

Chem 434 Instrumental Analysis Test 2

1. (10 points) What are the differences between $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in Energy (wavelength range), absorptivity (absorbance strength)? Which of these transitions undergo bathochromic or hypsochromic shifts?

$n \rightarrow \sigma^*$ - relatively high E (150-250 nm)
 - low to intermediate absorptivity ($100-3000 \text{ L cm}^{-1} \text{ mol}^{-1}$)
 - polar solvents shift to shorter λ so hypsochromic or blue shift

$n \rightarrow \pi^*$ - Low E (200-700nm)
 - low absorptivity (10-100)
 - polar solvents shift to shorter λ so hypsochromic or blue shift can be as large as 30 nm

$\pi \rightarrow \pi^*$ -Low E (200-700nm)
 -High absorptivity (1000-10000)
 - bathochromic or red shift usually small $\sim 5 \text{ nm}$

2. (10 points) The book gives the equation for quantum yield for fluorescence as:

$$\Phi = \frac{k_f}{k_f + k_i + k_{ec} + k_{ic} + k_{pd} + k_d}$$

What are all the different k's in this equation and what does the equation literally mean?

k_f = rate of fluorescence - singlet S_1 state relaxing to singlet ground state S_0 via release of a photon

k_i = rate of intersystem crossing - Singlet S_1 state converting to a excited triplet state

k_{ec} = rate of external conversion - Singlet S_1 state converting to S_0 ground state by passing energy in a non-radiative pathway to solvent molecules

k_{ic} = rate of internal conversion - Non-radiative conversion of a highly excited Singlet S_n state converting to vibrationally excited S_1 state or ground S_1 state converting to vibrationally excited S_0 state

k_{pd} = rate of predissociation - electron moves to a such a vibrationally excited, but electronically lower ground state that molecule falls apart

k_d = rate of dissociation energy of photon is enough to tear molecule apart directly

Quantum yield equation compares rate of fluorescence with total of all other possible decay rates. If fluorescence has the highest rate, then quantum yield will be large, and most of the photons hitting the molecule will be given off as fluorescence. If the fluorescence rate is low compared to the other mechanisms, then the quantum yield will be low, and few of the photons hitting the molecule will be released as fluorescence.

3. (10 points) Name and describe at least 3 different transducers used in an IR

machine.

Thermocouples - a pair of junctions between two different metals - both junctions kept in a vacuum, one junction a reference that is kept dark, the other is placed in the IR light beam. The junction between the metals creates a potential. As the junction in the IR beam gains or loses heat its potential shifts, and the difference between this potential and the reference potential is detected as a signal.

Bolometer - constructed from either strips of platinum and nickel or certain semiconductors. The material has a large change in resistance as a function of temperature. To monitor changes in temperature you monitor how much current this solid state device allows to pass in a circuit as its resistance changes.

Pyroelectric Transducers - single crystal of a pyroelectric material like DGGS acts like a heat sensitive capacitor, will bleed off charge quickly or slowly dependings on its tempaurate. Very fast response so ideal for FTIR

Photoconducting Transducer - A semiconducting material that will conduct electricity better when absorbs IR light. Also good for FTIR applications

4. (10 points) Describe how Raman Spectrosopy can give you IR information using visible light.

In Raman you are illuminating a sample with a near IR or visible light laser. Since this light is not at a wavelength near an absorbance band in the molecule, the light will not be absorbed. Instead some the light is scattered. The bulk of the scattered light will be at exactly the same wavelength and energy as the excitation light and will represent true elastic or Rayleigh scattering. However for a small fraction of the scattered light (~.001%) the energy of the photon will be increased or decreased by the energy of vibrations that occur in the molecule as during the light scattering event. This change in energy will be reflected in shifts of the wavelength of the scattered light. Thus by studying the changes in frequency of the scattered light you can detect energy absorption of vibrations that are usually associated with IR absorption.

