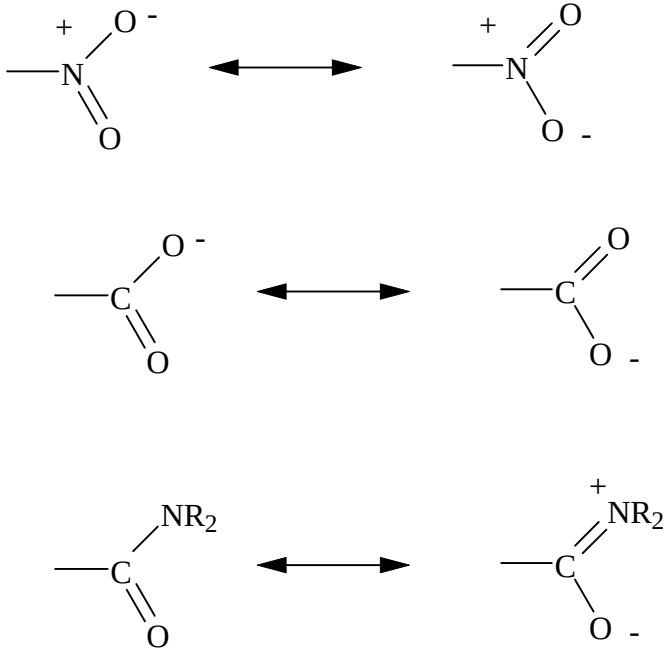
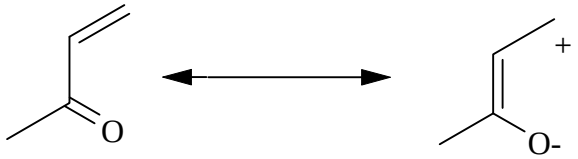
Factors affecting the frequency of infrared peaks

1. Resonance, symmetry and conjugation

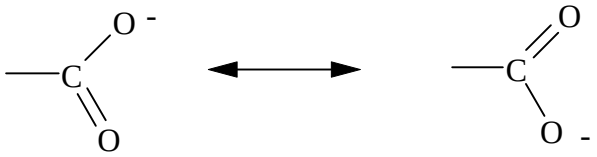
Effect of resonance, symmetry and conjugation on infrared frequencies



What about the effect of conjugation?



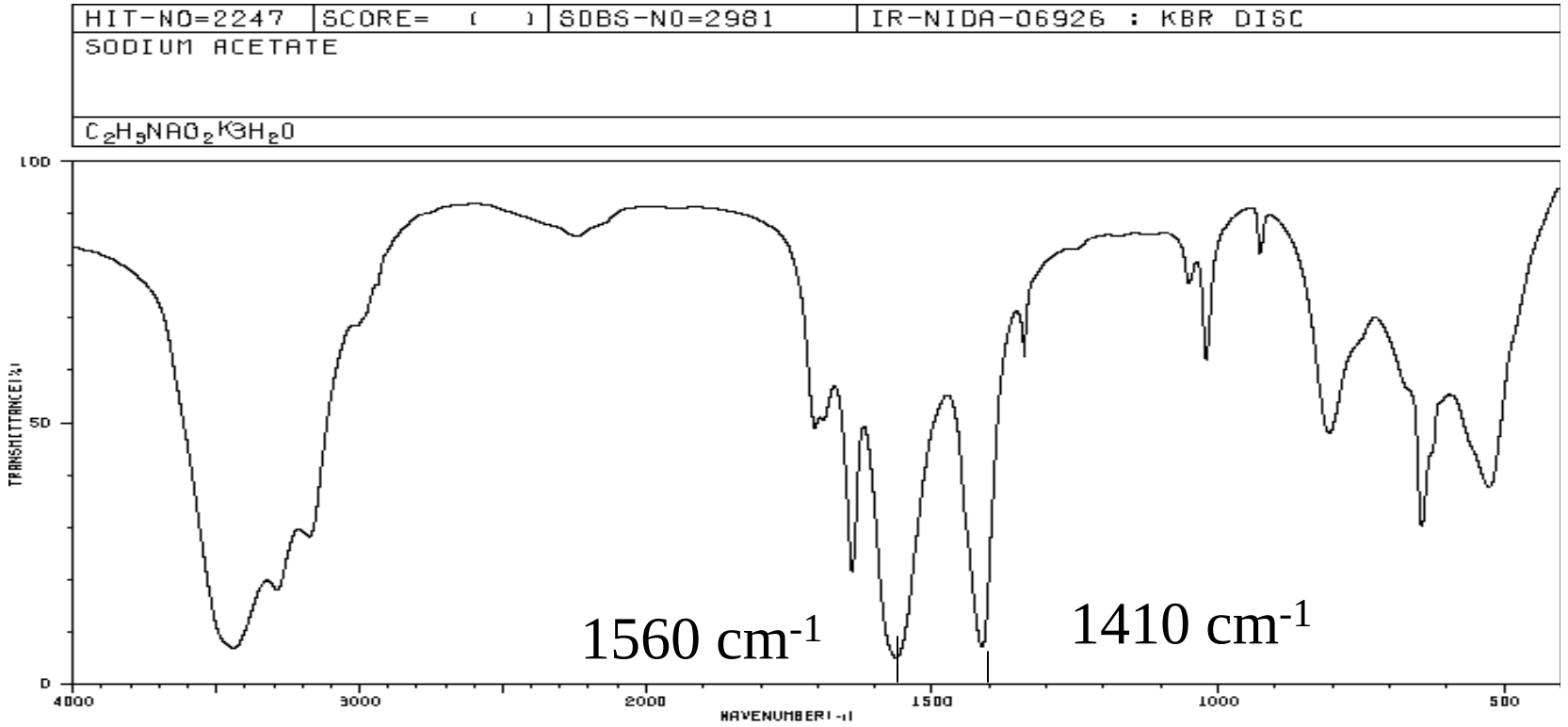
Do the facts support this interaction?



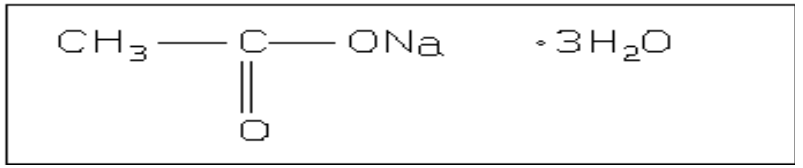
Carbonyl frequency: 1720-1680 (acid) ≈ 1700 cm^{-1}

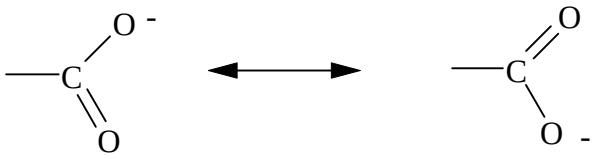
Ether frequency = 1000 to 1400 cm^{-1} ≈ 1200 cm^{-1}

Average of the two fundamentals = 1450 cm^{-1}



3436	6	1690	49	928	79
3287	17	1640	20	806	46
3176	26	1563	4	845	29
2252	81	1413	6	626	36
2242	81	1339	60		
1705	47	1051	74		
1696	49	1021	60		





