Experiment 29
Infra-Red Spectroscopy

Jay C. McLaughlin
Colorado Northwestern Community College

Name:

Date:

Key Objectives

1. Basic understanding of interaction of infra-red (IR) radiation and chemical bonds.
2. Create a flow chart to identify organic molecules using IR spectroscopy.
3. Identify functional groups in organic molecules.

Discussion

A. Infrared Spectroscopy Background

We recall (hopefully!!) from last semester that electrons around an atom can absorb and emit light of only specific colors (line spectra) due to the quantized nature of the electron orbitals. Each compound tested had a unique spectrum, and we used the intensity of the peak to give us information about the concentration of the compound using Beer's Law.

Figure 29.1 below shows the entire Electromagnetic Spectrum of which in this lab we will obviously focus on the IR region which is located to the right of the Visible region, and therefore is of lower energy, and longer wavelength.

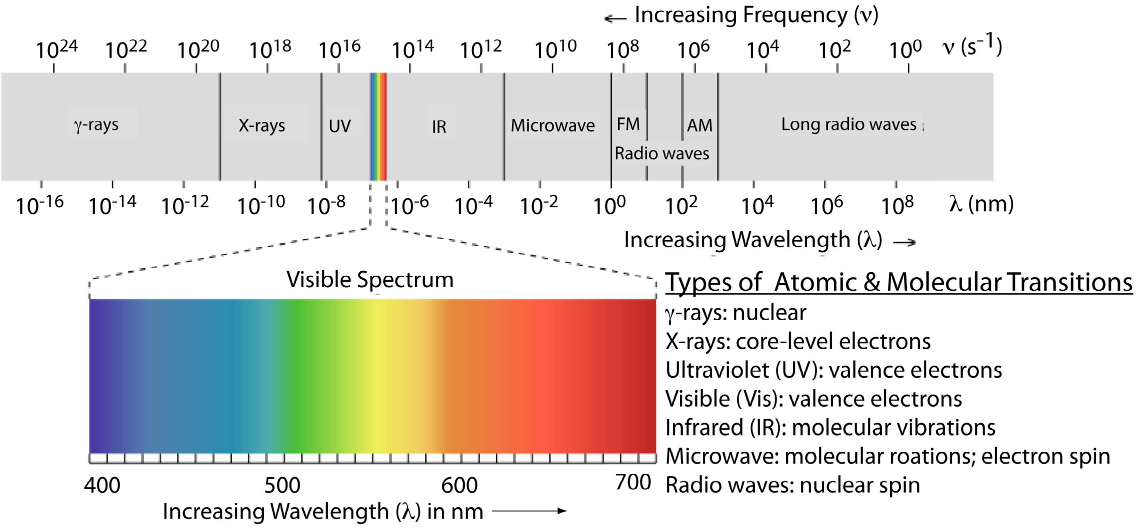


Figure 29.1: The Electromagnetic Spectrum. credit: "The Electromagnetic Spectrum" by LibreTexts is licensed under notset.

Scientists often like to use units which provide nice numbers to work with, thus for IR radiation we generally use the wavenumber (ν) instead of the wavelength (λ) of the radiation. The relationship between the two is shown in the equation below. This makes the mid IR range between 400-4000 cm^{-1}. Note that the wavenumber is proportional to energy of the radiation, as wavenumber increases so does the energy of the radiation.

$$\nu = \frac{1}{\lambda} \text{ where } \nu \text{ is measured in units of cm}^{-1}$$

The wavelength of the electromagnetic radiation determines how it interacts with a molecule. For the visible radiation we saw that the interaction correlated with the transitions of electrons between orbitals and gave rise to Line Spectra (and the color of compounds) that were unique for each element. IR radiation interacts with molecules primarily by being converted into different molecular vibrations, causing chemical bonds to stretch and bend.

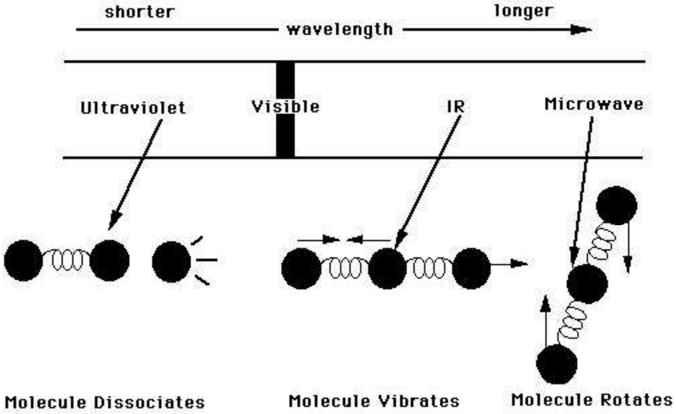


Figure 29.2: How Electromagnetic Radiation Interacts with Molecules. credit: unknown

Infrared radiation interacts with the chemical bonds between atoms, and produces a unique spectrum which can tell us information about the type of bonds in a compound. Our normal picture of a molecule (similar to the Lewis Structures/Models build in the previous lab) used rigid bonds between the atoms. This picture is a bit simplified, and instead of rigid bonds between atoms we should picture the bonds as a spring which can vibrate, stretch, and bend in many different ways. Infrared radiation causes vibrations of the atoms which cause the molecular bonds to stretch or bend. There are several types of bending and stretching motions illustrated in Figure 29.3 below (for an dynamic picture see `http://en.wikipedia.org/wiki/Infrared_spectroscopy`). As a molecule becomes larger and more complicated the number of vibrational modes (or degrees of freedom) increases as 3N-5 for linear molecules and 3N-6 for non-linear molecules, where N = number of atoms. Obviously very large molecules can give rise to complicated spectra.

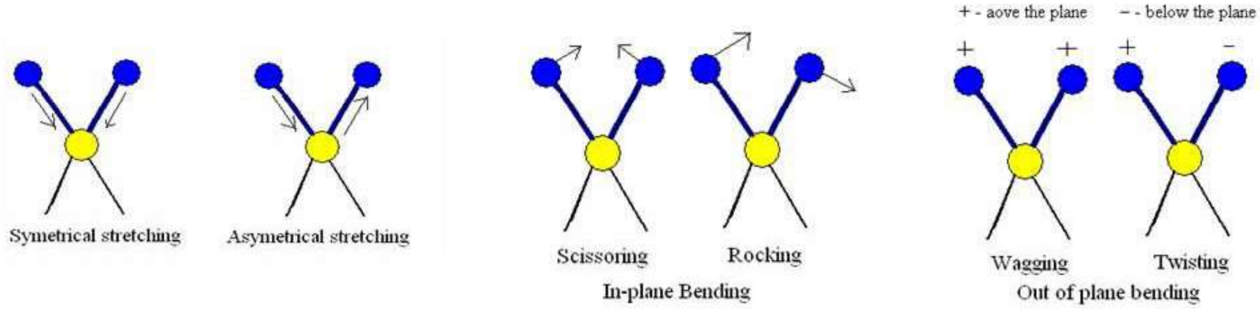


Figure 29.3: Basic Bending and Stretching Modes for a Molecule. Animations located at `https://en.wikipedia.org/wiki/Infrared_spectroscopy`. credit: unknown

A typical IR spectrum can be seen below in (Figure 29.4 and may seem incredibly complicated at first due to the large number of peaks compared to the visible spectra we took last semester. However, all is not lost, we will focus on learning only a few of the basic rules; enough to identify the functional group in most cases. The very complex looking region below 1500 cm^{-1} is called the **Fingerprint Region** and can mostly be ignored. The fingerprint region contains bond stretches between backbone atoms (C-C mostly) which almost all organic molecules have, and there are often too many overlaping absorptions to be any help. Instead, concentrate on the **Functional Group Region** between 1500-4000 cm^{-1}. This region contains peaks that correspond to stretches in functional groups, and is all that is usually needed to determine what type of compound we have. Table **??** on the next page lists each functional group and the most common absorption frequencies for each. By comparing between Table **??** and each IR spectra the functional group for each molecule can be determined and a model of the molecule can begin to take shape. In order to fully determine the structure of a molecule, it is generally necessary to have data from other techniques, such as chemical formula from a Mass Spectrometer (MS - Lab 32) or number and type of carbons and hydrogens from Nuclear Magnetic Resonance (NMR - Lab 33), to predict or confirm a specific structure.

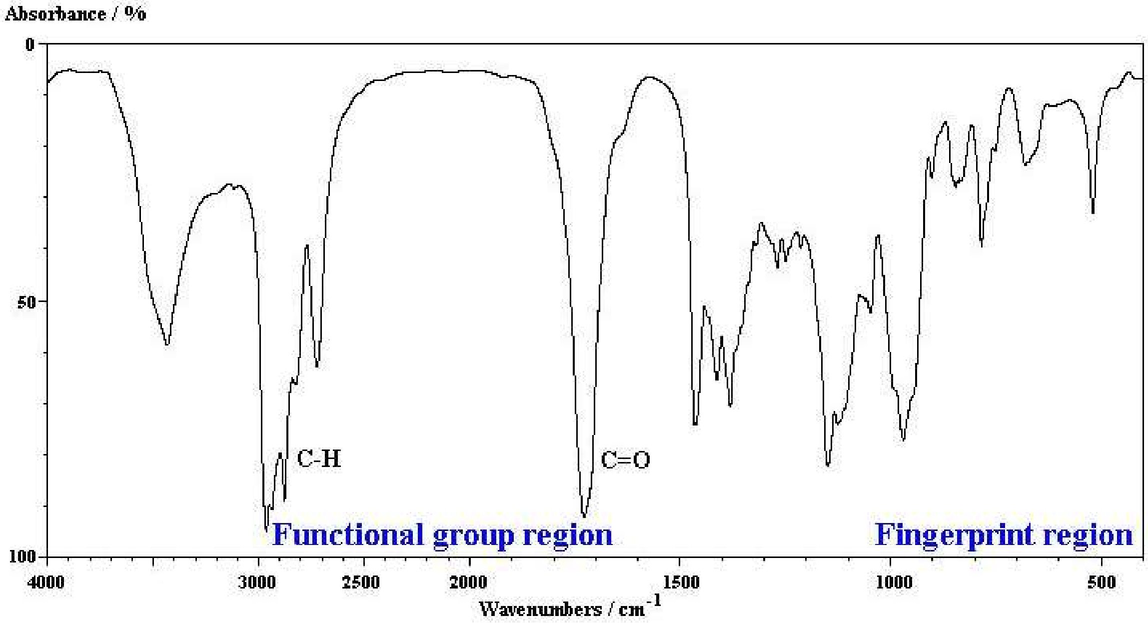


Figure 29.4: Example IR Spectrum. credit: `https://www.chem.ucalgary.ca/courses/351/Carey5th/Ch13/ch13-ir-1.html`

Organic chemists have observed and catalogued the types and locations of Infrared absorptions produced by variety of chemical bonds. The data is generally presented through Tables or Figures linking functional groups with specific regions of the Infrared Spectrum. These are general rules only, as the exact bonding, and nearby functional groups can all influence what frequencies a molecules will absorb. With the advent of computers, much of this information is online, and can even be searched to find a matching spectrum. We, however, will practice matching up spectra and functional groups the old fashioned way in order to gain a basic understanding of the technique.

