Group Frequencies

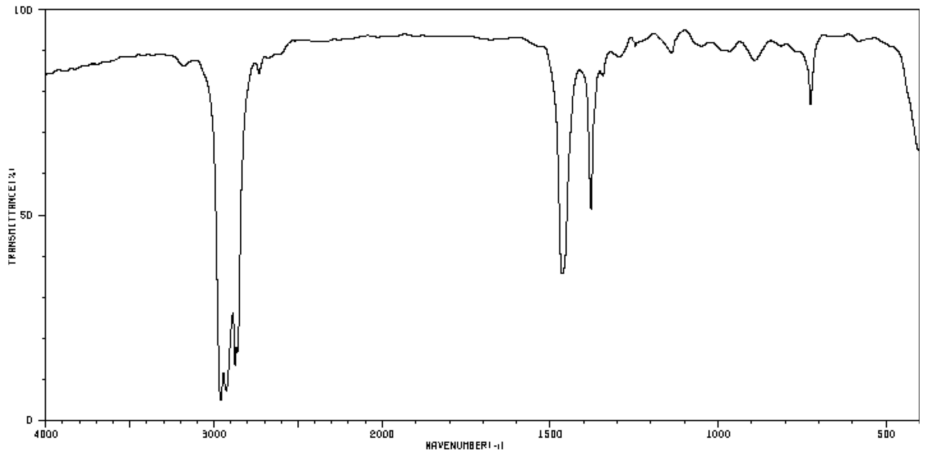
Functional Group Analysis

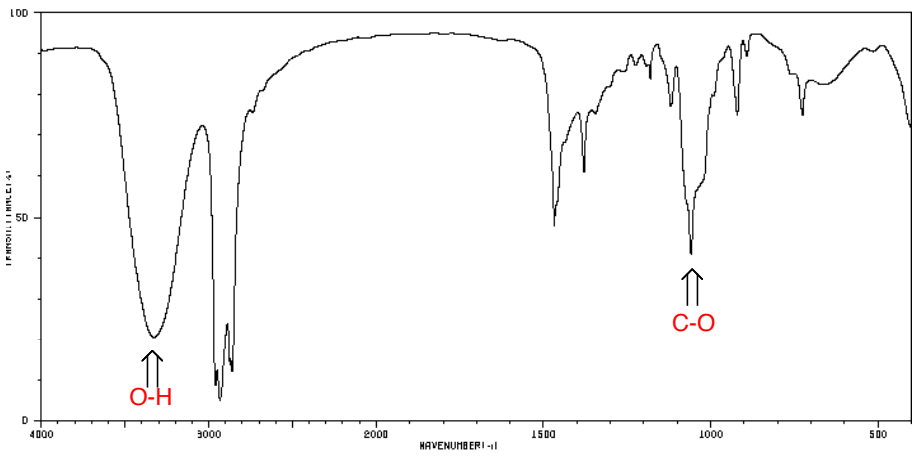
To Do's

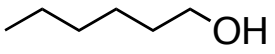
- Read Chapter 12. Skip Raman.
- Complete the end-of-chapter problems, 12-6, 12-7,12-8, 12-9 and 12-10

IR Peaks are Associated with Separate Functional Groups

Although all the bonds in a molecule vibrate, to a first approximation, they can be treated as if they vibrate independently.

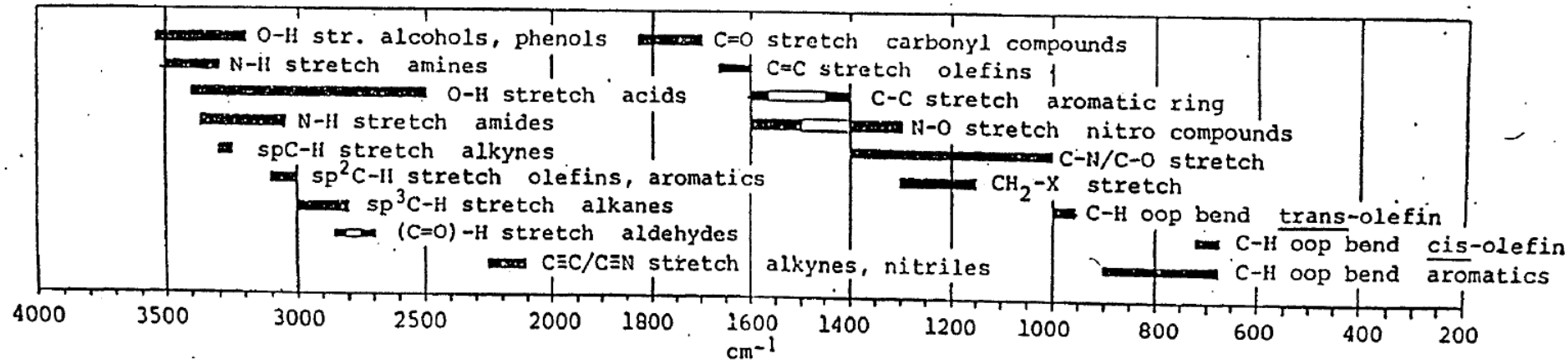






IR Group Frequencies

TABLE VII. Typical Absorption Regions for Some Common Functional Groups



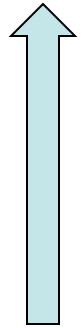
Hydrocarbons (overview)

(a) C -H stretch

R -C≡C-H 3300 cm^{-1}, more s-character & shorter bond length

R_2C=C-H 3000 ~ 3100 cm^{-1}

C-C-H(alkane) 2800 ~ 3000 cm^{-1}



s-charactor

(b) C-C Too week to observe

C=C medium 1620 ~ 1680 cm^{-1}

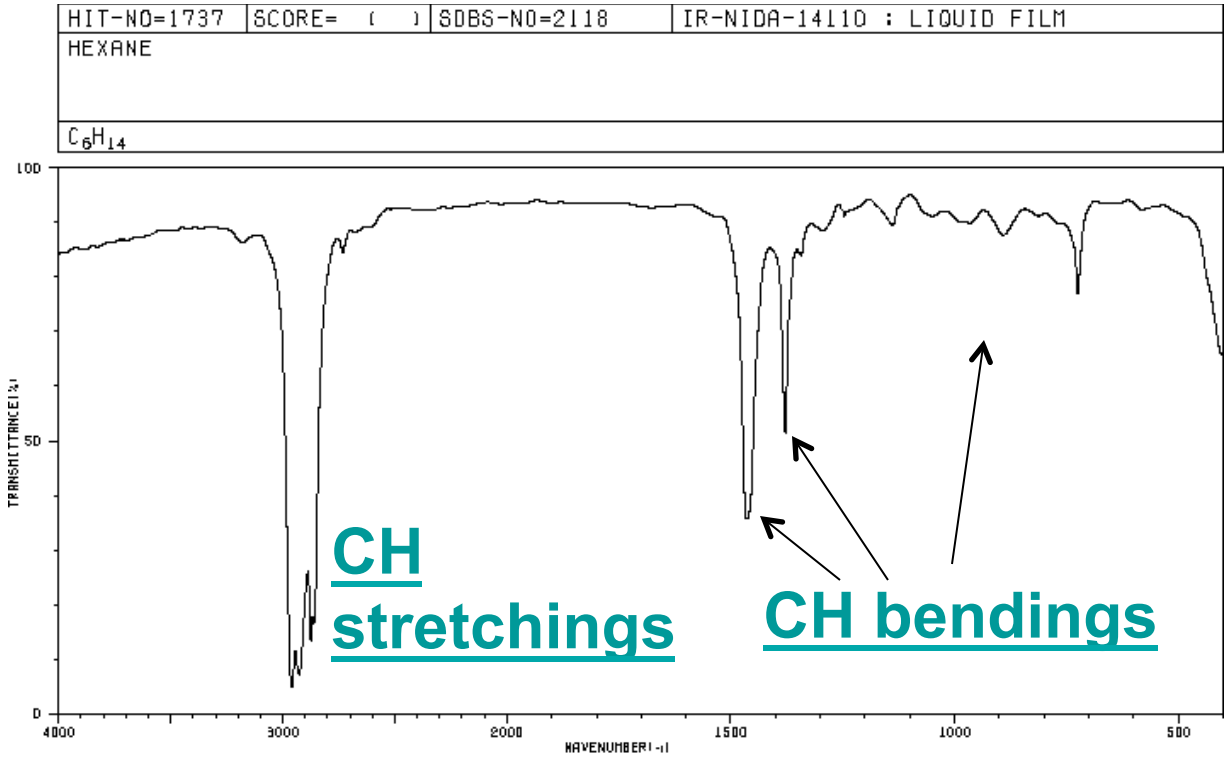
C≡C medium 2100 ~ 2600 cm^{-1}

aromatics 2 sharp peaks 1500 ~ 1600 cm^{-1}

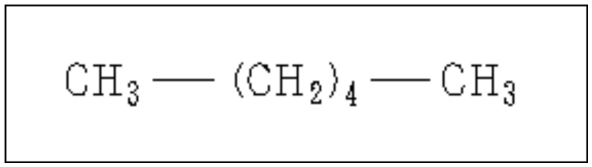
(c) out-of-plane bendings

Diagnostic to identify substitution patterns

Hexane

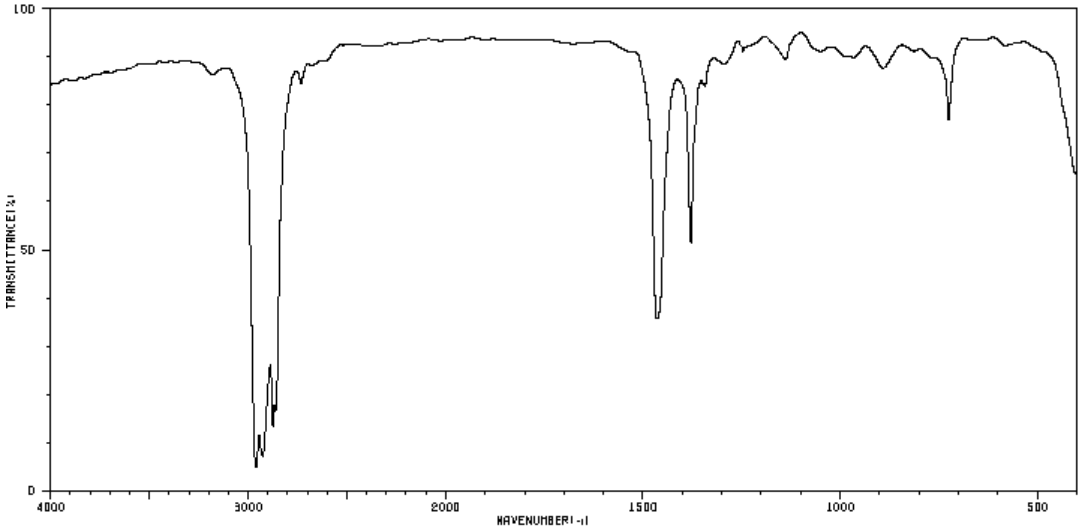


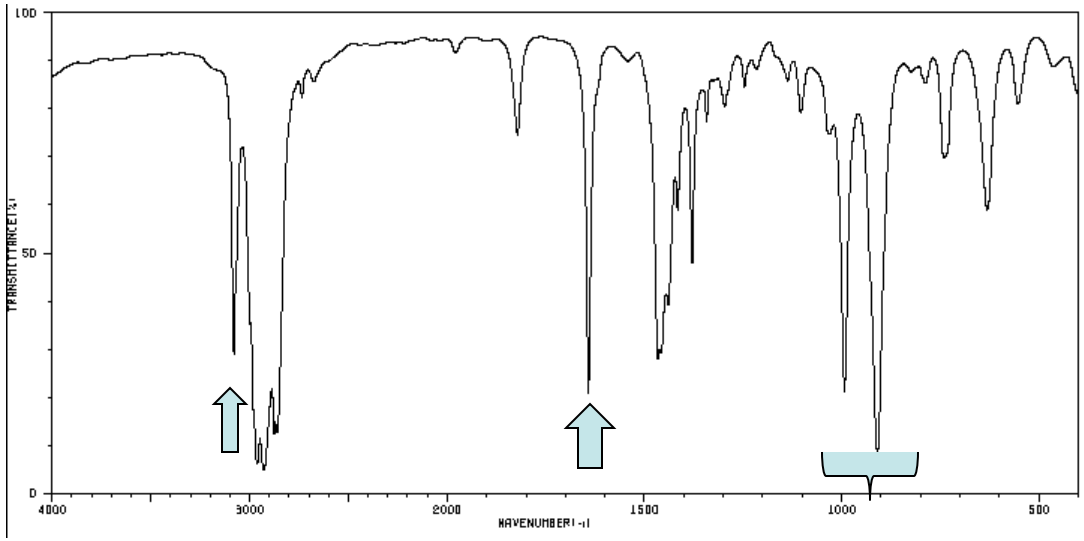
3187	84	1466	34	726	74
3176	84	1379	49		
2959	4	1300	84		
2928	7	1294	84		
2875	13	1138	86		
2862	15	891	84		
2734	81	884	84		

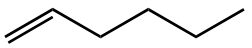


http://www.quimica3d.com/EN/IR/hexane.php

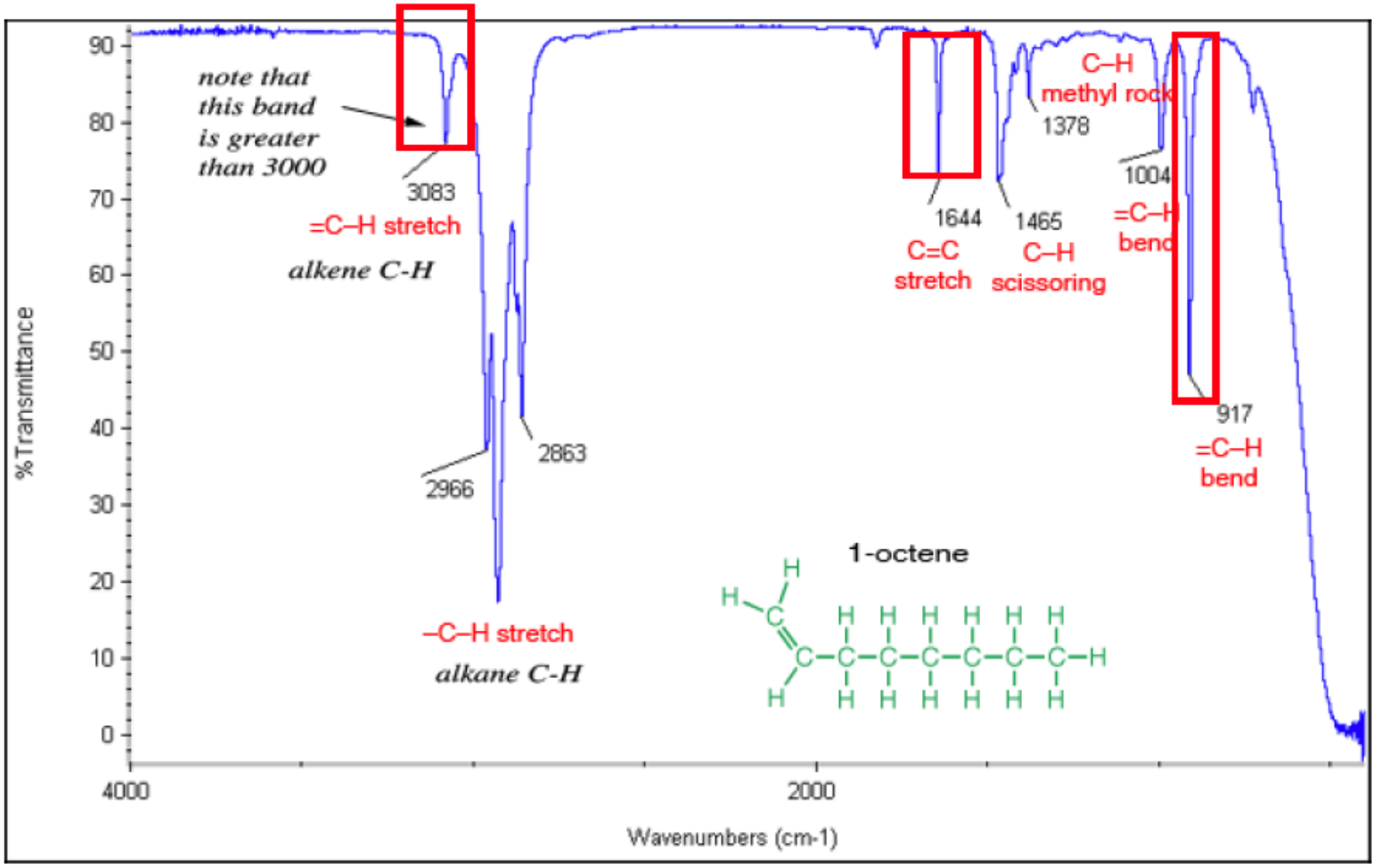
Hexane vs Hexene



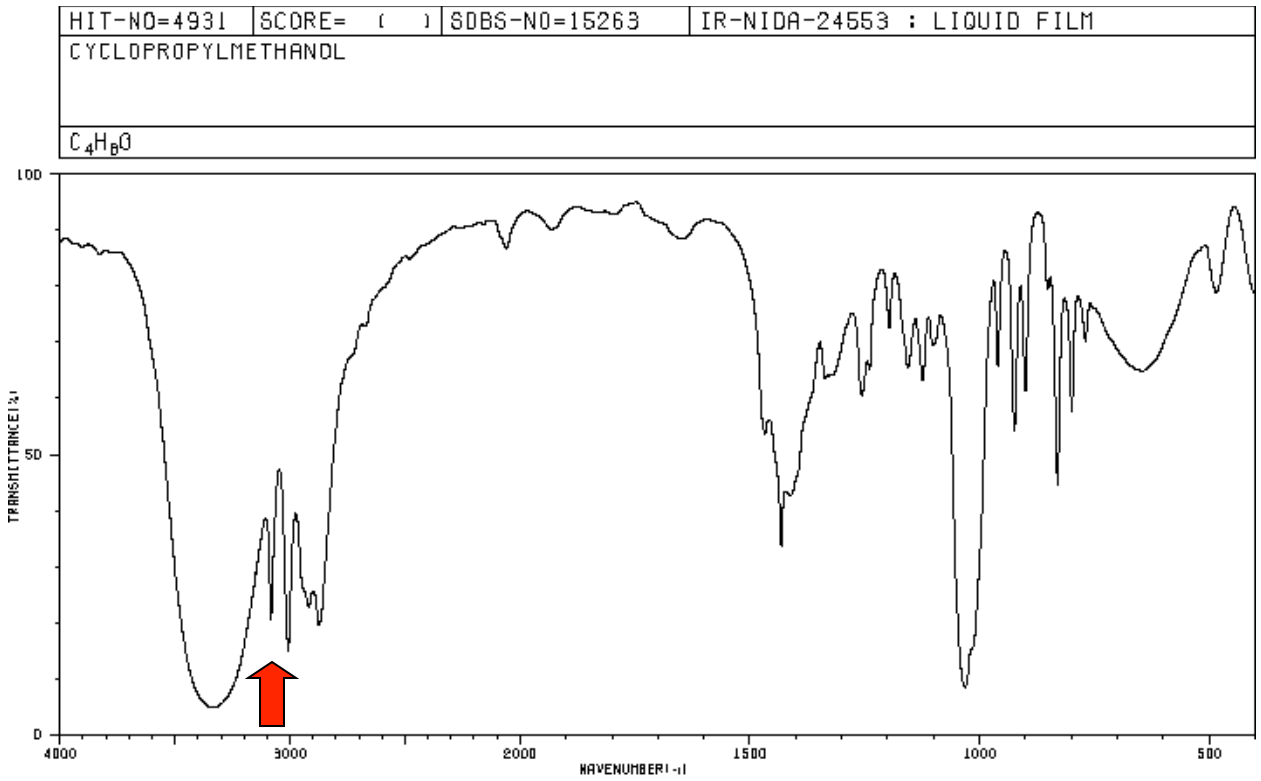




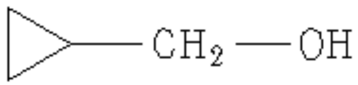
1-Octene

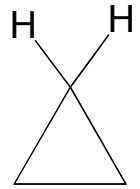

note that this band is greater than 3000
3083
=C–H stretch
alkene C-H
2966
2863
–C–H stretch
alkane C-H
1644
C=C stretch
1465
C–H scissoring
1378
C–H methyl rock
1004
=C–H bend
917
=C–H bend
1-octene
%Transmittance
Wavenumbers (cm-1)
4000
2000
90
80
70
60
50
40
30
20
10
0

Cyclopropane



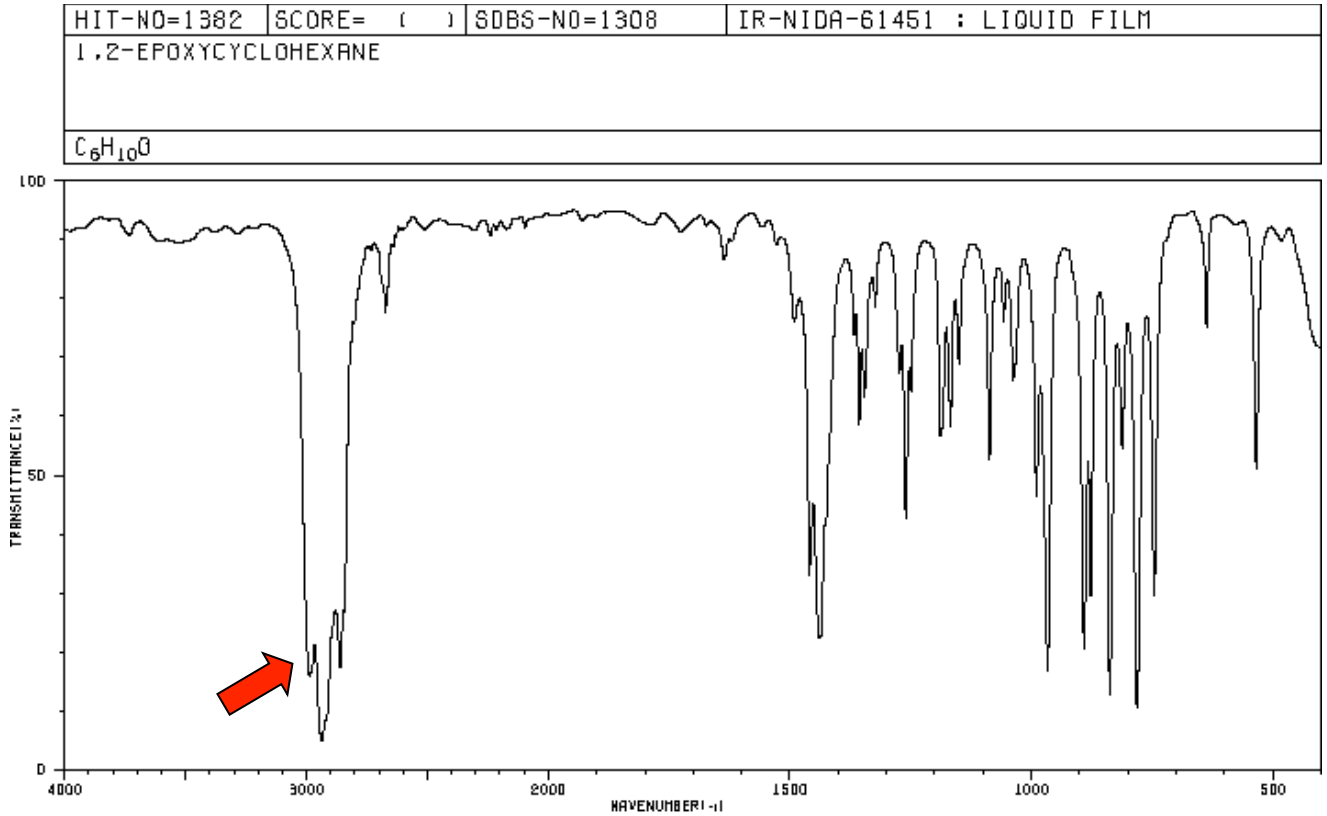
3330	4	1647	84	1321	62	1031	8	770	68
3082	20	1468	52	1256	58	960	64	650	62
3008	14	1432	32	1240	82	924	52	465	77
2919	21	1421	42	1197	70	900	68		
2873	18	1413	41	1156	62	852	77		
2059	84	1333	62	1124	80	830	49		
1662	84	1326	62	1103	66	799	66		



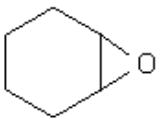


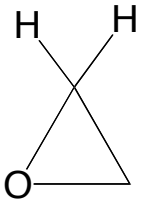
3100 ~ 3070 cm^{-1}

Epoxides



2987	15	1491	72	1323	74	1160	66	877	28
2936	4	1460	31	1274	64	1087	50	838	12
2861	16	1437	21	1260	41	1058	72	812	52
2674	74	1426	38	1249	62	1038	64	782	10
1637	84	1368	70	1189	55	990	44	746	28
1620	86	1357	57	1177	72	966	16	638	72
1628	86	1346	60	1168	67	891	20	636	49



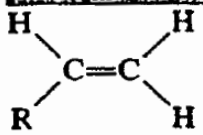


3060 ~ 3040 cm^{-1}

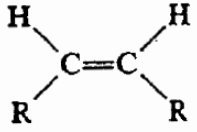
Alkene Substitution Patterns

Table D-1 (From Silverstein *et. al.*, pg. 163)

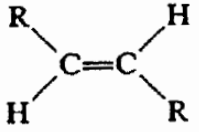
Alkene Absorptions[a]



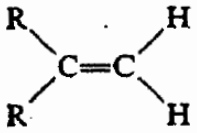
Vinyl
1648–1638 cm^{-1}
995–985 cm^{-1}(s)[b]
915–905 cm^{-1} (s)



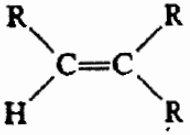
cis
1662–1626 cm^{-1} (v)
730–665 cm^{-1} (s)



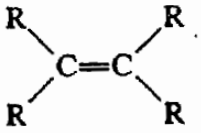
trans
1678–1668 cm^{-1} (v)
980–960 cm^{-1} (s)[c]



Vinylidine
1658–1648 cm^{-1} (m)
895–885 cm^{-1} (s)



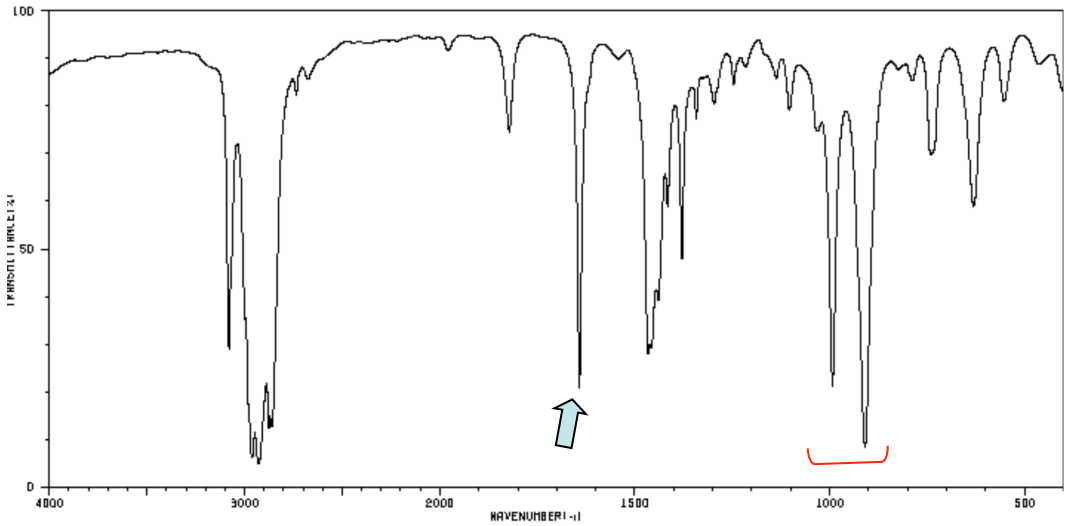
Trisubstituted
1675–1665 cm^{-1} (w)
840–790 cm^{-1} (m)

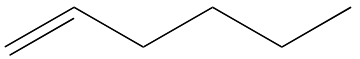


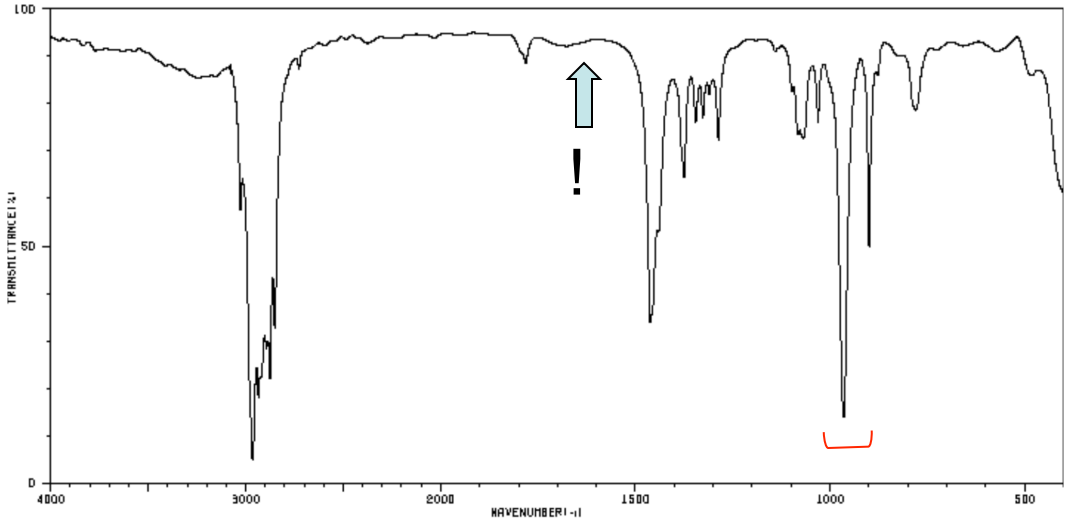
Tetrasubstituted
1675–1665 cm^{-1} very weak
or absent.

[a] s = strong, m = medium, w = weak, v = variable.
[b] This band also shows a strong overtone band.
[c] This band occurs near 1000 cm^{-1} in conjugated trans–trans systems such as the esters of sorbic acid.

