Lecture 9

Characterization Instruments

Fourier-transform infrared spectroscopy (FTIR)

- A technique used to obtain infrared spectrum of absorption or emission of a solid, liquid or gas

- To identify the presence of certain functional groups in a molecule, and to confirm the identity of a pure compound or to detect the presence of specific impurities

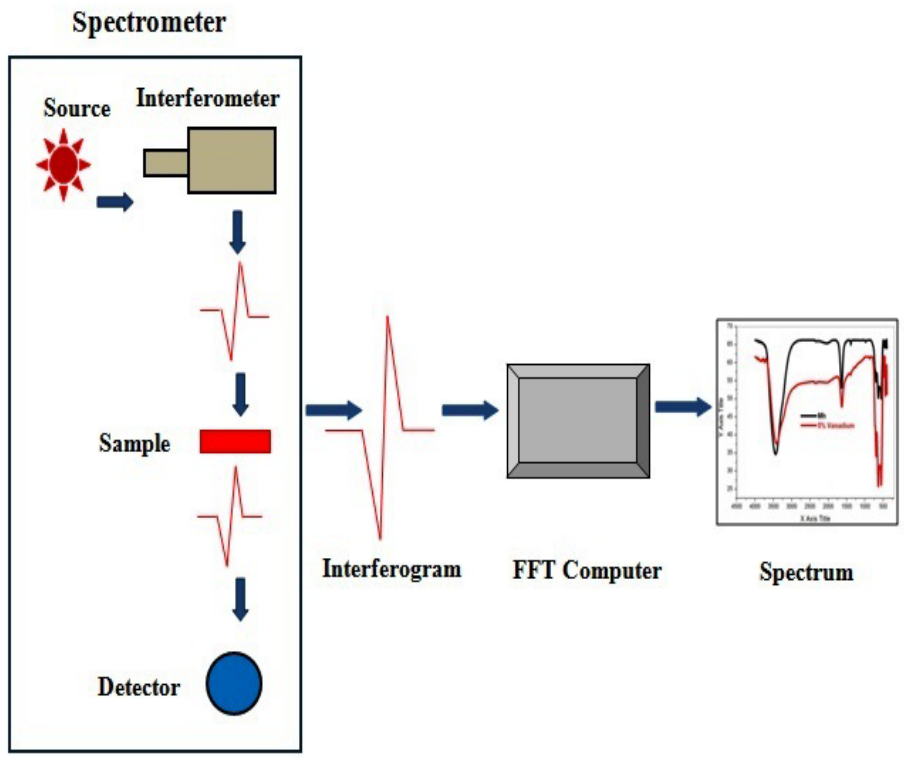
- FTIR spectrometers are mostly used for measurements in the mid and near IR regions. For the mid-IR region, 2−25 μm (5000–400 cm^{-1})

FTIR Spectrophotometer (Nicolet 5DX FT-IR, USA)

- Fourier transform spectrum is a single beam spectrum converted from an Interferogram, which includes both spectra from the sample and background.

- The background spectrum contains only the information from the instrument and the atmosphere, not from the sample being examined.

- The instrument contributions to background spectrum are from the detector, beam-splitter, mirror and the IR source. The atmospheric contributions are mainly from water vapor and carbon dioxide.



