IR Spectroscopy

Electromagnetic radiation has dual wave/particle properties. A photon is the particle of electromagnetic radiation. In a vacuum a photon travels at constant velocity $c = 2.998 \times 10^{8}\ \mathrm{m\ s^{-1}}$. The velocity is related to the frequency, v, and wavelength, λ:

$$c = \lambda v$$

The energy of a photon is proportional to its frequency, v. The proportionality constant is Planck's constant, $h = 6.626 \times 10^{-34}$ J s:

$$E = hv = \underline{hc/\lambda}$$

Photons with wavelengths from 100 nm to 800nm (frequency from $3.75 \times 10^{14}\ \mathrm{s^{-1}}$ to $3.00 \times 10^{15}\ \mathrm{s^{-1}}$) are sufficiently energetic to cause electronic transitions in molecules or atoms. These quantized transitions give information about atomic or molecular structure. The branch of spectroscopy known as electronic absorption spectroscopy is often called UV-VIS spectroscopy.

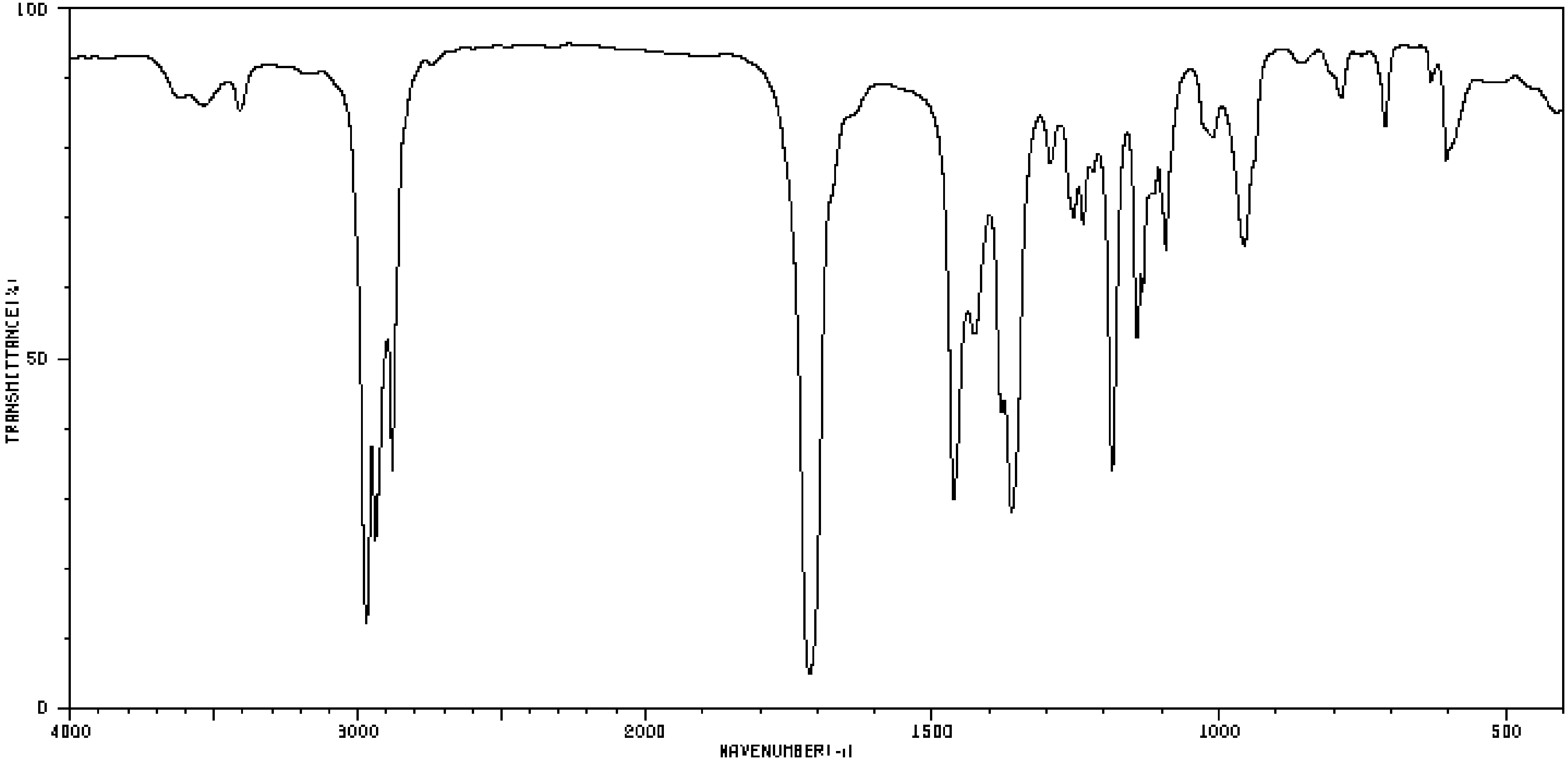
Less energetic radiation causes vibrational transitions within molecules. This vibrational motion is also quantized. Photons of wavelength from ca. 1000 nm to 30,000 nm cause these transitions. This infrared (IR) radiation is of longer wavelength (lower frequency) than visible red radiation. The practical range for infrared spectroscopy of organic compounds is about 2500 nm to 20,000 nm.

Frequency is more commonly used as a measurement in IR spectroscopy. The wavenumber ($\bar{v}$ expressed in units of cm^{-1}) is the standard frequency measure in IR spectroscopy:

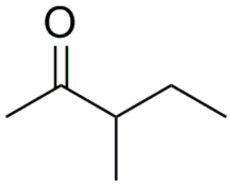
$$\bar{v}\ (\text{cm}^{-1}) = 1/\lambda\ (\text{cm}) = v\ (\text{s}^{-1})/c\ (\text{cm s}^{-1})$$

$\bar{v}$ is the frequency, v, divided by the speed of light in units of cm s^{-1}. The practical range of IR spectroscopy expressed in this unit is 4000 cm^{-1} to 500 cm^{-1}.

A typical IR spectrum is presented as % transmittance vs. $\bar{\nu}$, with higher frequency (higher energy) to the left:



3636	84	1426	62	1144	60	794	84
3411	81	1379	41	1133	57	787	84
2969	11	1362	26	1093	82	711	79
2938	23	1294	74	1027	79	631	86
2879	32	1254	68	1016	79	604	74
1714	4	1237	66	1011	79	599	77
1462	28	1187	32	956	64		



Functional groups such as OH or C=O tend to absorb radiation in a narrow frequency range in *any* compound in which they are found. These ranges are called functional group frequencies. A table of group frequencies has been provided for you. For organic compounds the functional group range lies between ca. 4000 to 1000 cm^{-1}.

The carbonyl stretching frequency is very important because there are many classes of compounds that have this group. You can identify which class by a detailed knowledge of how structural variations such as ring size and π-conjugation affect the frequency of absorption.