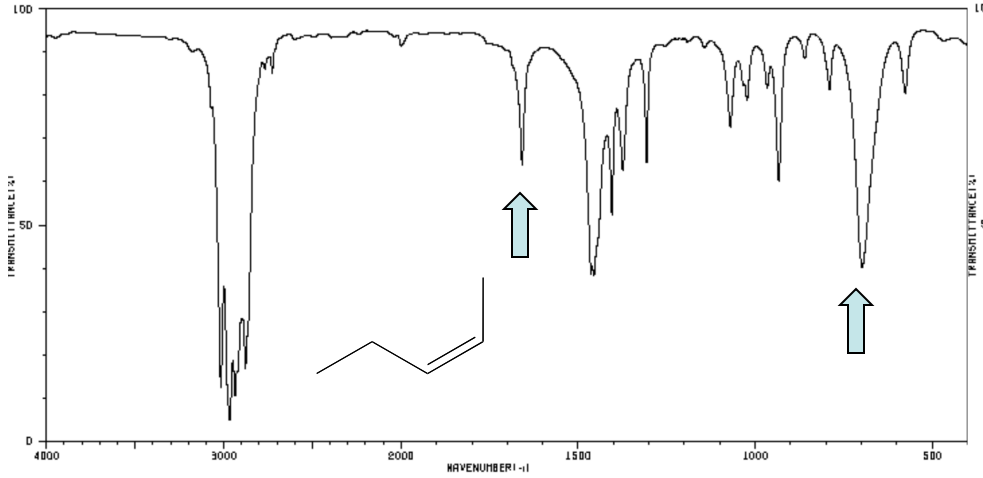
1-Hexene and 3-Hexene

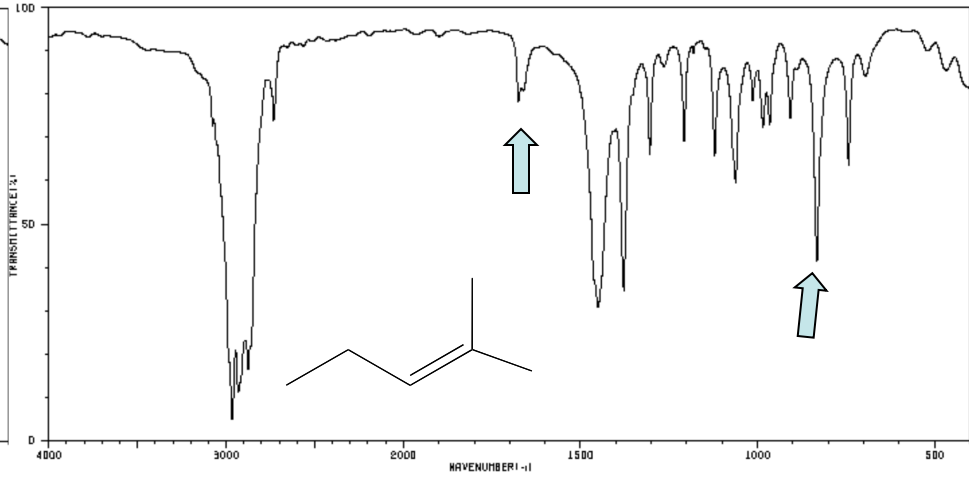


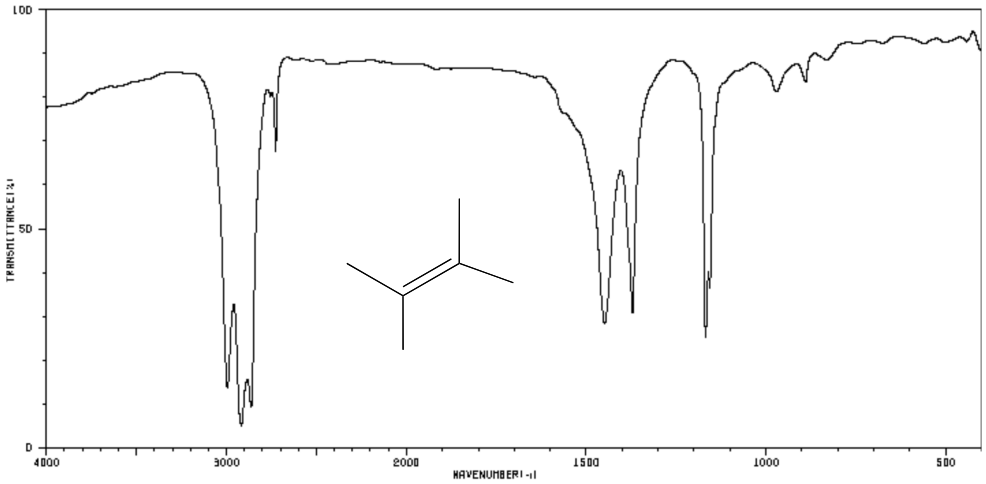




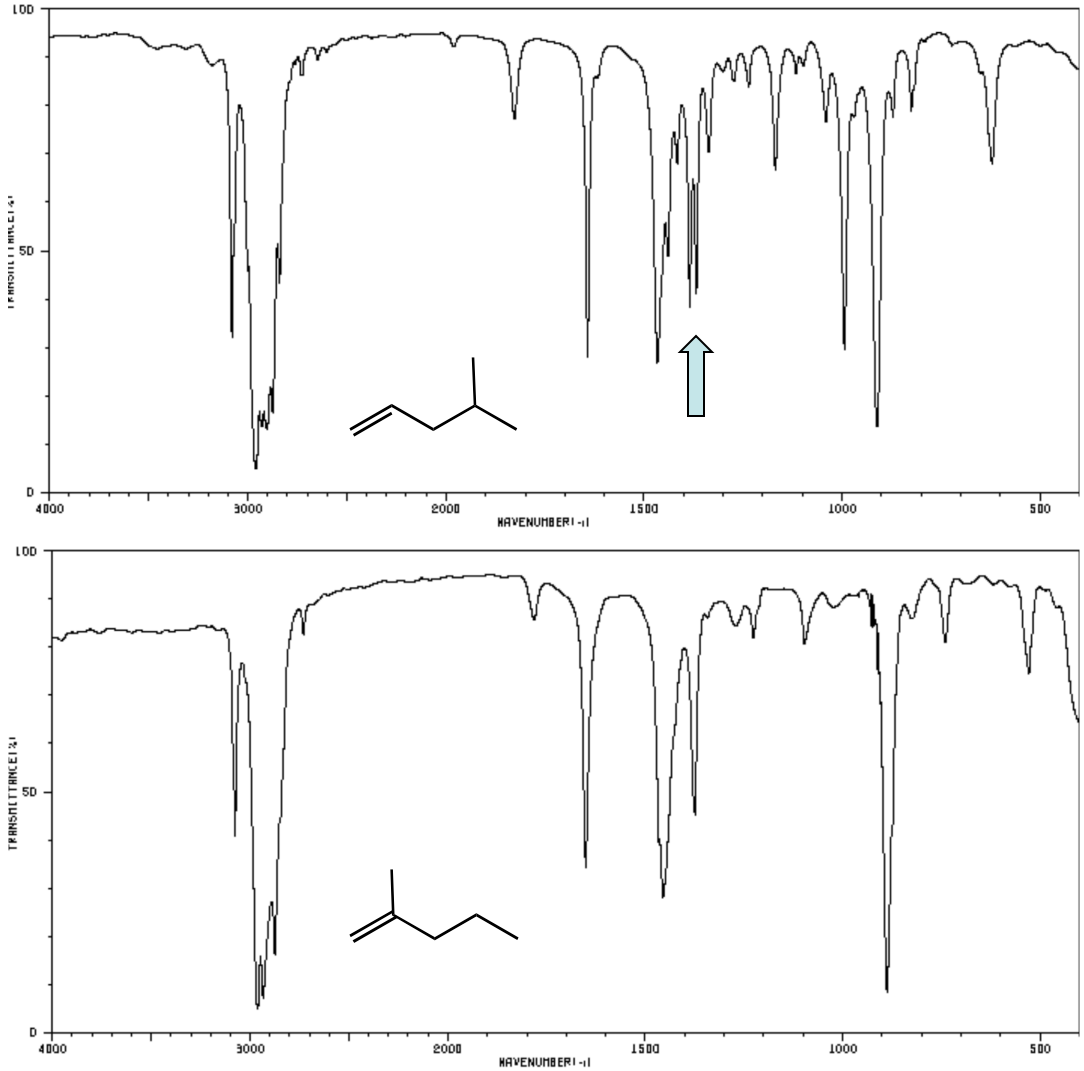
Other Alkenes

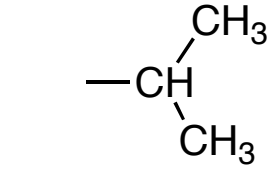




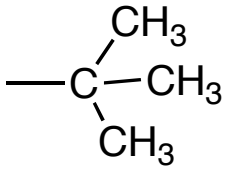


Methyl Pentenes



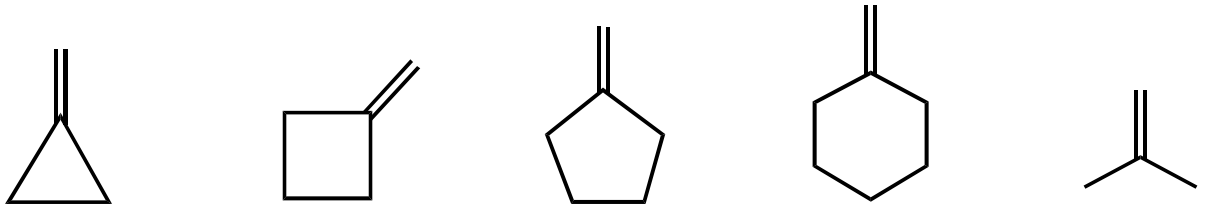


1370 & 1385 cm^{-1}



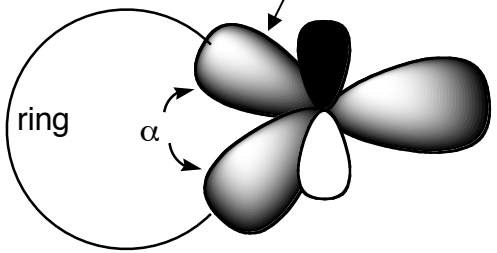
1370 & 1395 (weaker) cm^{-1}

Exocyclic Alkenes



$\bar{\nu}$ (C=C)	1780	1678	1657	1651	1655

cm^{-1}



α (bond angle)
sp 180
sp2 120
sp3 109

α ↓ → p-character ↑

↓

then, s-character ↑

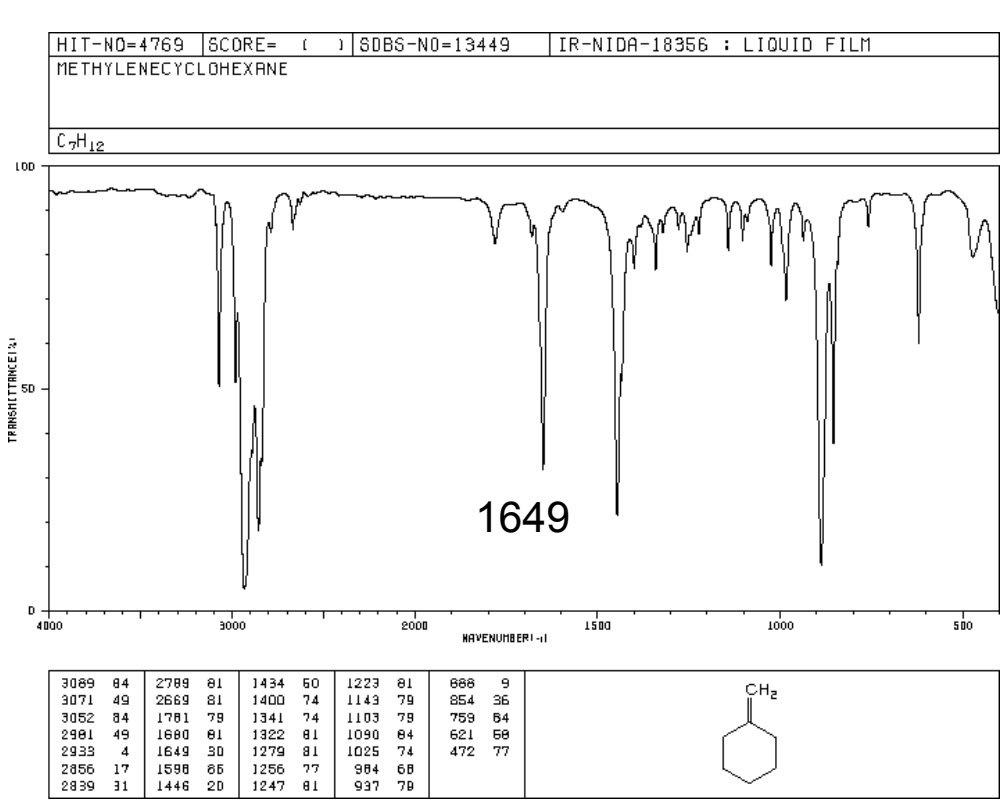
↓

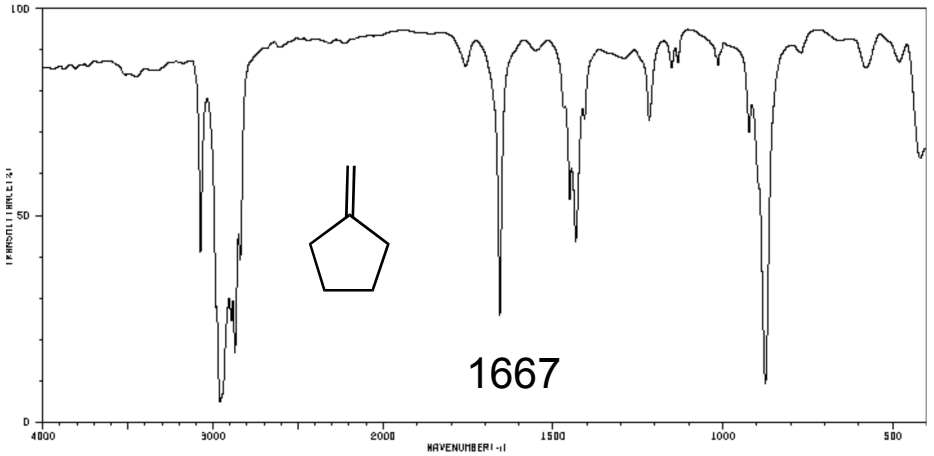
stronger C=C bond

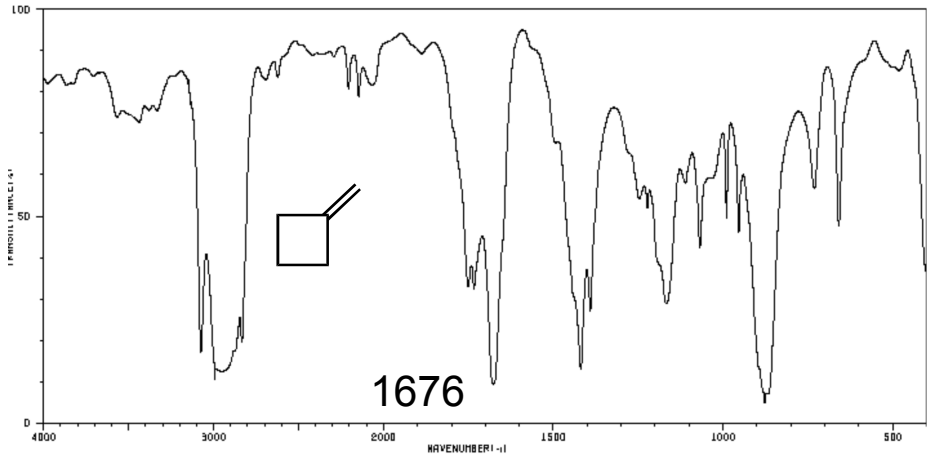
↓

$\bar{\nu}$ ↑

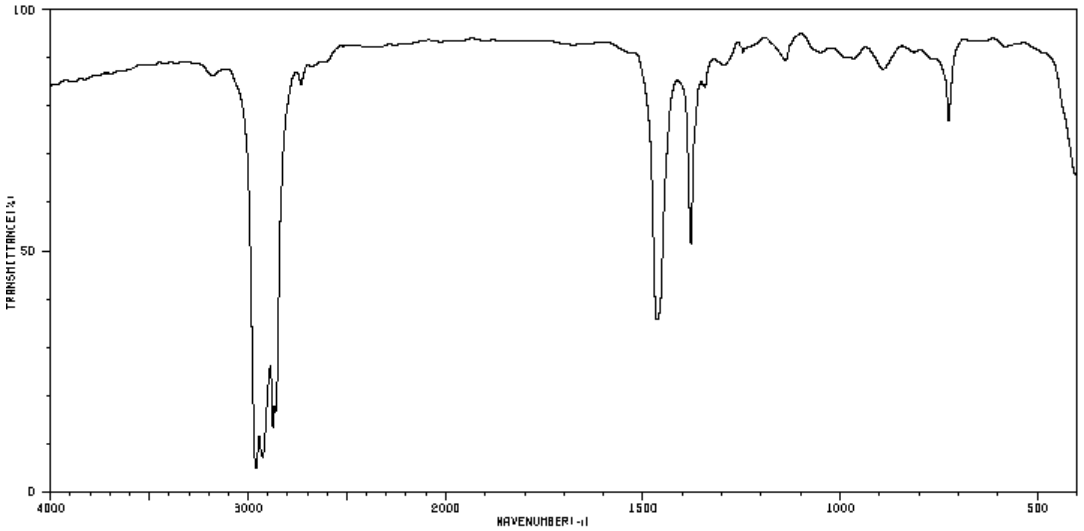
Exocyclic Alkene Examples

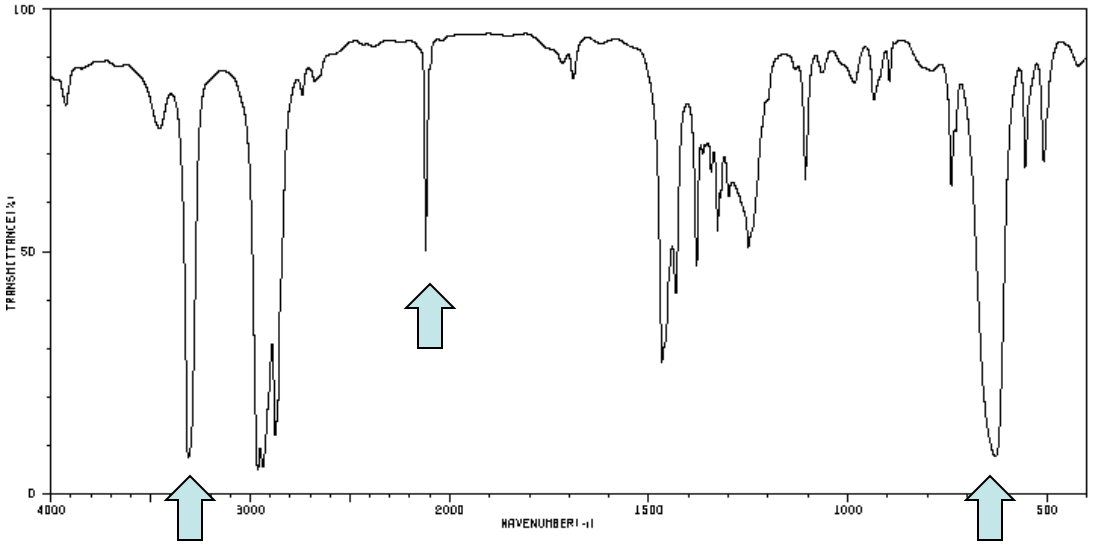


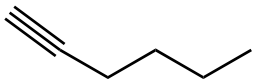




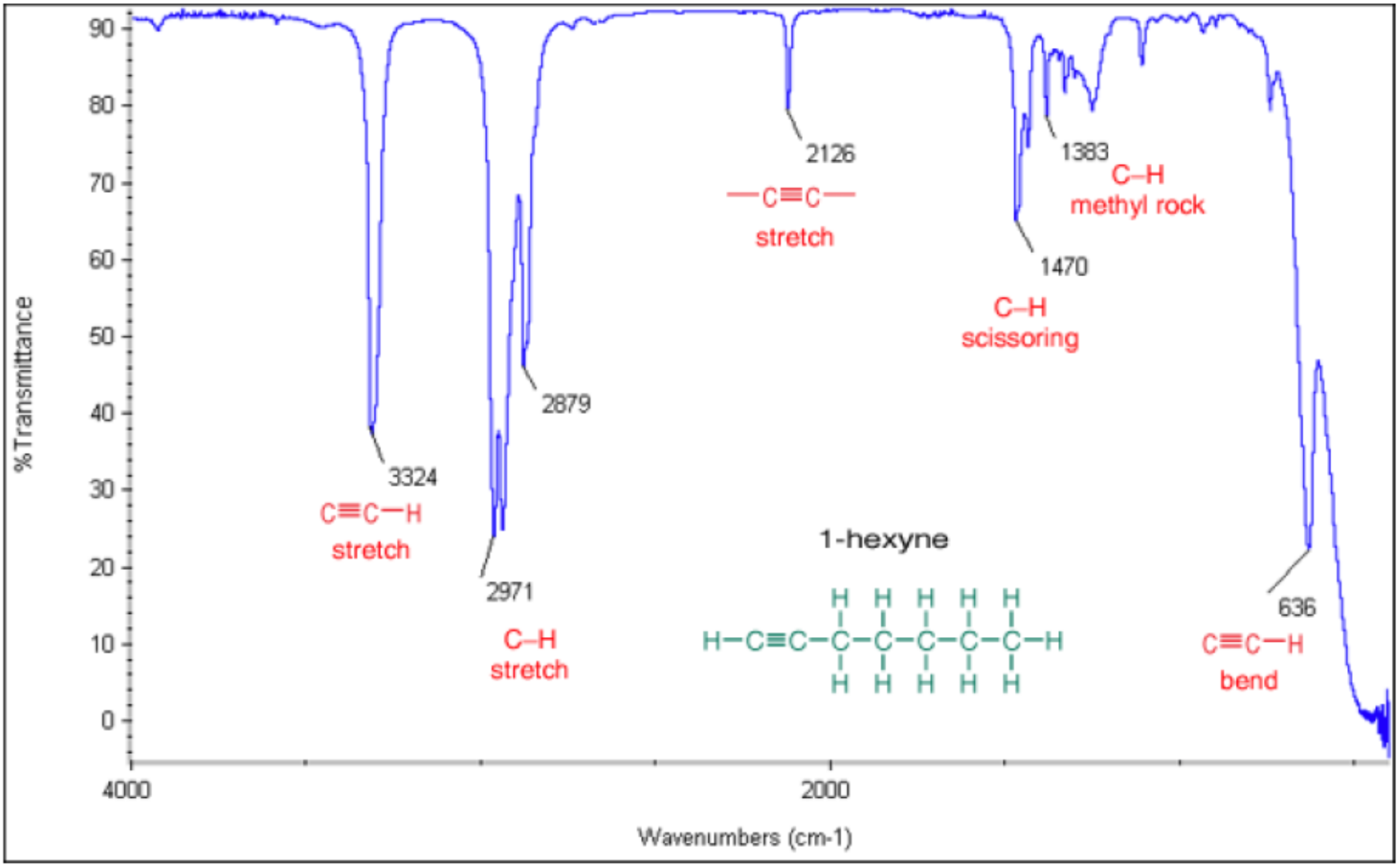
Hexane vs Hexyne



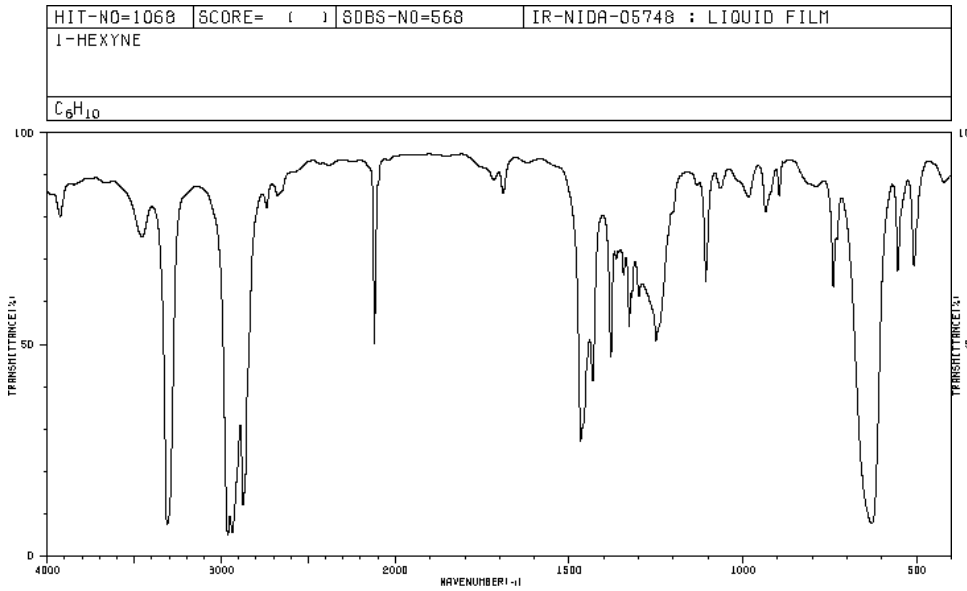




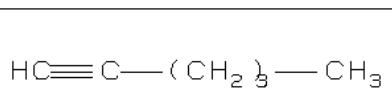
1-Hexyne

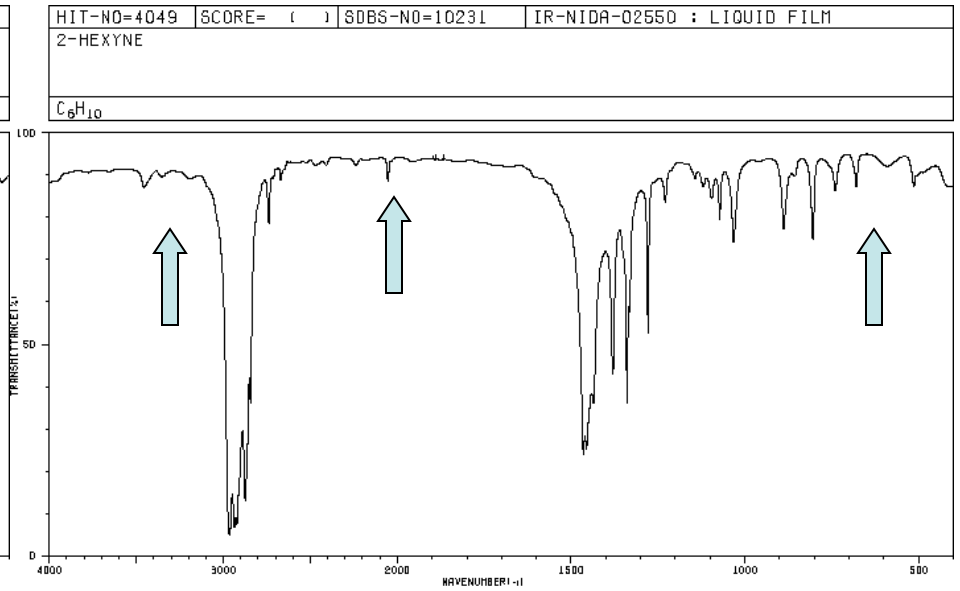

%Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
3324
C≡C–H
stretch
2971
C–H
stretch
2879
2126
—C≡C—
stretch
1470
C–H
scissoring
1383
C–H
methyl rock
636
C≡C–H
bend
1-hexyne

1-Hexyne and 2-Hexyne

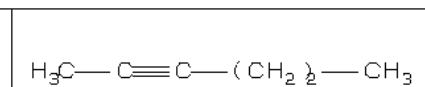


3926	77	2678	81	1432	39	1260	49	740	60
3455	72	2120	49	1380	46	1107	62	730	72
3311	7	2097	84	1366	68	1063	84	630	7
2962	4	1717	86	1344	64	983	81	666	64
2937	5	1690	81	1328	52	934	79	509	66
2876	11	1467	25	1320	58	895	81		
2738	79	1461	29	1300	58	793	84		





3468	84	2739	77	1340	35	1073	77	605	86
3354	86	2671	86	1333	55	1033	72		
2964	4	2054	84	1279	50	889	74		
2936	6	1466	29	1229	81	805	72		
2922	7	1456	24	1144	86	740	84		
2875	12	1436	34	1120	84	679	84		
2844	35	1380	41	1095	81	614	84		

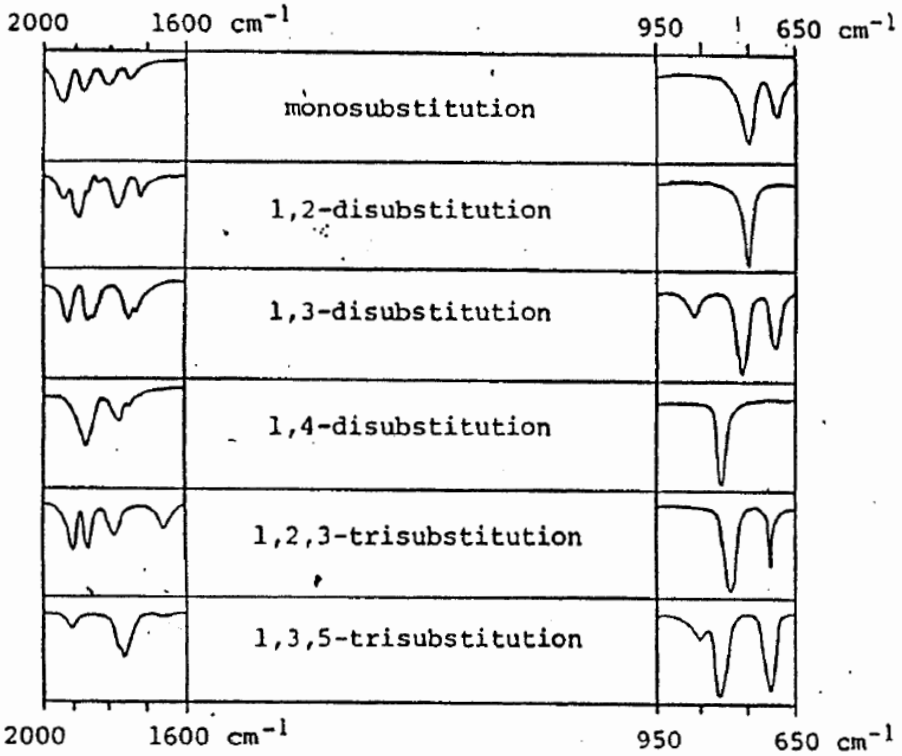


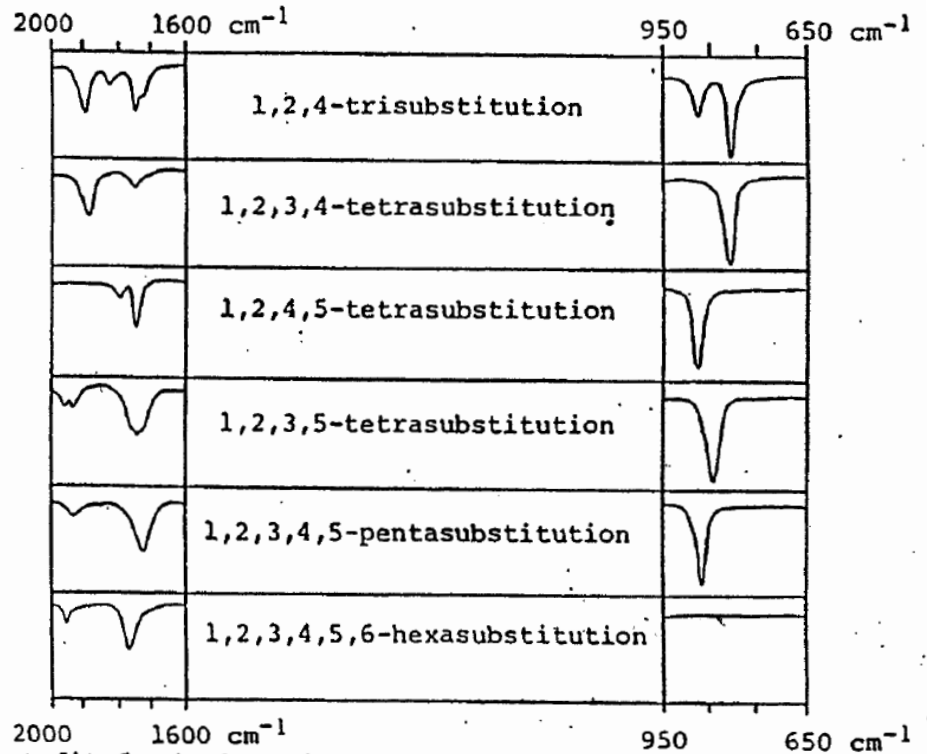
Aromatic Substitutions

- Mono-substituted
  2 peaks
  ~ 700 cm^{-1}
  730 ~ 770 cm^{-1}
- Disubstituted
  ortho- 1 peak 735 ~ 770 cm^{-1}
  meta- 2 peaks
  680 ~ 725 cm^{-1}
  750 ~ 810 cm^{-1}
  para- 1 peak 790 ~ 840 cm^{-1}

Benzene Substitution Patterns

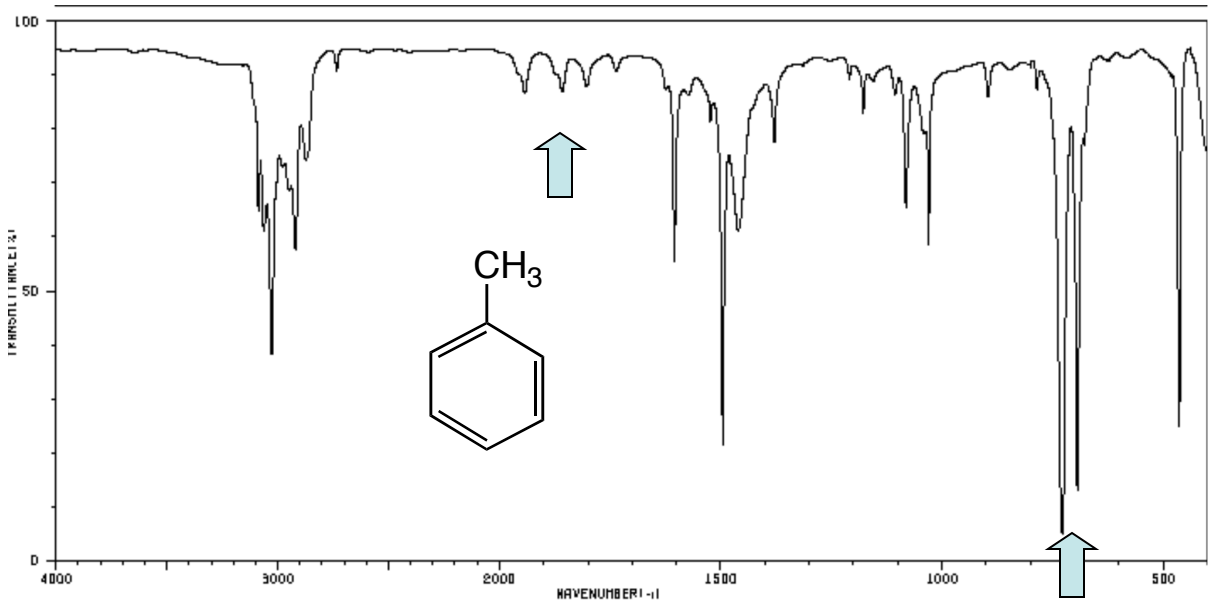
TABLE VI. Idealized Patterns Useful for Establishing the Substitution Pattern in Substituted Benzenes

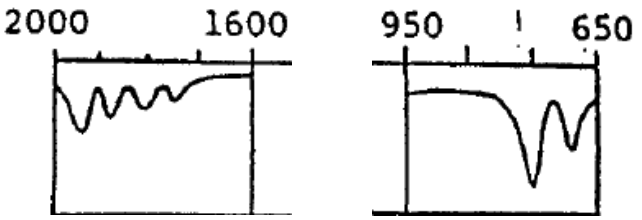


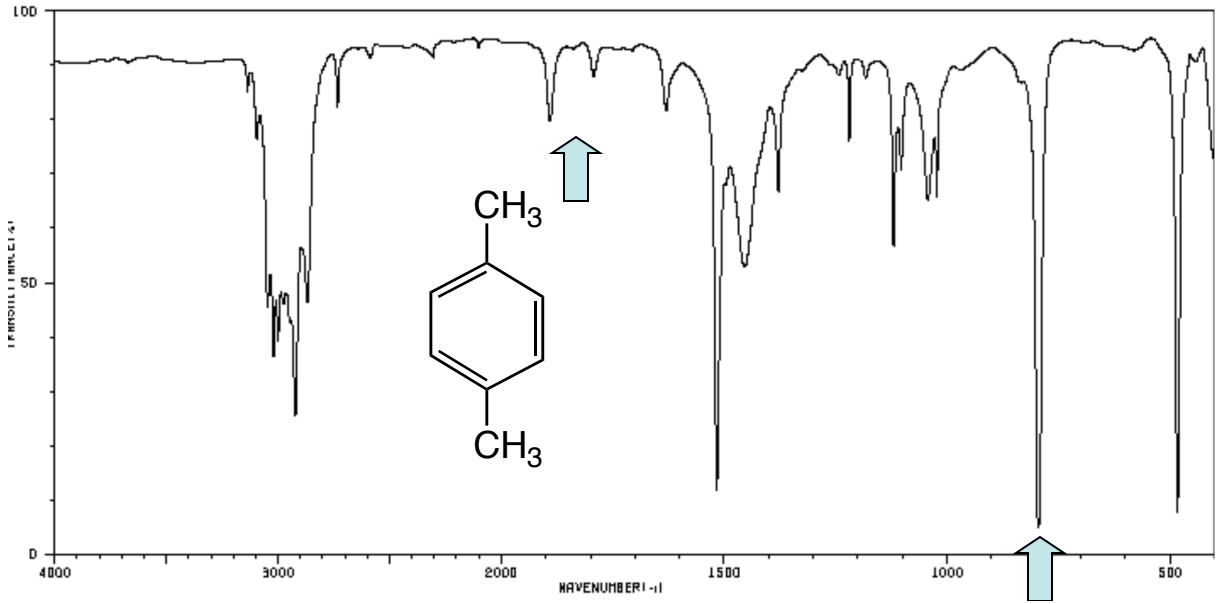


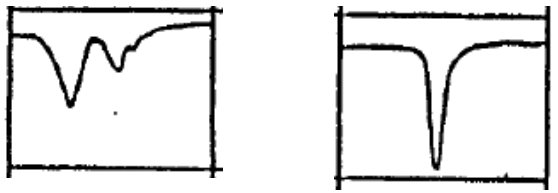
Both regions may be obscured by other absorptions and the best fit for both regions should be sought. Note that the intensity of the absorptions in the 2000 to 1600 cm^{-1} regions are exaggerated for clarity.