5. (10 points) I have an compound that gives a proton NMR spectrum that has peaks at 4.0 4.1, 2.1 and 2.2 ppm on a 60 MHz NMR. In this compound there are actually only 2 different protons, one that should have a chemical shift of 3.95 and a second that located at 2.15 ppm but both peaks have been split into a doublets due to spin-spin coupling. Describe what will happen to this spectrum if you run this same material in a 600 mHz spectrometer.

Due to the way we use the chemical shift scale the center of the doublet will be in exactly the same place, 3.95 and 2.15 ppm on the 600 MHz machine. However the coupling that appears to be .1 ppm wide on a 60 MHz machine is actually $60 \times 10^6 \text{ Hz} \times .1 \times 10^{-6} = \text{a } 6 \text{ Hz}$ coupling. Coupling is does not vary of magnetic field, so when you observe the same 6 Hz coupling in the 600 Mhz machine it will appear to be much smaller on the chemical shift scale. On a 600 MHz machine this 6 Hz coupling appears to be $6 \text{ Hz} / 600 \times 10^6 \text{ Hz} = .01 \times 10^{-6}$ or .01 ppm wide, thus you will have peaks at 3.96, 3.94, 2.16 and 2.14 ppm. In addition, if the sample is properly shimmed all peak will be much narrower and have a much higher S/N

Take home -

Calculation 1 (10 points): When we talked about IR solvents I said that water was a poor solvent because it both dissolves the common IR cells and because it absorbs lots of IR light. However, I actually did some of my graduate research doing IR spectroscopy in water. The trick is to use CaF_2 windows that don't dissolve in water, and to use deuterated water to shift the absorbance frequencies to a wavelength that would not interfere with my experiment. See if you can calculate this shift. Assume that the O-H single bond has a k of $5 \times 10^2 \text{ N/m}$. Determine the frequency (in cm^{-1}) for the stretching vibration for O-H and O-D.

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}; \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$m_H = \frac{1 \times 10^{-3} \text{ kg/mol}}{6.022 \times 10^{23} \text{ atom/mol}} = 1.66 \times 10^{-27} \text{ kg}$$

$$m_D = \frac{2 \times 10^{-3} \text{ kg/mol}}{6.022 \times 10^{23} \text{ atom/mol}} = 3.32 \times 10^{-27} \text{ kg}$$

$$m_O = \frac{16 \times 10^{-3} \text{ kg/mol}}{6.022 \times 10^{23} \text{ atom/mol}} = 2.66 \times 10^{-26} \text{ kg}$$

$$\mu_H = \frac{2.66 \times 10^{-26} \times 1.66 \times 10^{-27}}{2.66 \times 10^{-26} + 1.66 \times 10^{-27}} = 1.56 \times 10^{-27} \text{ kg}$$

$$\mu_D = \frac{2.66 \times 10^{-26} \times 3.32 \times 10^{-27}}{2.66 \times 10^{-26} + 3.32 \times 10^{-27}} = 2.95 \times 10^{-27} \text{ kg}$$

$$\bar{\nu}_H = \frac{1}{2 \times 3.14 \times 3 \times 10^8} \sqrt{\frac{500}{1.56 \times 10^{-27}}}$$

$$\bar{\nu}_H (\text{cm}^{-1}) = 5.3 \times 10^{-12} \sqrt{\frac{500}{1.56 \times 10^{-27}}} = 3000 \text{ cm}^{-1}$$

$$\bar{\nu}_D (\text{cm}^{-1}) = 5.3 \times 10^{-12} \sqrt{\frac{500}{2.95 \times 10^{-27}}} = 2180 \text{ cm}^{-1}$$

Calculation 2: (10 points) I have a laser tuned to 485.100 nm in my Raman Spectrometer. If I have a compound that has IR absorbances at 1000 and 3000 cm^{-1} , at what wavelengths (in nm) will I see Stokes and anti-Stokes scattered light?