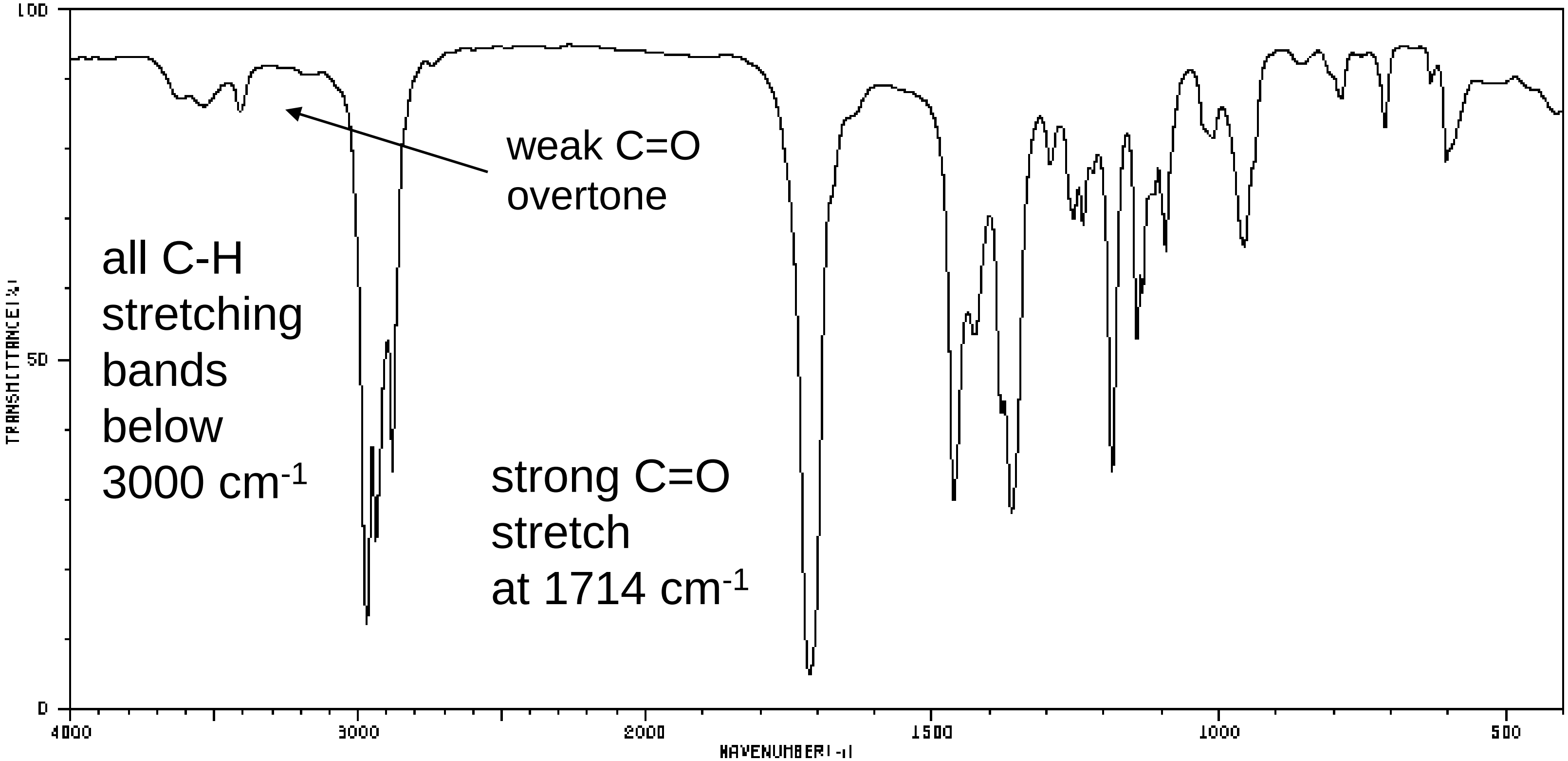
All distinct compounds afford unique IR spectra. A particularly useful part of the IR frequency range for establishing unique identity is the range from ca. 1500 cm^{-1} to 500 cm^{-1}. There is some overlap with the functional group range. This frequency range is called the fingerprint region because it appears that all compounds have a unique absorption spectrum in this region.

The carbonyl group in IR spectroscopy

The carbonyl group (C=O) occurs in a large number of organic compounds (ketones, aldehydes, carboxylic acids, and their ester, amide, anhydride, acid chloride, and thioester derivatives). IR spectroscopy is very useful for identifying these compounds because the carbonyl stretching band is very intense, and is located in a part of the IR spectrum (ca. 1650-1850 cm^{-1}) where there is very little interference from other functional groups. The characteristic carbonyl absorption frequency is sensitive to the type of carbonyl compound, and to ring size and π-conjugation effects, so it is very often possible to make an identification of the specific type of carbonyl compound from an investigation of its IR spectrum. On the next few pages we will examine the carbonyl absorption band in a number of common carbonyl containing functional groups.

Ketones

Aliphatic ketone: (1710 ± 10) cm^{-1} strong, sharp band

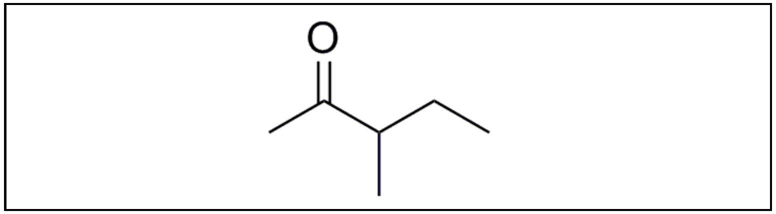


weak C=O overtone

all C-H stretching bands below 3000 cm^{-1}

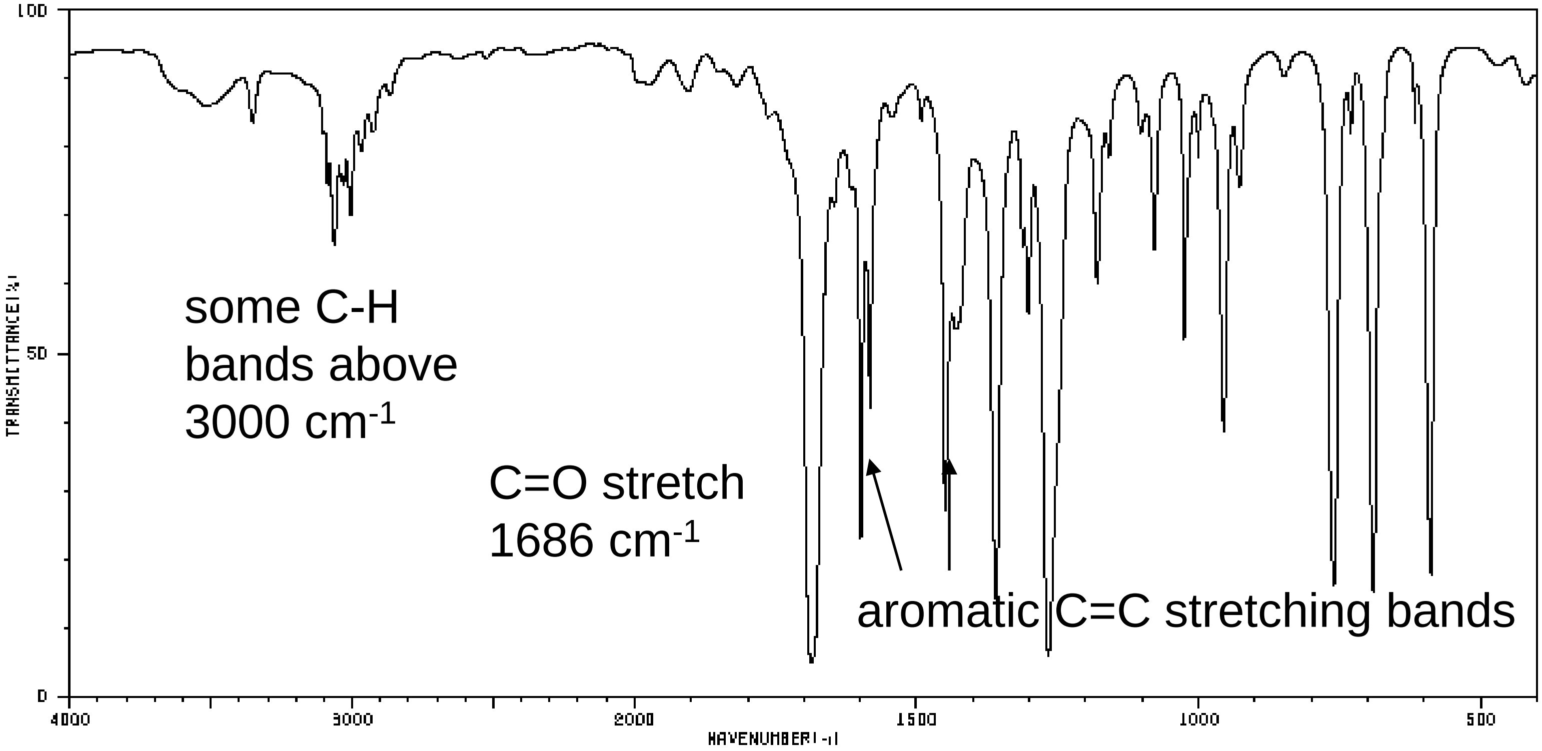
strong C=O stretch at 1714 cm^{-1}

3636	84	1426	62	1144	60	794	84
3411	81	1379	41	1133	57	787	84
2969	11	1362	26	1093	82	711	79
2938	23	1294	74	1027	79	631	86
2879	32	1254	68	1016	79	604	74
1714	4	1237	66	1011	79	599	77
1462	28	1187	32	966	64		



Conjugation

π-conjugation reduces the carbonyl absorption band frequency by ca. 30 cm^{-1} in ketones and other carbonyl compounds