Toluene and p-Xylene

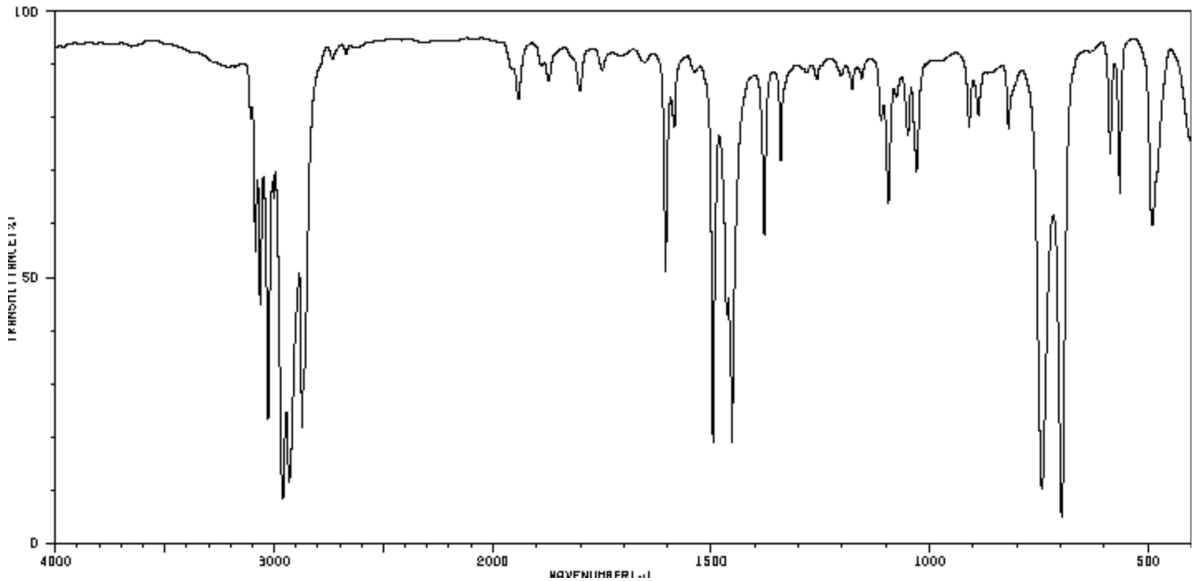


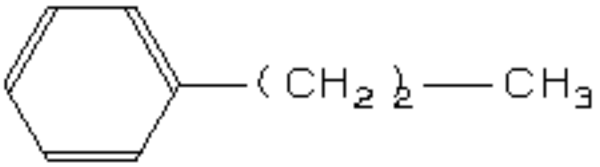


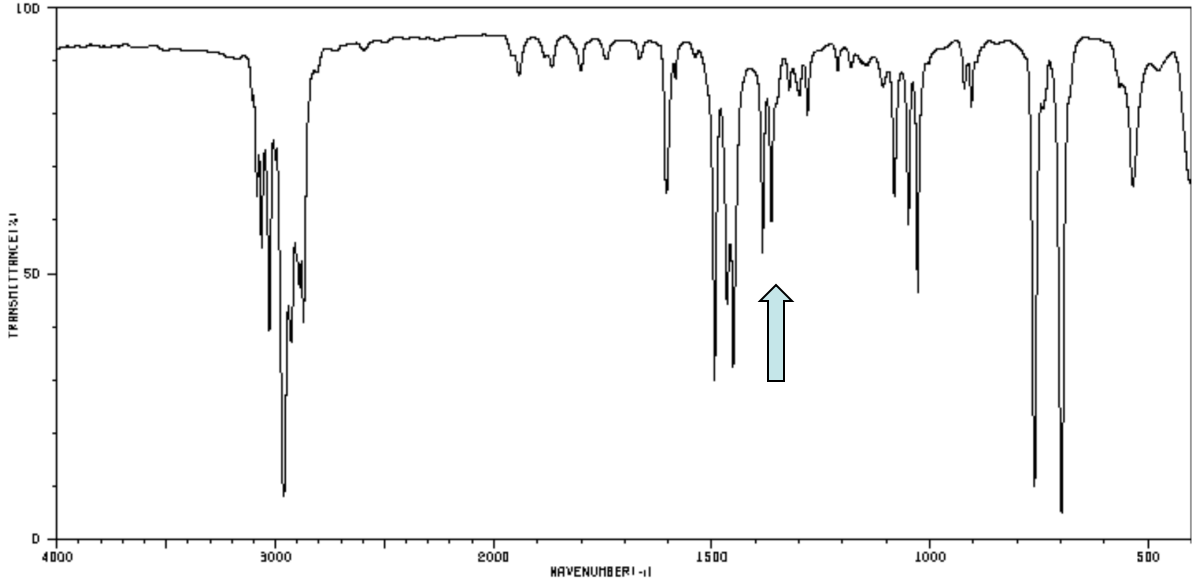


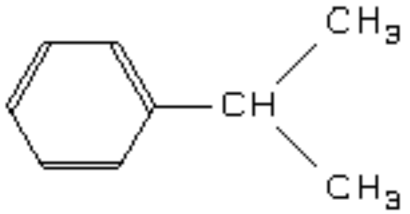


Propyl Benzene and Isopropyl Benzene







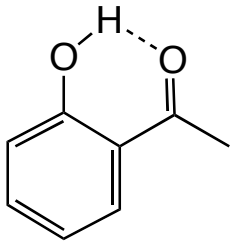


Alcohols & Phenols

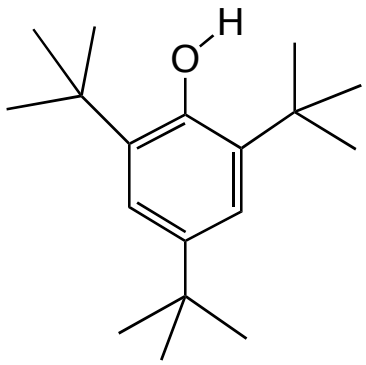
- O-H Stretch
  - 3650 ~ 3600 cm-1, sharp (monomeric)
  - 3500 ~ 3200 cm-1, broad (hydrogen bonded)

Usually concentration dependent

Some exceptions

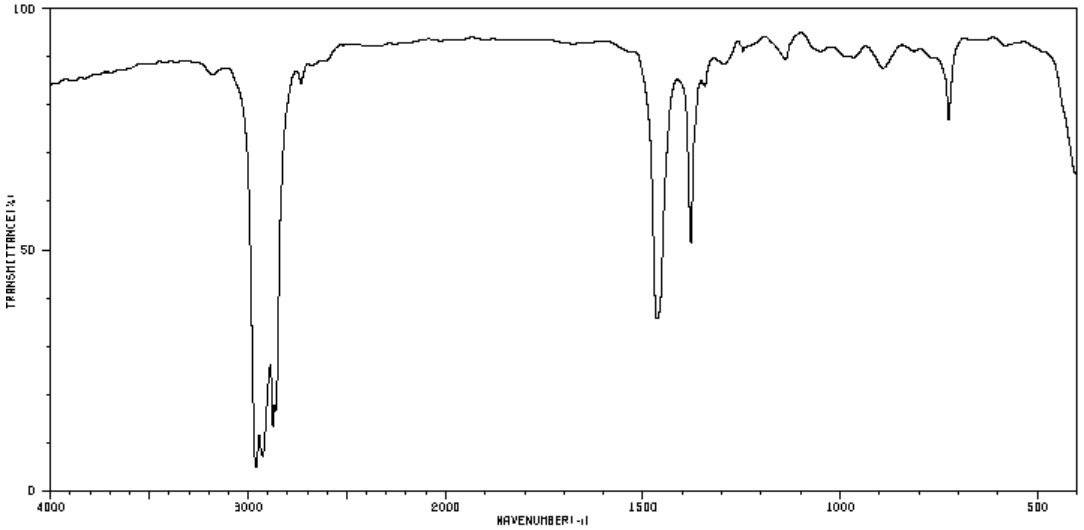


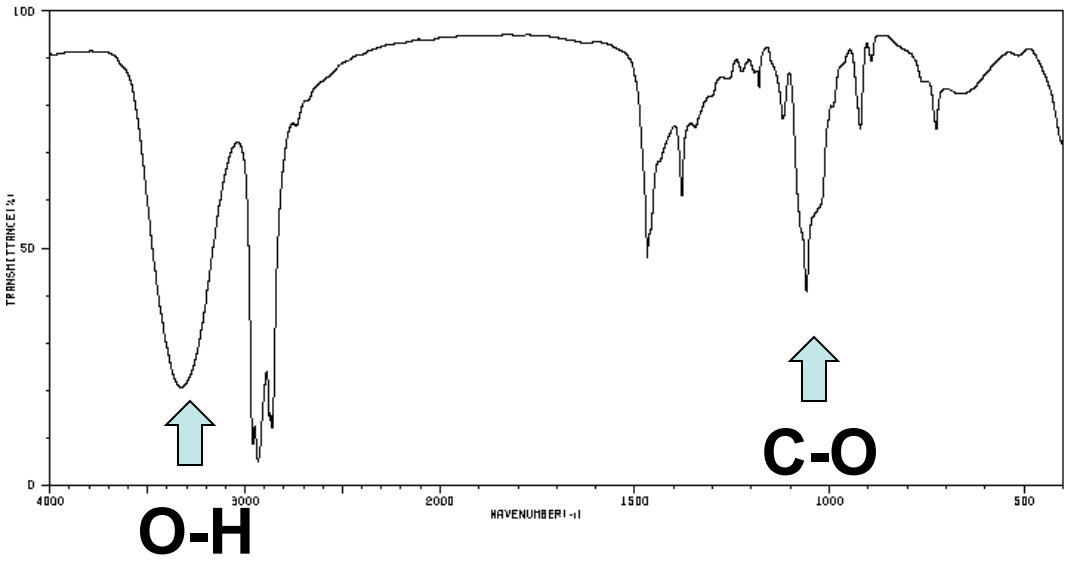
Always H-bonded

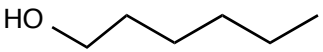


Always monomeric

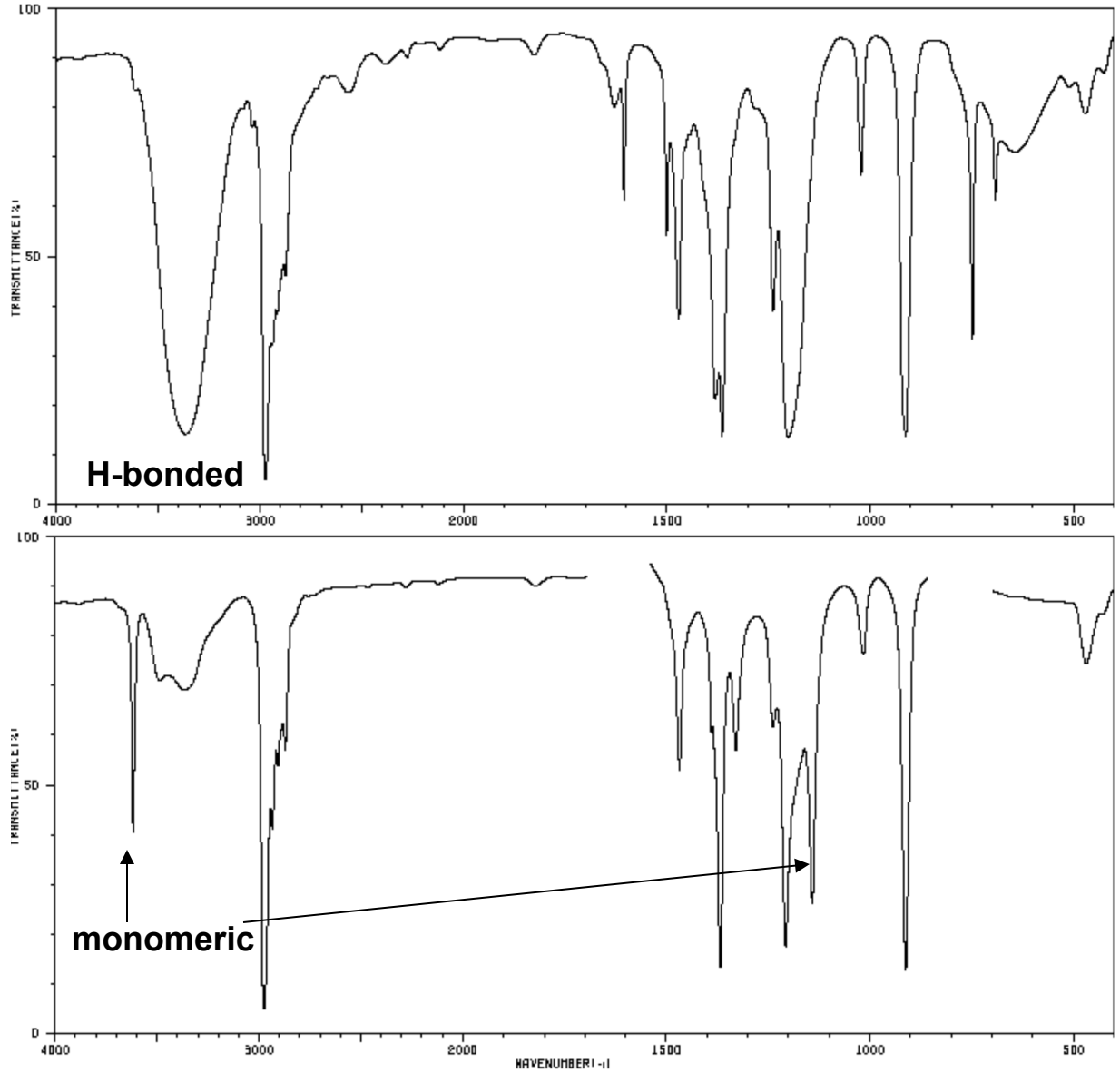
Hexane vs Hexanol







Tert-Butanol, Neat and solution



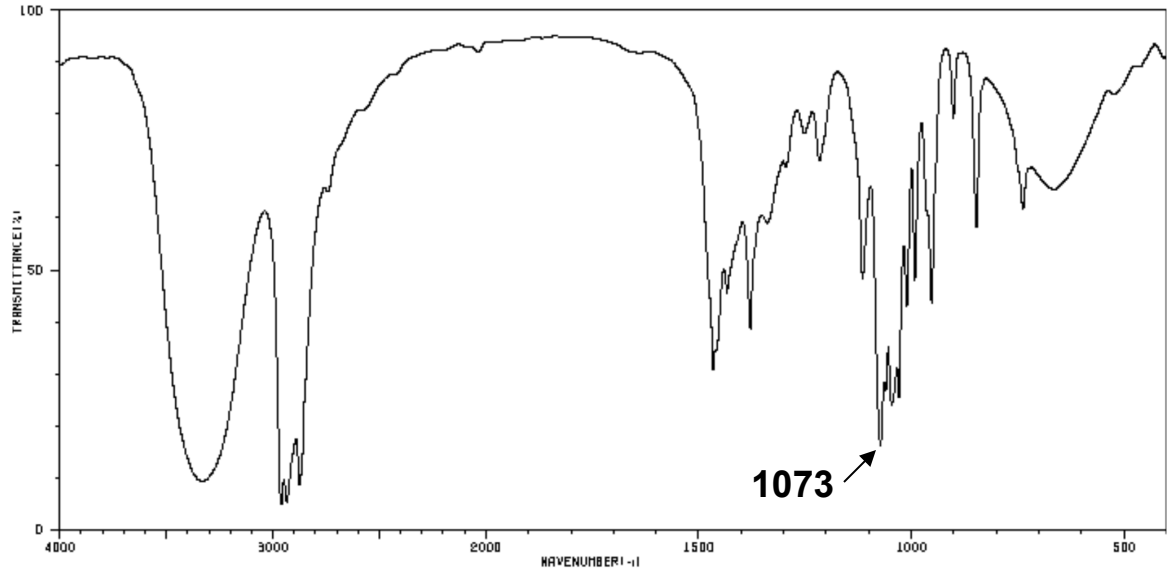
Neat

CCl_4 solution

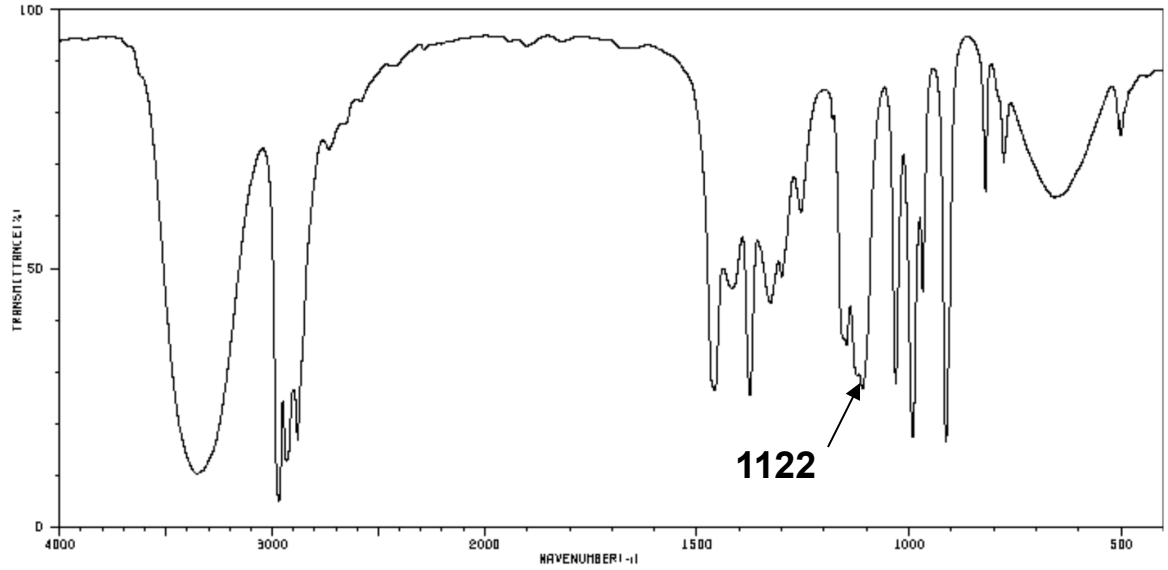
Alcohols & Phenols

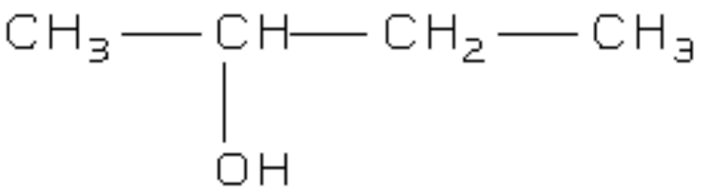
- C-O Stretch
  - Phenol 1220 cm-1
  - Tertiary alcohol 1150 cm-1
  - Secondary alcohol 1100 cm-1
  - Primary alcohol 1050 cm-1

1-Butanol and 2-Butanol

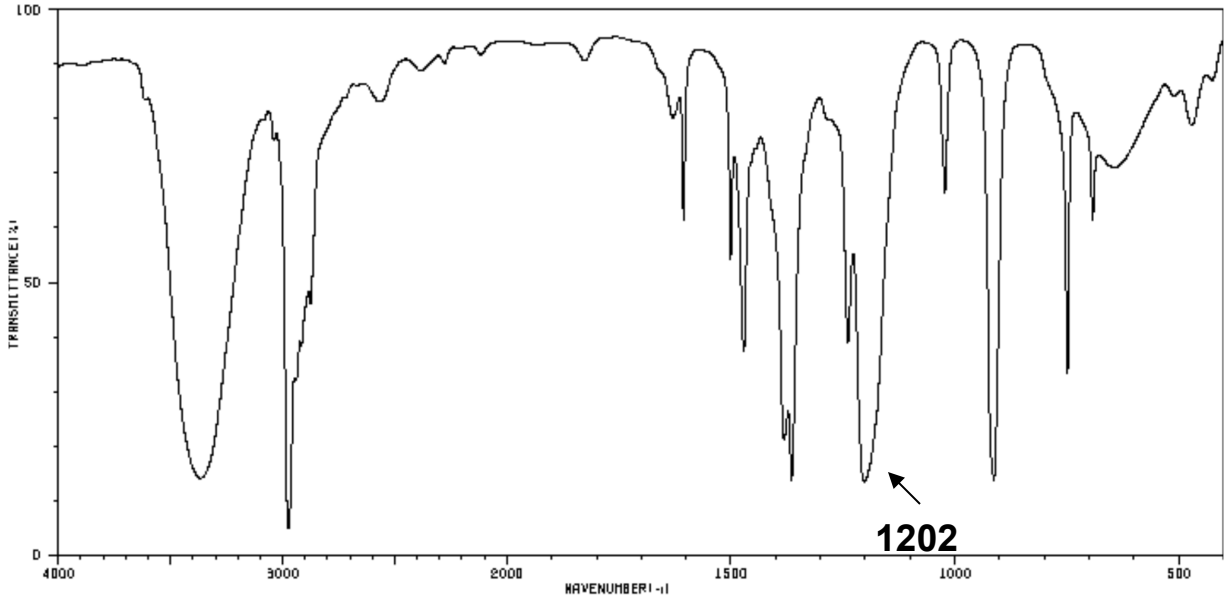


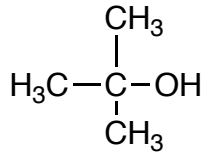
$CH_3 — (CH_2)_3 — OH$

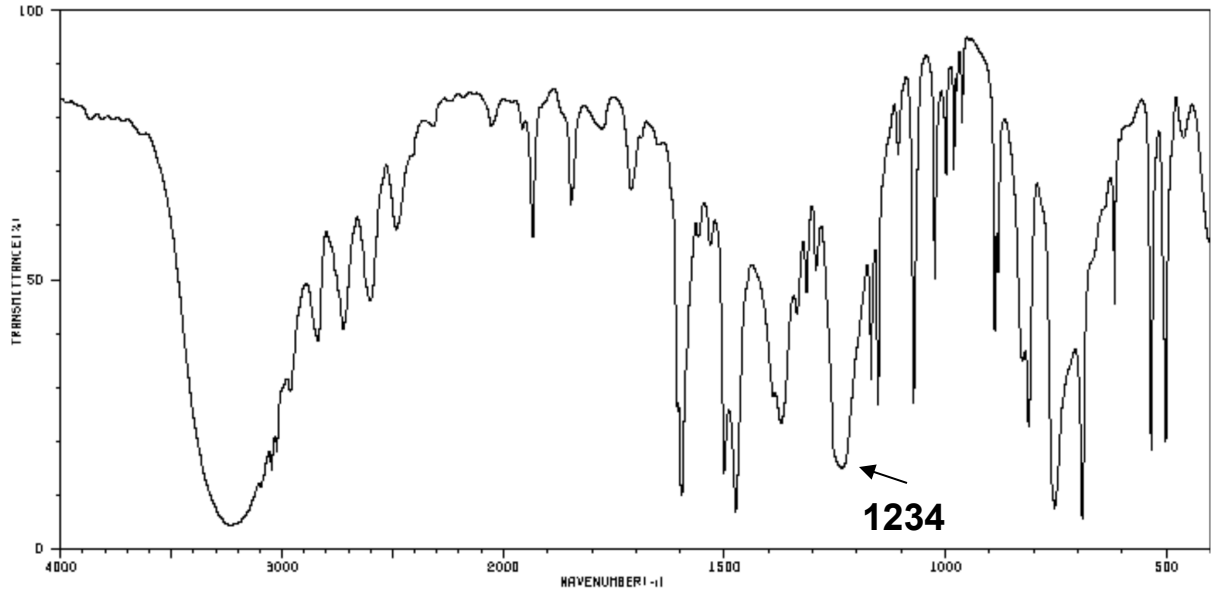


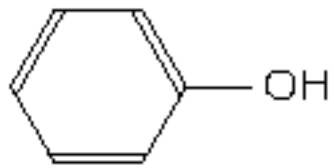


Tert-Butanol and Phenol



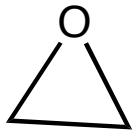






Ethers

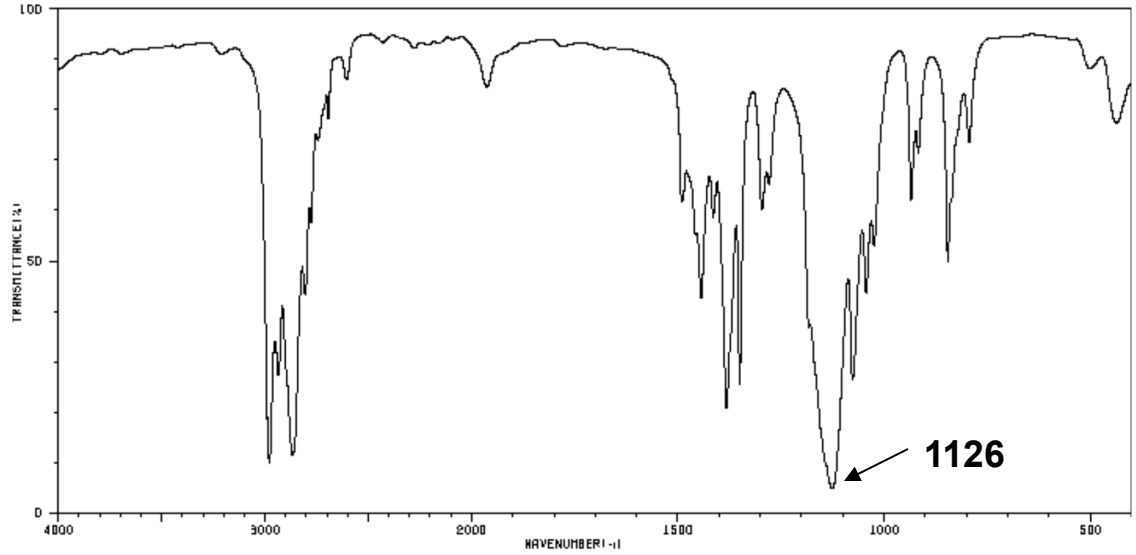
- C-O Stretch
  - Dialkyl 1120 & 850 cm-1
  - Diaryl & vinyl 1250 & 1040 cm-1

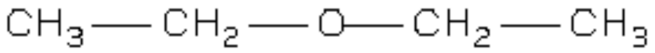


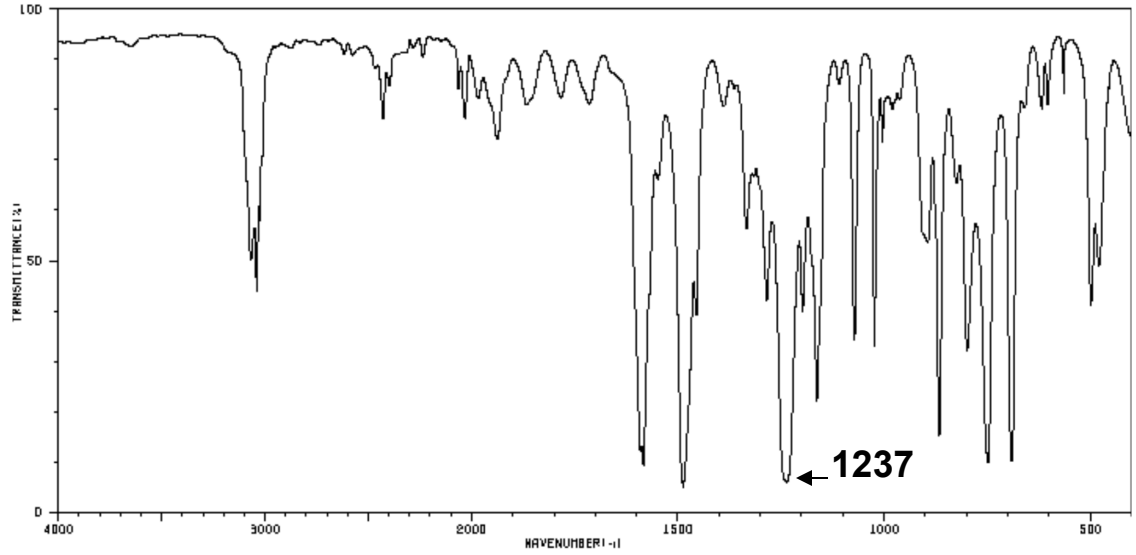
Three bands
1250 cm^{-1}
950 ~ 815 cm^{-1}
850 ~ 750 cm^{-1}