Schematic of a FTIR spectrometer

- The key component in the FTIR system is the Michelson interferometer.
- The infrared radiation from a source enters the Michelson interferometer. The interferometer is composed of one beam-splitter and two mirrors.
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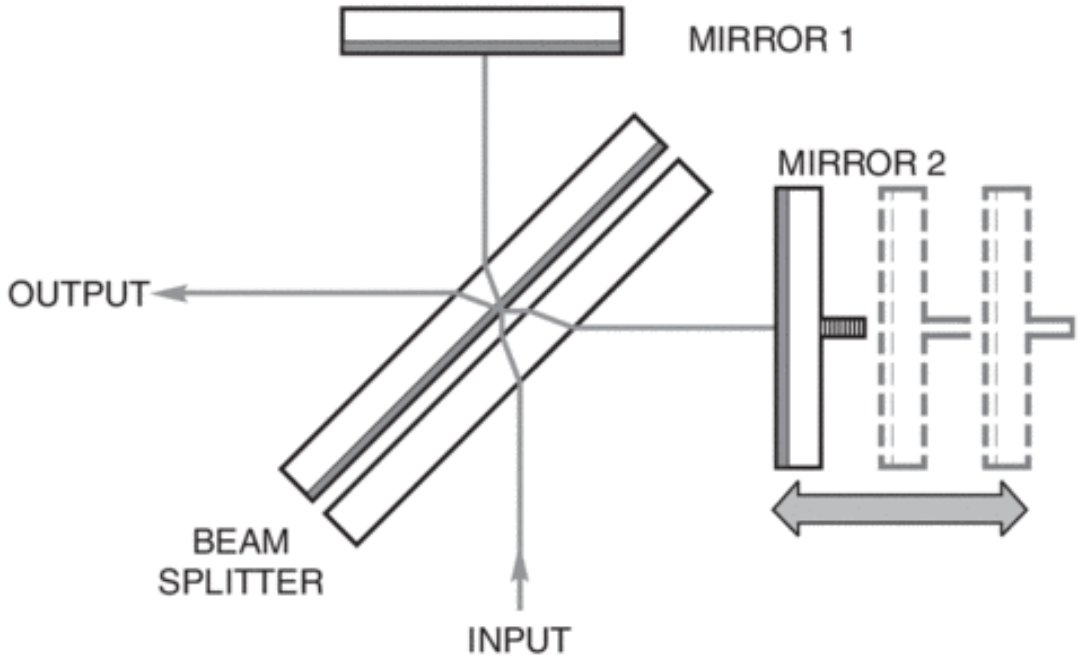
- The beam-splitter transmits half of the infrared (IR) beam from the source and reflects the other half. The two split beams strike a fixed mirror and a moving mirror, respectively.
- The function of the moving mirror is to change the optical path lengths in order to generate light interference between the two split beams.
- After reflecting from the mirrors, the two split beams combine at the beam-splitter again in order to irradiate the sample before the beams are received by a detector.



A Schematic of a generic Michelson interferometer

- The two split beams will show constructive and destructive interference periodically

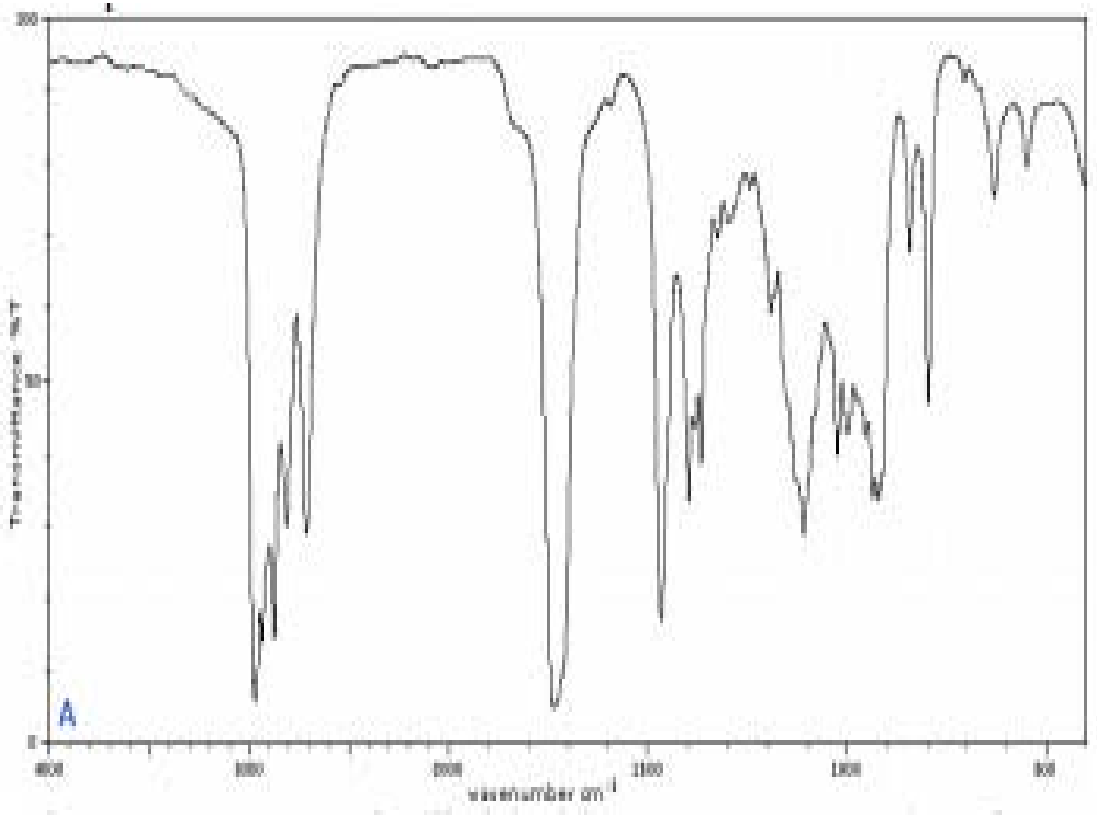
- Fourier transformation is necessary to convert an Interferogram into an infrared spectrum, which is a plot of the light intensity versus wavenumber.

