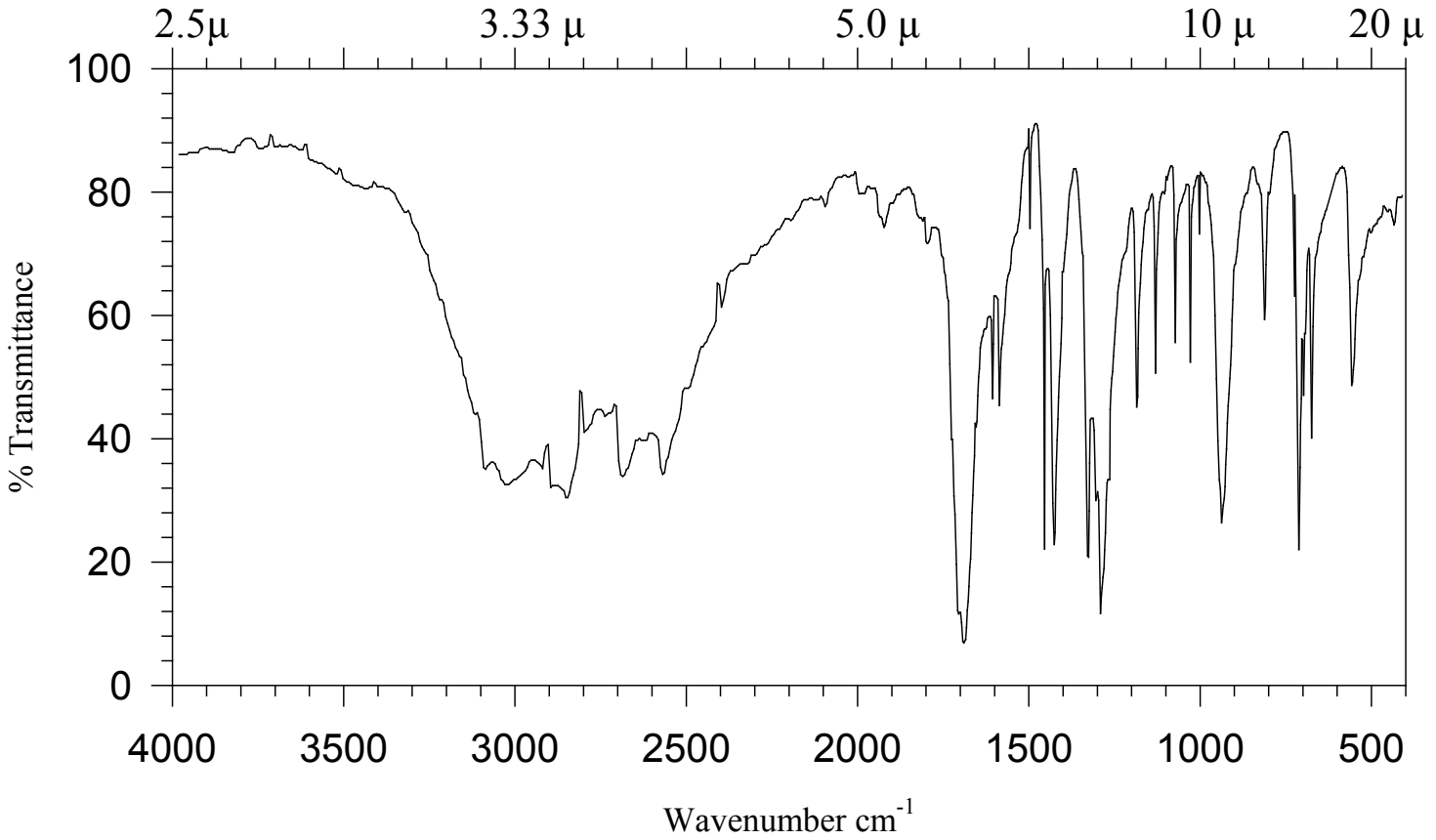
Infrared Spectroscopy

- Units
- The wavelength of light in the IR region varies from about 2.5 to 40 μ
- where 1 $\mu = 10^{-4}$ cm.



$2.5\mu = 2.5 \cdot 10^{-4}$ cm

$1/2.5\mu = 4000$ cm^{-1}

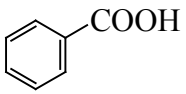


Figure IR-29. Benzoic acid; KBr disk

Units used in IR spectroscopy

The wavelength of light in the IR region varies from about 2.5 to 40 μ where 1 $\mu = 10^{-4}$ cm.

Since $\lambda_{cm}\nu_{sec\text{-}1} = c$; $\nu = c/\lambda$ and $E = h\nu$;

ν is proportional to $1/\lambda$, therefore E is proportional to $1/\lambda$ cm^{-1}

To convert to true energy units, cm^{-1} needs to be multiplied by the speed of light, $3*10^{-10}$ cm $sec^{-1,}$ and Planck's Constant, $h = 6.624*10^{-27}$ erg sec

The reason for using values proportional to energy is that overtones usually occur at approximately twice the energy of the main transition

Infrared Spectroscopy

$E_{vib} = (n+1/2)h(k/\mu)^{.5}/2\,\pi$ where $\mu = m_1m_2/(m_1+m_2)$

$E_{rot} = J(J+1)h^2/8\,\pi 2I$; where I = moment of inertia

$E_{vib\text{-}rot} = (n+1/2)h(k/\mu)^{.5}/2\,\pi + J(J+1)h^2/(8\,\pi^2 I)$; $n, J = \pm 1$.

In IR, the change in n is usually by +1, occasionally some + 2 also occurs (overtone). The number of molecules at room temperature that are in an $n = 1$ state is very small because the energy spacings are large.
The rotational energy spacings are considerably smaller; $J = \pm 1$

h is Planks constant
k is force constant

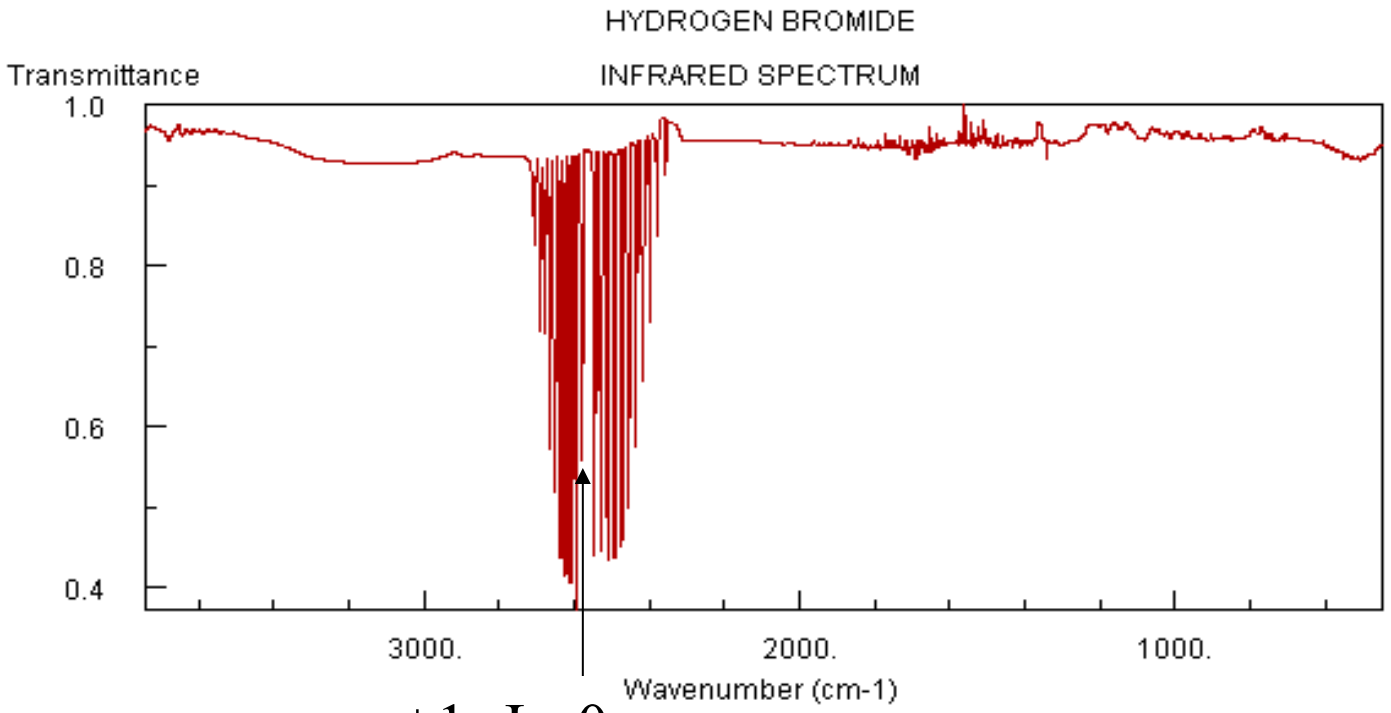
An example of a molecule with a small moment of inertia: HBr

$E_{vib\text{-}rot} = (n+1/2)h(k/\mu)^{.5}/2\,\pi + J(J+1)h^2/(8\,\pi^2 I)$; where I = moment of inertia

$n, J = \pm 1$. For most large molecules I is large. In this spectrum $n = +1$.

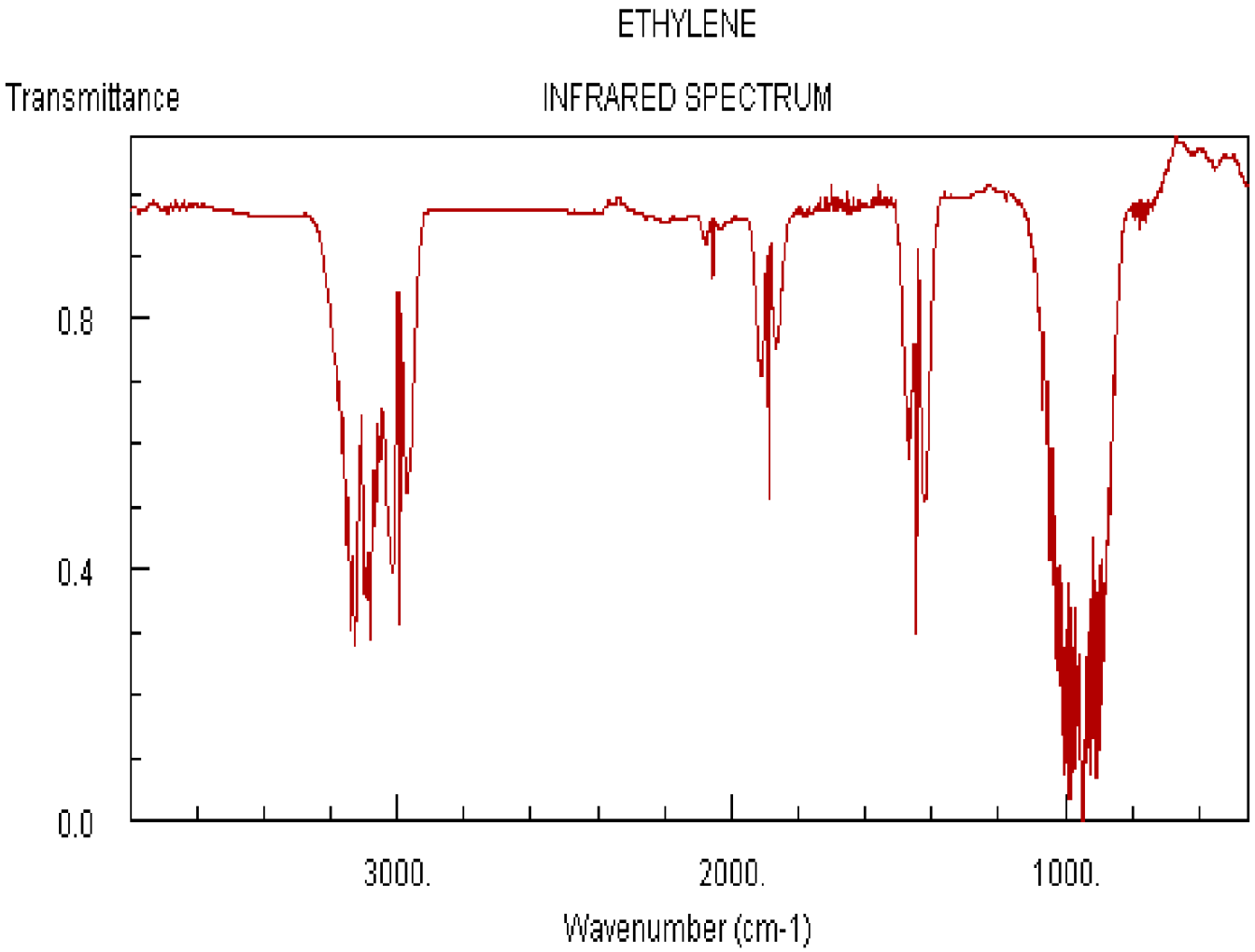
$J = \pm 1$

Gas Phase Spectrum

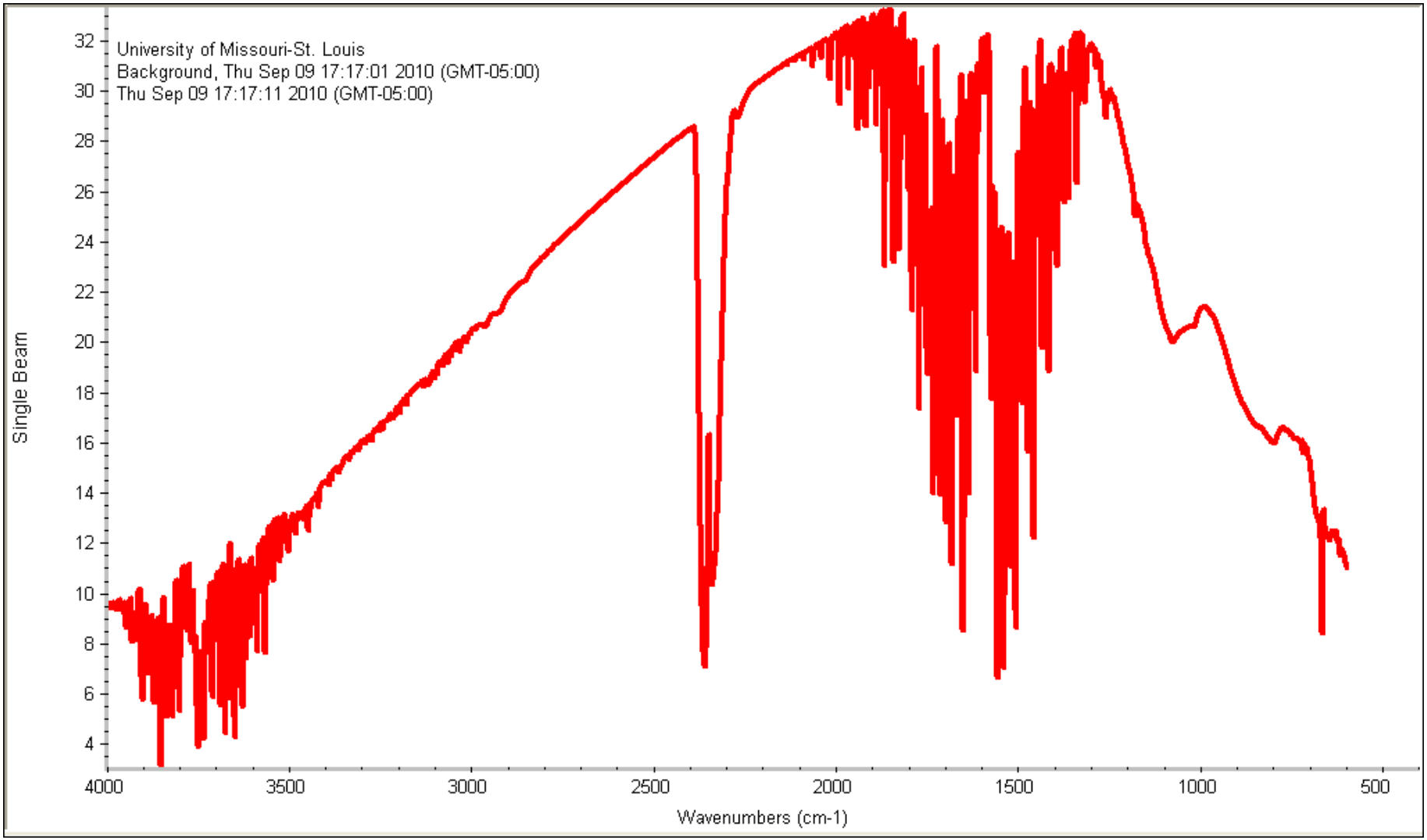


$n = +1$,J =0

Gas Phase Spectrum



In the condensed phase collision broadening also obcures the n=1, J =0 null


University of Missouri-St. Louis
Background, Thu Sep 09 17:17:01 2010 (GMT-05:00)
Thu Sep 09 17:17:11 2010 (GMT-05:00)
Single Beam
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

Windows

	IR Transmission Limit (cm^{-1})	H_2O
NaCl	650	sol
KCl	500	sol
KBr	400	sol
CsI	150	sol
CaF_2	1100	insol
BaF_2	850	insol
KRS-5 (TlBrI cmp*	200	insol

* toxic

IR TUTOR

A summary of the principle infrared bands and their assignments. R is an aliphatic group.

Funct. Group	Type		Frequencies cm^{-1}	Peak Intensity	Examples Figure No.
C-H	sp^3 hybridized	R_3C-H	2850-3000	M(sh)	6, 18, 22

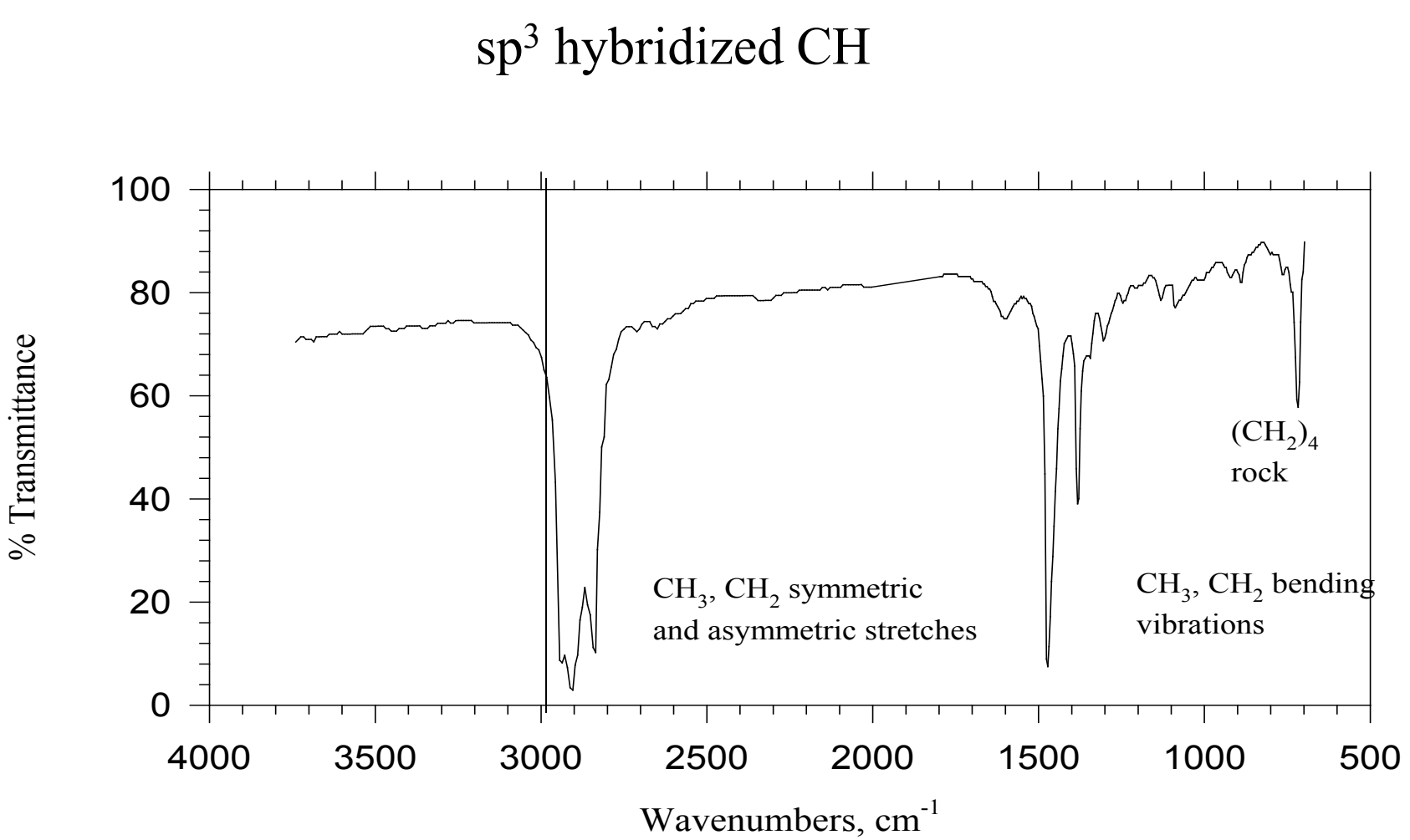


Figure IR-6. N-Decane, neat liquid, thin film: $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