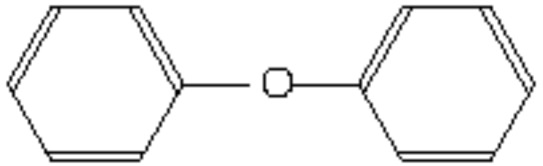
-O-CH_3 a sharp peak ~ 2830 cm^{-1}

Diethyl Ether and Diphenyl Ether

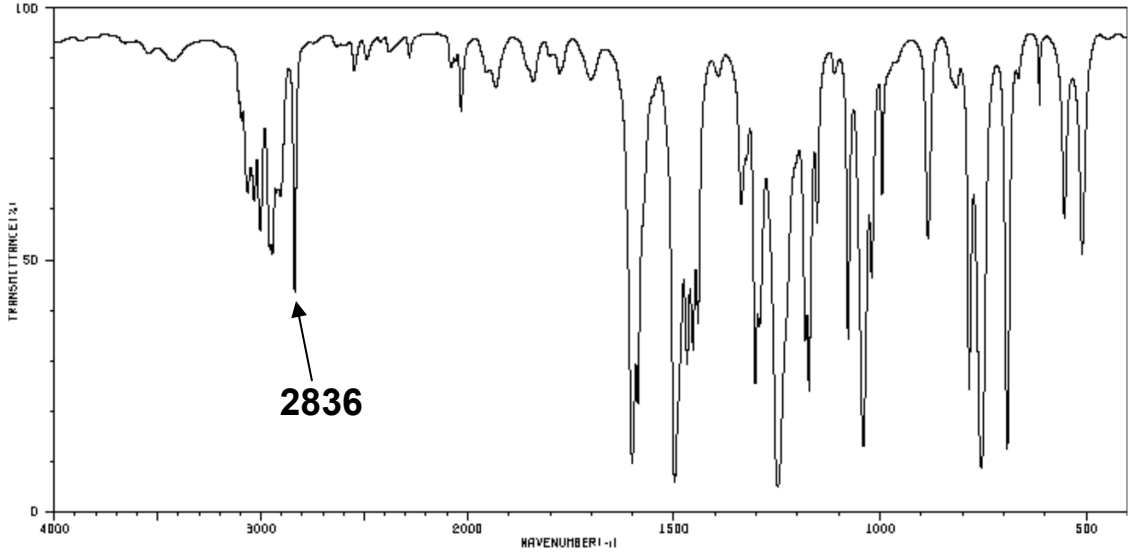


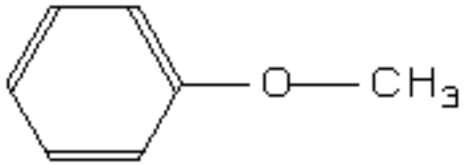


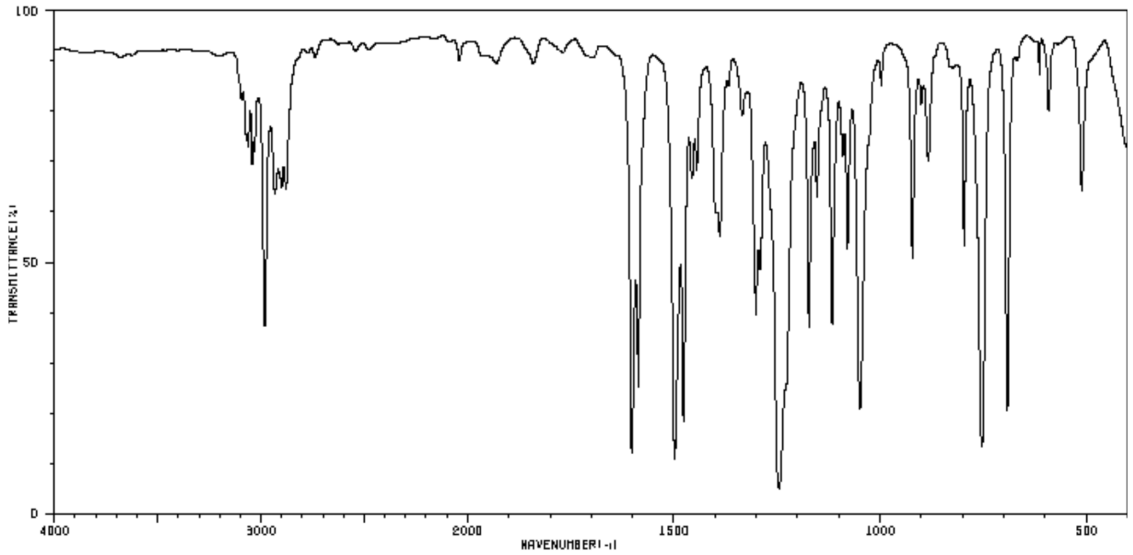


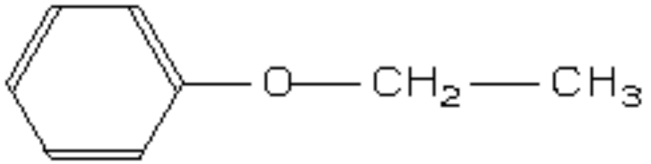


Anisole and Ethyl Phenyl Ether

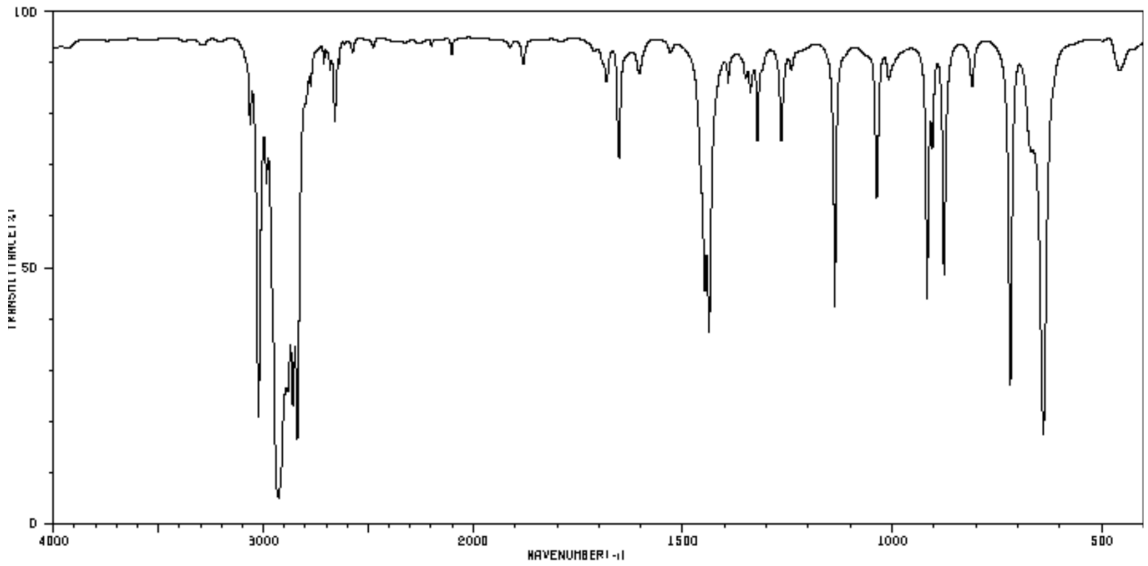


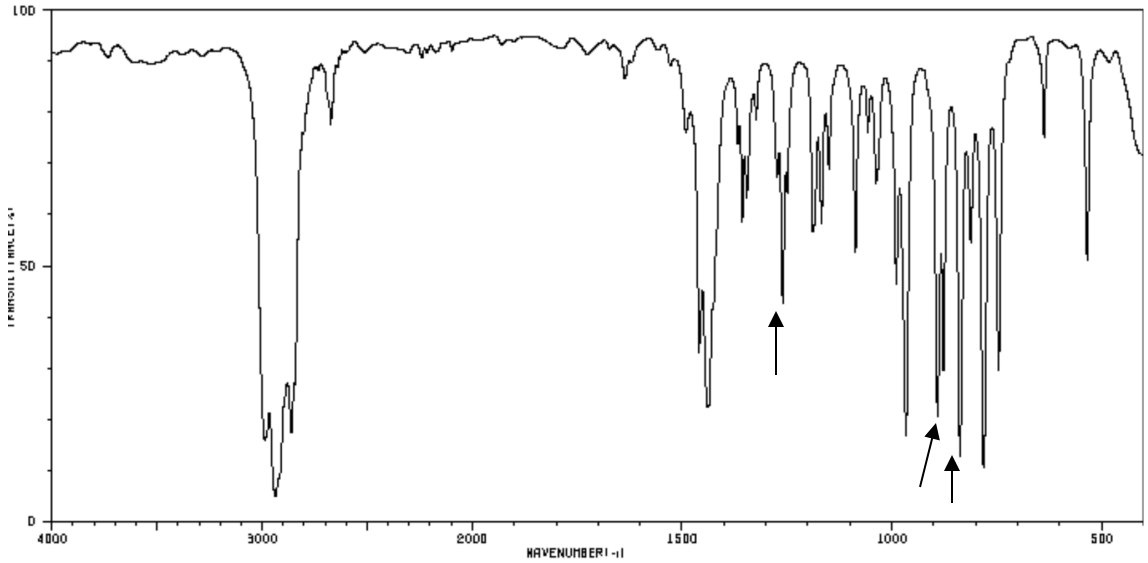


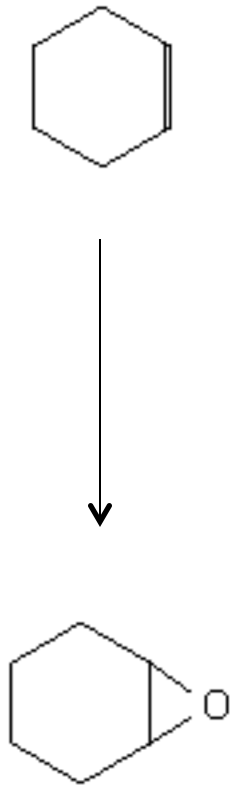




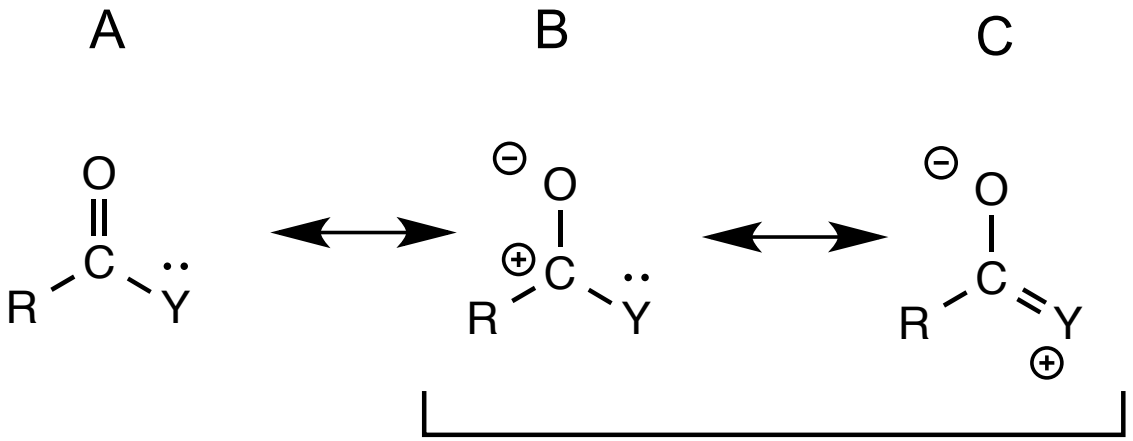
Cyclohexene and Cyclohexene Oxide





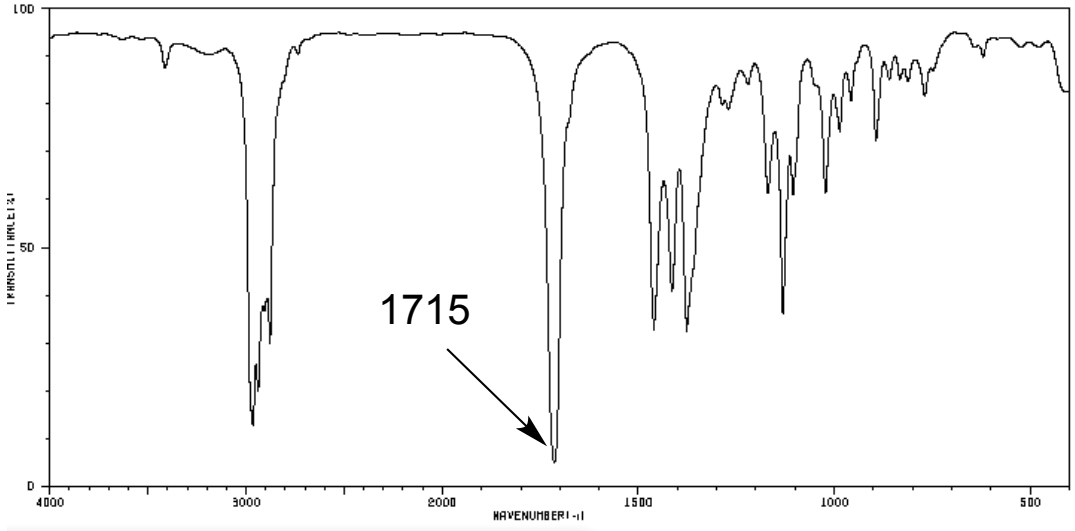


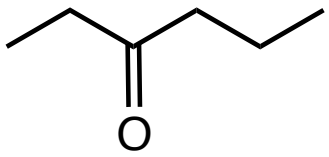
C=O Stretching Band

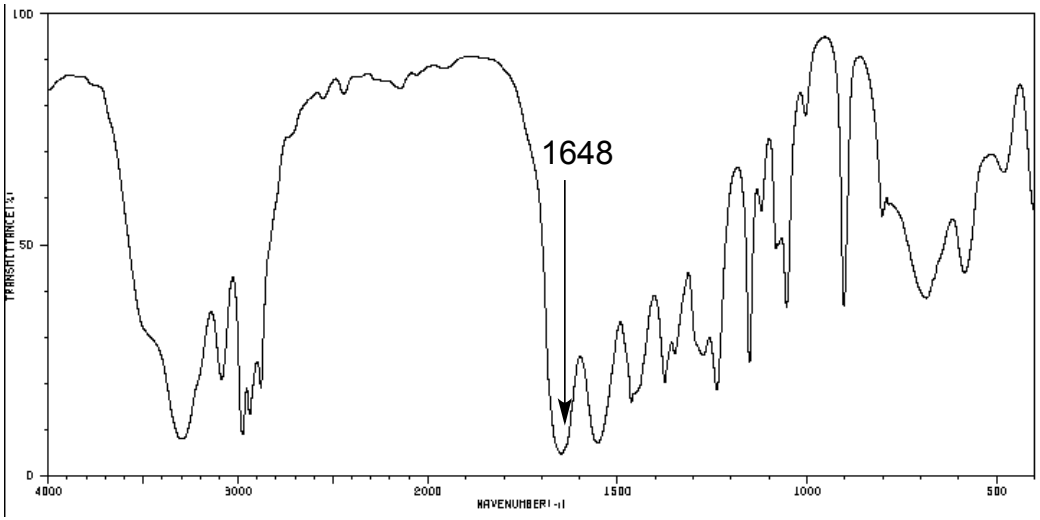


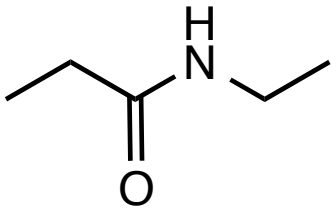
Increase $\bar{\nu}_{C=O}$ **Decrease $\bar{\nu}_{C=O}$**

Ketone vs Amide

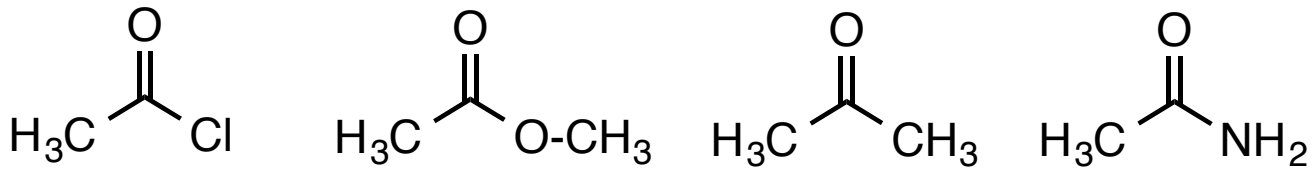






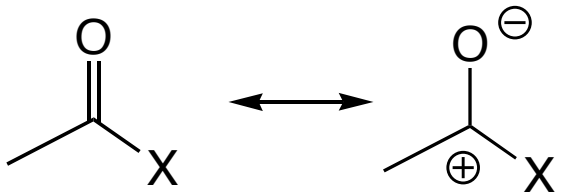


Carbonyl Compounds



$\bar{\nu}_{C=O}(cm^{-1})$ 1800 1740 1715 1650

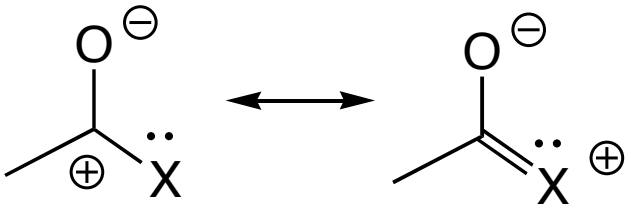
stronger bond



Inductive effect

O > N > Cl > C

3.5 3.1 2.8 2.5



Resonance effect

N > O > Cl

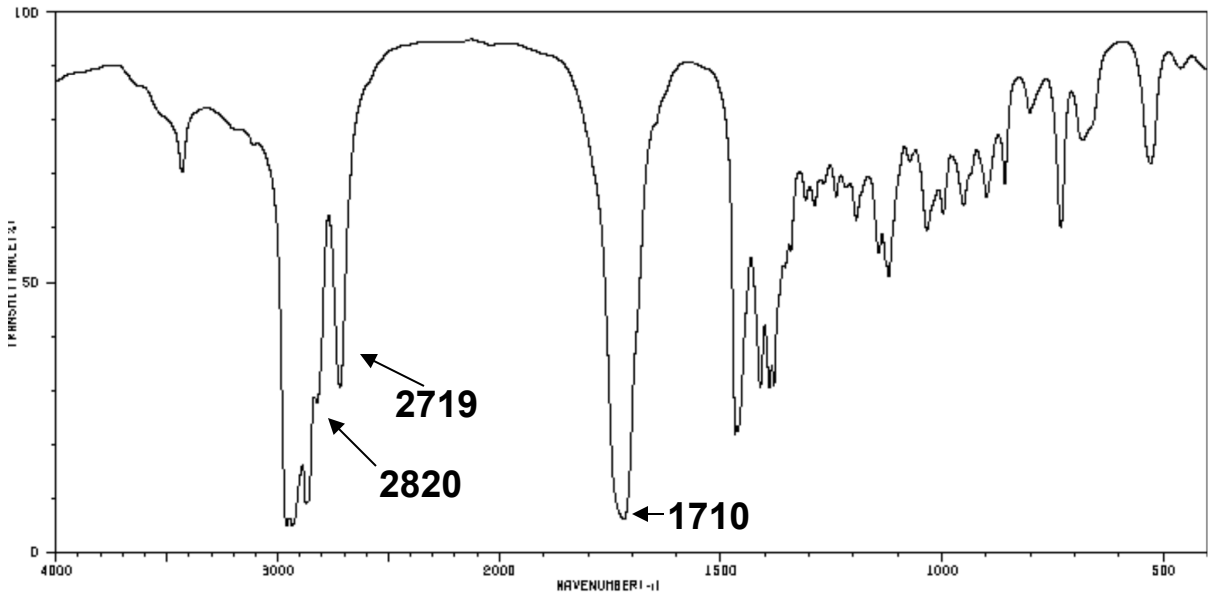
Aldehydes

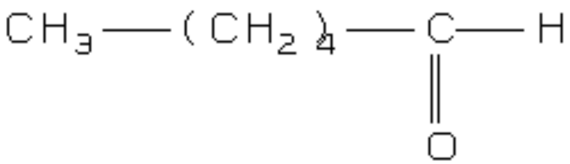
- C=O 1725 cm^{-1}
- C-H 2820 and 2710 cm^{-1},

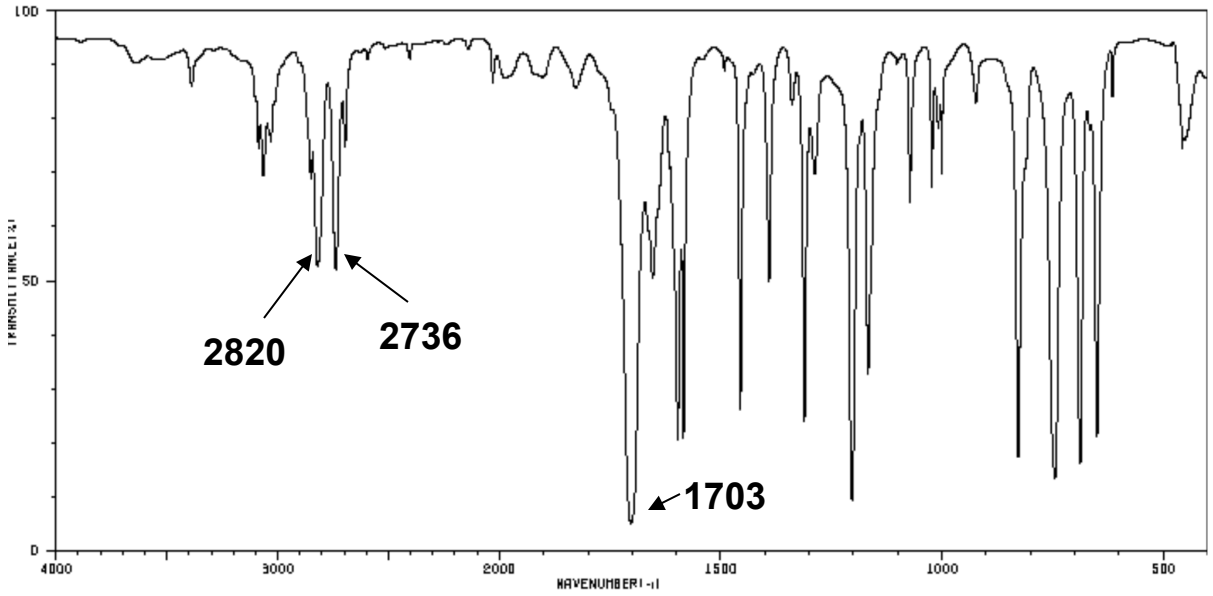
Fermi doublet

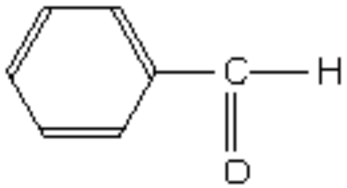
Important for ketone vs aldehyde

Hexanal & Benzaldehyde

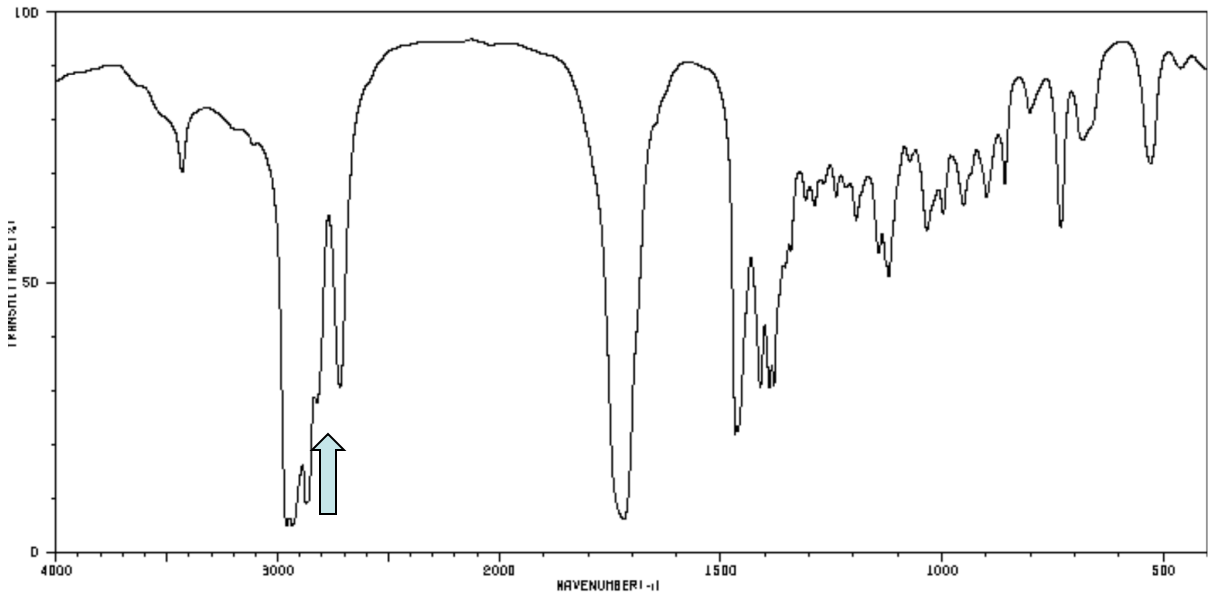


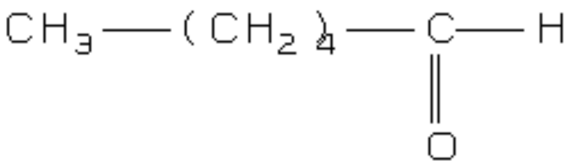


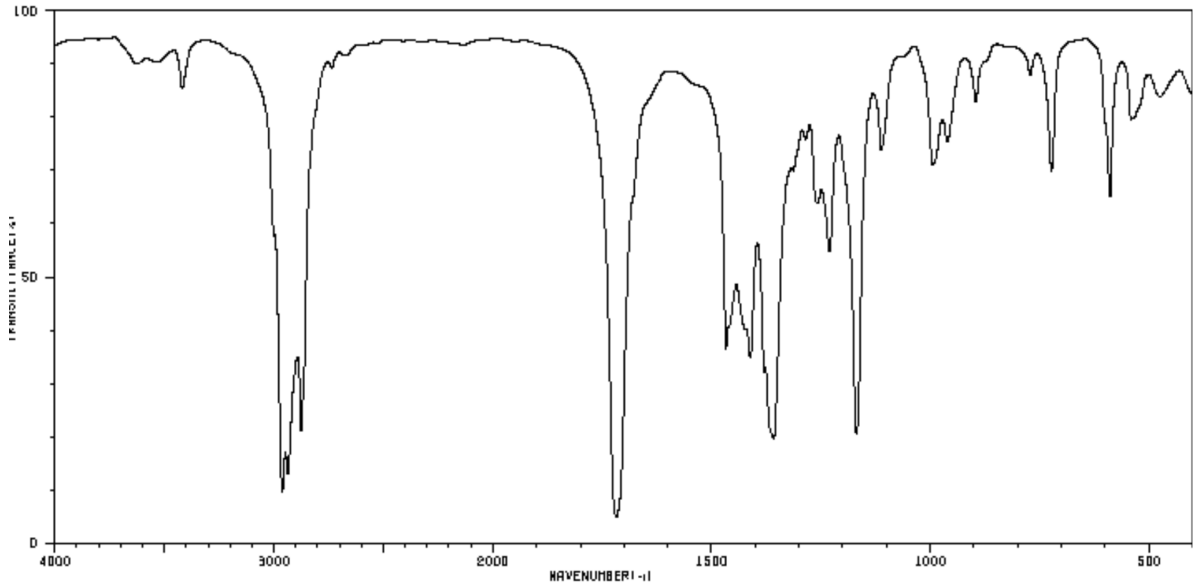


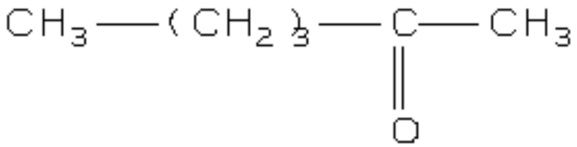


Ketone vs Aldehyde





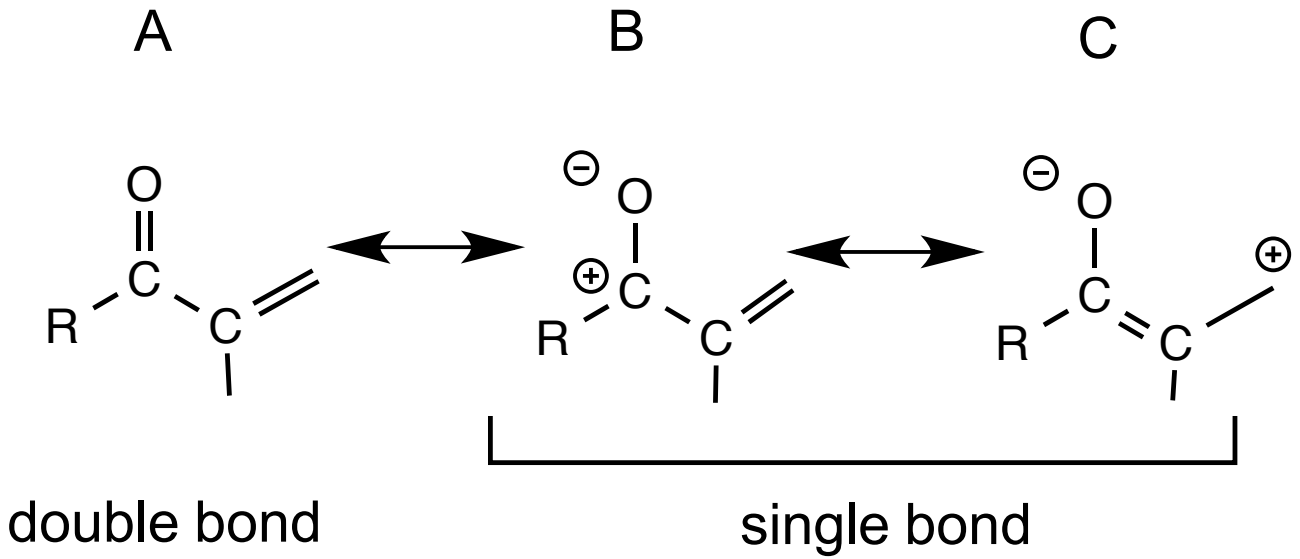




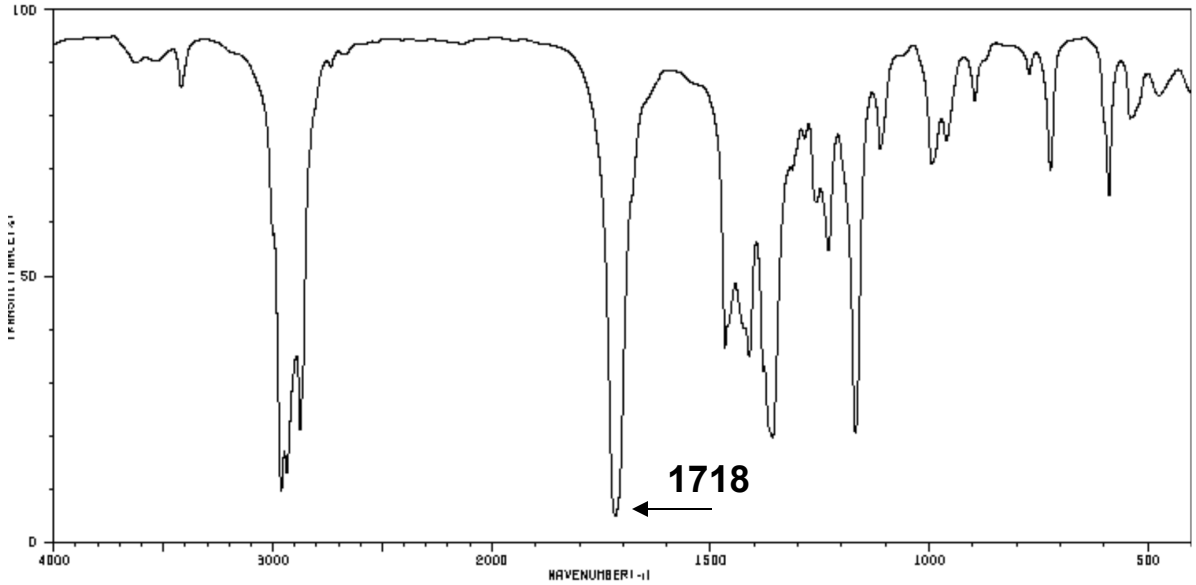
Ketones

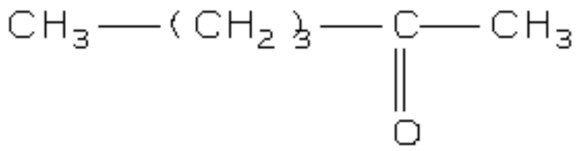
- C=O 1715 cm^{-1}

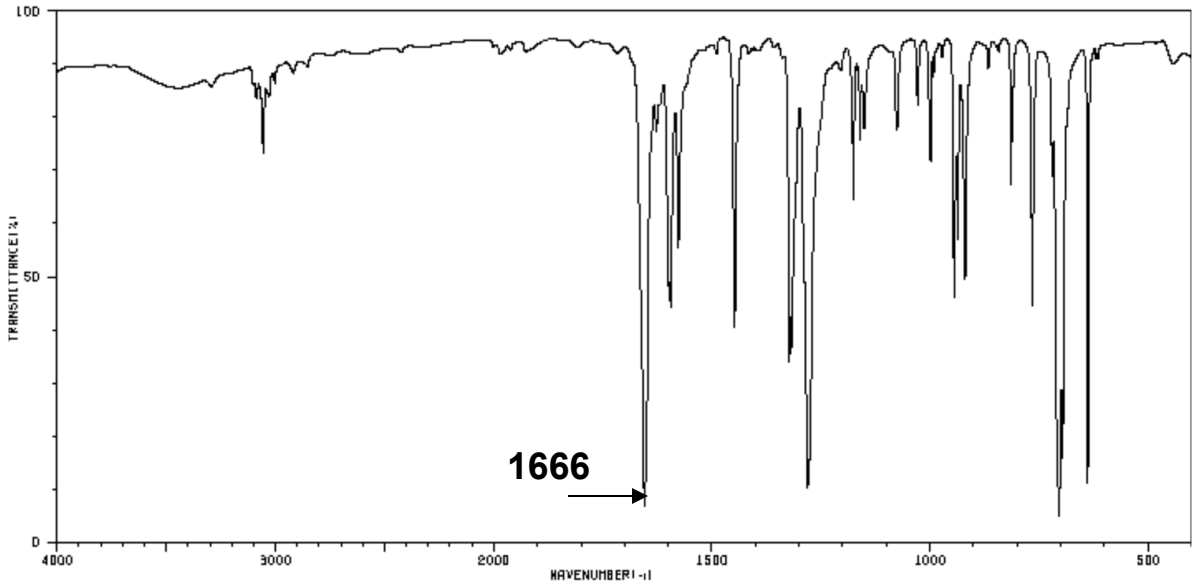
  Conjugation and ring size

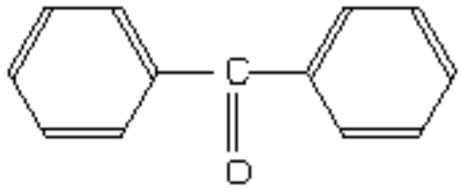


2-Hexanone & Benzophenone

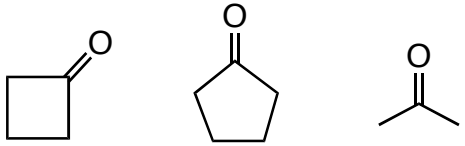




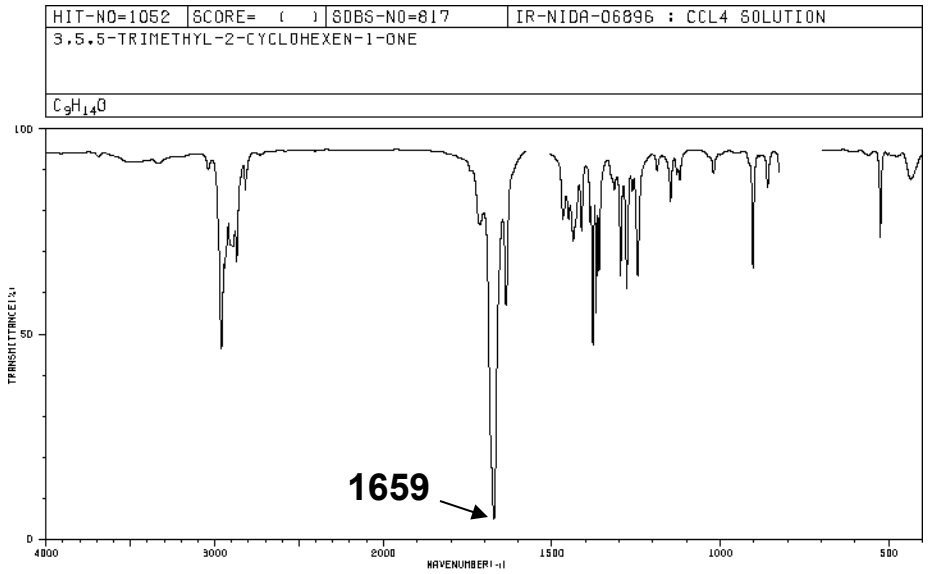




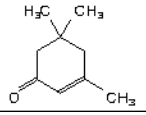
Ring Size Effects

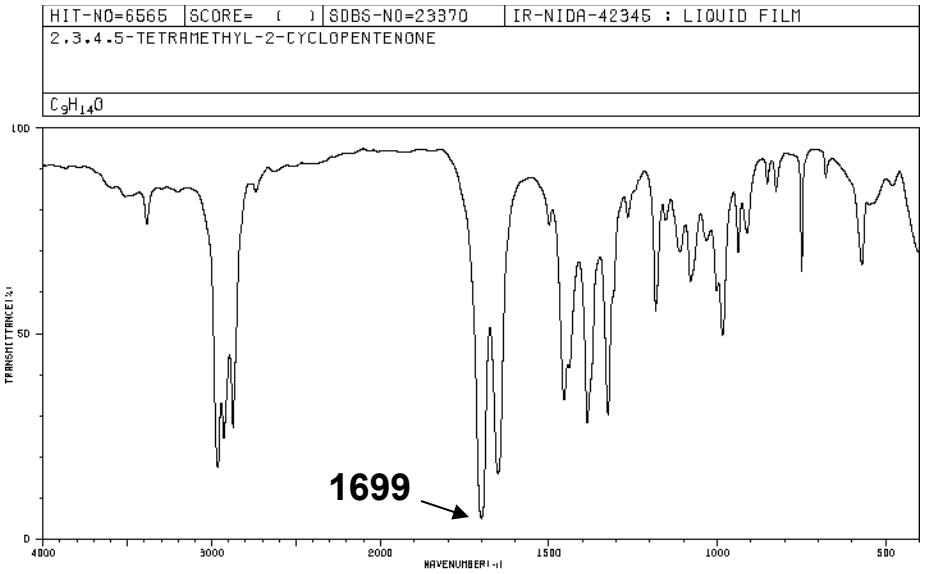


$\overline{\nu}$ (C=C) 1780 1645 1615

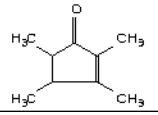


2960	44	1672	4	1379	46	1245	62	860	81
2941	64	1637	55	1369	53	1188	86	525	70
2903	86	1468	74	1360	62	1148	79	435	64
2893	68	1450	74	1315	81	1129	86		
2869	64	1437	70	1297	62	1121	84		
2819	81	1412	72	1278	56	1020	85		
1714	74	1387	74	1262	81	903	64		

