Infrared Spectroscopy – used to analyze the presence of functional groups (bond types) in organic molecules

The process for this analysis is two-fold:

1. Accurate analysis of infrared spectra to determine presence of specific bonds in a molecule.
2. The identification of functional groups based on bonds present leading to functional group recognition

**Infrared spectroscopy**: is the study of the interaction of infrared energy with organic molecules; the process analyzes molecules for molecular bond vibrations, measuring how fast bonds vibrate.

**How IR spectroscopy works:**

1. A sample is placed in the IR and allowed to interact with infrared energy. When the molecule has a bond vibration that matches that of the infrared energy, the molecule absorbs that energy. **EVERY TYPE OF BOND HAS A DIFFERENT VIBRATIONAL FREQUENCY.**
2. When the energy is absorbed, the instrument records that energy as not being entirely transmitted through a molecule. The energy that is absorbed has a specific frequency, thus identifying the (same) frequency of vibration of the bond in the molecule.
3. When the analysis is complete, every bond type has been noted on the spectra.
4. With every bond type present, functional groups can be identified.

When the sample is placed in the instrument and the instrument scans a range of frequencies, looking to match a frequency with a frequency of vibration within the molecule, two things could happen:

- When nothing matches, 100% of the energy just passes through the molecule (100% photon energy is transmitted)
- When the frequency of the energy from the instrument matches that of the frequency of the vibration of the bond, the molecule absorbs the energy (less than 100% is transmitted).

The IR shows the range of frequencies of energy (X-axis) and how much energy is passing through (Y-axis). **The peaks are those shown at frequencies when less than 100% energy is being transmitted (upside down peaks!).**
**Y Axis: Percent Transmittance:** Amount of energy that passes through the molecule
- If no bonds are vibrating at frequencies of energy, 100% energy photon transmittance occurs
- If bonds are vibrating at same frequency, energy is absorbed, less than 100% is transmitted.

**VIBRATION MODES IN MOLECULES:**

![symmetrical stretch](image)

![asymmetrical stretch](image)

![scissoring motion](image)

![wagging motion](image)

**X Axis: Wavenumbers:** Frequency of energy, expressed as reciprocal wavelength in centimeters (1/cm or cm\(^{-1}\))

There are **TWO** Factors that affect the FREQUENCY of vibration:
1. Size of the atoms attached to the bond. Larger atoms vibrate slower, at a lower frequency. Smaller atoms vibrate faster, higher frequency.
   
   \[ \text{C-H} \text{ versus } \text{C-Br} \]

2. Bond length (the strength of the bond). Shorter stronger bonds vibrate faster, at a higher frequency. Longer, weaker bonds vibrate slower, lower frequency.
   
   \[ -\text{C\equiv C} - \text{ versus } \text{C=C} \]
   
   \[ \text{sp } \text{C-H} \text{ versus } \text{sp}^2 \text{C-H} \text{ versus } \text{sp}^3 \text{C-H} \]
The INTENSITY (Size) of the Peak:
As far as molecules are concerned, the intensity of the peak (strong, medium, weak) is affected by the extent that the vibration changes the DIPOLE of the molecule. The greater the effect on the dipole moment while vibration occurs, the larger the peak will appear on the IR spectrum.

\[ \text{\text{C=C} \quad \text{C} = \text{C}} \text{ versus } \text{C=O} \quad \text{C} = \text{O} \]

Polar covalent bonds will be the largest (strongest) peaks on the IR spectrum.

The intensity of a peak is also affected by the number of any specific type of bond in a molecule. The more bonds of the same type will result in a larger number of data points acquired at a specific frequency, which will result in the appearance of a larger peak than one would normally expect.