Graphically the different regions can be seen in Figure 29.5 and 29.6 below. Specific regions and functional groups are discussed in more detail in several sections below.

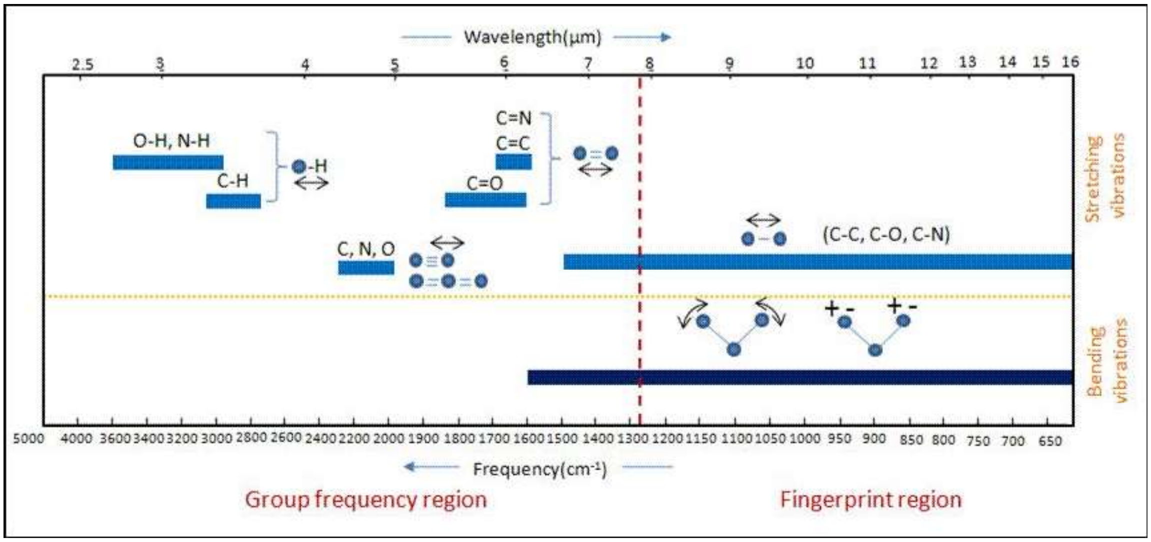


Figure 29.5: Graphical Representation of Typical IR Frequencies. credit: `InfraredSpectraofSomeCommonFunctionalGroups.(2019,September3).https://chem.libretexts.org/@go/page/183009`

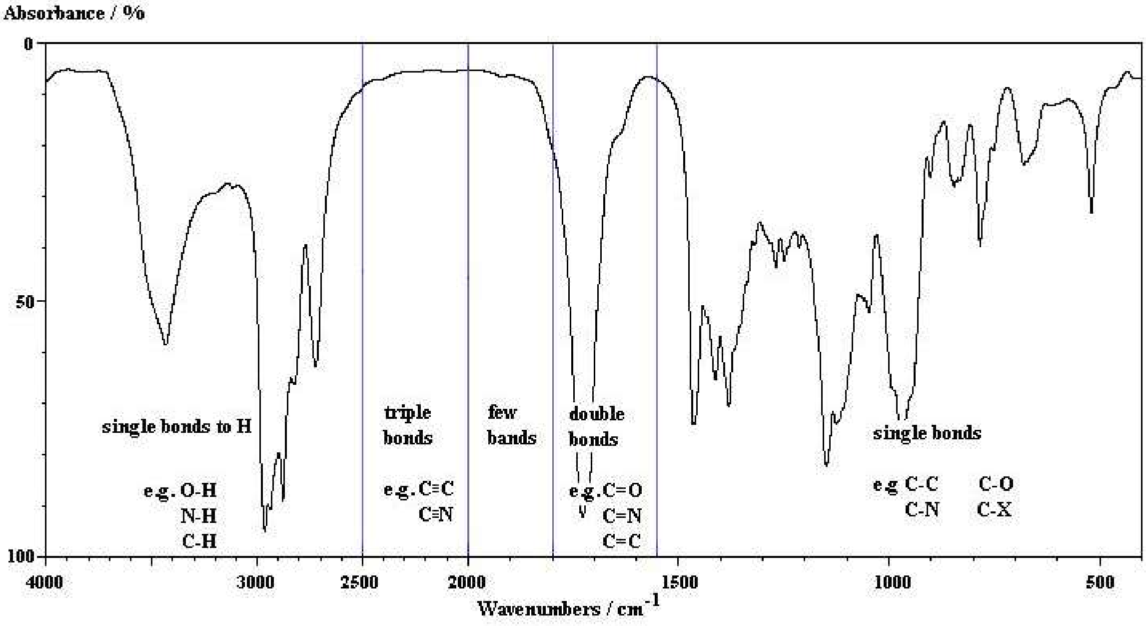


Figure 29.6: Graphical Representation of Typical IR Frequencies. credit: unknown

Alkanes, Alkenes, Alkynes and Aromatics

The absorption of the alkane part of a molecule consist primarily of C-H stretching and bending. When other functional groups are present these absorptions are often difficult to distinguish. It is often the lack of absorptions from other functional groups that leads one to identify a molecule as containing only an alkane functional group.

Functional Group	**Wavenumber (cm^{-1})**	**Intensity**	**Comments**
Alkane			
C-H stretch	2850-3000	strong	
-C-H bend	1350-1480	variable	
Alkene			
C=C stretch	1620-1680	variable (weak)	*Only alkenes and Aromatics show C-H absorption $>$ 3000
=C-H stretch	3000-3100	medium	
=C-H bend	650-1000	strong	
Alkyne			
$C\equiv C$ stretch	2100-2300	variable	
$C\equiv C-H$ stretch	3300	strong	*terminal only (can be obscured by other groups (OH)
$C\equiv C-H$ bend	600-700	strong	*terminal only
Aromatic			
=C-H stretch	3000-3100	medium	*Only alkenes and Aromatics show C-H absorption $>$ 3000
C-C stretch	1400-1600	medium, sharp	multiple bands (1400-1500 and 1585-1600)
overtones	1650-2000	weak	reflect substitution pattern on ring (ortho, meta, para)
C-H "oop"	675-900	weak	out-of-plane C-H bends reflects substitution patterns

Table 29.1: Alkanes, Alkenes, and Alkynes

The IR spectrum of octane is shown in Figure 29.7 below. Note the strong bands in the 3000-2850 cm^{-1} region due to C-H stretch. The C-H scissoring (1470 cm^{-1}), methyl rock (1383 cm^{-1}), and long-chain methyl rock (728 cm^{-1}) are noted on this spectrum. Since most organic compounds have these features, these C-H vibrations are usually not noted when interpreting a routine IR spectrum.

The addition of double bonds (C=C) gives rise to a new diagnostic peak, and shifts the frequency of the $C=C-H$ stretch to a high value than the $C-C-H$ stretch, generally slightly greater than 3000 cm^{-1}. This is a very useful diagnostic fact since only alkenes and aromatics show a C-H stretch $>$ 3000 cm^{-1}.

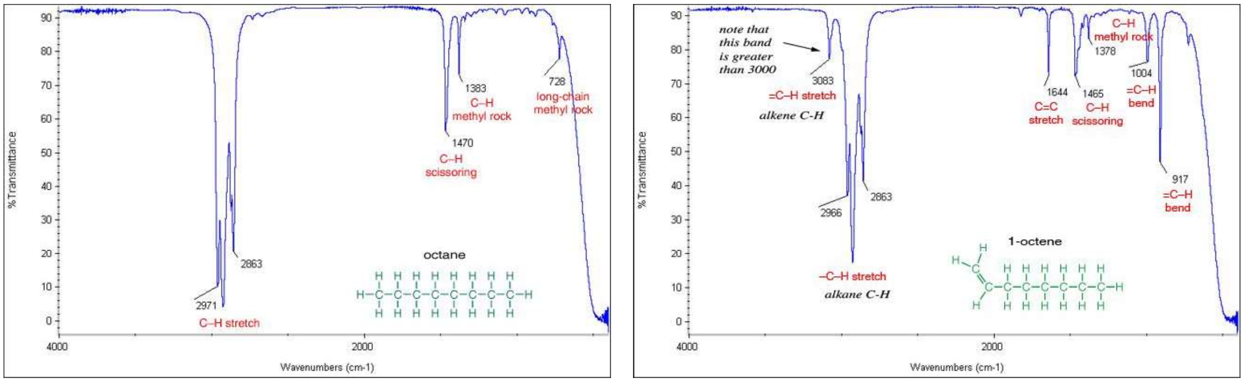


Figure 29.7: IR spectra of Octane and 1-octene. credit: credit: InfraredSpectraofSomeCommonFunctionalGroups.(2019,September3).https://chem.libretexts.org/@go/page/183009

Alkynes triple bonds (C≡C) provide additional features that can be identified. Typical bands are shown in Table 29.8. Triple bonds (C≡C and C≡N have a distinctive (sharp, though often small) absorption at 2200 cm^{-1}. Distinguishing between the two usually requires additional information, a terminal C≡C−H bond will have a peak at 3270-3330 cm^{-1} due to the C-H stretch, and a peak at 610-700 cm^{-1} due to C-H bend.

1-hexyne illustrates the typical features found in a compound with a triple bond (peak at 2260-2100 cm^{-1}), and also illustrates the terminal C≡C−H stretch for when the triple bond is located between 2nd and 3rd carbons.