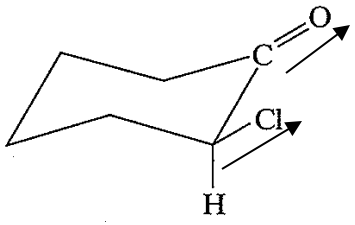




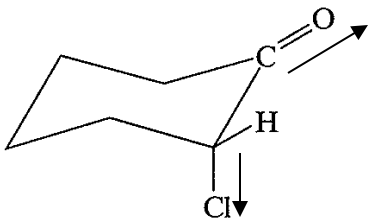
3385	74	1498	74	1154	74	911	72	480	81
2964	16	1456	32	1110	68	852	84		
2929	23	1440	39	1080	80	847	85		
2873	26	1386	26	1032	70	826	81		
2739	81	1325	29	1002	58	750	62		
1699	4	1268	74	985	47	678	84		
1660	16	1184	59	938	66	671	64		



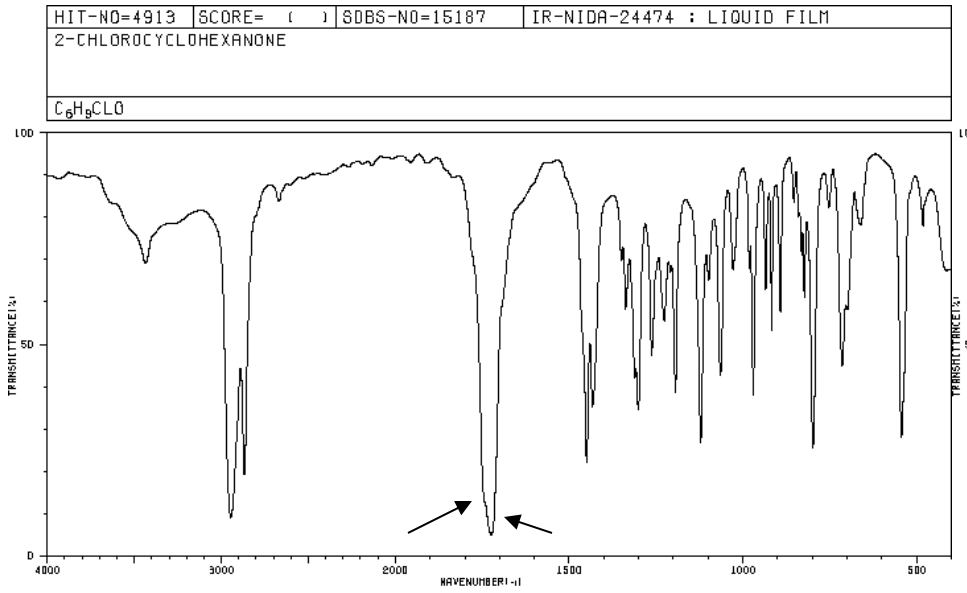
Alpha-substituents



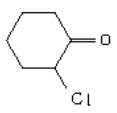
equatorial
$\nu_{CO} = 1745\ cm^{-1}$

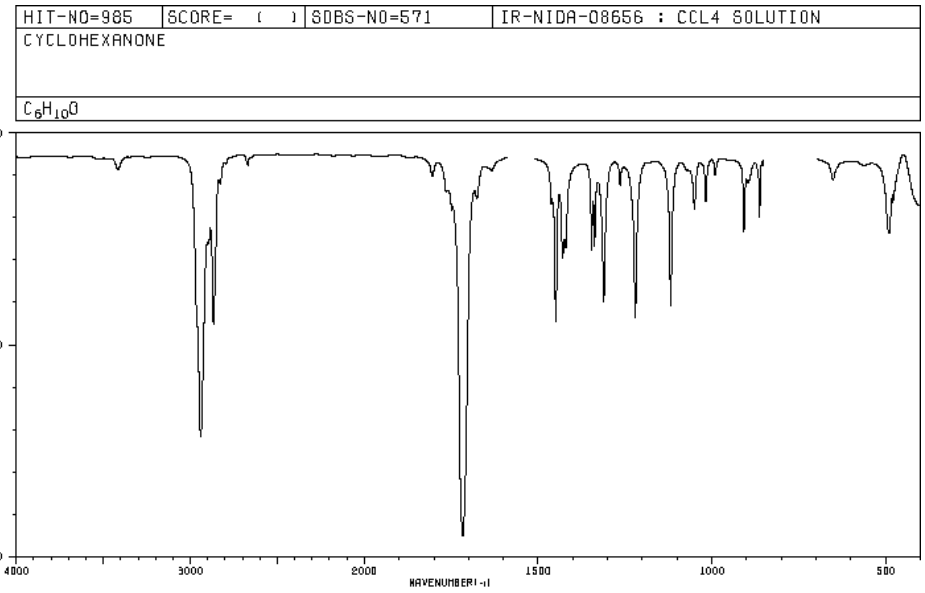


axial
$\nu_{CO} = 1725\ cm^{-1}$

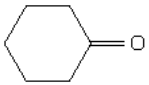


3436	66	1360	66	1196	37	936	60	763	79
2946	8	1338	55	1122	25	917	52	715	43
2867	16	1311	39	1098	82	893	55	700	55
2671	81	1302	39	1066	41	853	79	662	74
1723	4	1263	46	1029	66	831	68	544	26
1450	21	1227	59	982	86	823	58	482	74
1433	34	1209	64	971	36	798	24		



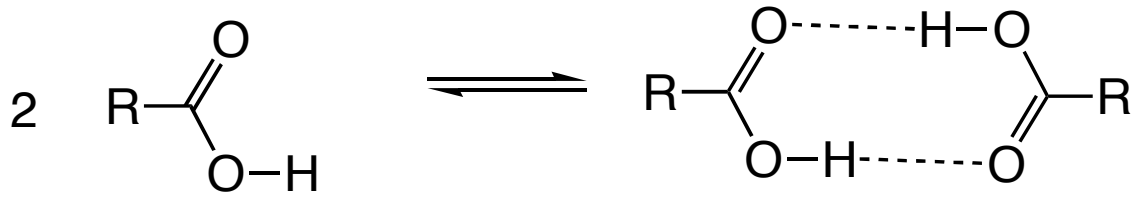


2940	26	1430	68	1119	67	491	72
2867	52	1422	70	1050	79	485	79
1804	86	1347	70	1018	81		
1717	4	1338	70	908	74		
1677	81	1311	58	896	84		
1463	79	1265	84	863	77		
1449	63	1221	69	852	86		



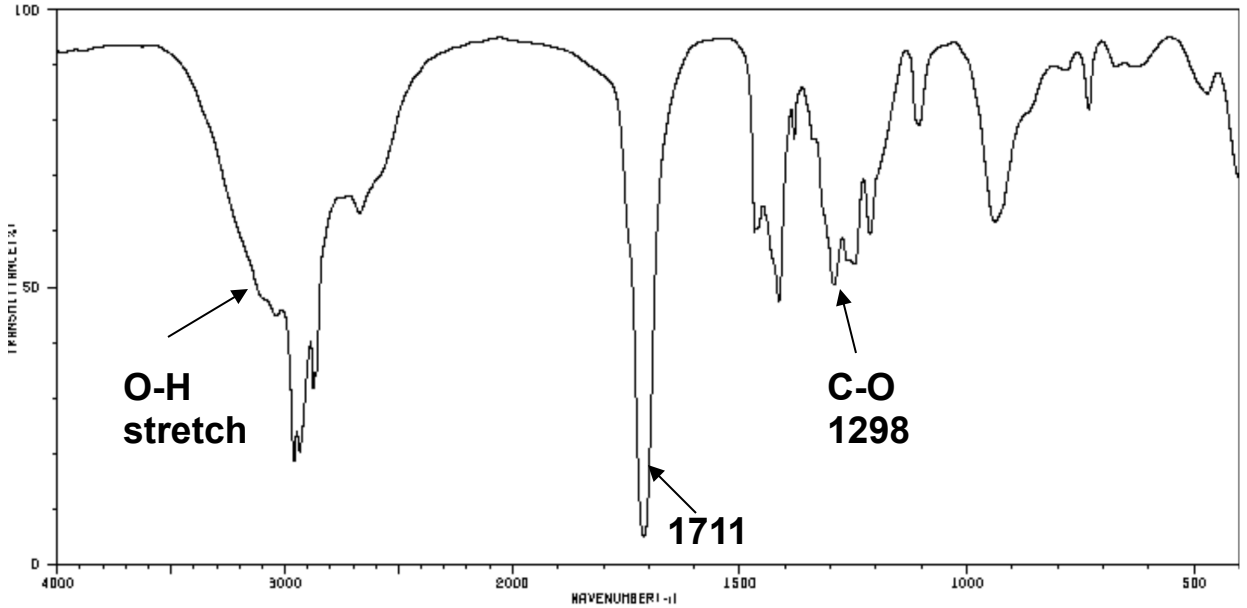
Carboxylic Acids

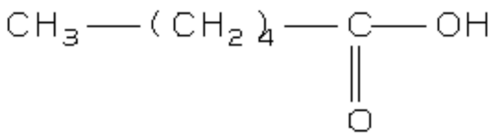
- O-H 3400 ~ 2400 cm^{-1}
- C=O 1730 ~ 1700 cm^{-1}
- C-O 1320 ~ 1210 cm^{-1}

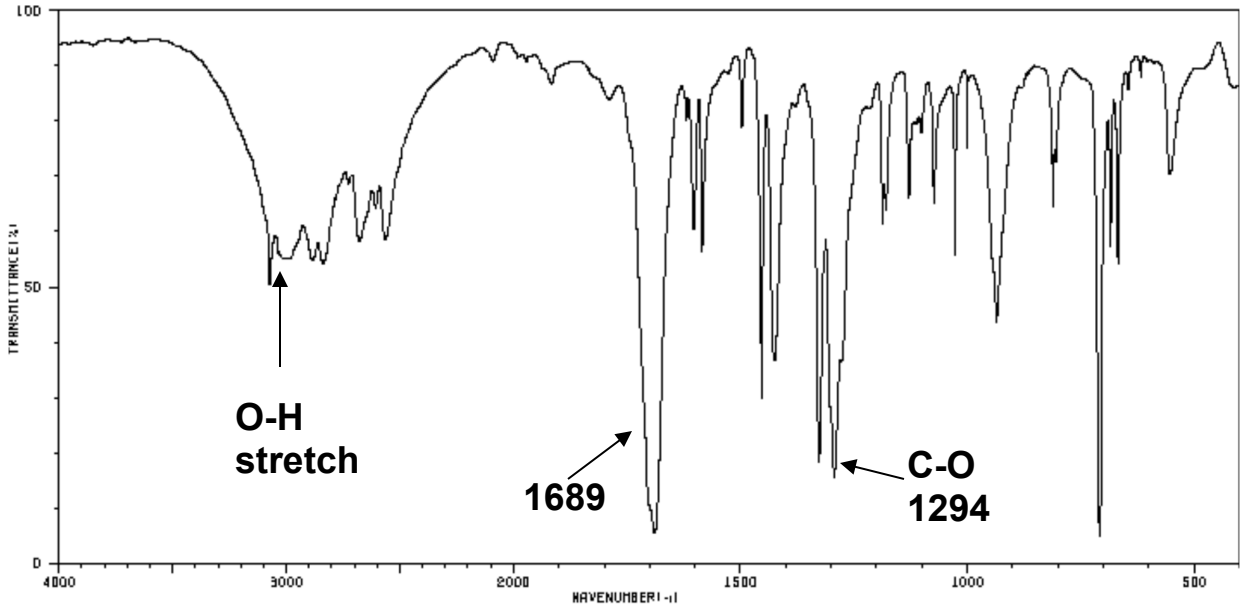


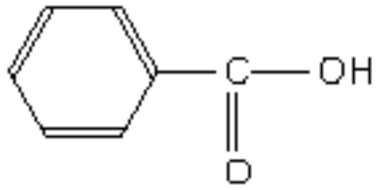
1760 cm^{-1} 1710 cm^{-1}

Hexanoic Acid and Benzoic Acid





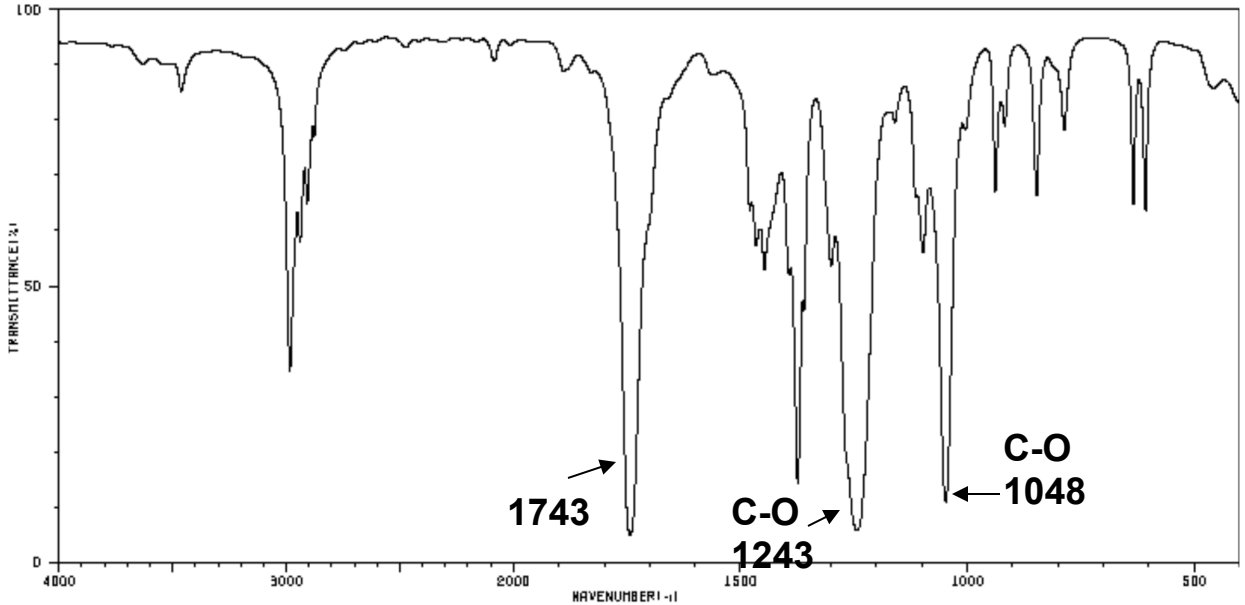


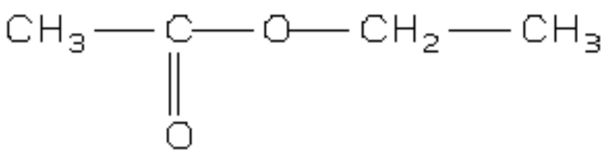


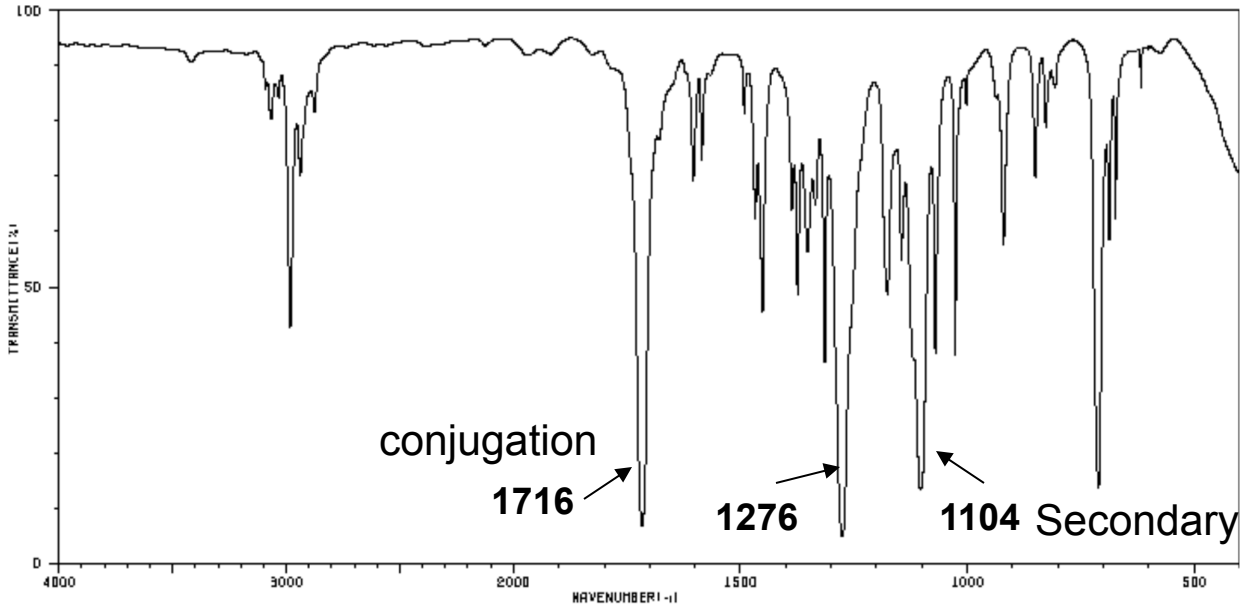
Esters

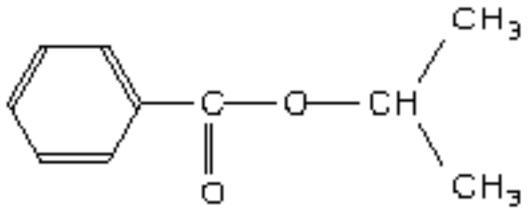
- C=O 1755 cm^{-1}
  Conjugation & ring size
- C-O 1300 ~ 1000 cm^{-1}

Ethyl Acetate & Isopropyl Benzoate



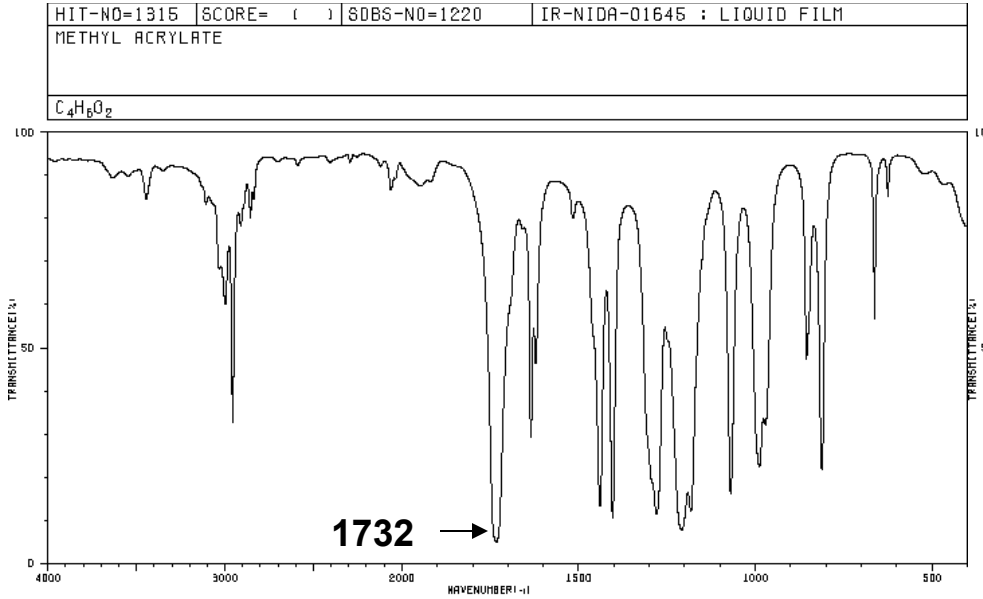




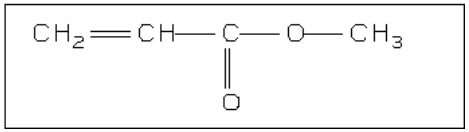


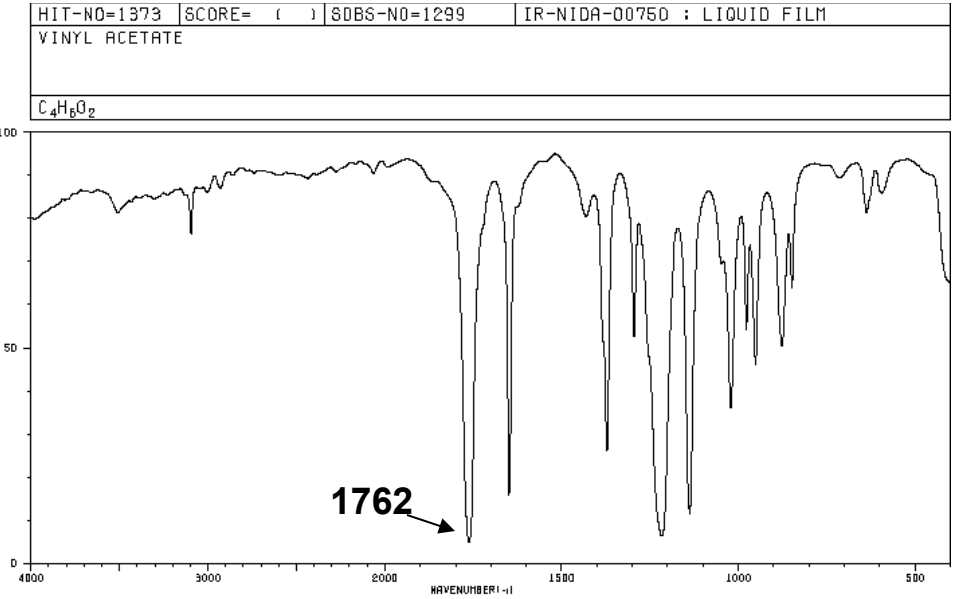
Secondary alcohol

Methyl Acrylate & Vinyl Acetate

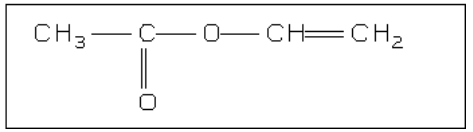


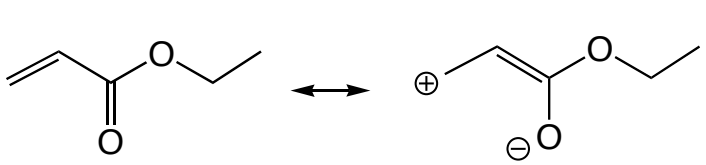
3632	86	2856	77	1621	44	1070	16
3444	81	2836	81	1516	77	988	21
3107	79	2061	84	1440	12	971	31
3031	66	2037	88	1404	10	866	46
2998	58	1945	84	1279	10	812	21
2956	31	1732	4	1209	7	663	55
2910	74	1636	27	1183	11	626	81



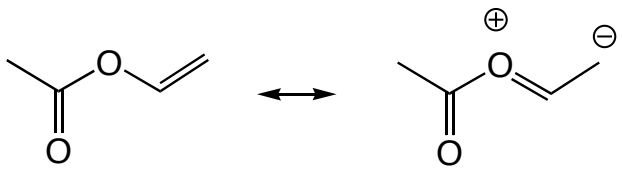


3609	79	1431	77	951	44		
3121	81	1372	25	877	49		
3095	74	1295	50	848	82		
3002	84	1217	6	714	86		
2931	84	1138	11	639	79		
1762	4	1021	35	595	81		
1649	16	977	52				

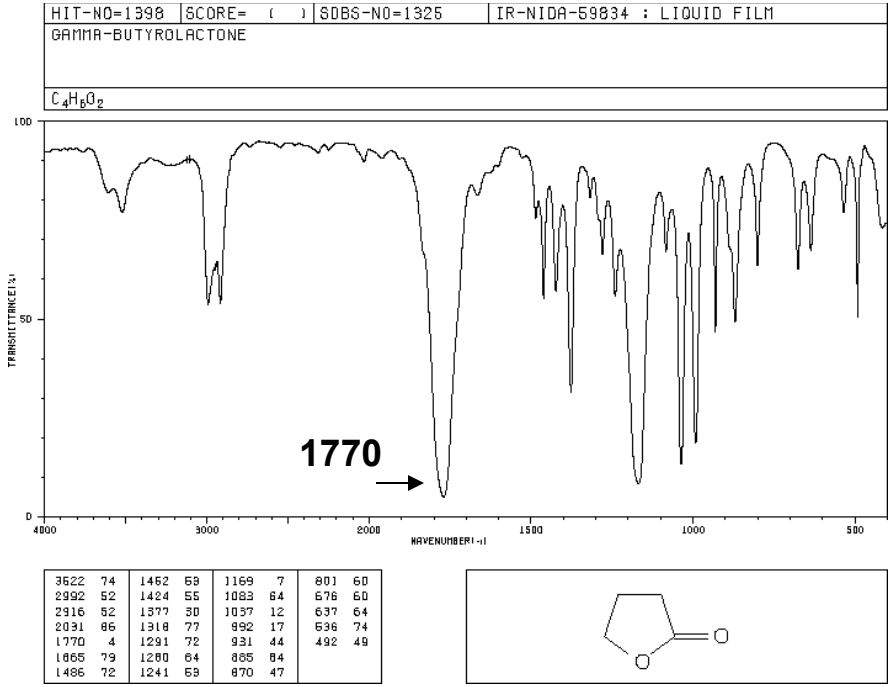




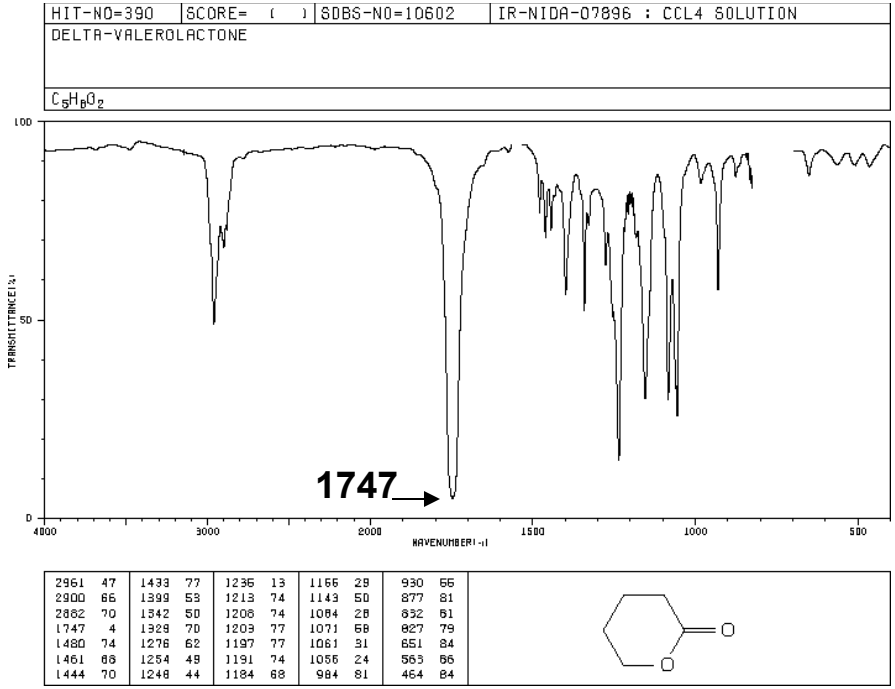
Ethyl acetate
1743 cm^{-1}



Lactones



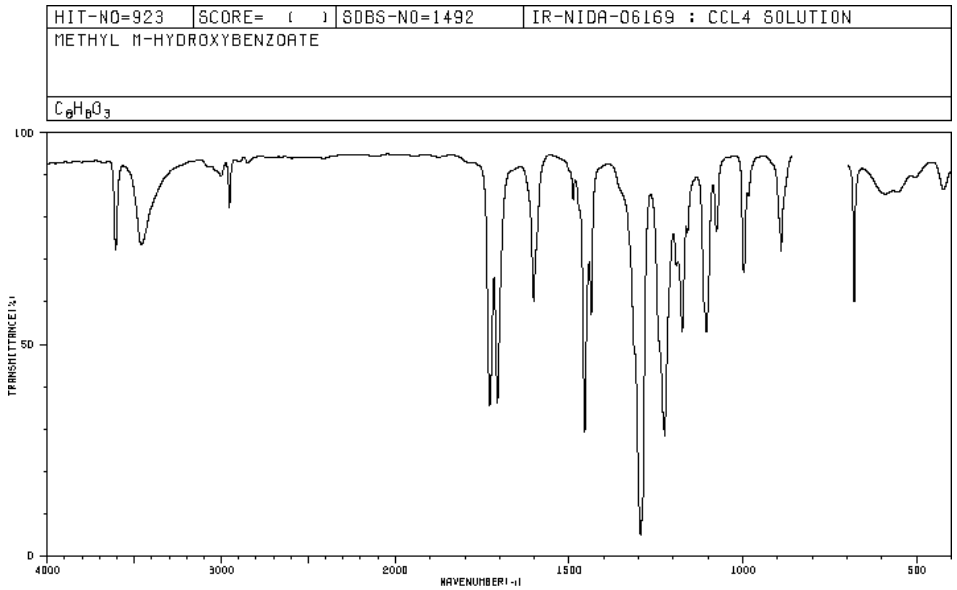
3622	74	1462	58	1169	7	801	60
2992	52	1424	55	1083	64	676	60
2916	52	1377	30	1037	12	637	64
2031	86	1318	77	992	17	536	74
1770	4	1291	72	931	44	492	49
1665	79	1280	64	885	84		
1486	72	1241	58	870	47		



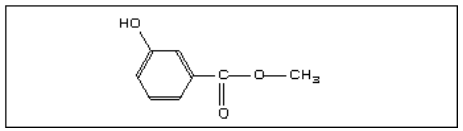
2961	47	1433	77	1236	13	1166	28	930	66
2900	86	1399	53	1213	74	1143	50	877	81
2862	70	1342	50	1208	74	1084	28	852	61
1747	4	1328	70	1203	77	1071	58	827	79
1480	74	1276	62	1197	77	1061	31	651	84
1461	66	1254	49	1191	74	1056	24	563	66
1444	70	1248	44	1184	68	984	81	464	84

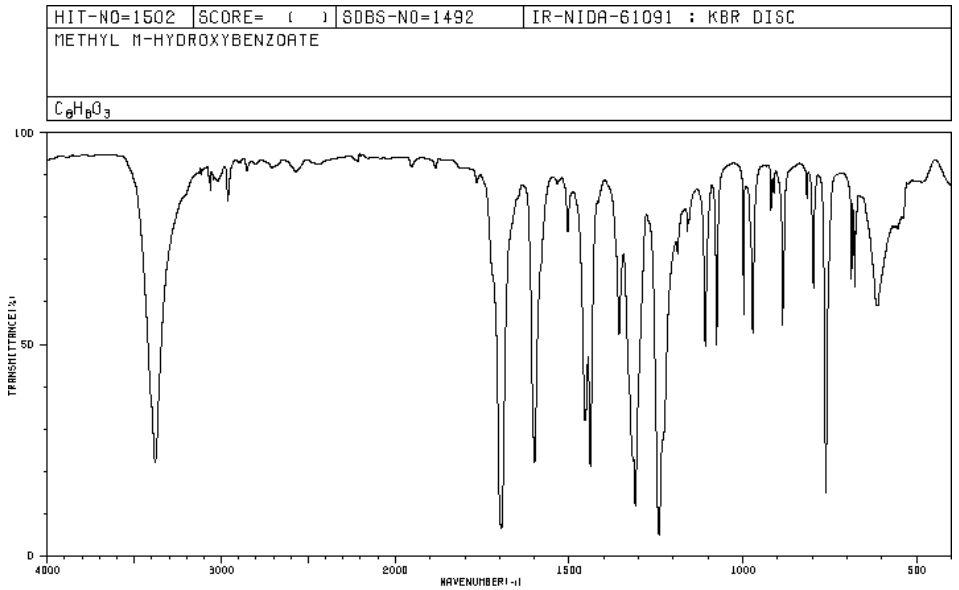
Ring size ↓ ⇒ $\overline{\nu}_{C=O}$ ↑

Methyl m-Hydroxybenzoate

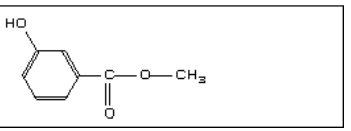


3607	70	1568	96	1160	74	680	68
3459	70	1489	81	1105	50		
3001	86	1458	27	1077	74		
2953	79	1437	66	997	64		
1728	34	1295	4	984	81		
1707	34	1228	25	896	77		
1602	58	1176	60	891	70		