(1560+ 1410)/2 = 1485 cm^{-1}

Resonance

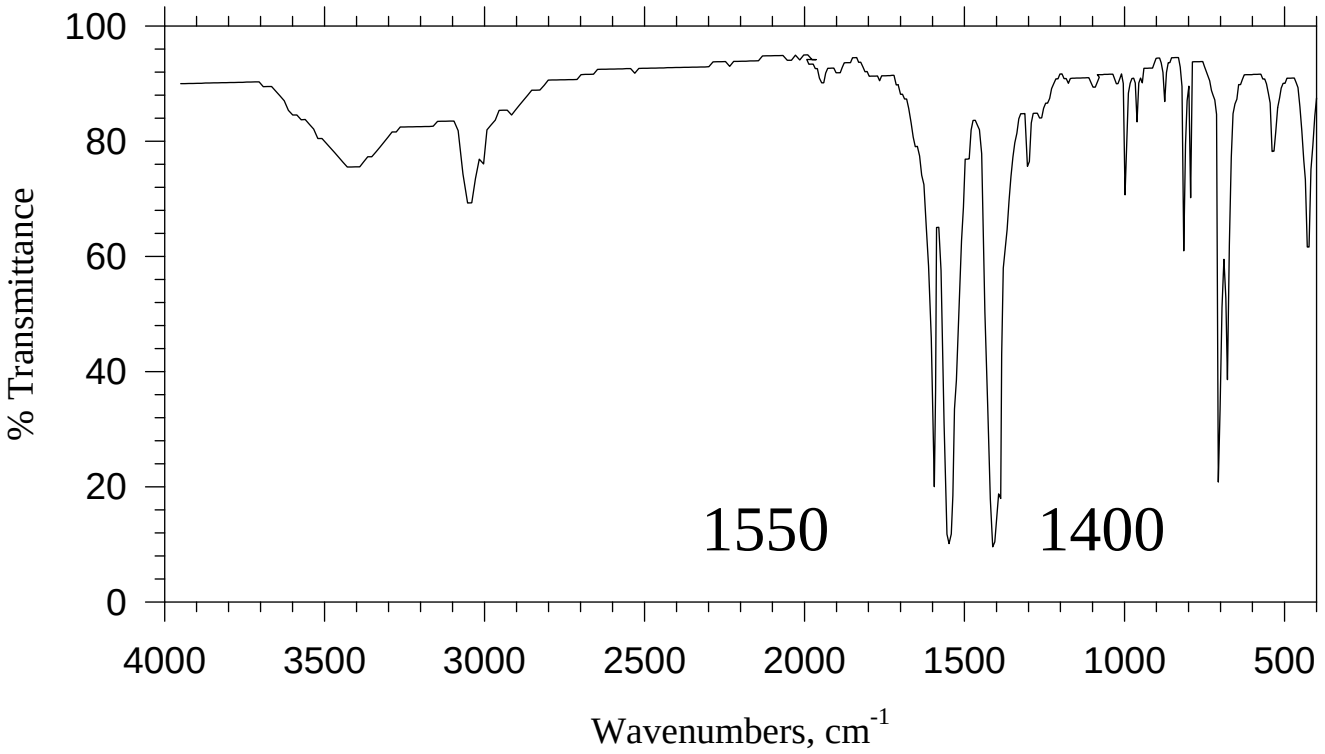
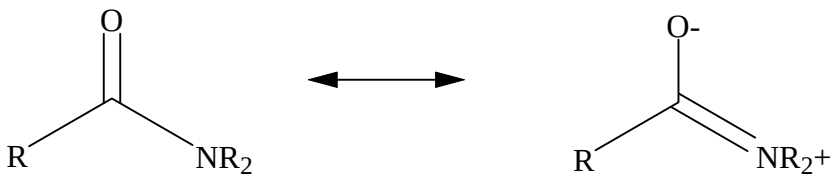


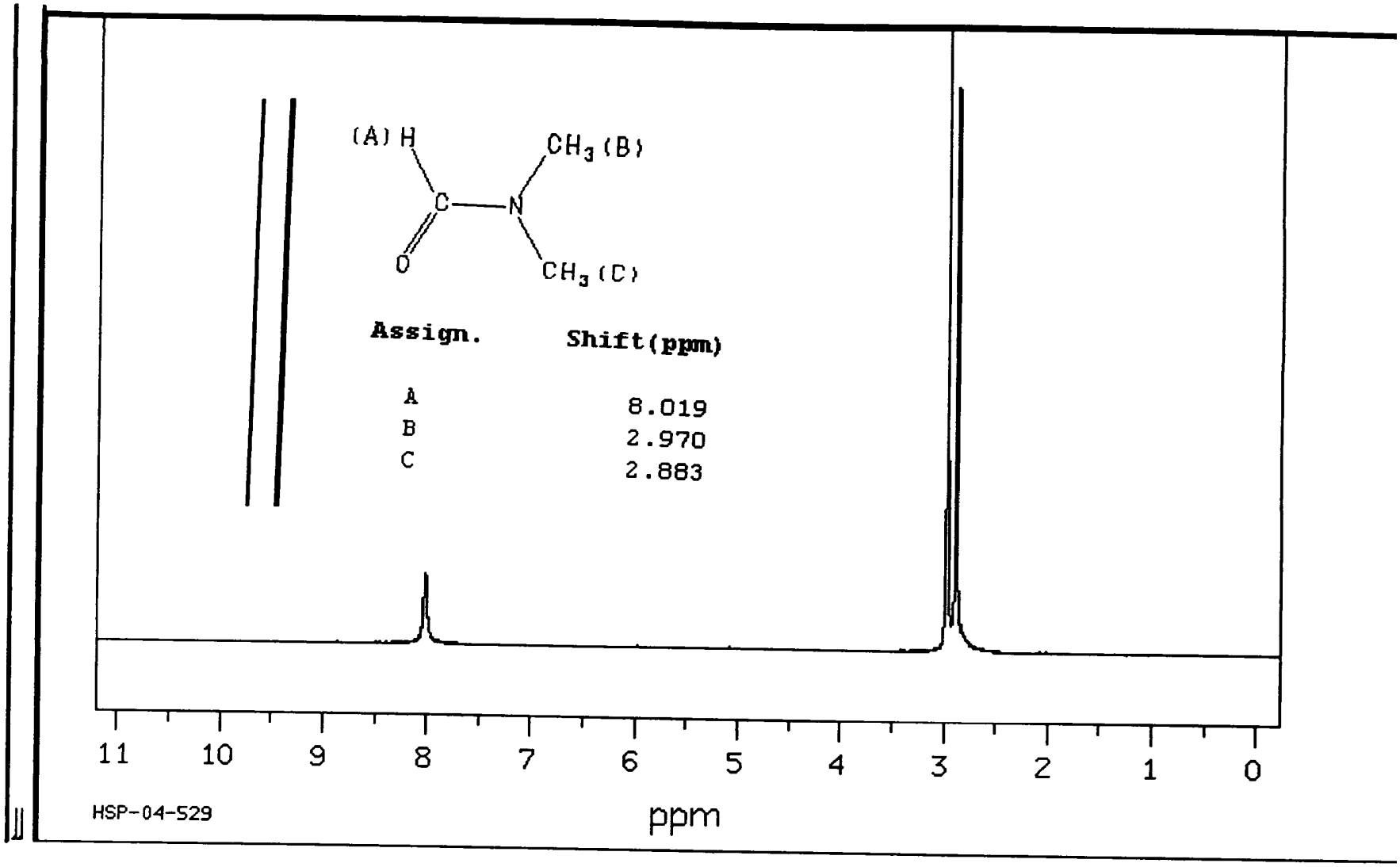
Figure IR-42. Sodium benzoate, KBr pellet:

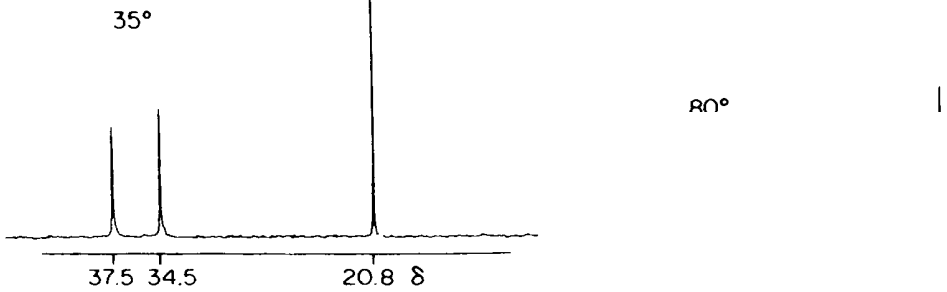
Sodium benzoate: (1550, 1400 cm^{-1}); Average : 1475 cm^{-1}

Sodium acetate: (1560, 1410 cm-1); Average : 1485 cm-1



How important is resonance in amides?