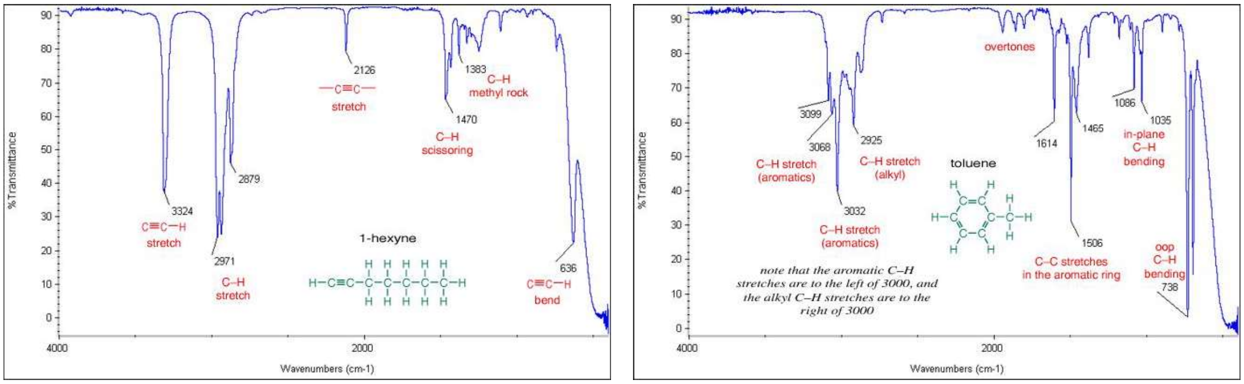


Figure 29.8: IR spectra of 1-hexyene and Toluene. credit: InfraredSpectraofSomeCommonFunctionalGroups.(2019,September3).https://chem.libretexts.org/@go/page/183009

The spectrum of toluene is shown in Figure 29.8. The =C−H stretches of aromatics (3100, 3070, 3030) and the C−H stretches of the alkyl (methyl) group (2925). The characteristic overtones are seen from about 1650-2000. Also note the carbon-carbon stretches in the aromatic ring (1620, 1510, 1470), the in-plane C−H bending (1090, 1040), and the C−H out-of-plane (740).

Aldehydes, Ketones, Carboxylic Acids and Esters

The typical frequencies for double bonds (C=C, C=O, and C=N) overlaps significantly and it is generally necessary to have additional information to identify them exactly. However, in this class, we can exclude C=N bonds and in conjunction with other information given identify them.

Functional Group	**Wavenumber (cm^{-1})**	**Intensity**	**Comments**
Aldehyde			
C=O	1720-1740	strong	
terminal C−H	2720-2750 and 2820-2850	medium	Two absorptions
Ketone			
C=O	1680-1750	strong/sharp	Lack of other bonds normally indicates a ketone
Carboxylic Acid			
C=O	1710-1780	strong	
O−H stretch	2500-3300	strong, broad	
O−H bend	900-955 and 1400-1450	medium	
C−O stretch	1210-1320	strong	
Ester			
C=O stretch	1735-1750	strong	
C−O stretch	1000-1300		Two or more absorptions
Amides			
C=O stretch	1630-1690	strong	
N−H stretch	3100-3500	medium	unsubstituted = 2 absorptions
N−H bend	1550-1640	medium	

Table 29.2: Double Bonds

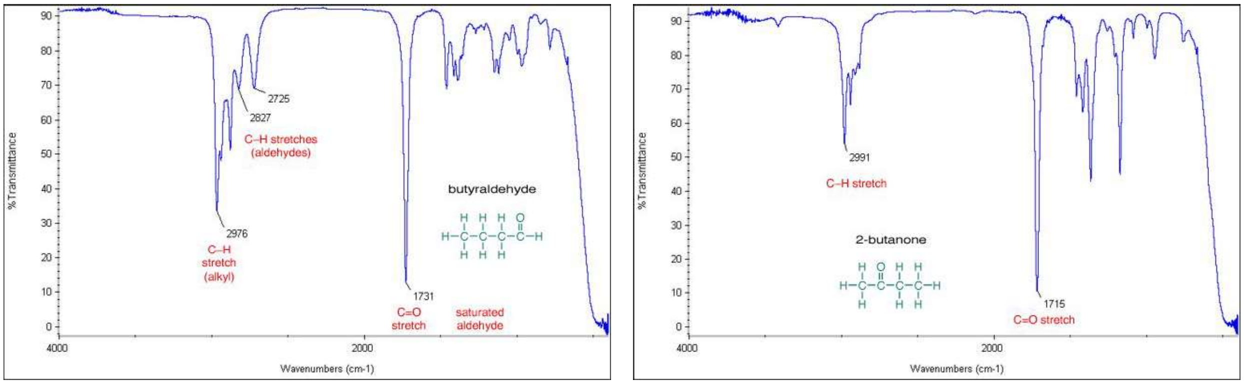


Figure 29.9: IR spectra Butanal and 2-butanone. credit: `InfraredSpectraofSomeCommonFunctionalGroups.(2019,September3).https://chem.libretexts.org/@go/page/183009`

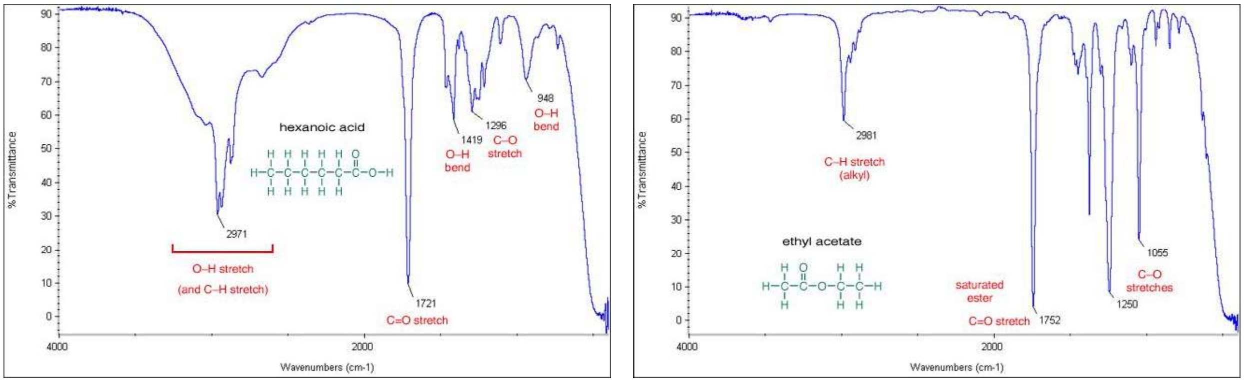


Figure 29.10: IR spectra Hexanoic Acid and Ethyl Ethanoate. credit: `https://orgchemboulder.com/Spectroscopy/irtutor/tutorial.shtml`

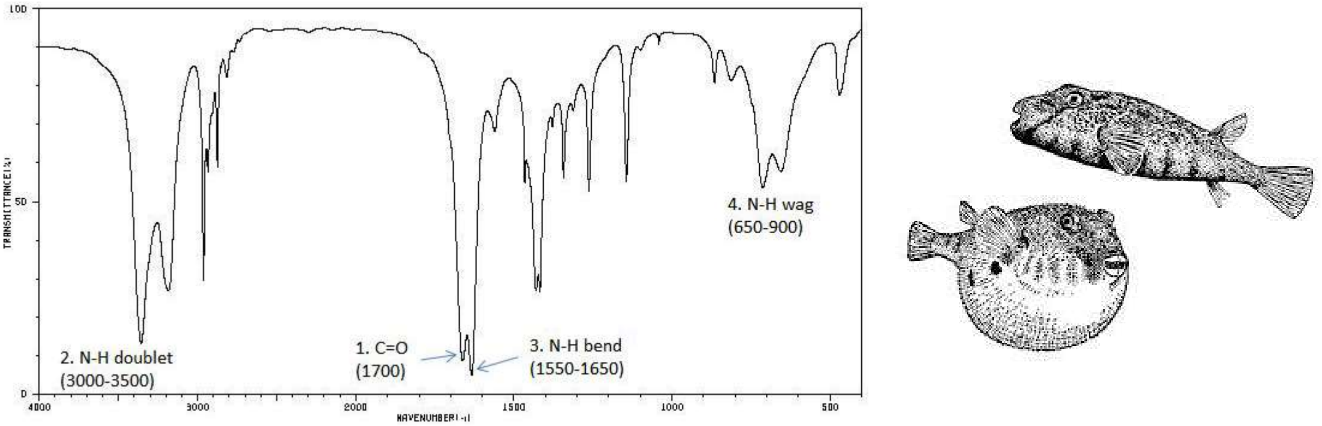


Figure 29.11: IR spectra for Butanamide and a Pufferfish. credit: Left - NIST Chemistry WebBook `http://webbook.nist.gov/chemistry` Right - `https://clipartix.com/clipart-fish-image-13780/`

Carbonyl Groups (C=O stretchs) typically have a sharp finger around 1715 for a ketone. The lack of additional features is indicative of a ketone.

Carboxylic acids show a strong, wide band for the O−H stretch. Unlike the O−H stretch band observed in alcohols, the carboxylic acid O−H stretch appears as a very broad band in the region 2500-3300, centered at about 3000. This is in the same region as the C−H stretching bands of both alkyl and aromatic groups. Thus a carboxylic acid shows a "messy" absorption pattern in the region 2500-3300, with the broad O−H band superimposed on the sharp C−H stretching bands. The reason that the O-H stretch band of carboxylic acids is so broad is because carboxylic acids usually exist as hydrogen-bonded dimers.

