1. Theory and properties
    1.1. IR is part of electromagnetic spectrum between visible and microwave
    1.2. 4000 to 400 cm^{-1} (wave numbers) most interesting to organic chemists
    1.3. wave number ($\bar{\nu}$) is inverse wavelength = $1/\lambda$
        1.3.1. magnitude is proportional to energy
            1.3.1.1. $c = \lambda\nu$, $\nu = c/\lambda$
            1.3.1.2. $E = h\nu = hc/\lambda$
        1.3.2. 2000 cm^{-1} is 5 μm = 5000 nm, red light (visible) is 500 nm or 20,000 cm^{-1}
        1.3.3. $\nu = c/\lambda = (2.998 \times 10^{8}\ \text{m/s})/(5 \times 10^{-6}\ \text{m}) = 6 \times 10^{13}\ \text{s}^{-1}$ = 60 THz (terahertz)
        1.3.4. Spectra are report as% transmittance $T = 100\left(\frac{I}{I_O}\right)$ or absorbance $A = log\left(\frac{I_O}{I}\right)$
    1.4. finger print method
        1.4.1. no two compounds are identical (except enantiomers)
        1.4.2. Comparison with genuine material
    1.5. molecular transition – vibrations, no change in center of mass
    1.6. at room temperature: ground to excited vibration
        1.6.1. stretching – changing in bond lengths
        1.6.2. bending – change in bond angle
        1.6.3. bent molecules have 3n-6 vibrations (-three translations and three rotations)
            1.6.3.1. water has 3
            1.6.3.2. symmetric and asymmetric stretch, scissoring bending
        1.6.4. linear molecules have 3n-5 vibrations
            1.6.4.1. CO_2 has 4
            1.6.4.2. Symmetric and asymmetric stretching, 2 degenerate bending

1.6.5. Some vibrations are not observed

  1.6.5.1. Forbidden transitions (no dipole change)

  1.6.5.2. Overlap with other peaks

  1.6.5.3. Outside of 4000-400 cm^{-1}

1.6.6. fundamental vibrations do not change center of mass

1.6.7. IR active vibrations must change dipole moment

  1.6.7.1. frequency matches oscillating field of light

1.7. frequency depends on mass and bond strength

1.8. Hooke's Law: $F = -k(d - d_0)$

1.8.1. mass attached to immovable object by a spring

1.8.2. F = force between atoms, k = force constant, d = distance between atoms

1.8.3. Frequency of oscillation: $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$

  1.8.3.1. The frequency in wavenumbers for a diatomic: $\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{f}{(m_x m_y)/(m_x + m_y)}}$

  f= molecular force constant, epage 84

  1.8.3.2. higher mass: lower frequency,(not linear)

  1.8.3.3. higher bond strength(k) – higher frequency

1.9. bonds to same atom couple and do not have same frequency as isolated bonds

1.9.1. C=O, ketone 1700 cm^{-1}

1.9.2. CO_2, two bonds couple to each other in symmetrical stretch (1340 cm^{-1}) and unsymmetrical stretch (2350 cm^{-1})

1.9.3. Coupling of two fundamental modes: two new modes of higher and lower frequencies than if no coupling occurred

1.9.4. Coupling also occurs with overtones and coupled modes

1.9.5. C-O stretch (1030 cm^{-1} for CH_3OH) couples to C-C in ethanol (1053 cm^{-1})

1.9.6. Coupling is negligible if groups are separated by one or more carbons

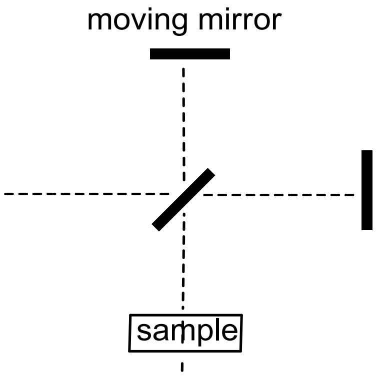
1.10. hydrogen bonding effect between Y-H and Z

1.10.1. lowers frequency Y-H peaks, broadens and increases intensity

1.10.2. lowers frequency of hydrogen bond acceptor, *i. e.* CO stretch, for CO- - -H

