CHE 231 AN INTRODUCTION TO LABORATORY PRACTICES IN ORGANIC CHEMISTRY

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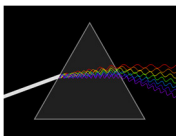
Infrared Spectroscopy



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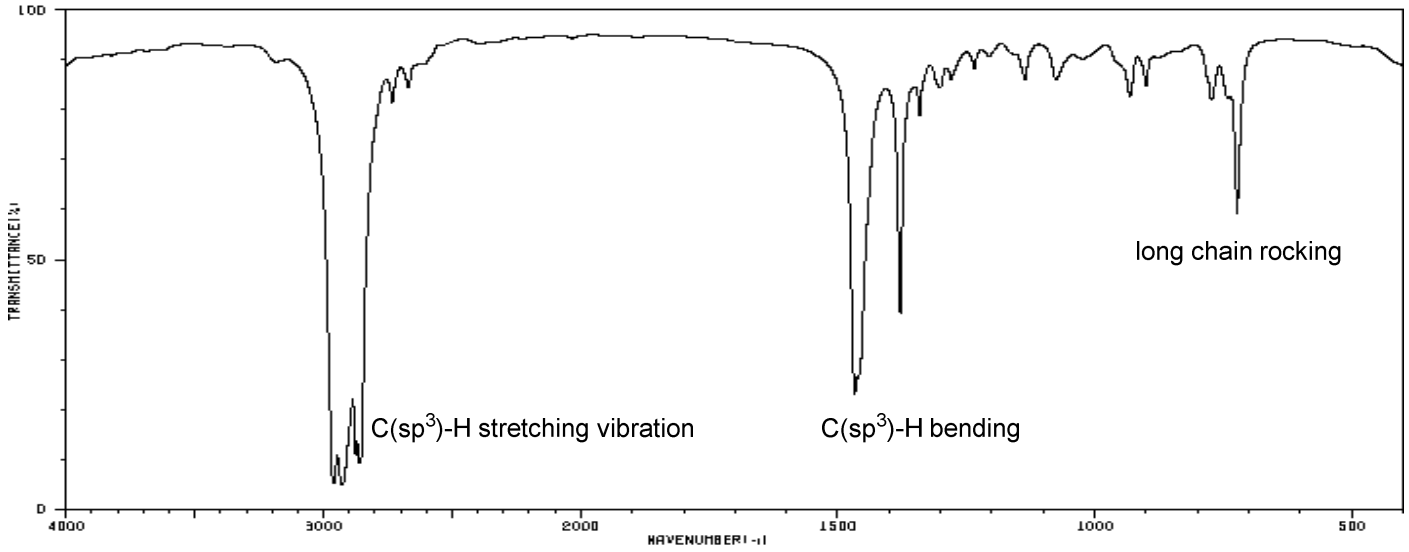
The Infrared Spectra of Alkanes

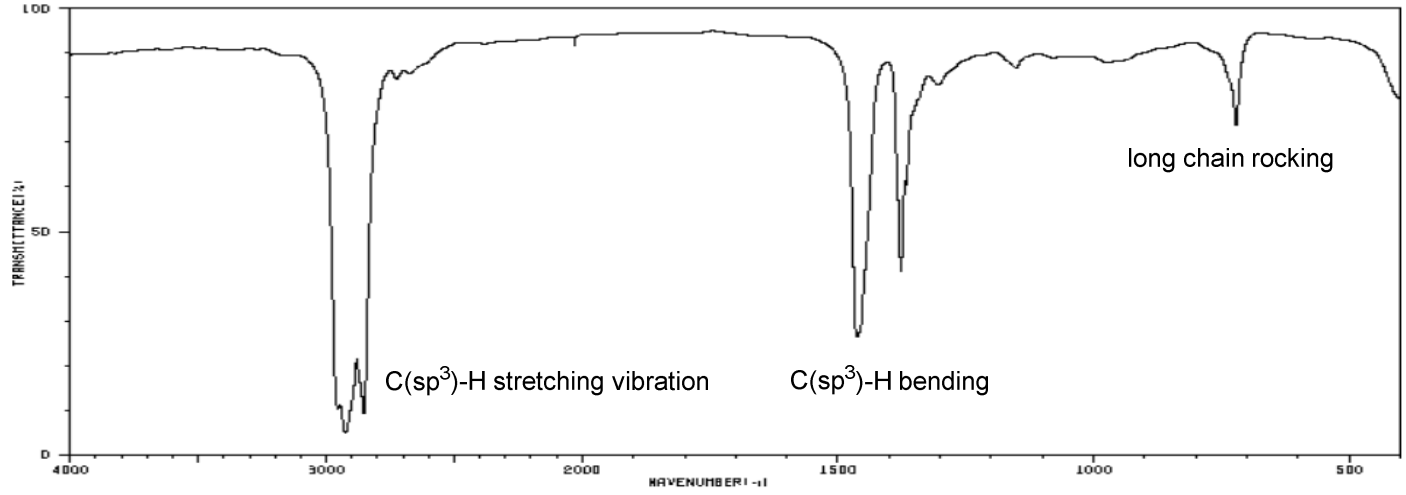
$C(sp^3)$-H stretching	2800 to 2960 cm^{-1}
CH_2 bending	1440 to 1500 cm^{-1}

Infrared spectrum of *n*-heptane: 2961, 2926, 1468, 1379 cm^{-1}.



SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015)

Infrared spectrum of nujol (paraffin wax, long chain hydrocarbon, C_nH_{2n+2}):

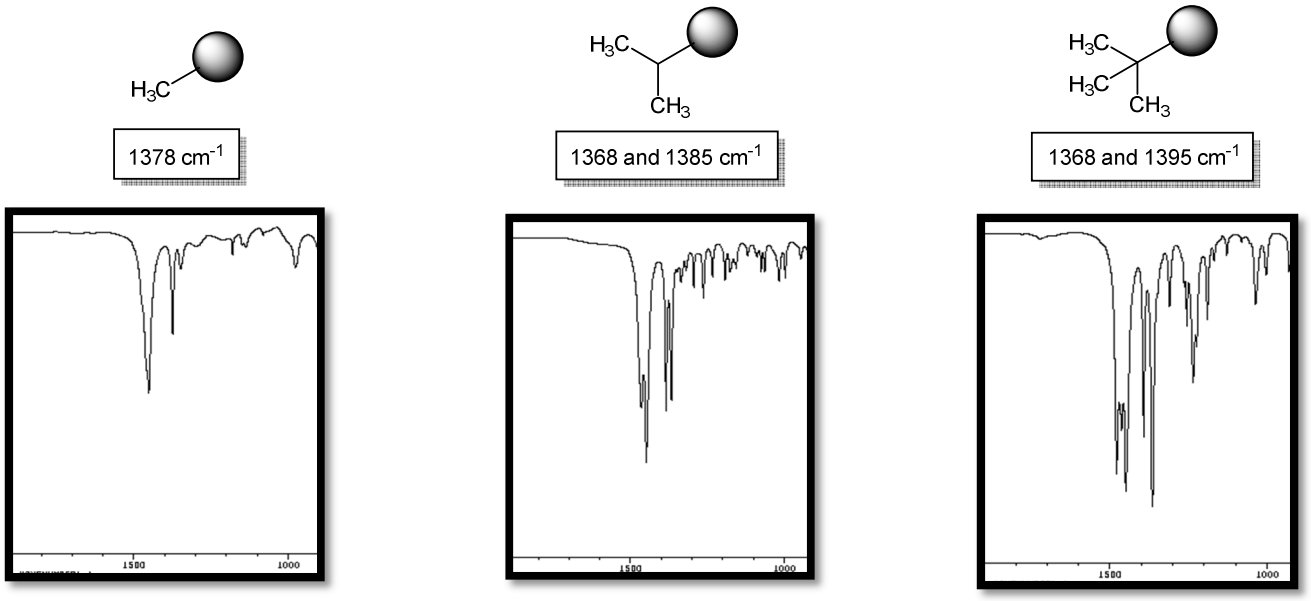


SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

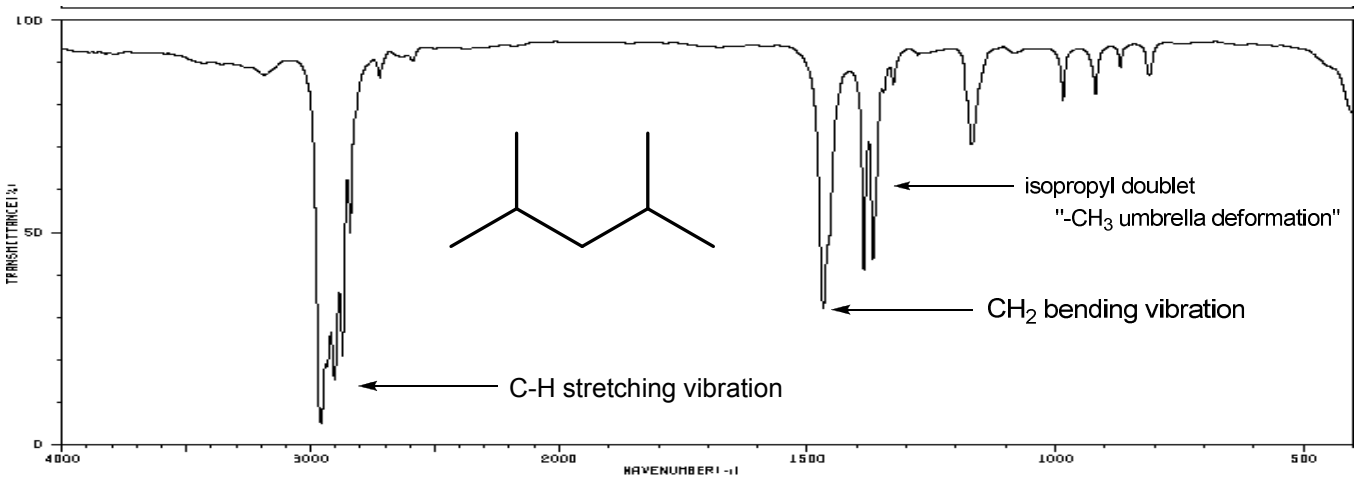
The Infrared Spectra of Alkanes

Different structural arrangements of methyl groups can be tentatively identified by inspection of the fingerprint region. These peaks should not be used as final diagnostics as there are other signals that may appear in this region.

The umbrella deformation of the methyl group.



Infrared spectrum of 2,4-dimethylpentane: 2968, 2935, 1466, 1368, 1361 cm^{-1}.



SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

The Infrared Spectra of Alkenes

Dominant Observable Vibrations

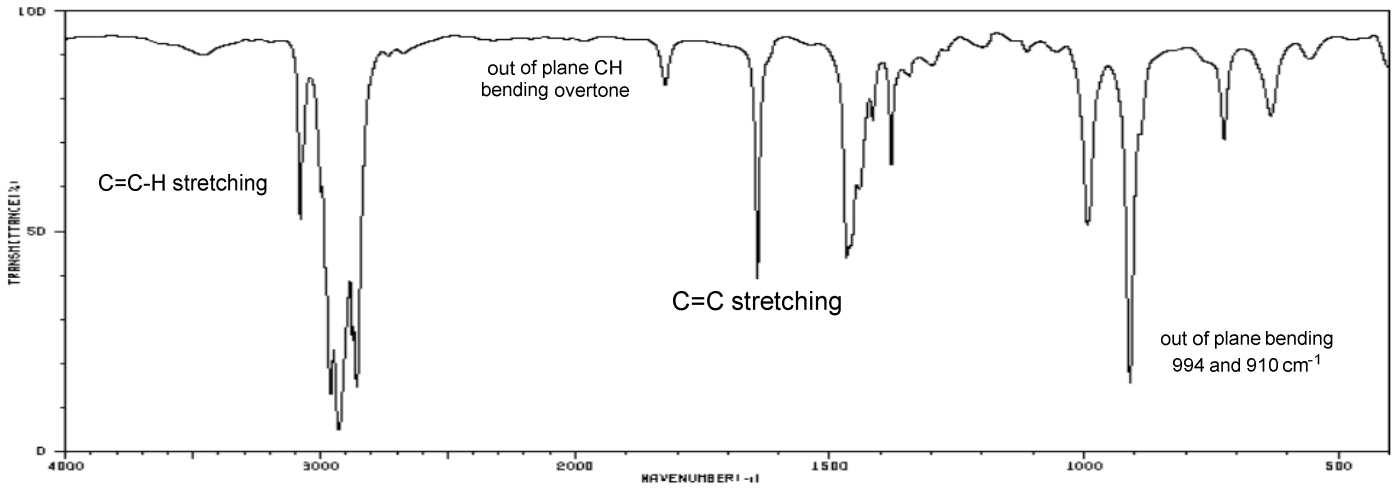
Stretching vibrations

C (sp^2)-H stretching	~3000 to 3100 cm^{-1}
C=C double bond stretch	~1600 to 1675 cm^{-1}

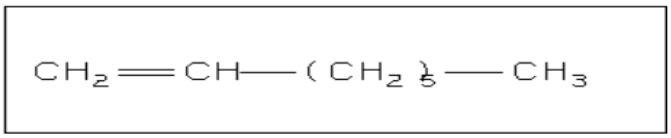
Out of plane C-H bending vibrations

monosubstituted alkenes	910 and 990 cm^{-1}
dibsubstituted terminal alkene	890 cm^{-1}
trans-alkene bending vibration	960-980 cm^{-1}
cis-alkene bending vibration	675-730 cm^{-1}
trisubstituted alkenes	800-840 cm^{-1}
tetrasubstituted alkenes	no C-H bending vibrational signal

An infrared spectrum of 1-octene: 3079, 2998, 1823, 1642, 994, 910 cm^{-1}.