Sample Infrared Spectrum:

Analysis of an IR Spectrum:
The Infrared Spectrum is divided into 6 Zones:

- **Zone 1: 3700-3200 cm\(^{-1}\)**
  - Alcohol O-H
  - Amine or Amide N-H
  - Terminal Alkyne sp \(\text{C-H (C} = \text{C-H)}\)

- **Zone 2: 3200-2700 cm\(^{-1}\)**
  - Aryl or vinyl sp\(^2\)C-H (\(>3000 \text{ cm}^{-1}\))
  - Alkyl sp\(^3\)C-H (\(<3000 \text{ cm}^{-1}\))
  - Aldehyde sp\(^2\)C-H
  - ALSO: Carboxylic Acid O-H
• **Zone 3**: 2300–2100 cm\(^{-1}\)
  - Alkyne \(\text{C}≡\text{C}\)
  - Nitrile \(\text{C}\equiv\text{N}\)
• **Zone 4**: 1850–1650 cm\(^{-1}\)
  - Carbonyl (\(\text{C}=\text{O}\)) functional groups
• **Zone 5**: 1680–1450 cm\(^{-1}\)
  - Alkene \(\text{C}=\text{C}\)
  - Aromatic ring pseudo double bonds
• **Zone 6**: “the Fingerprint Region” ~ 1500–600 cm\(^{-1}\)
  - Alcohol, Ester, Carboxylic Acid, Ether \(\text{C}-\text{O}\) (1300–1050 cm\(^{-1}\))
  - Amine, Amide \(\text{C}-\text{N}\)
  - Aromatic substitution patterns (680–860 cm\(^{-1}\))

Alkanes do not have any functional group but they do contain \(\text{sp}^3\text{C}-\text{H}\) (3000–2800 cm\(^{-1}\))

Each functional group in the infrared region has distinct characteristics

- **Alcohol and Amine**
  - Hydrogen-bonding capable - broad peaks - Zone 1 (3500–3200 cm\(^{-1}\))
- **Alcohol**: “U” shaped Zone 1
• Amine: 1° “W” shaped Zone 1

• Amine: 2° “V” shaped Zone 1

• Amine: 3° (no visible peak in Zone 1)

(Amides will also have “W” and “V” peaks for NH₂ and NH, as necessary.)
• Ether
  - C-O in Zone 6 (1250-1050 cm\(^{-1}\))

- Alkyl Halide
  - C-X in Zone 6
    - C-Cl 550-850 cm\(^{-1}\)
    - C-Br 500-650 cm\(^{-1}\)
- **Alkene**
  - $\text{C}=$ in Zone 5 (1680-1620 cm\(^{-1}\))
  - $\text{Sp}^2\text{C-H}$ in Zone 2 (unless tetrasubstituted)

- **Alkyne**
  - $\text{C}=$ in Zone 3 (visible in asymmetric alkynes) (2300-2100 cm\(^{-1}\))
  - $\text{Sp C-H}$ in Zone 2 (terminal alkyne only; 3300 cm\(^{-1}\))

- **Nitrile**
  - $\text{C}=$ in Zone 3 (more intense than $\text{C}=$)
- Carbonyl Groups
  - C=O is typically the most intense (largest, strongest) peak on an IR spectrum
  - Value shifts 30-50 cm\(^{-1}\) LOWER when next to aromatic ring
- Ketone
  - Carbonyl only (1725-1705 cm\(^{-1}\))

- Aldehyde
  - Two major types of bonds:
    - C=O in Zone 3 (1695-1725 cm\(^{-1}\))
    - Sp\(^2\)C-H "fangs" in Zone 2 (2830-2810 and 2740-2720 cm\(^{-1}\))
- **Carboxylic Acid**
  - Two major types of bonds:
    - Extremely broad OH (3500-2500 cm\(^{-1}\))
    - C=O in Zone 3 (1680-1710 cm\(^{-1}\))
    - C-O in Zone 6 (1050-1250 cm\(^{-1}\))

- **Ester**
  - C=O in Zone 3 (1730-1750 cm\(^{-1}\))
  - C-O in Zone 6 (1150-1300 cm\(^{-1}\))
- Acid Anhydride
  - Two C=O in Zone 3 (1710-1770; 1780-1850 cm\(^{-1}\))
  - C-O in Zone 6 (1150-1250 cm\(^{-1}\))

- Amides
  - C=O in Zone 3 (1640-1680 cm\(^{-1}\))
  - NH peak(s) in Zone 1 ("V" or "W" shaped) (3200-3500 cm\(^{-1}\))
• Acid Halides
  o C=O in Zone 3 (1790-1810 cm⁻¹)
  o C-X in Zone 6