$$485.1 \text{ nm} = .01/485.1 \times 10^{-9} = 20614.3 \text{ cm}^{-1}$$

$$20614.3 + 1000 = 21614.3 \text{ cm}^{-1}; .01/21614.3 = 4.6266 \times 10^{-7} \text{ m} = 462.66 \text{ nm}$$

$$- 1000 = 19614.3 \text{ cm}^{-1}; .01/19614.3 = 5.09832 \times 10^{-7} \text{ m} = 509.8 \text{ nm}$$

$$20614.3 + 3000 = 23614.3 \text{ cm}^{-1}; .01/23614.3 = 4.23472 \times 10^{-7} \text{ m} = 423.5 \text{ nm}$$

$$- 3000 = 17614.3 \text{ cm}^{-1}; .01/17614.3 = 5.6772 \times 10^{-7} \text{ m} = 567.7 \text{ nm}$$

Here are the empirical formulas, IR, ^1H and ^{13}C spectra of three compounds. For each compound:

What is the structure of the compound?

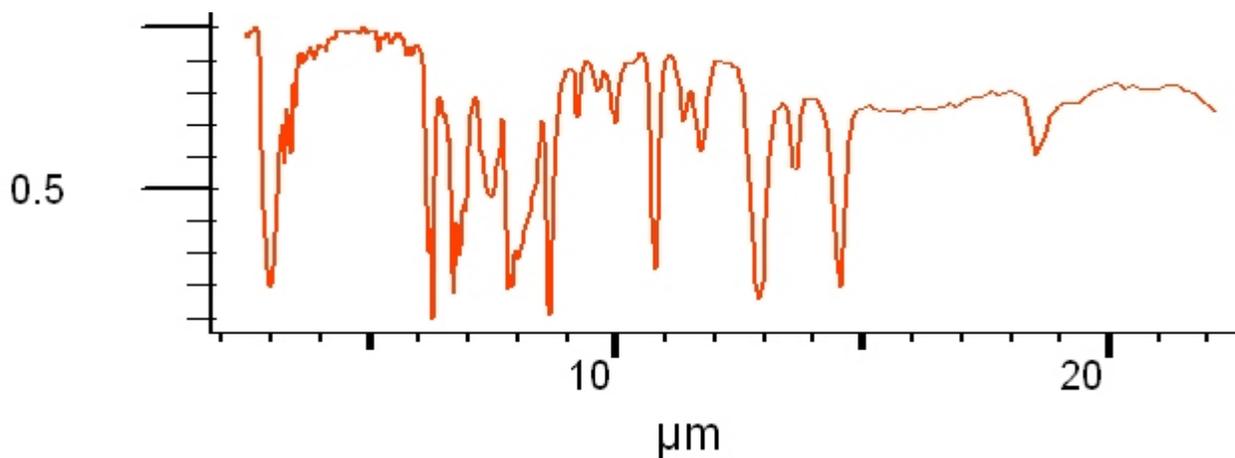
What are the characteristic group frequencies you observe in the IR for each

Based on the structure, assign as many proton and carbon resonances in the NMR spectra as possible.