Alcohols, Ethers, and Amines

Functional Group	**Wavenumber (cm^{-1})**	**Intensity**	**Comments**
Alcohol			
O–H stretch	3200-3500	broad, strong	H-bonding present
O–H stretch	3500-3700	strong, sharp	Free O-H (no H-bonding) (sometimes missing)
C–O stretch	1000-1300		Two or more absorptions
Ether			
C–O	1000-1300	strong	Lack of other absorptions
Amine			
N–H stretch	3000-3300	medium, sharp	Same region as O–H but weaker and sharper. 1° = 2 absorptions, 2° = 1 absorption (weak), and 3° = none
N–H bending	1550-1650	medium	1° only, 2° rarely seen, ° = none, often difficult to tell due to being near C=O region.
N–H wag	650-900	strong, sharp	1° and 2° only
C–N stretch	1050-1350	medium-weak	

Table 29.3: Alcohols, Ethers and Amines

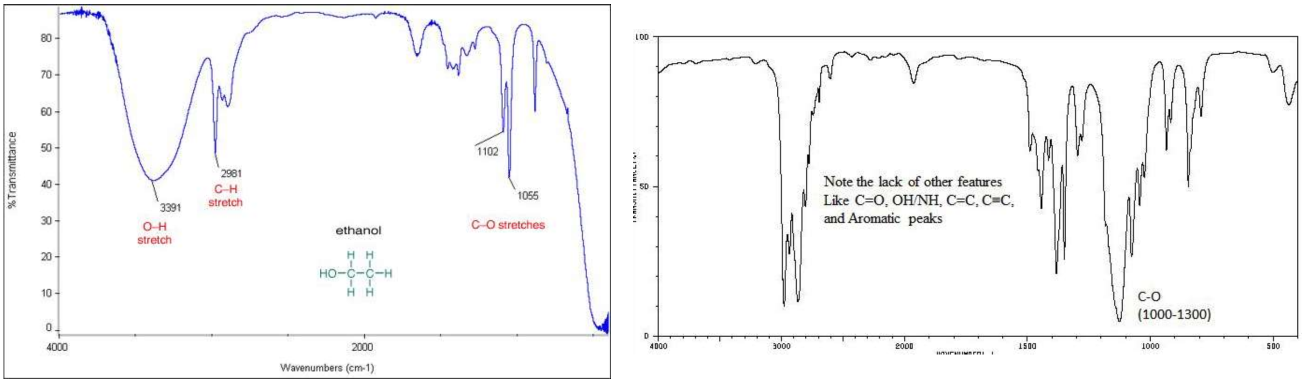


Figure 29.12: IR spectra Ethanol and Ethoxyethane. credit Left - `https://orgchemboulder.com/Spectroscopy/irtutor/tutorial.shtml` right - unknown

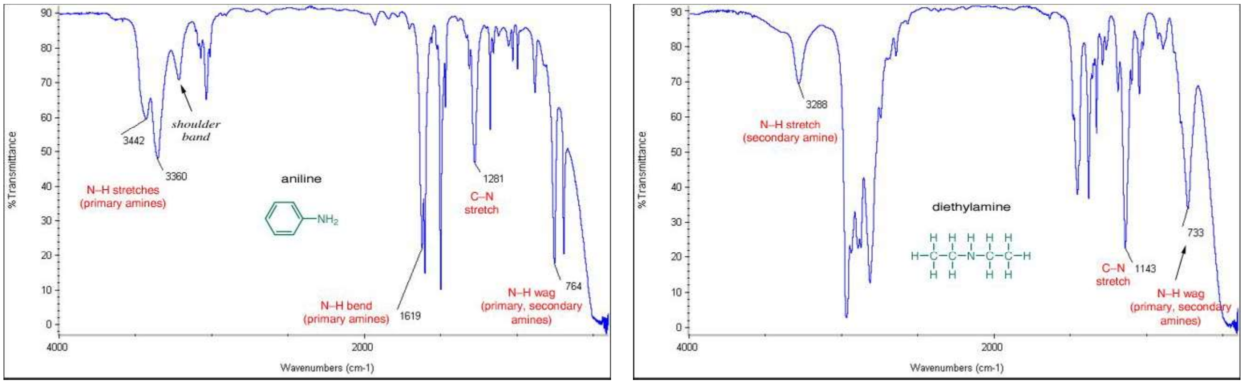


Figure 29.13: IR spectra for Analine (1°) and Ethylethanamine(2°). credit: `https://orgchemboulder.com/Spectroscopy/irtutor/tutorial.shtml`

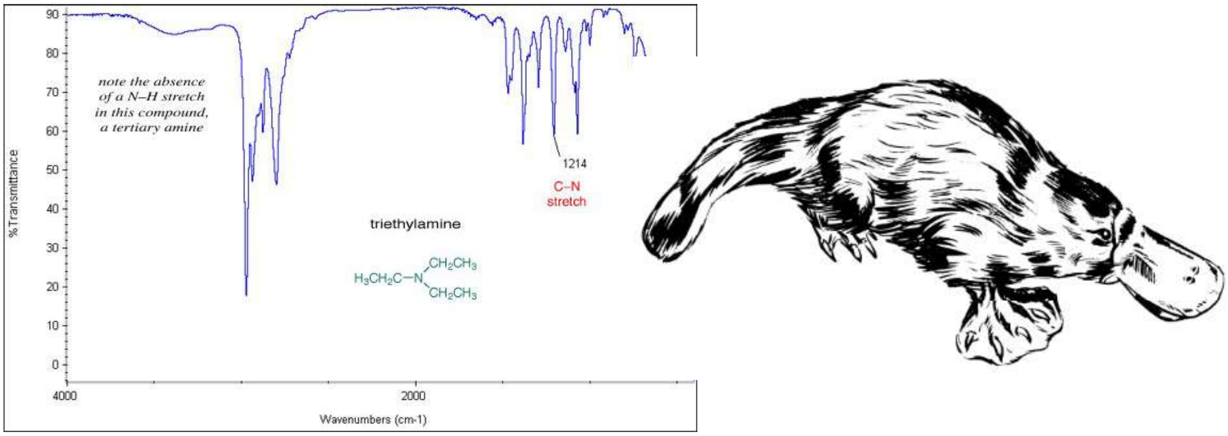


Figure 29.14: IR spectra for N,N-diethylethanamine (3°) and a Platypus. credit: left - `https://orgchemboulder.com/Spectroscopy/irtutor/tutorial.shtml` right - Public Domain

3200-3500 cm^{-1} Region

This region has several specific functional groups (Alcohols, Amines (1^o and 2^o) and Carboxylic Acids) which have characteristic peaks in this region. It is the shape of the peak, more than the position which gives clues as to the appropriate functional groups. If the region contains no absorption then these functional groups are likely missing.

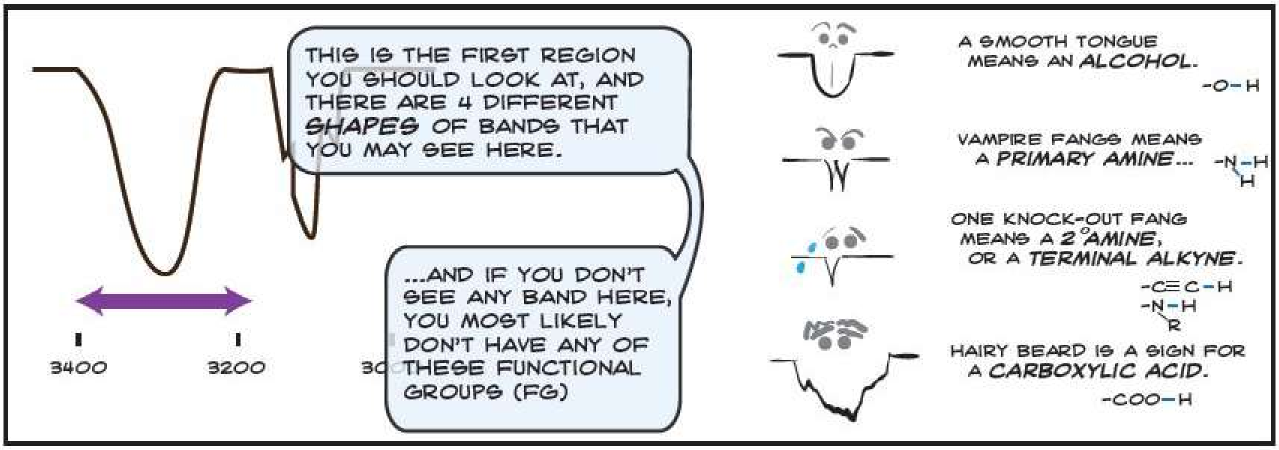


Figure 29.15: IR Identification in the 3500-3200 Region. credit - `https://toeholds.wordpress.com/2010/09/21/pictorial-guide-to-interpreting-infrared-spectra/`

How to Analyze an IR Spectrum

The task of anaylzing an IR spectrum can seem daunting as there are many functional groups and many different bending and stretching combinations present. There are many different approaches one may take to analyze a spectrum, the following is just one example.

Note that just as often as a specific absorption indicates a class of compounds, the lack of a specific absorption can also help exclude compounds from consideration.