(A) H
CH3 (B)
C
N
O
CH3 (C)
Assign.
Shift(ppm)
A
8.019
B
2.970
C
2.883
11
10
9
8
7
6
5
4
3
2
1
0
HSP-04-529
ppm



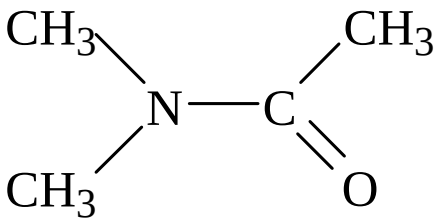
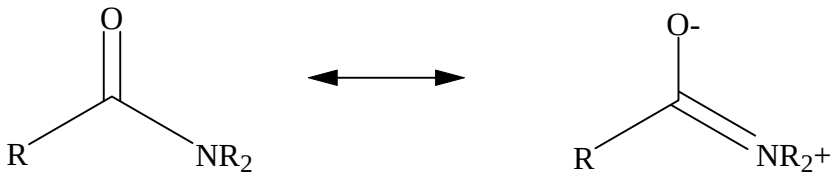
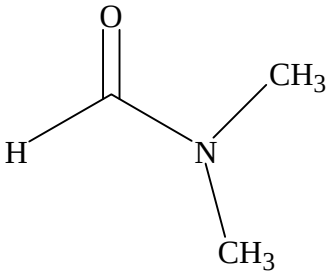


Fig. 7.16 The high-field part of the 25.2 MHz ^{13}C–{^{1}H} spectrum of *N*,*N*-dimethylacetamide at the temperatures indicated.



How important is resonance in amides?

In 

the barrier to rotation of the two CH_3 groups is approximately 18 kcal/mol

(A C-C π bond is worth about 60 kcal/mol)

Table 4. The effect of conjugation on carbonyl frequencies.

Non-conjugated Compound	Frequency cm^{-1}	Conjugated Compound	Frequency cm^{-1}		Frequency cm^{-1}
butanal	1725	2-butenal	1691	benzaldehyde	1702
2-butanone	1717	methyl vinyl ketone	1700, 1681	acetophenone	1685
propanoic acid	1715	propenoic acid	1702	benzoic acid	1688
ethyl propionate	1740	ethyl acrylate	1727	ethyl benzoate	1718
butanoic anhydride	1819, 1750	2-butenoic anhydride	1782, 1722	benzoic anhydride	1786, 1726
cis-cyclohexane-1,2-dicarboxylic anhydride	1857, 1786	1-cyclohexene-1,2-dicarboxylic anhydride	1844, 1767	phthalic anhydride	1852, 1762