3079	60	1642	37	994	49
2998	57	1468	42	910	14
2959	12	1460	44	725	86
2928	4	1416	72	633	72
2874	23	1379	62	558	86
2857	13	1344	81		
1823	79	1299	84		

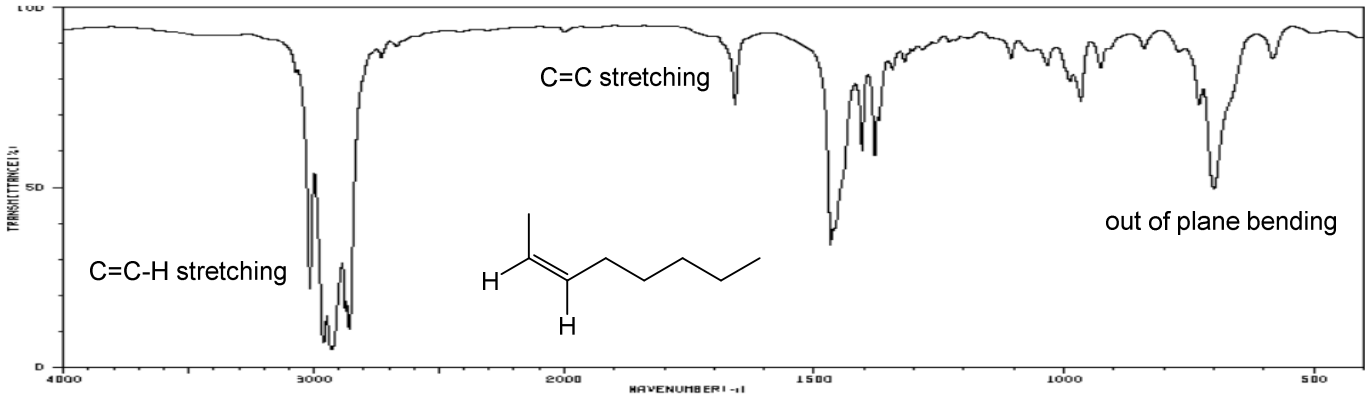


SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

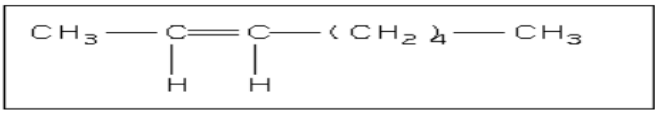
The Infrared Spectra of Alkenes

cis and *trans*-Alkenes may be distinguished based on two key features, the carbon-carbon double bond vibration and the out of plane bending of the vinylic protons.

An infrared spectrum for *cis*-2-octene

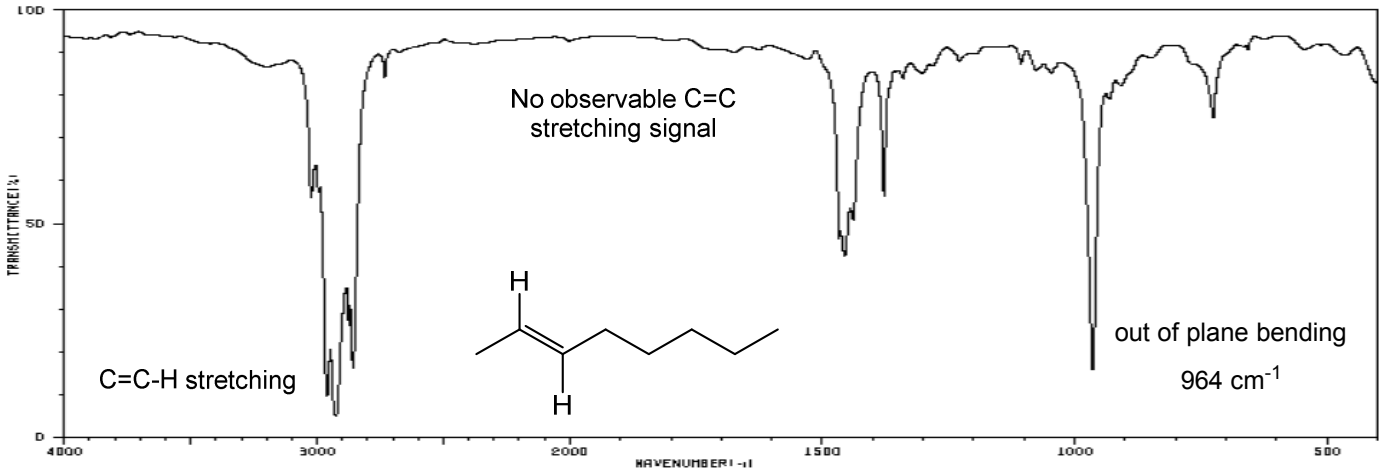


3015	21	1668	70	1319	81	772	84
2961	6	1468	32	1106	81	731	70
2929	4	1461	36	1034	81	701	47
2874	14	1404	67	989	77	691	84
2859	10	1379	57	966	70	583	81
2732	81	1371	66	926	79		
2668	86	1343	79	840	84		

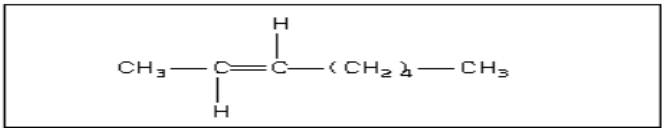


SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

An infrared spectrum for *trans*-2-octene



3024	63	1636	86	1307	81	931	77
2995	55	1530	84	1302	81	908	79
2960	9	1467	44	1229	84	726	72
2926	4	1456	41	1108	84	466	86
2874	25	1440	49	1076	81		
2858	15	1378	59	1047	81		
2733	81	1341	81	964	15		



SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

The Infrared Spectra of Alkynes

Dominant Observable Vibrations

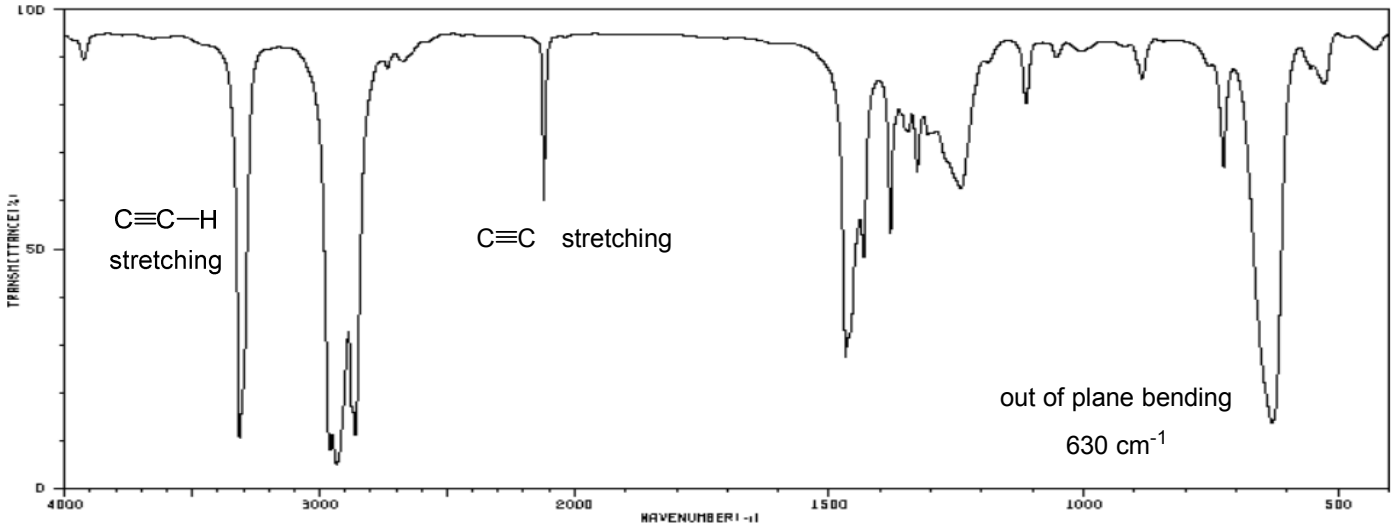
Stretching vibrations

C(sp)-H stretching vibration	~3250-3350 cm^{-1}
C≡C stretching vibration	~2100-2200 cm^{-1}

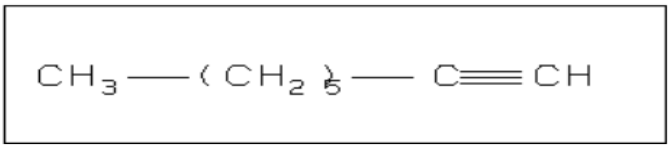
Out of plane C-H bending vibrations

C(sp)-H bending vibration	~610-700 cm^{-1}

Infrared spectrum of 1-octyne (a terminal alkyne): 3323, 3024, 2926, 1636, 1466, 630 cm^{-1}



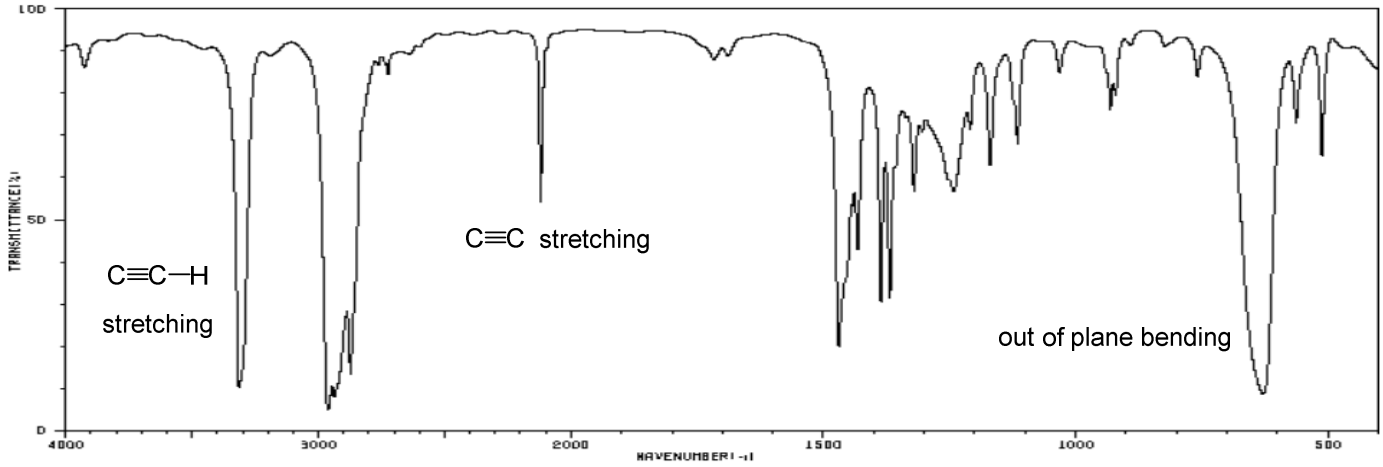
3926	86	2673	88	1327	64
3315	10	2120	58	1242	60
2959	7	1468	25	1113	77
2933	4	1461	30	886	81
2874	15	1432	46	725	64
2861	10	1380	52	630	13
2734	84	1346	72	628	81



SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

The Infrared Spectra of Alkynes

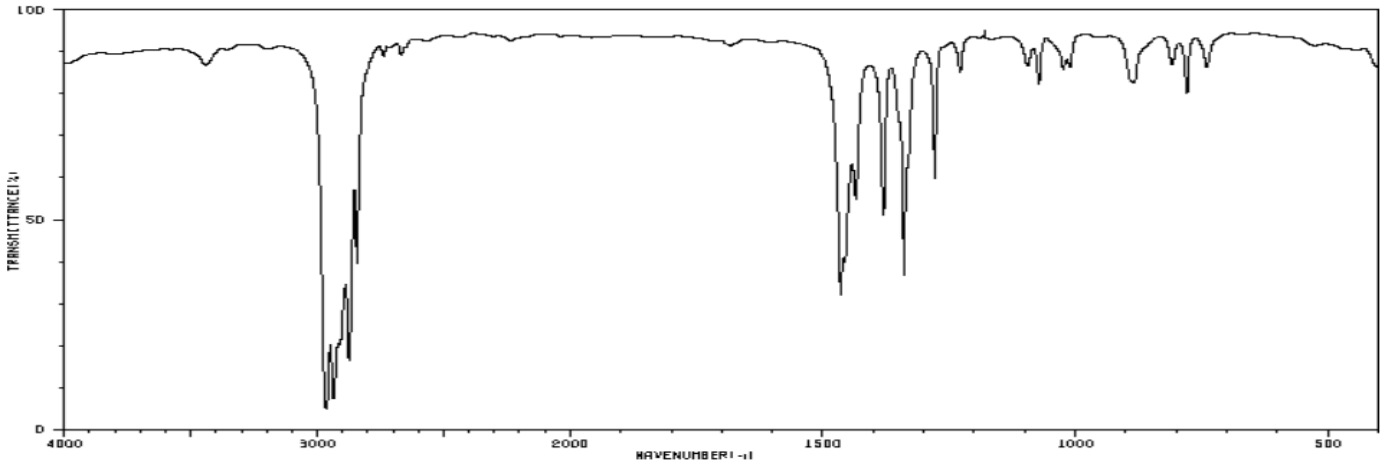
The infrared spectrum of 5-methyl-1-hexyne is illustrated below. The expected peaks are present. Notice the presence of the isopropyl group "doublet" at 1368 and 1388 cm^{-1}.



3927	84	2121	62	1368	60	1116	66	664	70	$CH_3-CH(-CH_3)-(CH_2)_2-C\equiv CH$
3314	9	1717	84	1321	55	1032	81	513	62	
2961	4	1689	86	1305	88	940	81			
2937	7	1470	19	1266	67	931	72			
2872	12	1432	41	1242	55	921	77			
2735	84	1388	28	1210	88	759	81			
2722	81	1368	30	1170	60	629	8			

SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

Infrared spectrum of 2-octyne (an internal alkyne): the alkyne C≡C stretching vibration is very weak and not observable due to symmetry and lack of changing dipole moment.