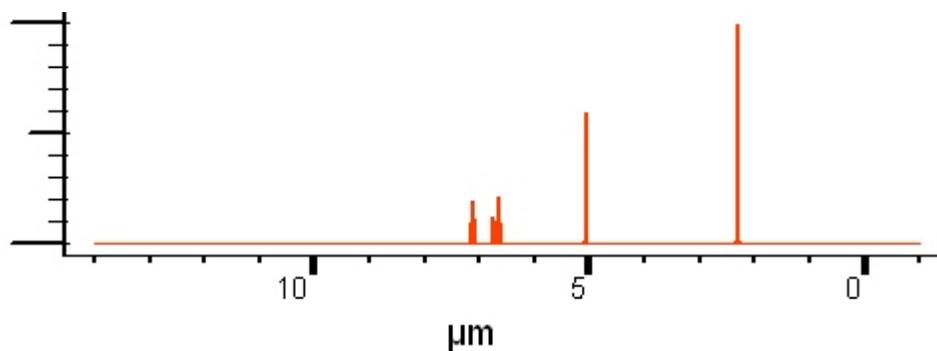
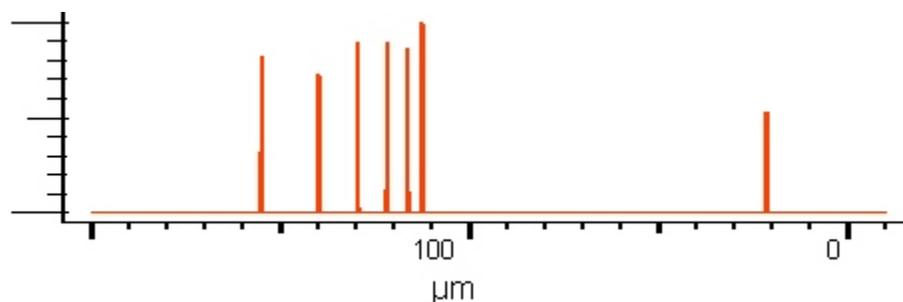
Hint: I will put the 'Aldrich Library of Infrared Spectra' on reserve in the library. You can use this to identify to help identify the IR spectrum of the compound.

Note that the labels are fouled up, only the IR spectrum is in units of μm , the NMR spectra are in the usual ppm.