sp^3 hybridized CH

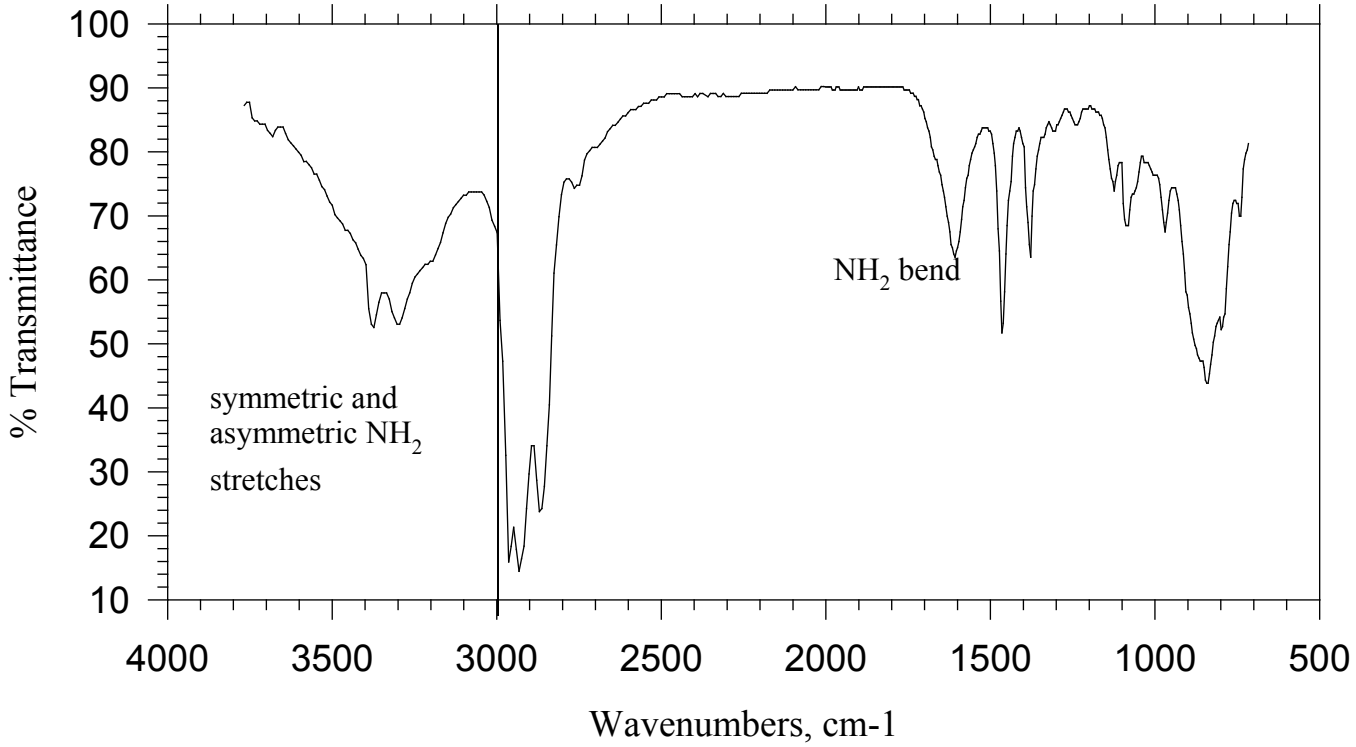


Figure IR-18. Butylamine, neat liquid; thin film: $CH_3CH_2CH_2CH_2NH_2$

sp^3 hybridized CH

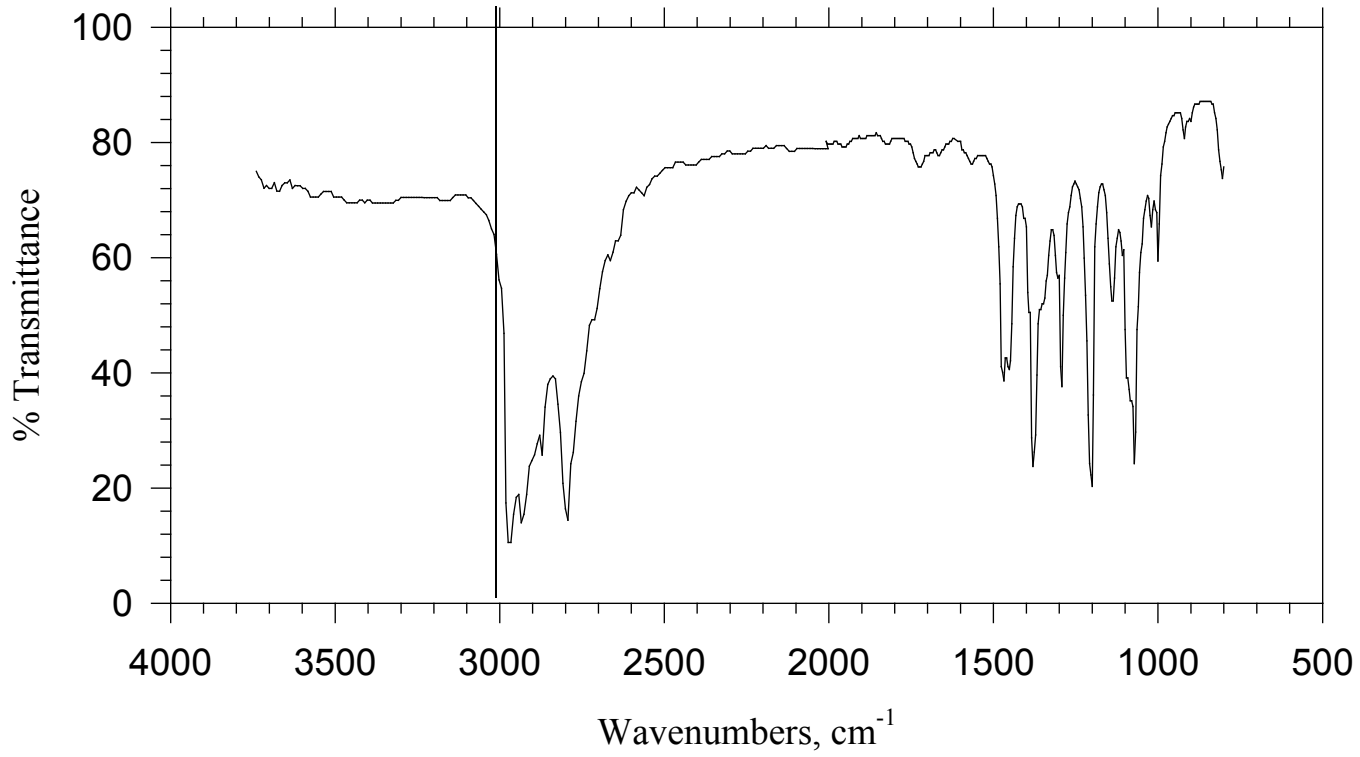


Figure IR-22. Triethylamine, neat liquid; thin film: $(CH_3CH_2)_3N$

A summary of the principle infrared bands and their assignments. R is an aliphatic group.

Funct. Group	Type		Frequencies cm^{-1}	Peak Intensity	Examples Figure No.
C-H					
	sp^2 hybridized	=CR-H	3000-3250	M(sh)	7, 13, 42

sp^2 hybridized CH

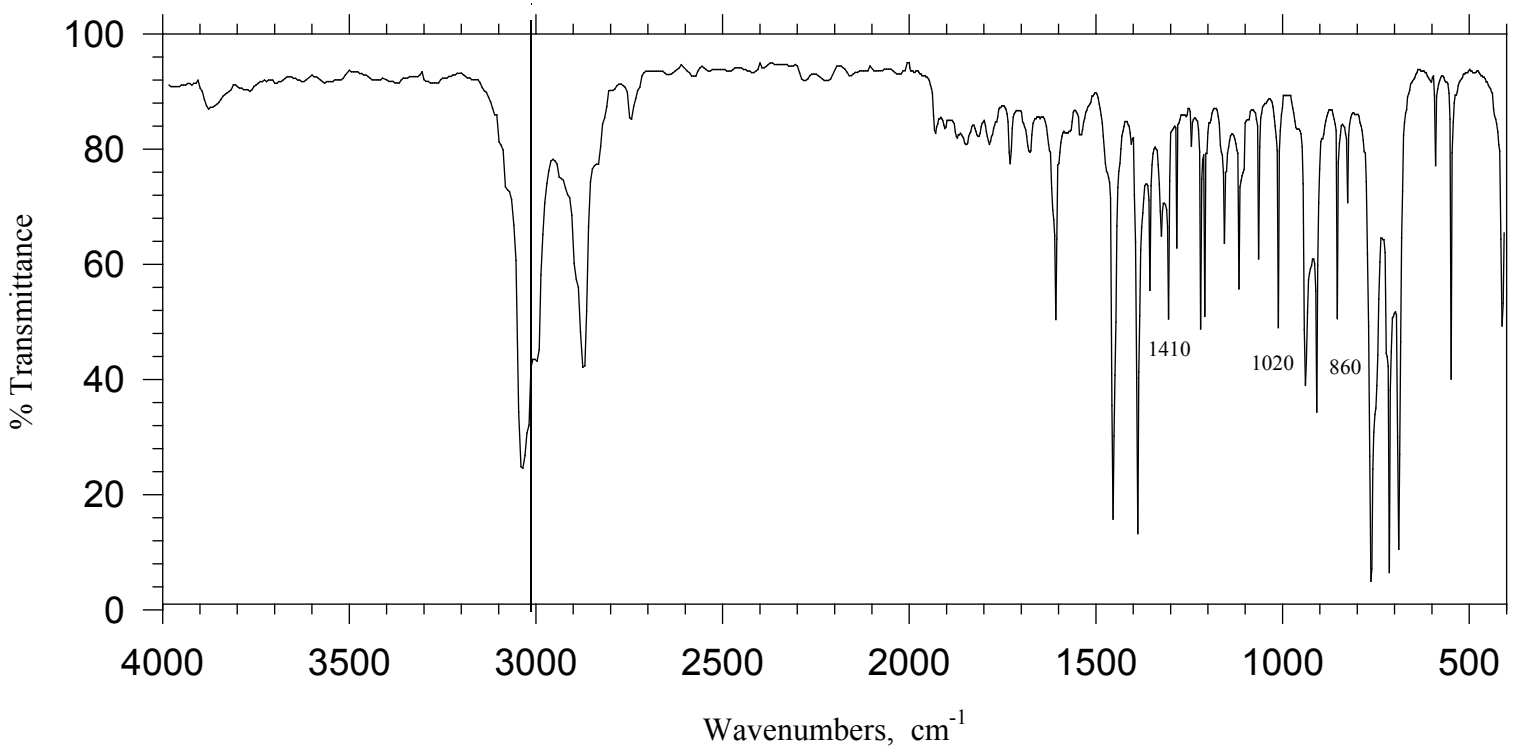
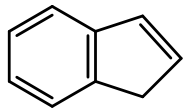


Figure IR-8. Indene; neat; 0.05 mm cell:



A summary of the principle infrared bands and their assignments. R is an aliphatic group.

Funct. Group	Type		Frequencies cm^{-1}	Peak Intensity	Examples Figure No.
C-H					
	sp hybridized	≡C-H	3300	M-S(sh)	13

sp and sp^2 hybridized CH

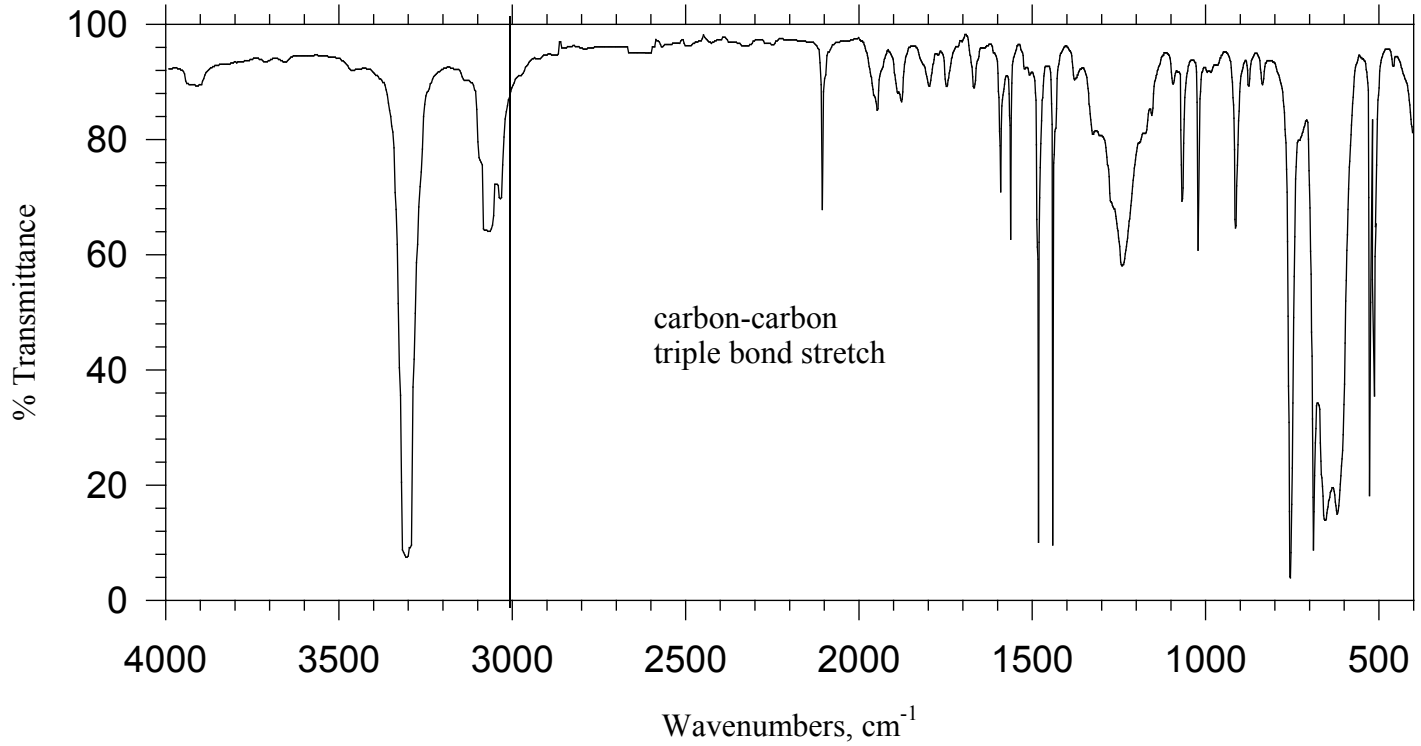
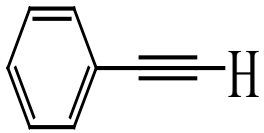


Figure IR-13. Phenylacetylene, neat liquid; thin film (note that R here is an aromatic group):



sp^2 hybridized CH

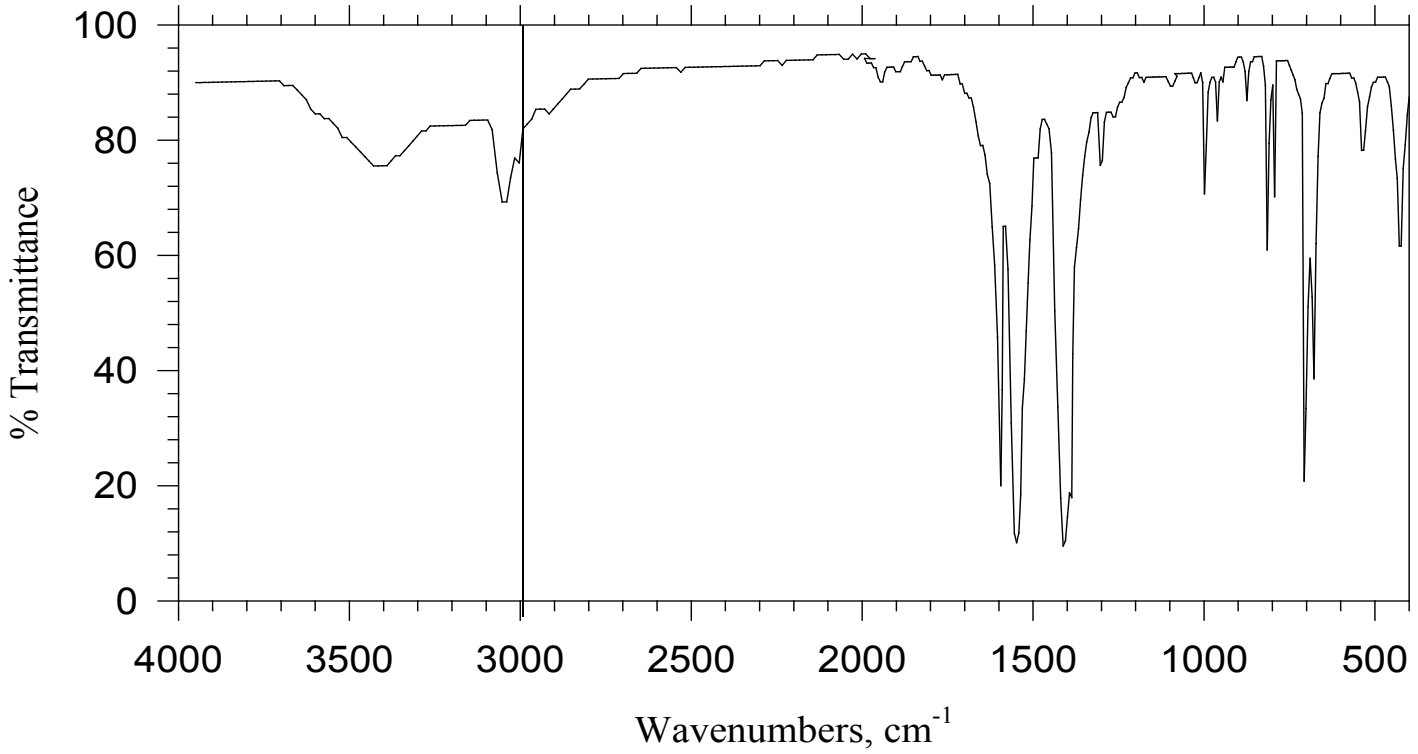
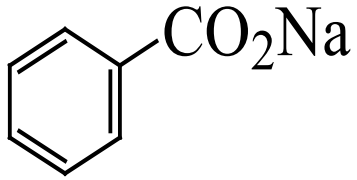


Figure IR-42. Sodium benzoate, KBr pellet:



Can the frequency dependence on hybridization be rationalized?

Table 2. Carbon Hydrogen Bond Strengths as a Function of Hybridization

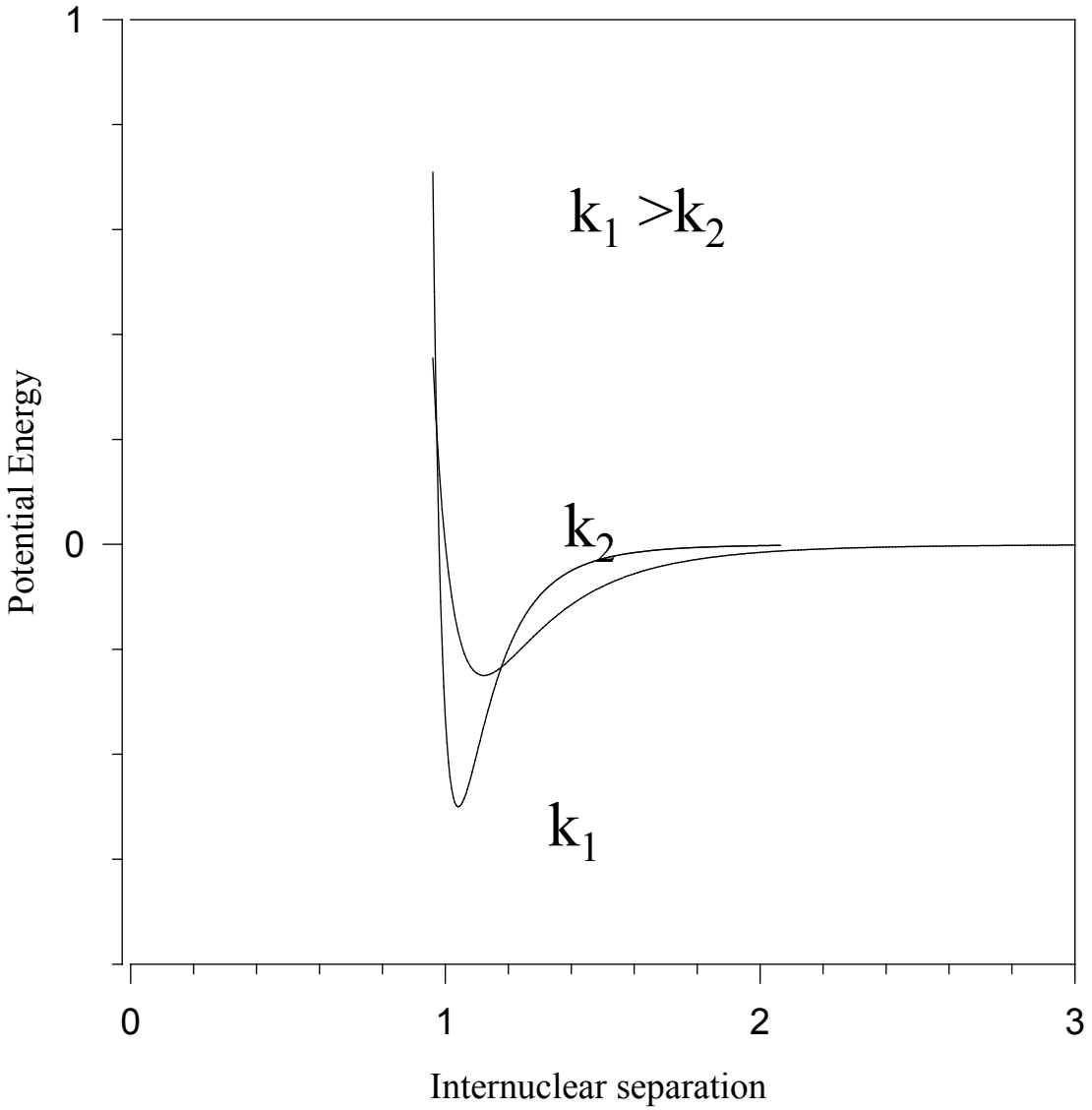
Type of C-H bond		Bond Strength kcal/mol	IR Frequency cm^{-1}
sp^3 hybridized C-H	$CH_3CH_2CH_2$-H	99	<3000
sp^2 hybridized C-H	CH_2=CH-H	108	>3000
sp hybridized C-H	HC≡C-H	128	3300

$$E = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}\left(n+\frac{1}{2}\right)$$