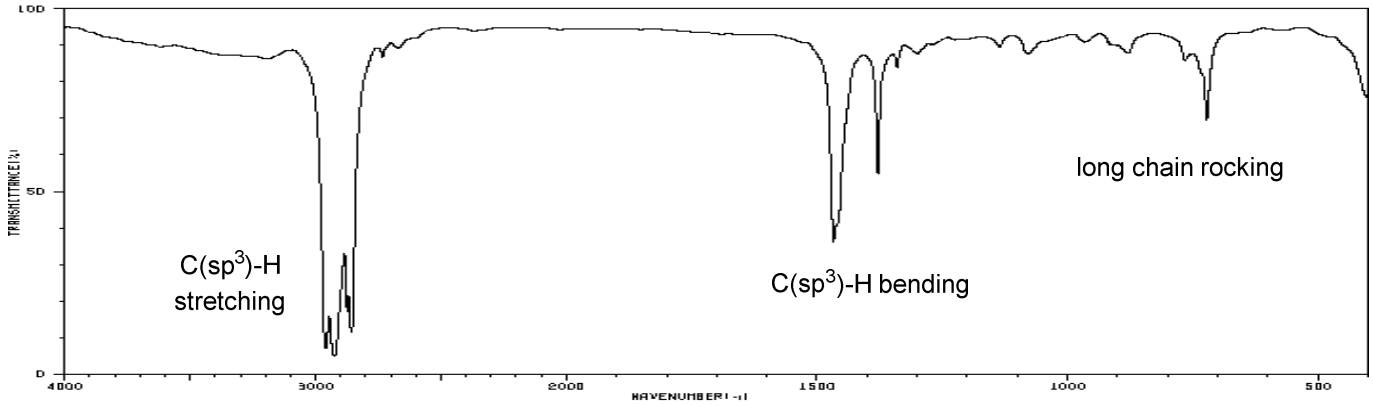


3441	84	1464	31	1229	81	809	84	$CH_3-(CH_2)_2-C\equiv C-(CH_2)_2-CH_3$
2963	4	1456	38	1094	84	779	77	
2936	7	1435	52	1072	79	740	84	
2874	16	1380	49	1024	81			
2842	38	1339	35	1018	84			
2736	86	1333	60	1010	84			
2669	86	1278	67	885	79			

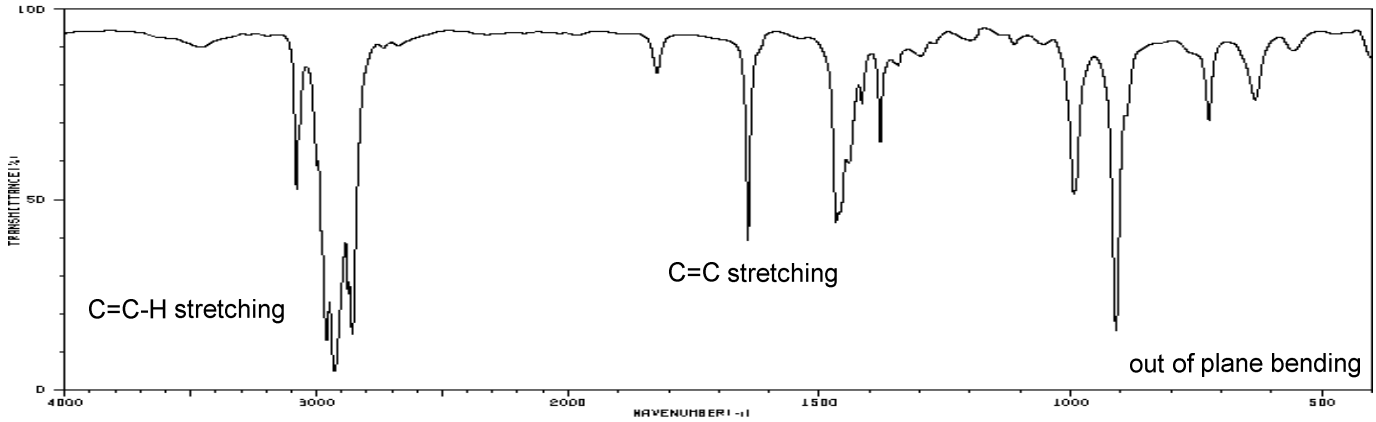
SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

A review of the aliphatic hydrocarbons

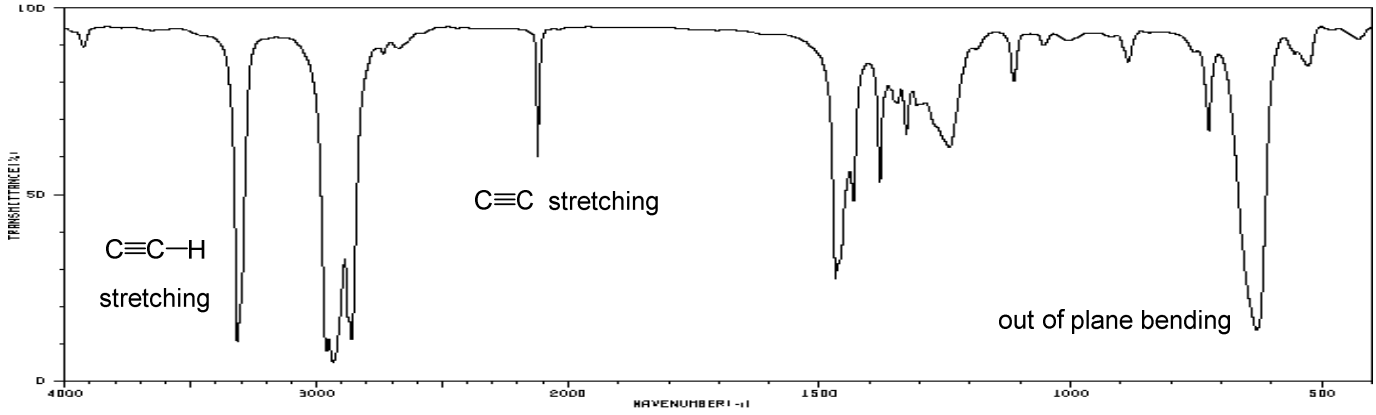
Infrared spectrum of 1-octane: A saturated hydrocarbon



Infrared spectrum of 1-octene: An unsaturated hydrocarbon



Infrared spectrum of 1-octyne: An unsaturated hydrocarbon



The Infrared Spectra of Aromatic Rings

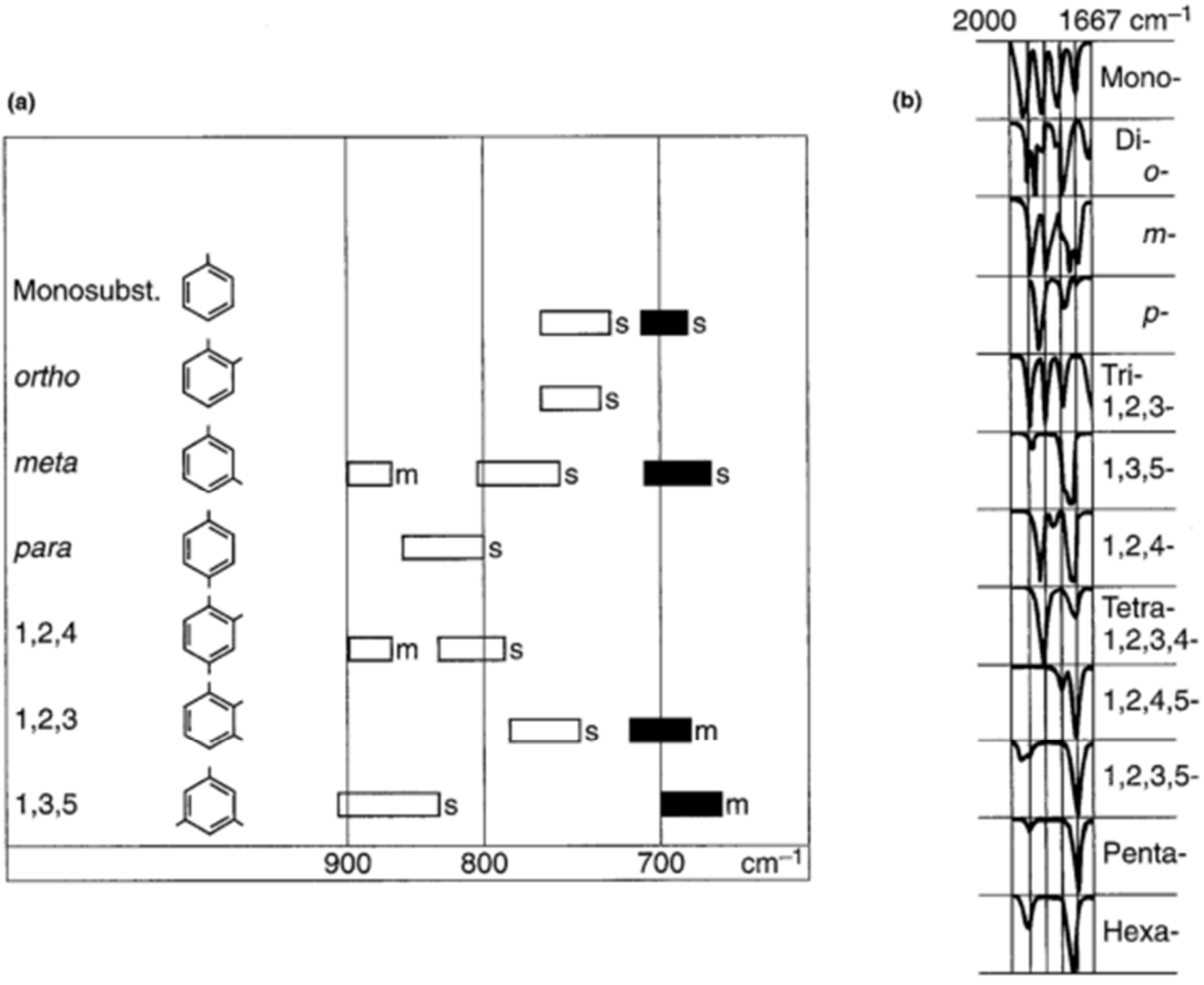
Dominant Observable Vibrations

Stretching vibrations

C(sp^2)-H stretching vibration	~3000-3100 cm^{-1}
C=C stretching vibration	~1500-1600 cm^{-1}

Out of plane C-H bending vibrations

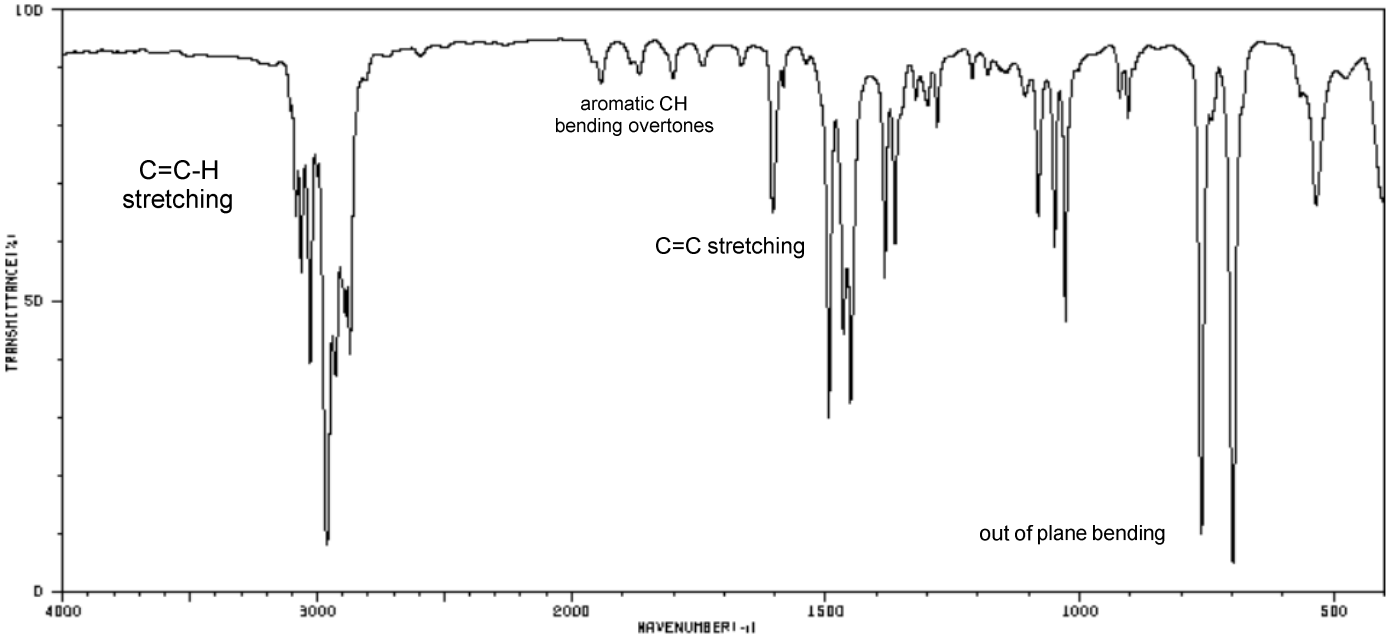
The substitution of aromatic rings can be tentatively assigned based on the observed aromatic out of plane CH bending overtones.



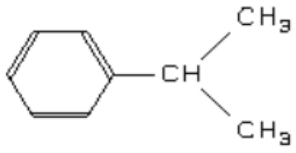
Taken from http://chemistrytextbookcrawl.blogspot.com/2012/12/infrared-spectra-of-aromatic-rings.html.

The Infrared Spectra of Aromatic Rings

Cumene (isopropylbenzene): There are a number of peaks that appear for aromatic systems. These peaks include aromatic C-H stretching, C=C from the aromatic ring, and out of plane bending. There are also out of plane CH bending overtones that appear between 2000 and 1667 cm^{-1}. The intensity and shape of these peaks varies with the substitution of the aromatic ring.



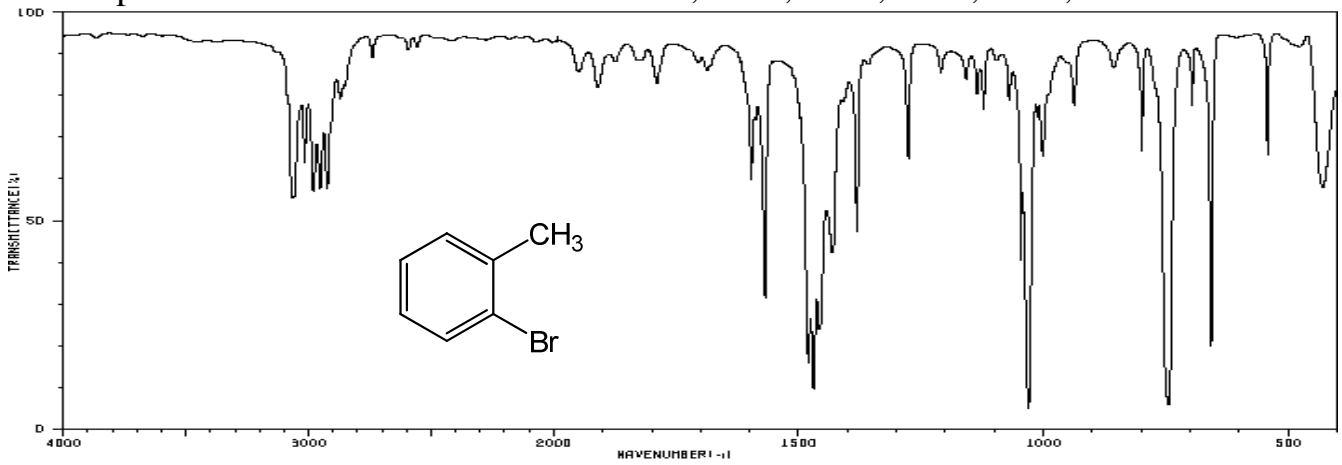
3084	62	2871	39	1466	42	1281	77	1028	44
3064	53	1942	84	1458	53	1213	84	922	81
3028	37	1868	86	1452	31	1150	86	905	79
3002	68	1800	84	1384	62	1144	86	761	9
2961	7	1604	62	1364	57	1108	81	699	4
2927	35	1583	84	1323	81	1082	62	535	64
2890	46	1494	28	1300	81	1060	57	478	84