- A computer equipped with FTIR constructs the infrared spectrum using a fast Fourier transform (FFT) algorithm which substantially reduces the computation time.

Infrared Spectrum is the plot of photon energy (x axis) versus the amount of photons (y axis)
X axis: the stretching frequency
Y axis: the amount of photons absorbed/ transmit.

The IR Spectrum is divided into 5 Zones and a Fingerprint Region

Each zone has a characteristic frequency and in each zone specific bonds have very specific peak intensities. Looking at the peak determines what functional group is present.

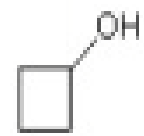


Characteristic Stretching Frequencies: The Five Zones (Table)

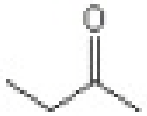
Bond	Stretching Frequency (cm^{-1})	Intensity and Shape
	ZONE 1: 3700-3200 cm^{-1}	
Alcohol O-H	3650-3200 cm^{-1}	Usually strong and broad
Alkyne ≡C-H	3340-3250	Usually strong and sharp
Amine or Amide N-H	3500-3200	Medium; often broad
	ZONE 2: 3200-2700 cm^{-1}	
Aryl or Vinyl sp^2 C-H	3100-3000	Variable
Alkyl sp^3 C-H	2960-2850	Variable
Aldehyde	~2900 and ~2700	Medium; two peaks
Carboxylic Acid O-H	3000-25000	Usually strong; very broad
	ZONE 3: 2300-2000 cm^{-1}	
Alkyne C≡C	2260-2000	Variable and sharp
Nitrile C≡N	2260-2220	Variable and sharp
	ZONE 4: 1850-1650 cm^{-1}	
Ketone C=O	1750-1705	Strong
Ester C=O	1750-1735	Strong
Aldehyde C=O	1740-1720	Strong
Carboxylic Acid C=O	1725-1700	Strong
Amide C=O	1690-1650	Strong
	ZONE 5: 1680-1450 cm^{-1}	
Alkene C=C	1680-1620	Variable
Benzene Ring C=C	~1600 and ~1500	~1600 often has 2 peaks

Attention: The functional group **BOLDED** are the ones that appear in more than one zone. They must be present in all characteristic zones to exist.

Practice Problem: Using what you have just learned. Decide which of the following 5 molecules the IR Spectrum below depicts.