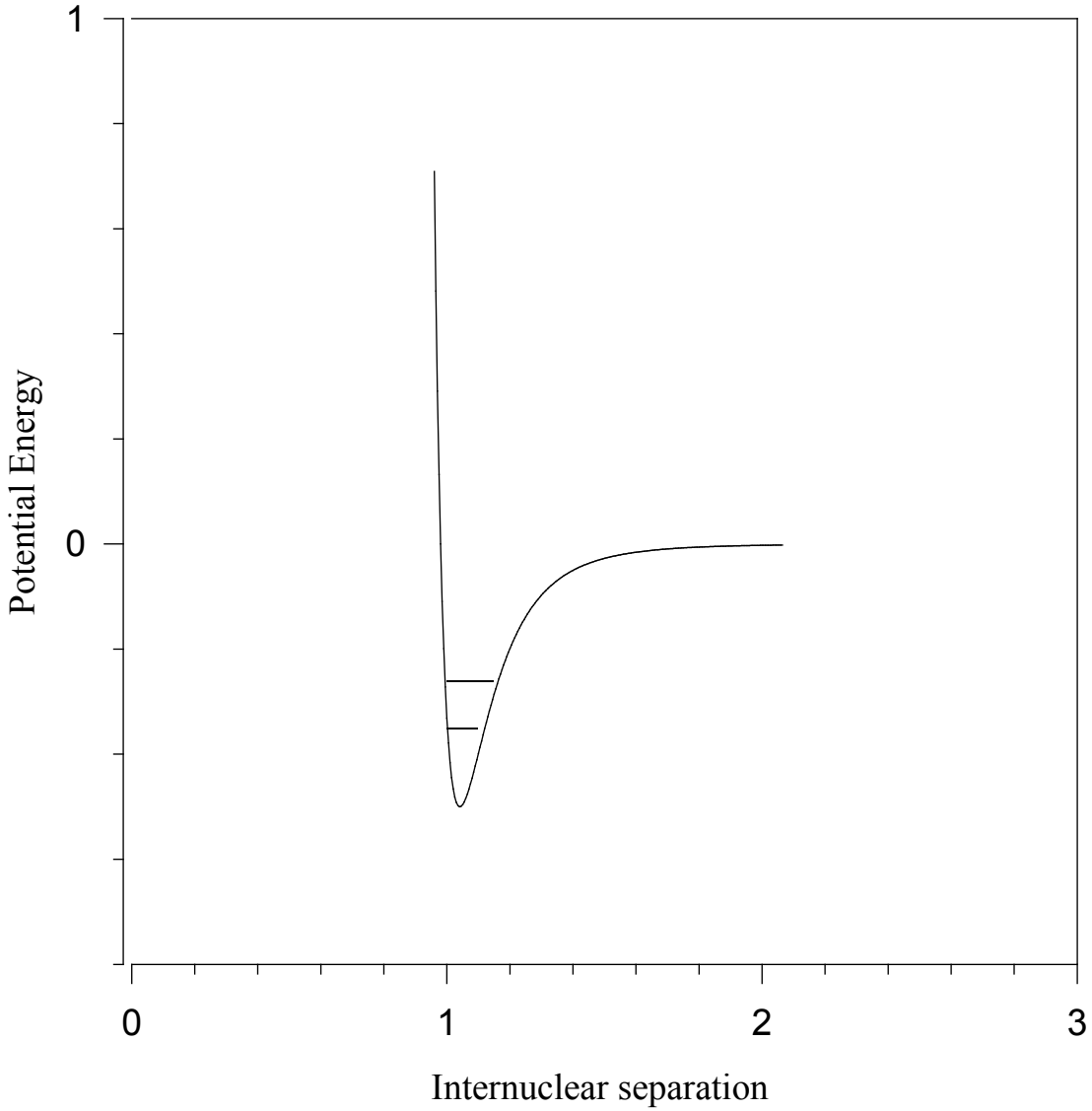
μ is the same for all C-H bonds

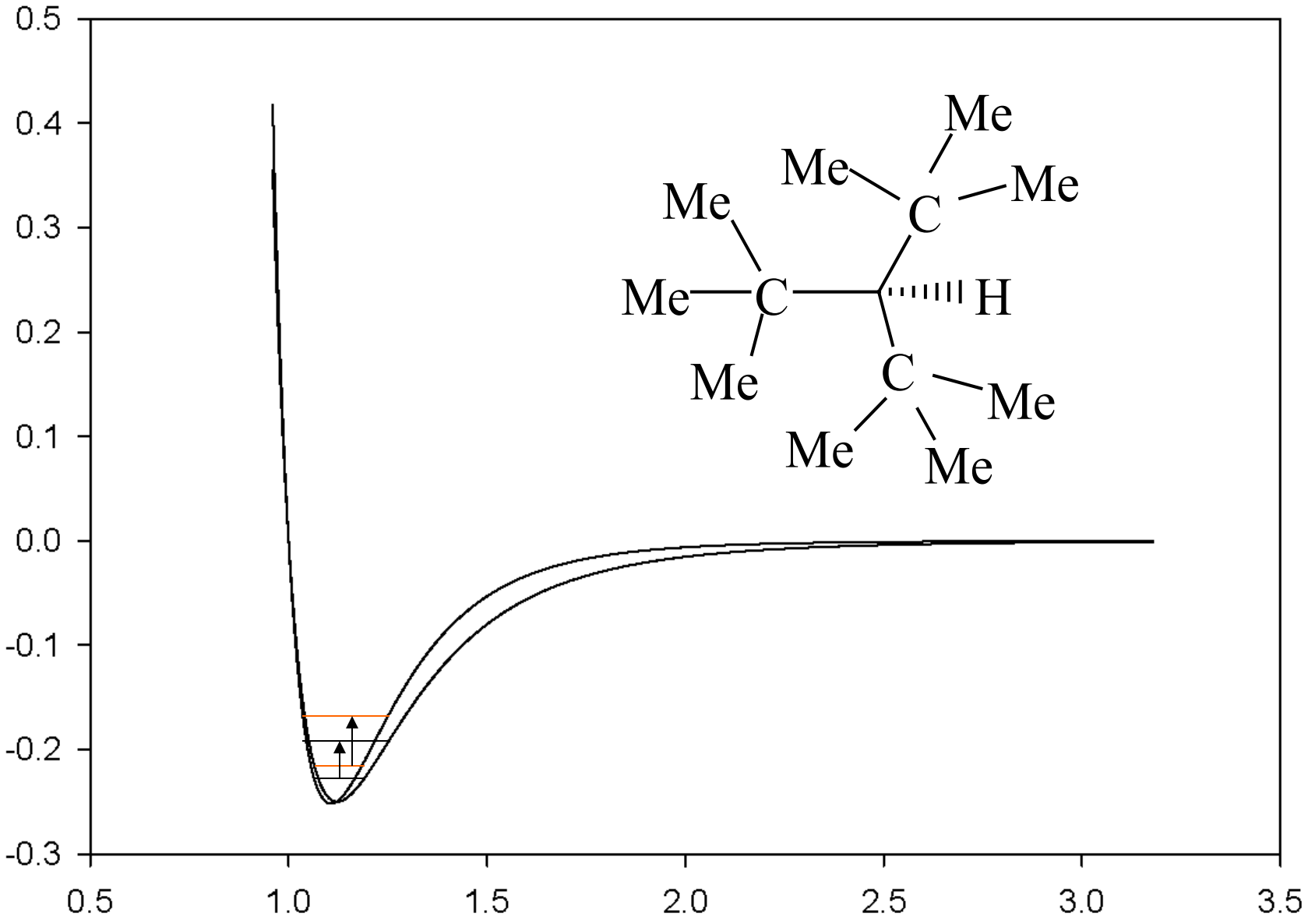
$\mu = m_{CR}m_H/(m_{CR}+m_H) \approx m_H$

The bond strength seems dependent of the amount of s character in the bond

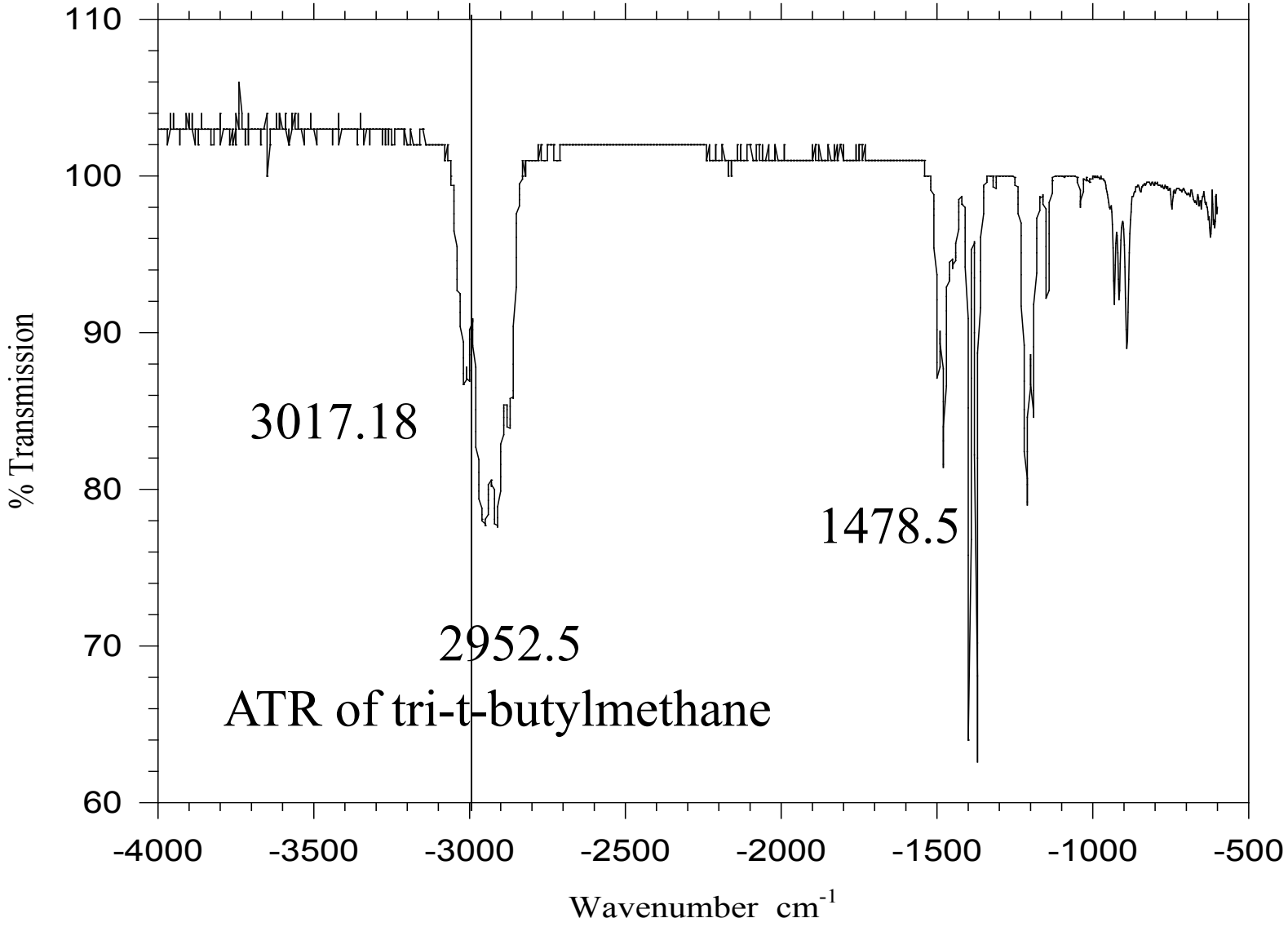

1
0
Potential Energy
$k_1 > k_2$
k_2
k_1
0
1
2
3
Internuclear separation

What would happen to k (force constant) if **stretching** a bond resulted in severe steric interactions?




0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Me
Me
Me
Me
C
Me
Me
C
H
Me
C
Me
Me
Me
Me

Hindered sp^3 C-H



The force constant seems dependent of the amount of s character in the bond;

C-H bond acidity is likewise related to the amount of s character

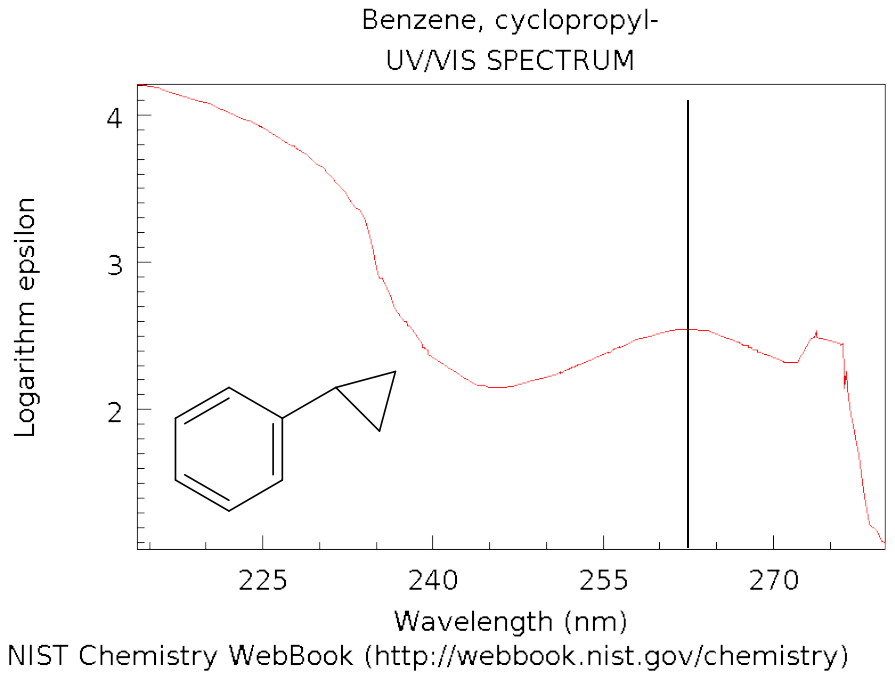
CH_3CH_3	C-H sp^3 hydridization	2850-3000 cm^{-1}
$H_2C{=}CH_2$	C-H sp^2 hydridization	3000-3250 cm^{-1}
H-C≡C-H	C-H sp hybridization	3300 cm^{-1}

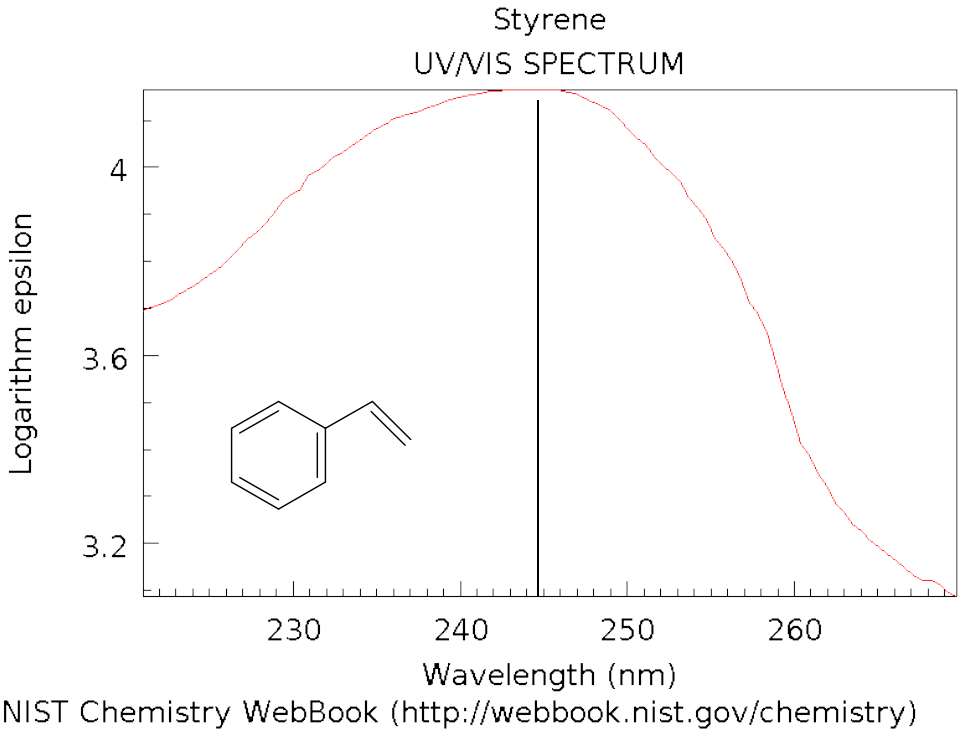
cyclopropanes C-H hybridization in cyclopropane?

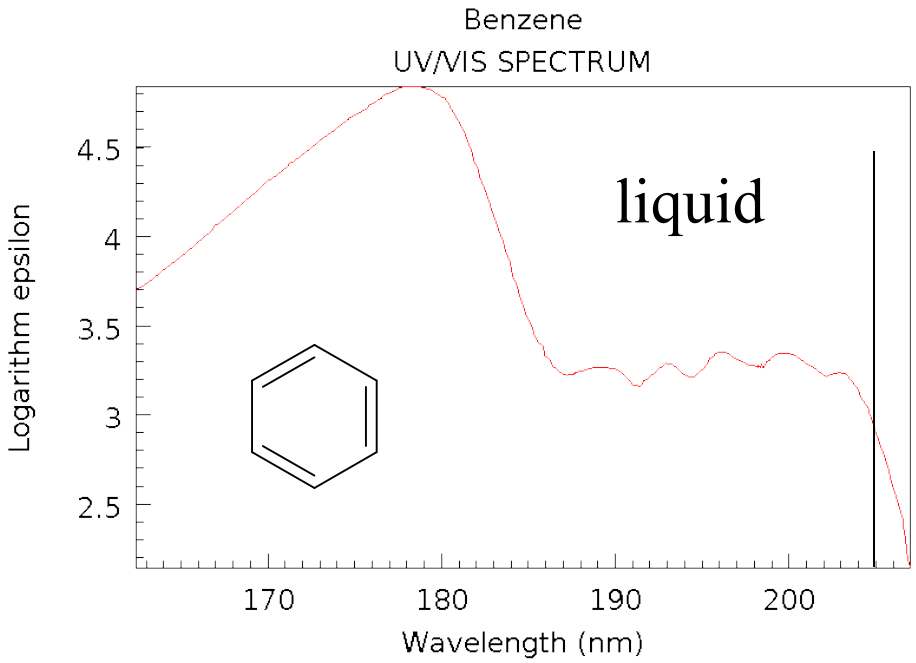
what is the C-C hybridization?

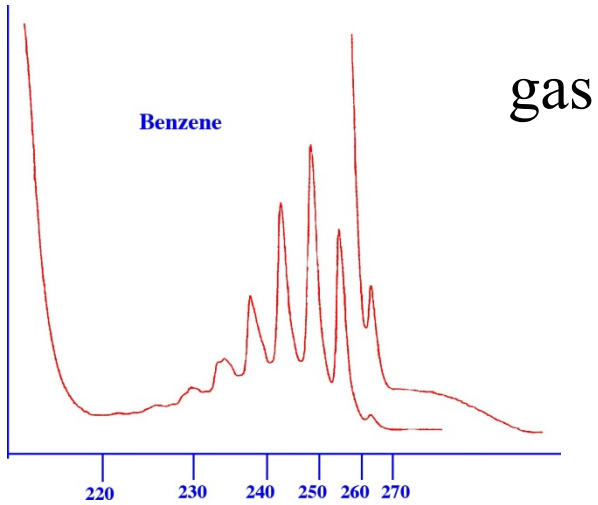
what is the C-H hybridization?

halogenated alkanes


Benzene, cyclopropyl-
UV/VIS SPECTRUM
Logarithm epsilon
4
3
2
225
240
255
270
Wavelength (nm)
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)


Styrene
UV/VIS SPECTRUM
Logarithm epsilon
4
3.6
3.2
230
240
250
260
Wavelength (nm)
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)


Benzene
UV/VIS SPECTRUM
liquid
Logarithm epsilon
4.5
4
3.5
3
2.5
170
180
190
200
Wavelength (nm)
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)


gas
Benzene
220
230
240
250
260
270

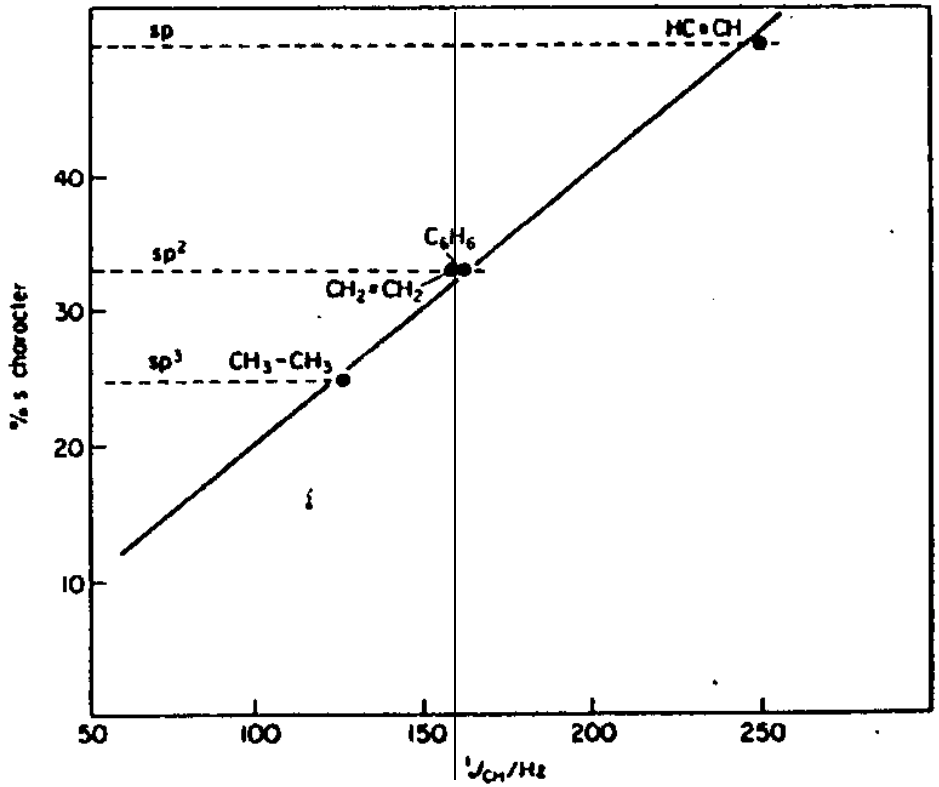


Fig. 2.6 Dependence of $^1J_{CH}$ on s character of carbon. The straight line corresponds to Eqn (2

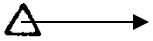
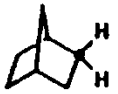
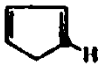
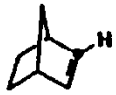
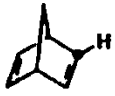
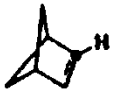
ONE-BOND C—H COUPLINGS

Empirically it has been found that the one-bond coupling constant $^1J_{CH}$ can be approximated by the following simple relationship:[59]

$$^1J_{CH} = 5 \times (\%s)\,[\mathrm{Hz}] \qquad (2.17)$$

‡ Index n in $^nJ_{NK}$ refers to the number of bonds by which nuclei N and K are separated.