3398	32	1766	84	1367	50	1076	47	797	50
3380	21	1695	6	1317	21	998	55	791	84
3064	84	1600	21	1310	11	972	50	762	14
3046	86	1534	84	1242	4	919	79	698	62
3030	86	1504	74	1188	68	911	81	679	62
3016	84	1455	31	1160	74	886	52	614	57
2962	81	1439	20	1108	47	816	81		

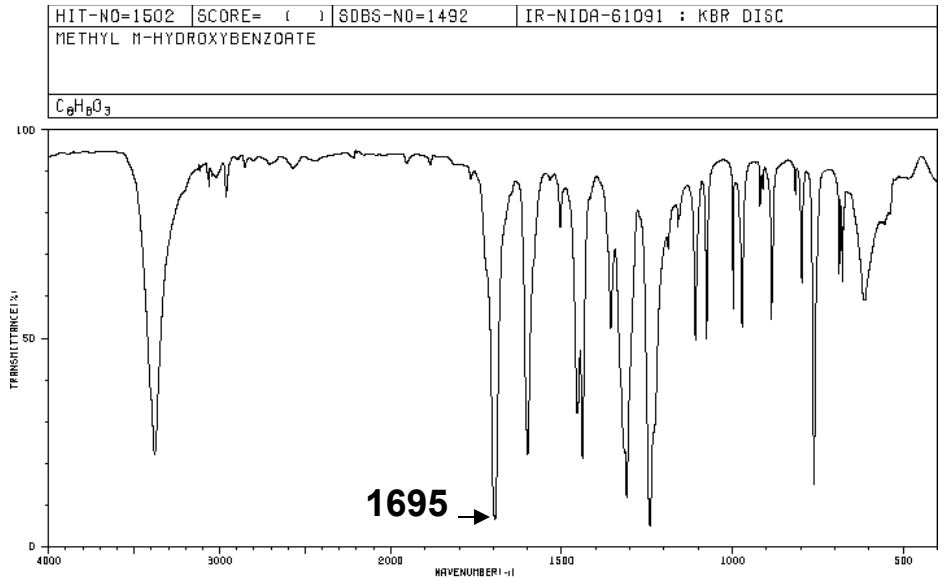


CCl_4 solution

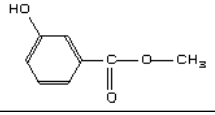
KBr pellet

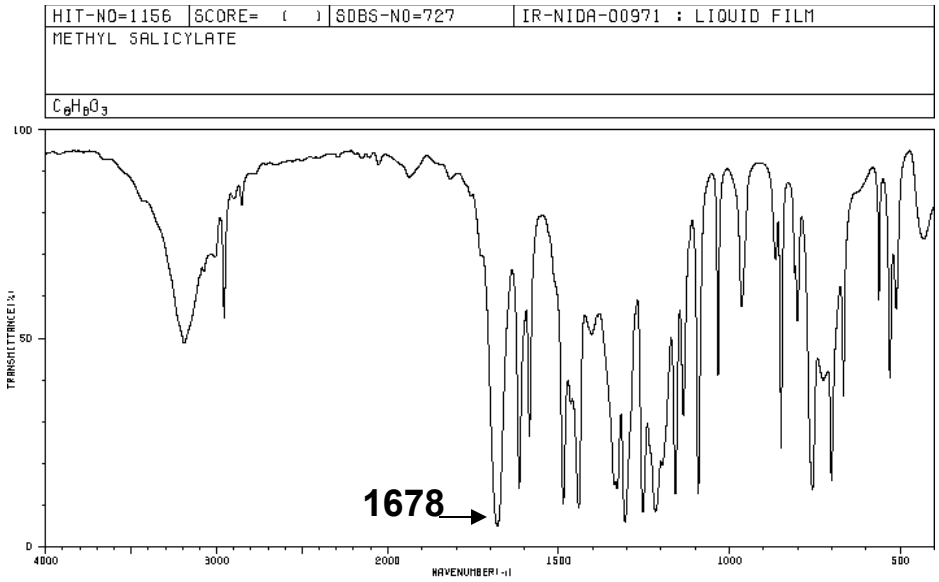
H-bonding ⇒ $\bar{\nu}_{C=O}\downarrow$

Methyl o- or m-hydroxybenzoate

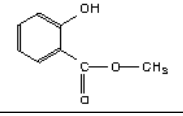


3398	32	1766	84	1367	60	1076	47	797	60
3380	21	1695	6	1317	21	998	55	791	84
3064	84	1600	21	1310	11	972	50	762	14
3046	86	1534	84	1242	4	919	78	688	62
3030	86	1504	74	1188	68	911	81	679	62
3016	84	1455	31	1160	74	886	52	614	57
2962	81	1439	20	1108	47	816	81		





3190	47	1679	4	1329	13	1033	39	726	38
3074	64	1615	13	1306	5	964	55	702	15
2956	52	1586	25	1254	8	865	66	667	34
2898	79	1487	10	1217	7	849	22	663	57
2855	79	1441	8	1159	12	810	62	531	38
1936	84	1403	49	1135	30	801	52	512	55
1818	84	1338	14	1091	12	757	19	431	70



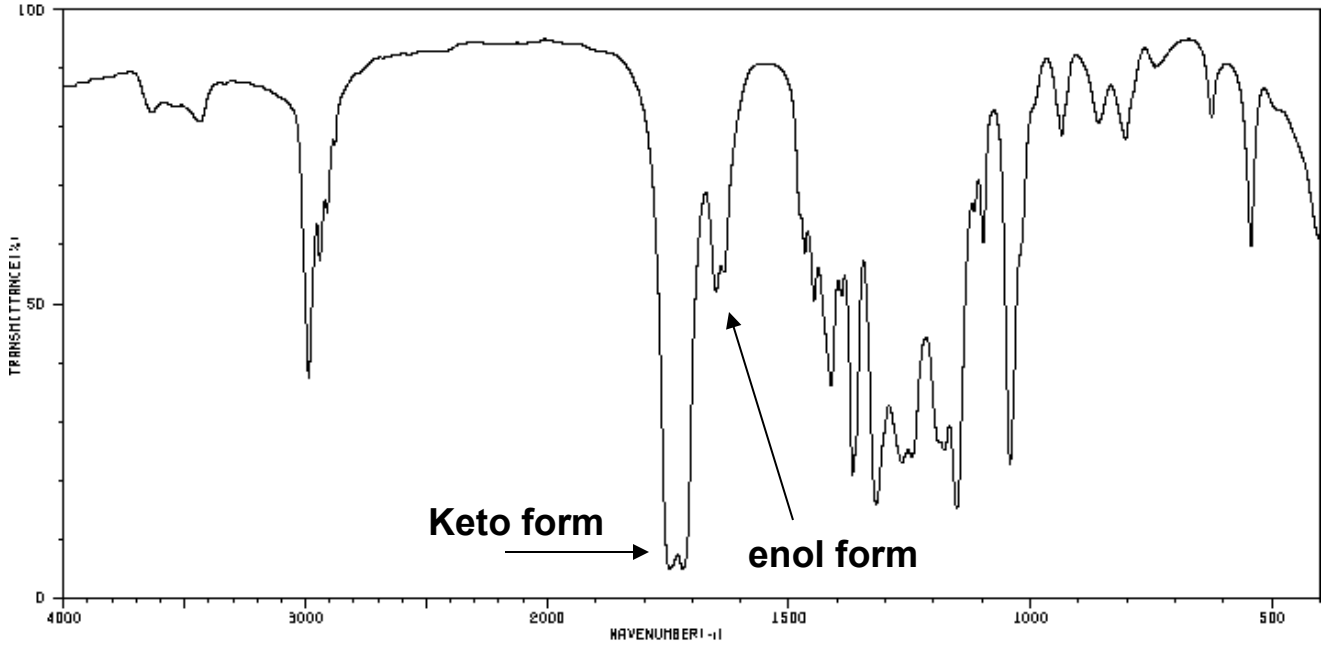
Methyl benzoate
1724 cm^{-1}

Keto and Enol Forms

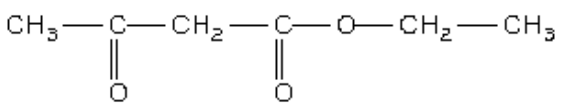
HIT-NO=1071	SCORE= ( )	SDBS-NO=573	IR-NIDA-00054 : LIQUID FILM

ETHYL ACETOACETATE

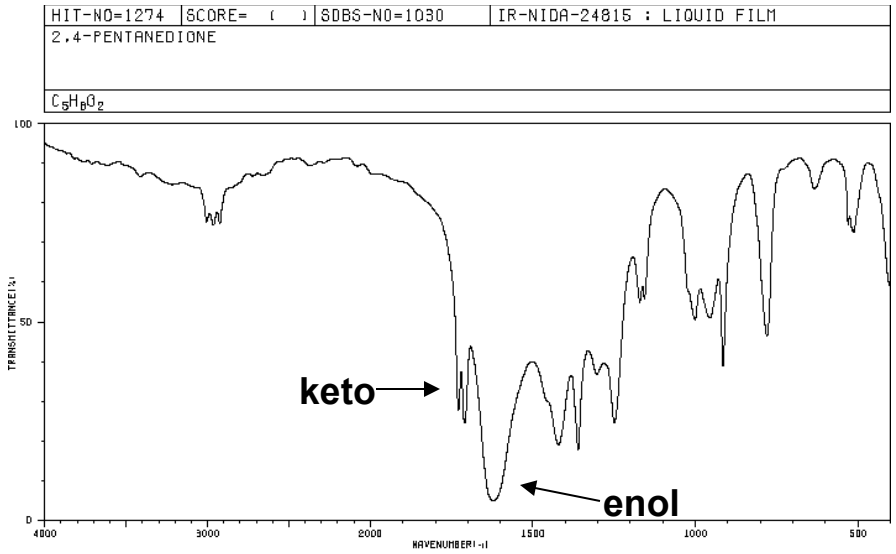
$C_6H_{10}O_3$



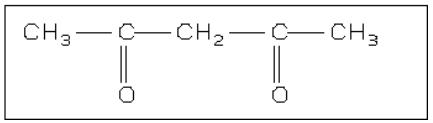
3634	79	1731	7	1391	49	1163	14	625	79
3438	77	1719	4	1368	20	1116	62	543	57
2985	35	1651	50	1319	15	1097	58		
2941	66	1634	69	1266	21	1042	21		
2910	62	1467	57	1245	23	935	77		
2878	74	1448	49	1189	25	859	77		
1746	4	1413	34	1179	23	803	74		

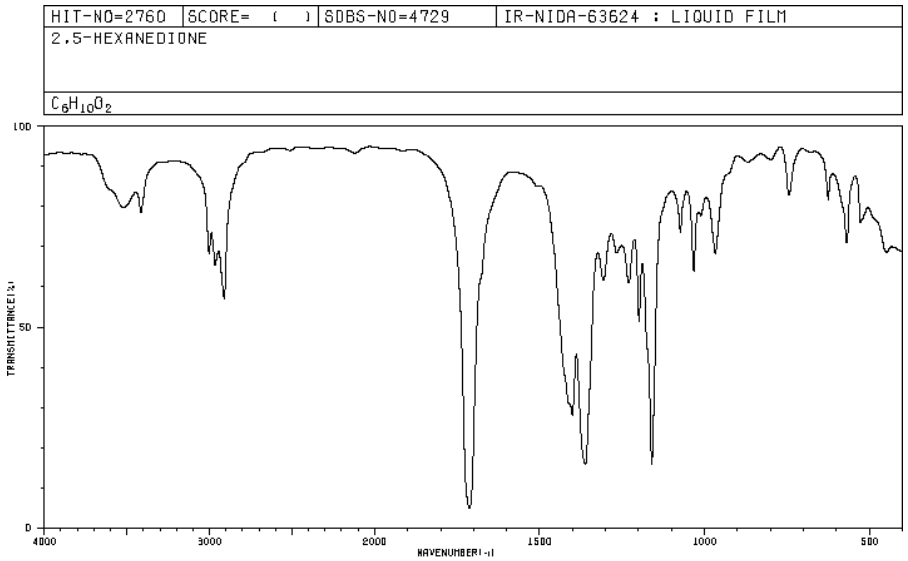


Diones

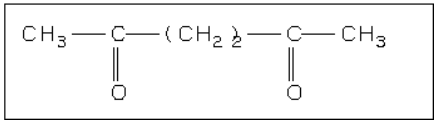


3006	72	1422	18	966	49
2964	72	1361	17	915	37
2924	72	1304	35	780	44
2367	86	1249	29	634	81
1729	26	1172	53	531	72
1710	23	1157	55	519	70
1622	4	1001	49	512	70





3619	77	1401	28	1079	70	621	74
3414	77	1362	15	1033	62	449	66
3002	86	1307	58	967	86		
2966	62	1267	66	744	79		
2912	55	1230	58	626	79		
1715	4	1199	49	569	66		
1409	29	1160	15	528	72		



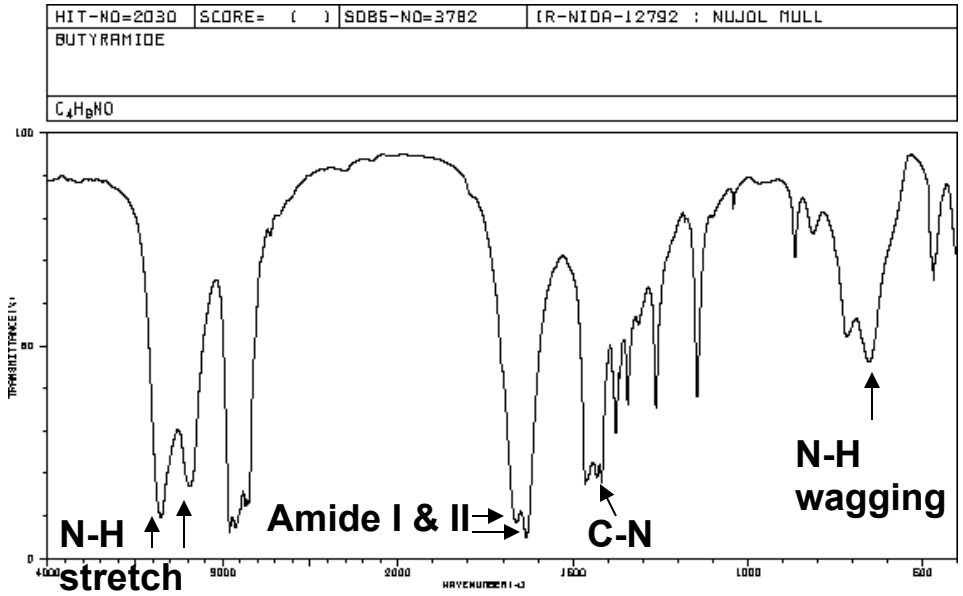
Amides

- C=O stretch (amide I) 1680 ~ 1630 cm^{-1}
- N-H bending (amide II) 1640 ~ 1550 cm^{-1}
  I° and II° amides only
  often overlaps with amide I
- N-H stretch 3350 ~ 3180 cm^{-1}(H-bonded)
  I° (two bands) and II°(one band) amides only

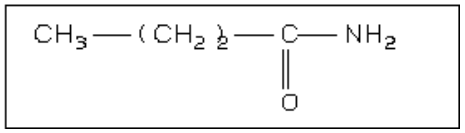
Other bands

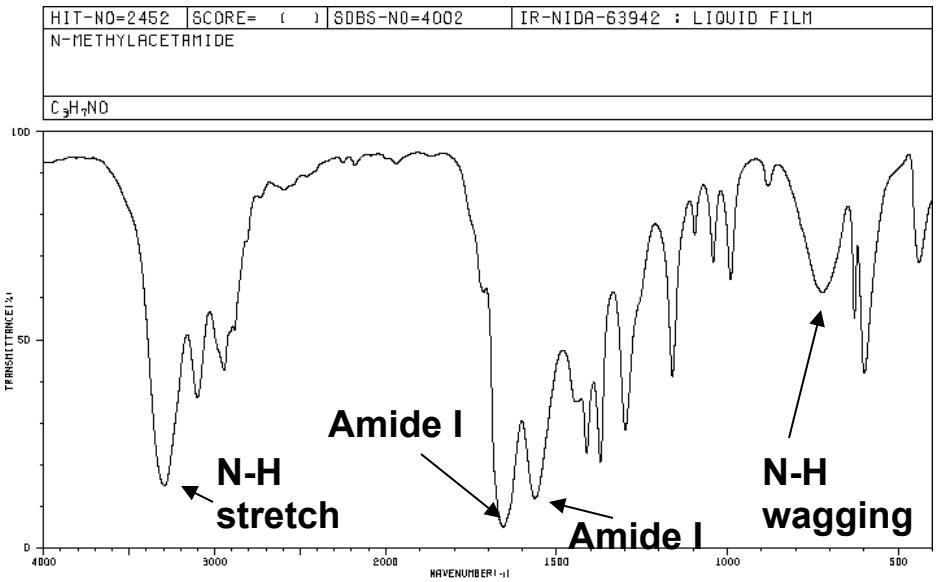
- C-N stretch ~1400 cm^{-1}
- N-H wagging 800 ~ 660 cm^{-1} broad

Butanamide and N-Methyl Acetamide

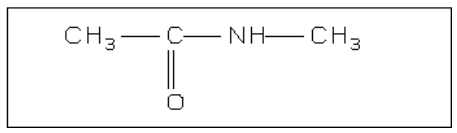


3364	9	2728	72	1577	28	1042	79
3187	15	1652	7	1468	41	866	68
2961	5	1633	4	1343	36	816	74
2946	9	1466	16	1312	63	721	60
2928	7	1460	17	1263	34	664	44
2873	11	1431	18	1181	77	469	62
2865	12	1418	17	1145	36		

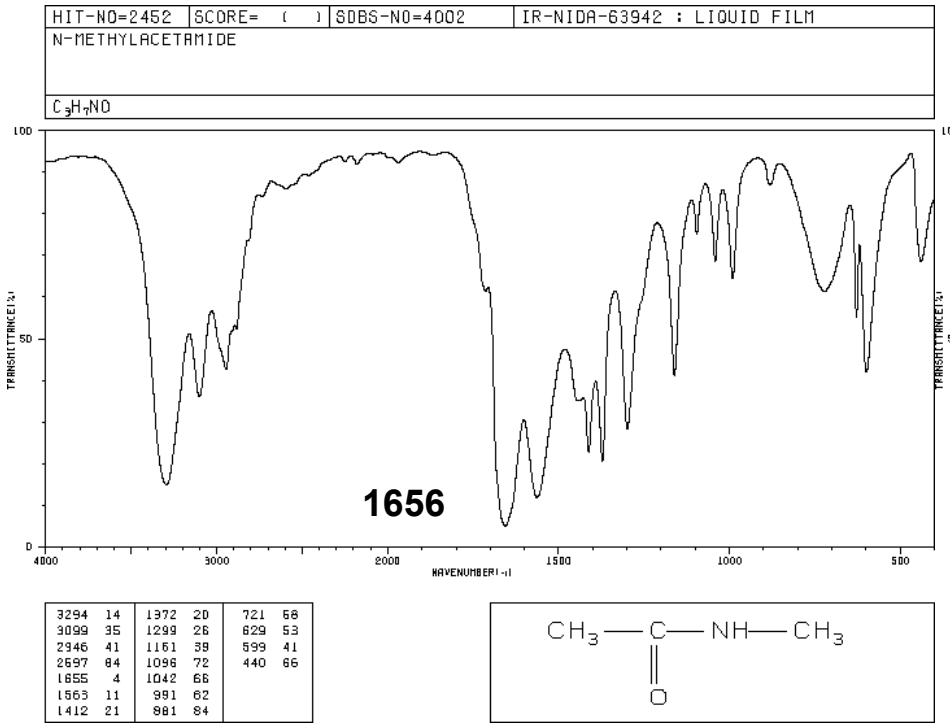




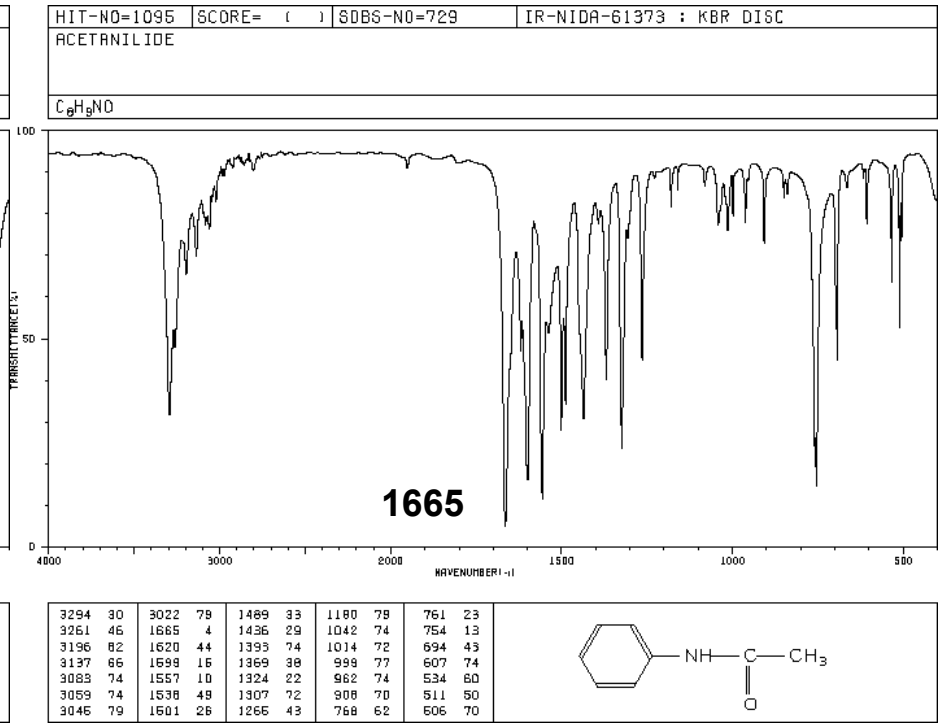
3294	14	1372	20	721	68
3099	35	1299	26	629	53
2946	41	1161	38	599	41
2697	84	1096	72	440	66
1655	4	1042	66		
1565	11	991	62		
1412	21	881	84		



N-Methyl and N-Phenyl Acetamide



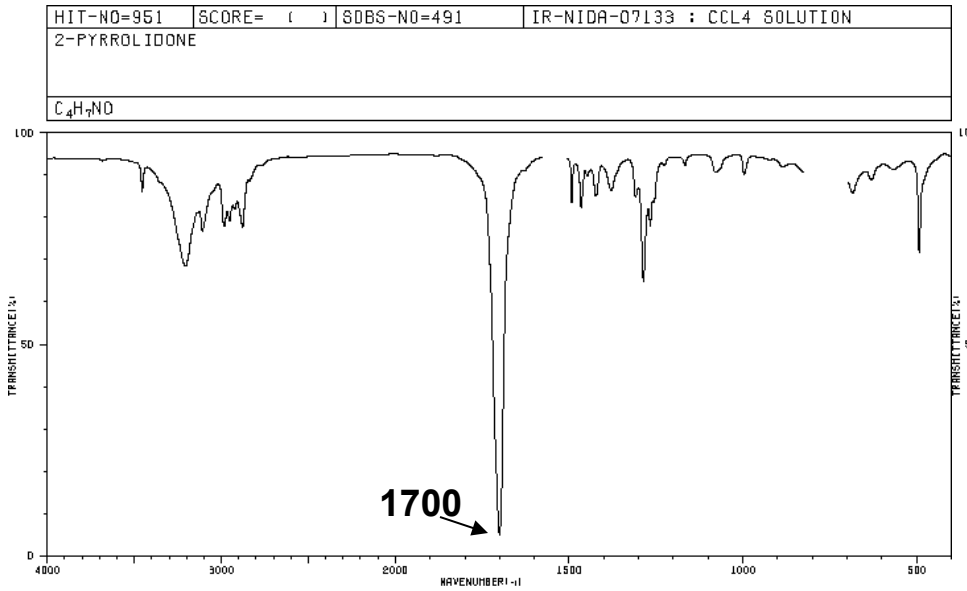
3294	14	1372	20	721	58
3099	35	1299	26	629	53
2946	41	1161	39	599	41
2697	84	1096	72	440	66
1655	4	1042	66		
1563	11	991	62		
1412	21	881	84		



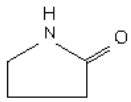
3294	30	3022	78	1489	33	1180	78	761	23
3261	46	1665	4	1436	29	1042	74	754	13
3196	62	1620	44	1393	74	1014	72	694	43
3137	66	1599	15	1369	38	999	77	607	74
3083	74	1557	10	1324	22	982	74	534	60
3059	74	1538	48	1307	72	908	70	511	50
3046	79	1501	26	1265	43	768	62	506	70

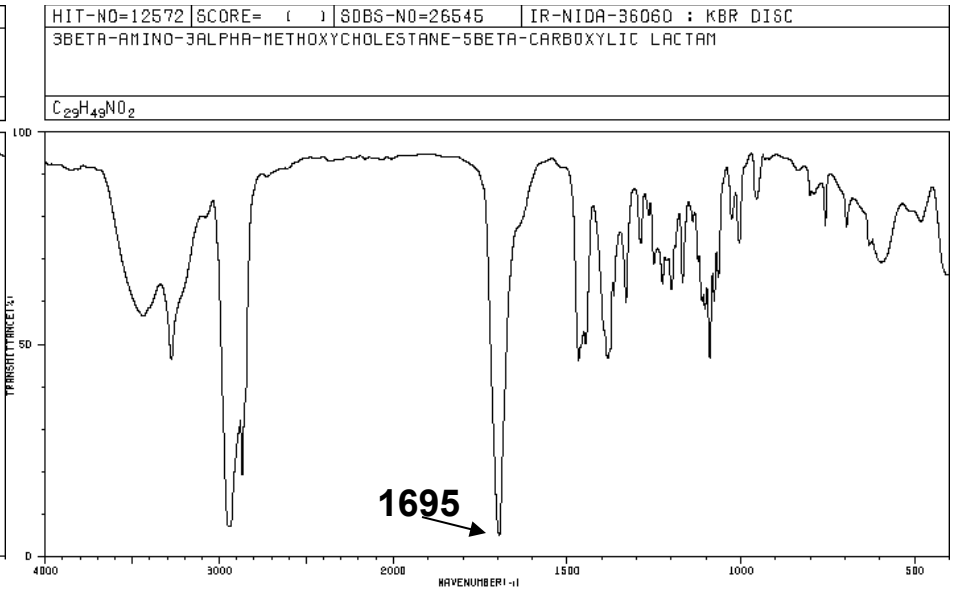
Conjugation to N ⟹ $\bar{\nu}_{C=O}$ ↑

Lactams

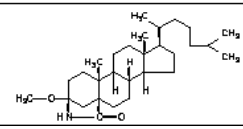


3455	84	1700	4	1287	62		
3207	66	1493	79	1267	74		
3108	74	1466	79	997	86		
2982	74	1449	86	686	81		
2966	79	1425	81	630	86		
2953	77	1376	84	495	86		
2878	74	1309	81				

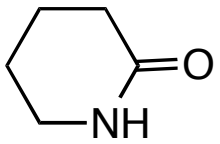




3435	55	1383	44	1226	62	1104	57	802	81
3275	44	1378	47	1213	68	1089	44	757	74
2942	6	1368	58	1200	80	1077	58	697	74
2868	18	1331	68	1168	62	1065	64	692	79
1695	4	1289	70	1139	77	1027	77	632	70
1466	44	1258	77	1124	86	1004	70	597	66
1447	49	1251	68	1112	68	966	81	483	77

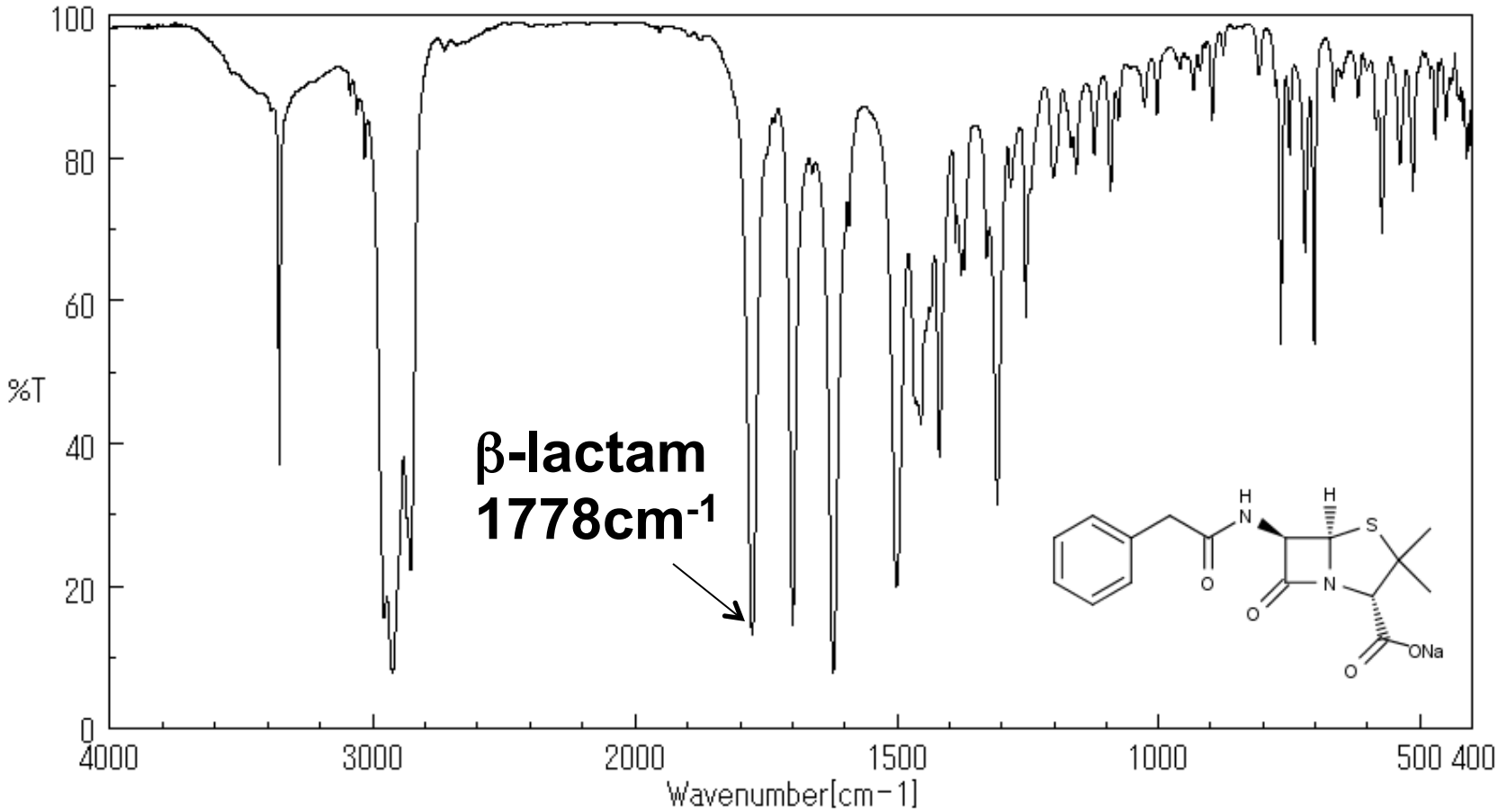


N-Ethyl acetamide
1655 cm^{-1}



1673 cm^{-1}

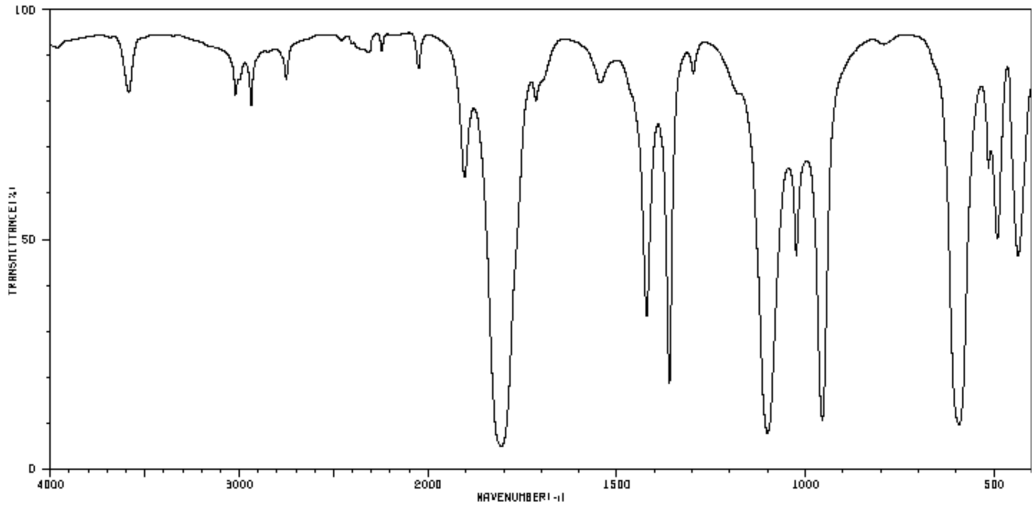
Penicillin G Sodium Salt

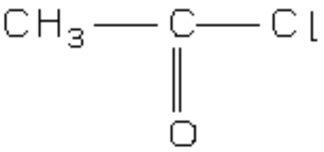


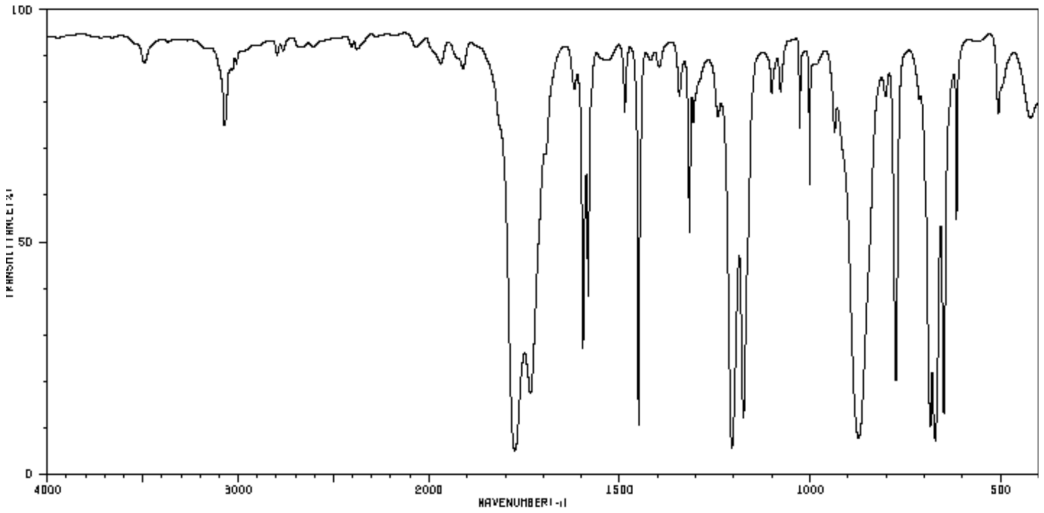
Acid Chlorides and Anhydrides

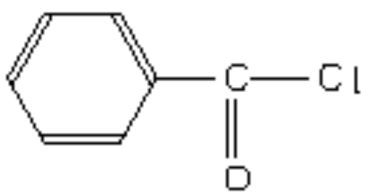
- Acid chlorides
  - C=O 1800 cm^{-1}, Fermi doublet sometime
- Carboxylic acid anhydrides
  - C=O Two bands, 1830 ~ 1800 cm^{-1}
    1775 ~ 1740 cm^{-1}
  - C-O 1300 ~ 900 cm^{-1}

