

CHEM 8L, Experiment 4 – Infrared (IR) Spectroscopy

Experiment 4 – Infrared Spectroscopy

- Bond vibration (stretch & bend) frequency
- Relationship of vibrational frequency to absorbance of IR
- Functional group identification
- Predicting and interpreting IR spectra of a given structure

Wave nature of energy...

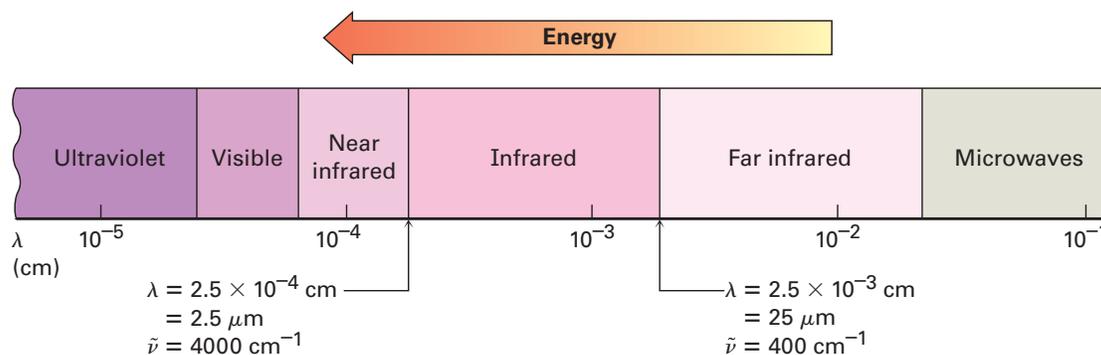


Figure 12.13 The infrared and adjacent regions of the electromagnetic spectrum.

$$E = h\nu$$

E - Energy of radiation,

h - Planck's constant, $6.62607015 \times 10^{-34}$ Js

ν - frequency (cycles per second, s^{-1})

$$\nu\lambda = c$$

ν - frequency (cycles per second, s^{-1})

λ - wavelength (distance, m)

c - speed of light, 3×10^8 m / s

IR Spectroscopy identifies bonds within specific functional groups

Ex. Stretching vibration of alcohol O-H bond occurs $\sim 10^{14}$ cycles / sec, $\nu = 10^{14} s^{-1}$

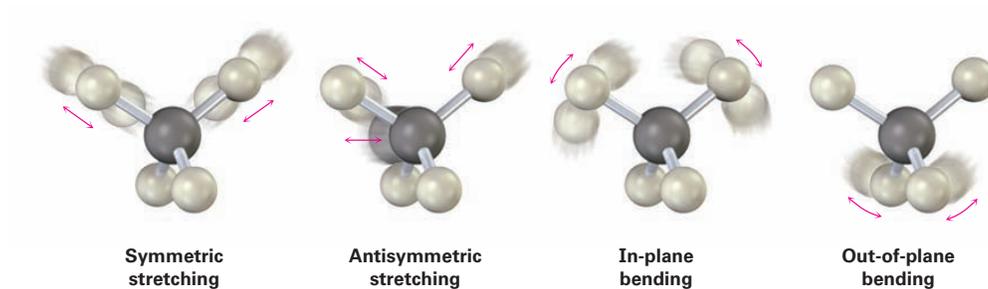
Wavelength

Wavenumber

Wavenumber – unit of choice for IR spectroscopy

$$\bar{\nu} = \frac{1}{\lambda}$$

Types of Bond Vibrations



J. McMurry, Organic Chemistry, 8th Edition. Cengage: Belmont. 2008.

- Frequency of vibration depends on **bond length**
- Longer bonds take longer to expand/contract = slower frequency, $\downarrow \nu$

Vibrational Frequency and Wavenumber

Bond Stretching

Fully expanded

Fully contracted

Stretching wave represents oscillation between expanded & contracted bond

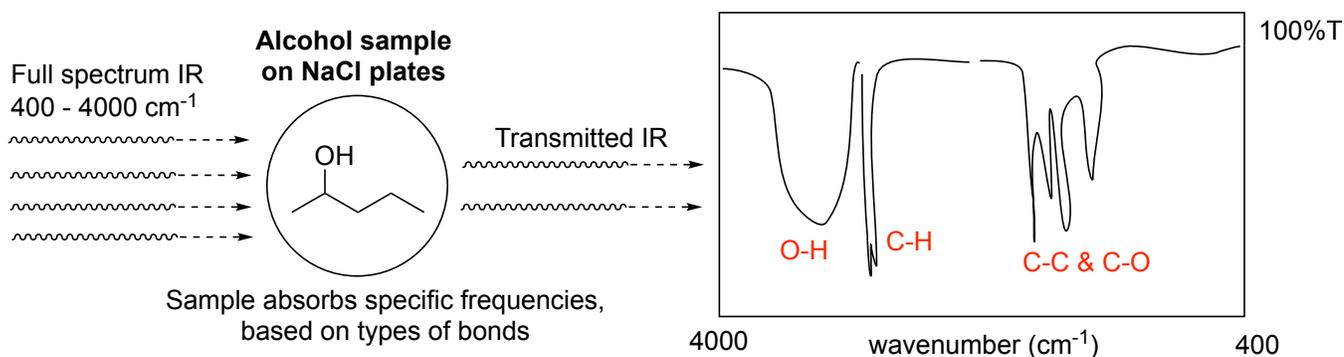
Wavelength of bond stretching wave is converted into wavenumber

What role does the IR spectrometer play?