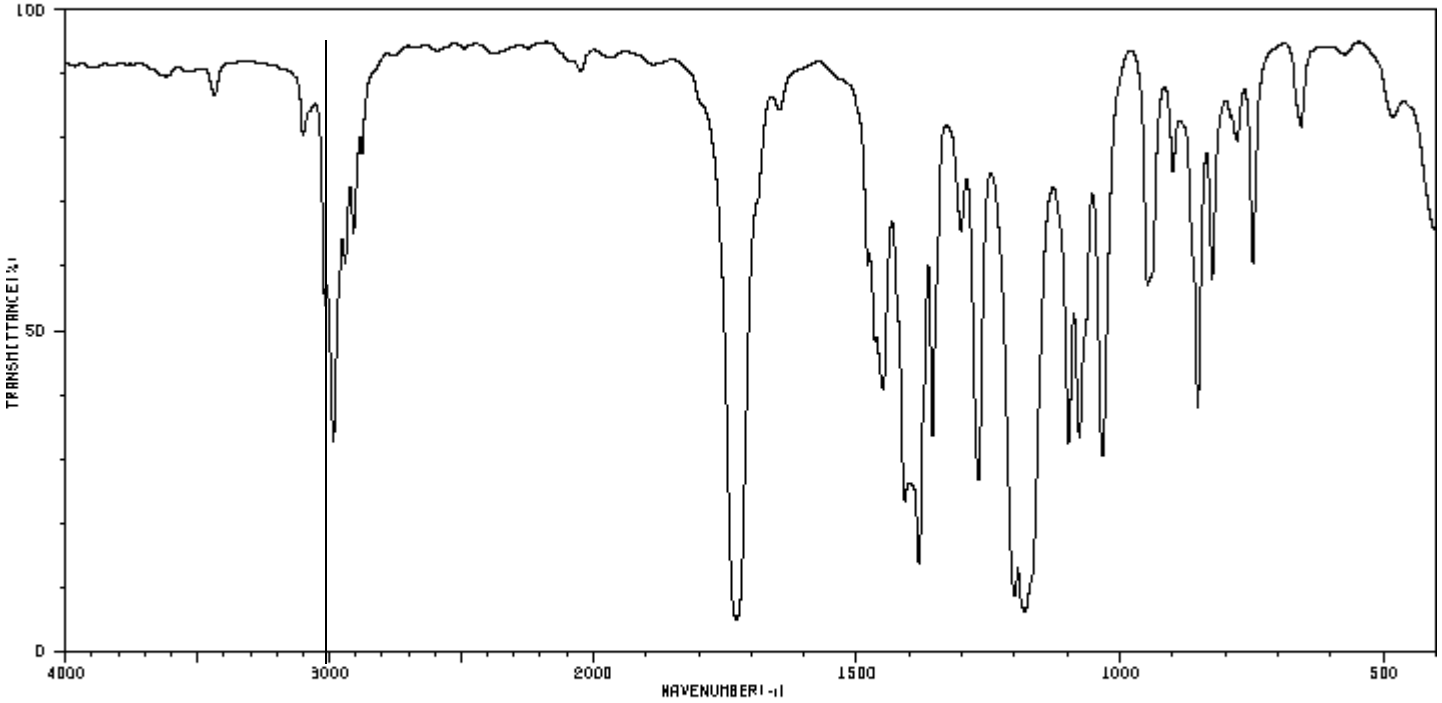
TABLE 2.15 $^1J_{CH}$ in hydrocarbons (values from Ref. unless otherwise noted)

sp^3		sp^2	
H_3C-CH_3	125	$H_2C=CH_2$	156
	123		157
	128		159
	136		160
	161		
	130[61]		170
	130		170
	142[61]		166
	142[61]		173
	179		177
	205		

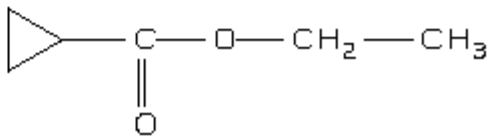
HIT-NO=4954	SCORE= ( )	SDBS-NO=15380	IR-NIDA-24694 : LIQUID FILM

ETHYL CYCLOPROPANECARBOXYLATE

$C_6H_{10}O_2$



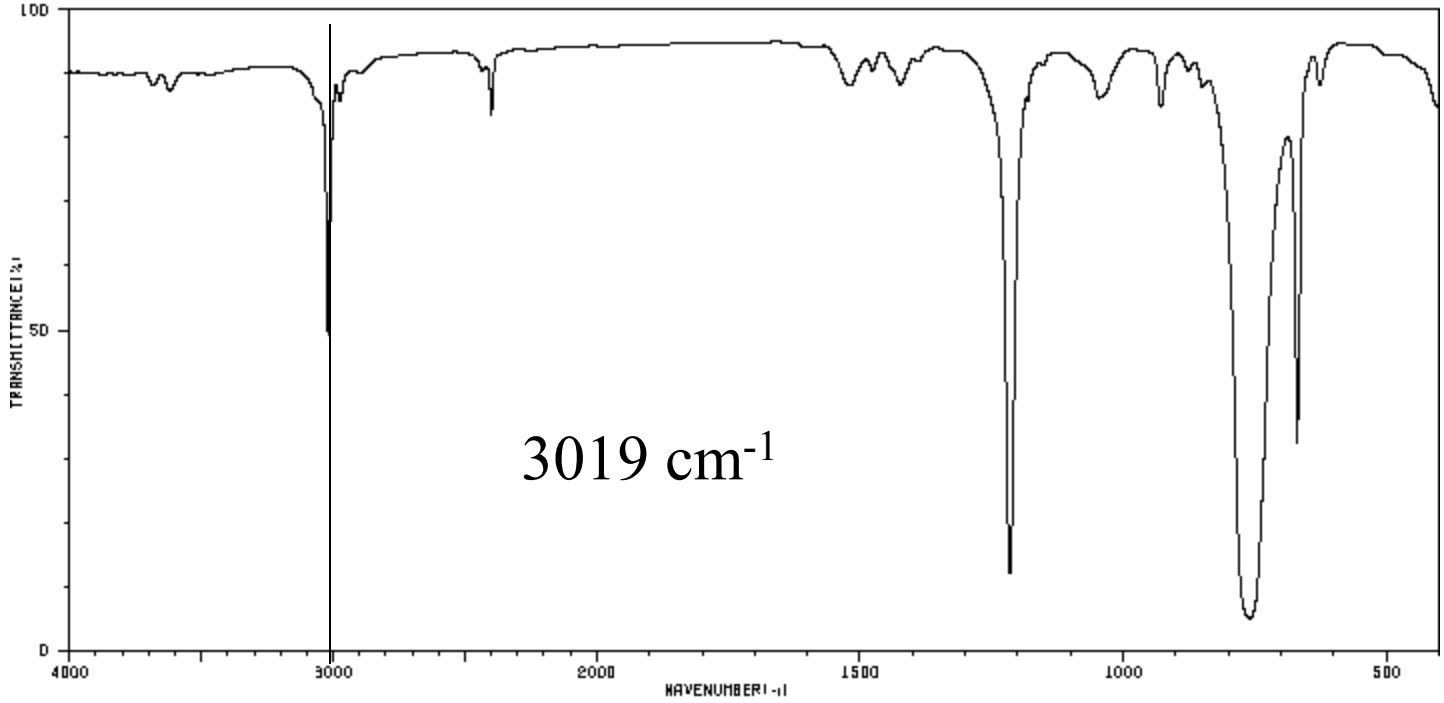
3630	86	2909	62	1409	22	1182	6	863	36
3618	86	2876	74	1401	25	1097	31	825	55
3455	84	1728	4	1382	13	1077	32	778	77
3100	77	1646	81	1366	32	1033	29	749	68
3017	52	1479	58	1302	82	948	55	657	79
2984	31	1465	46	1269	25	900	72	482	79
2941	68	1460	39	1200	8	861	68		



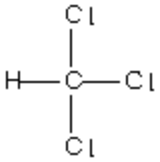
HIT-NO=1233	SCORE= ( )	SDBS-NO=894	IR-NIDA-01674 : LIQUID FILM

CHLOROFORM

$CHCl_3$



3683	84	1216	11
3618	84	1047	84
3019	47	1041	84
2975	81	929	81
2400	79	760	4
1520	84	671	31
1423	84	627	84



A summary of the principle infrared bands and their assignments. R is an aliphatic group.

Funct. Group	Type		Frequencies cm^{-1}	Peak Intensity	Examples Figure No.
C-H	sp^3 hybridized	R_3C-H	2850-3000	M(sh)	6, 18, 22
	sp^2 hybridized	=CR-H	3000-3250	M(sh)	7, 13, 42
	sp hybridized	≡C-H	3300	M-S(sh)	13
	aldehyde C-H	H-(C=O)R	2750, 2850	M(sh)	14, 15

aldehyde C-H

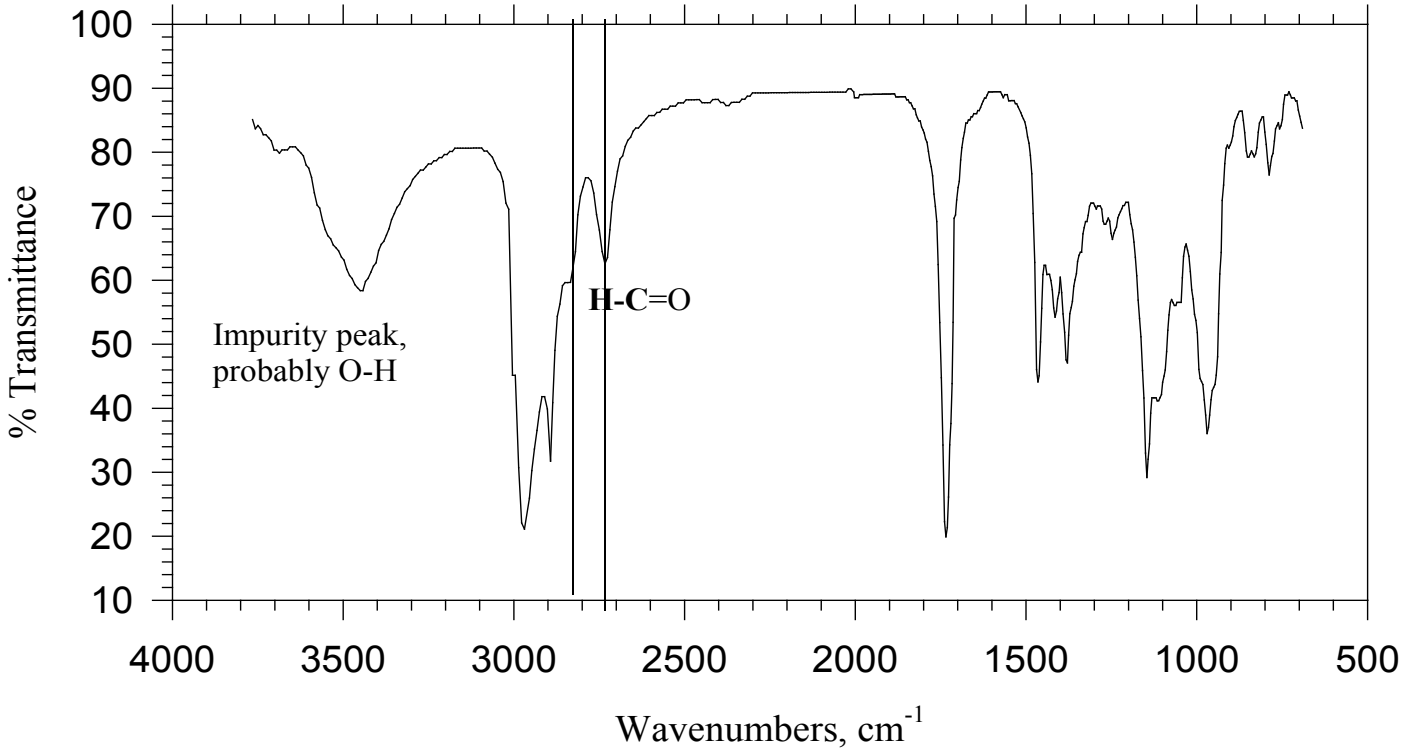
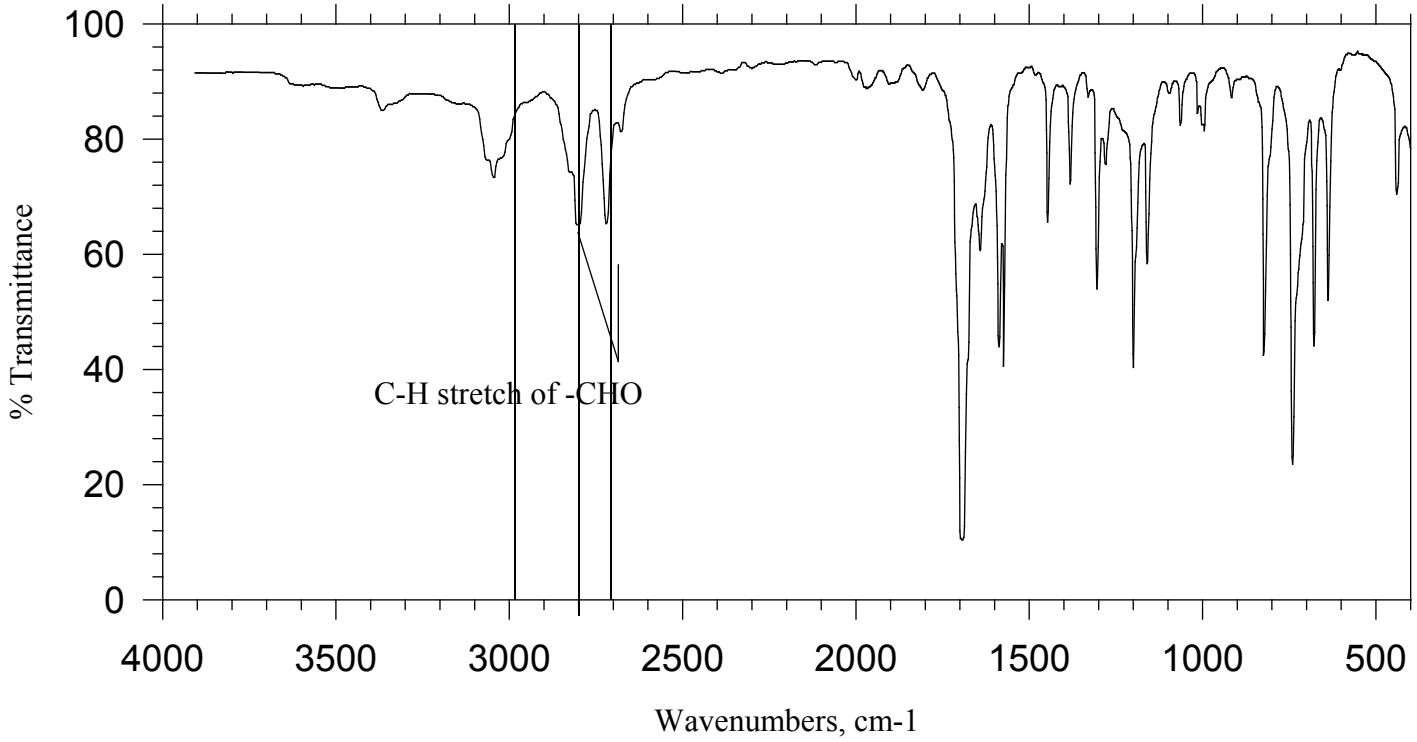


Figure IR-14. Butanal, neat liquid, thin film: $CH_3CH_2CH_2CHO$

aldehyde C-H



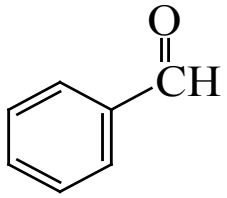


Figure IR-15. Benzaldehyde, neat, thin film

(R here is an aromatic group):

Focusing on $-NH_2$

remember the
CH_2

A summary of the principle infrared bands and their assignments. R is an aliphatic group.

Funct. Group	Type		Frequencies cm^{-1}	Peak Intensity	Examples Figure No.
C-H	sp^3 hybridized	R_3C-H	2850-3000	M(sh)	6, 18, 22
	sp^2 hybridized	=CR-H	3000-3250	M(sh)	7, 13, 42
	sp hybridized	≡C-H	3300	M-S(sh)	13
	aldehyde C-H	H-(C=O)R	2750, 2850	M(sh)	14, 15
N-H	primary amine, amide	$RN-H_2$, $RCONH_2$	3300, 3340	S,S(br)	18, 19

NH_2- Stretching Frequencies

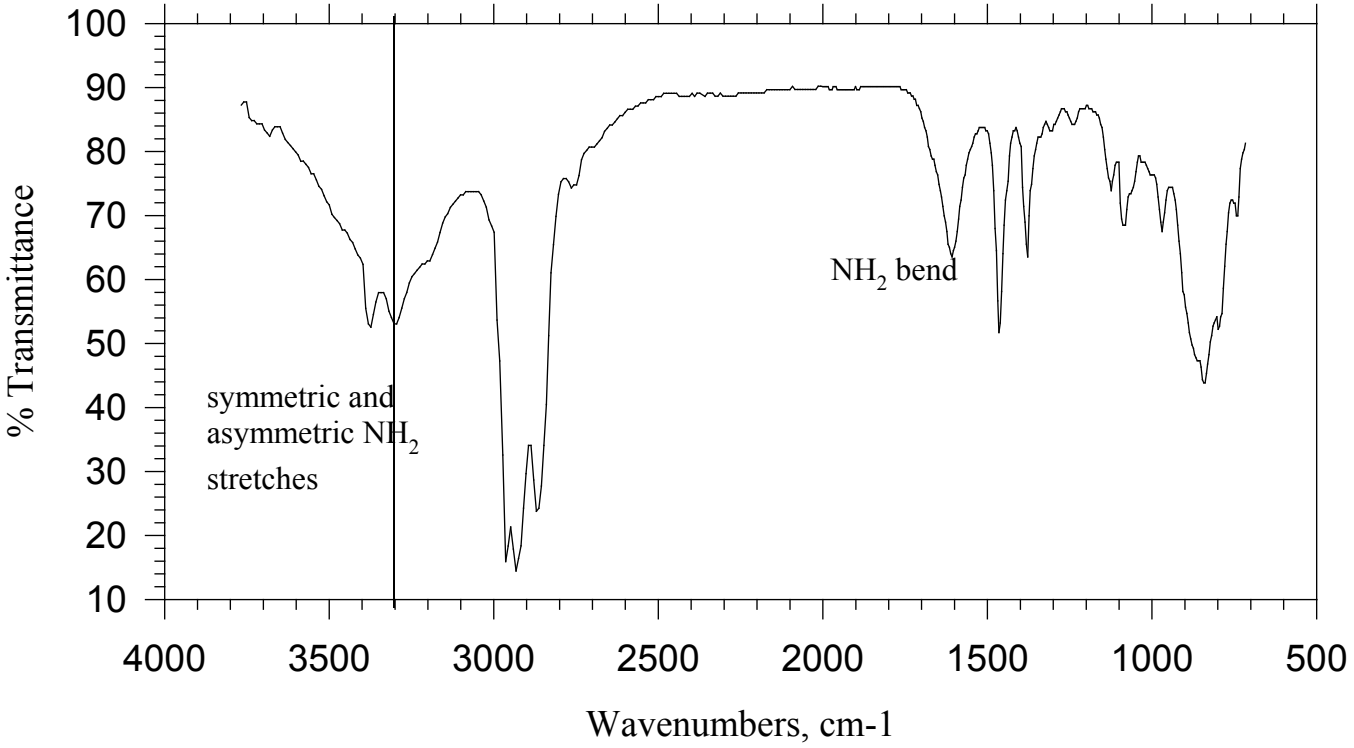
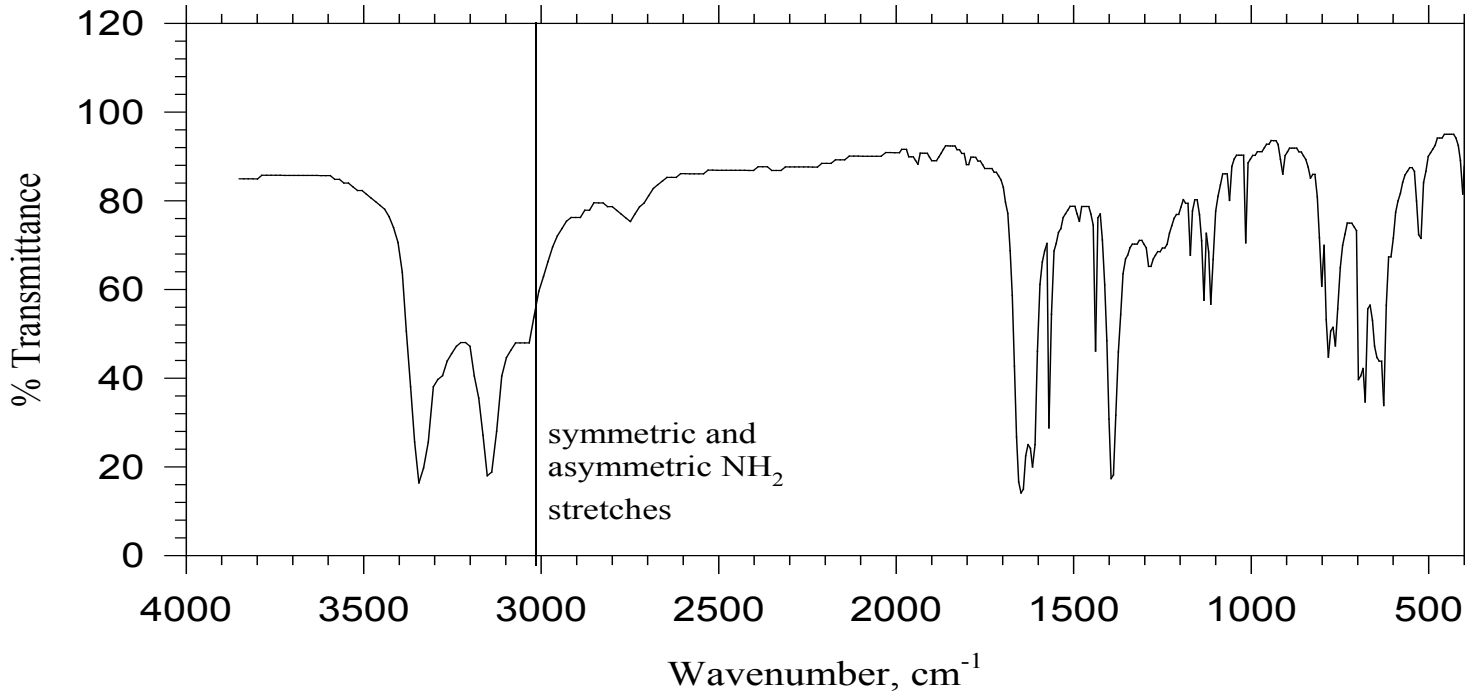


Figure IR-18. Butylamine, neat liquid; thin film: $CH_3CH_2CH_2CH_2NH_2$

NH_2- Stretching Frequencies



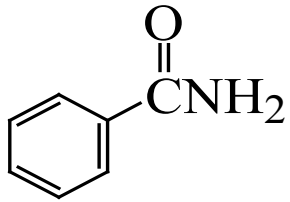


Figure IR-19. Benzamide, KBr pellet

(R here is an aromatic group):

Focusing on –NHR

A summary of the principle infrared bands and their assignments. R is an aliphatic group.