Other effects of conjugation on carbonyl frequencies

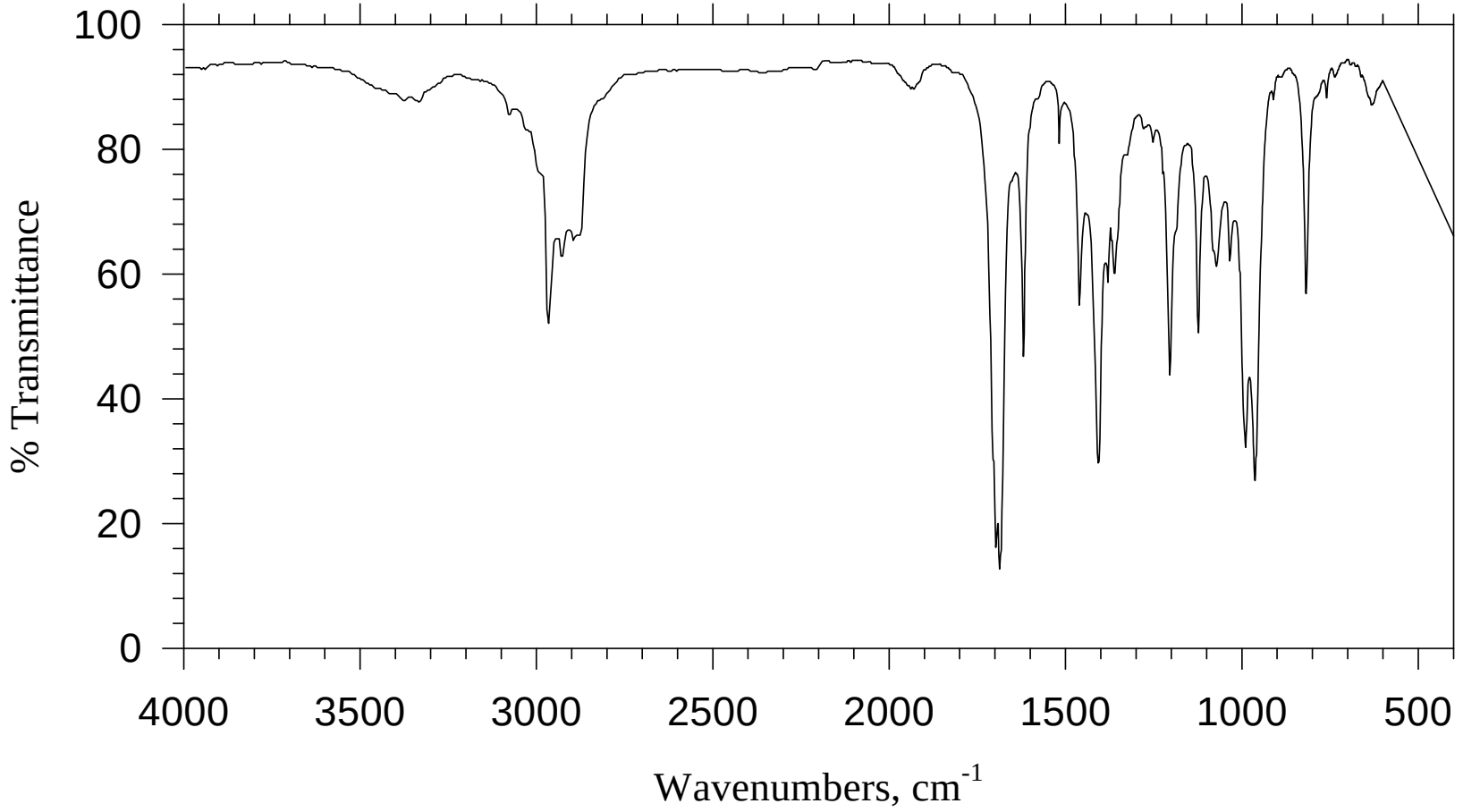


Figure IR-45. Ethyl vinyl ketone, neat liquid: $CH_3CH_2COCH{=}CH_2$

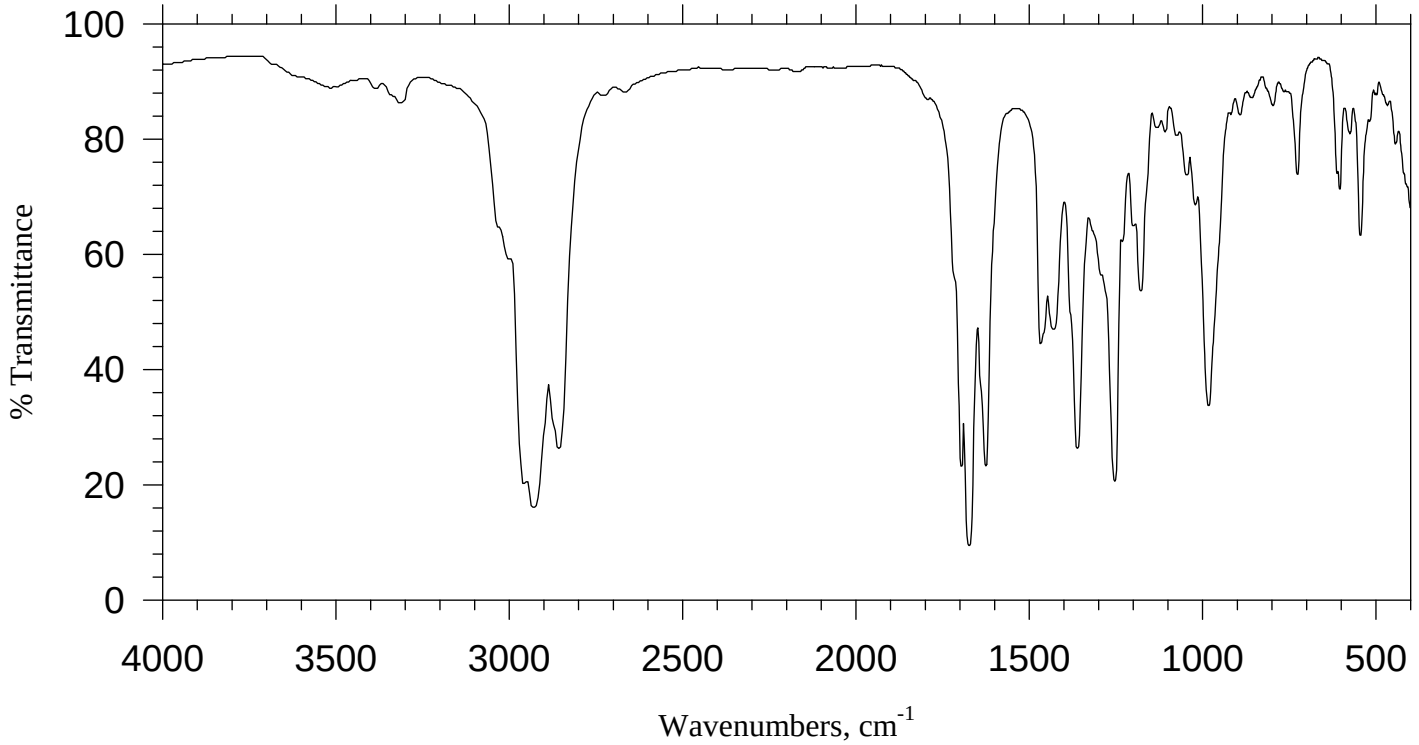
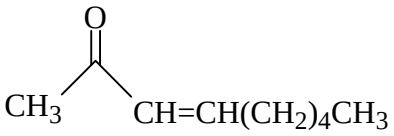
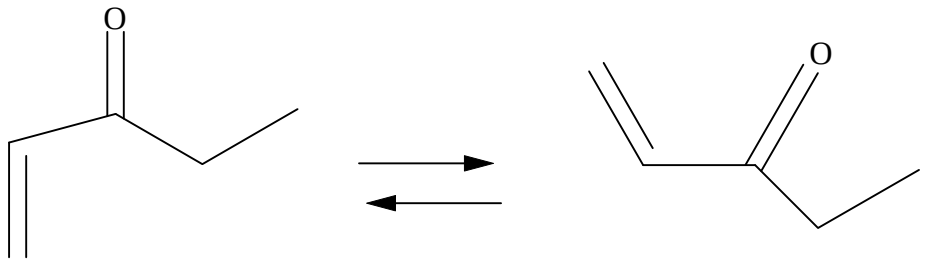


Figure IR-44. 3-Nonen-2-one, 95%; neat liquid, thin film:

Why the extra carbonyl peaks?

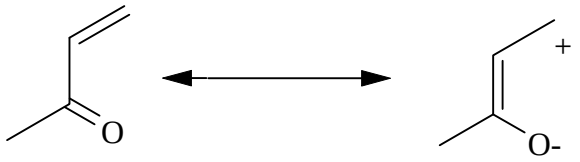




Factors affecting the intensities :

Extent of interaction (dipole moment change)

Concentration of each conformer

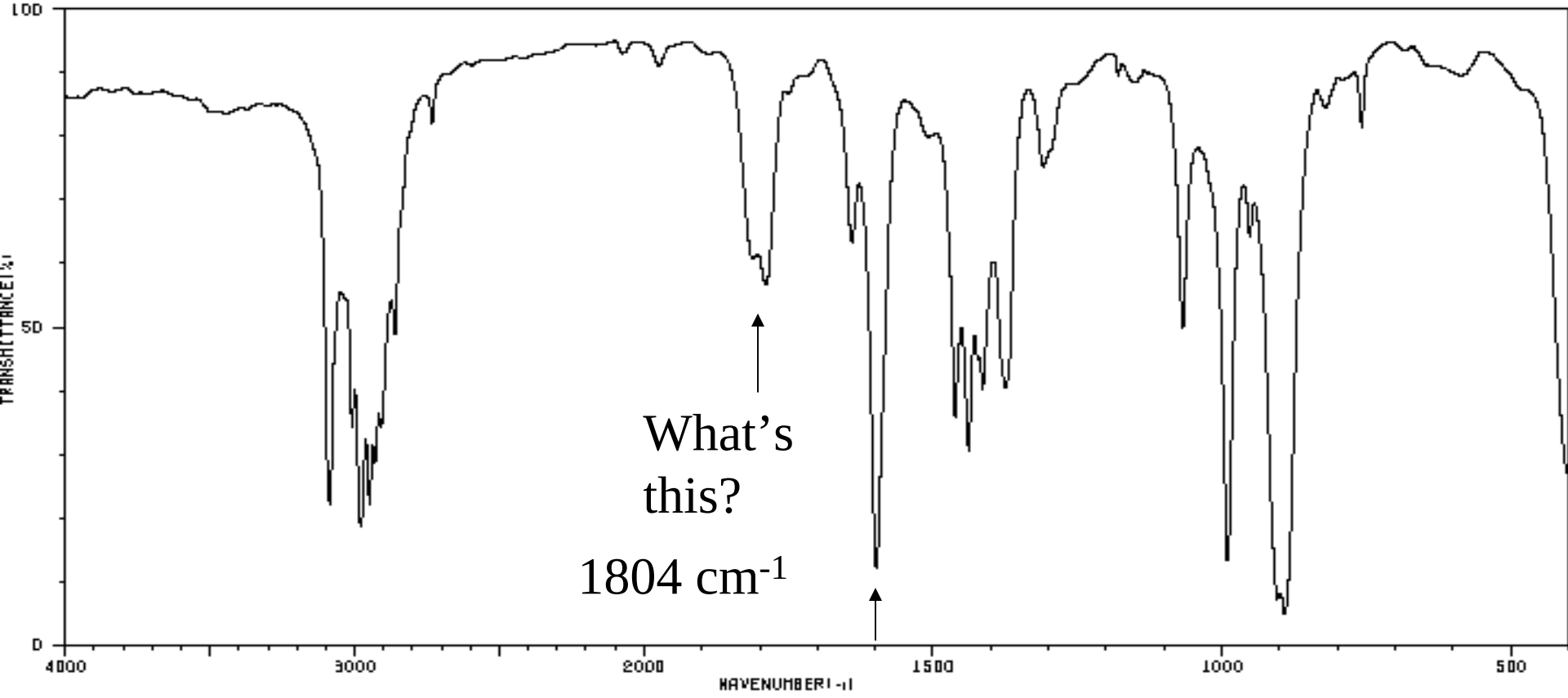


Overtones in terminal olefins

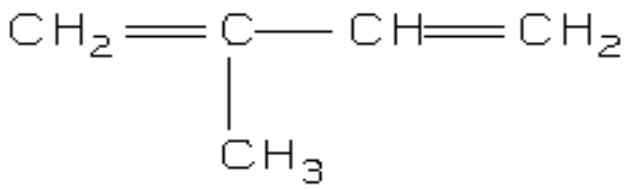
HIT-NO=3871	SCORE= ( )	SDBS-NO=7940	IR-NIDA-13460 : LIQUID FILM