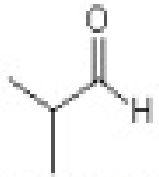
cyclobutanol



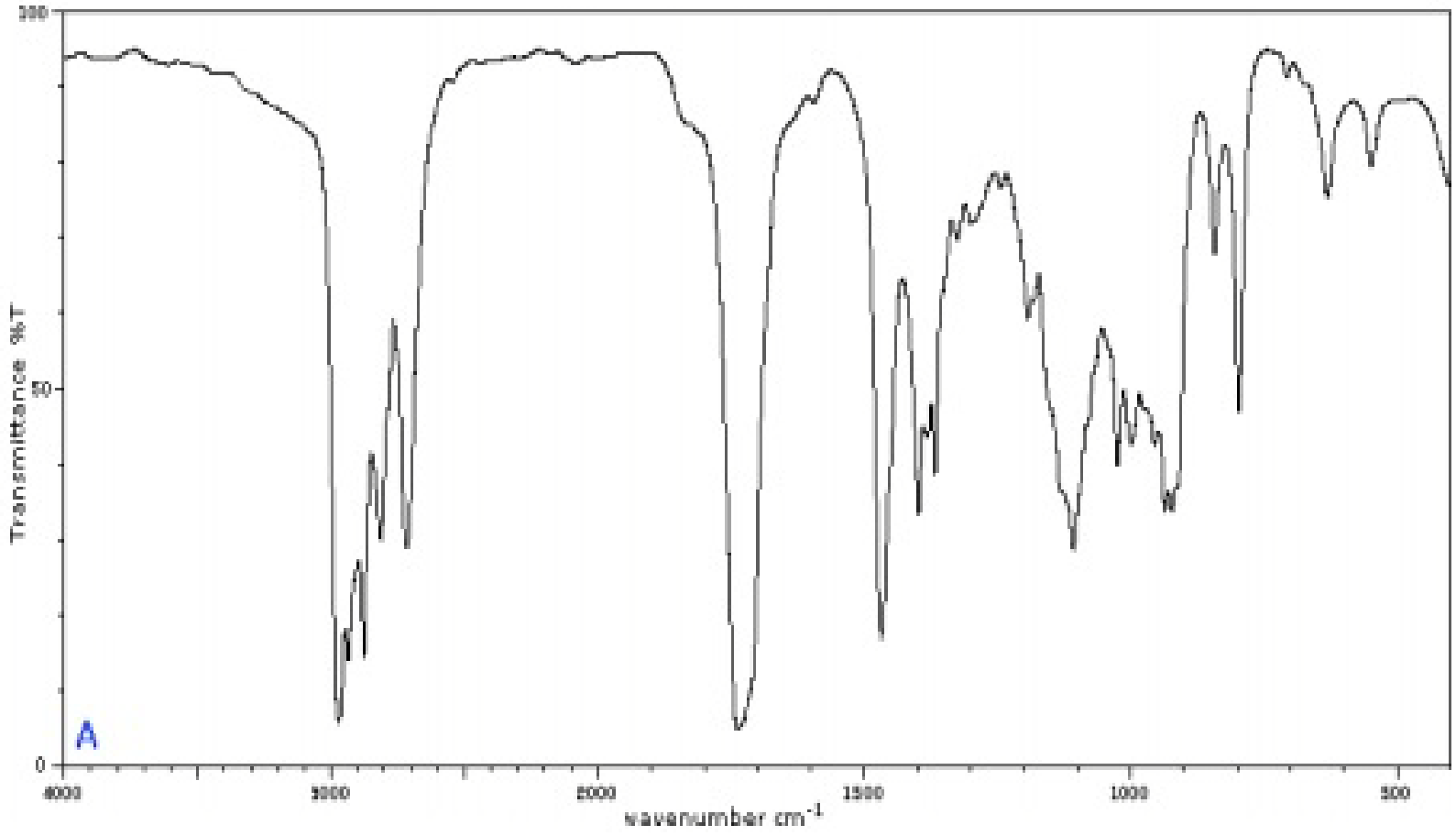
2-butanone

ethyl vinyl ether

2-methyl-2-propen-1-ol



2-methylpropanal



Solution: You can solve this problem by process of elimination.

1. By looking at the IR Spectrum you can eliminate all molecules with an alcohol in it (cyclobutanol and 2-methyl-2-propen-1-ol). This is because the IR spectrum does not show an alcohol present. (Remember: You need a broad peak at about 3300. Hint: Alcohol peak looks like a tongue.)
2. Now you have three choices left. 2-butanone has a ketone present in the molecule. (Remember: A ketone is a Carbon double bonded to an oxygen. The carbon is bonded to two other Carbons). Ethyl Vinyl Ether has an ether present in the molecule (An ether is one functional group that is not identified on within the 5 zones so move on to the next molecule). 2-methylpropanal has an aldehyde in its molecule. (Remember: An aldehyde is a carbon double bonded to oxygen. The carbon is bonded to a carbon and hydrogen).
3. So by looking at the IR Spectrum above, do you see a ketone or an aldehyde present? We can immediately tell that the molecule portrayed by the IR spectrum must be the last molecule (2-methylpropanal) because the IR spectrum has a peak in Zone 2 at 2700 and 2900. This signifies that an Aldehyde is present.

Answer: 2-methylpropanal ☺