Funct. Group	Type		Frequencies cm^{-1}	Peak Intensity	Examples Figure No.
C-H	sp^3 hybridized	R_3C-H	2850-3000	M(sh)	6, 18, 22
	sp^2 hybridized	=CR-H	3000-3250	M(sh)	7, 13, 42
	sp hybridized	≡C-H	3300	M-S(sh)	13
	aldehyde C-H	H-(C=O)R	2750, 2850	M(sh)	14, 15
N-H	primary amine, amide	$RN-H_2$, $RCONH_2$	3300, 3340	S,S(br)	18, 19
	secondary amine, amide	RNR-H, RCONHR	3300-3500	S(br)	20, 21

NH- Stretching Frequencies

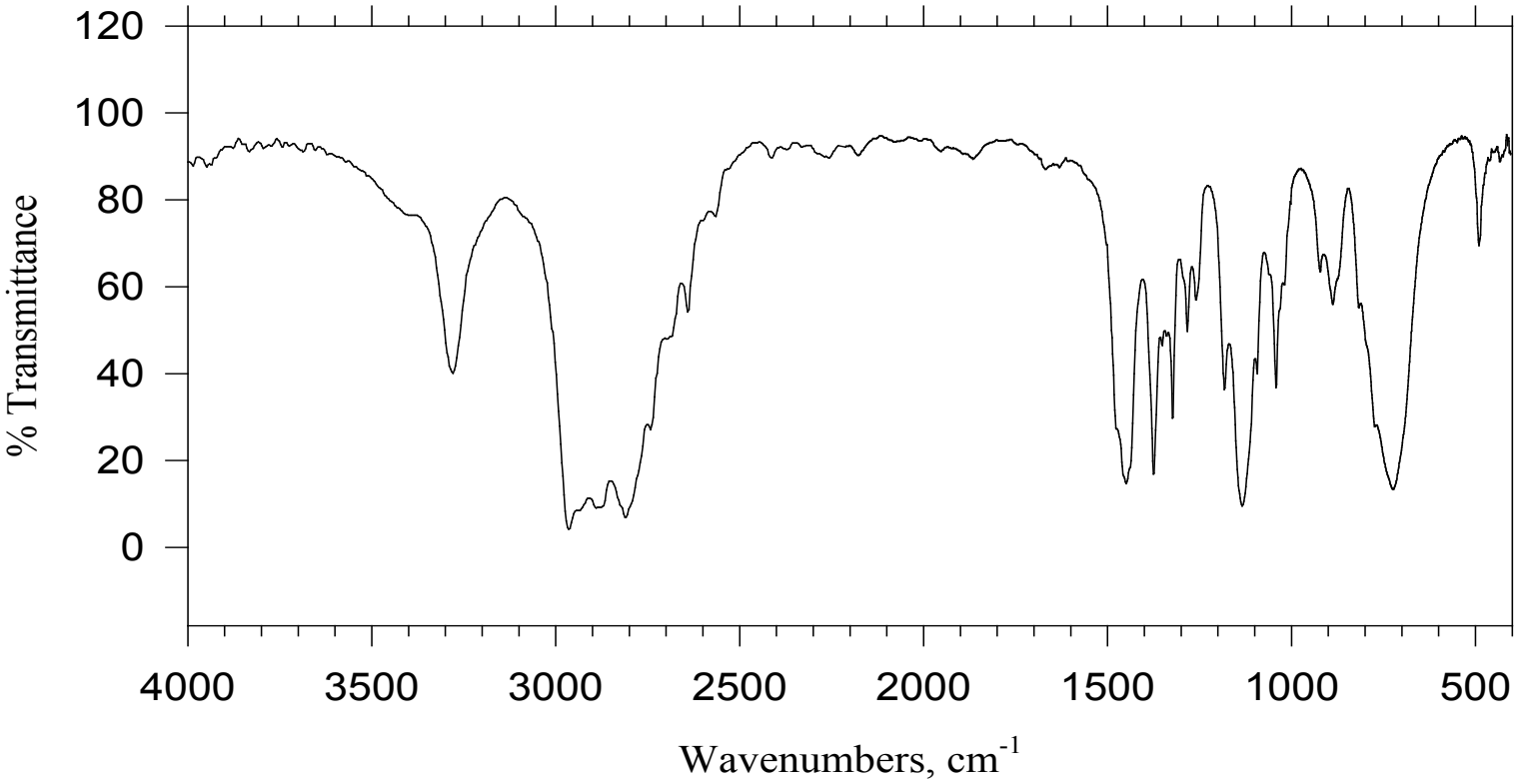


Figure IR-20. Diethylamine, neat liquid; thin film: $CH_3CH_2NHCH_2CH_3$

NH- Stretching Frequencies

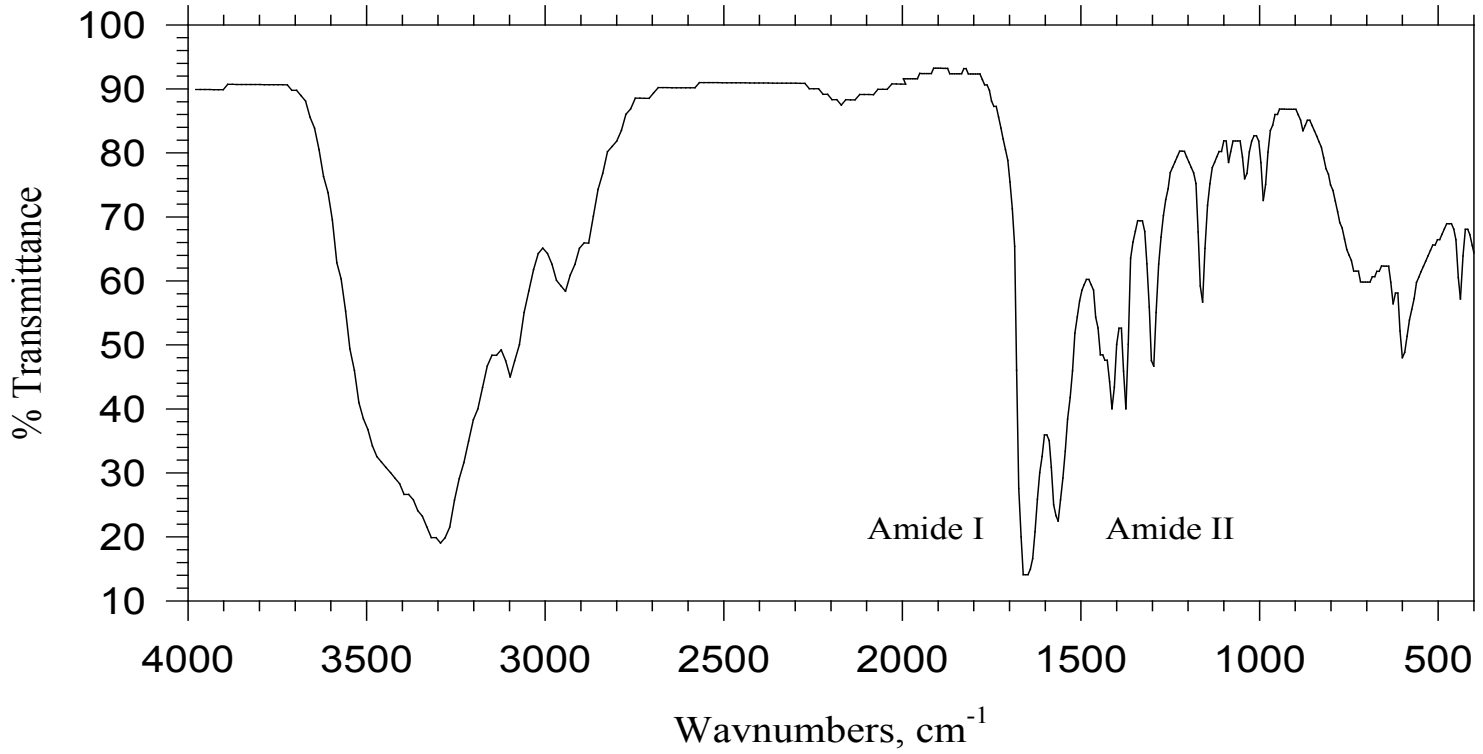


Figure IR-21. N-Methyl acetamide, neat liquid; thin film: $CH_3CONHCH_3$

Focusing on $-NR_2$

A summary of the principle infrared bands and their assignments. R is an aliphatic group.

Funct. Group	Type		Frequencies cm^{-1}	Peak Intensity	Examples Figure No.
C-H	sp^3 hybridized	R_3C-H	2850-3000	M(sh)	6, 18, 22
	sp^2 hybridized	=CR-H	3000-3250	M(sh)	7, 13, 42
	sp hybridized	≡C-H	3300	M-S(sh)	13
	aldehyde C-H	H-(C=O)R	2750, 2850	M(sh)	14, 15
N-H	primary amine, amide	$RN-H_2$, $RCONH_2$	3300, 3340	S,S(br)	18, 19
	secondary amine, amide	RNR-H, RCONHR	3300-3500	S(br)	20, 21
	tertiary amine, amide	$RN(R_3)$, $RCONR_2$	none		22, 23

Tertiary Amines

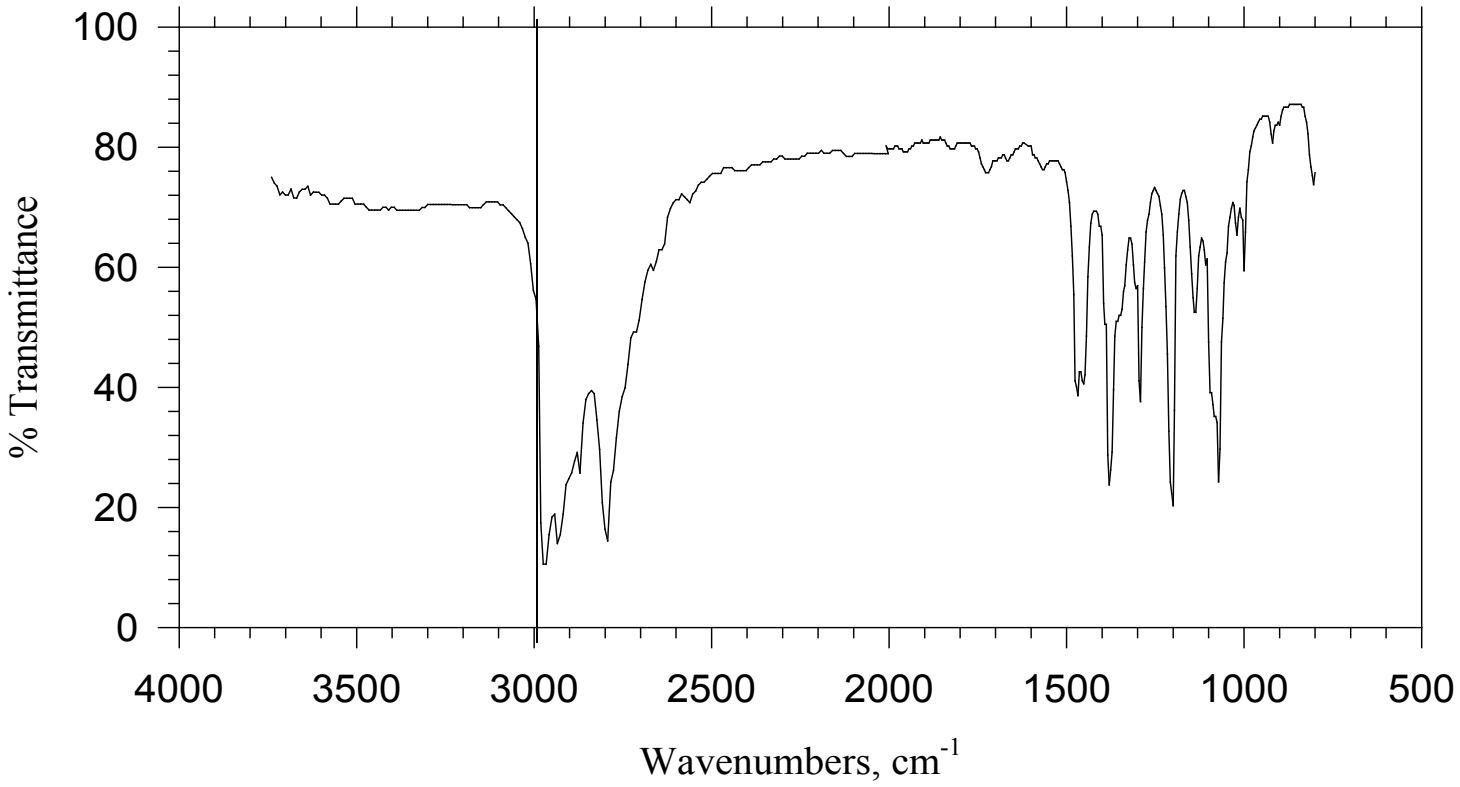


Figure IR-22. Triethylamine, neat liquid; thin film: $(CH_3CH_2)_3N$

Tertiary Amides

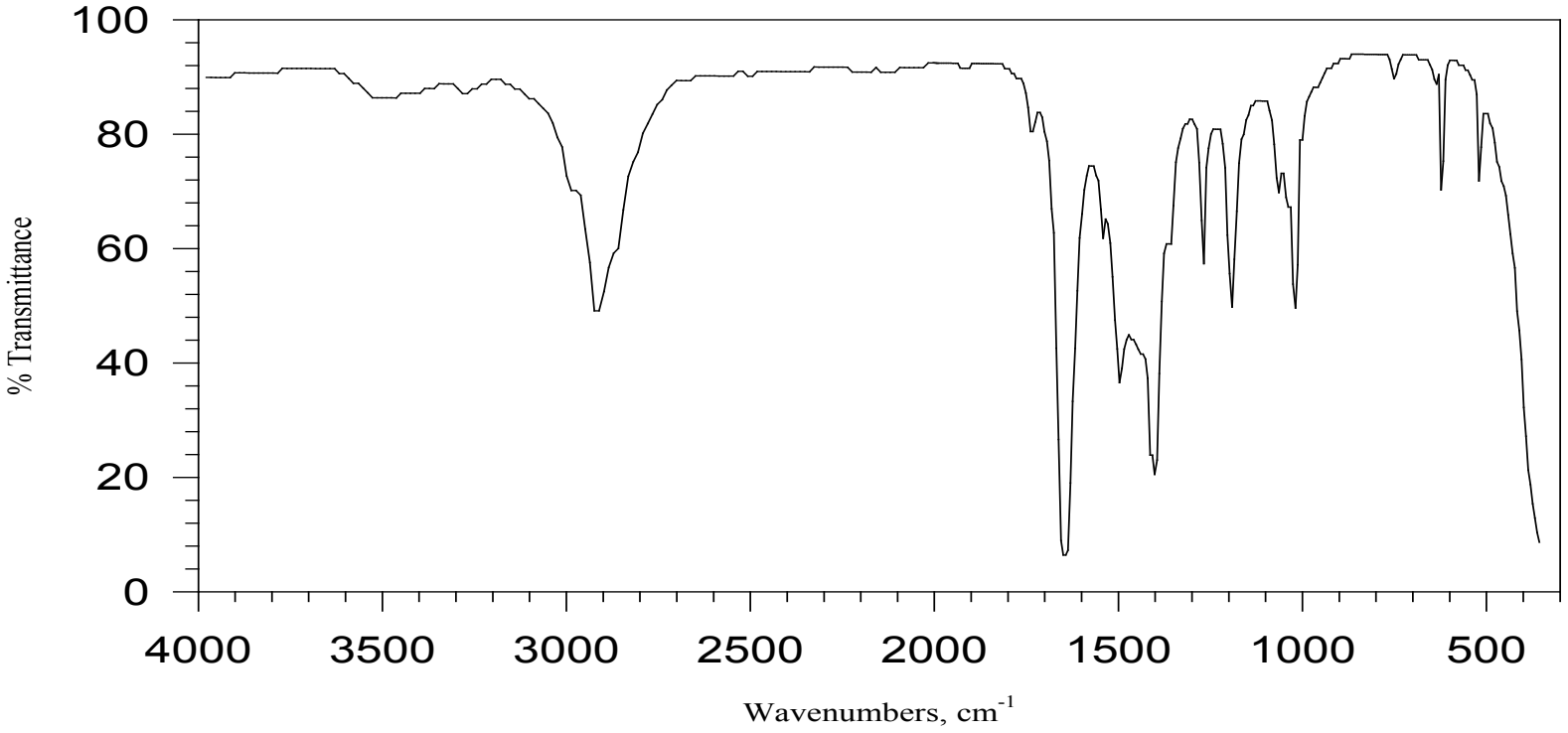


Figure IR-23. N,N-Dimethylacetamide, neat liquid; thin film: $CH_3CON(CH_3)_2$

A summary of the principle infrared bands and their assignments. R is an aliphatic group.

Funct. Group	Type		Frequencies cm^{-1}	Peak Intensity	Examples Figure No.
C-H	sp^3 hybridized	R_3C-H	2850-3000	M(sh)	6, 18, 22
	sp^2 hybridized	=CR-H	3000-3250	M(sh)	7, 13, 42
	sp hybridized	≡C-H	3300	M-S(sh)	13
	aldehyde C-H	H-(C=O)R	2750, 2850	M(sh)	14, 15
N-H	primary amine, amide	RN-H_2, RCONH_2	3300, 3340	S,S(br)	18, 19
	secondary amine, amide	RNR-H, RCONHR	3300-3500	S(br)	20, 21
	tertiary amine, amide	RN(R_3), RCONR_2	none		22, 23
O-H	alcohols, phenols	free O-H	3620-3580	W(sh)	17, 24, 25
		hydrogen bonded	3600-3650	S(br)	24, 25, 28
	carboxylic acids	R(C=O)O-H	3500-2400	S(br)	26, 27, 29, 30

Free and Hydrogen Bonded H-O-R

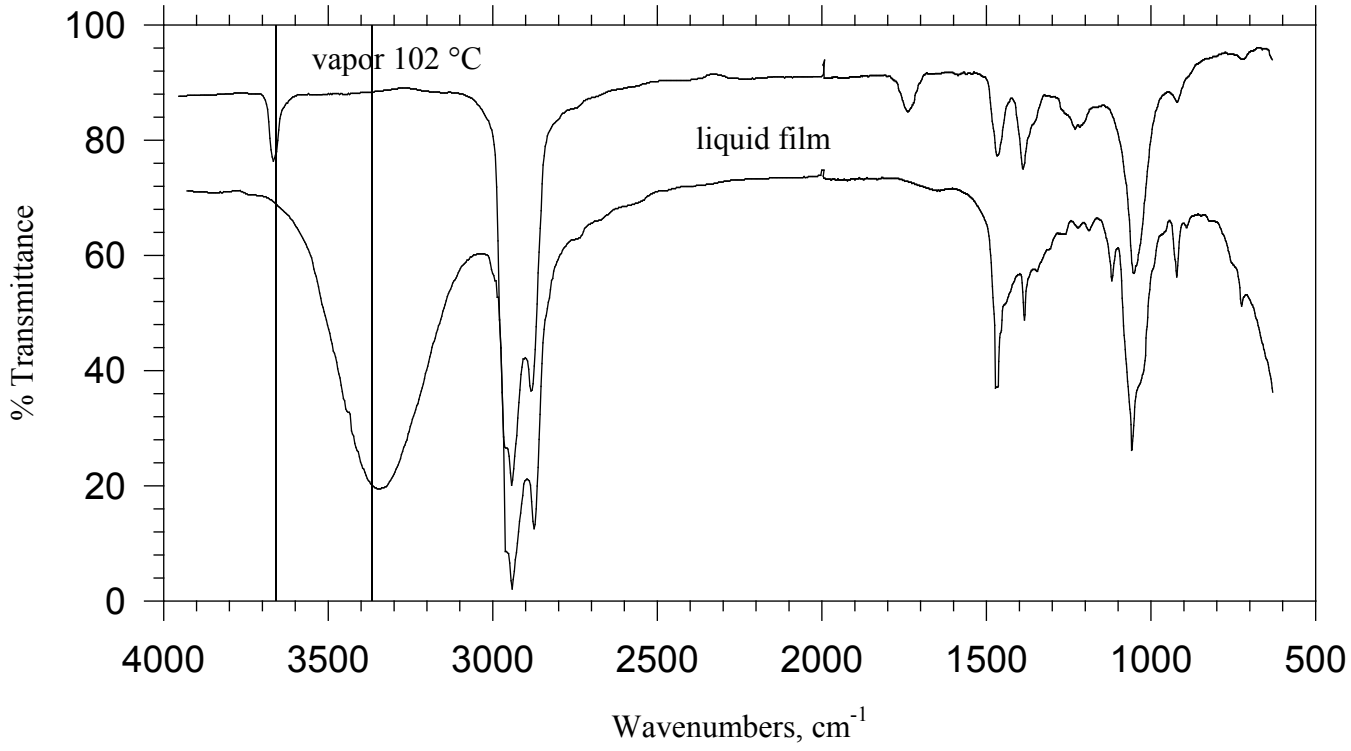


Figure IR-24. The liquid and vapor spectra of n-hexanol.