1.10.3. intra-versus intermolecular H-bonds detected by dilution

2. Design of Fourier Transform IR spectrometer



2.1. Light is split and rejoined by beam splitter.

2.2. Moving mirror makes light of specific frequency go in and out of phases

2.3. Constructive/destructive interference causes intensity of light to oscillate

2.4. Frequency of intensity oscillation depends on wavelength and mirror velocity

2.5. For constant velocity, intensity of each IR frequency (4000-400 cm^{-1}) has a unique oscillating frequency, computer calculates which frequency match each wavenumber

2.6. If a sample is in the beam, sample reduces the intensity at specific vibrations

2.7. Spectrum with no sample is subtracted to get sample spectrum. Why?

2.8. Raw data is superposition of sine waves

2.9. Fourier transform converts time domain to frequency domain spectrum

2.9.1. How do time dependent, oscillating, signals get converted to frequencies

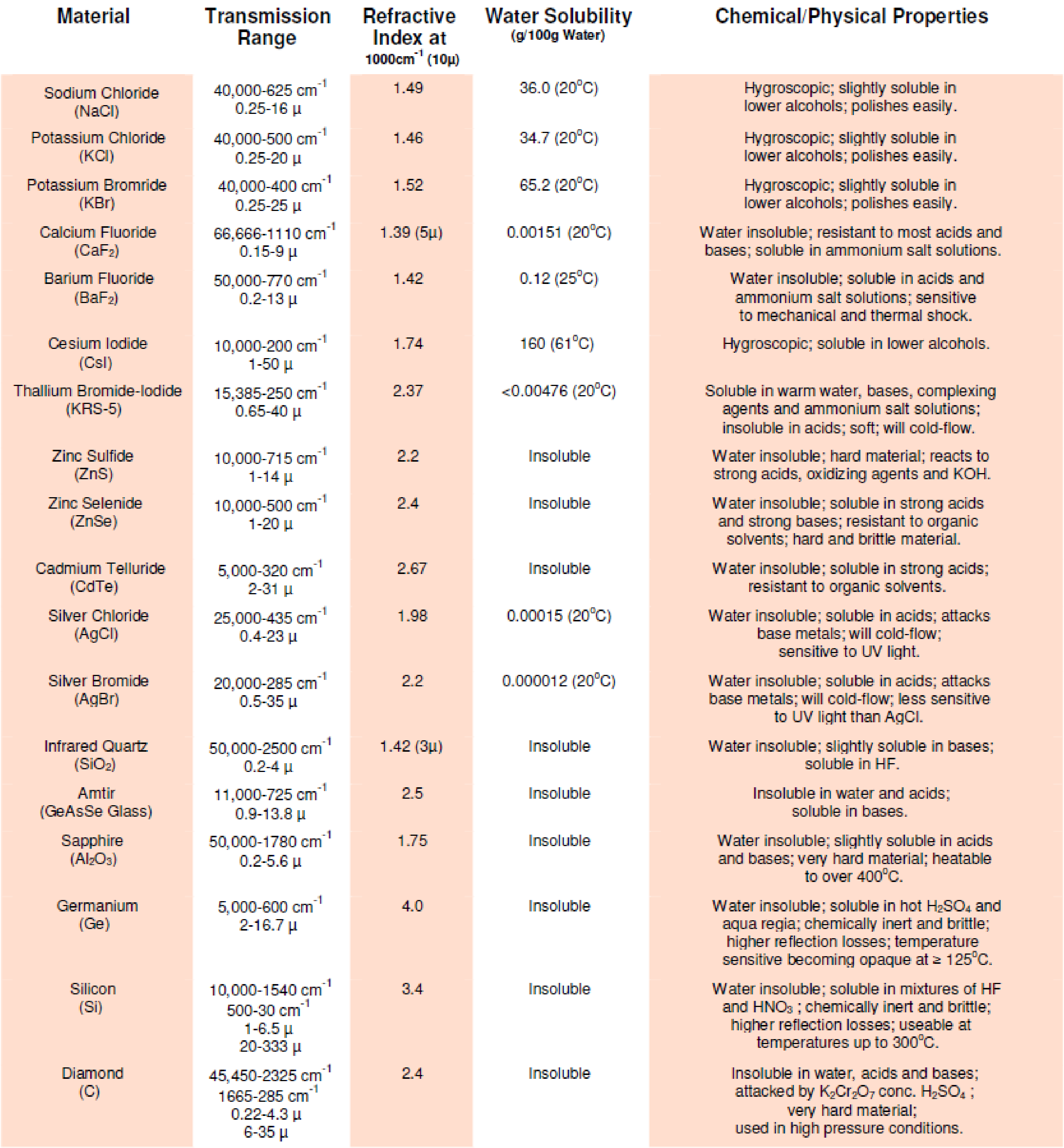
2.9.2. $I(\omega) = \int_0^\infty M_y(t)\cos(\omega t)dt$