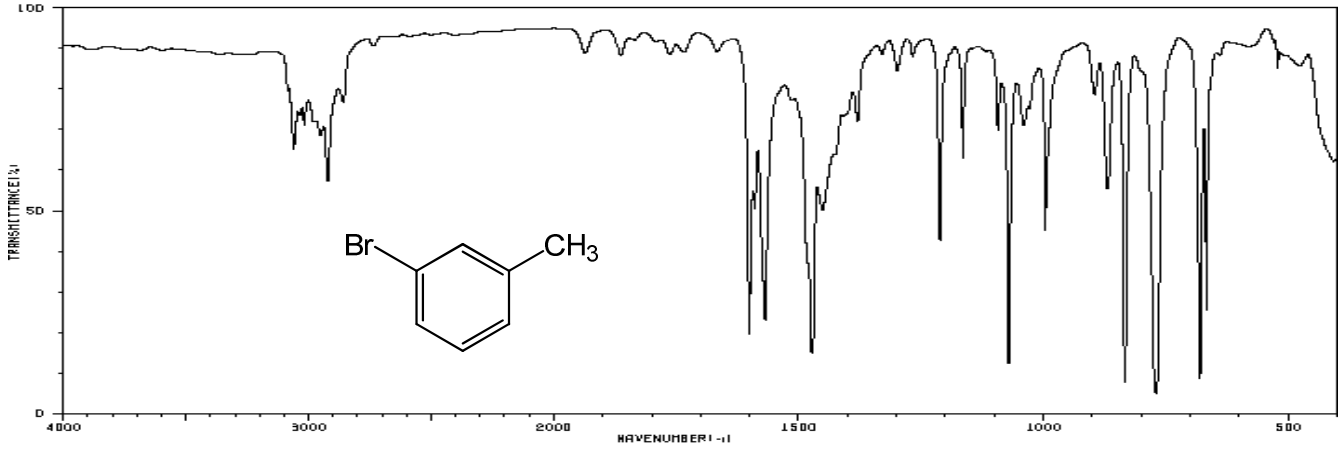
SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

Disubstituted aromatic rings

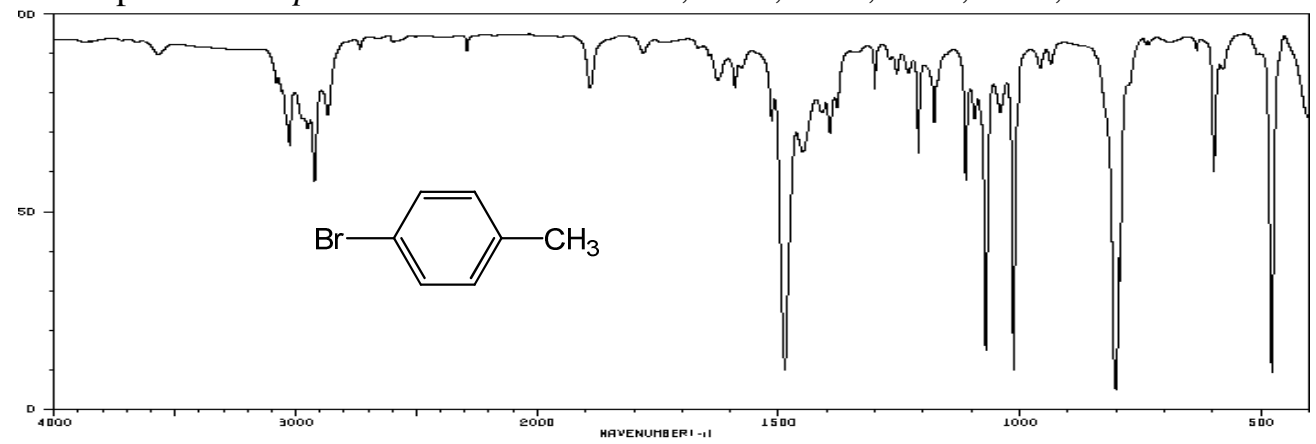
Infrared spectrum of *ortho*-bromotoluene: 3061, 3016, 2924, 1470, 1031, 745 cm^{-1}



Infrared spectrum of *meta*-bromotoluene: 3061, 3017, 2932, 1564, 834, 770, 681 cm^{-1}



Infrared spectrum of *para*-bromotoluene: 3081, 3026, 2923, 1487, 1013, 801 cm^{-1}

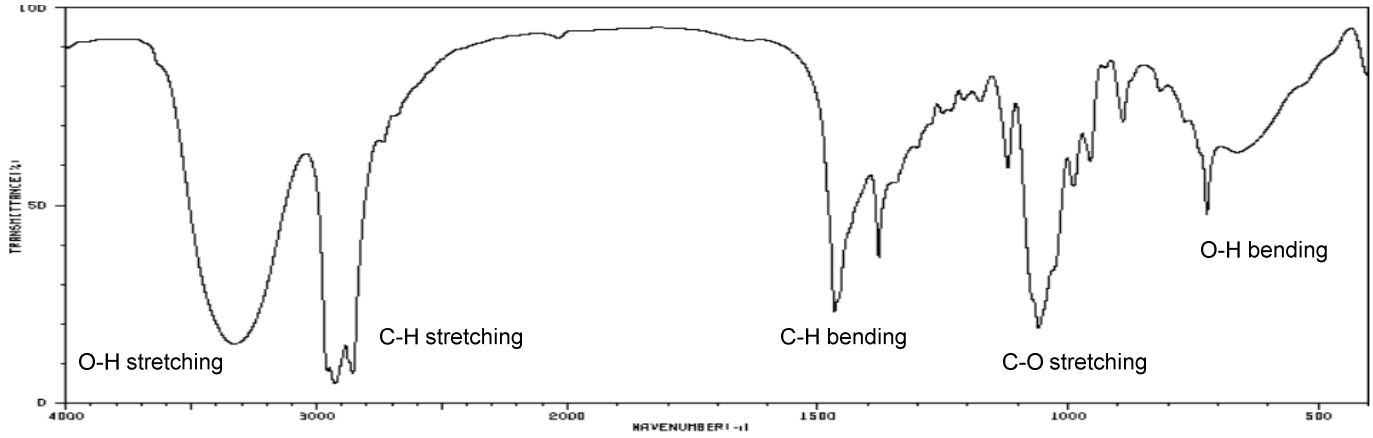


The Infrared Spectra of The Alcohols (ROH)

Dominant Observable Vibrations:

O-H stretching	~3200-3600 cm^{-1}
C-O stretching	~1000-1200 cm^{-1}

Infrared spectrum of 1-octanol



3338	14	1246	70	956	58
3327	14	1235	70	890	68
2927	4	1209	74	816	77
2870	10	1176	74	723	46
2856	7	1120	57	662	60
1467	21	1059	18		
1379	36	989	62		

SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

Hydrogen bonding is an important phenomenon in the infrared spectra of alcohols. The frequency and shape of the peak is directly proportional to the level of hydrogen bonding.

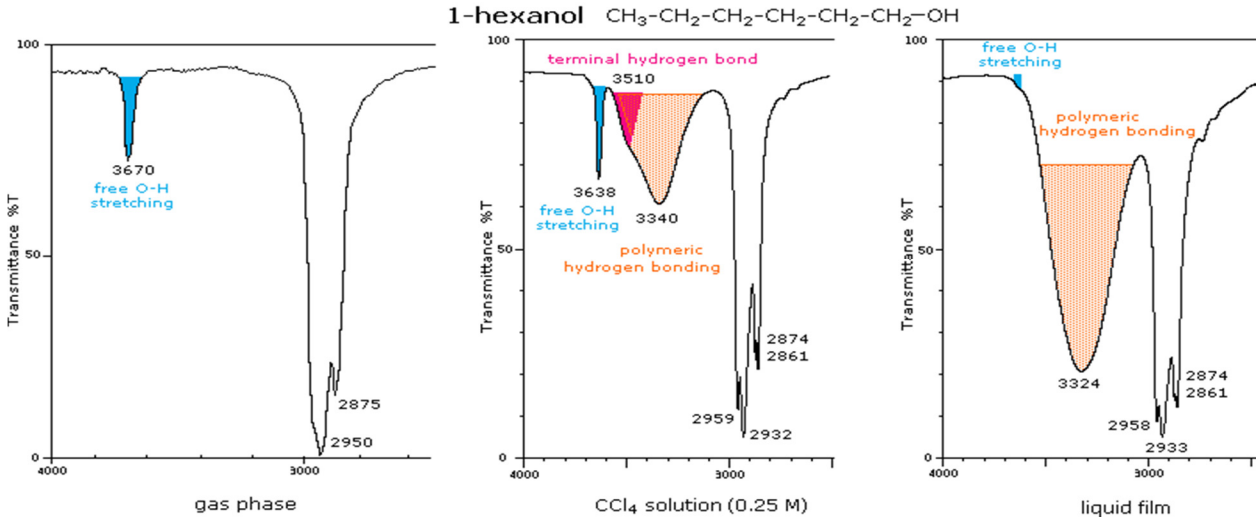
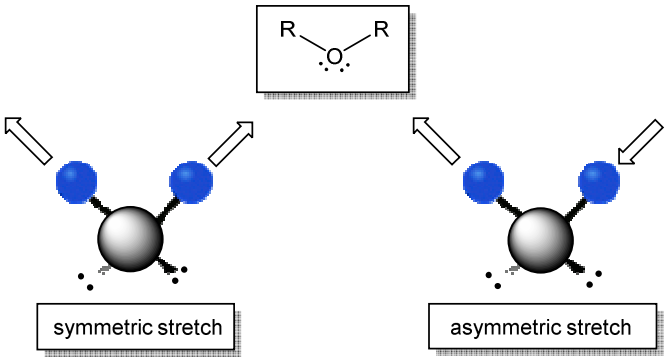


Image taken from https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/Spectrpy/InfraRed/irspec1.htm

The Infrared Spectra of The Ethers

Dominant Observable Vibrations

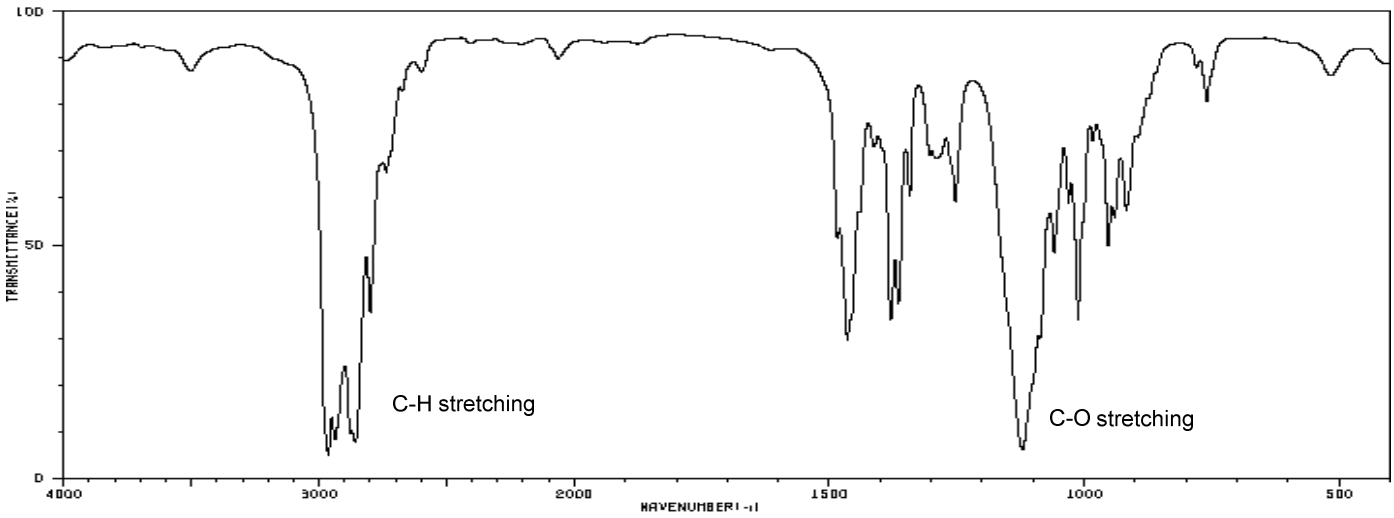
Stretching vibrations



strong band due to asymmetrical stretching, 1150-1085 cm^{-1} (usually 1125 cm^{-1})

weak band due to symmetrical stretching, 820-890 cm^{-1}

Infrared spectrum of di-*n*-propyl ether ($CH_3CH_2CH_2$-O-$CH_2CH_2CH_3$)



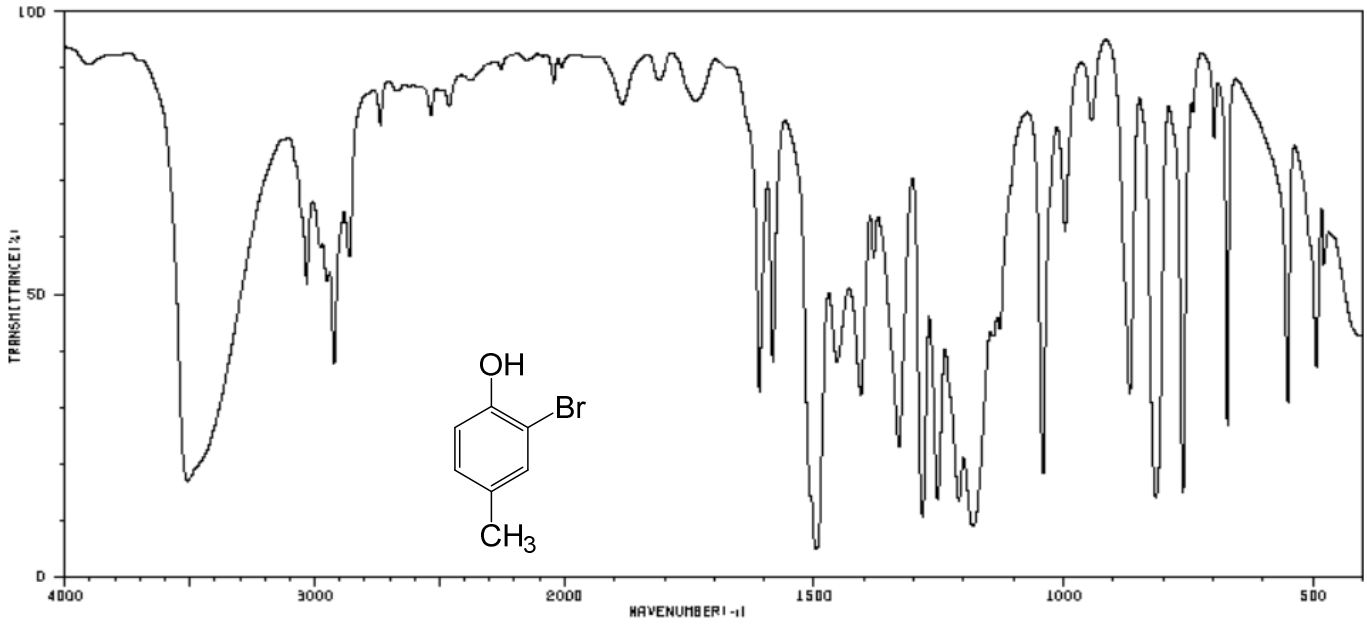
3504	84	2698	84	1343	68	1012	32	620	84	$CH_3-(CH_2)_2-O-(CH_2)_2-CH_3$	
2963	4	2063	86	1303	86	983	70	513	84		
2936	7	1464	49	1269	86	953	47				
2878	9	1466	28	1263	67	941	69				
2858	7	1413	68	1121	5	917	55				
2799	34	1380	32	1059	46	780	84				
2736	82	1366	36	1031	67	760	77				

SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

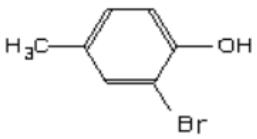
The Infrared Spectra of The Phenols

Dominant Observable Vibrations

Phenols will have an appearance that is very similar to that of alcohols. There is a broad absorption that appears in the region of 3600 to 3100 cm^{-1}. The following infrared spectrum is that of 2-bromo-4-methylphenol.