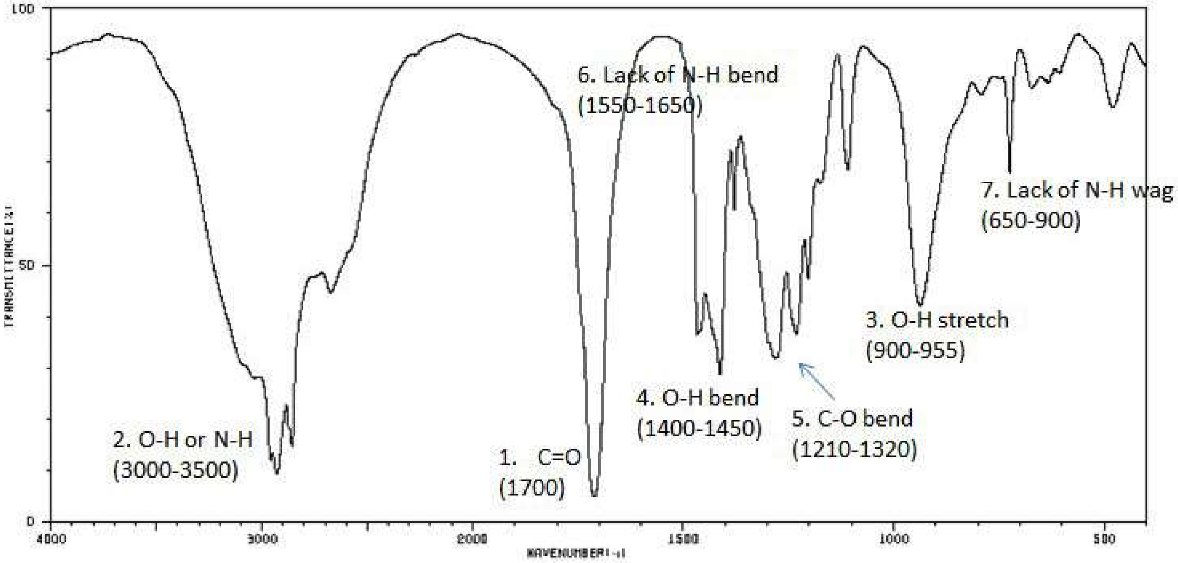
1. Examine the 1700 ± 1000 cm^{-1} carbonyl region. If a carbonyl group is present, look for the different secondary absorptions associated with each specific functional group to verify your assignment.
   (a) Aldehyde: C−H sharp absorption at 2720 and 2820 cm^{-1} (sometimes seen as shoulders)
   (b) Ketone: no additional absorptions (i.e. lack of Aldehyde/Carboxylic Acid/Ester/Amide peaks)
   (c) Carboxylic Acid: broad O−H absorption 3000-3500 cm^{-1} + others
   (d) Ester: C−O absorption 1000-1300 cm^{-1} (1 or more)
   (e) Amide: broad N−H absorption 3000-3500 cm^{-1} + others
2. Examine the 3000-3500 cm^{-1} region for broad features (not the C-H stretches).
   (a) Alcohol: broad, smooth absorption, confirmation of free O-H hydrogen bonds at 3500-3700 cm^{-1} (sometimes missing) (smooth tongue)
   (b) 1° Amide/Amine: 2 medium/sharp absorptions (fangs)
   (c) 2° Amide/Amine: 1 medium/sharp absorption (missing a tooth)
   (d) Carboxylic Acid: broad, jagged absorption (beard)
3. 3000 region - C-H stretching frequencies (sharp peaks)
   (a) Alkene/Aromatic: C-H absorptions > 3000 cm^{-1}
   (b) Alkane: C-H absorptions < 3000 cm^{-1}
4. Miscellaneous
   (a) Ether: strong C−O absorption at 1000-1300 cm^{-1} and lack of other absorptions
   (b) Alkynes: C≡C absorption at 2200 cm^{-1} (sharp, but can be smallish)
   (c) Aromatic: Overtones (1650-2000 cm^{-1}) and OOP (675-900 cm^{-1}) pattern

Some functional groups (Carboxylic Acid/Amide, Alcohol/Amine, Alkenes/Aromatics and Alkanes/Ethers) can be particularly hard to differentiate between because many absorptions overlap. In those cases one must often look to secondary or even tertiary absorptions to tell the difference. Don't be afraid to narrow your results down to 1 or 2 types of molecules and then find the other spectrum that is similar and compare the two and determine which spectra is best representative of each.

Procedure

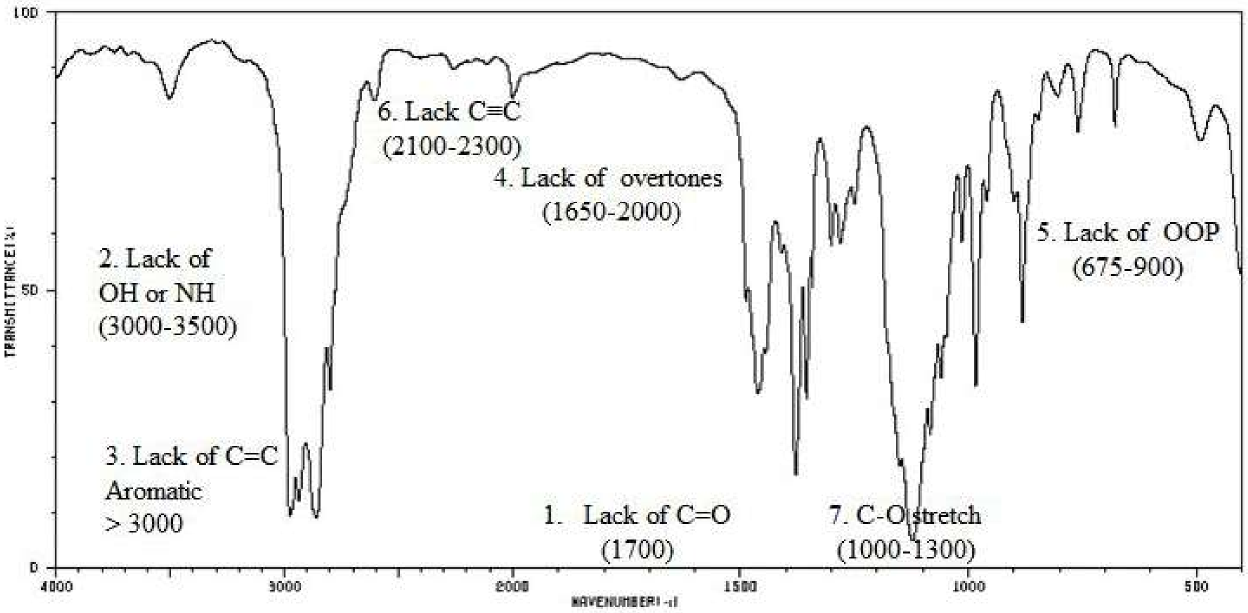
1. Assign as many features as possible to each functional group.
    (a) Indicate the order of identification
    (b) Identification can be inclusive or exclusive (i.e. C=O present, or missing)
    (c) Label secondary absorptions that help to verify each assignment.
2. Finally label (and circle it) your final assignment by functional group.
3. The spectra in Problems 1-12 are (a) 2,2-dimethylbutane, (b) 2-pentene (c) 2-pentyne (d) ortho-methyltoluene (e) 2-pentanol (f) butoxybutane (g) hexanal (h) 2-hexanone (i) pentanoic acid (j) 1-ethylhexyl butanoate (k) ethylamine (l) propanamide
4. Two example are provided on the next page.

Example 1



Examining the first spectra, we first noted the carbonyl peak 1700 cm^{-1} which indicates an Aldehyde, Ketone, Carboxylic Acid, Ester or Amide is present. We then looked at the 3000-3500 cm^{-1} region and noted the presence of an O-H or N-H, which indicates a Carboxylic Acid or Amide. We then begin looking at the secondary peaks (in the fingerprint region) and can clearly see 3 absorptions associated with Carboxylic Acids. Lastly we note the absence of any N-H absorptions. We then conclude we have a Carboxylic Acid.

Example 2



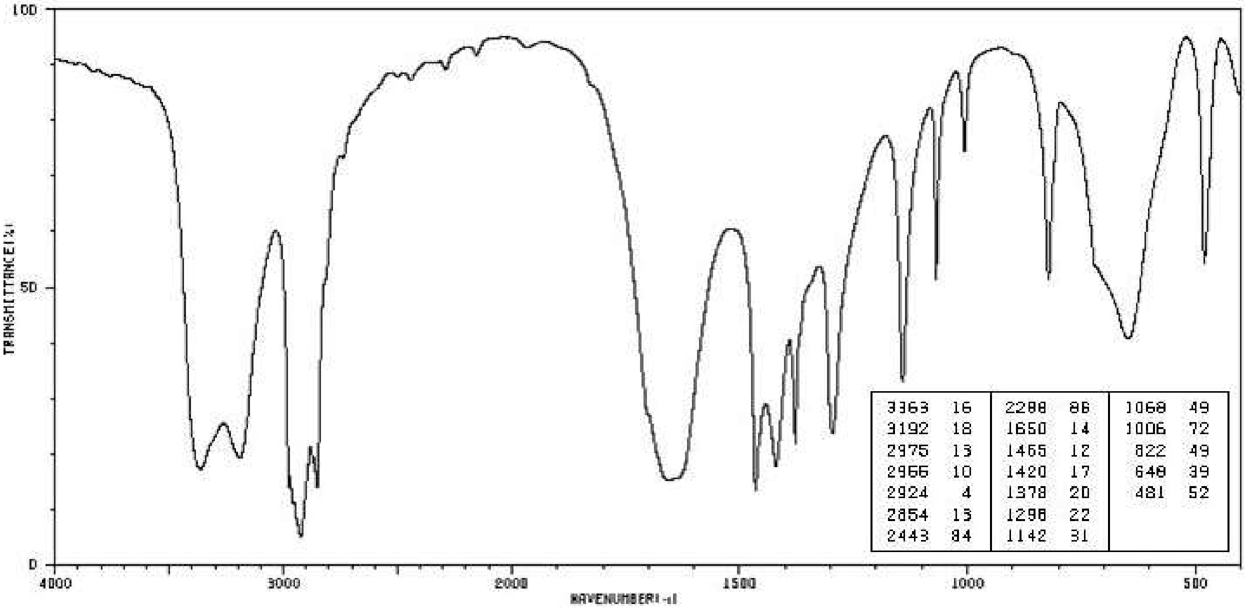
Examining the second specra, we first note the lack of many features, most specifically at 1700 cm^{-1} and between 3000-3500 cm^{-1}. This indicates we most likely have an alkane of some sort or possibly an ether. We next looked for absorptions indicating different alkane features. The lack of intensity $>$ 3000 cm^{-1} along with the lack of Overtones and C-H oop means we are unlikely to have a C=C therefore we don't have an alkene or aromatic. The lack of a peak near 2100-2300 cm^{-1} means we don't have an alkyne either. This leaves us with the possibility of a simple alkane or ether. We not a large absorption between 1000-1300 cm^{-1} which is indicative of a C-O stretch and conclude that we have an Ether.