2.9.3. let $M_y(t) = m\cos(\omega_1 t)$

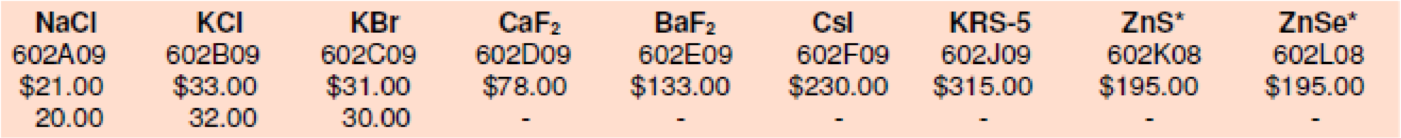
where m_1 = amplitude for ω_1 = IR frequency, then $I(\omega) = \int_0^\infty m_1\cos(\omega_1 t)m_2\cos(\omega_2 t)dt$

- 2.9.4. integrate the product of two cosωt functions to infinity and repeat for all frequencies
- 2.9.5. **Don’t move the mirrors**
  - 2.9.5.1. For $\omega_1 = \omega_2$, integral will be non zero only if two cosine functions have the same frequencies
  - 2.9.5.2. For $\omega_1 \neq \omega_2$, integrals are zero because the functions go in and out of phase
- **2.9.6. move one mirror**
- 2.9.7. whenever $\omega_1 = \omega_2$, two cosine functions go in and out of phase with time
- 2.9.8. each IR frequency creates an amplitude modulation at a unique frequency:0-20,000 hz depending on mirror speed
- 2.9.9. create a new spectrum is an interferogram – each point corresponds to an IR frequency
- 2.9.10. difference between reference (no sample) and sample interferograms
- 2.9.11. speed of mirror is important, calibrate with HeNe laser
- 2.9.12. advantage – point by point versus FT

3. Sample preparation
   - 3.1. Gas cells
   - 3.2. salt plates- thin liquid layer
   - 3.3. sealed liquid cell (0.1- 1 mm path) – dilute solid or liquid in solvent – reproducible
   - 3.4. pellets- liquid and solid – not reproducible
   - 3.5. background and scattering
   - 3.6. window properties