Constructive Interference

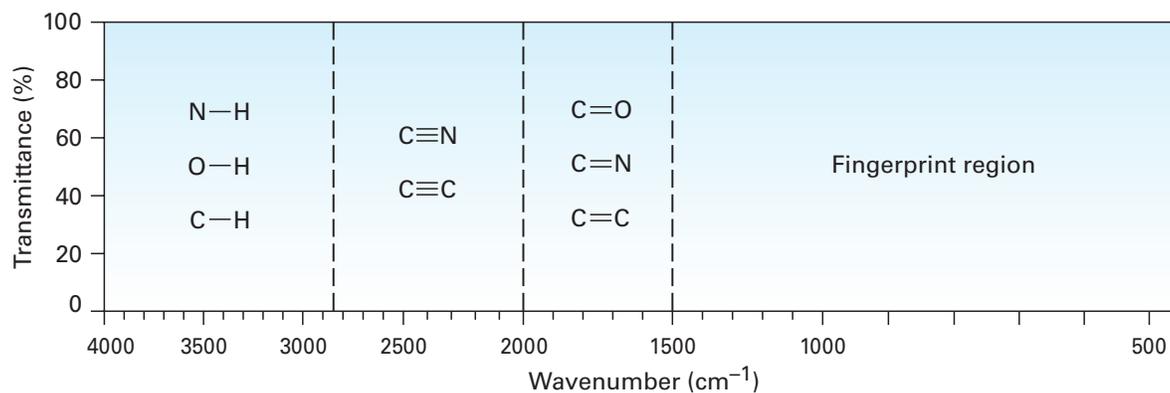
Instrument detects transmitted wavenumbers (energy not absorbed by compound) & plots on spectrum

IR vibrations of a bond + IR radiation from the instrument → Amplified wave



**** IR Table of Values gives expected ranges each bond vibration within functional groups *****

General areas of interest in IR spectrum...



* C-H bending & C-X stretching occurs less than 1000 cm⁻¹

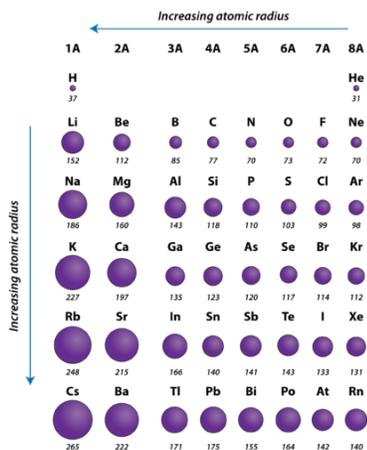
* C-C, C-N, and C-O bonds stretch between 1500 – 1000 cm⁻¹ (ignore)

Longer Bond = Slower (↓) Stretching Frequency

	O-H	C-H	C=O
Bond Length (pm)	100	110	120
Stretching Frequency (cm ⁻¹)	3300	2900	1700

Factors Effecting Bond Length – refer to IR Table of Values

- Atomic Radius

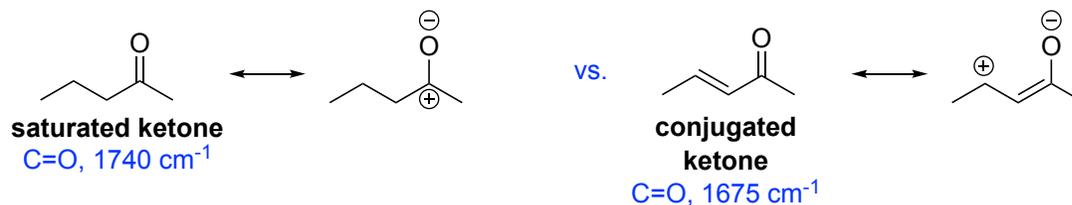


- Hybridization / Type of bond

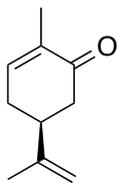
Ex. C-H bonds alkane vs. alkene

Ex. C-C in alkene vs. alkyne

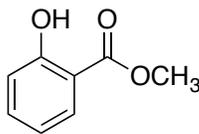
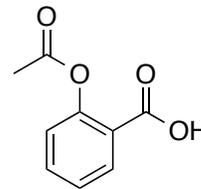
- Conjugation / Resonance



Experiment 4 Preparation – Predicting IR Spectra



Carvone

Methyl Salicylate
(Wintergreen Oil)Acetylsalicylic Acid
(Aspirin)

Make three IR tables – one for each compound above.