Name: ______________________________ Date: __________________ Score: _____/80

Results

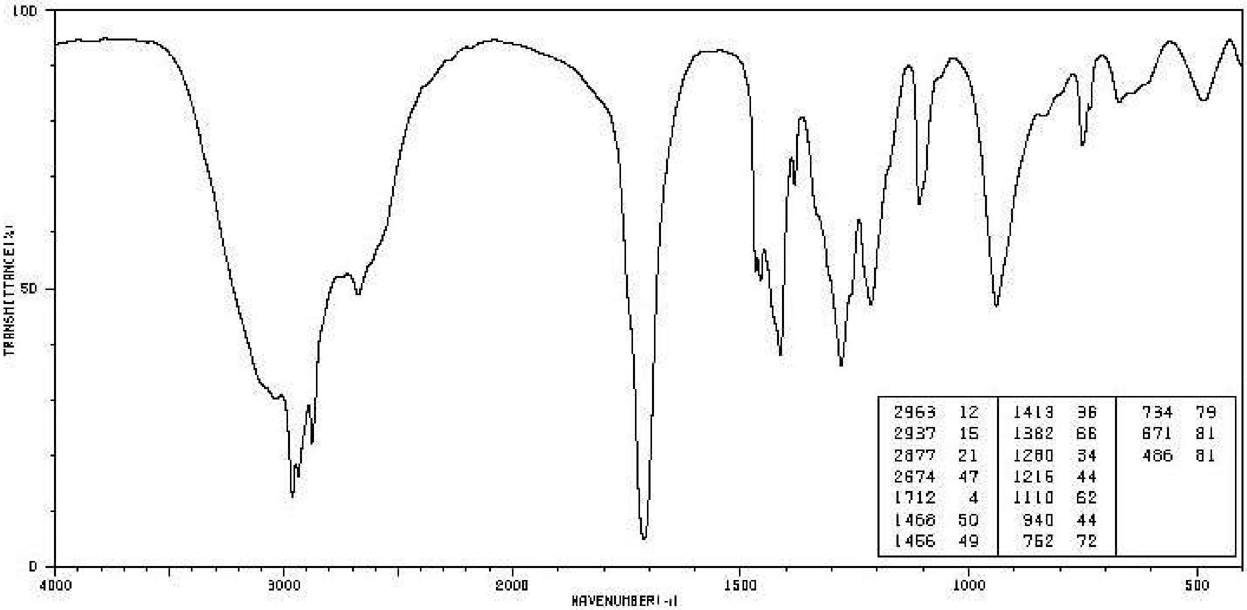
Credit for all spectra in results section - Source: SDBSWeb : `http://riodb01.ibase.aist.go.jp/sdbs/` (National Institute of Advanced Industrial Science and Technology of Japan, 14 July 2008)

Spectrum 1



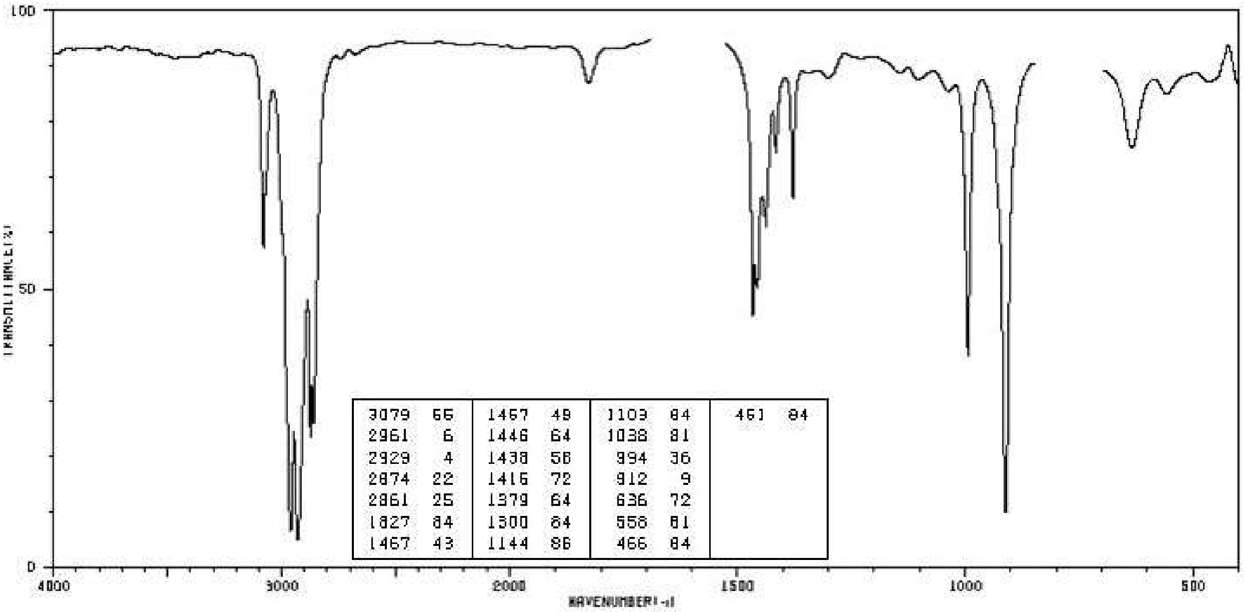
3363	16	2288	86	1068	49
3192	18	1650	14	1006	72
2975	13	1465	12	822	49
2966	10	1420	17	648	39
2924	4	1378	20	481	52
2854	13	1298	22		
2443	84	1142	31		

Spectrum 2



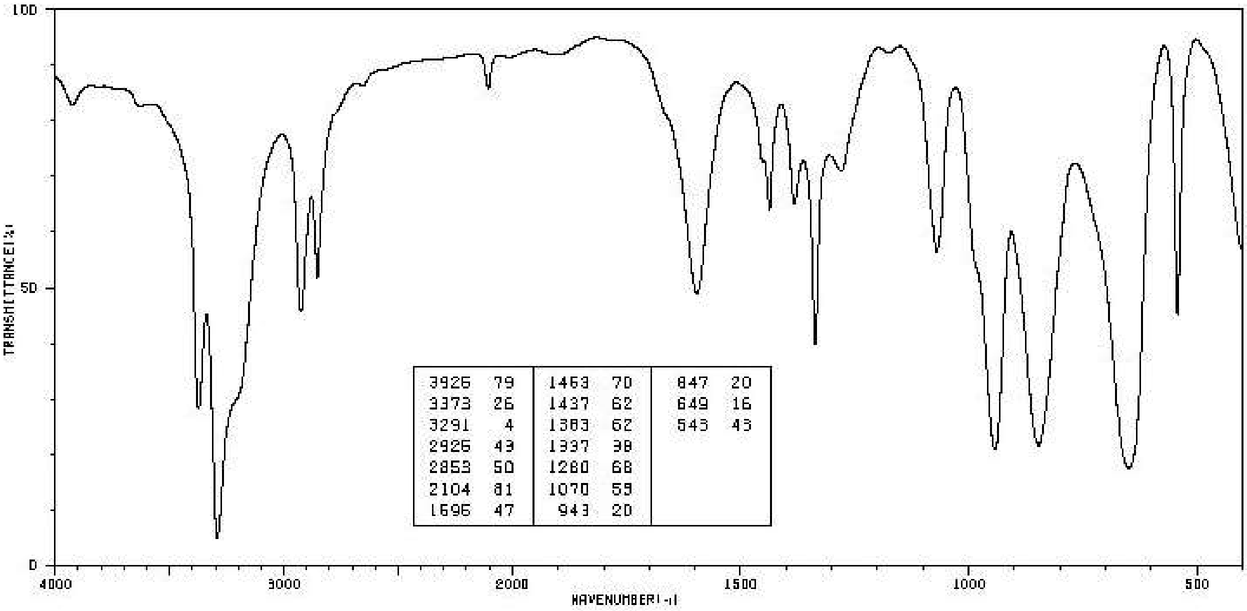
2963	12	1413	36	734	79
2937	15	1382	66	671	81
2877	21	1280	34	486	81
2674	47	1216	44		
1712	4	1110	62		
1468	50	940	44		
1466	49	762	72		

Spectrum 3



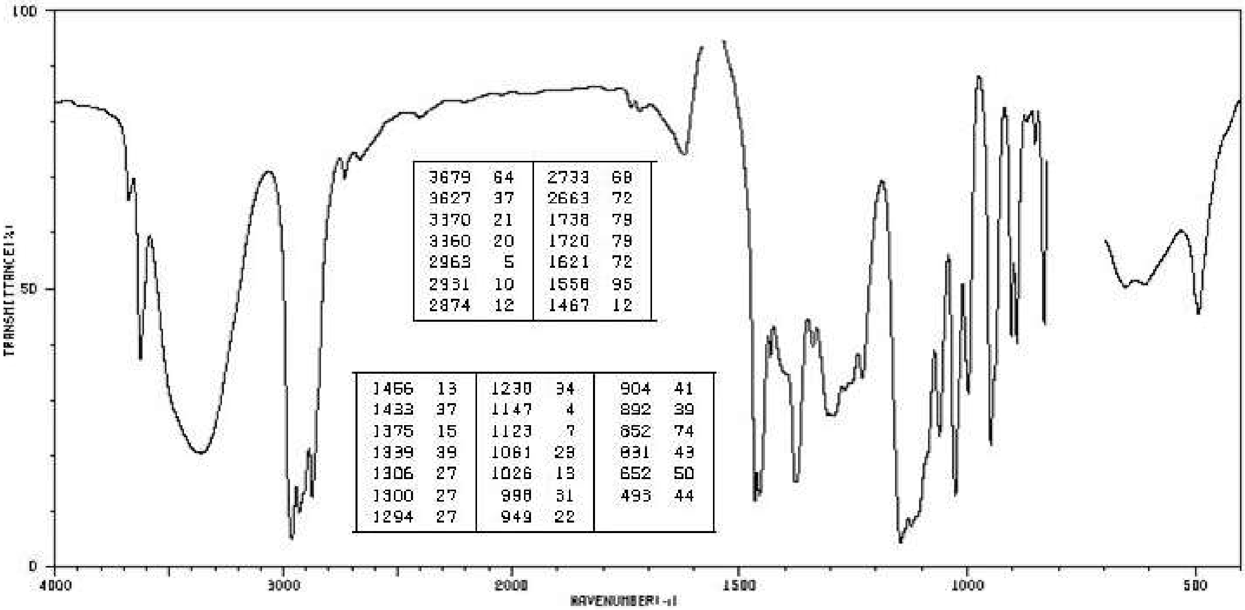
3079	66	1467	49	1103	84	461	84
2961	6	1446	64	1038	81		
2929	4	1438	56	994	36		
2874	22	1416	72	912	9		
2861	25	1379	64	636	72		
1827	84	1300	84	558	81		
1467	43	1144	86	466	84		

Spectrum 4



3926	79	1463	70	847	20
3373	26	1437	62	649	16
3291	4	1383	62	543	43
2926	43	1337	38		
2853	50	1280	68		
2104	81	1070	59		
1696	47	943	20		