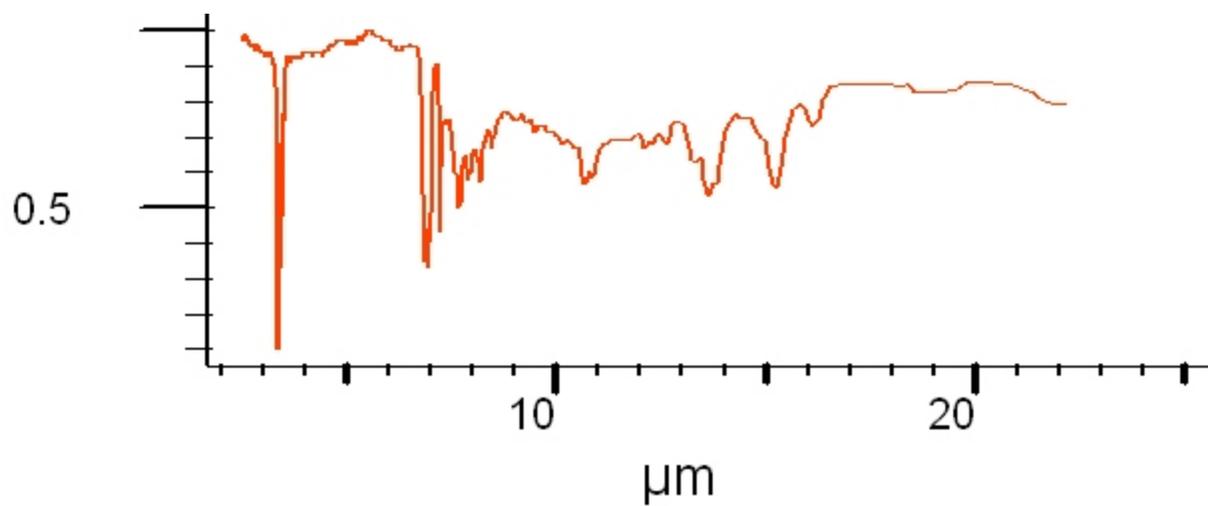
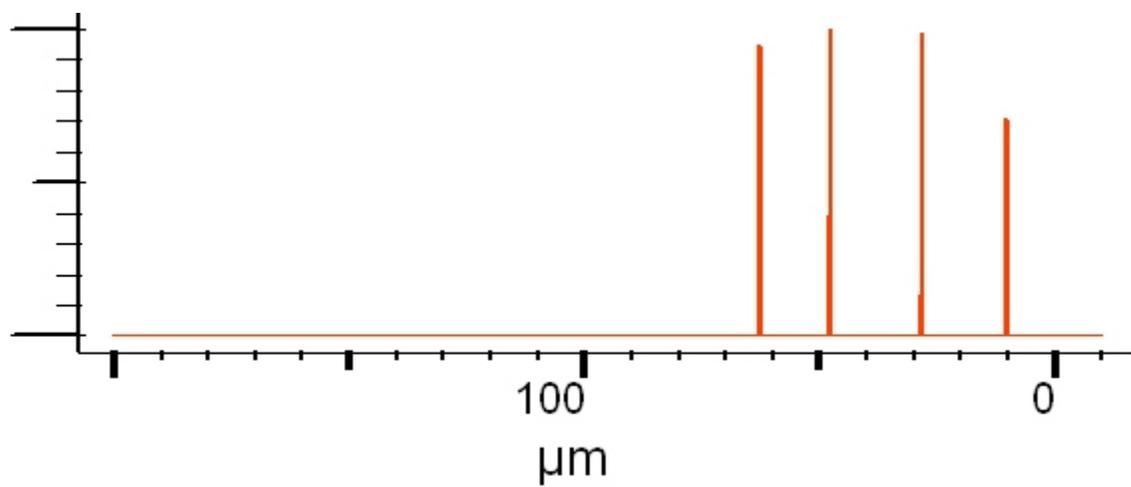
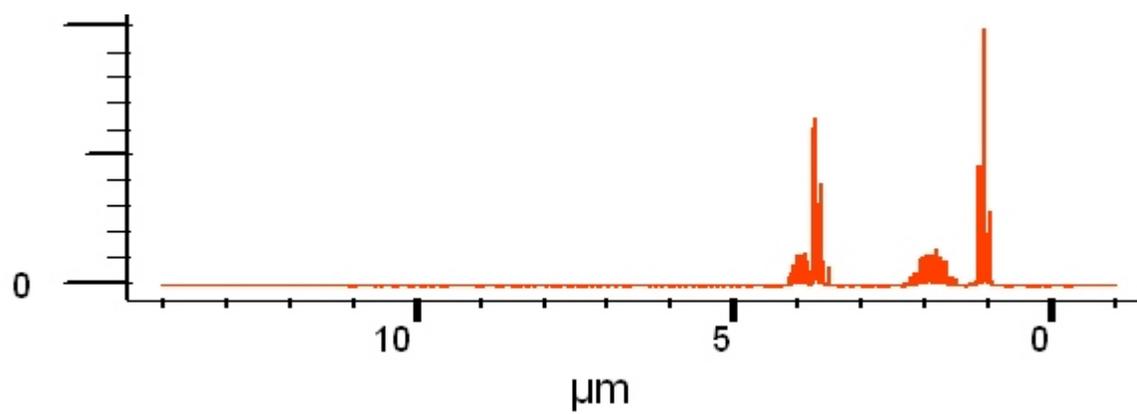
$\text{C}_7\text{H}_8\text{O}$

