

Ch 12 Structure Determination (Mass Spectroscopy and Infrared)

Part 2: Infrared Spectroscopy (IR)

The Electromagnetic Spectrum

- The [electromagnetic spectrum](#) can be divided into regions.

In order of increasing energy/frequency and decreasing wavelength, they are:

Low E

High E

radio, microwave, infrared (IR), visible light, ultraviolet (UV), x-rays, gamma rays

- Visible light (380 - 780 nm) is only a small portion of the overall spectrum, and is located between infrared ($E < \text{red}$) and ultraviolet ($E > \text{violet}$).
- Electromagnetic radiation behaves partially like a particle (a photon) that can be absorbed or released, and partially like a wave that has a sine-wave cycle with a crest and a trough.
- A photon has a **wavelength** (λ or lambda), measured in m (or μm for IR, where $10^6 \mu\text{m} = 1 \text{ m}$), as well as a **frequency** (ν or nu) in s^{-1} or cm^{-1} (**wavenumbers**).
- The velocity of a photon is the speed of light, $c = 3 \times 10^8 \text{ m/s} = \nu\lambda$.
- The energy of a photon is found by $\epsilon = h\nu = hc/\lambda$, where h is Planck's constant, and $h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$.

On a molar basis, this becomes $E = N_A(hc/\lambda)$, where N_A is Avogadro's number.

- Energy absorbed or released is quantized, that is it happens only at specific ΔE 's.
- Molecules absorb and release energy as they change energy states. The molecules have four different types of energies that can change: translational (kinetic energy), electronic, vibrational, and rotational.
- **IR** radiation corresponds to changes in molecular (or functional group) **vibration**.
- The IR spectrum extends from 2.5 to 25 μm , or 4000 – 400 cm^{-1} .
- Typically, the spectrum is plotted as **Transmission** (% T) on the y-axis vs. **wavenumbers** (cm^{-1}) on the x-axis.
- Fig 12.12 in McMurry shows that where a molecule absorbs IR radiation, the % T will decrease as less IR radiation is transmitted through the sample. More absorption is less transmission.

Molecular Vibrations

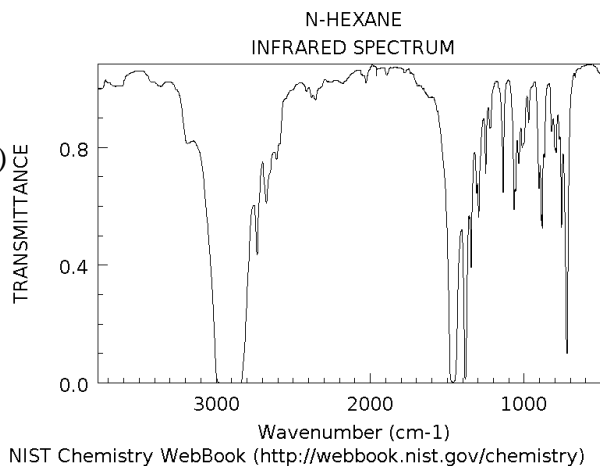
- Chemical bonds are like springs, and they vibrate at characteristic frequencies.
- Vibrations are either stretches (along with accompanying compressions) or bends.
- Two bonds (with 3 atoms: X-Y-Z) can vibrate simultaneously (in phase).
In this case, both stretching and bending can be either symmetric (like mirror images) or anti-symmetric (one bond compresses while the other expands).
- Bending can additionally be in-plane (flat/planar) or out-of-plane (not flat).
For instance, in-plane symmetric bending is called scissoring, in-plane anti-symmetric bending is called wagging, out-of-plane symmetrical bending is called rocking, and out-of-plane anti-symmetrical bending is called twisting.

IR Interpretation

- Functional groups have the same **characteristic IR absorptions**, practically regardless of the remainder of the molecule.
- The IR spectrum can be divided into four sections (see Fig12.15).
- 4000 to 2500 cm^{-1} (left side of spectrum) are due to bonds (of C, N, and O) to H atoms.
- 2500 to 2000 cm^{-1} are due to triple bonds ($\text{C}\equiv\text{C}$ or $\text{C}\equiv\text{N}$).
- 2000 to 1500 cm^{-1} are due to double bonds ($\text{C}=\text{C}$, $\text{C}=\text{N}$, or $\text{C}=\text{O}$).
- Less than 1500 (right side of spectrum) is called the fingerprint region, where all molecules have different absorptions. These absorptions are often complex and difficult to diagnose.