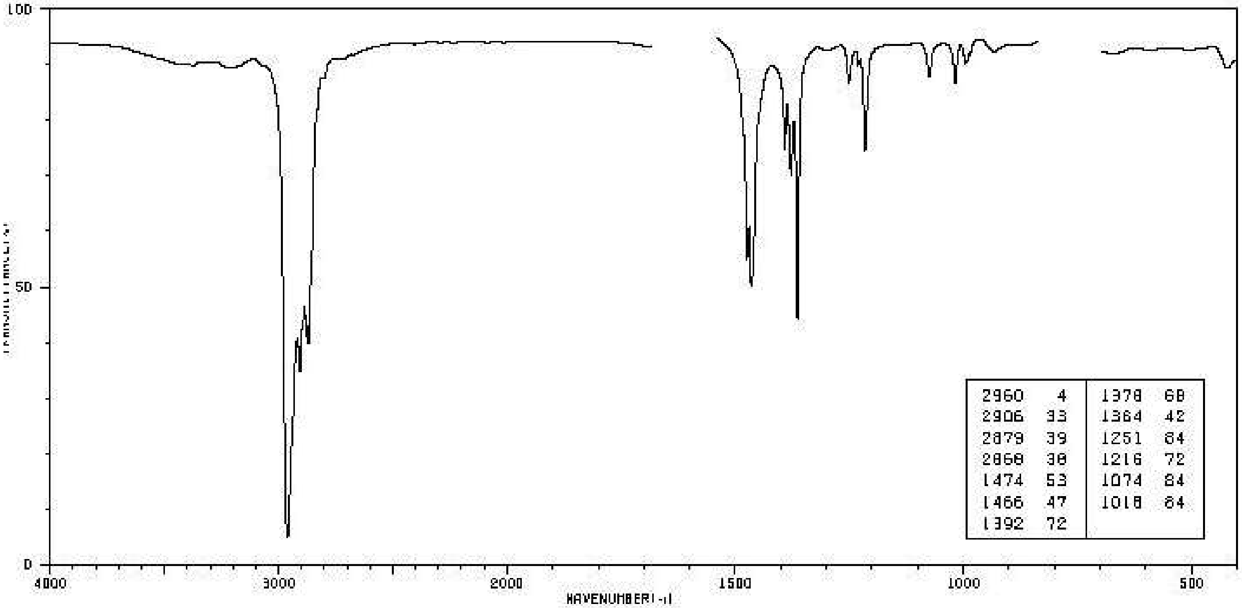
Spectrum 5



3679	64	2733	68
3627	37	2663	72
3370	21	1738	79
3360	20	1720	79
2963	5	1621	72
2931	10	1558	95
2874	12	1467	12

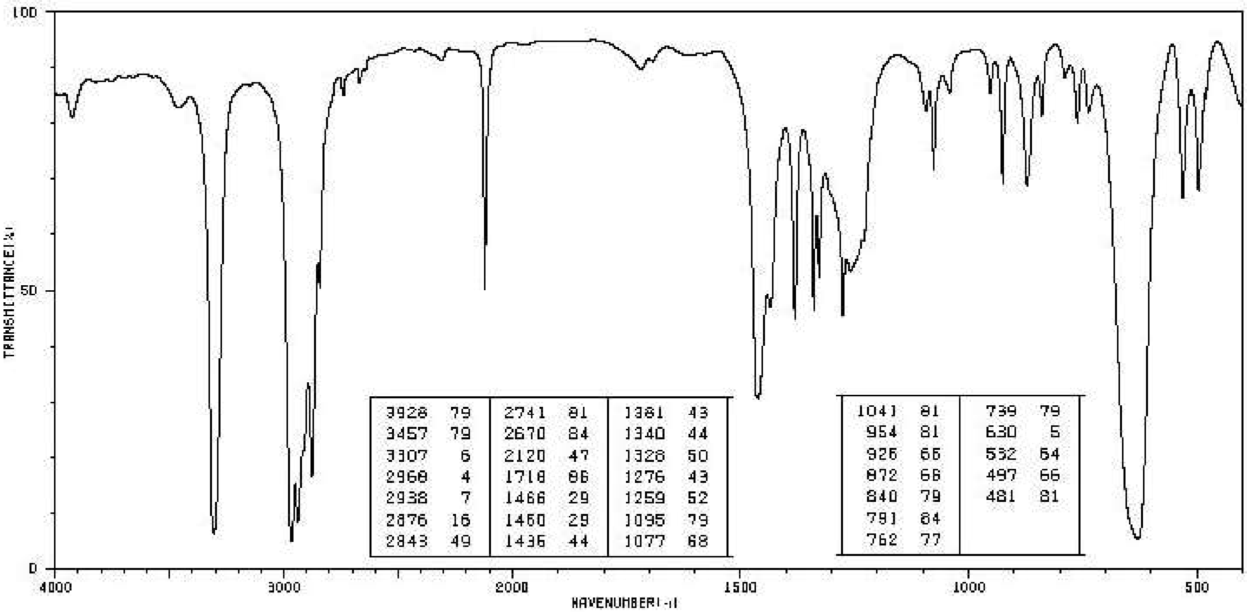
1466	13	1230	34	904	41
1433	37	1147	4	892	39
1375	15	1123	7	852	74
1339	39	1061	28	831	43
1306	27	1026	13	652	50
1300	27	998	31	493	44
1294	27	949	22		

Spectrum 6



2960	4	1378	68
2906	33	1364	42
2879	39	1251	64
2868	38	1216	72
1474	53	1074	84
1466	47	1018	64
1392	72		

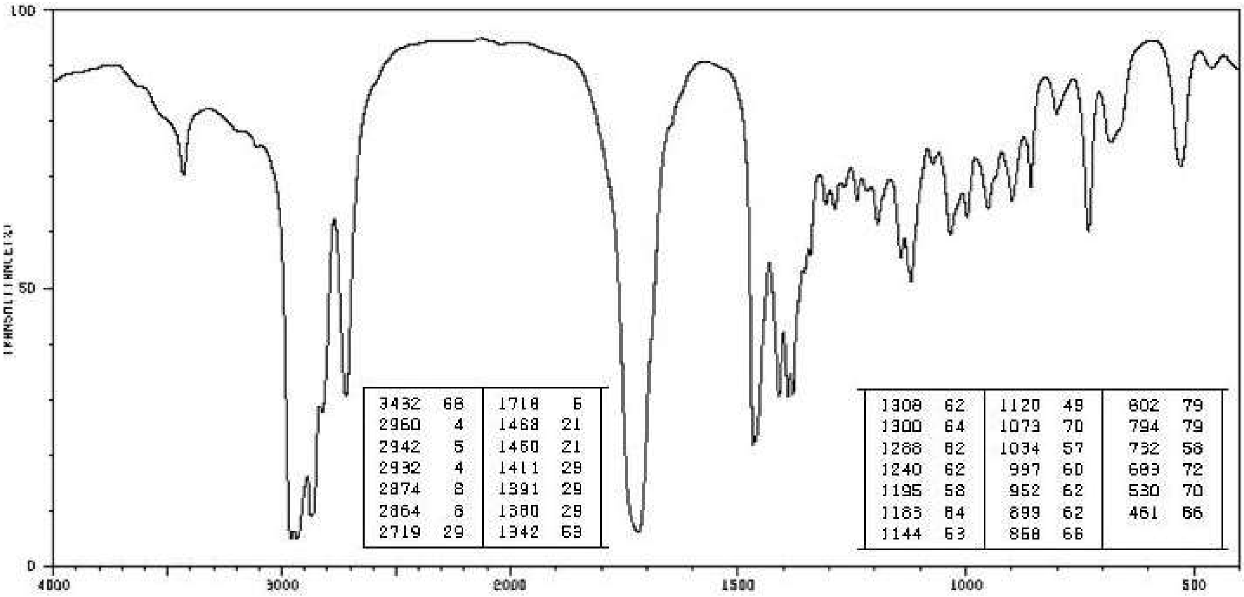
Spectrum 7



3928	79	2741	81	1381	43
3457	79	2670	84	1340	44
3307	6	2120	47	1328	50
2968	4	1718	86	1276	43
2938	7	1466	29	1259	52
2876	16	1460	29	1095	79
2843	49	1436	44	1077	68

1041	81	739	79
954	81	630	5
926	66	532	64
872	66	497	66
840	79	481	81
791	84		
762	77		

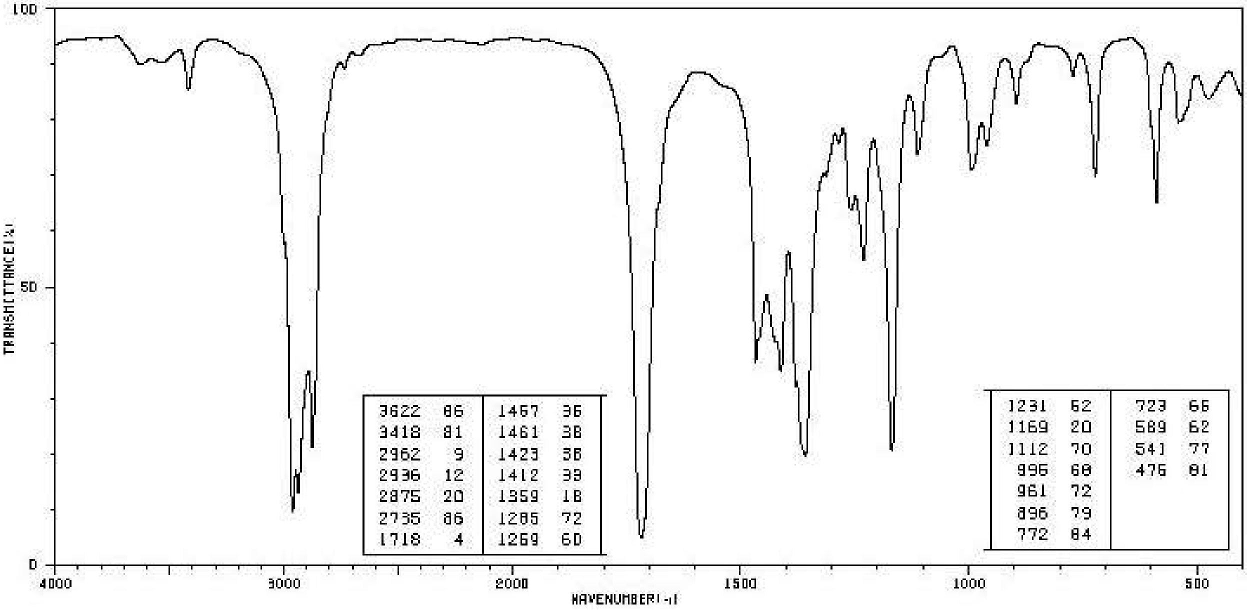
Spectrum 8



3432	68	1718	6
2960	4	1468	21
2942	5	1460	21
2932	4	1411	29
2874	8	1391	29
2864	6	1380	29
2719	29	1342	63