Material	Transmission Range	Refractive Index at 1000cm^{-1} (10µ)	Water Solubility (g/100g Water)	Chemical/Physical Properties
Sodium Chloride (NaCl)	40,000-625 cm^{-1} 0.25-16 µ	1.49	36.0 (20°C)	Hygroscopic; slightly soluble in lower alcohols; polishes easily.
Potassium Chloride (KCl)	40,000-500 cm^{-1} 0.25-20 µ	1.46	34.7 (20°C)	Hygroscopic; slightly soluble in lower alcohols; polishes easily.
Potassium Bromride (KBr)	40,000-400 cm^{-1} 0.25-25 µ	1.52	65.2 (20°C)	Hygroscopic; slightly soluble in lower alcohols; polishes easily.
Calcium Fluoride (CaF_2)	66,666-1110 cm^{-1} 0.15-9 µ	1.39 (5µ)	0.00151 (20°C)	Water insoluble; resistant to most acids and bases; soluble in ammonium salt solutions.
Barium Fluoride (BaF_2)	50,000-770 cm^{-1} 0.2-13 µ	1.42	0.12 (25°C)	Water insoluble; soluble in acids and ammonium salt solutions; sensitive to mechanical and thermal shock.
Cesium Iodide (CsI)	10,000-200 cm^{-1} 1-50 µ	1.74	160 (61°C)	Hygroscopic; soluble in lower alcohols.
Thallium Bromide-Iodide (KRS-5)	15,385-250 cm^{-1} 0.65-40 µ	2.37	<0.00476 (20°C)	Soluble in warm water, bases, complexing agents and ammonium salt solutions; insoluble in acids; soft; will cold-flow.
Zinc Sulfide (ZnS)	10,000-715 cm^{-1} 1-14 µ	2.2	Insoluble	Water insoluble; hard material; reacts to strong acids, oxidizing agents and KOH.
Zinc Selenide (ZnSe)	10,000-500 cm^{-1} 1-20 µ	2.4	Insoluble	Water insoluble; soluble in strong acids and strong bases; resistant to organic solvents; hard and brittle material.
Cadmium Telluride (CdTe)	5,000-320 cm^{-1} 2-31 µ	2.67	Insoluble	Water insoluble; soluble in strong acids; resistant to organic solvents.
Silver Chloride (AgCl)	25,000-435 cm^{-1} 0.4-23 µ	1.98	0.00015 (20°C)	Water insoluble; soluble in acids; attacks base metals; will cold-flow; sensitive to UV light.
Silver Bromide (AgBr)	20,000-285 cm^{-1} 0.5-35 µ	2.2	0.000012 (20°C)	Water insoluble; soluble in acids; attacks base metals; will cold-flow; less sensitive to UV light than AgCl.
Infrared Quartz (SiO_2)	50,000-2500 cm^{-1} 0.2-4 µ	1.42 (3µ)	Insoluble	Water insoluble; slightly soluble in bases; soluble in HF.
Amtir (GeAsSe Glass)	11,000-725 cm^{-1} 0.9-13.8 µ	2.5	Insoluble	Insoluble in water and acids; soluble in bases.
Sapphire (Al_2O_3)	50,000-1780 cm^{-1} 0.2-5.6 µ	1.75	Insoluble	Water insoluble; slightly soluble in acids and bases; very hard material; heatable to over 400°C.
Germanium (Ge)	5,000-600 cm^{-1} 2-16.7 µ	4.0	Insoluble	Water insoluble; soluble in hot H_2SO_4 and aqua regia; chemically inert and brittle; higher reflection losses; temperature sensitive becoming opaque at ≥ 125°C.
Silicon (Si)	10,000-1540 cm^{-1} 500-30 cm^{-1} 1-6.5 µ 20-333 µ	3.4	Insoluble	Water insoluble; soluble in mixtures of HF and HNO_3 ; chemically inert and brittle; higher reflection losses; useable at temperatures up to 300°C.
Diamond (C)	45,450-2325 cm^{-1} 1665-285 cm^{-1} 0.22-4.3 µ 6-35 µ	2.4	Insoluble	Insoluble in water, acids and bases; attacked by $K_2Cr_2O_7$ conc. H_2SO_4 ; very hard material; used in high pressure conditions.



NaCl	KCl	KBr	CaF_2	BaF_2	CsI	KRS-5	ZnS*	ZnSe*
602A09	602B09	602C09	602D09	602E09	602F09	602J09	602K08	602L08
\$21.00	\$33.00	\$31.00	\$78.00	\$133.00	\$230.00	\$315.00	\$195.00	\$195.00
20.00	32.00	30.00	-	-	-	-	-	-

3.7. Reflection spectroscopy – solid placed against light guide -

4. Peak Assignments – note mass and force constant (bond strength)

4.1. IR most useful for identification of functional groups (See Appendix B epage 131)

4.2. Peaks are not solely due to one functional group – interaction with rest of molecule

4.3. high frequency region dominated by specific functional groups

4.3.1. Characteristic frequency – depends on coupling to molecule and conditions

4.3.2. Some functional groups have large range – see amines on epage 133

4.3.3. search specific frequencies – identify functional groups

4.3.4. search functional group – confirm frequency

4.4. specific functional group region – 4000-1400 cm^{-1}

4.5. CH stretch – low mass of H

4.5.1. alkyl/sp^3: 2840-3000 cm^{-1}

4.5.2. alkene/sp^2: 3000-3100 cm^{-1}

4.5.3. alkyne/sp: 3267-3333 cm^{-1}

4.6. OH

4.6.1. 3584-3650 cm^{-1}, sharp and strong for free OH

4.6.2. 3200-3550 cm^{-1} very broad for hydrogen bonded OH

4.7. NH – where is it likely to be?

4.8. C=C increase mass and bond energy

4.8.1. Most are in 1640-1670 cm^{-1}

4.8.2. depends on substitution and strain

4.8.3. See Appendix C – epage 136 (125), Table C-1

4.8.4. Distinguish vinyl, cis, trans, vinylidine, trisubstituted and tetrasubstituted

4.8.5. Effect of ring Appendix C- epage 136 (125)

4.8.6. 1678^{-1}?