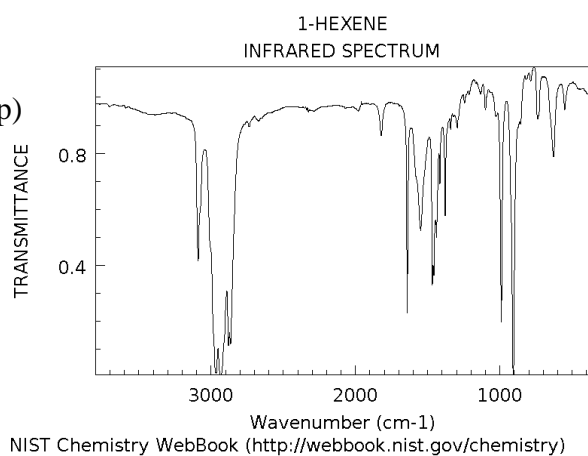
Characteristic IR Absorptions of Hydrocarbons

- **Alkanes** display the following absorptions:
 - C-H stretches at **2850 - 2960** (strong/medium)
 - C-H bend at **1500** (medium)
 - CH₂ rock at **750** (weak)
- These vibrations tend to be apparent in the IR for most organic substances.
- The C-C vibration at 800 - 1300 (section 12.8) is weak and difficult to diagnose. **Ignore** this vibration completely.

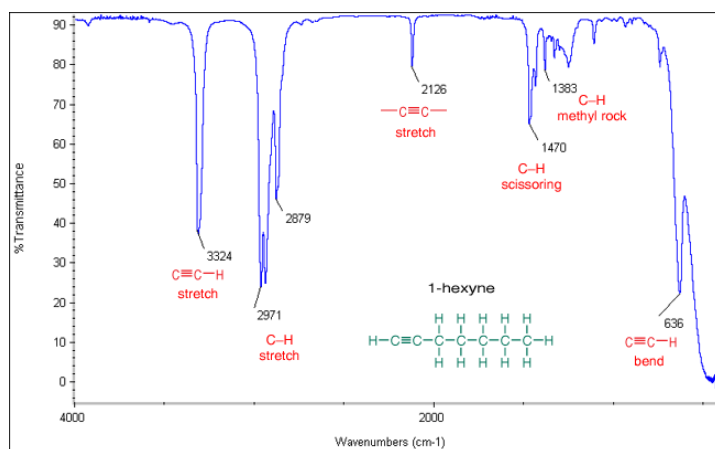


- See also Figure 12.20a (12.14a in 8e) and Problem 12.32 in McMurry 9e.

- **Alkenes** display the following absorptions:
 - =C-H bond at **3020 - 3100** (medium and sharp)
 - C=C at **1640 - 1680** (medium - weak).
- **Mono-substituted alkenes** (RCH=CH₂) have two strong absorptions at **910** and **990**.
- **2,2-disubstituted alkenes** (R₂C=CH₂) have a strong absorption at **890**.
- See also Figure 12.20b (12.14b in 8e) and Problem 12.32.

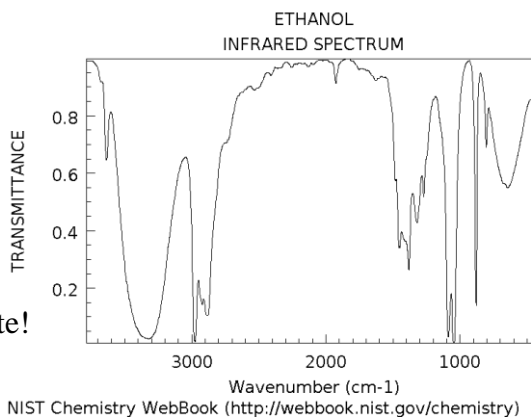


- **Alkynes** display their C≡C bond at **2100 - 2260** (medium).
- **Terminal Alkynes** (RC≡CH) show their ≡C-H bond at **3300** (strong).
- See also Figures 12.20c and 12.17 (12.14c and 12.28 in 8e), as well as Problem 12.41.