ISOPRENE

C_5H_8



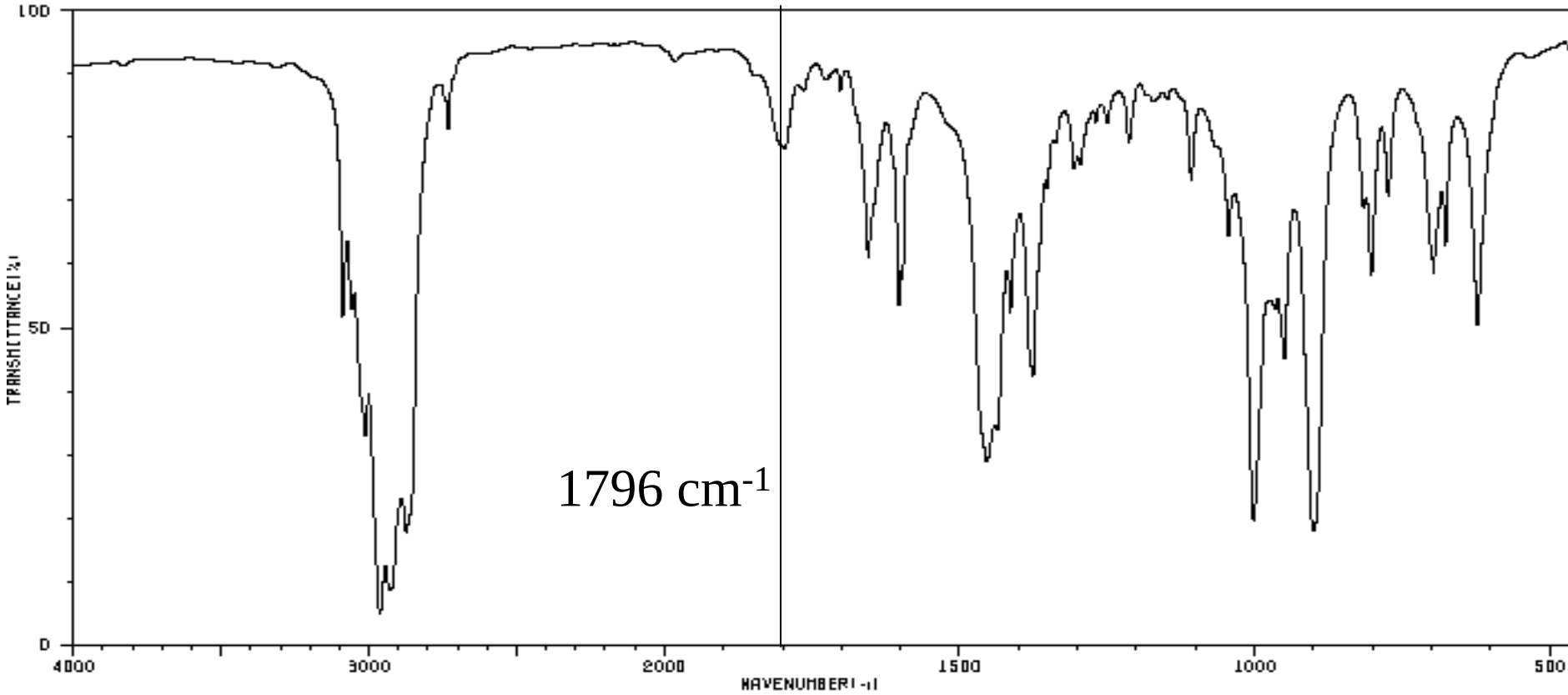
3086	21	2732	79	1423	43	991	12	769	79
3009	33	1804	58	1414	38	952	62	587	86
2977	18	1790	55	1375	38	906	6		
2949	21	1639	60	1309	72	899	7		
2931	27	1598	11	1181	86	892	4		
2909	33	1462	34	1152	84	825	61		
2861	47	1439	29	1068	47	820	81		



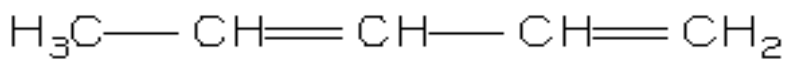
HIT-NO=4169	SCORE= ( )	SDBS-NO=10477	IR-NIDA-03079 : LIQUID FILM

1,3-PENTADIENE

C_5H_8



3089	49	1796	74	1376	41	1172	81	816	66
3058	50	1702	84	1352	70	1164	84	802	55
3011	31	1655	58	1306	72	1107	70	774	66
2963	4	1603	62	1296	72	1044	62	698	67
2928	8	1597	55	1270	79	1002	18	677	60
2874	17	1454	27	1250	79	950	45	623	49
2731	79	1414	60	1213	77	900	17	448	84