4.9. C=C–C=C, 1600 cm^{-1}, why?

4.10. C=C=C, 1900-2000 cm^{-1} why?

4.11. C≡C, 2100-2260 cm^{-1}, weak

  4.11.1. 2100-2140 cm^{-1} for monosubstituted

  4.11.2. 2190-2260 cm^{-1} for disubstituted

4.12. C=O, 1540 – 1870 cm^{-1} intense!

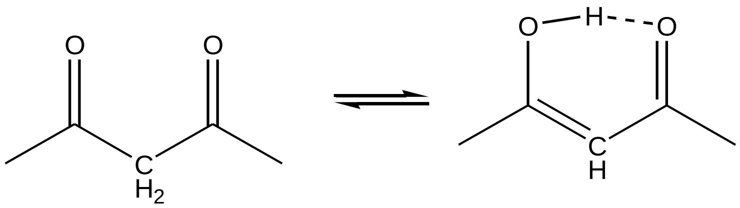
  4.12.1. 1715 cm^{-1}, aliphatic ketone, note it is higher than C=C!

  4.12.2. 1735-1750 cm^{-1}, ester OR

  4.12.3. 1650-1695 cm^{-1}, amide NR_2

  4.12.4. 1666-1685 cm^{-1}, conjugation with C=C or phenyl

  4.12.5. 1580-1640 cm^{-1}, broad and intense, β -dicarbonyls: CO conjugated with enol



more than hydrogen bond is responsible for low frequency?

  4.12.6. resonance, reduces double bond character → lower frequency

  4.12.7. electron withdrawing increases bond strength → higher frequency

4.13. C-O alcohols (1180 cm^{-1}) ethers (1150 cm^{-1}), esters (1240 cm^{-1}?)

4.14. C≡N, weak to medium

  4.14.1. 2240-2260 cm^{-1}

  4.14.2. 2222-2240 cm^{-1}, conjugated

4.15. <u>Lack of strong bands in 900-650 cm^{-1}, indicates no aromatic rings</u>

5. Alkanes

- 5.1. Stretching and bending of CH and CC bonds
- 5.2. CC stretching (1200-800 cm^{-1}) are useless, weak and overlap many other groups
- 5.3. CH bending at 1460 and 720 (scissoring and rocking, respectively)
- 5.4. Inspect dodecane - , Figure 2.8 (e94) 83
- 5.5. 3 CH stretching bands
- 5.6. CH frequency increasing in strained rings. Why?
- 5.7. Compare isooctane – mostly methyl – one methylene Figure 2.9 epage 95 (84)
- 5.8. Isopropyl - 1385-1380 cm^{-1}, 1370-1365 cm^{-1}
- 5.9. tert-butyl – 1395-1385 cm^{-1} and 1370 cm^{-1}