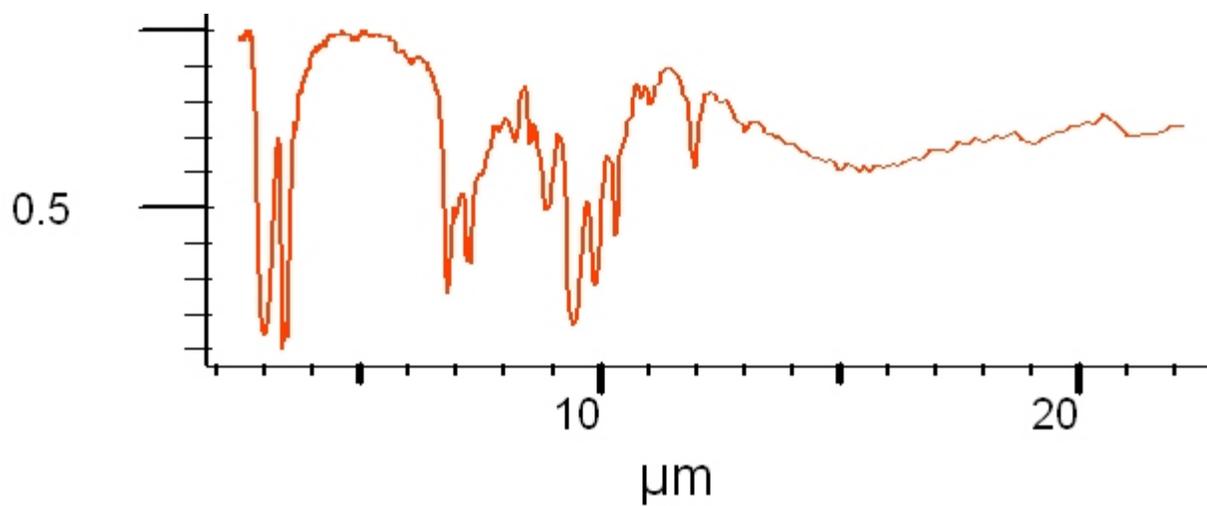
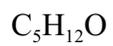
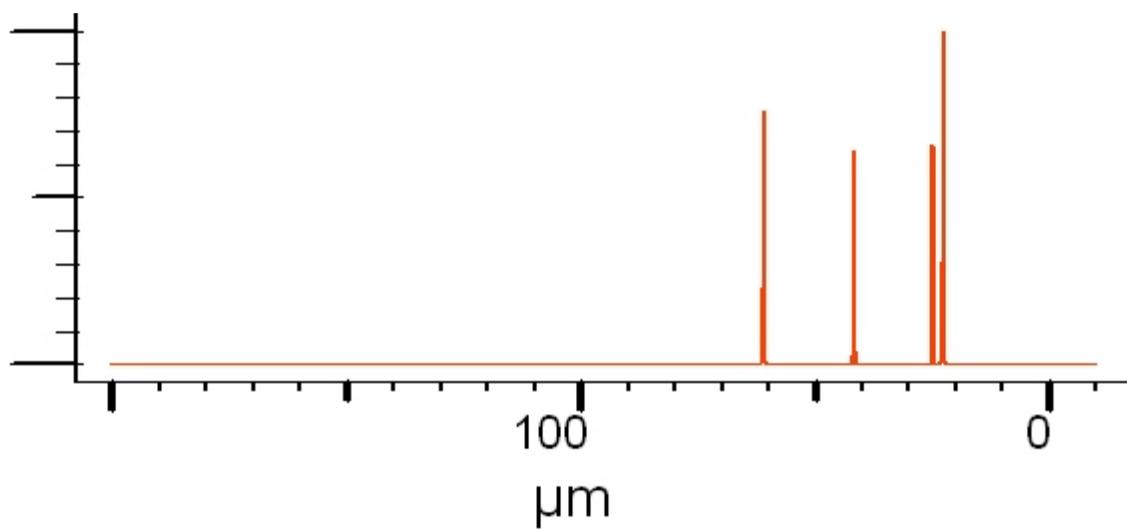
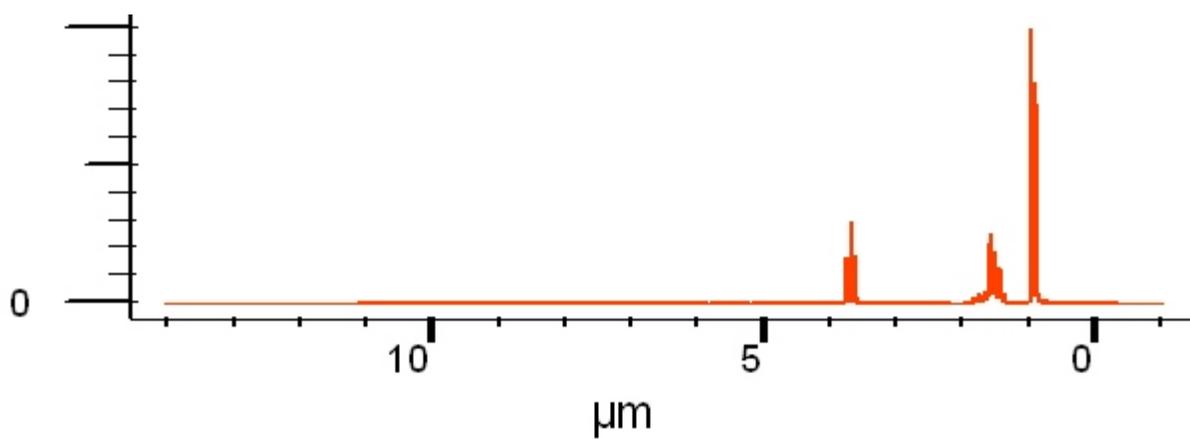