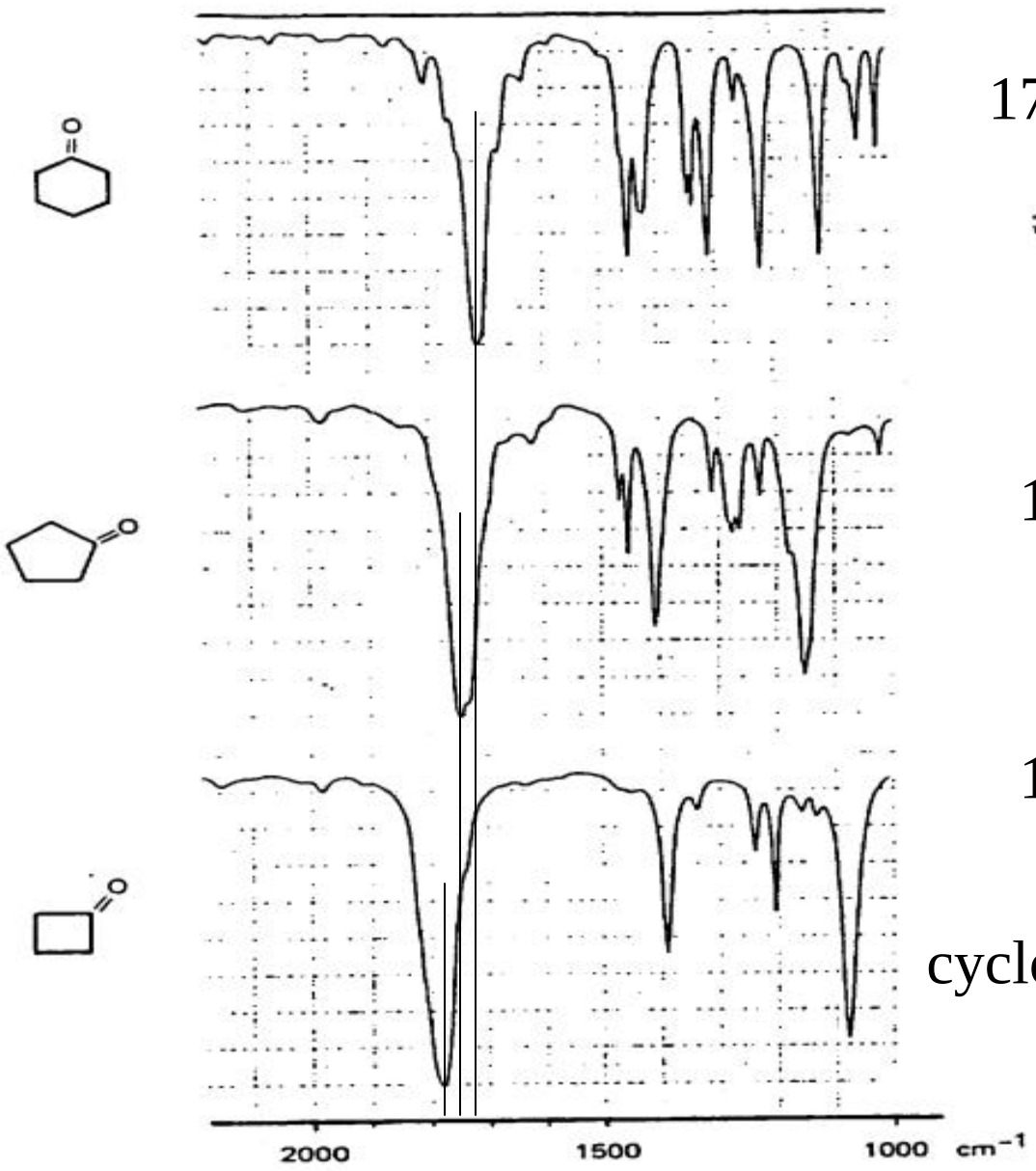


Factors affecting the frequency of infrared peaks

1. Resonance and conjugation

2. Ring strain:

A: on carbonyl frequencies



1720 cm^{-1}

1750 cm^{-1}

1775 cm^{-1}

cyclopropanone

1800 cm^{-1}

Table. The Effect of Ring Strain on the Carbonyl Frequencies of Some Cyclic Molecules

Ring Size	ketone:	cm^{-1}	lactone:	cm^{-1}	lactam:	cm^{-1}
3	cyclopropanone:	1800				
4	cyclobutanone:	1775	β-propiolactone:	1840		
5	cyclopentanone:	1751	γ-butyrolactone:	1750	γ-butyrolactam:	1690
6	cyclohexanone:	1715	δ-valerolactone:	1740	δ-valerolactam:	1668
7	cycloheptanone:	1702	ε–caprolactone:	1730	ε–caprolactam:	1658

Factors affecting the frequency of infrared peaks

1. Resonance and conjugation

2. **Ring strain:**

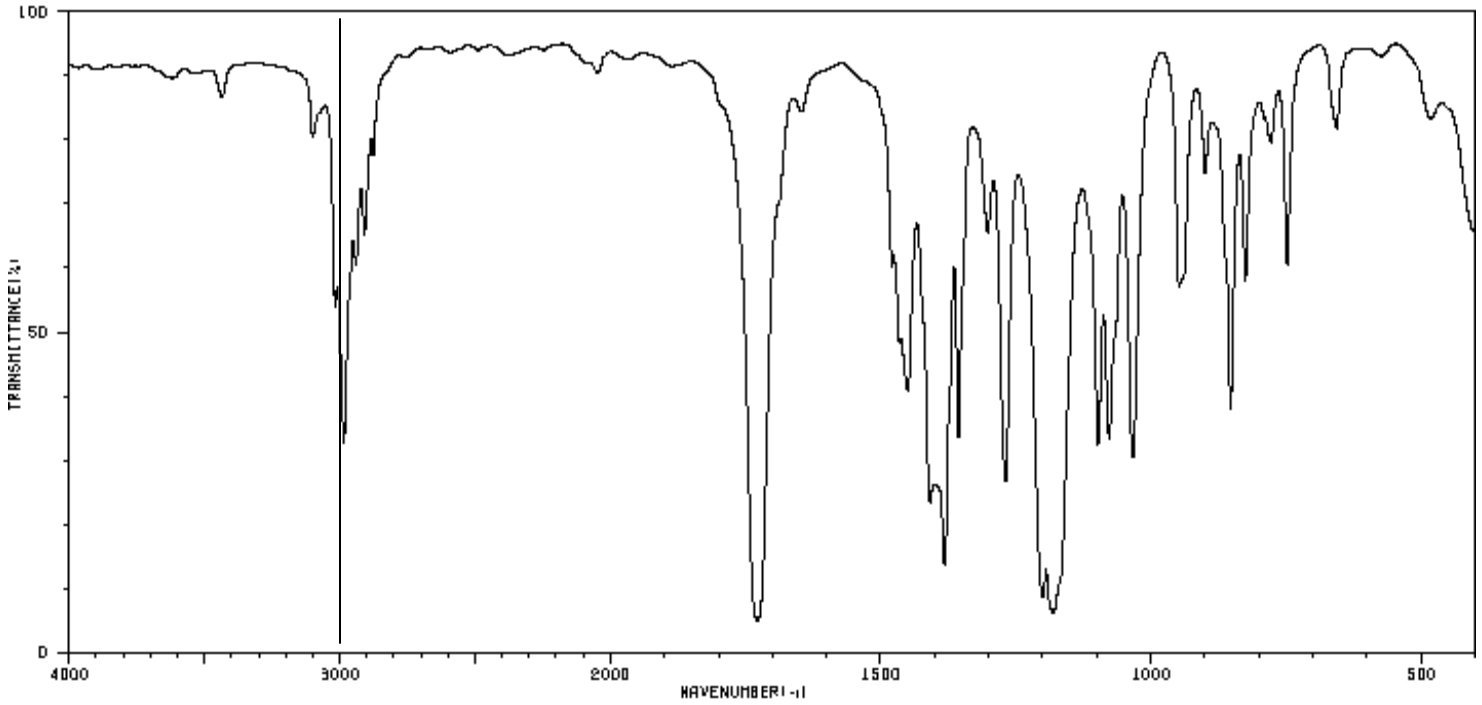
A: on carbonyl frequencies

B. on C-H stretching frequencies

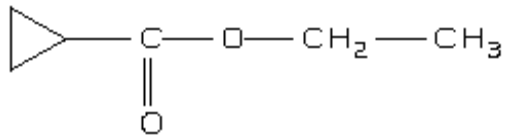
HIT-NO=4954	SCORE= ( )	SDBS-NO=15380	IR-NIDA-24694 : LIQUID FILM

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
3435	84	1728	4	1382	13	1077	32	776	77
3100	77	1646	81	1366	32	1033	29	749	60
3017	52	1479	58	1302	62	948	55	657	79
2984	31	1465	46	1269	25	900	72	462	79
2941	68	1460	39	1200	8	861	68		