• Aromatic Rings
  o Pseudo double bond peaks - one must appear ~1600 cm⁻¹ and 1-2 more
    ~1500-1450 cm⁻¹ (Zone 5)
  o Sp²C-H peak (Zone 2, 3100-3000 cm⁻¹)
  o Substitution patterns for monosubstituted and disubstituted aromatic
    rings (Zone 6)

• Mono Substituted (Zone 6: 680-710, 730-770 cm⁻¹)
- Ortho Substituted (Zone 6: 735-770 cm\(^{-1}\))

- Meta Substituted (Zone 6: 810-750, 725-680 cm\(^{-1}\))

- Para Substituted (Zone 6: 860-800 cm\(^{-1}\))
- Nitro (-NO₂) - Spans Zones 5 and 6
  - N=O/N-O (1300-1390 and 1500-1600 cm⁻¹)

So - How do you SOLVE an IR?
You need to break the IR up into the basic Zones, moving from left to right and only delving into the Fingerprint Zone if need be (i.e. you think you have a functional group that applies).

Example 1:

Zone 1: (3700-3200 cm⁻¹)
  - Alcohol OH present ("U") (note the C-O in Zone 6)
  - Amine or Amide absent - no "V" or "W"
  - No sharp stretch at 3300 cm⁻¹

Zone 2: (3200-2700 cm⁻¹)
  - No Aryl/vinyl sp²C-H (>3000 cm⁻¹)
  - Sp³C-H present (<3000 cm⁻¹)
  - No aldehyde "fangs" between 2800-2700
No broad OH of carboxylic acid (no C=O in Zone 4)

Zone 3: (2300-2100 cm$^{-1}$)
No $\equiv$C or $\equiv$N

Zone 4: (1850-1650 cm$^{-1}$)
No C=O peak (must be longest, strongest peak)

Zone 5: (1680-1450 cm$^{-1}$)
No peak at 1600, etc - no aromatic ring
No peak 1680-1620 - no alkene

Functional group? Alcohol (2-propanol)

Example 2:

Zone 1: (3700-3200 cm$^{-1}$)
Alcohol OH absent ("U")
Amine or Amide absent - no "V" or "W"
No spC-H - sharp stretch at 3300 cm$^{-1}$

Zone 2: (3200-2700 cm$^{-1}$)
No Aryl/vinyl sp$^2$C-H (>3000 cm$^{-1}$)
Sp$^3$C-H present (<3000 cm$^{-1}$)
No aldehyde "fangs" between 2800-2700
No broad OH of carboxylic acid (no C=O in Zone 4)

Zone 3: (2300-2100 cm$^{-1}$)
No $\equiv$C or $\equiv$N

Zone 4: (1850-1650 cm$^{-1}$)
C=O present (note the C-O in Zone 6)

Zone 5: (1680-1450 cm$^{-1}$)
No peak at 1600, etc - no aromatic ring
No peak 1680-1620 - no alkene

Functional group? Ester (Ethyl Acetate)
Example 3:

Zone 1: (3700-3200 cm\(^{-1}\))
- Alcohol OH absent ("U")
- Amine or Amide absent - no "V" or "W"
- No spC-H - sharp stretch at 3300 cm\(^{-1}\)

Zone 2: (3200-2700 cm\(^{-1}\))
- Aryl/vinyl sp\(^2\)C-H present (>3000 cm\(^{-1}\))
- Sp\(^3\)C-H present (<3000 cm\(^{-1}\))
- No aldehyde "fangs" between 2800-2700
- No broad OH of carboxylic acid (no C=O in Zone 4)

Zone 3: (2300-2100 cm\(^{-1}\))
- No C≡C or C≡N

Zone 4: (1850-1650 cm\(^{-1}\))
- No C=O present

Zone 5: (1680-1450 cm\(^{-1}\))
- Peak at 1600, etc - Aromatic Ring
- No peak 1680-1620 - no alkene

Zone 6: (850-680 cm\(^{-1}\))
- Peaks ~690, 750 - monosubstituted aromatic ring

Functional group? Monosubstituted aromatic ring (Ethyl Benzene)