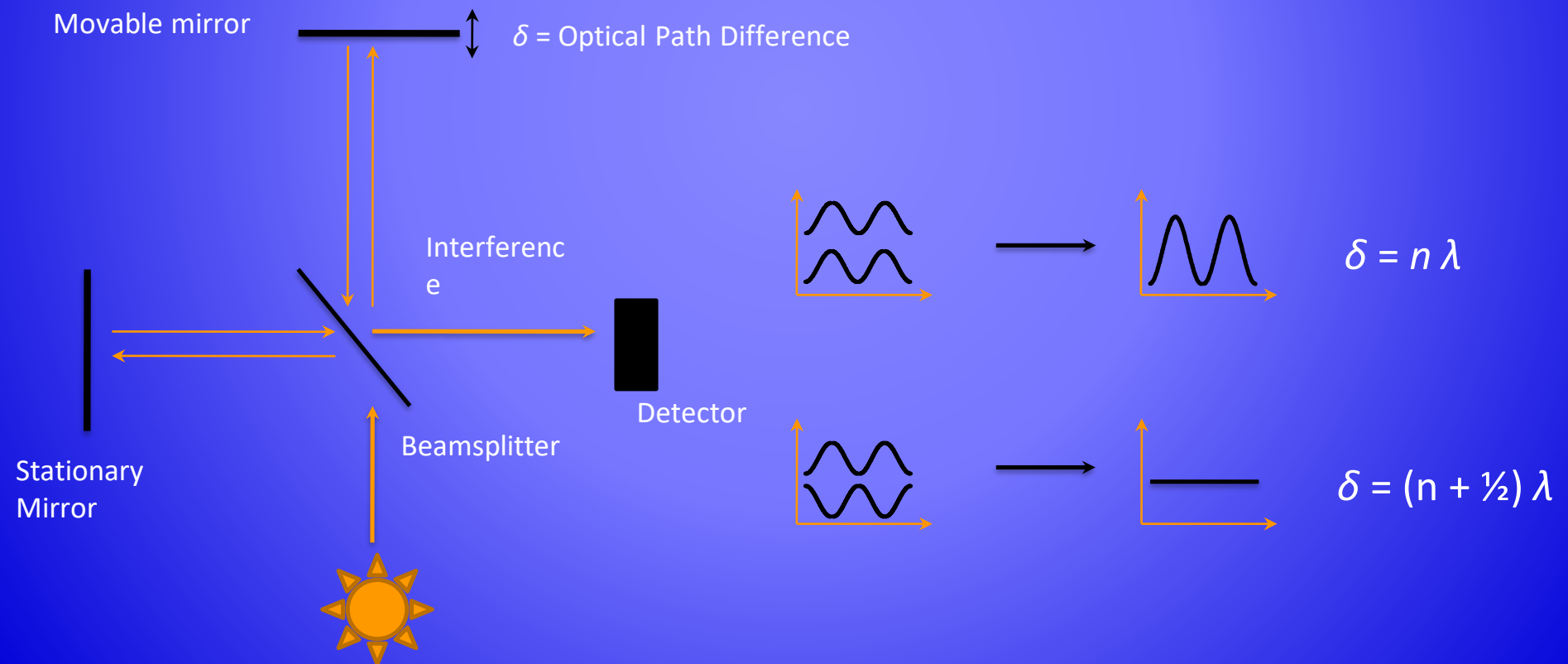


# Theory and Instrumentation



- Light enters the spectrometer and is split by the beam splitter. The figure above shows what is referred to as the Michelson interferometer

- The Michelson interferometer principle



# Theory and Instrumentation(contd.)

- The light originates from the He-Ne laser
- Half of the light is reflected 90 degrees and hits a fixed mirror, while the other half passes through the beam splitter and hits the moving mirror
- The split beams are recombined, but having traveled different distances, they exhibit an interference pattern with each other
- As they pass through the sample, the detector collects the interfering signals and returns a plot of response with mirror displacement known as an interferogram