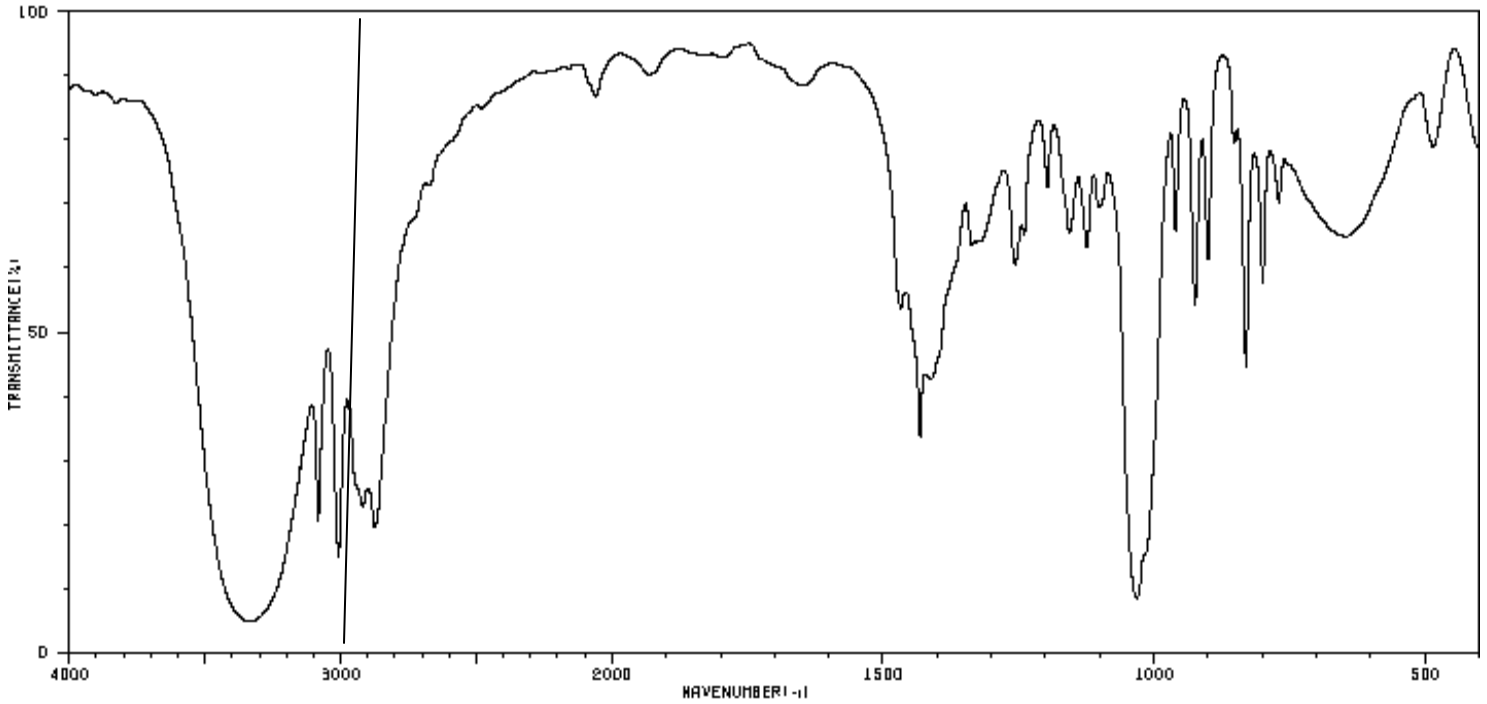


What is the hybridization of a C-H bond in cyclopropane?

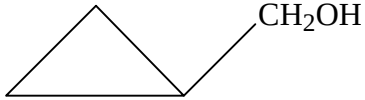
HIT-NO=4931	SCORE= ( )	SDBS-NO=15263	IR-NIDA-24553 : LIQUID FILM

CYCLOPROPYLMETHANOL

C_4H_8O



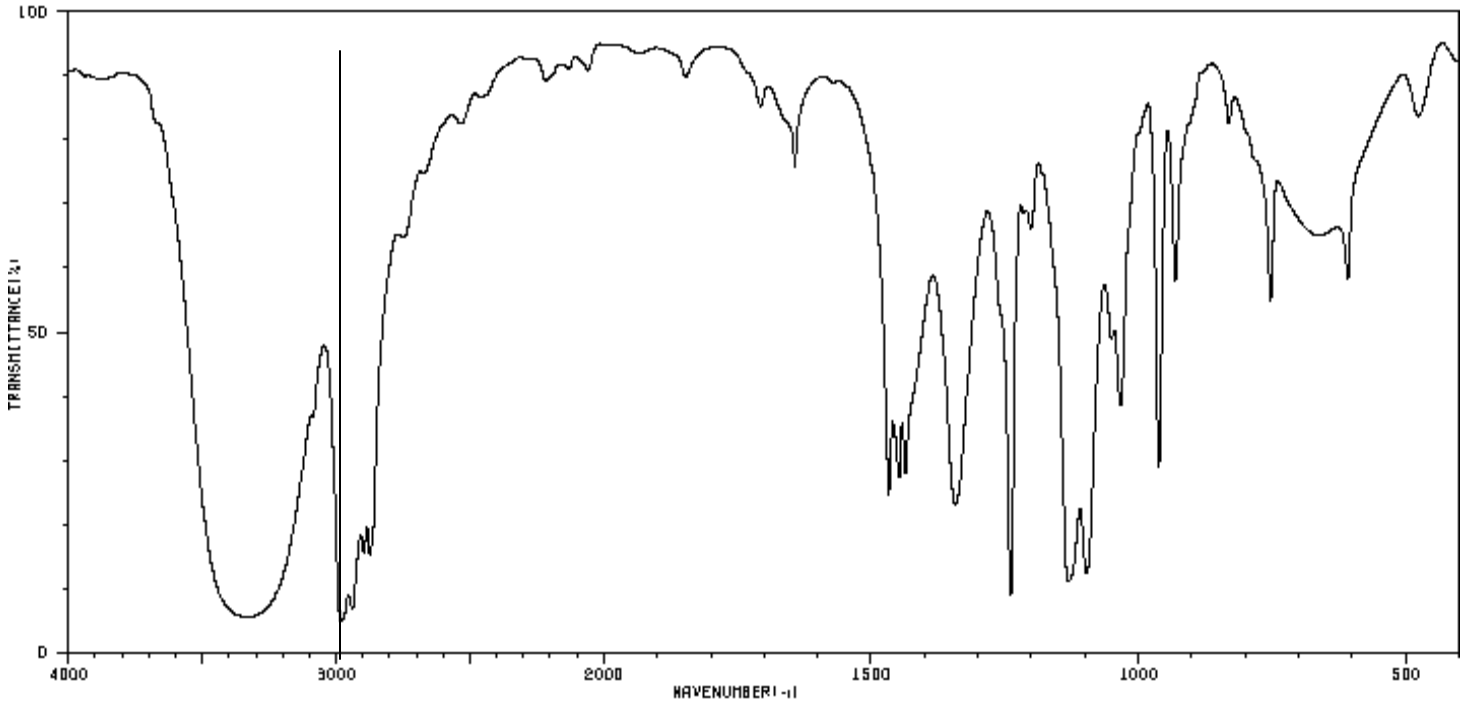
3330	4	1647	84	1321	62	1031	8	770	68
3082	20	1468	52	1256	58	960	64	650	62
3006	14	1432	32	1240	82	924	52	465	77
2919	21	1421	42	1197	70	900	68		
2873	18	1413	41	1156	62	852	77		
2059	84	1333	62	1124	80	830	45		
1652	84	1326	62	1103	66	799	55		



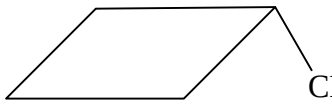
HIT-NO=4216	SCORE= ( )	SDBS-NO=10603	IR-NIDA-03249 : LIQUID FILM

CYCLOBUTANOL

C_4H_8O



2978	4	2196	86	1343	22	962	27
2939	6	1847	86	1239	8	931	55
2896	14	1707	81	1201	84	831	79
2874	14	1643	72	1130	10	763	62
2533	79	1467	23	1097	12	663	62
2218	86	1448	26	1050	47	609	55
2207	86	1436	26	1033	37	476	81