3609	16	2462	79	1407	31	1127	42	741	79
3032	50	1884	81	1381	55	1041	17	698	74
2951	50	1738	81	1330	22	997	58	672	26
2923	36	1610	32	1289	10	944	77	661	29
2862	55	1583	36	1253	13	867	31	505	57
2737	77	1495	4	1210	15	815	19	494	36
2636	79	1464	36	1182	8	761	14	480	63

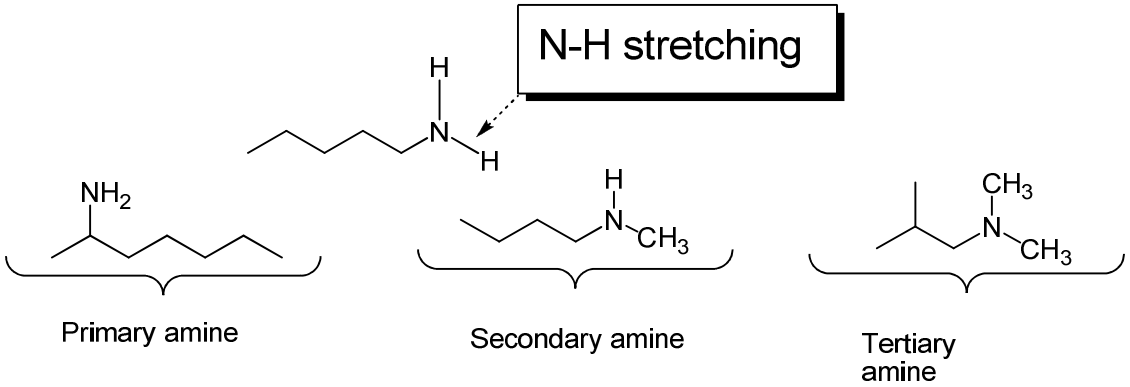


Spectrum obtained from SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, December 16, 2014).

The Infrared Spectra of The Amines

Dominant Observable Vibrations:

N-H stretching	~3200-3500 cm^{-1}
N-H bend	~1550-1650 cm^{-1}



Comments:

Shows the –N-H stretch for NH_2 as two signals between 3200-3500 cm^{-1} (s-m); symmetric and anti-symmetric modes NH_2 group shows a deformation band from 1590-1650 cm^{-1}. Additionally there is a "wag" band at 780-820 cm^{-1} that is not diagnostic

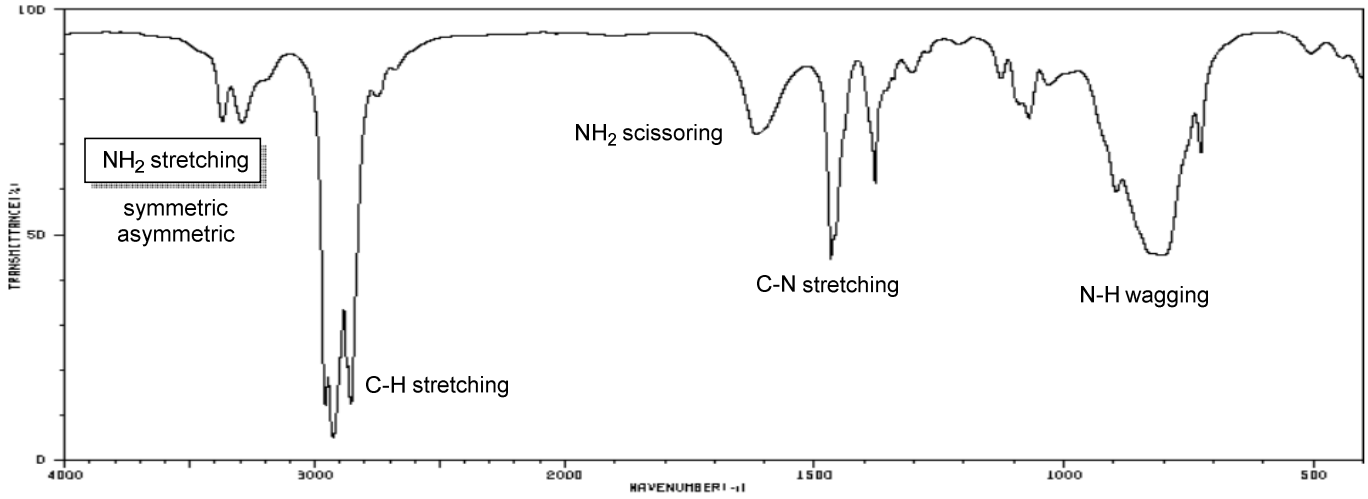
- The N-H stretching vibration varies in intensity.
- **Primary amines** have two N-H signals in the region between 3200 and 3500 cm^{-1}.
- **Secondary amines** have only one N-H signal in this region.
- **Tertiary amines** do not have an N-H signal.

Sometimes, amines are mistaken for alkenes because of the N-H bending vibration that appears near 1600 cm^{-1}.

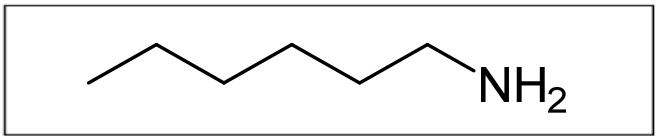
The Infrared Spectra of Amines

The infrared spectra of amines have only a few peaks that can be considered to be of diagnostic value. The symmetric and asymmetric N-H stretch is of greatest value. The NH_2 scissoring peak will vary in intensity and may be obscured by other peaks.

Primary amine: *n*-hexylamine



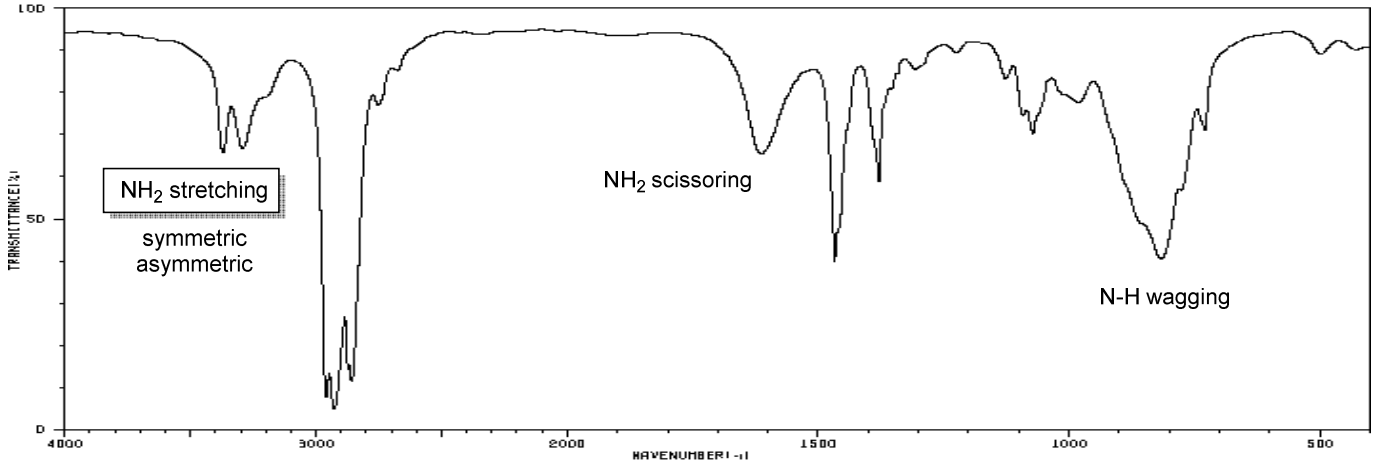
3369	72	1617	70	1070	72
3291	72	1468	42	1031	79
2956	11	1461	47	895	57
2927	4	1379	58	812	43
2873	19	1303	84	726	66
2856	12	1128	61		
2763	77	1086	77		



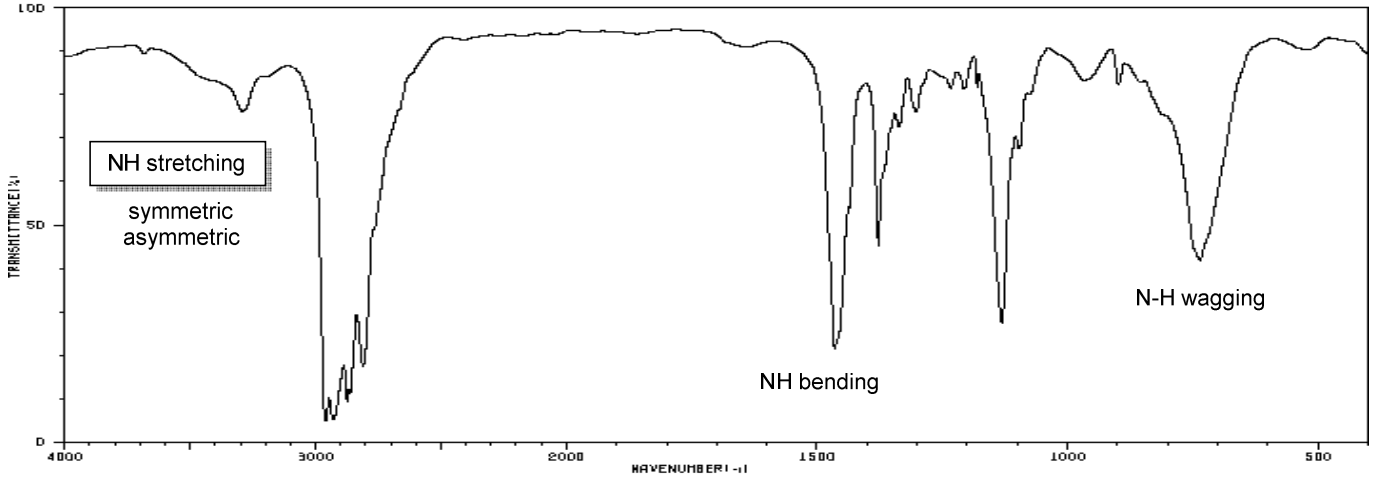
SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

The Infrared Spectra of the Amines (primary, secondary, tertiary)

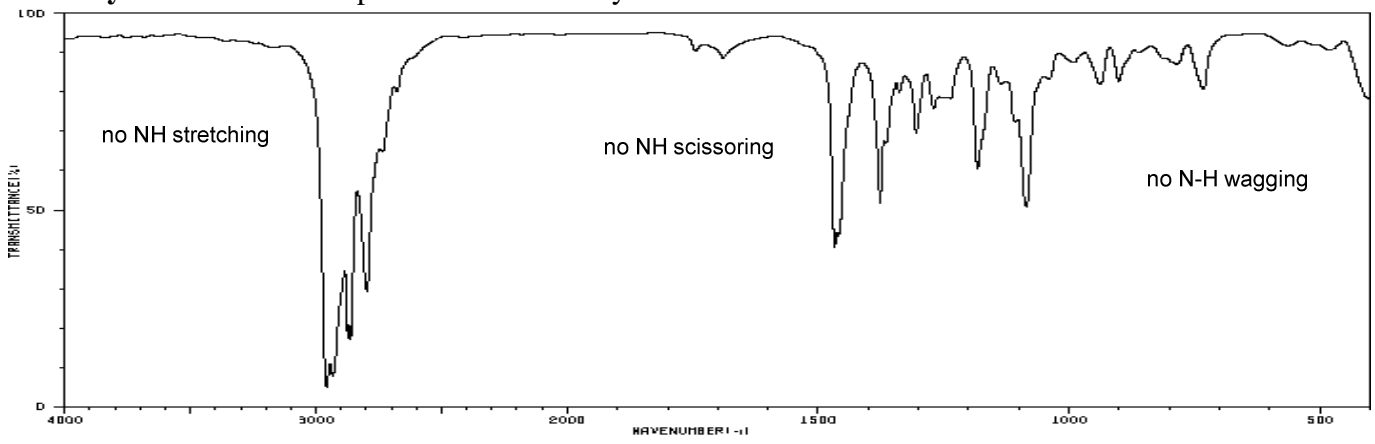
Primary amine: Infrared spectrum of *n*-pentyl amine



Secondary amine: Infrared spectrum of di-*n*-butyl amine

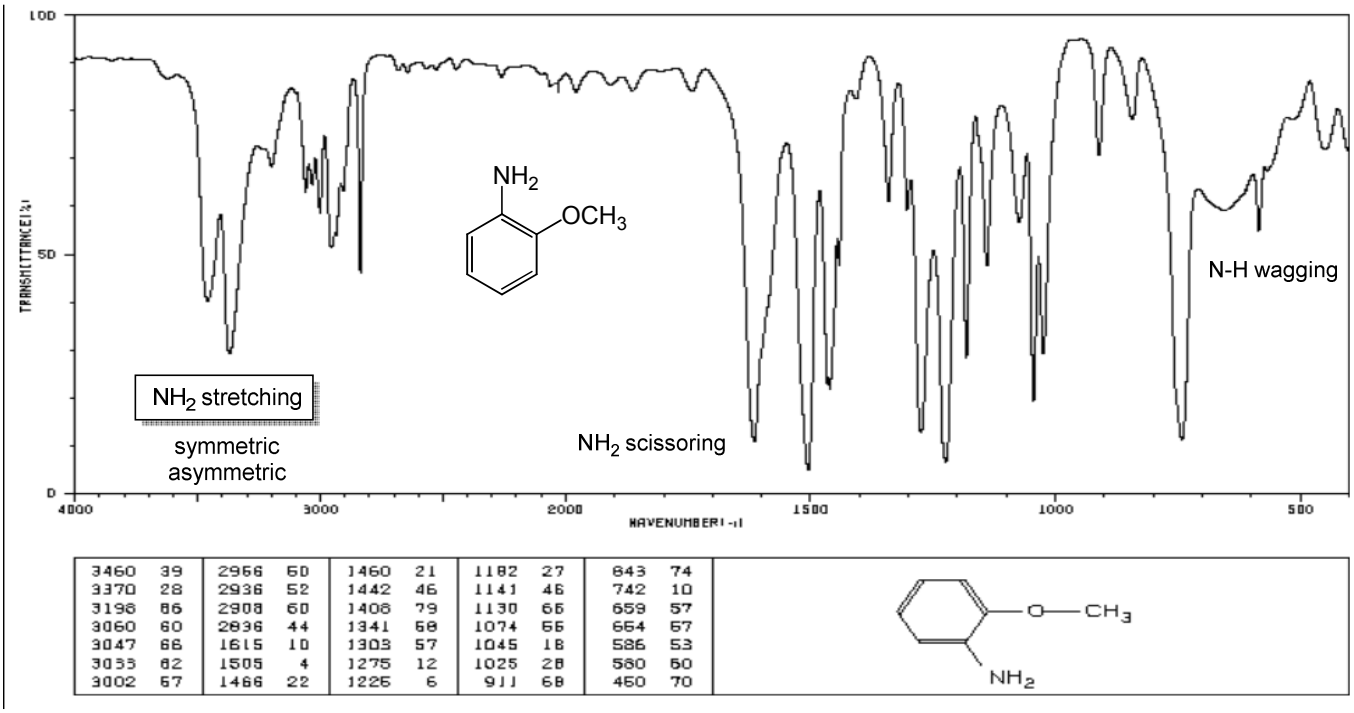


Tertiary amine: Infrared spectrum of tri-*n*-butyl amine



The Infrared Spectra of Aromatic Amines (Anilines)