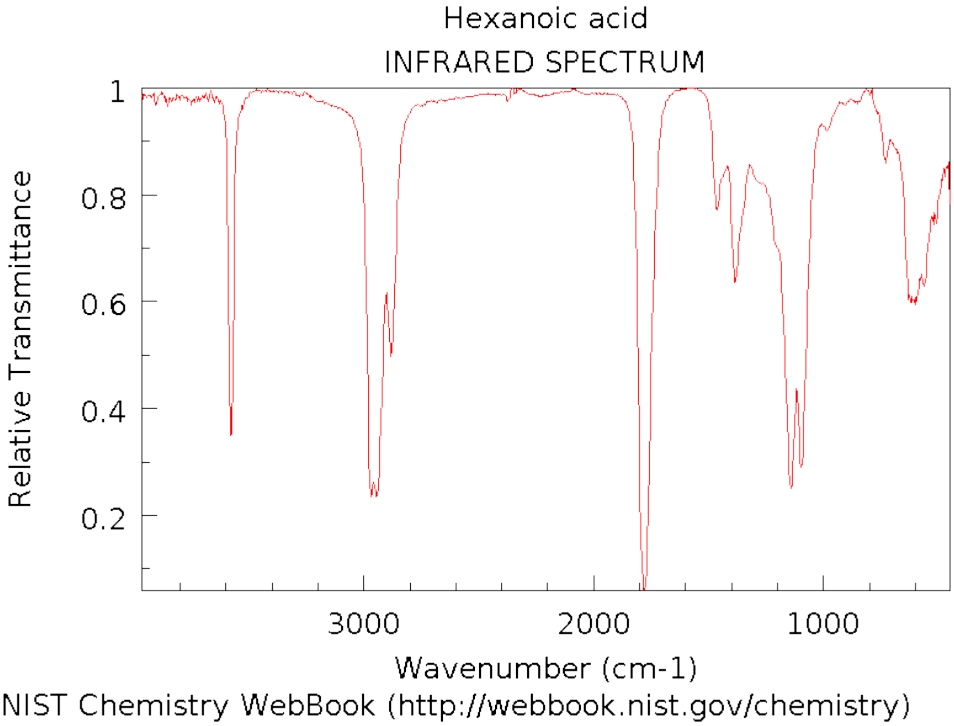
6. Alkenes
    - 6.1. 1-dodecene, Figure 2.10
        - 6.1.1. C=C 1648 cm^{-1}, weak?
        - 6.1.2. C-H stretch, 3082 cm^{-1}, weak
        - 6.1.3. C-H stretch, 2928 and 2859 cm^{-1}, methylene, strong
        - 6.1.4. Methyl CH stretch, 2962 cm^{-1}
        - 6.1.5. Out of plane CH bend, 1000 cm^{-1}, 915 cm^{-1}
        - 6.1.6. Alkene
        - 6.1.7. 1470? 730?
    - 6.2. Dienes, 2-methyl-1,3-butatdiene, isoprene, Figure 2.11
        - 6.2.1. Unsymmetrical diene- two C=C stretches, 1601 and 1640 cm^{-1}
        - 6.2.2. Unsymmetrical and symmetrical stretch, respectively – why so weak?
        - 6.2.3. Cumulated dienes 1900-2000 cm^{-1}, why so high?
        - 6.2.4. 992, 899 cm^{-1}, out of plane CH bending, why so intense compared to dodecene?

- 6.3. 1-heptyne, Figure 2.12
    - 6.3.1. 3314 cm^{-1}?
    - 6.3.2. 2126 cm^{-1}? No competition, weak?
    - 6.3.3. Disubstituted alkyne CC stretch often not detected
    - 6.3.4. 1463 cm^{-1}?
    - 6.3.5. 637 cm^{-1}? sp CH bend, 1247 cm^{-1} overtone

7. Aromatic, 1,2-dimethylbenzene, Figure 2.13
    - 7.1. 3017 cm^{-1}?
    - 7.2. 2970 cm^{-1}?
    - 7.3. 2940, 2878 cm^{-1}?
    - 7.4. 1605, 1497, 1466 aromatic CC stretch
    - 7.5. 1050 and 1019 cm^{-1}? In plane CH bend
    - 7.6. 741 cm^{-1} out of plane CH bend
8. Alcohols – benzyl alcohol, Figure 2.16m(e100)
    - 8.1. 3329 cm^{-1}?, why is it broad?
    - 8.2. 3067 and 3036 cm^{-1}?
    - 8.3. 2936 and 2882 cm^{-1}?
    - 8.4. 1501 and 1455 cm^{-1}, ring CC stretch
    - 8.5. 1208 cm^{-1}, in plane CH bend
    - 8.6. 1023 cm^{-1}, CCO stretch
    - 8.7. 745 cm^{-1}, out of plane CH bend
    - 8.8. 707 cm^{-1}, ring bend
    - 8.9. Phenol: 1378 cm^{-1}, OH bend; 1231 cm^{-1}, CCO stretch
9. Ketones

- 9.1. Acetone, Figure 2.20
  - 9.1.1. 1715 cm^{-1}, C=O
  - ~~9.1.2. 2500 cm^{-1}~~
  - 9.1.3. 1213 cm^{-1}, C-CO-C bend/stretch
  - 9.1.4. 1,3-diketones, form enol and hydrogen bond, C=O 1640-1580 cm^{-1}
- 9.2. Acetophenone, Figure 2.21
  - 9.2.1. 1686 cm^{-1}, shift in C=O
  - 9.2.2. 3352 cm^{-1}, C=O overtone
- 9.3. Octanal, Figure 2.22
- 9.4. 1728 cm^{-1}, C=O
- 9.5. 2715 cm^{-1}, aldehyde C-H, sp^2, often two peaks, Fermi resonance with CH bend overtone
- 9.6. 1381 cm^{-1}, aldehyde, CH bend