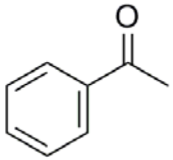


some C-H bands above 3000 cm^{-1}

C=O stretch 1686 cm^{-1}

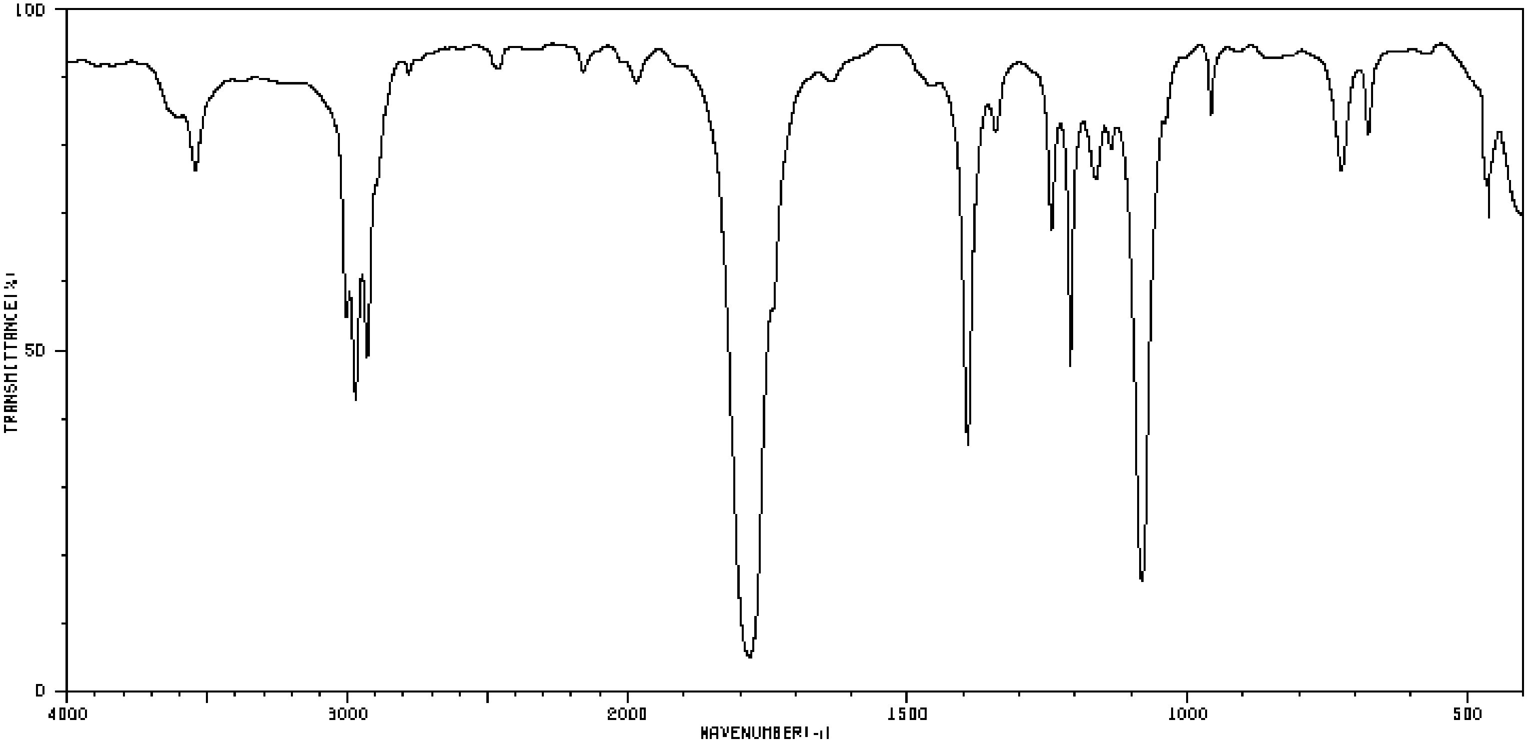
aromatic C=C stretching bands

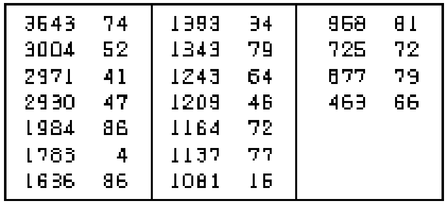
3604	84	2967	77	1646	81	1267	6	966	37
3352	81	2925	79	1492	81	1181	58	928	72
3087	72	2867	84	1450	26	1160	74	761	15
3063	64	1686	4	1430	62	1103	79	731	79
3040	72	1646	68	1360	13	1079	62	691	14
3029	72	1599	21	1313	82	1025	50	618	61
3006	68	1583	41	1303	63	1001	74	588	17



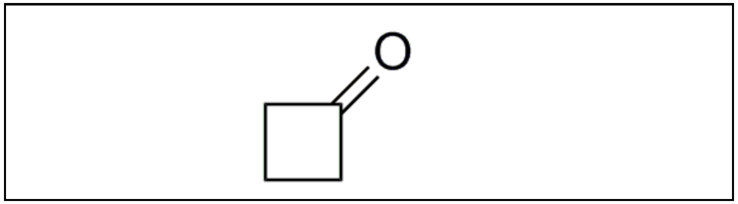
Ring size effects

Decreasing ring size (< 6 member ring) increases C=O stretching frequency: Cyclohexanone 1710 cm^{-1} Cyclopentanone 1747 cm^{-1} Cyclobutanone 1783 cm^{-1}



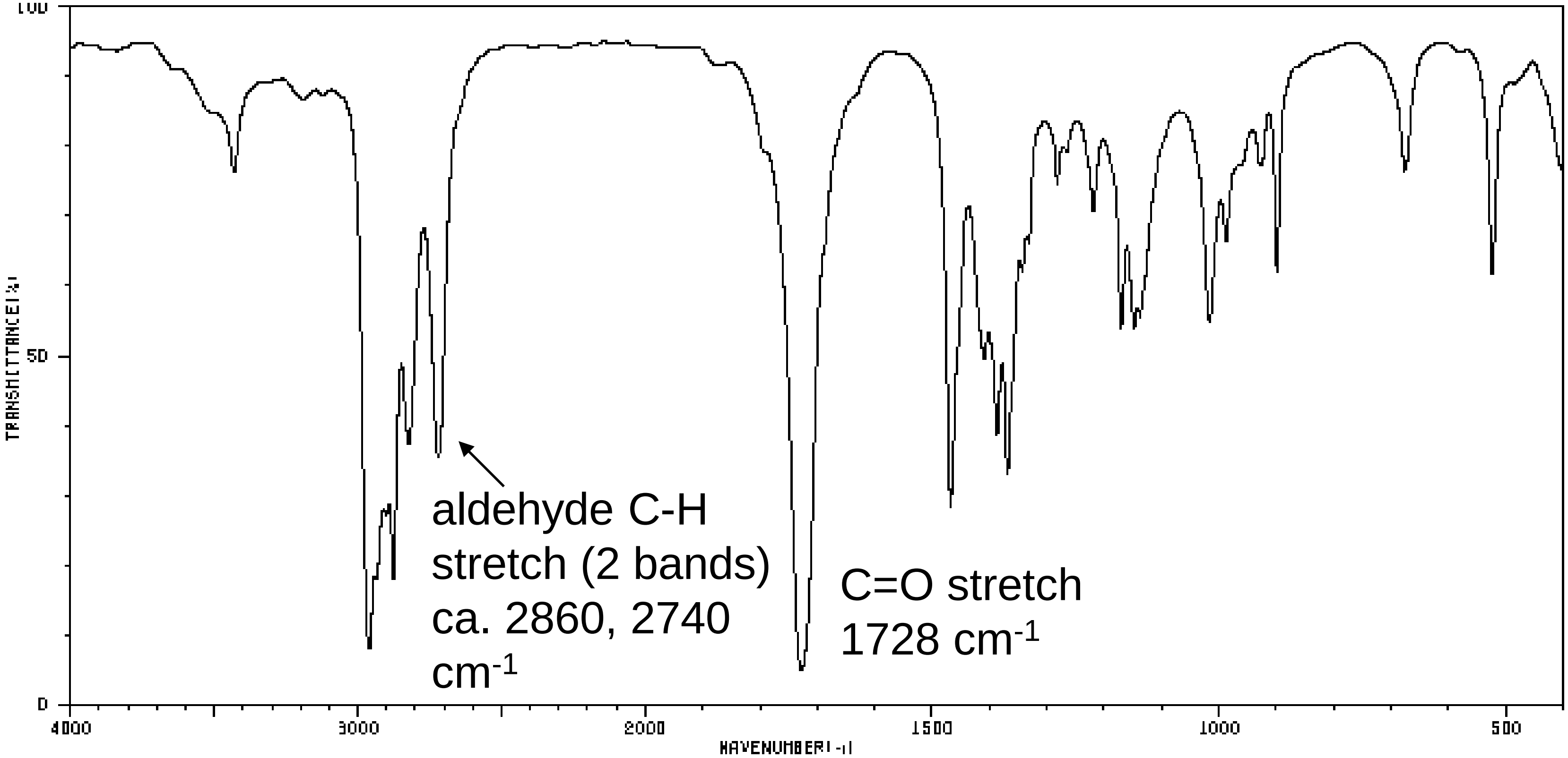


3643	74	1393	34	968	81
3004	52	1343	79	725	72
2971	41	1243	64	877	79
2930	47	1209	46	463	66
1984	86	1164	72		
1783	4	1137	77		
1636	86	1081	16		