1308	62	1120	49	802	79
1300	64	1073	70	794	79
1288	82	1034	57	732	58
1240	62	997	60	683	72
1195	58	952	62	530	70
1183	84	899	62	461	66
1144	63	868	66		

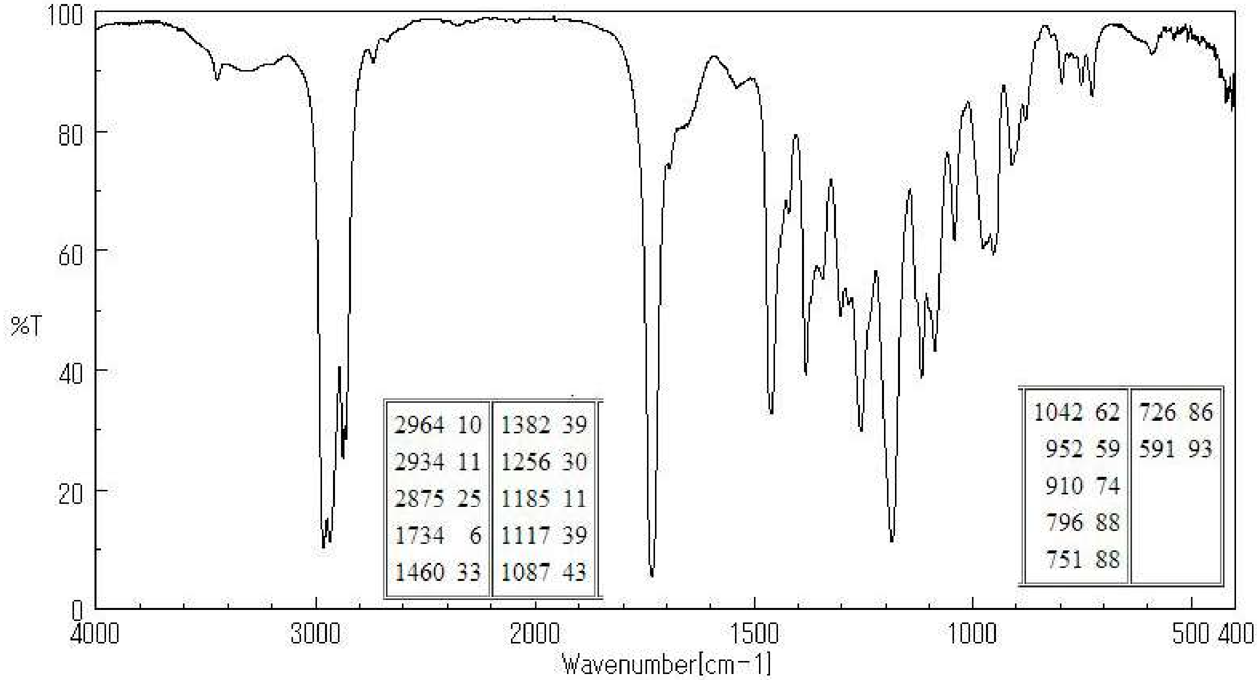
Spectrum 9



3622	86	1467	36
3418	81	1461	38
2962	9	1423	38
2936	12	1412	33
2875	20	1359	18
2735	86	1285	72
1718	4	1269	60

1231	62	723	66
1169	20	589	62
1112	70	541	77
996	68	476	81
961	72		
896	79		
772	84		

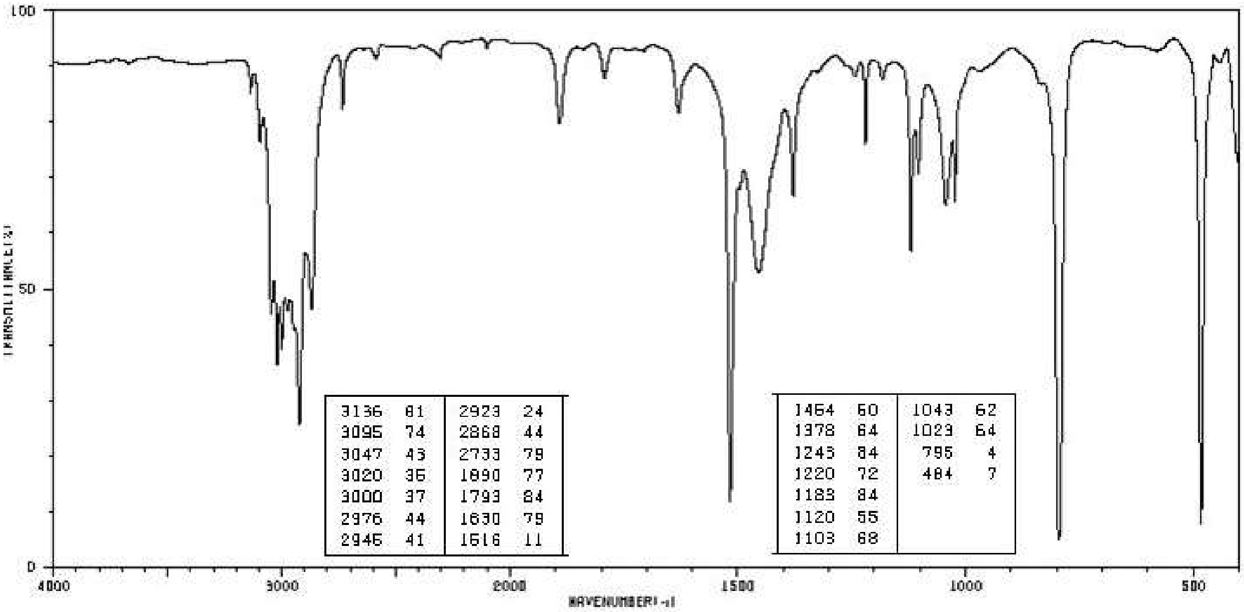
Spectrum 10



2964	10	1382	39
2934	11	1256	30
2875	25	1185	11
1734	6	1117	39
1460	33	1087	43

1042	62	726	86
952	59	591	93
910	74		
796	88		
751	88		

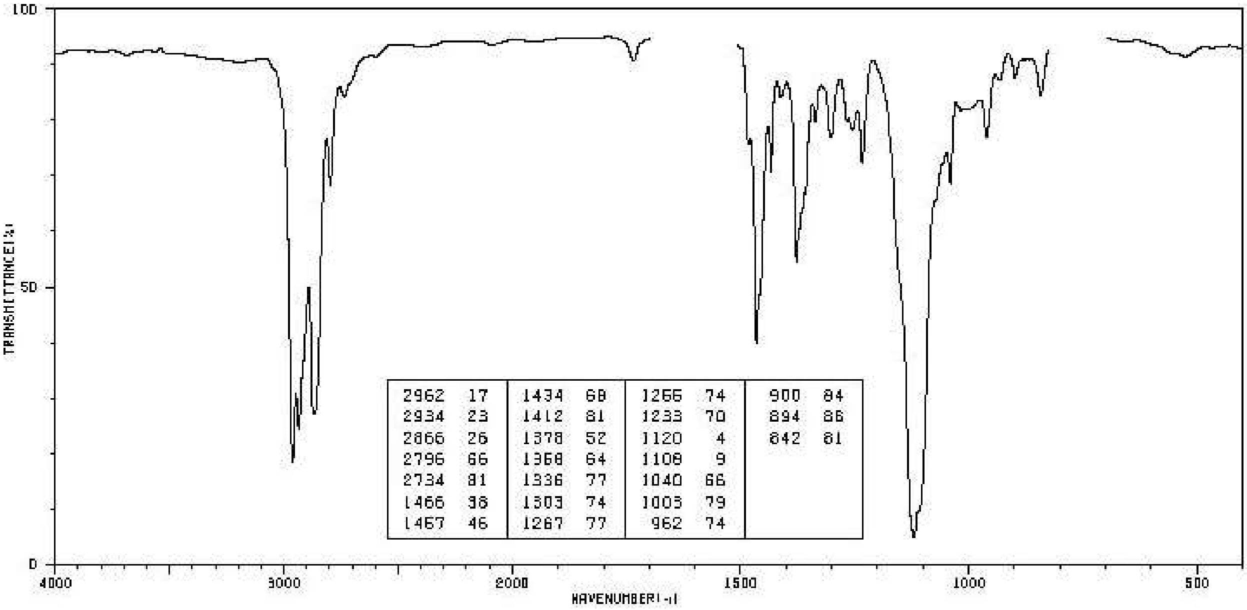
Spectrum 11



3136	81	2923	24
3095	74	2868	44
3047	43	2733	79
3020	36	1890	77
3000	37	1793	84
2976	44	1630	79
2946	41	1616	11

1464	60	1043	62
1378	64	1023	64
1243	84	795	4
1220	72	484	7
1183	84		
1120	55		
1103	68		

Spectrum 12



2962	17	1434	68	1266	74	900	84
2934	23	1412	81	1233	70	894	86
2866	26	1378	52	1120	4	842	81
2796	66	1368	64	1108	9		
2734	81	1336	77	1040	66		
1466	38	1303	74	1003	79		
1467	46	1267	77	962	74		

Name: ________________________________ Date: ___________________ Score: _____/20

Prelab Questions

1. Define the term "Functional Group Region" **AND** "Fingerprint Region".

2. Complete the table below by drawing a each of the molecules in the procedure section in the appropriate category below.

Name	**Structure**	**Name**	**Structure**
Alkane		Aldehye	
Alkene		Ketone	
Alkyne		Carboxylic Acid	
Aromatic		Ester	
Alcohol		Amine	
Ether		Amide	

Hello!