Free and Hydrogen Bonded H-O-R

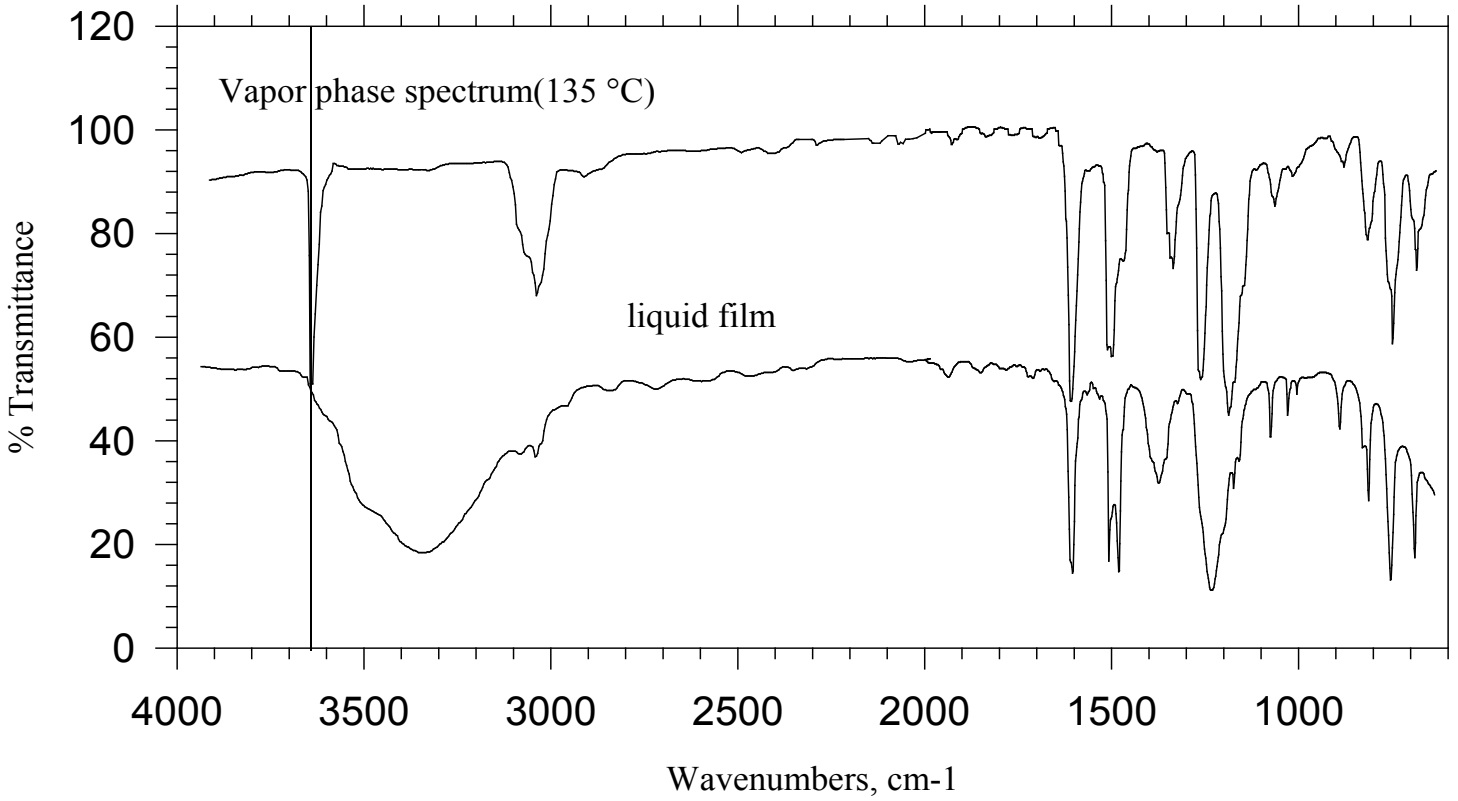
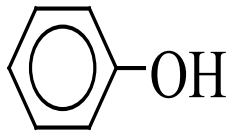


Figure IR-25. The liquid and vapor spectra of phenol.



Free and Hydrogen Bonded H-O-R

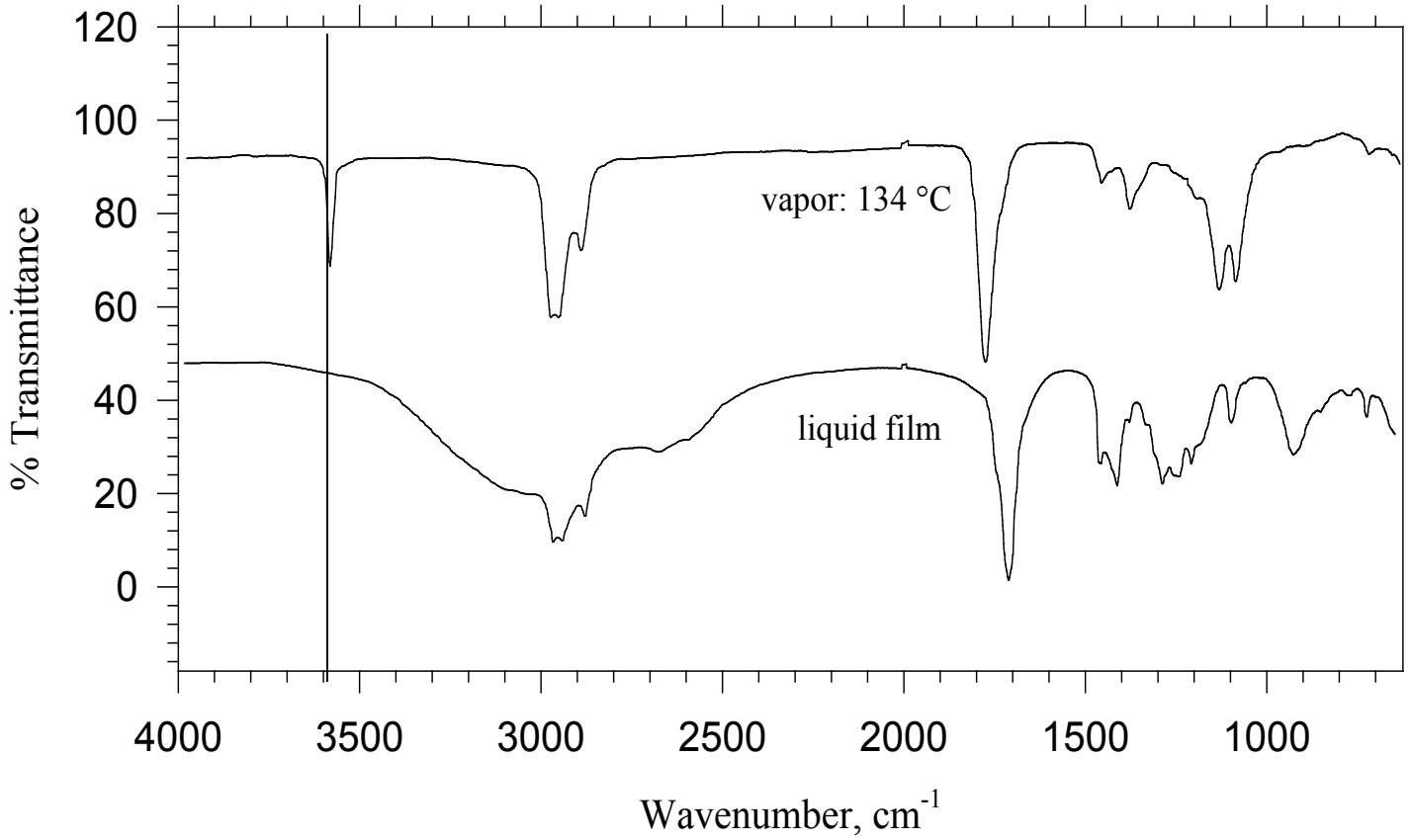


Figure IR-26. The liquid and vapor spectra of hexanoic acid: $CH_3(CH_2)_4\ CO_2H$

A summary of the principle infrared bands and their assignments. R is an aliphatic group.

Funct. Group	Type		Frequencies cm^{-1}	Peak Intensity	Examples Figure No.
C-H	sp^3 hybridized	R_3C-H	2850-3000	M(sh)	6, 18, 22
	sp^2 hybridized	=CR-H	3000-3250	M(sh)	7, 13, 42
	sp hybridized	≡C-H	3300	M-S(sh)	13
	aldehyde C-H	H-(C=O)R	2750, 2850	M(sh)	14, 15
N-H	primary amine, amide	RN-H_2, RCONH_2	3300, 3340	S,S(br)	18, 19
	secondary amine, amide	RNR-H, RCONHR	3300-3500	S(br)	20, 21
	tertiary amine, amide	RN(R_3), RCONR_2	none		22, 23
O-H	alcohols, phenols	free O-H	3620-3580	W(sh)	17, 24, 25
		hydrogen bonded	3600-3650	S(br)	24, 25, 28
	carboxylic acids	R(C=O)O-H	3500-2400	S(br)	26, 27, 29, 30

Hydrogen Bonded H-O-R

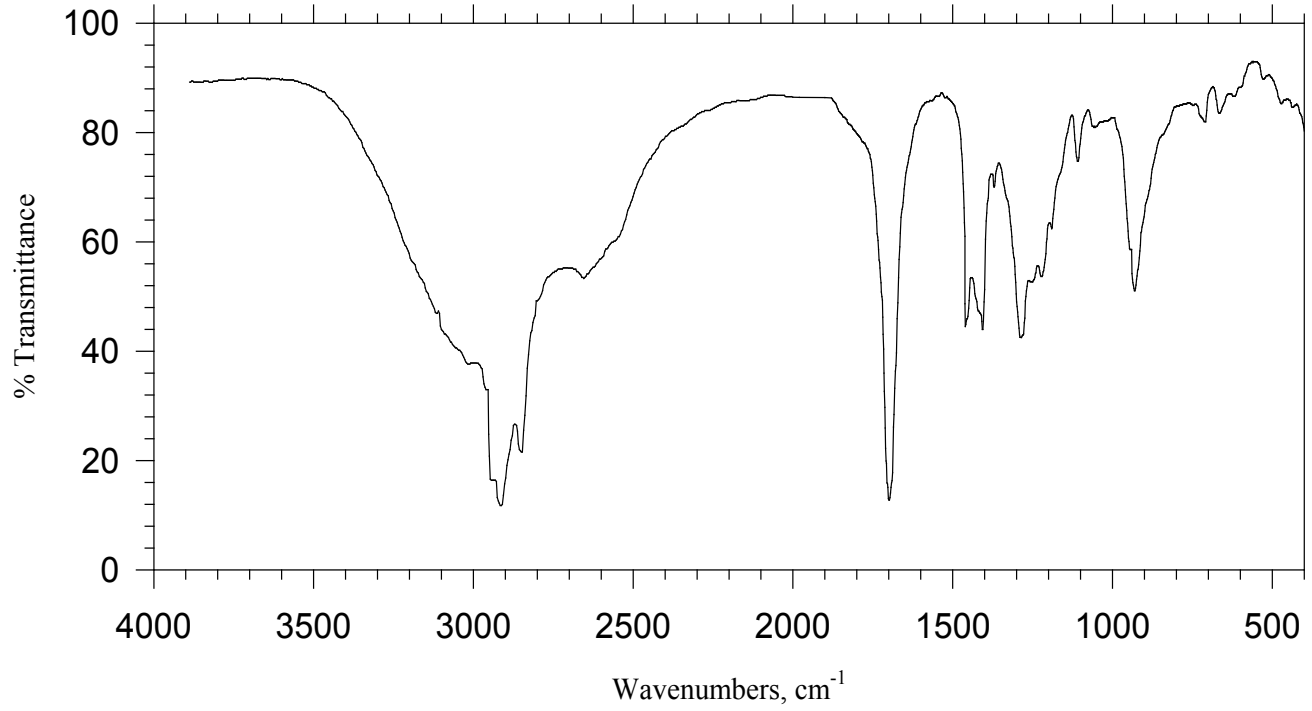


Figure IR-27. Decanoic acid, neat liquid, thin film: $CH_3(CH_2)_8CO_2H$

Hydrogen Bonded H-O-R

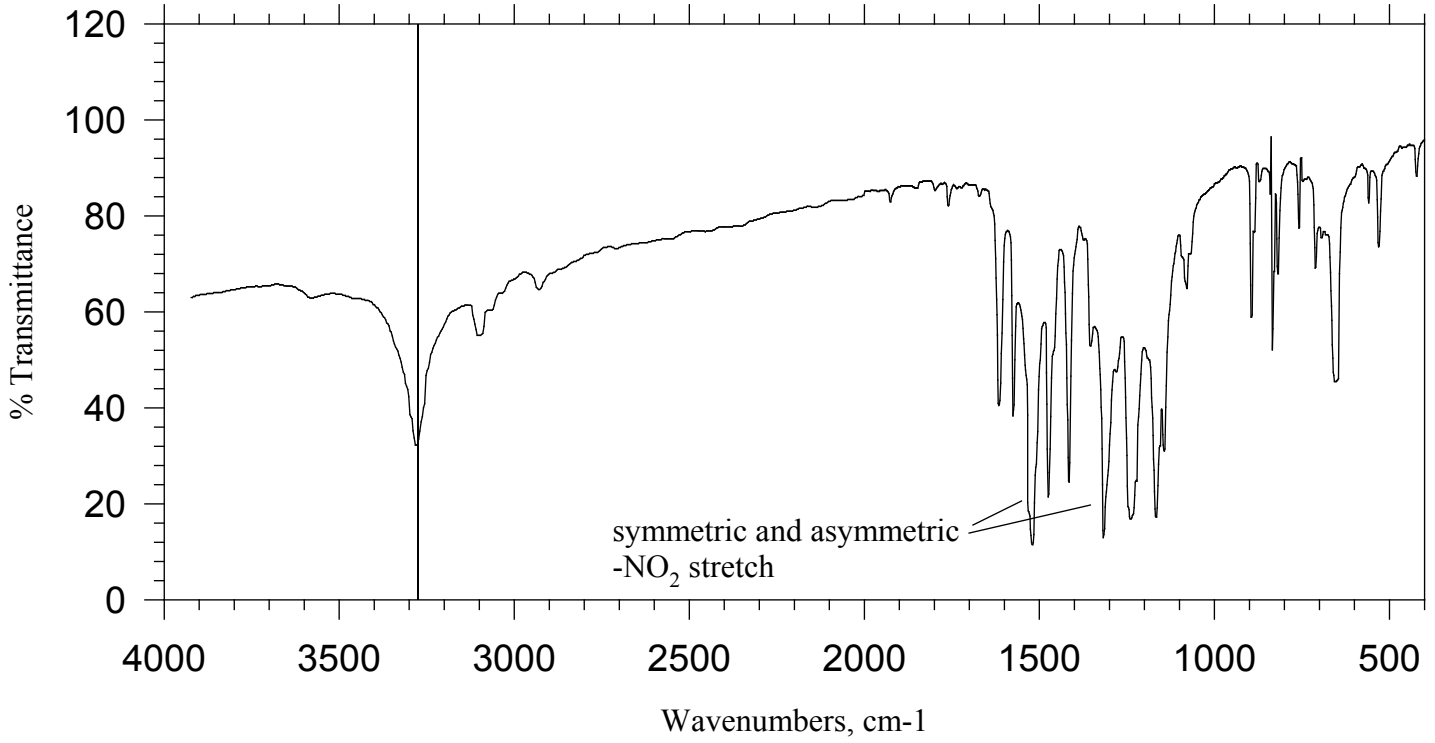
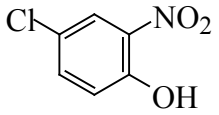


Figure IR-28. 4-Chloro-2-nitrophenol, KBr pellet:



Hydrogen Bonded H-O-R

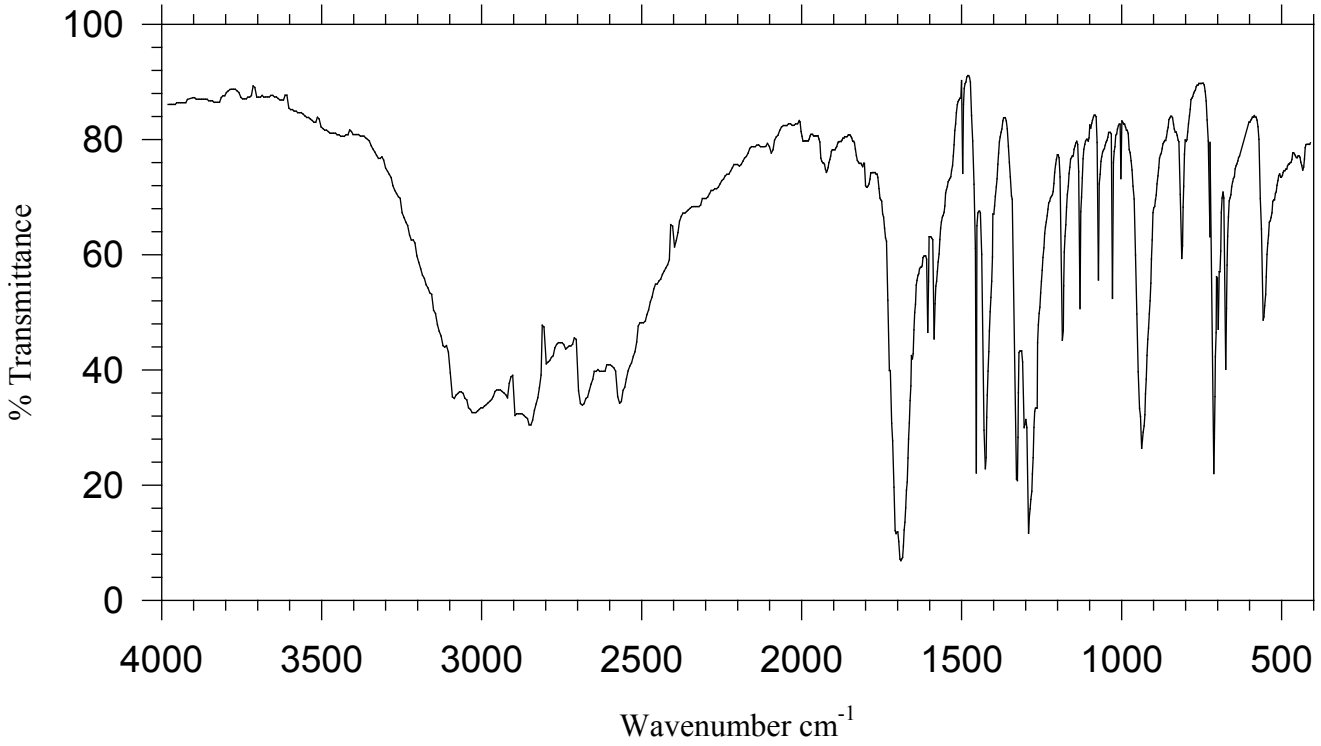
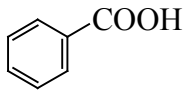


Figure IR-29. Benzoic acid; KBr disk



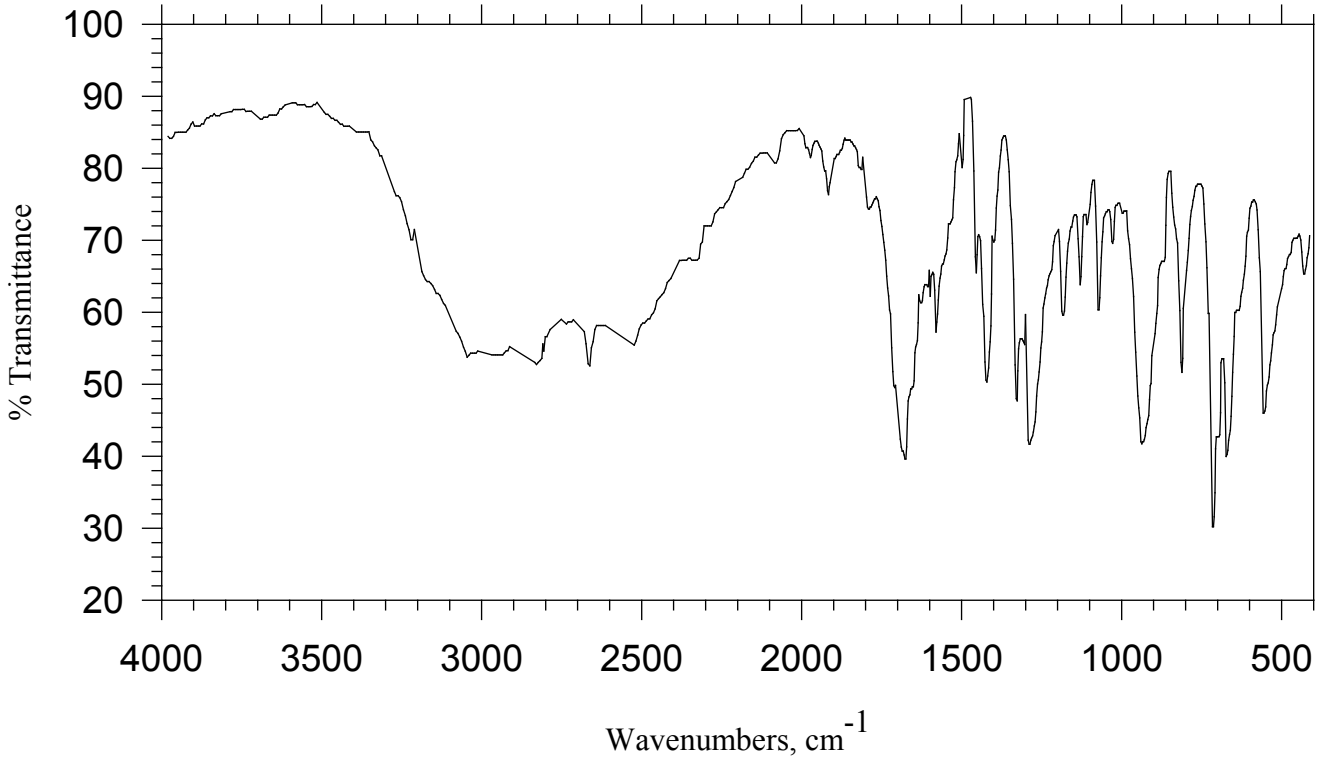


Figure IR-30. Benzoic acid, KBr; band distortions and broadening caused by poor grinding, compare to Figure 29.