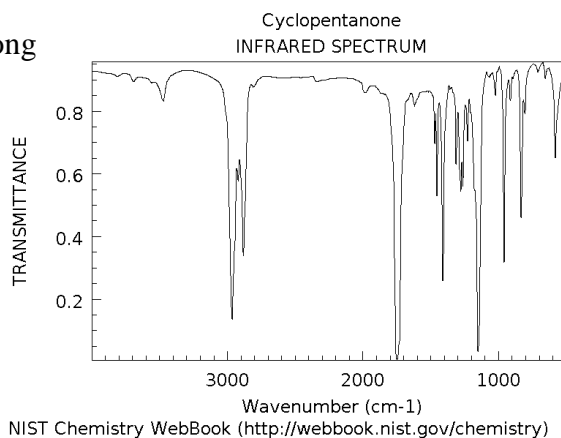


- Alkyl Halides have absorptions below 800 cm^{-1} . However, these are **not seen** if the sample is analyzed with **NaCl salt plates**, which become **opaque to IR below 800 cm^{-1}** .

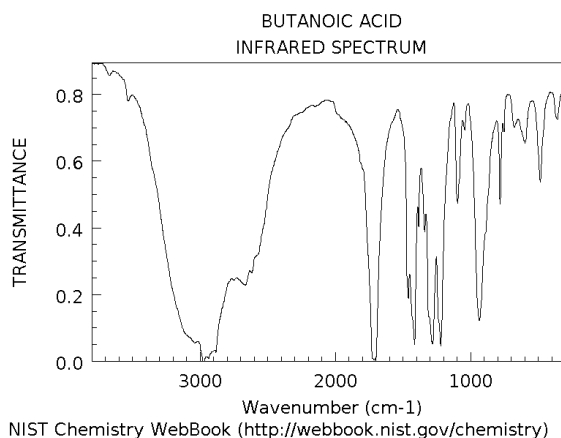
- **Alcohols** (ROH) show their O-H bond at **3200 – 3500** (strong and very broad).
- One cautionary note here is that water displays this same vibration as well, and is a common contaminant in organic samples.
- One more cautionary note about water... Never ever put an aqueous sample on a salt plate! (What happens to NaCl in water?)
- Alcohols also show the C-O bond at **1050 – 1150** (strong).
- Both absorptions are visible in Figure 12.18 (12.12 in 8e). See also Worked Example 12.5a and Figure 17.11.



- **Carbonyl** (C=O) compounds have a very strong prominent absorption at **1670 – 1780**.
- The exact position depends on the nature of the compound - that is whether the compound is an aldehyde, ketone, ester, carboxylic acid, etc.
- See Worked Examples 12.5b and 12.6, as well as Figure 19.14 and Table 19.2.



- **Carboxylic Acids** (RCOOH) have an OH attached to the carbonyl C.
- The acid's O-H bond has a very strong and very broad absorption at **3300 – 2500**.
- See Figure 20.5.



IR Absorptions for Functional Groups

Alkane or Alkyl Group (sp^3)	C-H	3000 – 2850	broad
	C-H	1500	
	H-C-H	750	
Alkene (sp^2 C, same as vinylic)	=C-H	3100 – 3020	
	C=C	1680 – 1630	
	RC-H=CH ₂	910 and 990	
	R ₂ C=CH ₂	890	
	R ₂ C=CHR	840 – 790	
	trans (C-H)	980 – 960	
	cis (C-H)	730 – 665	
Alkyne (sp C)	\equiv C-H	3300	sharp
	C \equiv C	2300 – 2100	small / sharp
Alcohol	O-H	3650 – 3200	broad
Alcohol or Ether	C-O	1200 – 1050	
Aromatic (sp^2 ring w/ alternating dbl bonds)	C-H	3030	
	Ring	2000 – 1660	small bumps
	Ring	1600 – 1450	usually two
Amine	N-H	3500 – 3300	sharp
	C-N	1230 – 1030	
Carbonyl	C=O	1800 – 1650	strong
Aldehyde	O=C-H	2850 – 2700	
Carboxylic Acid (O-H)	O=C-O-H	3300 – 2500	very broad
Nitrile	C \equiv N	2260 – 2210	