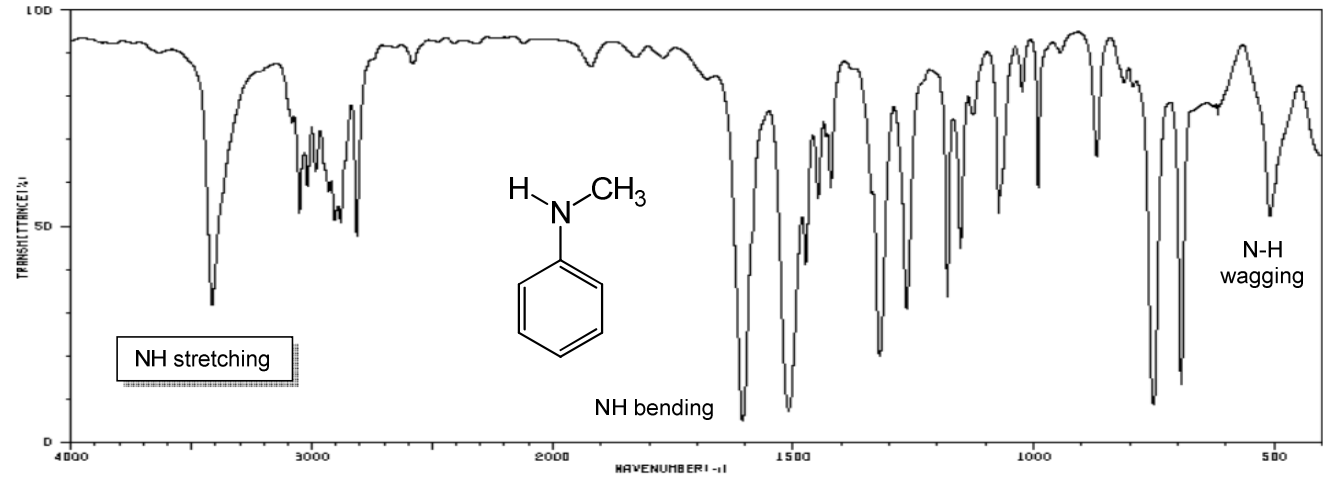
The following example represents an aromatic primary amine. Notice that the NH_2 symmetric and anti-symmetric stretches near 3400 cm^{-1} are significantly larger than the corresponding peaks in the aliphatic amines.



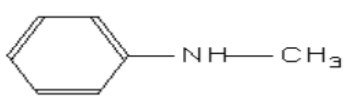
3460	39	2966	60	1460	21	1182	27	843	74
3370	28	2936	52	1442	46	1141	46	742	10
3198	86	2908	60	1408	79	1130	66	659	57
3060	60	2836	44	1341	68	1074	66	654	67
3047	66	1615	10	1303	57	1045	18	586	53
3033	62	1505	4	1275	12	1025	28	580	60
3002	67	1466	22	1225	6	911	68	450	70

SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

The following example represents an aromatic secondary amine.



3415	31	2880	49	1610	7	1163	48	796	79
3083	72	2813	46	1474	39	1126	72	751	8
3052	52	2580	84	1448	55	1073	50	693	13
3018	67	1920	84	1422	67	1024	79	623	74
2983	60	1825	86	1320	19	991	57	617	72
2930	55	1769	86	1264	30	869	64	509	50
2906	49	1606	4	1180	32	813	79		

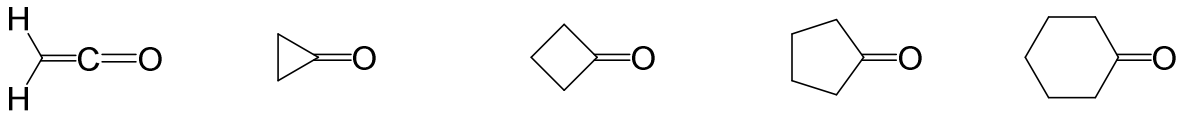


SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

The Infrared Spectra of The Ketones

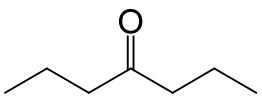
Dominant Observable Vibration

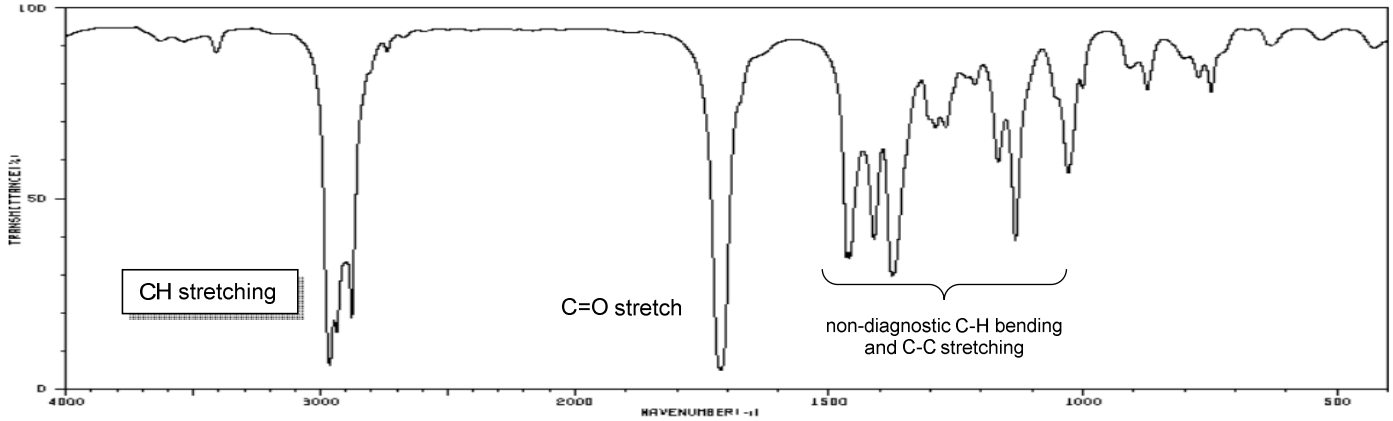
The most important vibration associated with ketones is the C=O stretching vibration. This vibration occurs in the region of ~1710-1725 cm^{-1}. The frequency of the carbonyl peak will vary based on the structure of the carbonyl.



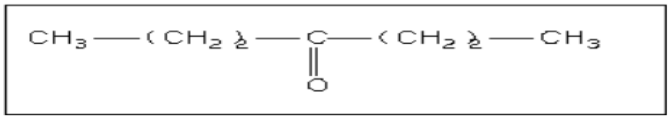
2140 cm^{-1} 1815 cm^{-1} 1780 cm^{-1} 1742 cm^{-1} 1715 cm^{-1}

Infrared spectrum of 4-heptanone: key carbonyl vibration at 1713 cm^{-1}.





3409	84	1460	38	1168	67	748	74
2964	6	1412	37	1134	37	427	86
2937	14	1377	26	1030	55		
2877	17	1291	66	1001	77		
2737	84	1271	66	907	81		
1713	4	1228	79	874	74		
1466	33	1213	77	774	79		

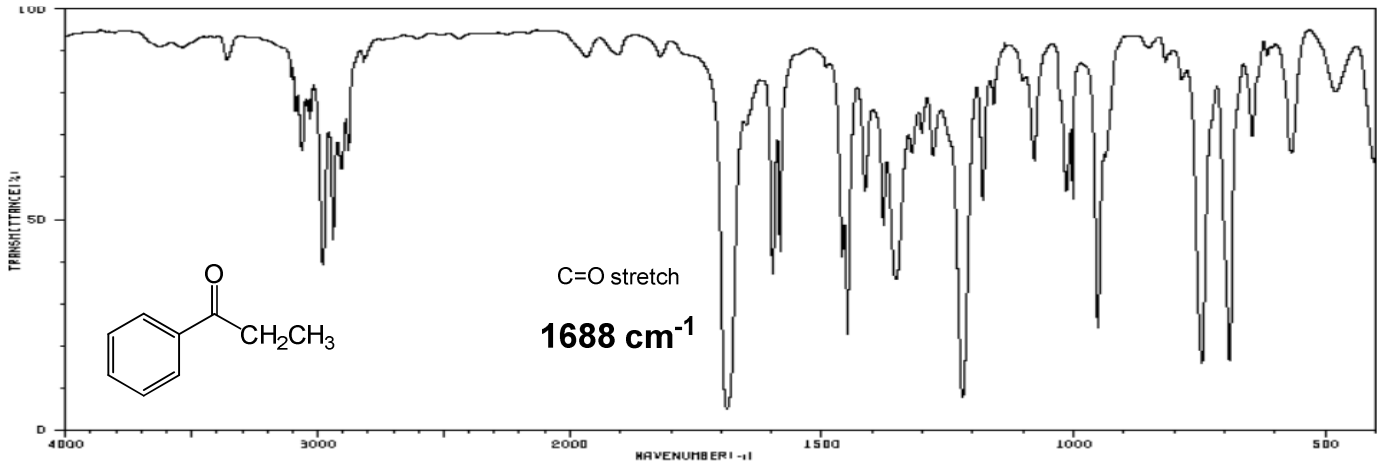


SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

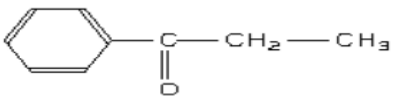
The Infrared Spectra of Aromatic ketones

The frequency of the C=O stretching vibration for ketones will decrease to about 1690-1666 cm^{-1} if the C=O functional group is immediately next to an alkene or an aromatic ring.

Infrared spectrum of propiophenone:

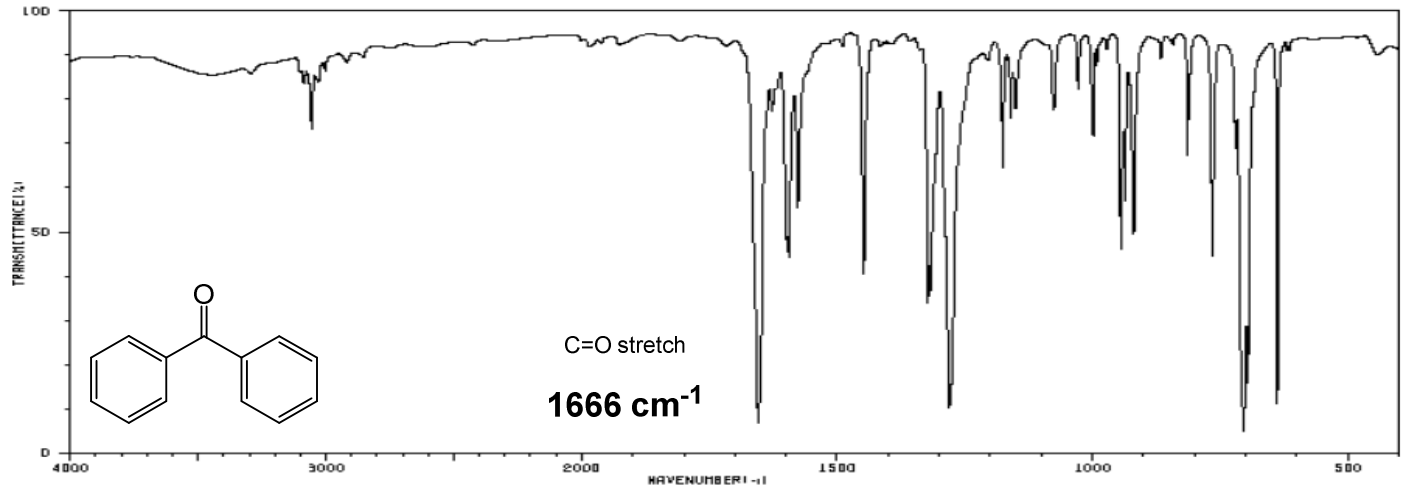


3102	79	2879	64	1378	46	1159	74	786	79
3087	72	1688	4	1353	34	1102	79	746	15
3062	84	1598	55	1321	84	1078	62	691	15
3030	70	1583	41	1302	68	1015	66	646	68
2979	37	1460	39	1279	62	1002	52	636	79
2940	43	1449	21	1221	7	952	29	568	64
2906	60	1414	65	1181	62	937	62	480	77

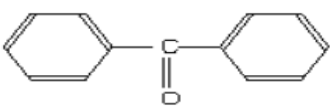


SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

Infrared spectrum of benzophenone:



3291	81	1665	6	1206	86	992	84	720	66
3088	81	1627	74	1176	62	945	44	705	4
3067	79	1595	42	1162	72	936	55	697	15
3057	70	1577	69	1161	74	919	47	639	10
3030	81	1449	38	1076	74	867	86		
3003	84	1323	32	1026	79	814	64		
2919	84	1281	10	999	68	765	42		



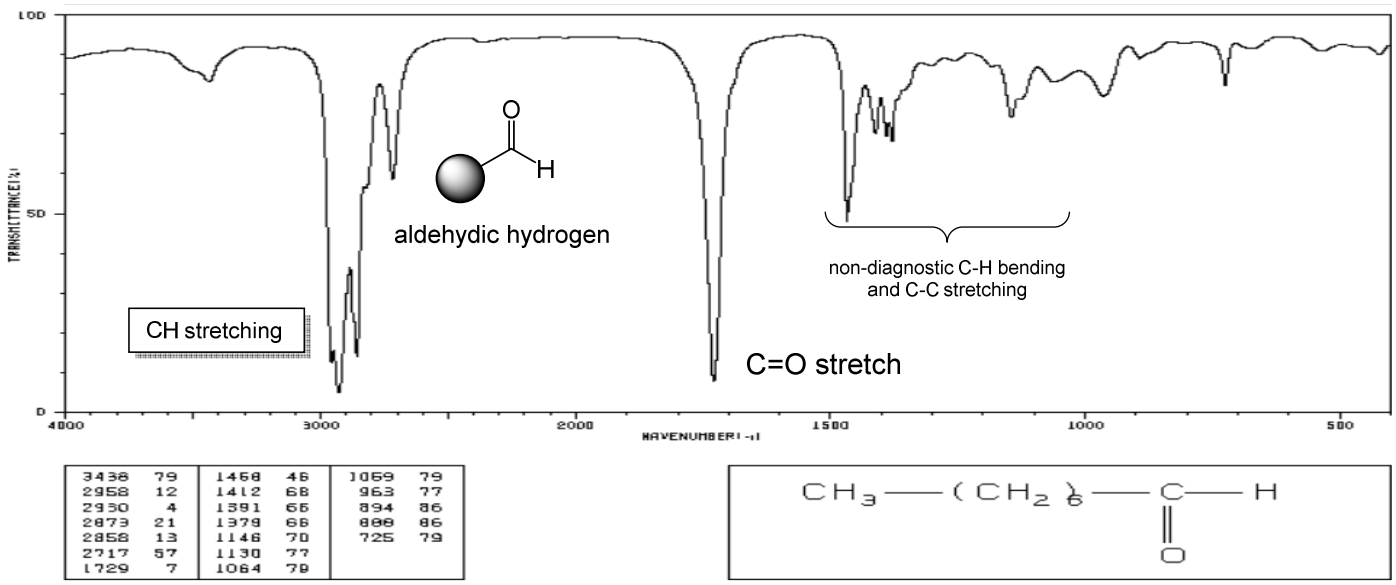
SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

The Infrared Spectra of the Aldehydes

The most important vibration associated with ketones is the C=O stretching vibration. This vibration occurs in the region of ~1725-1735 cm^{-1}. The frequency of the carbonyl peak will vary based on the structure of the carbonyl.