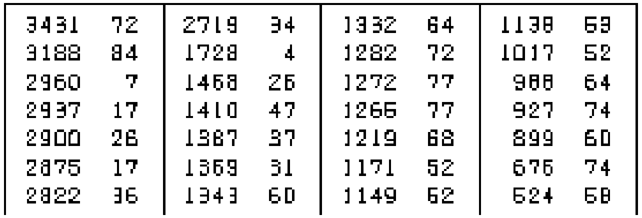
Aldehydes

Aliphatic aldehyde: 1725 ± 10 cm^{-1} strong, sharp band

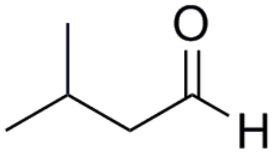


aldehyde C-H stretch (2 bands) ca. 2860, 2740 cm^{-1}

C=O stretch 1728 cm^{-1}

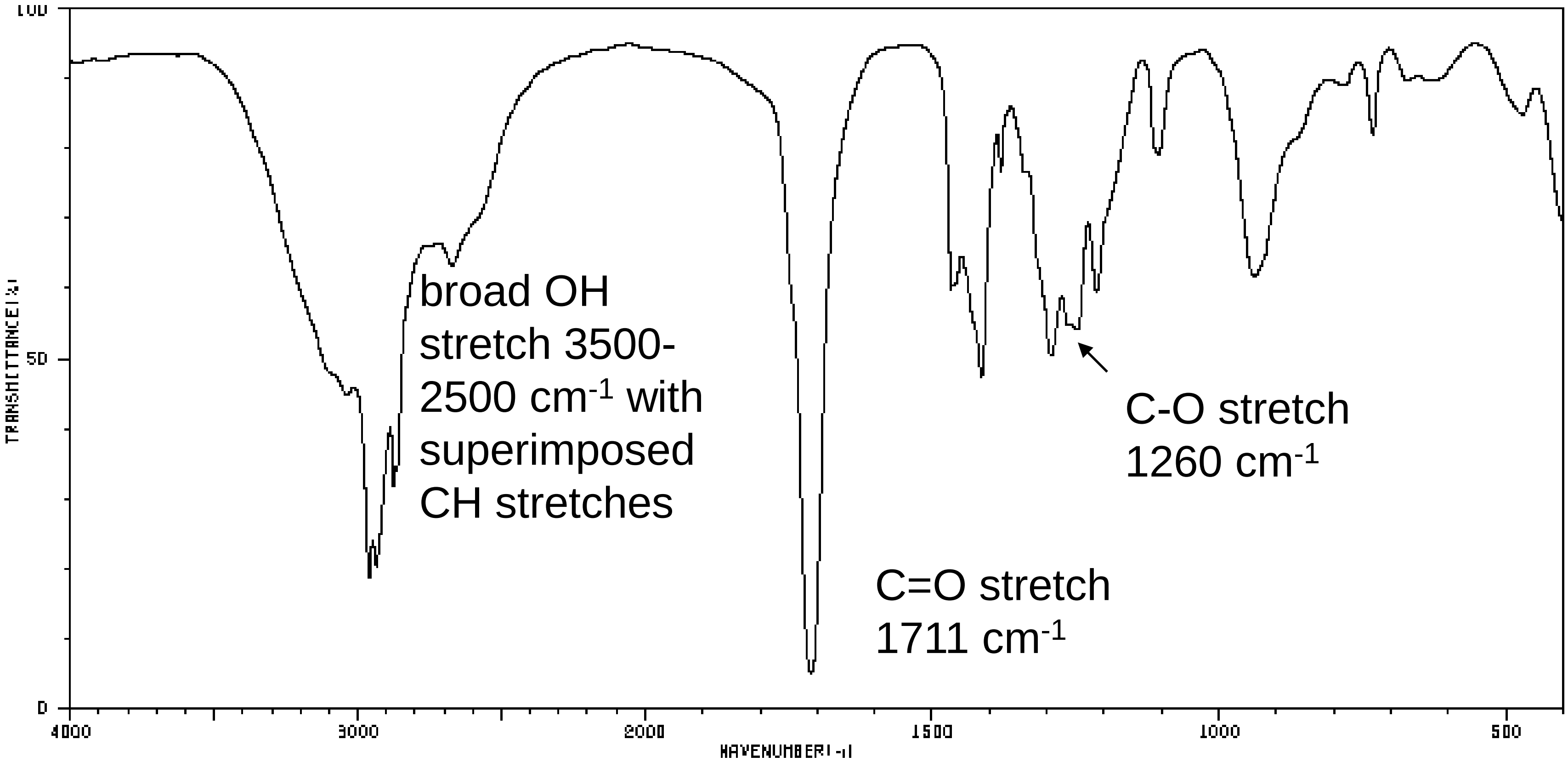


3431	72	2719	34	1332	64	1138	69
3188	84	1728	4	1282	72	1017	52
2960	7	1468	26	1272	77	988	64
2937	17	1410	47	1266	77	927	74
2900	26	1387	37	1219	68	899	60
2875	17	1369	31	1171	52	676	74
2822	36	1343	60	1149	62	624	68



Carboxylic Acids

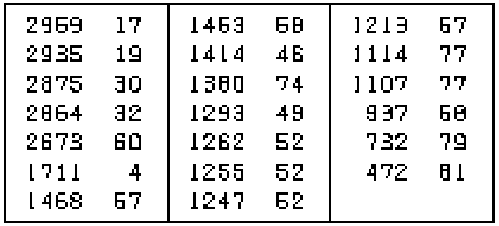
Aliphatic acid: (1710 ± 10) cm^{-1}



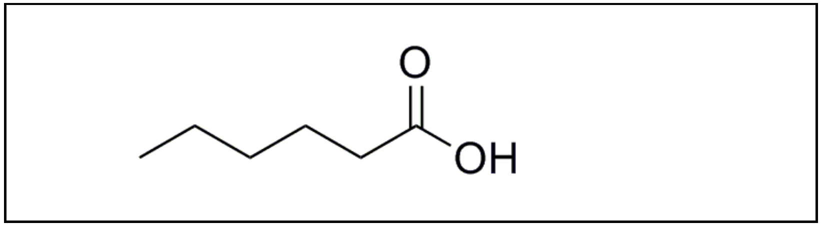
broad OH stretch 3500-2500 cm^{-1} with superimposed CH stretches