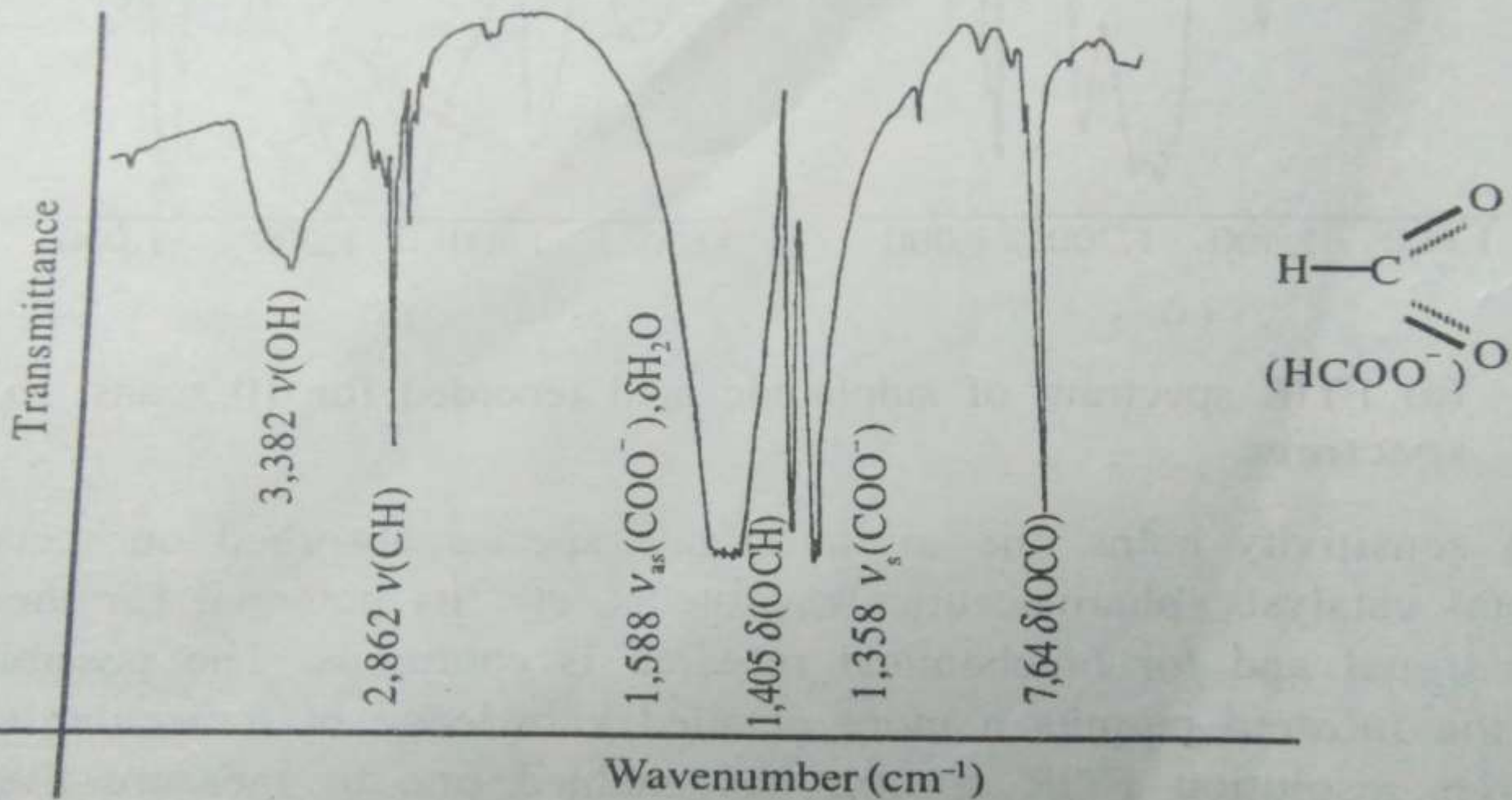
# Advantages of FTIR

- very high resolution ( $< 0.1 \text{ cm}^{-1}$ )
- very high sensitivity (nanogram quantity)
- High S/N ratios - high throughput
- Rapid Scanning ( $< 10 \text{ s}$ )
- Reproducible and • Inexpensive

# APPLICATIONS OF FTIR

- Identification of molecular constituents
- Elucidation of molecular structure
- Characterization of the transition phases of ceramics
- Biological applications

# INFRARED SPECTRUM



**Figure 7.15** Infrared spectrum of  $\text{Cd}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$

THANK YOU