-C=O stretching	~1725-1735 cm^{-1}
Aldehydic C-H	~2700-2800 cm^{-1}

Infrared spectrum of *n*-hexanal:



3438	79	1468	46	1069	79
2958	12	1412	68	963	77
2930	4	1391	66	894	86
2873	21	1379	66	808	86
2858	13	1146	70	725	79
2717	57	1130	77		
1729	7	1064	79		

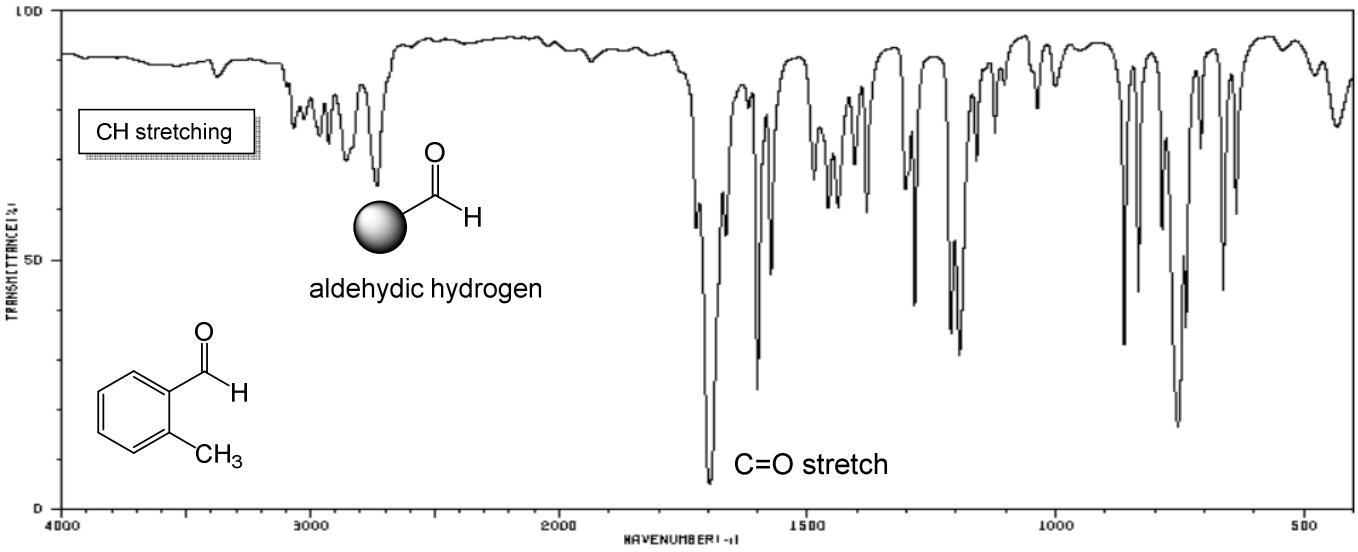
SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

The Infrared Spectra of the Aromatic Aldehydes

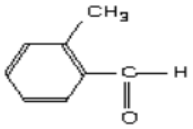
Aromatic Aldehydes

The frequency of the C=O stretching vibration for aldehydes will decrease to about 1685-1666 cm^{-1} if the C=O functional group is conjugated to an alkene or an aromatic ring.

Infrared spectrum of 4-methoxybenzaldehyde (*para*-anisaldehdye)



3068	74	1724	63	1468	68	1211	34	786	63
3041	77	1697	4	1438	58	1194	29	754	15
3029	74	1664	52	1405	86	1160	68	736	35
2963	72	1619	77	1381	67	1122	72	708	70
2926	70	1601	23	1304	62	1037	77	663	42
2856	66	1573	44	1298	84	862	31	637	57
2733	62	1487	64	1285	39	834	42	434	74

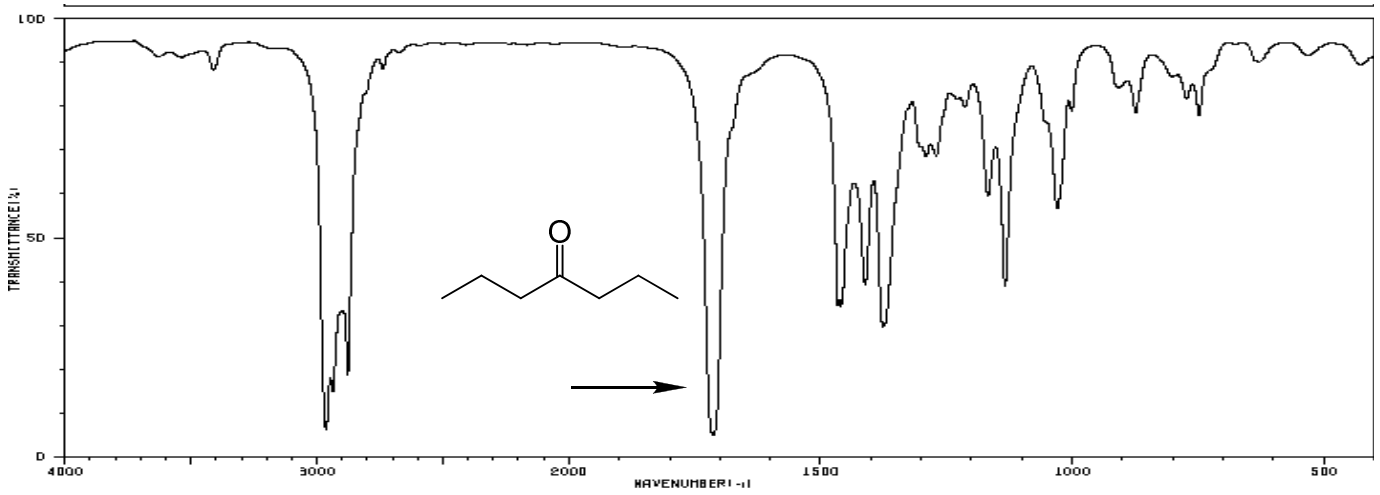


SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

The Ketones and the Aldehydes: A Comparison

The Ketones

Infrared spectrum of 4-heptanone:

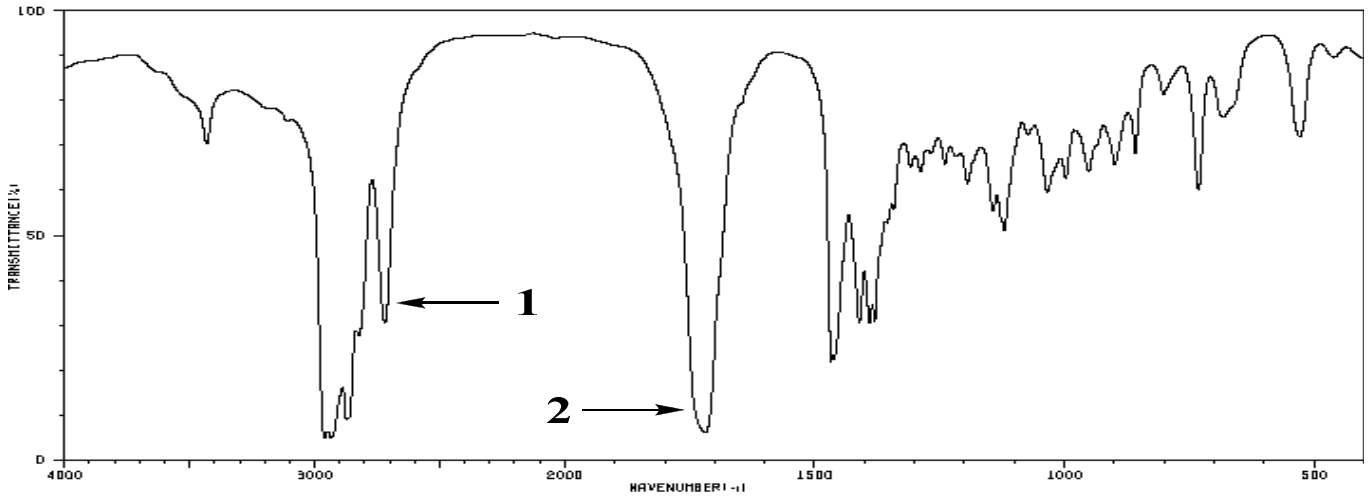


SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

The Aldehydes

The Aldehyde C-H stretch at ~2700-2800 cm^{-1} serves as a marker in terms of distinguishing aldehydes from ketones.

Infrared spectrum of *n*-hexanal:

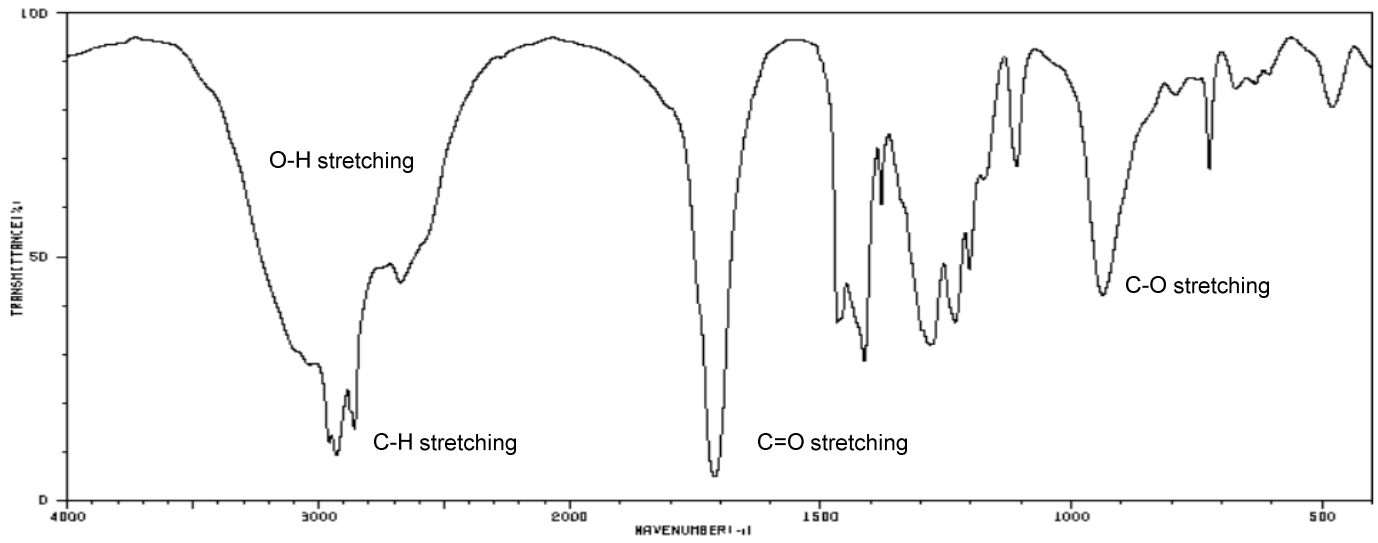


SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

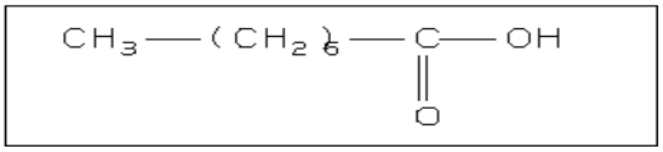
The Infrared Spectra of Carboxylic Acids

C=O stretching ~1710 cm^{-1} O-H stretching ~2500-3100 cm^{-1}

Infrared spectrum of octanoic acid:



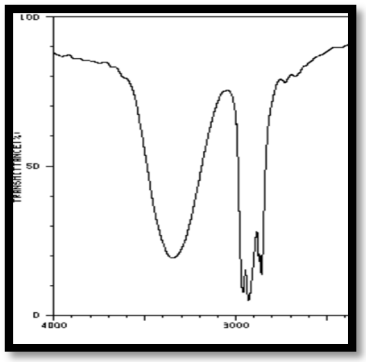
2967	11	1461	35	938	41
2930	8	1413	27	792	79
2873	17	1379	58	725	86
2859	13	1282	30	673	81
2673	43	1232	35	633	81
1711	4	1204	45	607	84
1468	35	1109	66	480	77



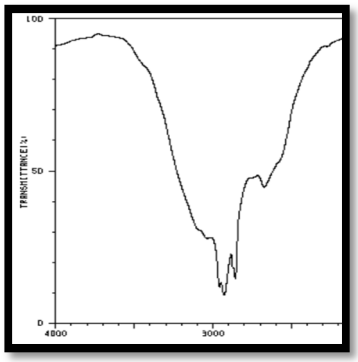
SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

Comparison with aliphatic alcohols

Both carboxylic acids and alcohols possess the –OH group, although their reactivities are very different as the carboxylic acid –OH group is bound to a carbonyl group. The vibrational frequency of an –OH group of an alcohol is shifted to higher frequencies.