10. Carboxylic acids
  - 10.1. Hexanoic acid, Figure 2.23
  - 10.2. 3000 cm^{-1}, hydrogen bond dimer, broadens and lower



10.3. 946 cm^{-1}, OH out of plane bending,

10.4. 1717 cm^{-1}, C=O, monomer 1760 cm^{-1}

11. Ammonium benzoate, Figure 2.24

    11.1. 1550 and 1385 cm^{-1}, CO_2, stretches

    11.2. 1600 cm^{-1}, ring/CO_2 combination

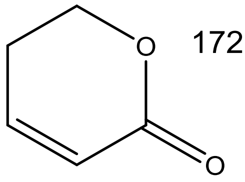
12. Esters – aliphatics – 1735-1750 cm^{-1}

    12.1. phenyl acetate, Figure 2.25 (e109)

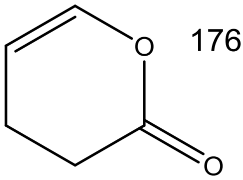
        12.1.1. 1223 and 1200 cm^{-1}, two coupled asymmetric C-O stretches [C-C(=O)-O ~1200 cm^{-1} and O-C-C ~ 1100 cm^{-1}): carbonyl and aryl

        12.1.2. 1771 cm^{-1}, C=O, higher than ketone, O electron withdrawing dominates

        12.1.3. Direct conjugation lowers frequency



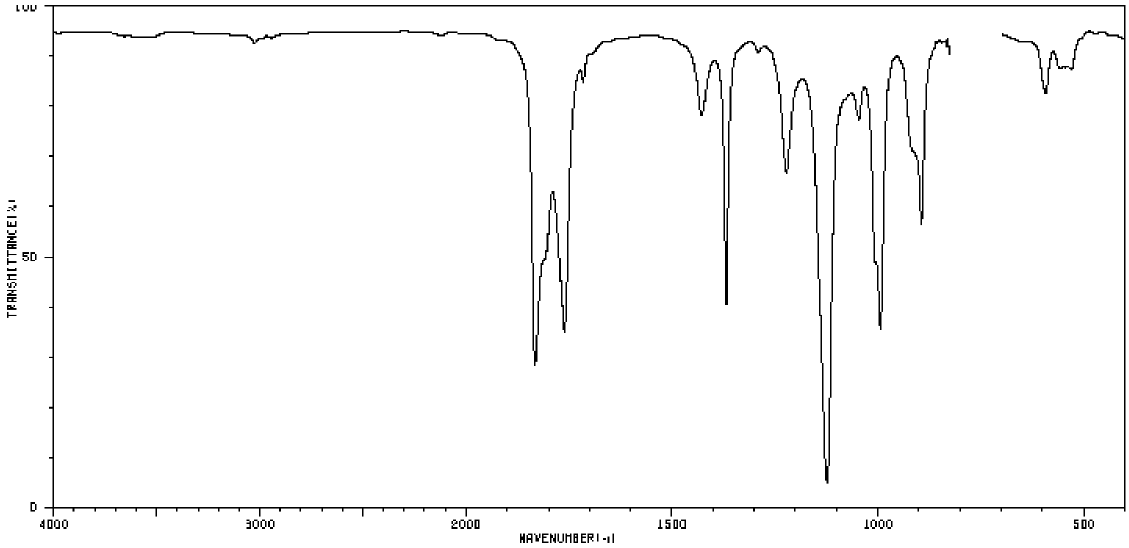
1720 cm^{-1}



1760 cm^{-1}

12.2. Acetic anhydride

12.2.1. Two C=CO stretches, 1832, 1761 cm^{-1}



12.2.2. 1124 cm^{-1}, C-O stretch

13. Amides, Acrylamide, Figure 2.28

13.1. 3352, 3198 cm^{-1}, Primary amide, 2 NH stretching bands

13.2. Secondary amides, only one NH, one NH band

13.3. 1679, Amide I, and CO stretch, lower than ketone

13.4. 1617 cm^{-1}, Amide II, N-H coupled bending

13.5. Hydrogen bonding lowers Amide I and II frequencies

13.6. 660 cm^{-1}, NH out of plane wagging

13.7. 1432 cm^{-1}, NH bending

14. Amines, 2-methyl-1,5-pentadiamine, Figure 2.29 (e112)

14.1. 3368, 3291 cm^{-1}?