1. Identify all functional groups
2. Use the IR table of values to find the corresponding bond(s) and stretches / bends.

Table x. IR Analysis of Carvone

Functional Group	Bond Assignment (C=O, N-H, etc.) from IR Table	Expected Wavenumber from IR Table	Observed Wavenumber

Table 1. Characteristic IR Absorption Peaks of Functional Groupsⁱ

Functional Group & Bond Vibration	Position (cm ⁻¹)	Intensity*	Notes
Alkanes			
C-H stretch	2990 – 2850	m to s	
Alkenes			
=C-H stretch	3100 – 3000	m	
C=C stretch	1680 – 1620 (sat.) 1650 – 1600 (conj.)	w to m	
=C-H bend	995 – 685	s	See Table 2 for detail
Alkynes			
≡C-H stretch	3310 – 3200	s	
C≡C stretch	2250 – 2100	m to w	
Aromatic Compounds			
C-H stretch	3100 – 3000	m to w	
C=C stretch	1625 – 1440	m to w	Hidden in fingerprint region
C-H bend	900 – 680	s	See Table 2 for detail
Alcohols**			
O-H stretch	3550 – 3200	br, s	Hydrogen bonded (typical)
Amines			
N-H stretch	3550 – 3250	br, m	Primary (two bands) Secondary (one band)
Nitriles			
C≡N stretch	2280 – 2200	s	
Aldehydes			
C-H stretch	2900 – 2800 & 2800 – 2700	s	H-C=O Fermi doublet
C=O stretch	1740 – 1720 (sat.) 1715 – 1680 (conj.)	s	
Ketones			
C=O stretch	1750 – 1705 (sat.) 1700 – 1665 (conj.)	s	
Esters**			
C=O stretch	1765 – 1735 (sat.) 1730 – 1715 (conj.)	s	
Carboxylic Acids**			
O-H stretch	3200 – 2500	br, m to w	
C=O stretch	1725 – 1700 (sat.) 1715 – 1680 (conj.)	s	
Amides			
N-H stretch	3500 – 3150	m	Primary (two bands) Secondary (one band)
C=O stretch	1700 – 1630	s	

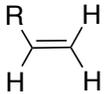
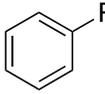
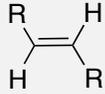
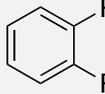
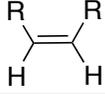
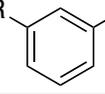
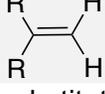
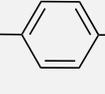
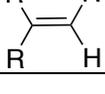
Table 1 cont'd

Vibration	Position (cm ⁻¹)	Intensity	Notes
Anhydrides**			
C=O stretch	1850 – 1800 & 1790 – 1740	s	
Acid Chlorides			
C=O stretch	1815 – 1770	s	
Nitro Compounds			
NO ₂ stretch	1570 – 1490 & 1390 – 1300	s	
Thiolsⁱⁱ			
R-S-H stretch	2550 – 2600		
Alkyl & Aryl Halides[†]			
C-F stretch	1000 – 1400		Hidden in fingerprint region
C-Cl stretch	< 600 – 840		
C-Br stretch	< 700		
C-I stretch	< 600		

* Abbreviations: s = strong; m = medium; w = weak; br = broad; sat. = saturated; conj. = conjugated

** Alcohols, Esters, Carboxylic Acids, and Anhydrides also absorb in the fingerprint region due to the C-O stretch (1300 – 1000, s).

Table 2. Out-of-Plane C-H Bending Vibrations in Alkenes and Aromatics

Alkene Structure	Position (cm ⁻¹)	Phenyl Structure	Position (cm ⁻¹)
Mono-substituted 	997 – 985 & 915 – 905	Mono-substituted 	770 – 730 & 720 – 680
Disubstituted, <i>trans</i> 	980 – 960	Disubstituted, <i>ortho</i> 	770 – 735
Disubstituted, <i>cis</i> 	730 – 665	Disubstituted, <i>meta</i> 	810 – 750 & 725 – 680
Disubstituted, <i>symm.</i> 	895 – 885	Disubstituted, <i>para</i> 	860 – 800
Trisubstituted 	840 – 790		

ⁱ Adapted from...Mohrig, J. R.; Hammond, C. N.; Schatz, P. F. "Infrared Spectroscopy" in *Techniques in Organic Chemistry*. Freeman: New York, **2006**.

ⁱⁱ Palleros, D. R. "Infrared Spectroscopy" in *Experimental Organic Chemistry*. Wiley: New York, **2000**. p. 688.