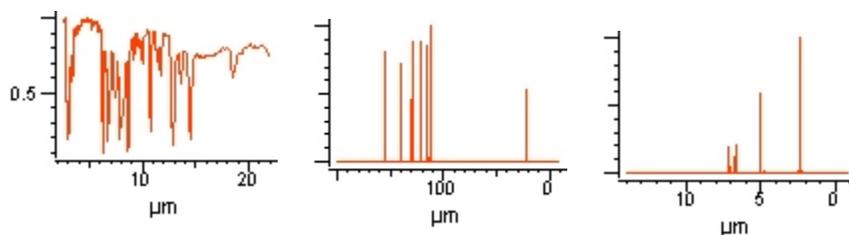
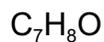
^{13}C



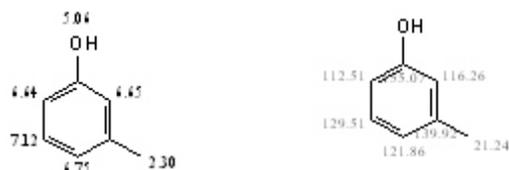
^1H

 ^{13}C  1H 

 ^{13}C  ^1H 



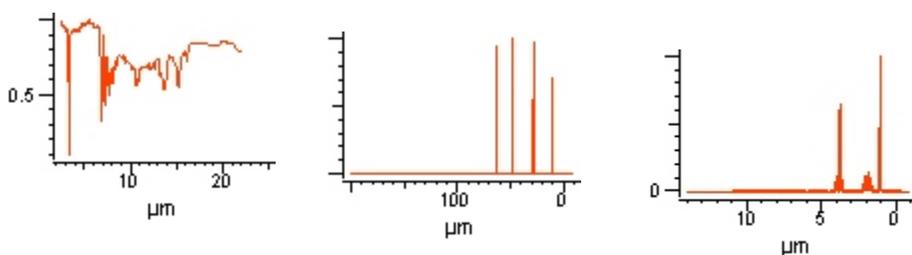
m-cresol



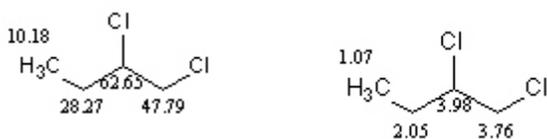
Phenols

1. 1. O-H stretching vibration:
 - O-H stretching (free), $3650\text{-}3590\text{ cm}^{-1}$ (sharp)
 - O-H stretching (intermolecular H-bonds, dimeric), near 3500 cm^{-1} (broad strong intensity)
 - O-H stretching (intermolecular H-bonds, polymeric), near 3320 cm^{-1} (broad strong intensity)
 - O-H stretching (intramolecular H-bonds, single bridge), $3570\text{-}3450\text{ cm}^{-1}$ (broad)
2. C-OH stretching vibration:
 - C-OH stretching, $1260\text{-}1180\text{ cm}^{-1}$
3. O-H deformation vibration:
 - O-H deformation, $1390\text{-}1330\text{ cm}^{-1}$ (medium intensity)