Acetyl Chloride and Benzoyl Chloride

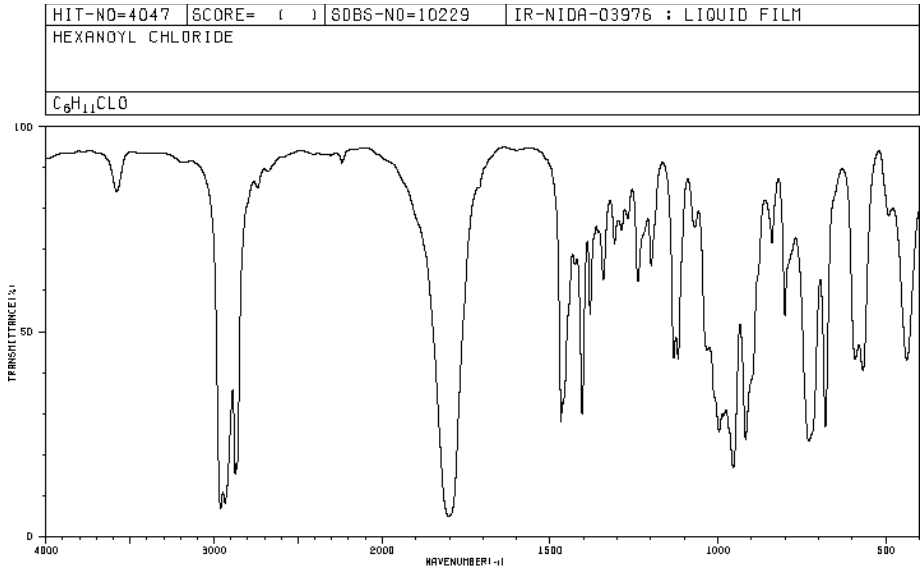




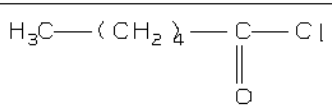


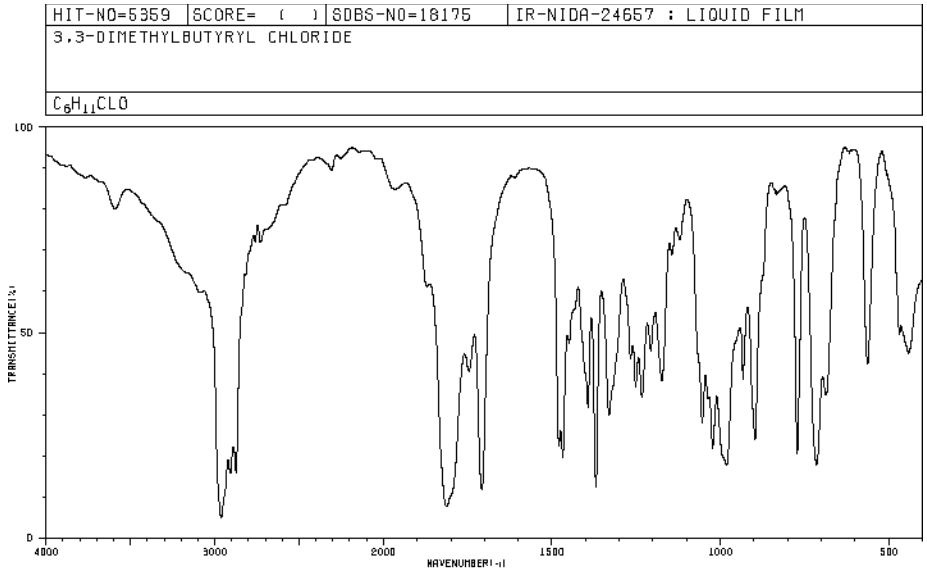


Hexanoyl Chloride & 3,3-Dimethylbutyl chloride

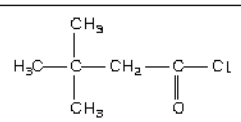


3680	81	1468	28	1288	72	997	24	692	42
2961	6	1461	31	1269	74	955	16	584	43
2935	7	1427	64	1239	80	918	22	577	42
2875	14	1405	28	1199	64	840	68	569	38
2864	15	1381	52	1132	42	801	52	491	74
2739	81	1342	60	1119	42	730	22	436	41
1800	4	1308	68	1069	72	680	26		

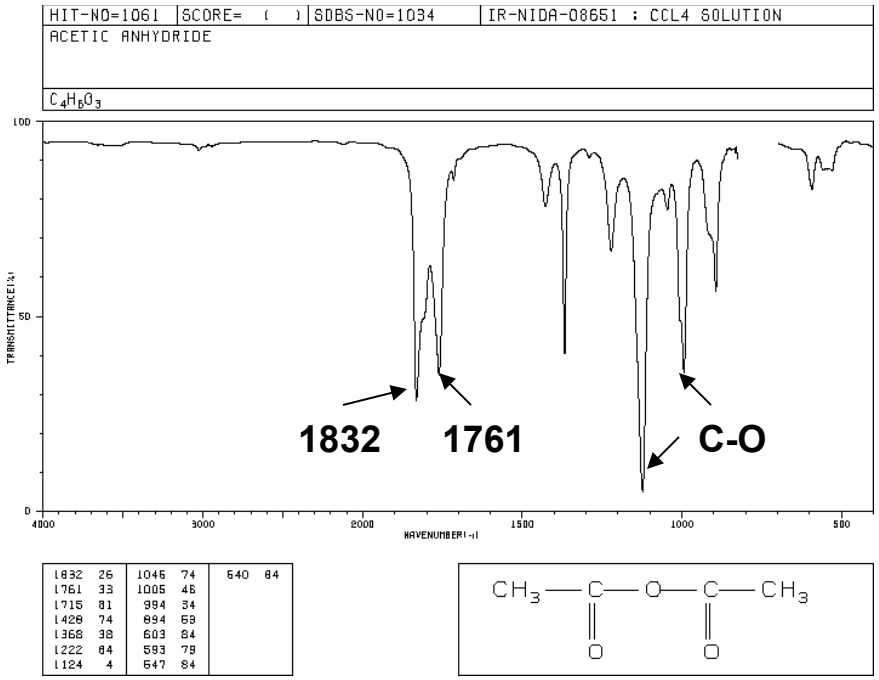




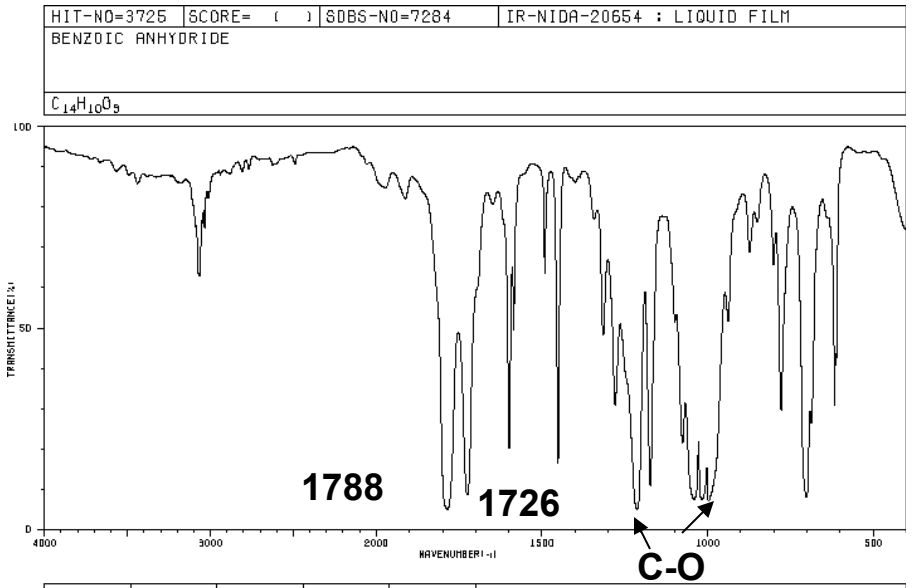
3589	77	1965	81	1393	30	1174	36	898	23
2961	4	1813	7	1369	12	1145	66	772	20
2908	15	1748	36	1331	26	1120	70	715	17
2874	16	1708	11	1267	42	1064	26	687	33
2760	70	1480	21	1252	35	1023	21	564	41
2729	66	1466	18	1233	33	981	17	469	47
2708	72	1449	46	1207	43	933	37	442	43



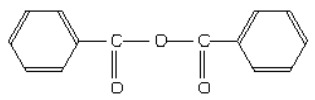
Acetytic Anhydride & Benzoic Anhydride



1832	26	1045	74	640	84		
1761	33	1005	46				
1715	81	994	34				
1428	74	894	59				
1368	38	603	84				
1222	84	583	79				
1124	4	547	84				



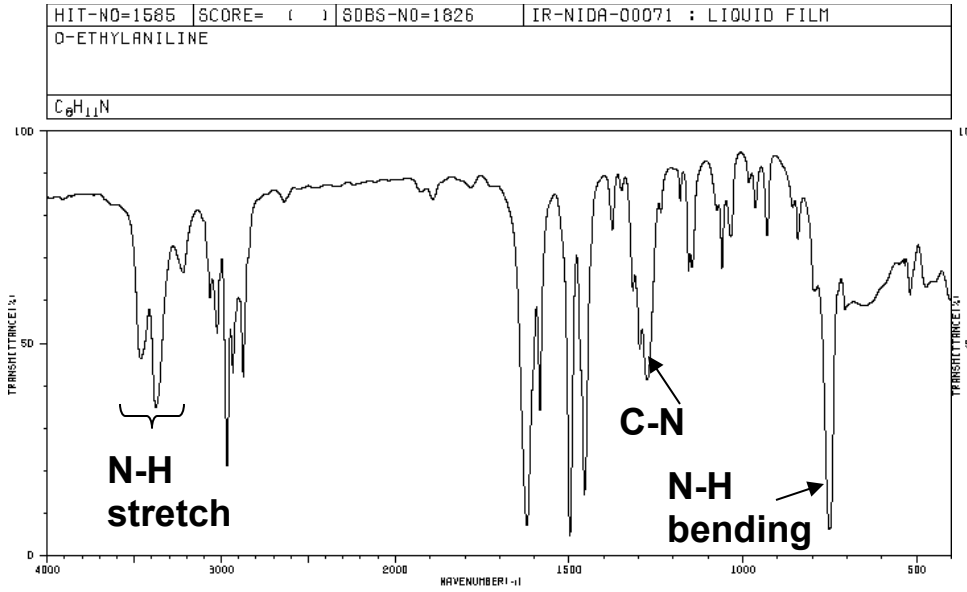
3440	81	1973	81	1492	60	1173	10	874	56
3089	72	1912	79	1452	15	1099	49	850	74
3065	80	1788	4	1406	84	1076	20	802	54
3048	72	1726	8	1344	74	1041	7	779	28
3034	72	1649	77	1315	46	1016	7	702	7
3010	79	1599	19	1280	29	997	6	686	25
1979	81	1586	47	1213	4	938	49	617	29



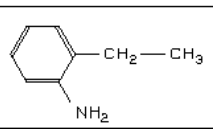
Amines

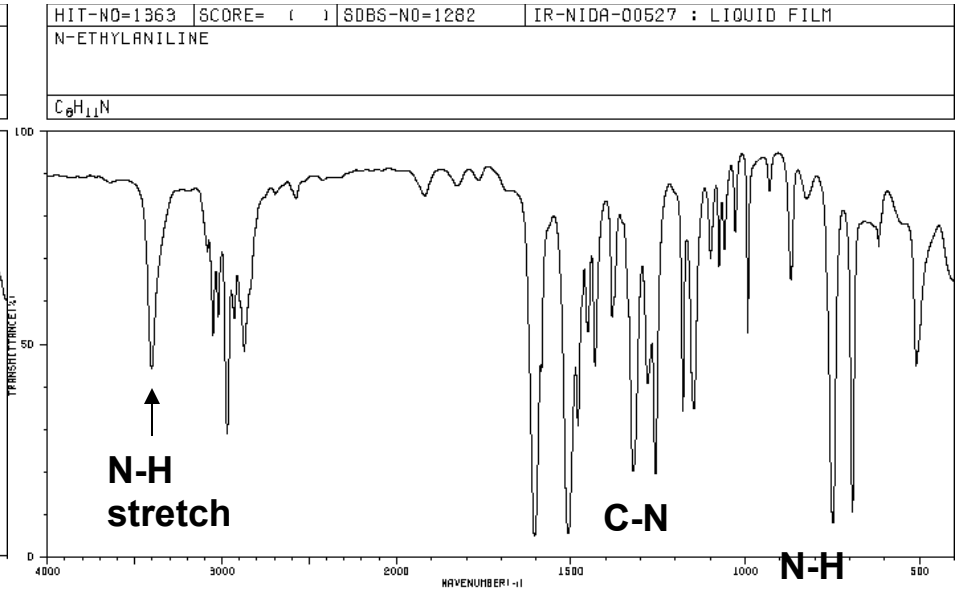
- N-H stretch 3500 ~ 3300 cm^{-1}
  - Primary two bands
  - Secondary one band
  - Tertiary no N-H stretch
- N-H bending ~800 cm^{-1}
- C-N stretch 1350 ~ 1300 cm^{-1}

Ethyl Anilines

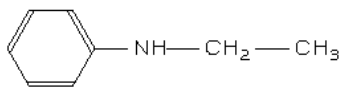


3462	46	2873	41	1317	60	1050	65	750	6
3377	34	1622	7	1298	47	1035	72	707	57
3220	64	1584	34	1276	41	963	79	535	66
3065	68	1498	4	1236	79	930	72	526	64
3023	50	1466	43	1157	66	857	79	520	60
2966	21	1458	14	1147	66	842	72	474	62
2933	42	1376	74	1076	79	793	60	459	62



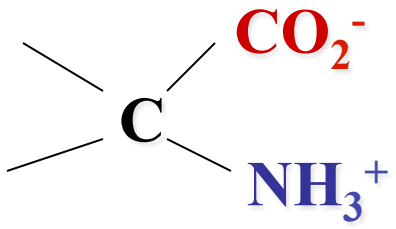


3403	43	2696	81	1451	52	1147	34	825	81
3083	70	2576	81	1431	43	1100	68	749	8
3052	50	1918	81	1382	55	1075	66	693	10
3021	66	1604	4	1321	19	1060	70	629	74
2970	28	1585	42	1280	39	1028	74	618	70
2929	53	1509	5	1256	19	993	50	510	43
2872	47	1480	30	1179	33	869	62	506	46



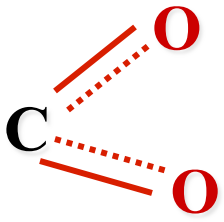
Amino Acid

Exist as zwitterions



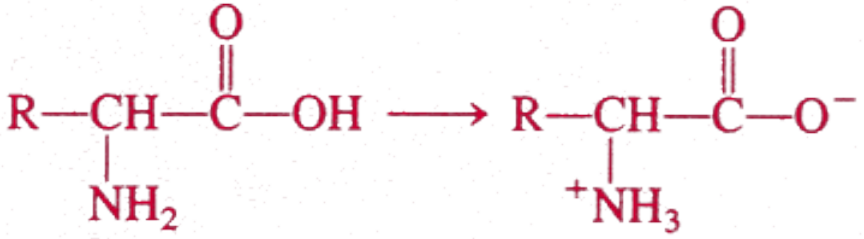
NH_3^+ : very broad 3330-2380

(OH + NH_3^+)



1600 – 1590 strong
Asymmetric stretching

Amino Acid



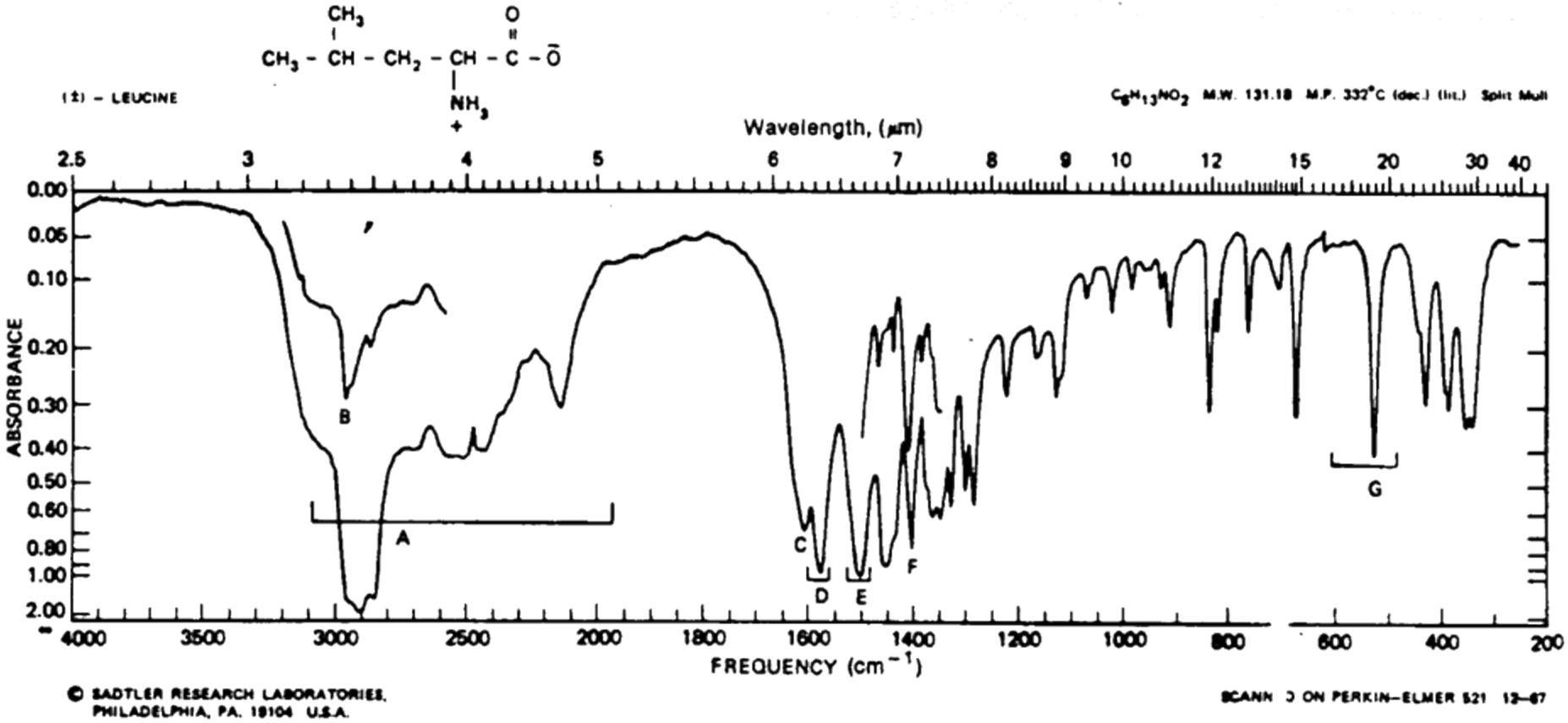
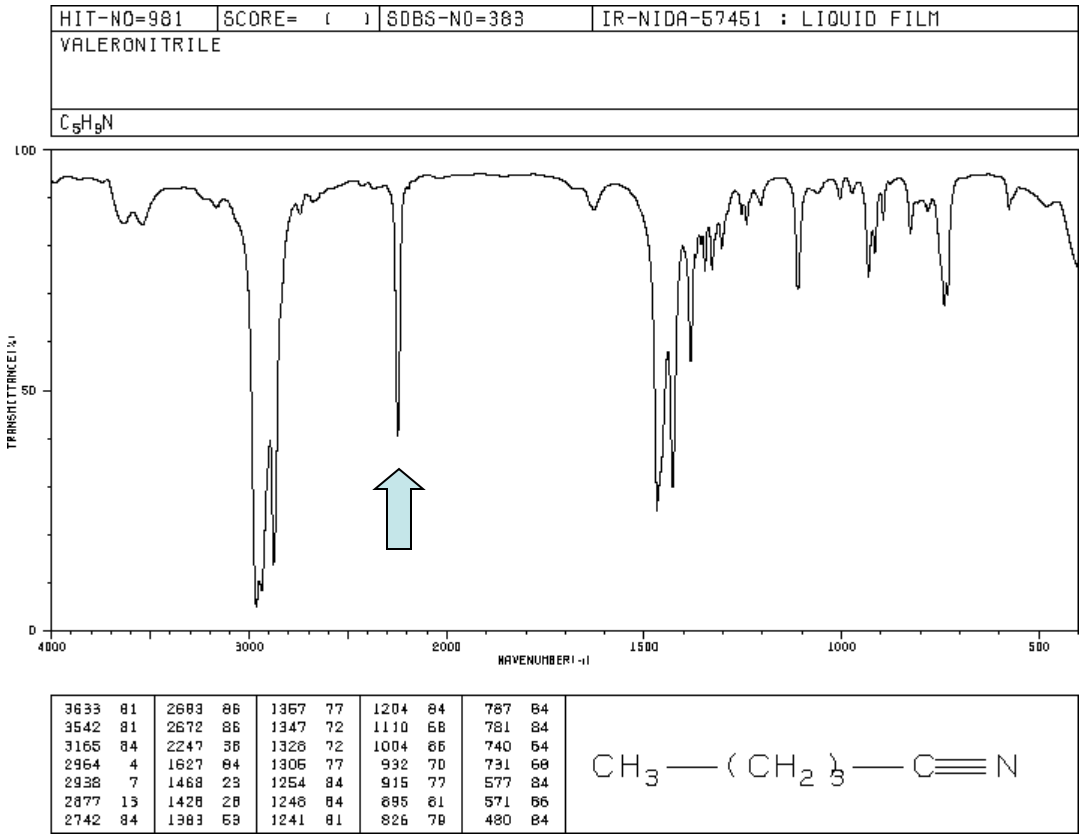


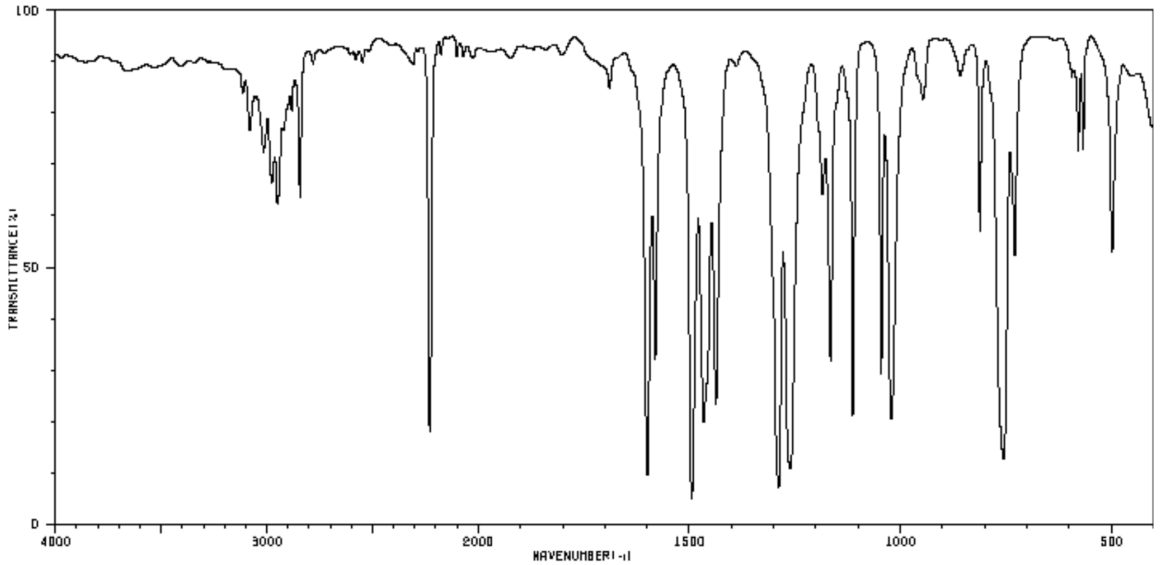
FIGURE 3.30. (±)-Leucine. A. Broad ($—NH_3^+$) N—H stretch, 3100–2000 cm^{-1}, extended by combination band at 2140 cm^{-1}, and other combination-overtone bands. B. Aliphatic C—H stretch (superimposed on N—H stretch), 2967 cm^{-1}. C. Asymmetric ($—NH_3^+$) N—H bend, 1610 cm^{-1}. D. Asymmetric carboxylate $(C{=}O)_2$ stretch, 1580 cm^{-1}. E. Symmetric ($—NH_3^+$) N—H bend, 1505 cm^{-1}. F. Symmetric carboxylate $(C{=}O)_2$ stretch, 1405 cm^{-1}. G. Torsional ($—NH_3^+$) N—H oscillation, 525 cm^{-1}.

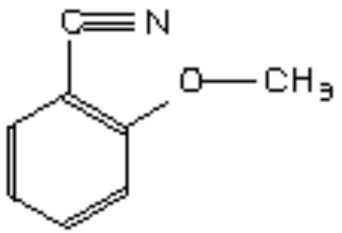
Nitriles

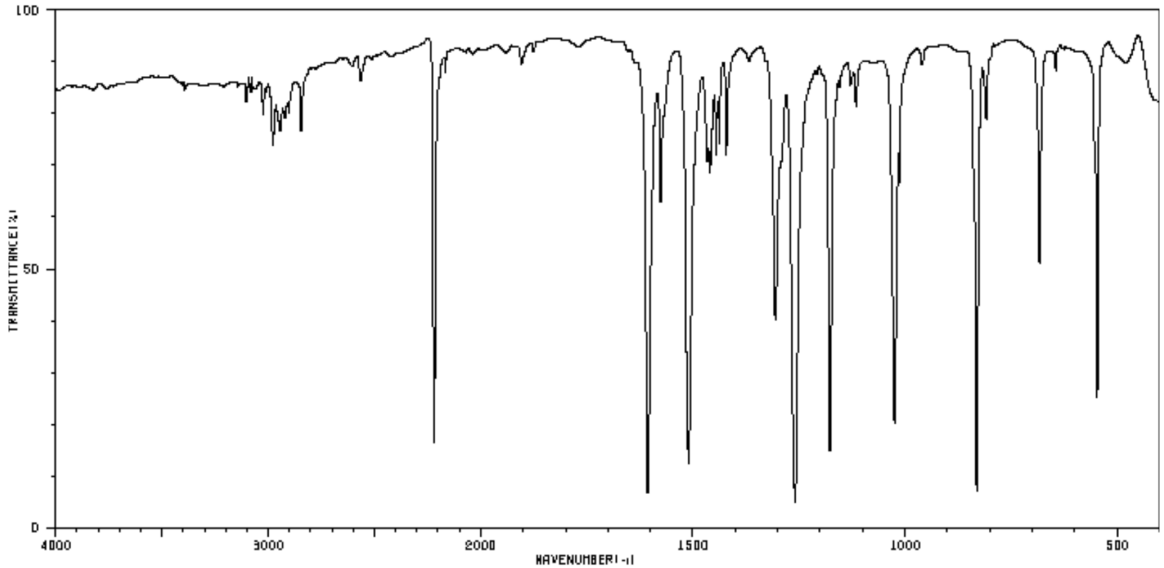
- C≡N ~ 2250 cm^{-1}

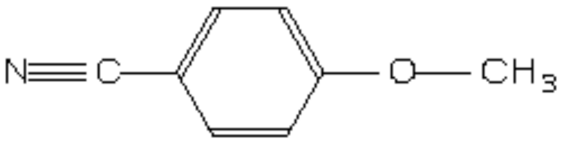


2- or 4-methoxybenzonitrile



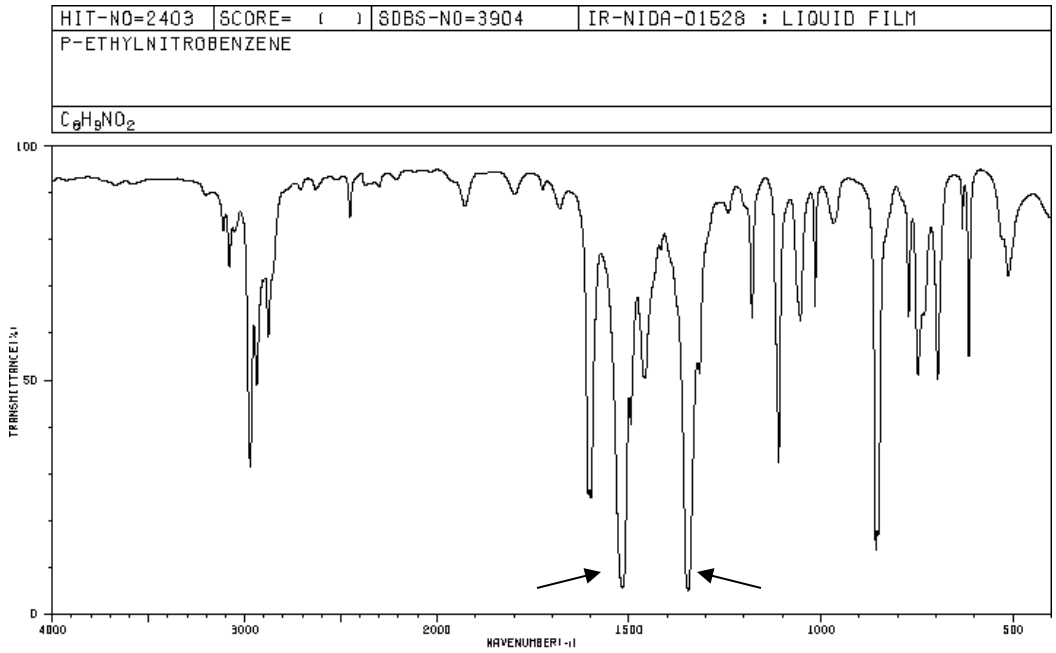




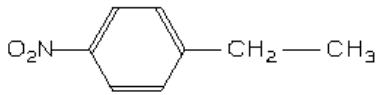


Nitro Compounds

- Two N-O stertching bands
  - Aliphatic 1550 and 1380 cm^{-1}
  - Aromatic 1520 and 1350 cm^{-1}



3111	79	1927	84	1460	49	1064	60	732	62
3079	70	1797	86	1346	4	1016	64	696	47
3053	79	1680	84	1317	49	967	78	632	79
2971	30	1606	24	1242	81	857	13	615	63
2937	47	1600	23	1180	60	852	16	512	70
2877	57	1517	5	1117	55	772	60		
2461	81	1496	38	1110	31	748	49		



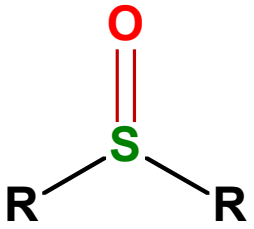
Sulfur

Mercaptans **S – H : weak 2600-2550 cm^{-1}**

Since only few absorption in that range it confirm its presence

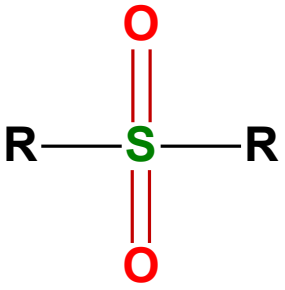
Sulfides,Disulfides : no useful information