When does one see a free –OH in the condensed phase?

Free H-O-R

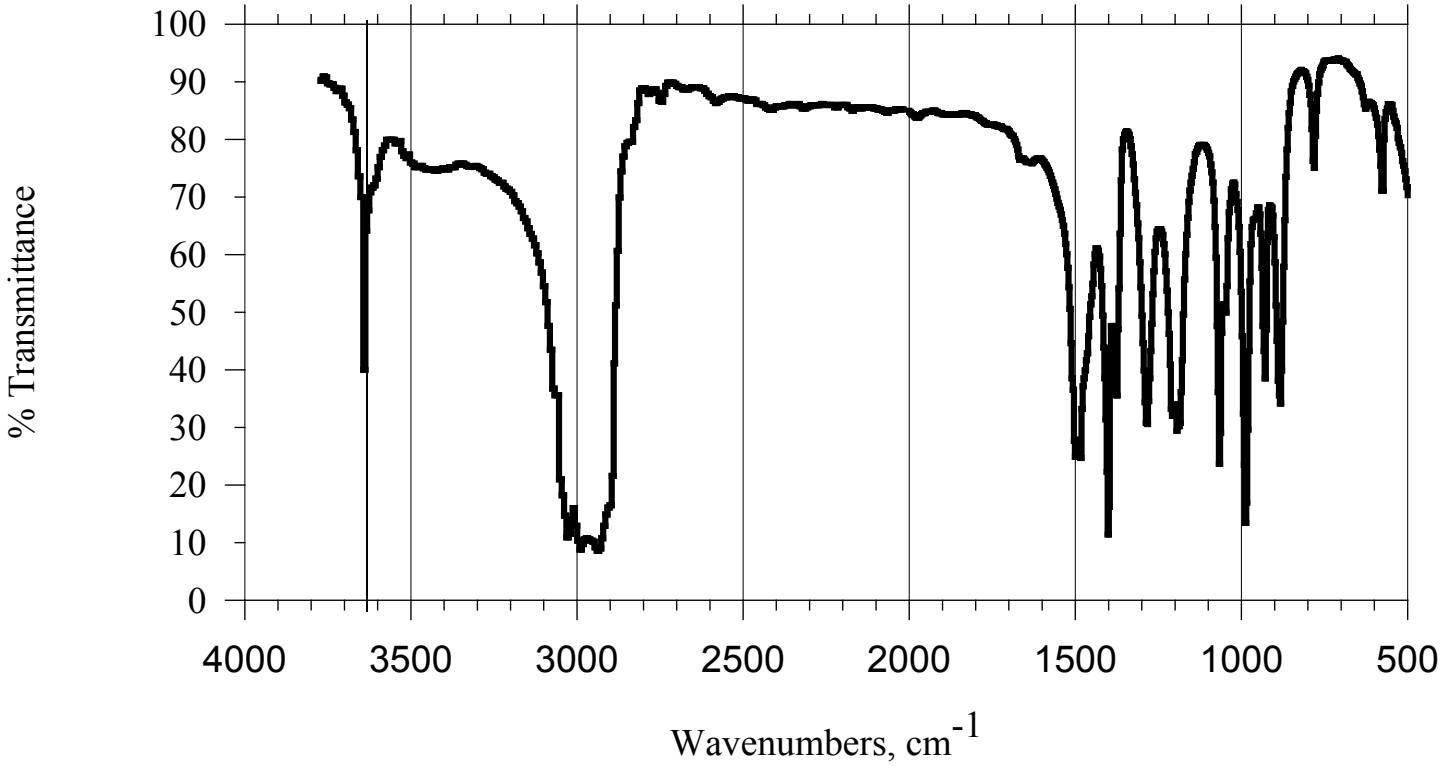
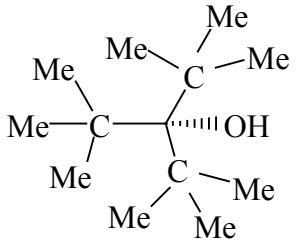


Figure IR-17. Tri-t-butylmethanol, KBr pellet:



The –CN triple bond

A summary of the principle infrared bands and their assignments. R is an aliphatic group.

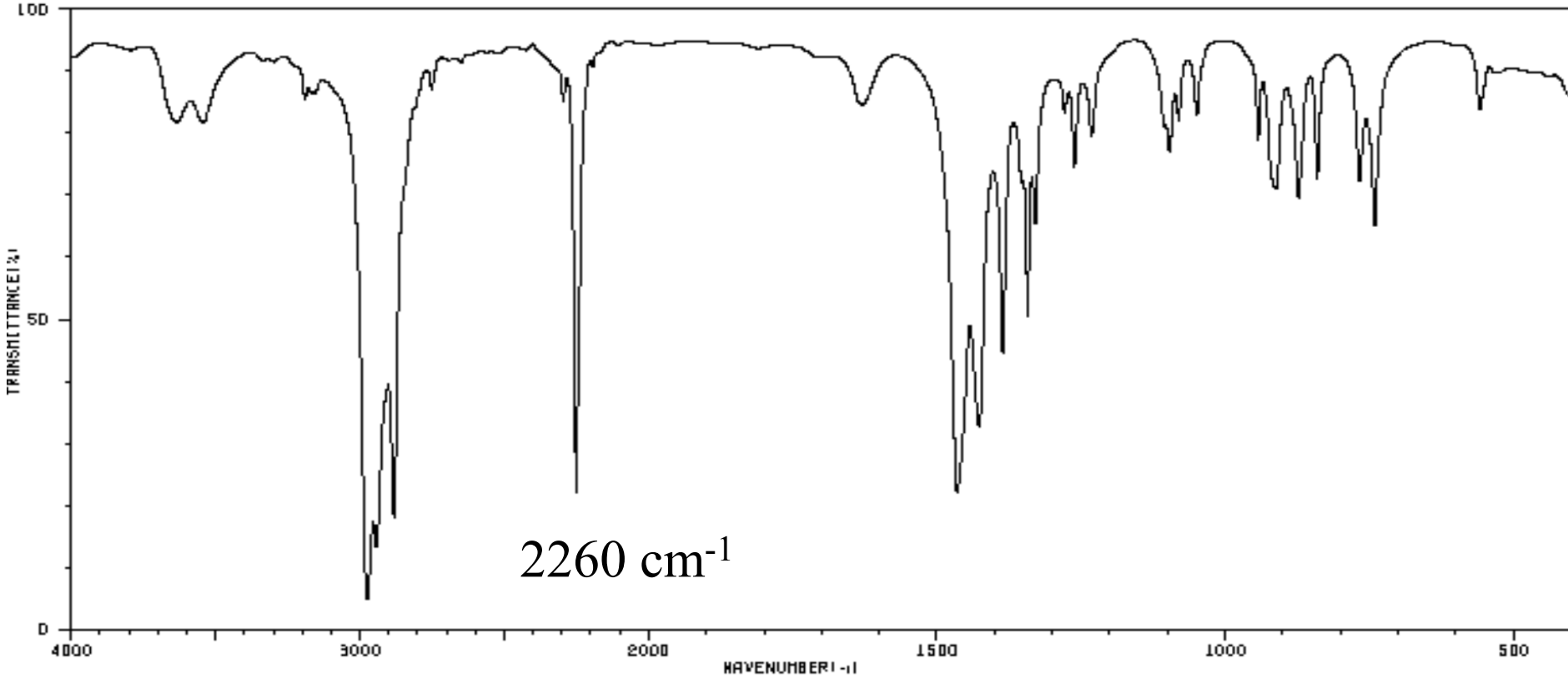
Funct. Group	Type		Frequencies cm^{-1}	Peak Intensity	Examples Figure No.
C-H	sp^3 hybridized	R_3C-H	2850-3000	M(sh)	6, 18, 22
	sp^2 hybridized	=CR-H	3000-3250	M(sh)	7, 13, 42
	sp hybridized	≡C-H	3300	M-S(sh)	13
	aldehyde C-H	H-(C=O)R	2750, 2850	M(sh)	14, 15
N-H	primary amine, amide	RN-H_2, RCONH_2	3300, 3340	S,S(br)	18, 19
	secondary amine, amide	RNR-H, RCONHR	3300-3500	S(br)	20, 21
	tertiary amine, amide	RN(R_3), RCONR_2	none		22, 23
O-H	alcohols, phenols	free O-H	3620-3580	W(sh)	17, 24, 25
		hydrogen bonded	3600-3650	S(br)	24, 25, 28
	carboxylic acids	R(C=O)O-H	3500-2400	S(br)	26, 27, 29, 30
C≡N	nitriles	RC≡N	2280-2200	S(sh)	31
C≡C	acetylenes	R-C≡C-R	2260-2180	W(sh)	32
		R-C≡C-H	2160-2100	M(sh)	13

br: broad; sh: sharp

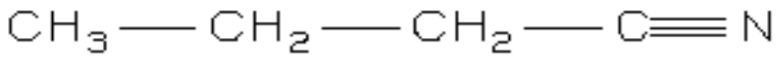
HIT-NO=1318	SCORE= ( )	SDBS-NO=1223	IR-NIDA-04692 : LIQUID FILM

BUTYRONITRILE

C_4H_7N



3634	79	2882	17	1386	42	1096	74	767	70
3543	79	2751	84	1343	49	1081	79	741	62
3191	81	2295	81	1330	82	1049	79	559	61
3176	84	2260	21	1279	79	943	77		
3161	84	1629	81	1262	72	913	68		
2974	4	1465	21	1232	77	873	66		
2943	12	1427	31	1106	77	840	70		



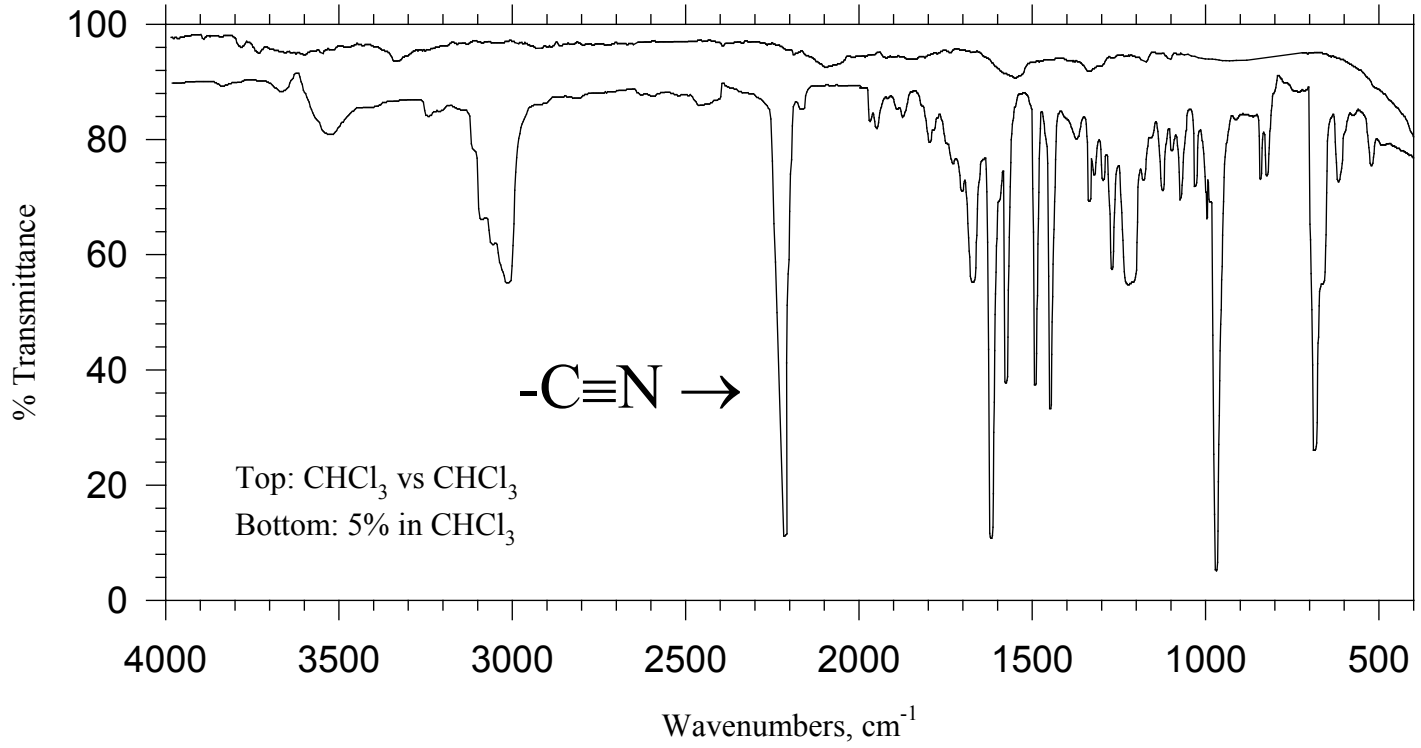
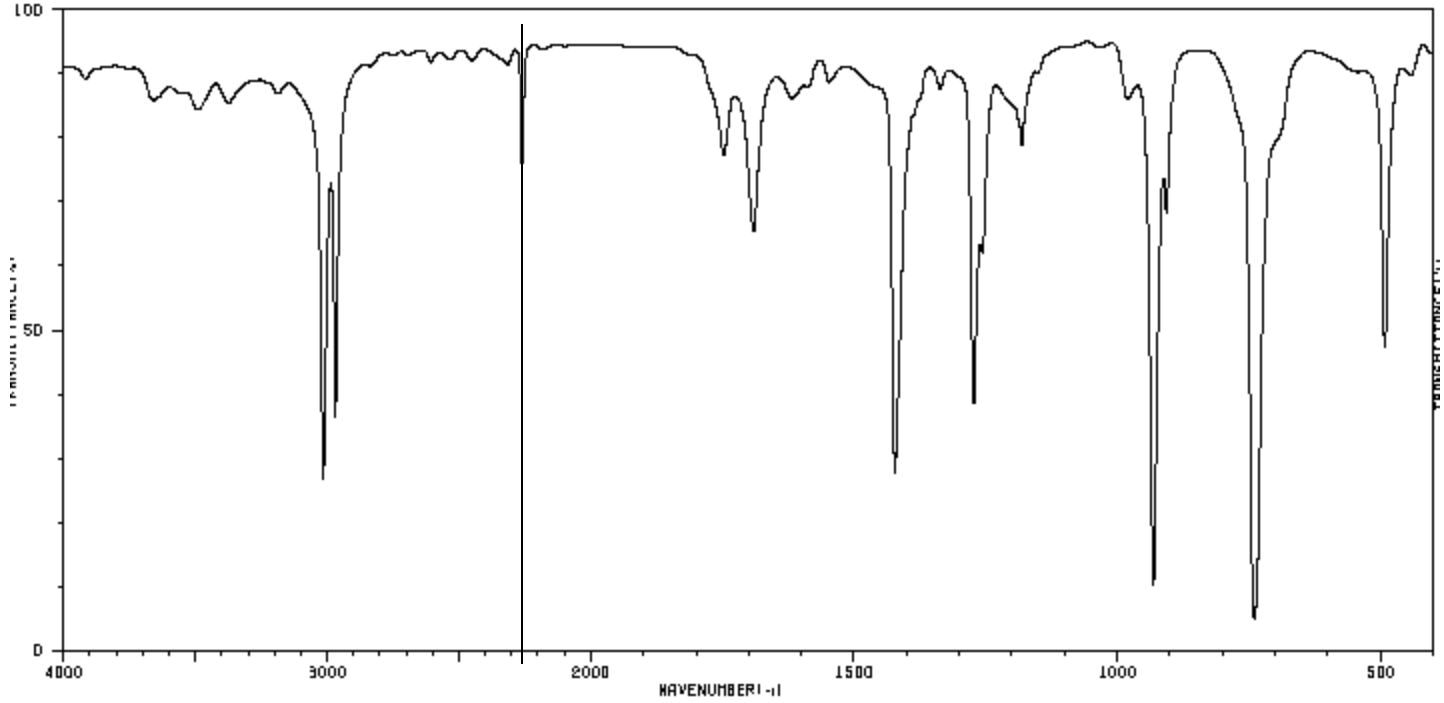


Figure IR-31. *trans*-2-Phenyl-1-cyanoethene, in $CHCl_3$ solution: Ph-CH=CH-CN

HIT-NO=2496	SCORE= ( )	SDBS-NO=4104	IR-NIDA-03296 : LIQUID FILM
CHLOROACETONITRILE			
C_2H_2CLN			



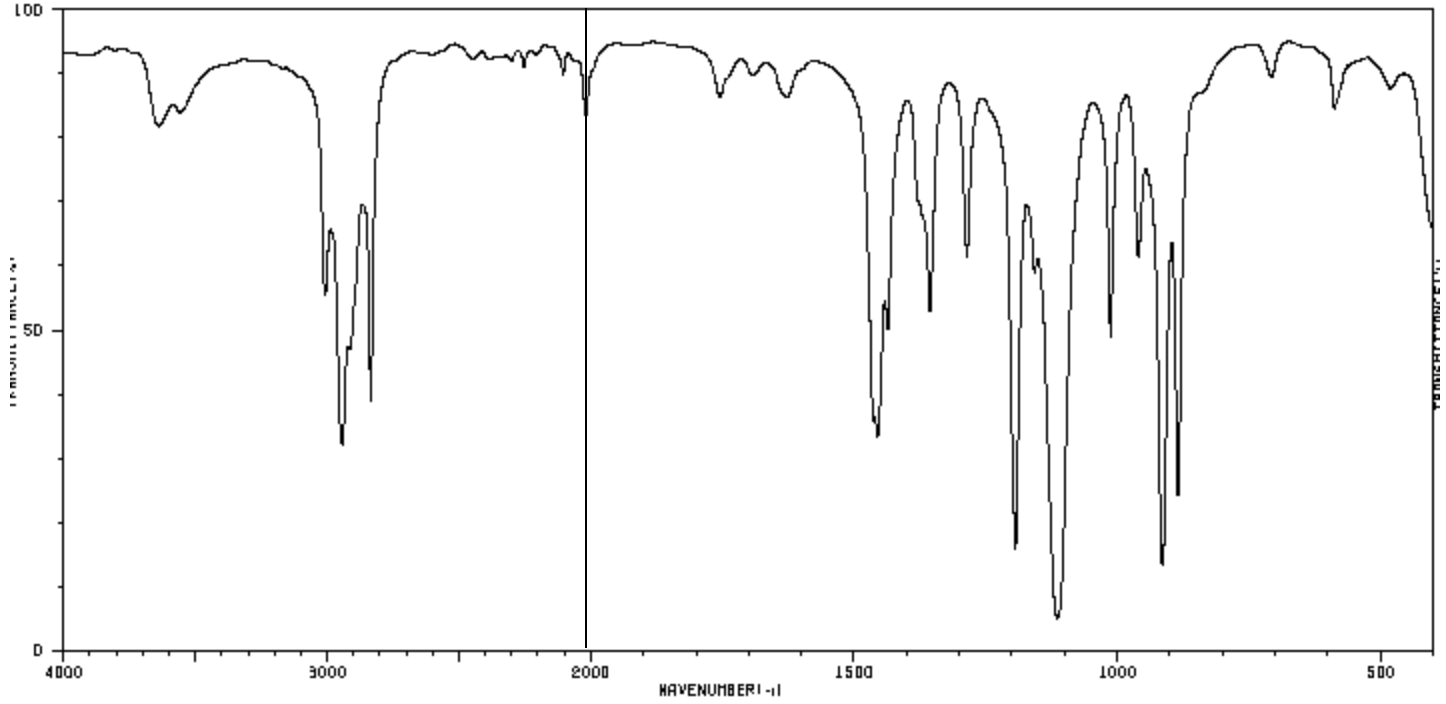
3917	86	2261	72	1273	37	492	44
3655	81	1747	74	1257	58	443	86
3490	81	1691	62	1162	77		
3374	81	1618	84	981	84		
3187	84	1548	84	931	9		
3014	26	1423	26	907	86		
2969	36	1337	84	740	4		