C-O stretch 1260 cm^{-1}

C=O stretch 1711 cm^{-1}

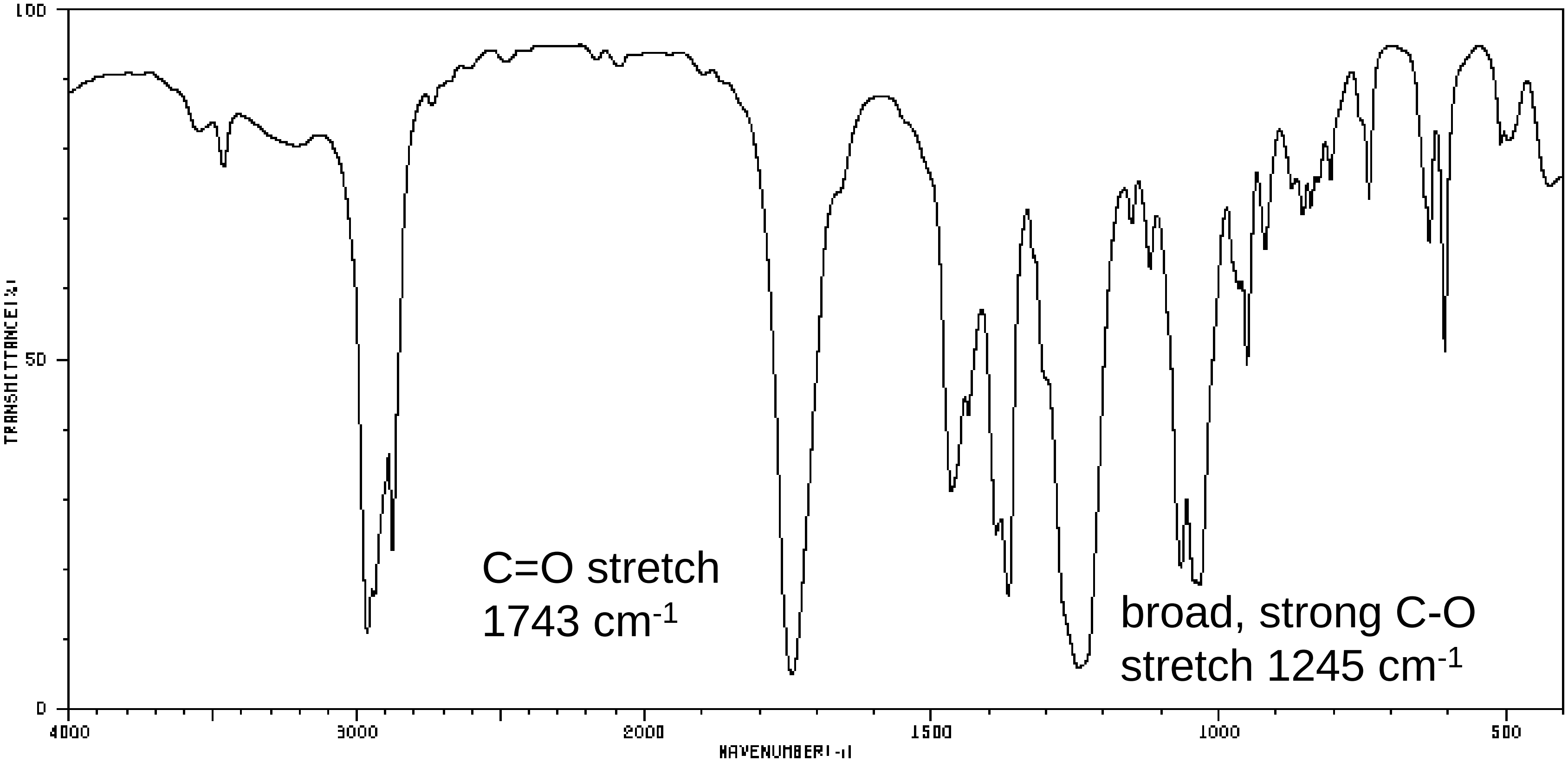


2969	17	1463	68	1213	67
2935	19	1414	46	1114	77
2875	30	1380	74	1107	77
2864	32	1293	49	937	68
2673	60	1262	52	732	79
1711	4	1255	52	472	81
1468	67	1247	62		



Esters

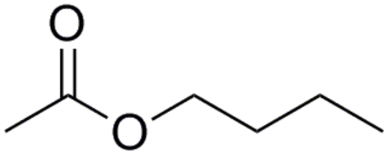
Aliphatic ester: 1740 ± 10 cm^{-1}



C=O stretch
1743 cm^{-1}

broad, strong C-O
stretch 1245 cm^{-1}

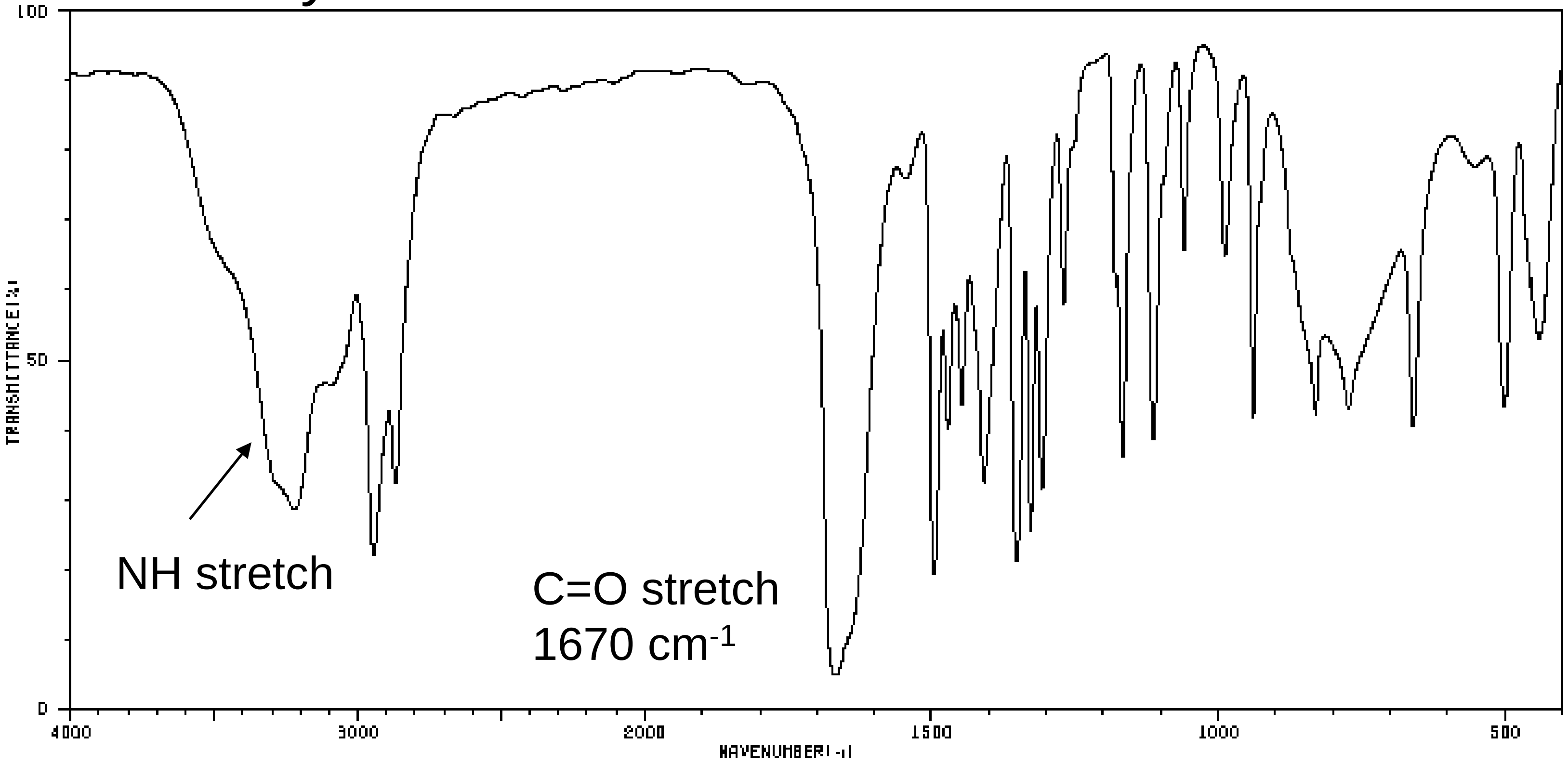
3646	79	1467	30	1066	19	874	72	609	77
3463	74	1436	41	1044	17	853	68	495	79
2963	10	1388	25	1038	17	840	68	425	72
2938	16	1367	16	1032	17	806	72		
2876	21	1244	5	965	58	739	70		
2738	84	1152	66	951	47	634	64		
1743	4	1120	60	919	64	606	48		



Amides

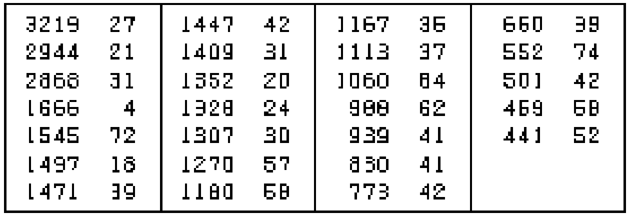
Aliphatic amide: (1660 ± 10) cm^{-1}

A secondary amide:

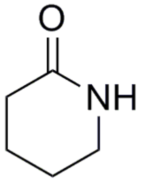


NH stretch

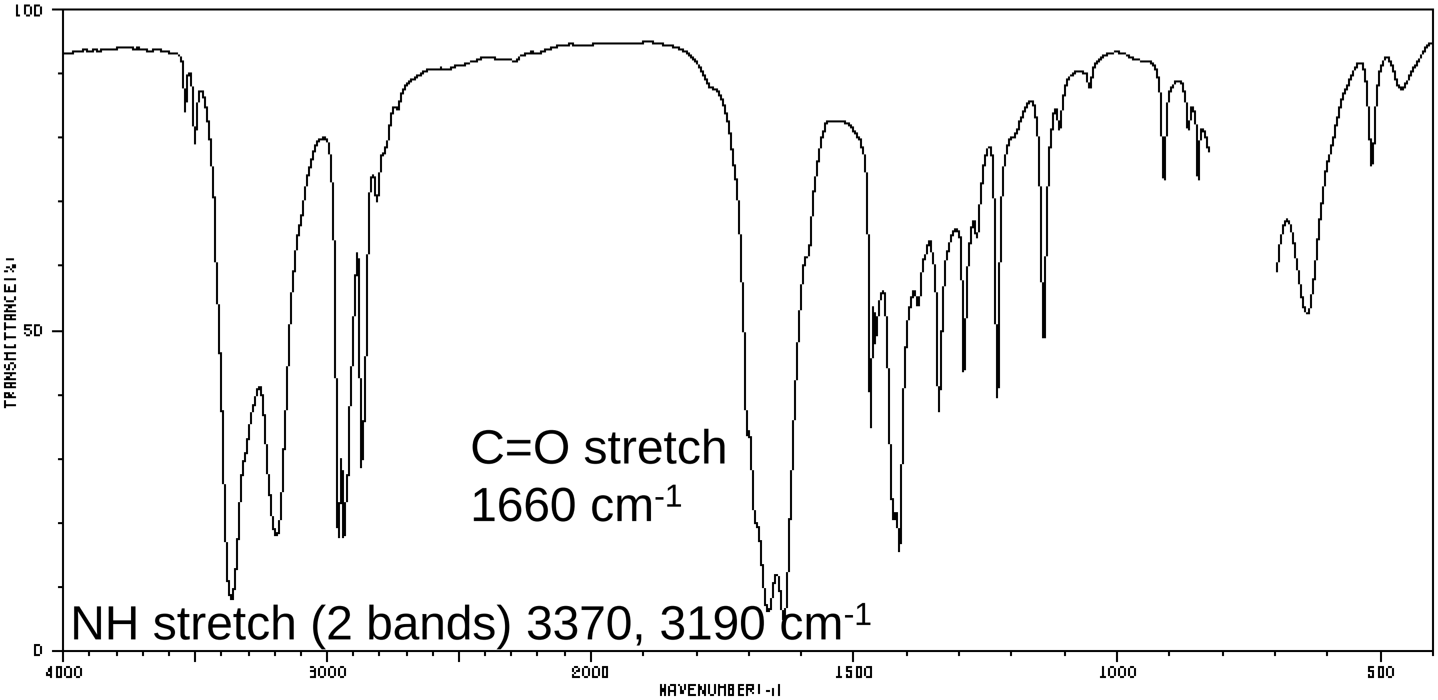
C=O stretch
1670 cm^{-1}



3219	27	1447	42	1167	36	660	39
2944	21	1409	31	1113	37	552	74
2868	31	1352	20	1060	84	501	42
1666	4	1328	24	988	62	469	68
1545	72	1307	30	939	41	441	52
1497	18	1270	57	830	41		
1471	39	1180	68	773	42		



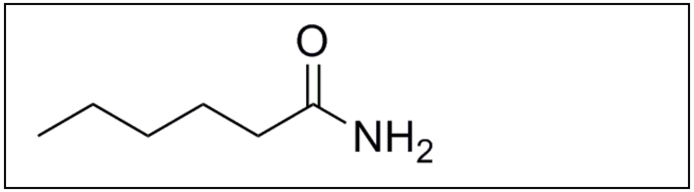
A primary amide:



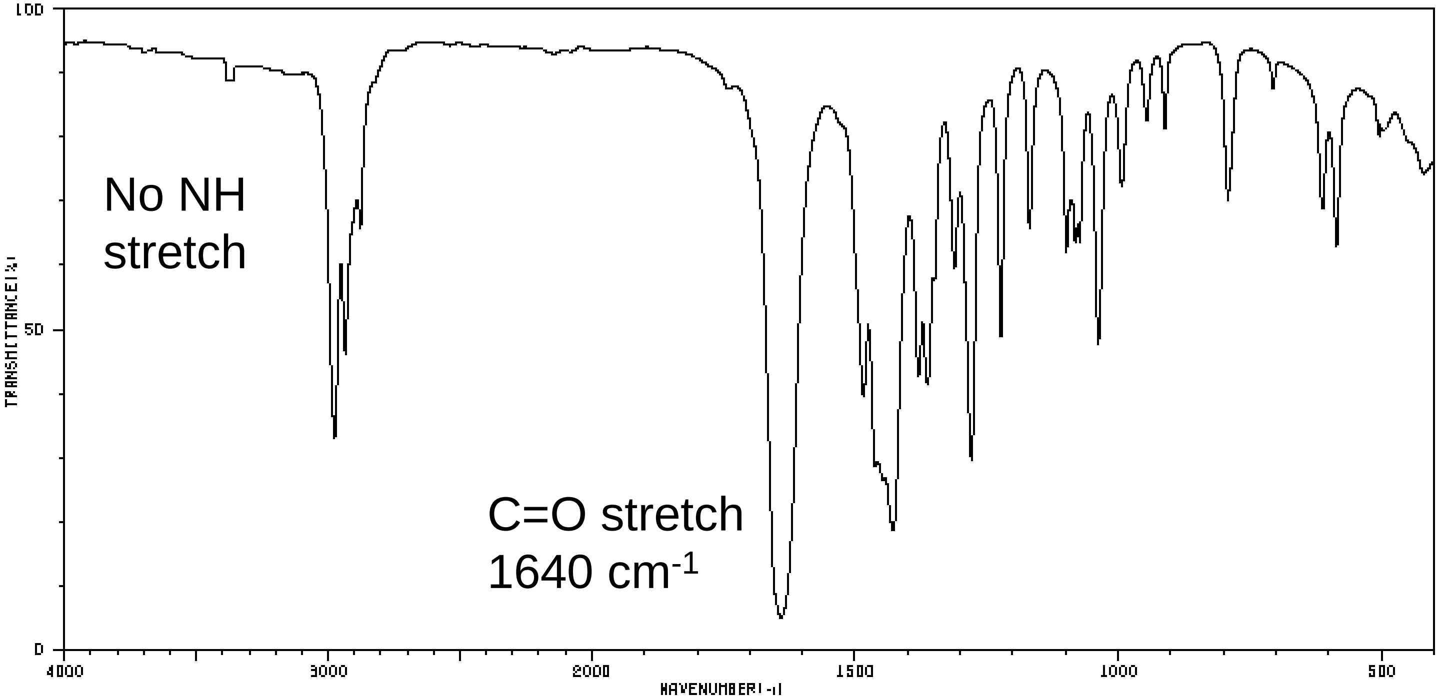
C=O stretch
1660 cm^{-1}

NH stretch (2 bands) 3370, 3190 cm^{-1}

3639	81	2811	68	1379	62	1062	84
3501	77	1663	5	1339	36	911	70
3363	7	1633	4	1292	42	866	79
3193	17	1469	33	1267	62	846	70
2957	17	1460	46	1228	38	639	50
2937	17	1424	20	1140	47	517	72
2870	27	1414	14	1110	79	460	84



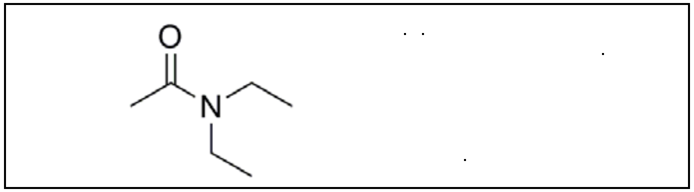
A tertiary amide:



No NH
stretch

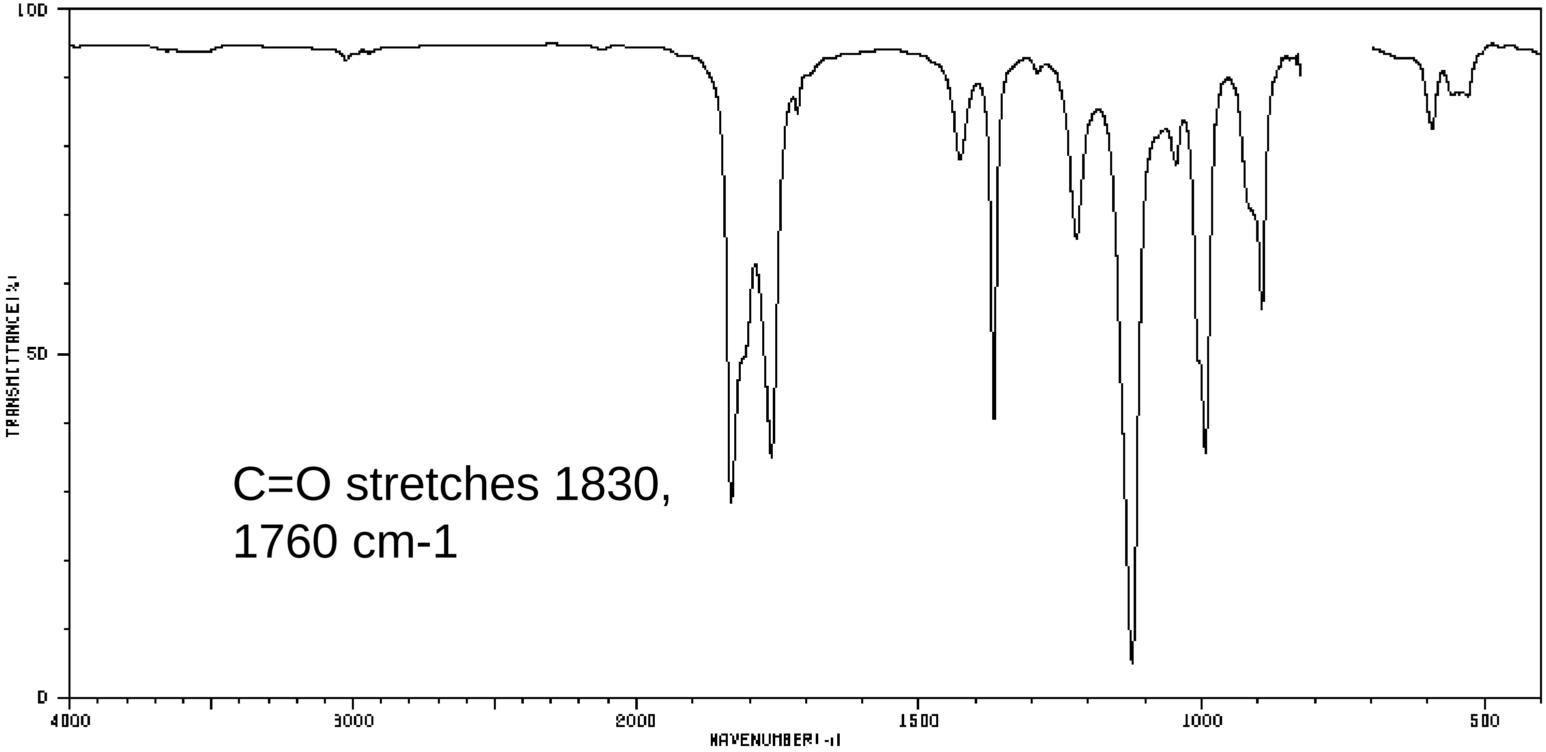
C=O stretch
1640 cm^{-1}

3471	68	1428	18	1098	60	792	68
2975	32	1380	41	1082	60	706	84
2934	44	1363	39	1074	80	612	66
2877	64	1311	67	1038	46	586	60
1640	4	1279	28	993	70	505	77
1484	38	1223	47	946	79	496	79
1443	26	1169	64	911	79		



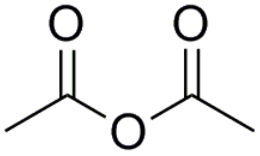
Anhydrides

Aliphatic anhydride: 1820, 1760 cm^{-1} (two bands)



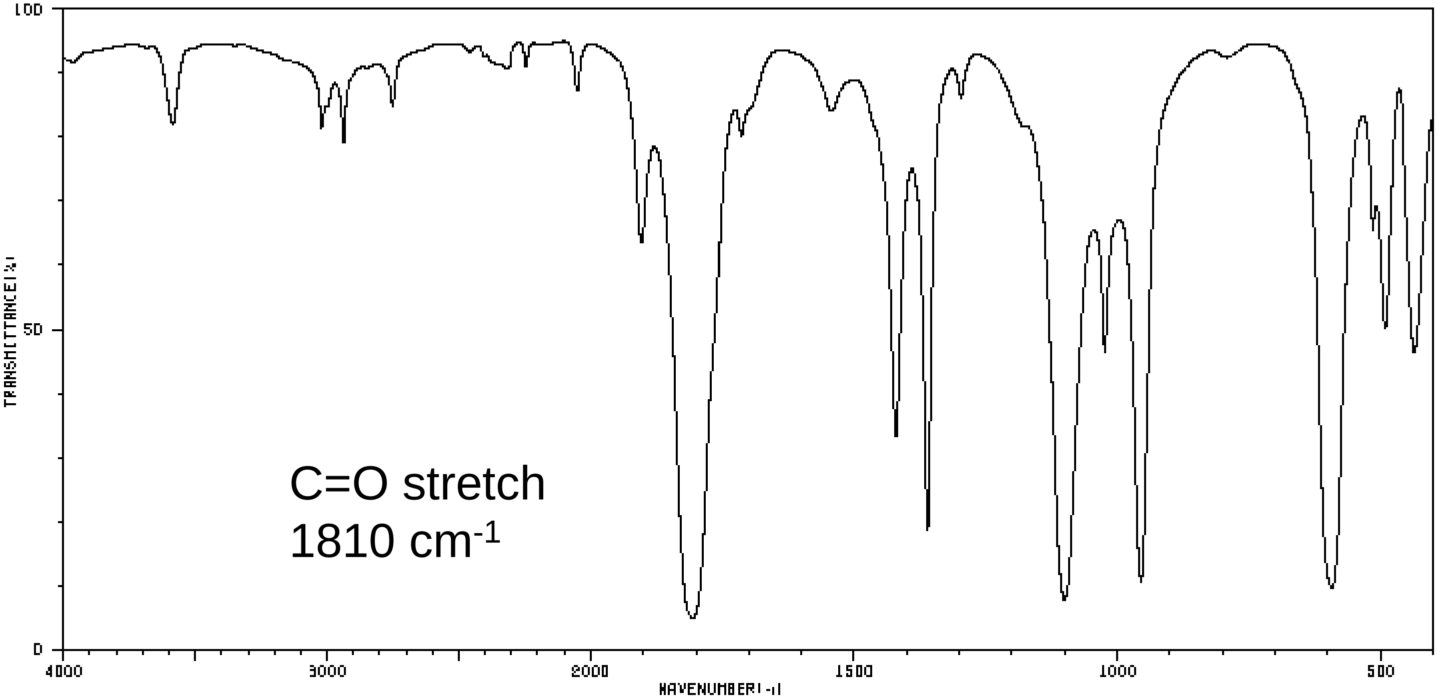
C=O stretches 1830, 1760 cm-1

1832	26	1046	74	640	84
1761	33	1005	46		
1715	81	994	34		
1428	74	894	63		
1368	38	603	84		
1222	84	593	79		
1124	4	647	84		



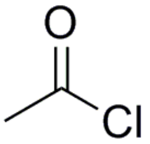
Acid Chlorides

Aliphatic acid chloride: (1820 ± 10) cm^{-1}



C=O stretch
1810 cm^{-1}

3686	79	1806	4	1024	44
3020	79	1714	77	955	10
2997	81	1542	81	595	9
2937	77	1421	32	616	62
2751	81	1361	18	491	47
2051	84	1297	84	481	84
1903	60	1100	7	436	44



Other easily detected functional groups

Alcohols, ROH

OH stretch 3200 - 3600 cm^{-1} strong, often broad

OH bend 1050 - 1200 cm^{-1} strong, frequency increases in order 1°, 2°, 3°, phenol

C-O stretch 1260 - 1410 cm^{-1}

Nitriles RCN

C≡N stretch 2210-2260 cm^{-1} medium intensity, sharp

Alkynes RC≡CR

C≡C stretch 2100 – 2260 cm^{-1} variable intensity, sharp

≡C-H stretch 3300 cm^{-1} strong, terminal alkynes only

USING A MOLECULAR FORMULA AND SPECTROSCOPIC DATA TO SOLVE STRUCTURAL PROBLEMS

EMPIRICAL FORMULA: obtained from whole number ratio of elements in a particular molecule.