Sulfoxides:



Strong ~ 1050 cm^{-1}

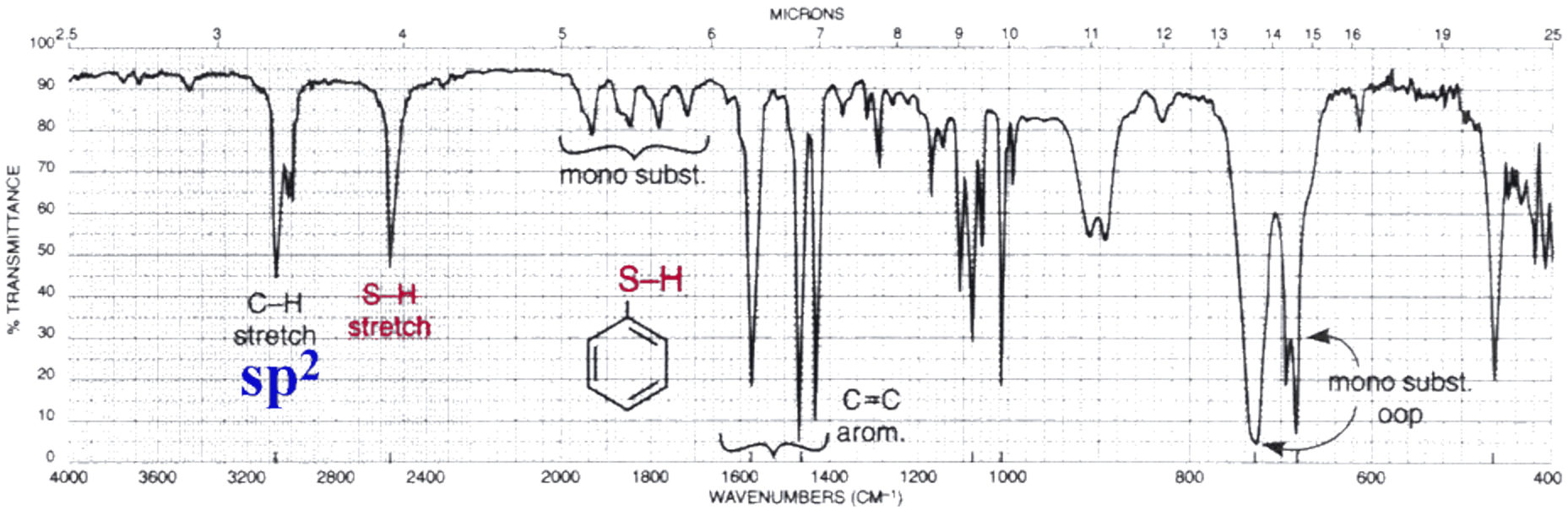
Sulfones:



2 bands :

- **Asymetrical ~ 1300 cm^{-1}**
- **Symetrical ~ 1150 cm^{-1}**

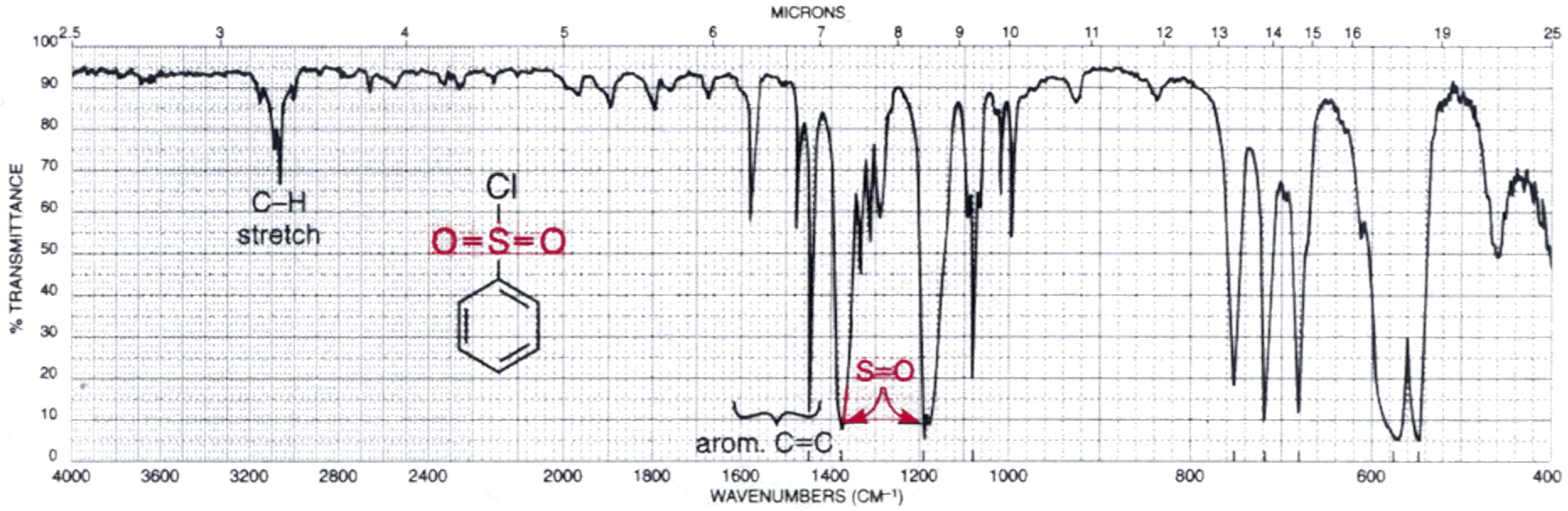
Sulfur: Mercaptan R-S-H



▶ **FIGURE 2.68** The infrared spectrum of benzenethiol (neat liquid, KBr plates).

Sulfur: Sulfonyl Chloride

S=O : Asymmetrical stretch: 1375 cm-1
Symmetrical Stretch : 1185 cm-1

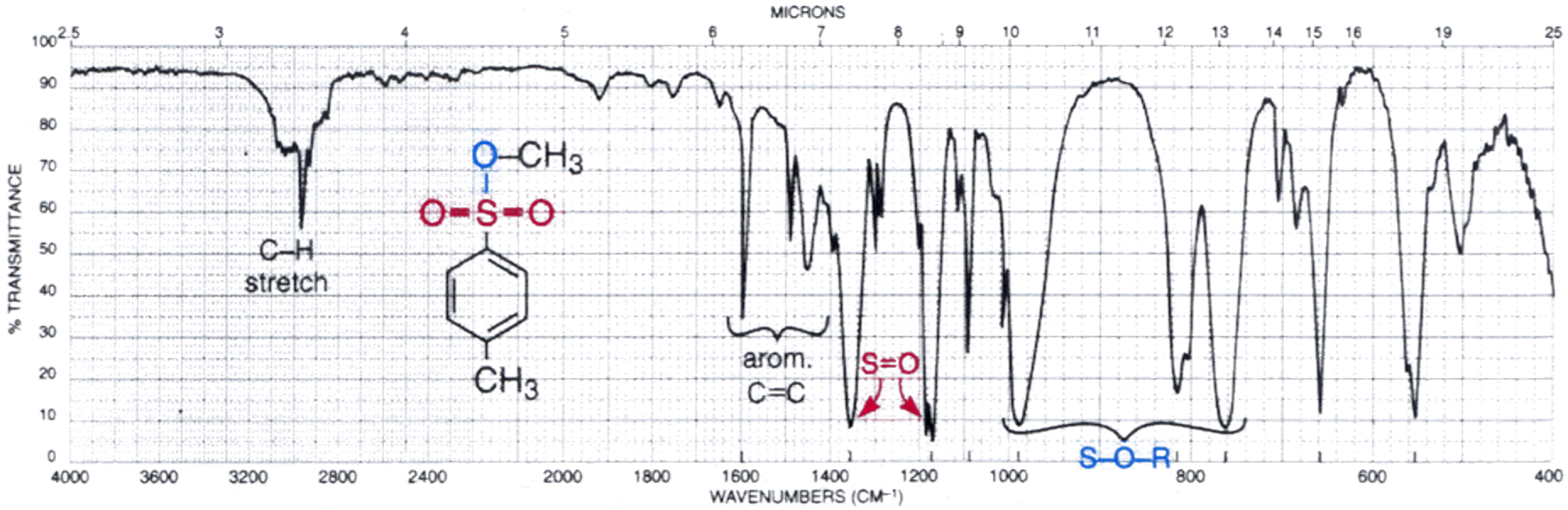


▶ **FIGURE 2.69** The infrared spectrum of benzenesulfonyl chloride (neat liquid, KBr plates).

Sulfur: Sulfonate

S=O : Asymmetrical stretch: 1350 cm-1
Symmetrical Stretch : 1175 cm-1

S-O : several bands between 1000 – 750 cm^{-1}

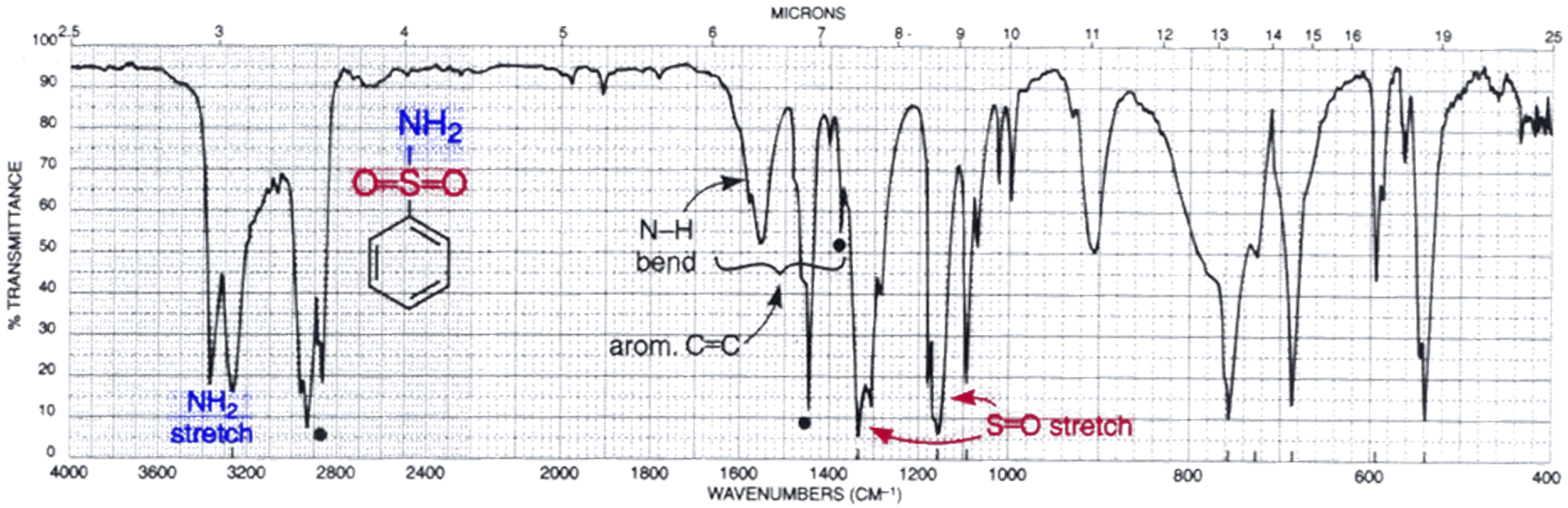


► **FIGURE 2.70** The infrared spectrum of methyl *p*-toluenesulfonate (neat liquid, KBr plates).

Sulfur: Sulfonamide

S=O : Asymmetrical stretch: 1325 cm-1
Symmetrical Stretch : 1140 cm-1

NH_2 stretch: 3350 and 3250 cm^{-1} **NH Bend: 1550 cm^{-1}**



▶ **FIGURE 2.71** The infrared spectrum of benzenesulfonamide (Nujol mull, KBr plates). Dots indicate the Nujol (mineral oil) absorption bands (see Fig. 2.8).

Halogens

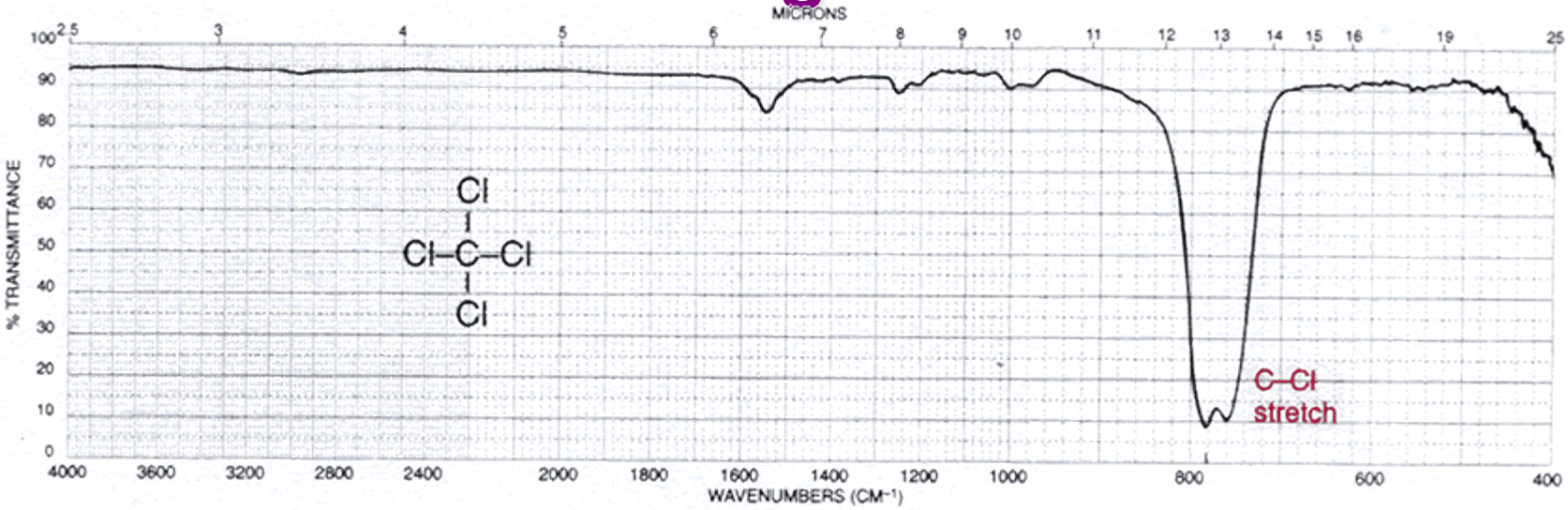
C—F : 1400 – 1000 cm^{-1}

C—Cl : strong 785 – 540 cm^{-1}

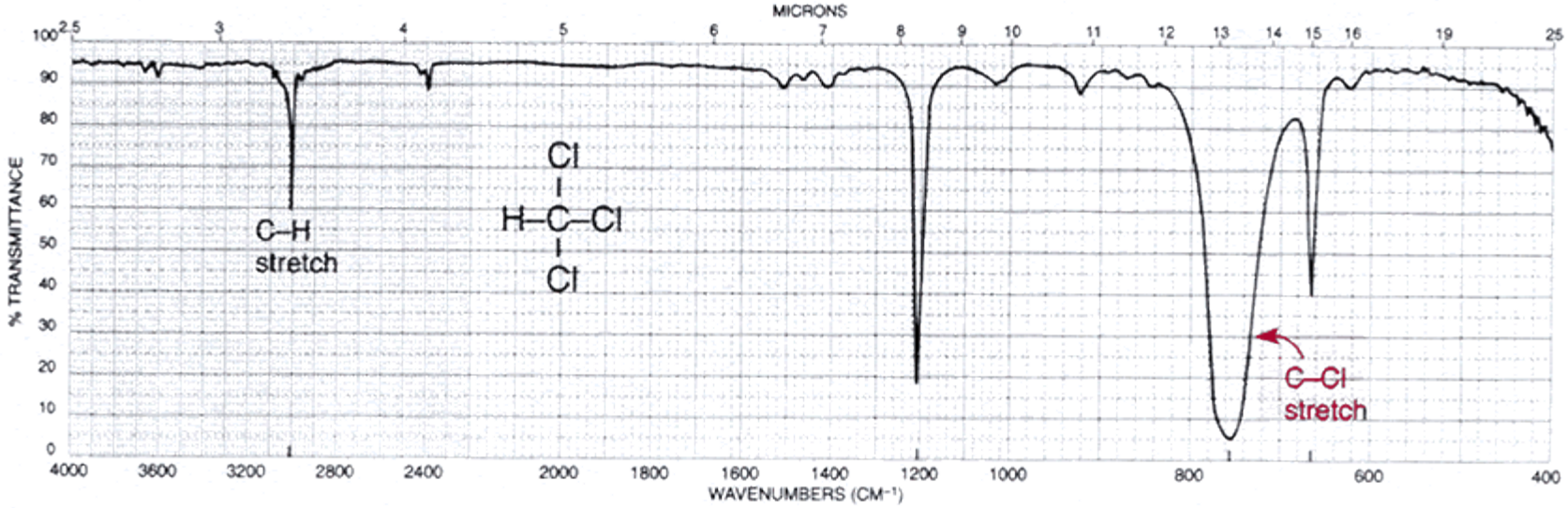
C—Br : 650 – 510 cm^{-1} (out of range with NaCl plates)

C—I : 600 – 485 cm^{-1} (out of range)

Halogens

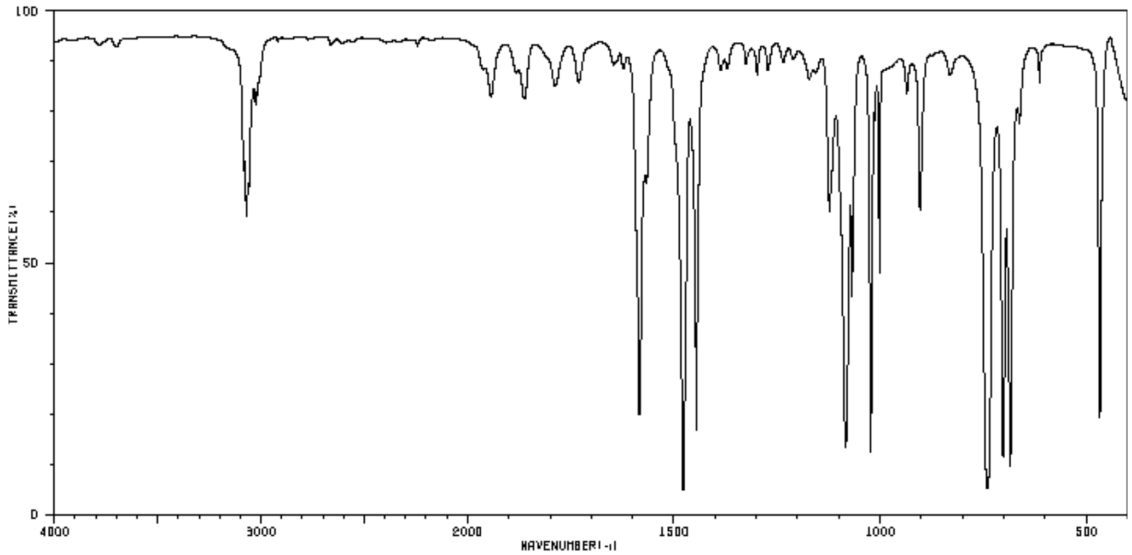


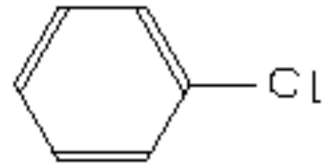
▶ **FIGURE 2.72** The infrared spectrum of carbon tetrachloride (neat liquid, KBr plates).

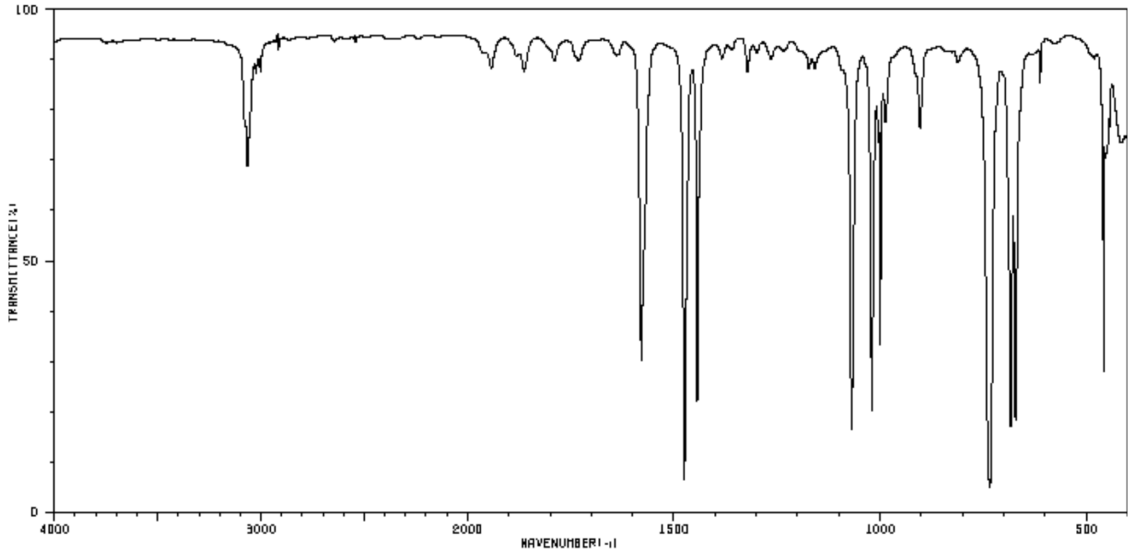


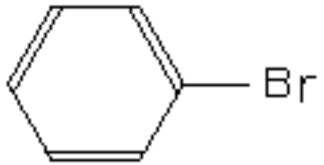
▶ **FIGURE 2.73** The infrared spectrum of chloroform (neat liquid, KBr plates).

Chloro- and Bromo-benzenes

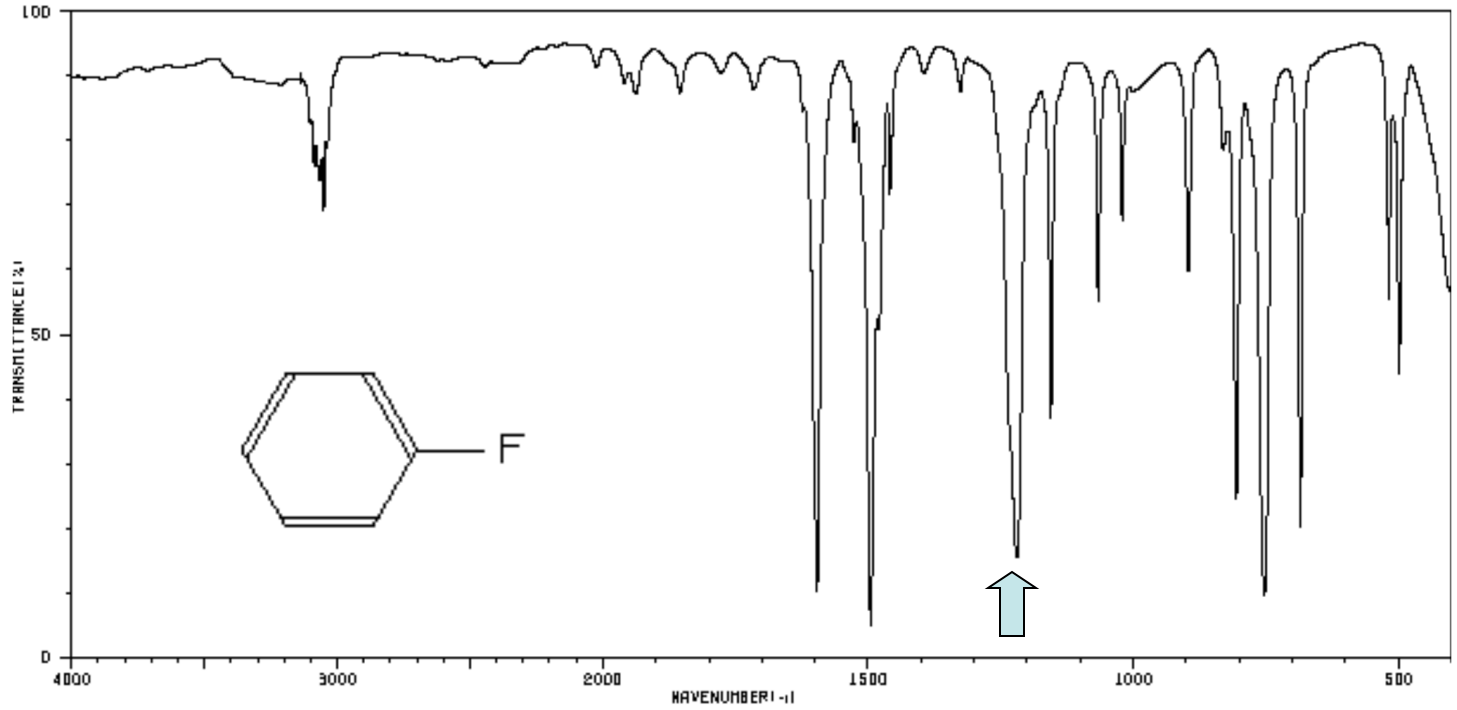








Fluorobenzene



C-Br 650 ~ 500 cm^{-1}
C-Cl 850 ~ 550 cm^{-1}
C-F 1400 ~ 1000 cm^{-1}

Silicon

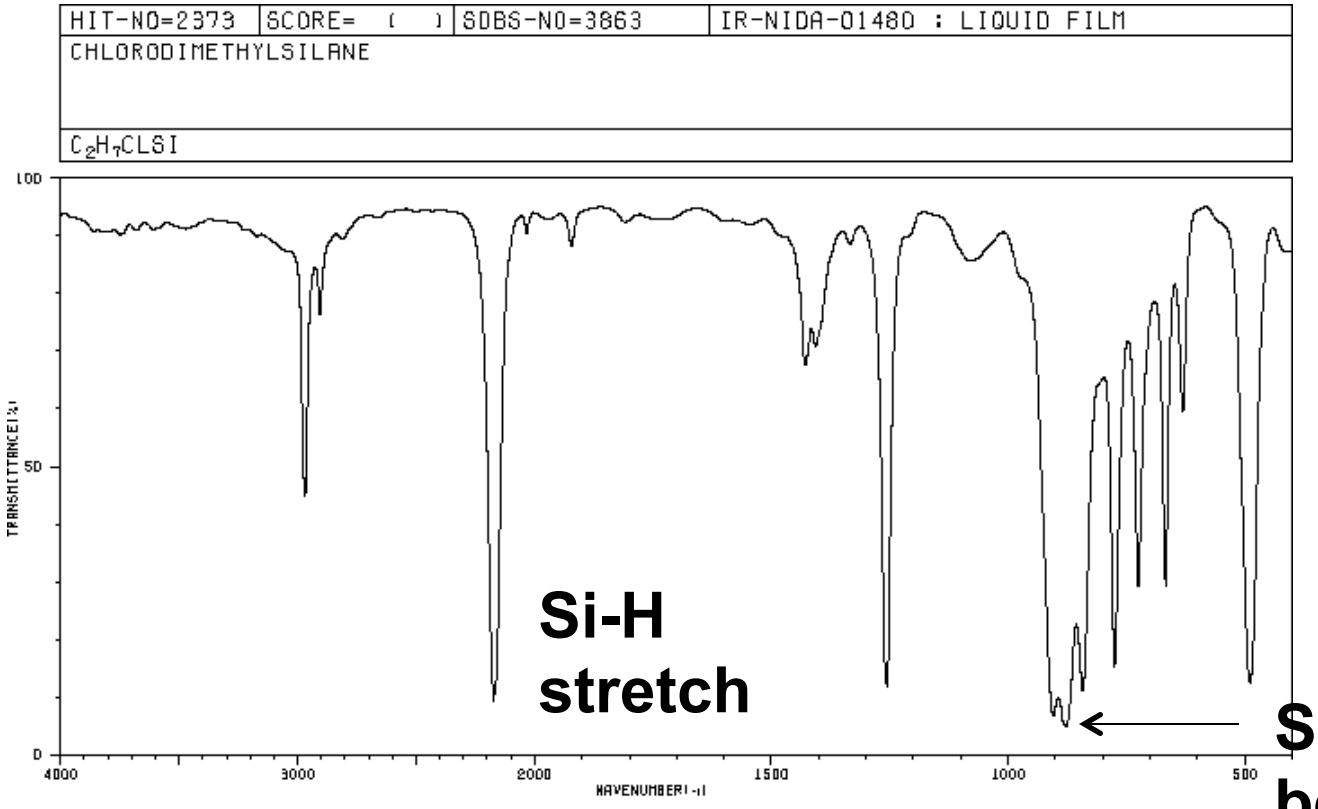
Si-H :

- **2200 cm^{-1} (Stretch)**
- **950 – 800 cm^{-1} (bend)**

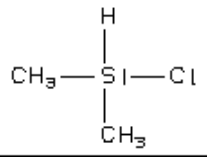
Si-O-H :

- **OH: 3700 – 3200 cm^{-1} (Stretch)**
- **Si-O : 830 – 1110 cm^{-1}**

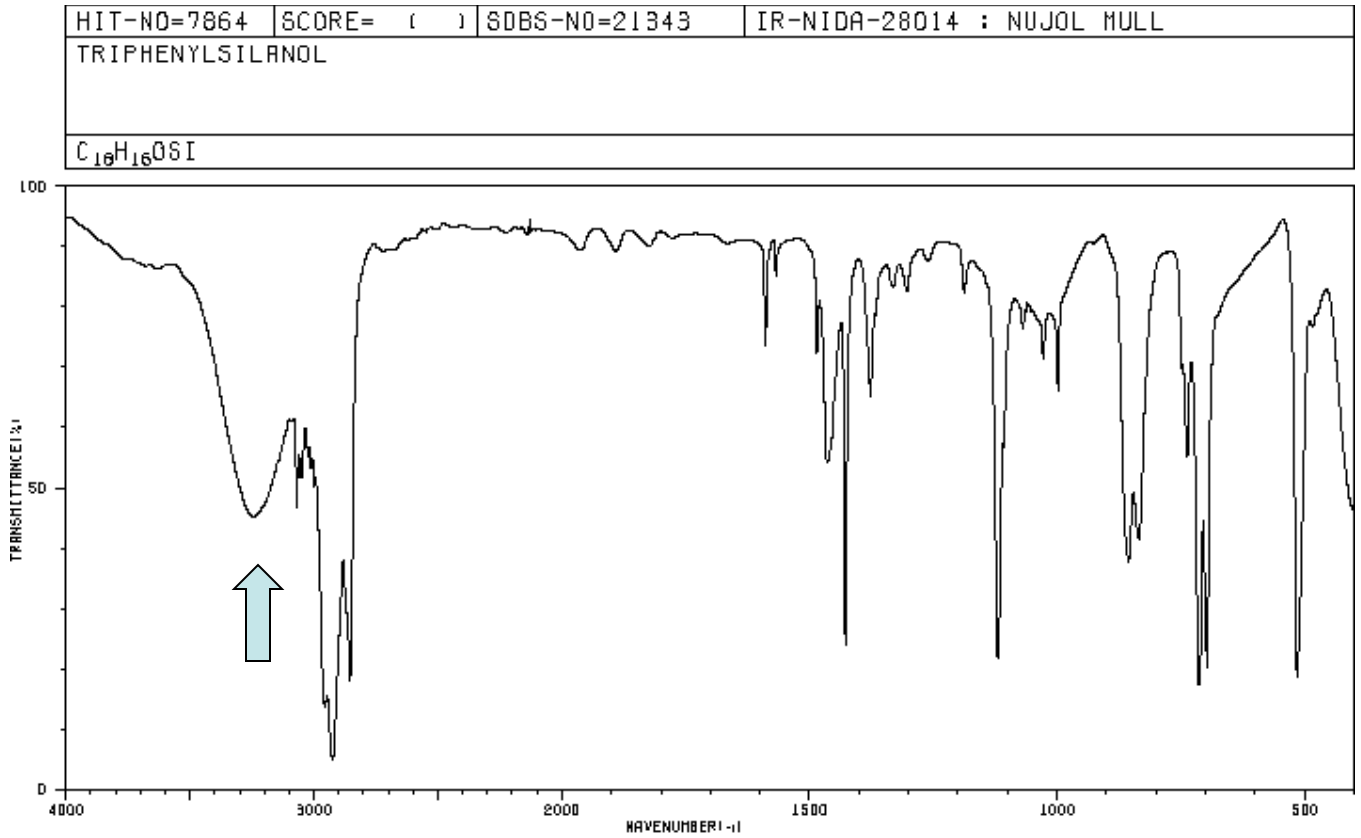
Chlorodimethylysilane



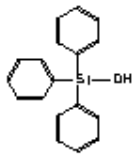
2968	43	1256	11	667	27
2906	74	1077	81	631	57
2176	9	905	6	490	12
1922	84	878	4		
1429	64	843	10		
1407	66	778	14		
1336	84	726	28		



Triphenylsilanol



3242	43	2926	4	1464	62	1188	79	836	39
3069	44	2854	17	1427	23	1120	20	737	53
3051	49	1962	86	1378	82	1108	55	714	16
3024	53	1890	86	1367	77	1070	72	698	19
3012	50	1589	70	1332	79	1028	68	516	18
2999	47	1568	81	1304	79	998	64	485	74
2956	13	1486	70	1261	84	866	36		



Analyzing IR
or “What You Can Tell at a Glance”

(1) Is a carbonyl present?

(2) If C=O is present, what type?

(3) If C=O is absent, check

Alcohols, amines, ethers

(4) Double bonds and/or aromatic

(5) Triple bonds

(6) Nitro compounds

(7) Hydrocarbons, sulfer, silicone etc