   14.2. 1601 cm^{-1}, NH bend - scissoring

   14.3. 1069 cm^{-1}, CN stretch

15. Nitriles, (1-cyano-ethyl)benzene Figure 2.31

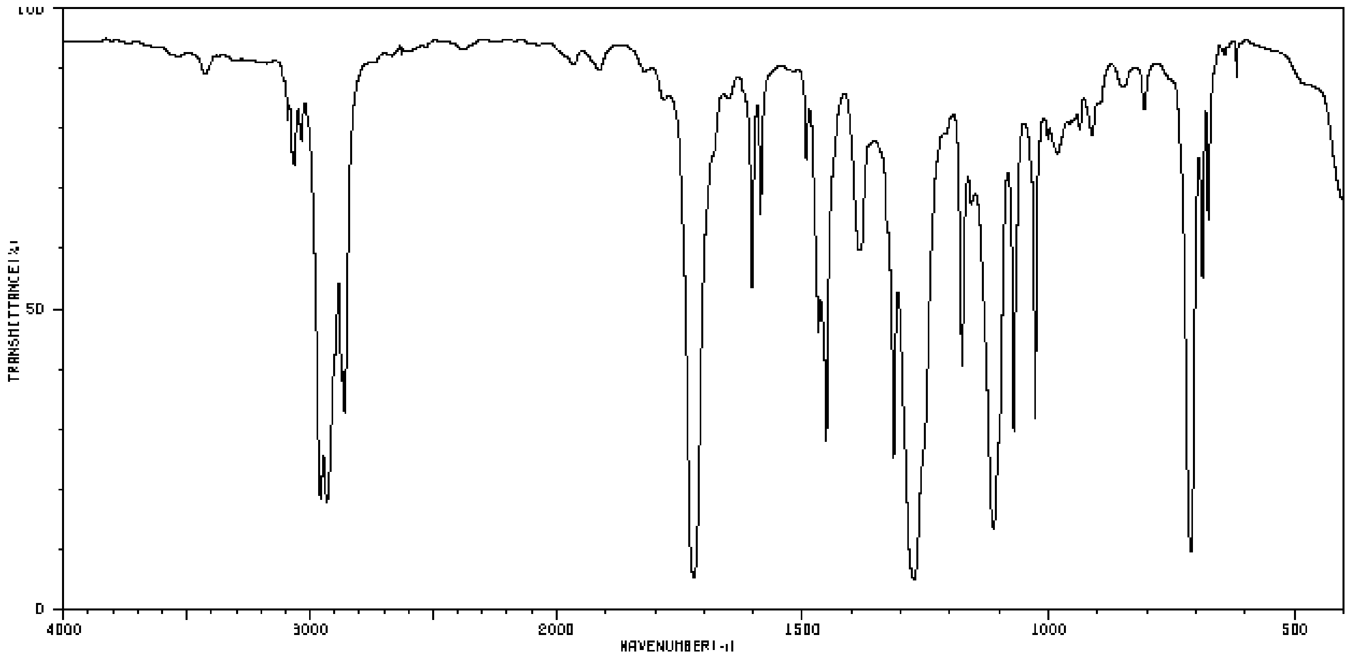
   15.1. 2249 cm^{-1}?

16. Thiols, Figure 2.33, 1,6-hexanedithiol

   16.1. 2558 cm^{-1}, SH, see 1.8.3.1 – reduced mass

   16.2. 730 cm^{-1}, C-S stretch

   16.3. Suggest a structure for the following spectrum: $C_{13}H_{18}O_2$.



http://www.aist.go.jp/RIODB/SDBS/cgi-bin/cre_index.cgi

17. Suggest a structure for the problem 2.7 Spectrum S (Chapter 2 spectra) for C_2H_3NS :

   http://bcs.wiley.com/he-bcs/Books?action=index&itemId=0471393622&bcsId=2174

   http://higheredbcs.wiley.com/legacy/college/silverstein/0471393622/add_probs/ch02.pdf

18. http://www.chem.ucalgary.ca/courses/351/WebContent/spectroscopy/index.html