Example: C_3H_6O

The empirical formula is determined as shown below from quantitative elemental analysis data usually expressed as a weight% of each element present:

Convert to whole number ratios:

62.04% $C/12.01 = 5.17$ $5.17/1.72 = 3.01 \approx 3$

10.42% $H/1.008 = 10.34$ $10.34/1.72 = 6.01 \approx 6$

27.55% $O/16.00 = 1.72$ $1.72/1.72 = 1$

MOLECULAR FORMULA: the formula that expresses the number of moles of each element in a mole of the molecule.

The Empirical Formula **is not** the Molecular Formula. Any multiple of the empirical formula would also give the same elemental analysis:

Possible Molecular Formulae for this example:

C_3H_6O $C_6H_{12}O_2$ $C_9H_{18}O_3$ $C_{12}H_{24}O_4$ etc.

Corresponding (Whole Number) Molecular Mass:

58 116 174 232

To determine the molecular formula it is also necessary to know the molecular mass (mass spectrometry provides this information). In the present example, if the molecular mass is 116, the molecular formula must be:

$C_6H_{12}O_2$ twice the empirical formula.

Index of Hydrogen Deficiency or Index of Unsaturation (I):

Defined for formula $\alpha_{\mathrm{I}}\beta_{\mathrm{II}}\gamma_{\mathrm{III}}\delta_{\mathrm{IV}}$:

$\mathrm{I} = \mathrm{IV} - \mathrm{I}/2 + \mathrm{III}/2 + 1$

Where:

α = all elements of valence 1 (H, D, halogens)

β = all elements of valence 2 (O, S, etc.)

γ = all elements of valence 3 (N, P, etc.)

δ = all elements of valence 4 (C, Si, etc.)

The Index of Unsaturation provides the number of double bonds or double bond equivalents in the molecule:

C=C, C=O, $\mathrm{I} = 1$, One saturated ring (cyclohexane, etc.), $\mathrm{I} = 1$

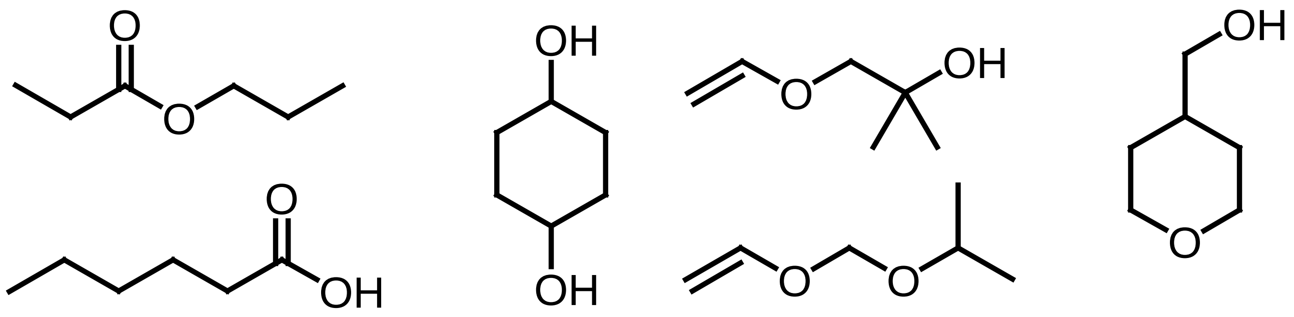
C≡C, C≡N, $\mathrm{I} = 2$, One benzene ring, $\mathrm{I} = 4$

A value of $I = 2$ would mean that the structure has 2 double bonds, or one double bond and one ring, or two rings, or one triple bond. A structure with one double bond and one triple bond, for example, would be impossible for a molecular formula with $I = 2$, because the double bond and triple bond would require $I = 3$.

In the present case of $C_6H_{12}O_2$:

$I = 6 – 12/2 + 1 = 1$ (Note that oxygens and other divalent atoms do not enter into the equation).

Some possible structures consistent with the formula:



Once you have the molecular formula and an IR spectrum you can solve structural problems using the following algorithm:

A. Calculate the Index of Unsaturation for the molecular formula. All structures must be consistent with the Index you have calculated.

B. Use the formula and Index to eliminate classes of compounds. For example, if the formula includes one O, all classes of compounds containing two O (such as esters or carboxylic acids) can be eliminated. If $I = 0$, your compound has no multiple bonds and no rings.

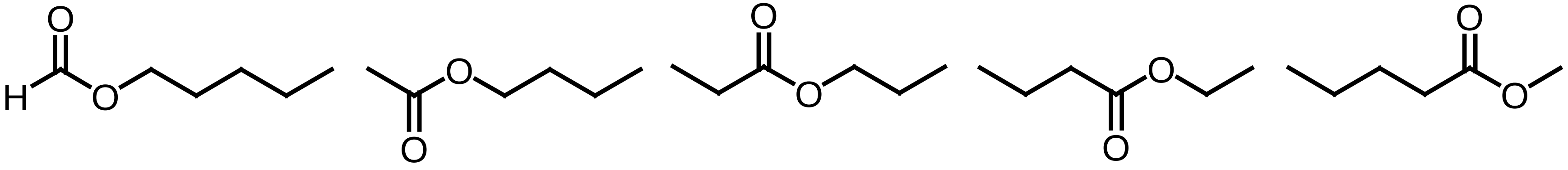
C. Use the IR data to establish the presence (or absence) of relatively easily established functional groups such as C=O (try to distinguish the type of carbonyl compound), C=C (careful, often weak), aromatic rings, C≡C (careful, often weak), C≡N, OH and/or NH or NH_2(molecular formula can help you distinguish these).

D. Draw provisional structures that contain the functional group(s) and that are consistent with the molecular formula and index of unsaturation. Start by drawing the functional groups, subtract those atoms from the molecular formula, and use the remaining atoms to form connections. Isomers of the structures you draw containing the same functional groups are also possible structures.

E. Go back to the IR to look for evidence of less readily observed functional groups (C-N, C-O, NO_2 etc.) if any of your provisional structures contain these. Look in the C-H region for C-H stretches of the frequency range required for the structure(s) you have drawn. Look for evidence you may have missed the first time for other functional groups if they appear in your provisional structures. C=C and C≡C are easy to miss in symmetric cases (they actually disappear in completely symmetric molecules). Rings have the same effect on the molecular formula as do multiple bonds.

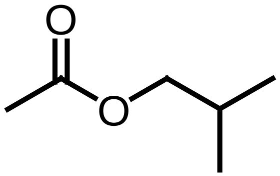
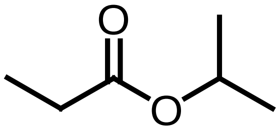
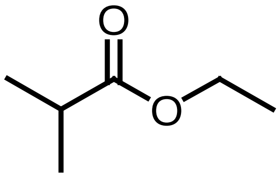
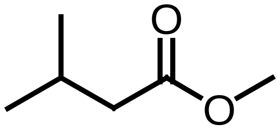
F. Refine/eliminate structures based on your re-examination of the IR data. With only a molecular formula and an IR spectrum it will rarely be possible to determine a unique structure. You will probably find yourself with a series of isomers containing the same functional group(s). NMR data discussed later this semester will allow you to readily distinguish isomers.

In our example of $C_6H_{12}O_2$ we already know that I = 1, indicating one double bond or one ring. If your IR data included strong sharp peaks at 1745 cm^{-1} and 1240 cm^{-1}, and no evidence of OH, you could confidently conclude that your compound is a saturated ester. This would still leave you with a significant number of possible structures, though:



This only includes unbranched isomers.

Some possible isomers with branched structures:

This is not a complete list of possible structures. We will be able to readily distinguish these structures by analysis of NMR spectra.

This week’s experiment

Part 1: analysis of characteristic functional group frequencies found in spectra of **known compounds** performed in **groups of 4 students**.

Part 2: identification of an unknown from its IR spectrum performed **individually**.

As always, the notebook entries and answers to the end of lab questions are prepared **individually**. Students may discuss questions posed during the experiment in Part 1 within the group.

Students turn in notebook pages with answers to questions as a **summary report**. **A copy of the IR spectrum of the unknown must be permanently attached to the notebook, and submitted as part of the summary report**.