Increases in the strength of H-bonds are accompanied by shifts to lower frequencies of the absorption bands due to O-H stretching vibration. The occurrence of multiple absorption bands at the O-H stretching region in the spectra of samples examined in the neat or solid form is indicative of an involvement of the OH group in more than one type of hydrogen bonding



1,2-dichlorobutane



Halogenated Hydrocarbons

1. Chlorinated

Chlorinated Aliphatic Hydrocarbons

1. C-Cl stretching vibration:

C-Cl stretching, (range) $800\text{-}600\text{ cm}^{-1}$ (intense absorption)

C-Cl stretching, (liquid consisting of more than one conformational isomer)
 $800\text{-}600\text{ cm}^{-1}$ (intense absorption)

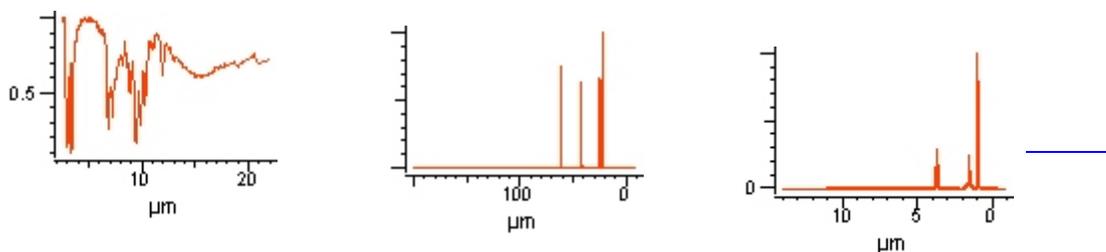
C-Cl stretching, (trans isomer) $750\text{-}700\text{ cm}^{-1}$

C-Cl stretching, (gauche isomer) near 650 cm^{-1}

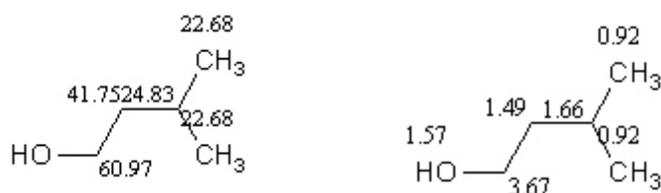
C-Cl stretching, (cyclohexane rings);

equatorial $800\text{-}700\text{ cm}^{-1}$

axial $710\text{-}650\text{ cm}^{-1}$



3-methyl-1-butanol



Alcohols

1. Primary

1. O-H stretching vibration:

- O-H stretching (free), $3650\text{-}3590\text{ cm}^{-1}$
(sharp medium strong intensity)
- OH stretching (intermolecular H-bonds, dimeric),
near 3500 cm^{-1} (broad strong intensity)
- OH stretching (intermolecular H-bonds, polymeric),
near 3320 cm^{-1} (broad strong intensity)
- OH stretching (intramolecular H-bonds, single bridge),
 $3570\text{-}3450\text{ cm}^{-1}$ (broad)

2. C-OH stretching vibration:

- C-OH stretching, $1075\text{-}1000\text{ cm}^{-1}$
(limited diagnostic value)

3. O-H deformation vibration:

- O-H in-plane deformation, near 1400 cm^{-1}
(limited diagnostic value)

The absorption band location given for the C-OH stretching vibration of primary alcohols ($1075\text{-}1000\text{ cm}^{-1}$) is not restricted to this class of alcohols alone. Some secondary alcohols, because of the environmental effect of neighboring structures on the -CHOH group, have a C-OH stretching vibration that cause absorption at the $1075\text{-}1000\text{ cm}^{-1}$ region. As a consequence, the presence of a characteristic C-OH absorption band at the designated region in the spectra of alcohols has doubtful diagnostic value. It is valid as an indication of a primary alcohol group only when it can be supported by additional structural information. (See secondary alcohols.)