$ClCH_2C{\equiv}N$

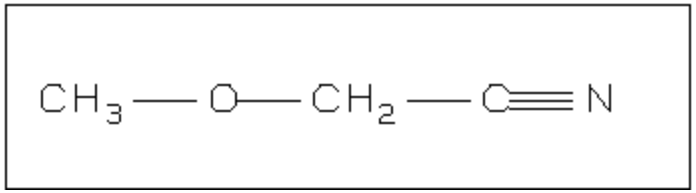
HIT-NO=1309	SCORE= ( )	SDBS-NO=1214	IR-NIDA-60882 : LIQUID FILM

METHOXYACETONITRILE

C_3H_5NO



3638	79	2019	79	1366	60	914	12
3556	81	1755	84	1286	58	885	23
3007	53	1691	86	1194	15	708	86
2942	31	1628	84	1157	67	688	81
2914	44	1463	34	1114	4	582	84
2854	37	1458	32	1015	47	481	84
2105	86	1437	47	960	68		



The C-C triple bond in terminal acetylenes

C≡C Triple Bond Stretch

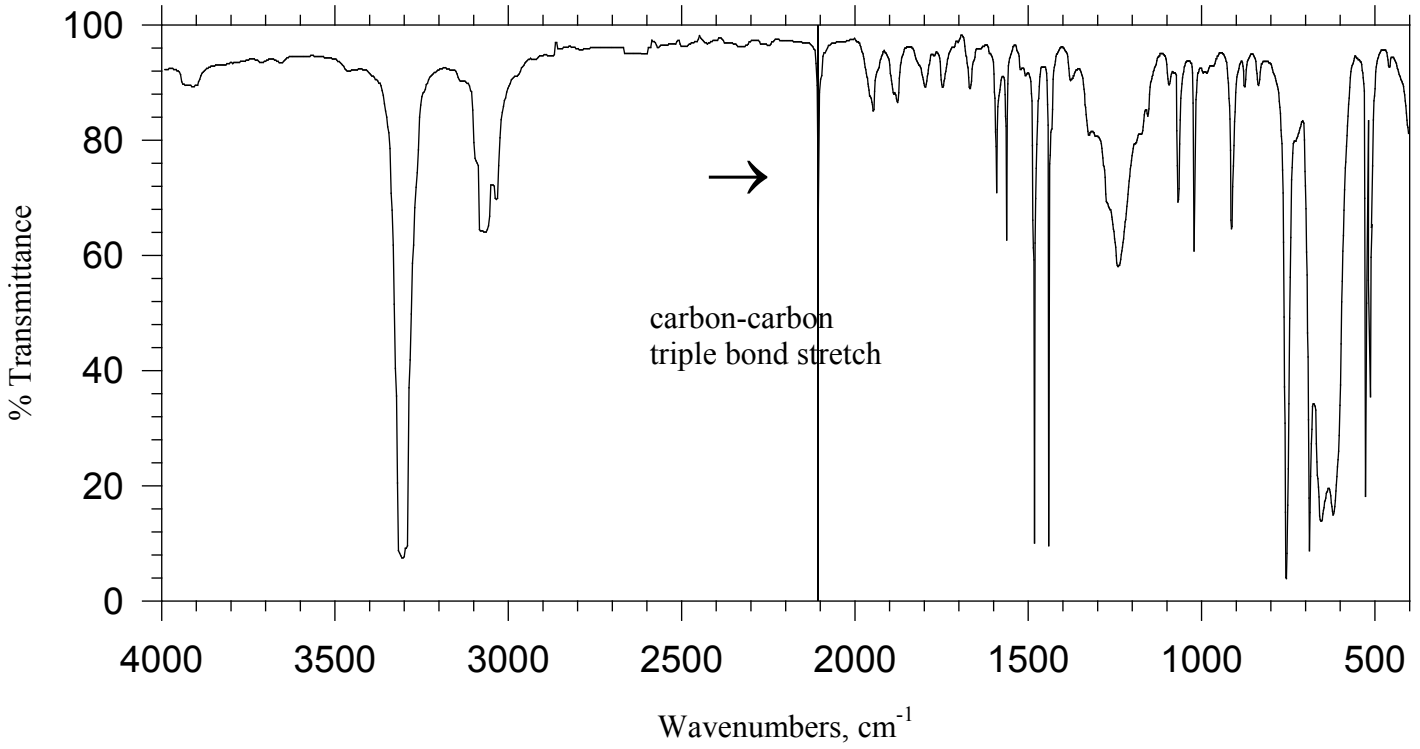
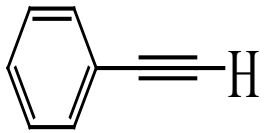


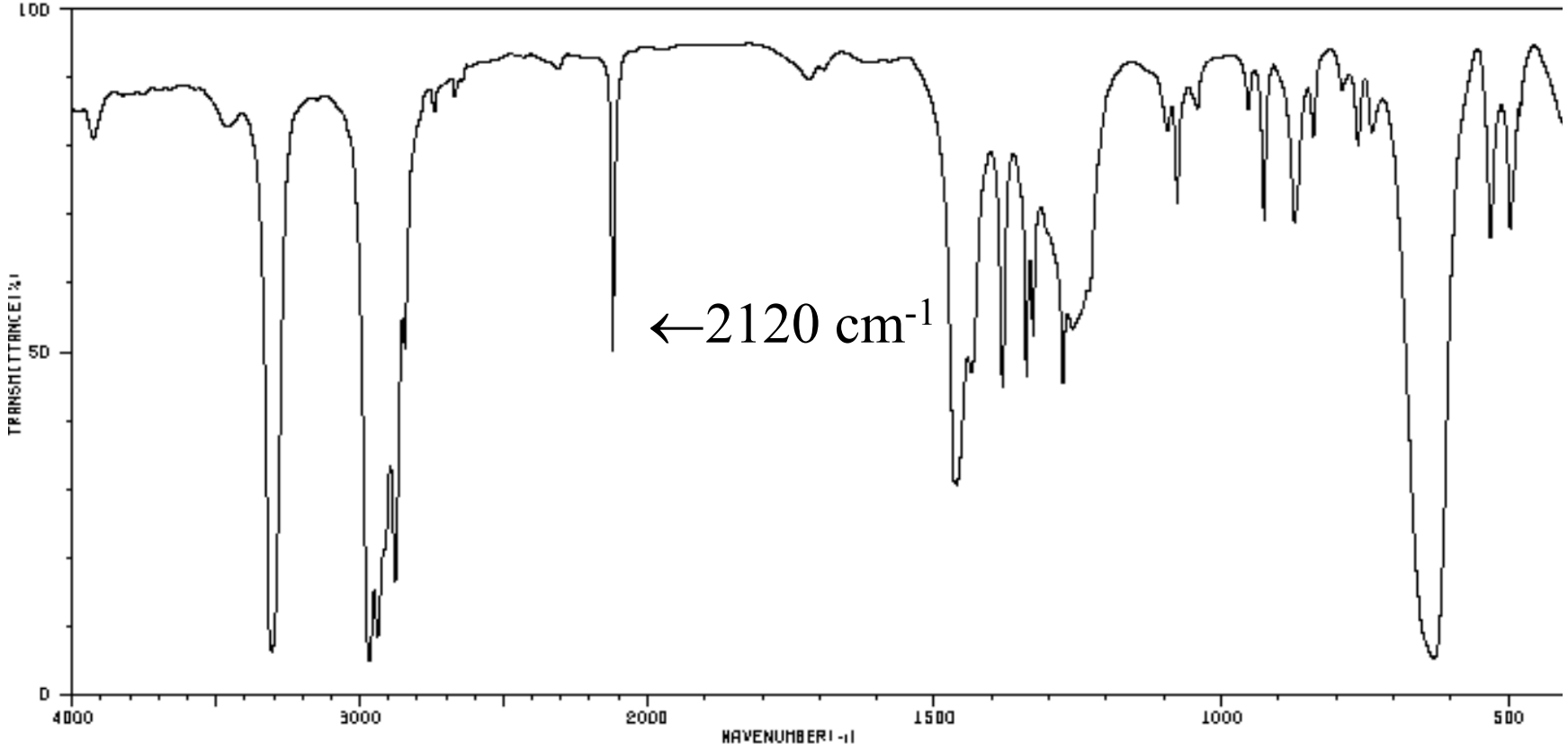
Figure IR-13. Phenylacetylene, neat liquid; thin film:



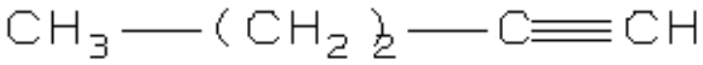
HIT-NO=2943	SCORE= ( )	SDBS-NO=5386	IR-NIDA-13676 : LIQUID FILM

1-PENTYNE

C_5H_8



3928	79	2741	81	1381	43	1041	81	739	79
3457	79	2670	84	1340	44	954	81	630	5
3307	6	2120	47	1328	50	926	66	532	64
2968	4	1718	86	1276	43	872	66	497	66
2938	7	1466	29	1259	52	840	79	481	81
2876	16	1460	29	1095	79	791	64		
2843	49	1436	44	1077	68	762	77		



The C≡C triple bond in symmetrical acetylenes

C≡C Triple Bond Stretch

Where is it?

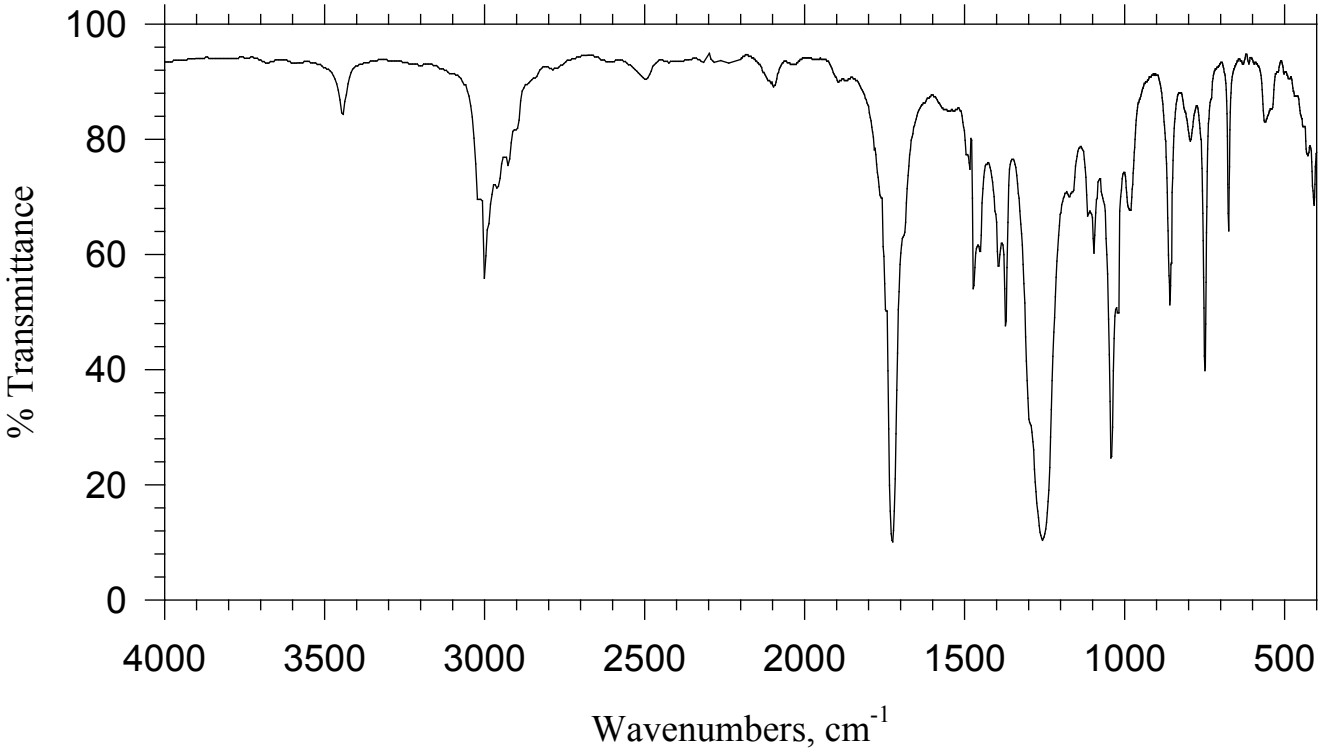


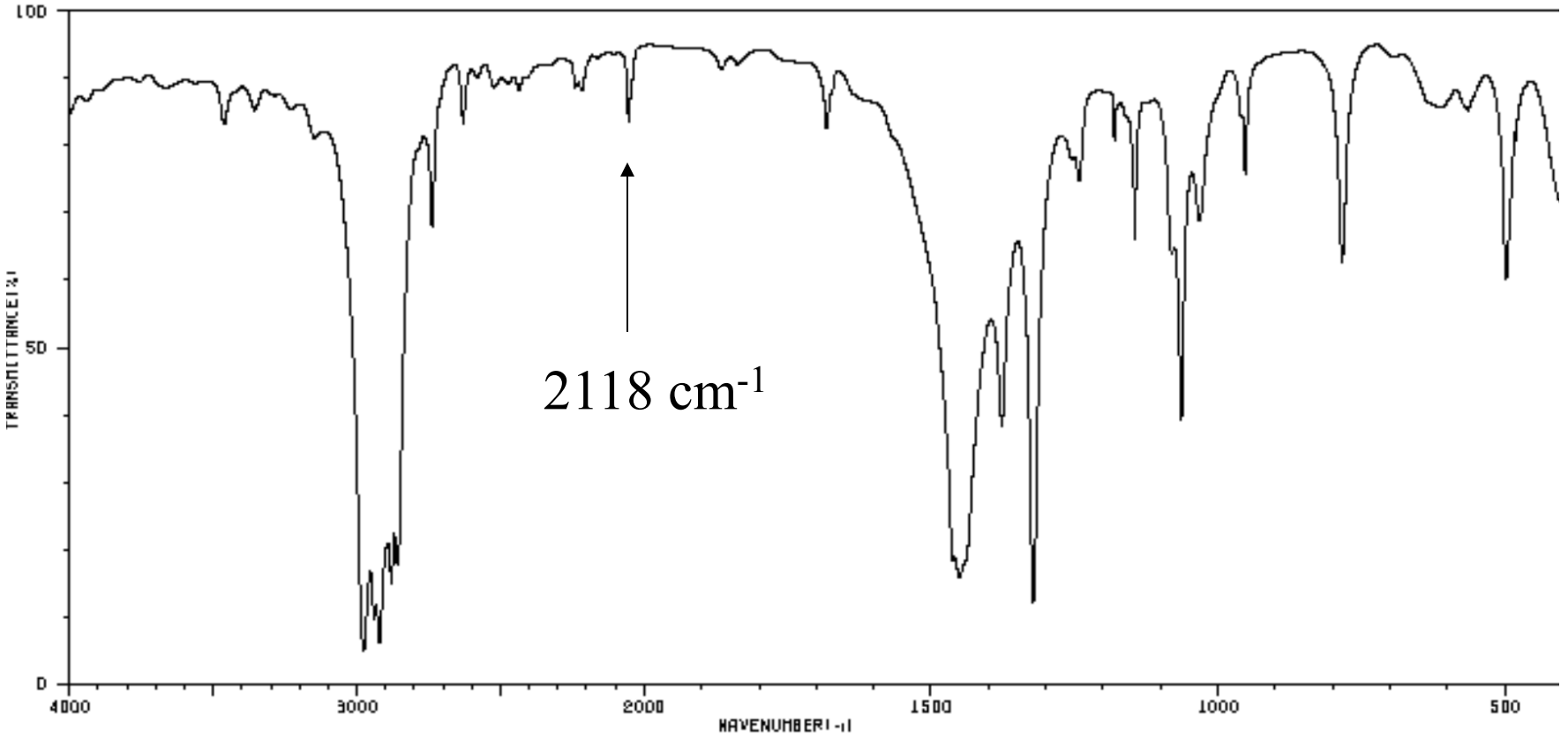
Figure IR-32. Diethyl acetylenedicarboxylate; neat liquid: $C_2H_5OCO\text{-}C{\equiv}C\text{-}CO_2CH_2CH_3$

The C≡C triple bond in internal acetylenes

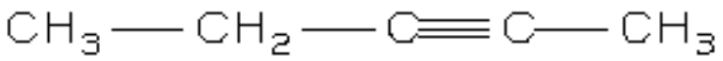
HIT-NO=2944	SCORE= ( )	SDBS-NO=5387	IR-NIDA-13678 : LIQUID FILM

2-PENTYNE

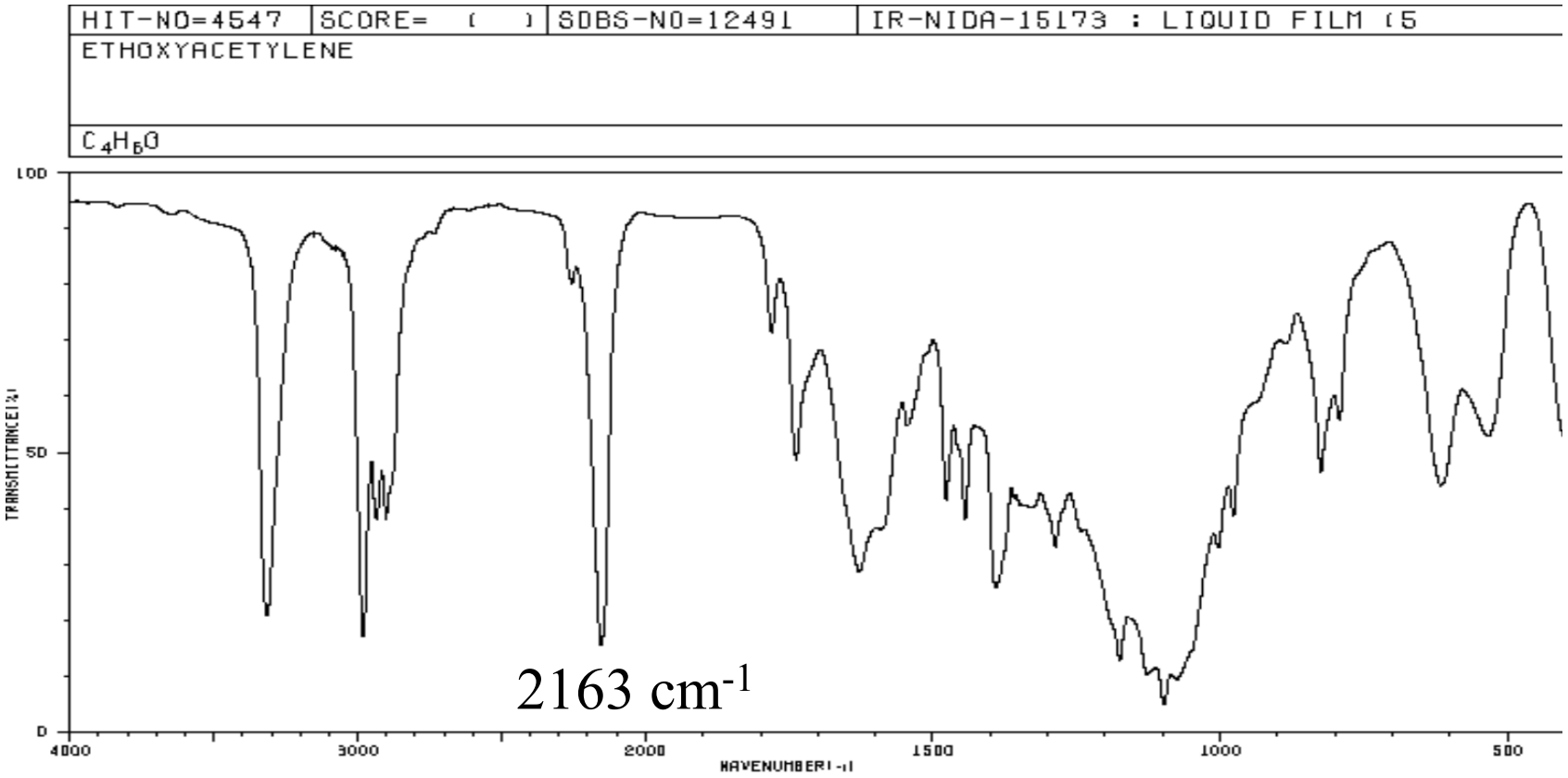
C_5H_8



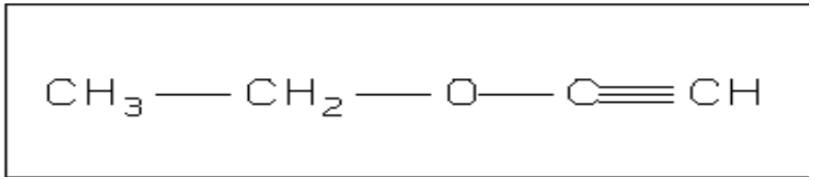
3669	84	2860	17	1682	79	1181	77	963	72
3463	79	2739	66	1463	17	1158	81	784	60
3354	81	2629	79	1451	15	1145	64	619	61
2975	4	2436	84	1377	37	1081	62	613	81
2940	9	2239	84	1322	11	1064	37	563	81
2922	6	2218	84	1256	74	1032	66	499	57
2879	14	2063	81	1243	72	960	81	481	77



The C≡C triple bond when next to a heteroatom



3316	20	1781	68	1339	38	1003	31
2981	16	1738	46	1334	38	977	37
2960	42	1628	27	1329	36	825	44
2933	36	1644	62	1287	31	793	69
2901	36	1477	39	1176	12	616	42
2256	77	1444	36	1128	10	535	50
2163	14	1391	24	1098	4		



Spectrum in hexanes (50%)