Alcohol



Carboxylic acid

The Infrared Spectra of Esters

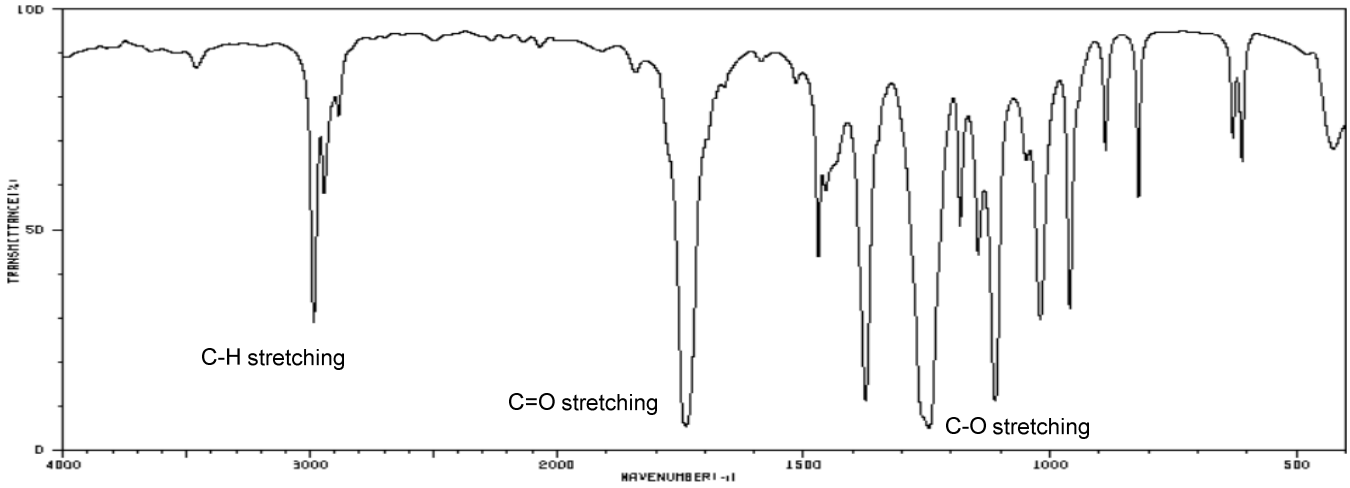
C=O stretch

- saturated aliphatic esters: C=O: 1750–1735 cm^{-1}
- formates, a,b-unsaturated, and benzoate esters: 1730-1715 cm^{-1}
- phenyl or vinyl esters: 1770-1780 cm^{-1}

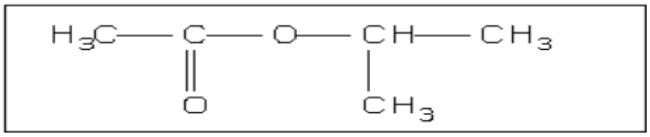
C–O stretches (strong absorptions; asymmetrical coupled vibrations)

- saturated aliphatic esters (except acetates): C–O: 1210–1163 cm^{-1}
- acetates: 1240 cm^{-1}
- α,β-unsaturated esters: 1300–1160 cm^{-1}
- benzoate esters: 1310–1250 cm^{-1}

Infrared spectrum of isopropyl acetate:



3460	84	1684	84	1146	42	629	68
2984	27	1514	79	1111	10	611	62
2944	55	1470	42	1049	84	426	66
2884	72	1466	67	1020	28		
1841	81	1374	10	960	31		
1736	5	1248	4	866	86		
1690	86	1183	49	821	66		



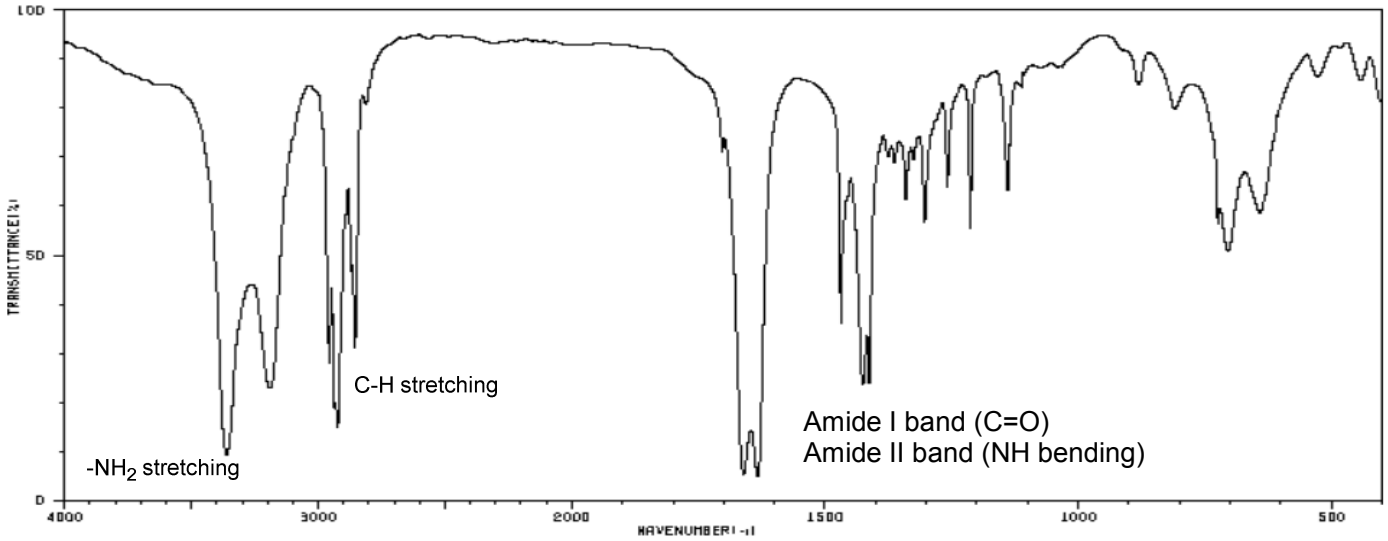
SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

The Infrared Spectra of Amides

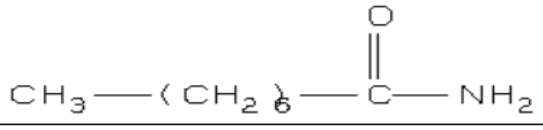
Dominant Observable Vibrations:

C=O stretching	~1660-1680 cm^{-1}
N-H stretching	~3200-3500 cm^{-1}

Infrared spectrum of octanamide:



3362	9	2811	77	1375	68	1140	60	705	49
3190	22	1703	68	1363	66	1112	81	641	57
2956	26	1661	5	1341	58	881	81	528	64
2936	18	1633	4	1326	66	872	84	442	81
2923	14	1469	35	1304	55	810	77		
2871	44	1428	22	1259	82	798	79		
2855	30	1413	29	1214	63	724	69		

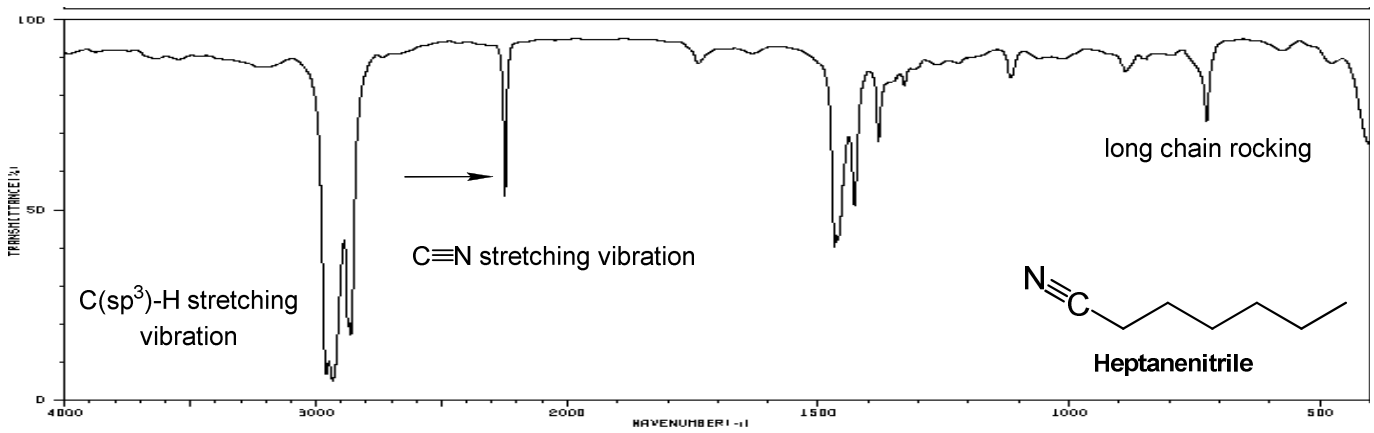


SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

The Infrared Spectra of Nitriles

-C≡N triple bond stretch ~2240-2280 cm^{-1}

Infrared spectrum of heptanenitrile:

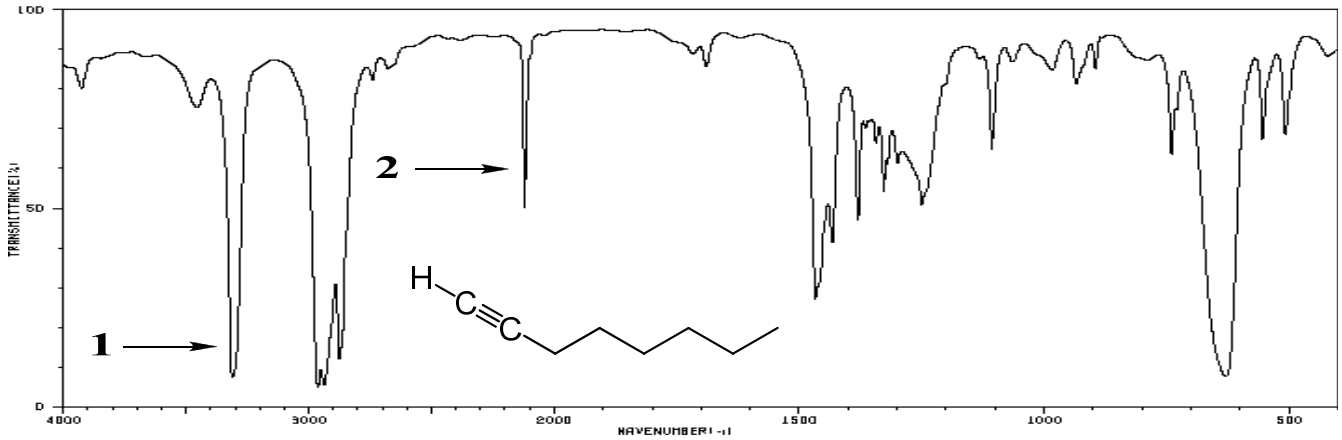


SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).

Comparison with terminal alkynes (R-C≡C-H)

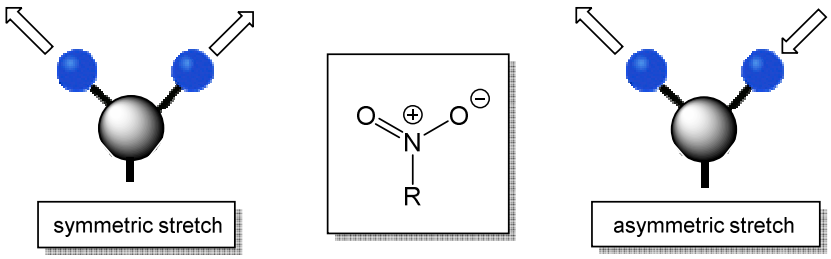
Both alkynes and nitriles possess triple bonded functional groups that appear in nearly the same region in the infrared spectrum. A key difference is that the alkynes (if they are terminal alkynes) will possess additional features that should readily allow for diagnostic confirmation for one functional group or the other.

1-octyne (a terminal alkyne): 3323, 3024, 2926, 1636, 1466, 964 cm^{-1}.



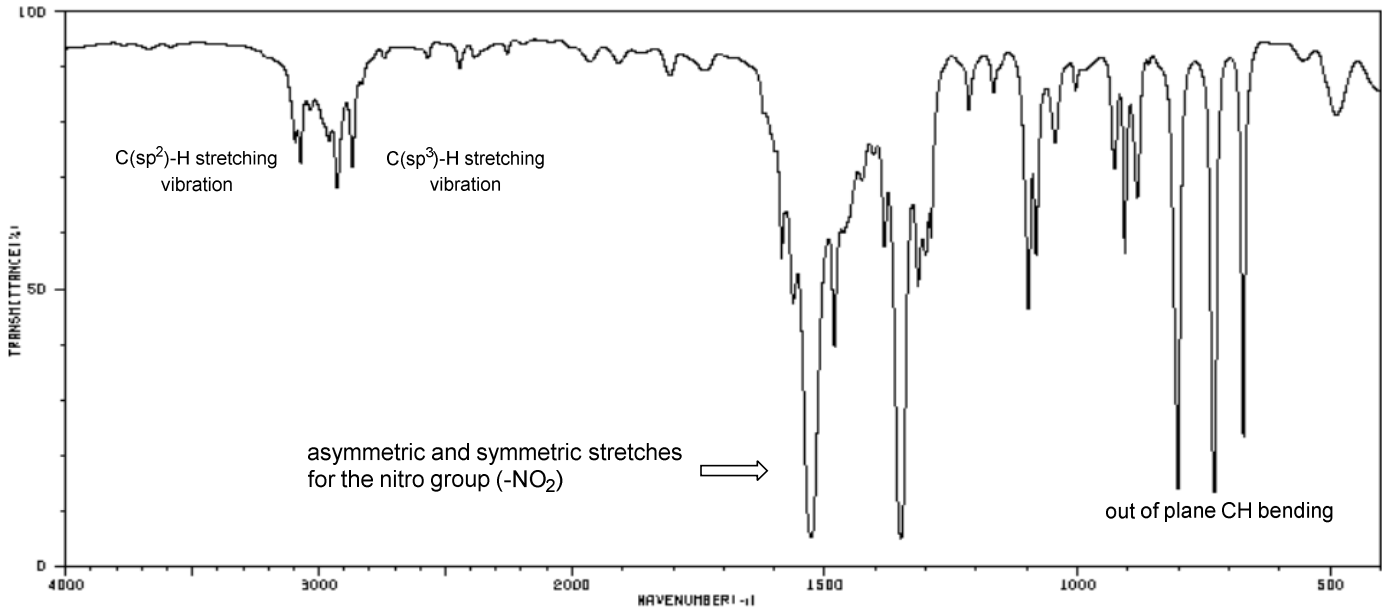
The Infrared Spectra of Nitrocompounds

Dominant Observable Vibrations

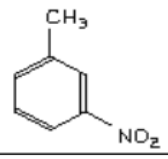


Two bands are observed in the spectrum (symmetric and asymmetric) at 1300-1380 cm^{-1} (m-s) and 1500-1570 cm^{-1} (m-s).

Infrared spectrum of *meta*-nitrotoluene



3094	74	1740	86	1403	72	1167	81	927	68
3072	70	1735	86	1382	55	1097	44	906	53
3032	79	1588	55	1350	4	1082	59	862	64
2960	74	1562	46	1316	49	1044	74	802	13
2927	66	1527	4	1301	53	1004	81	729	12
2867	70	1482	58	1290	57	993	86	672	22
1806	84	1427	66	1216	79	988	86	488	79



SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, January 8, 2015).