Factors affecting the frequency of infrared peaks

1. Resonance and conjugation

2. Ring strain:

A: on carbonyl frequencies

B. on C-H stretching frequencies

3. Halogens

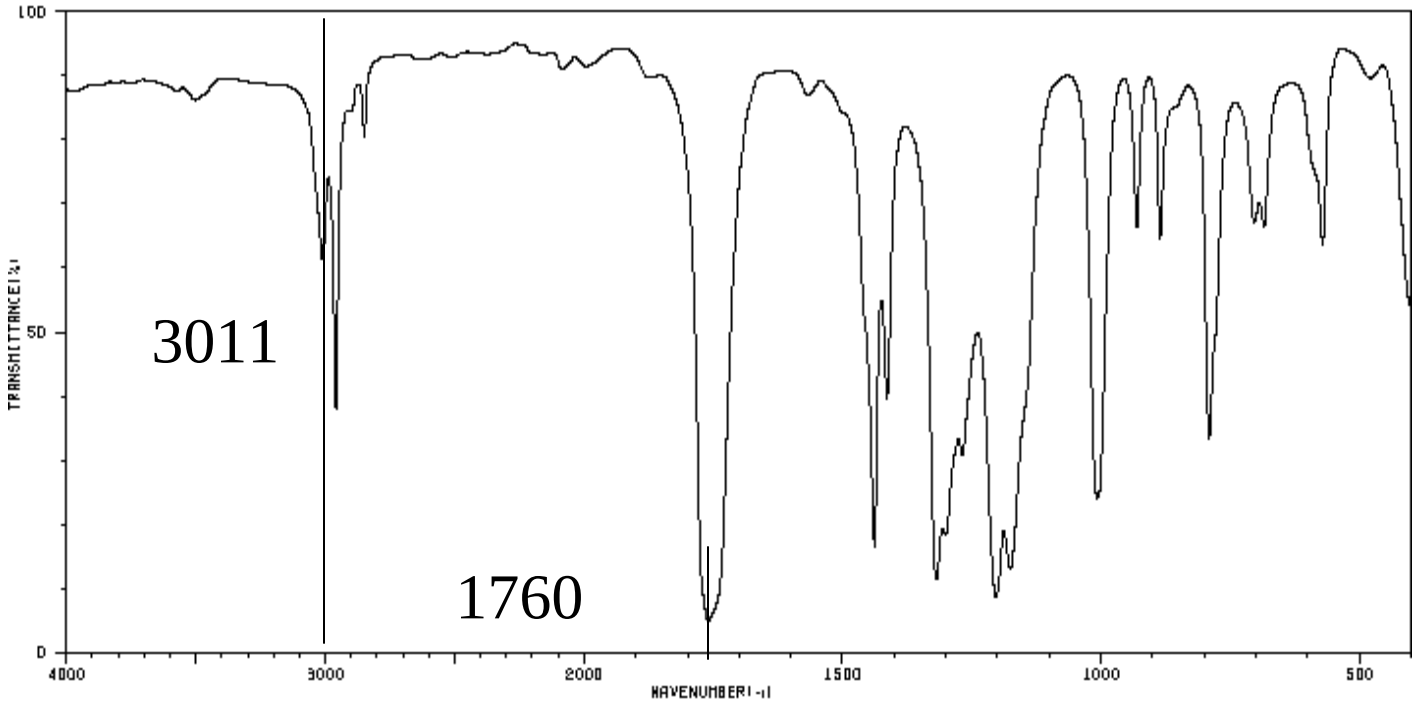
A: on carbonyl frequencies

B. on C-H stretching frequencies

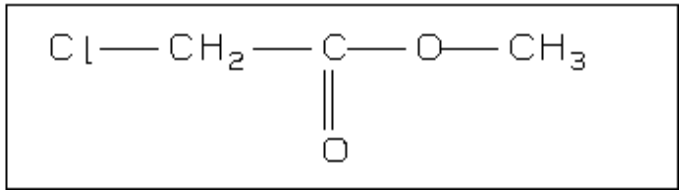
HIT-NO=1303	SCORE= ( )	SDBS-NO=1204	IR-NIDA-63537 : LIQUID FILM

METHYL CHLOROACETATE

$C_3H_5ClO_2$



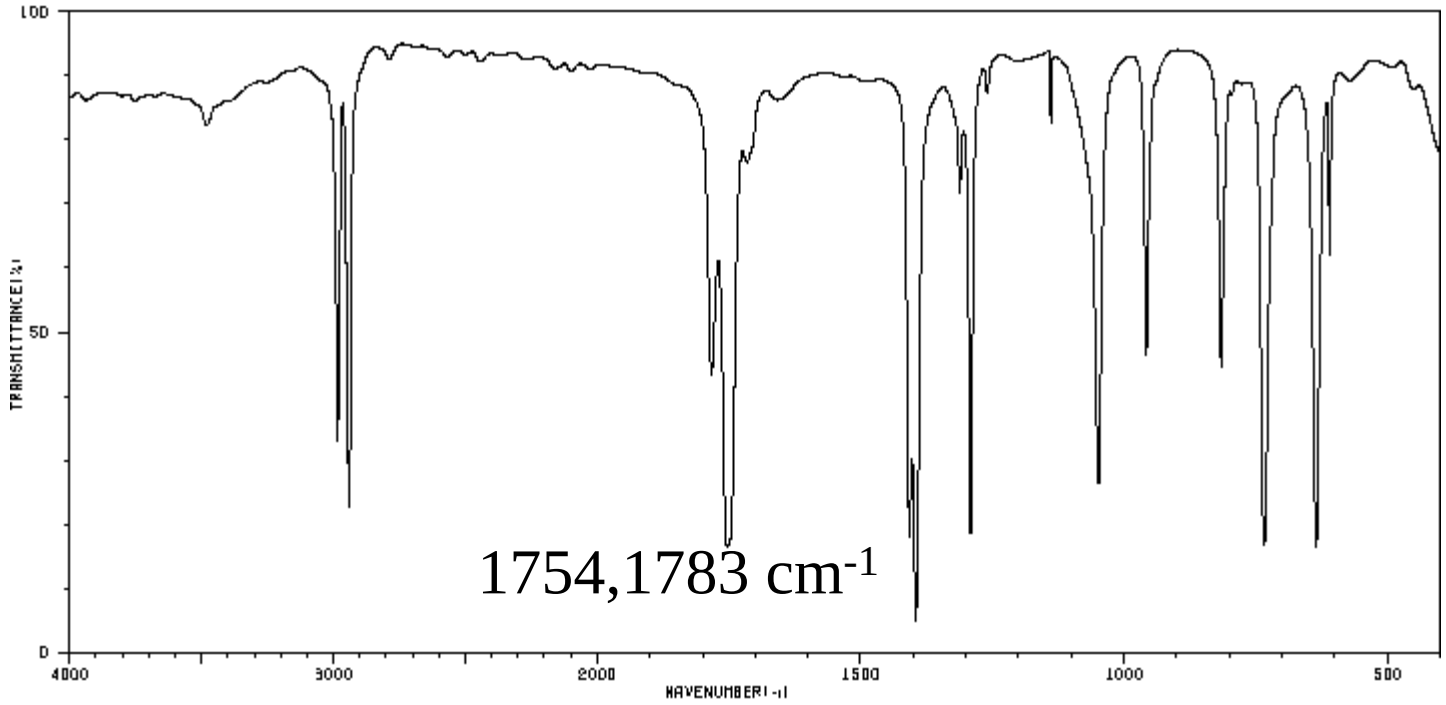
3602	84	1414	38	931	64	479	86
3011	58	1318	10	886	62		
2959	36	1301	17	791	32		
2848	77	1269	29	704	64		
1759	4	1203	8	698	66		
1568	84	1178	12	665	84		
1439	15	1007	29	572	60		



HIT-NO=1461	SCORE= ( )	SDBS-NO=1534	IR-NIDA-02596 : LIQUID FILM

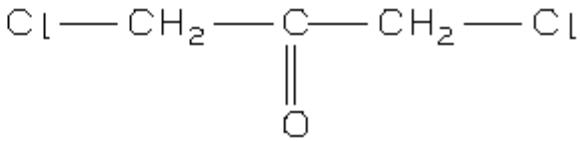
1,3-DICHLORO-2-PROPANONE

$C_3H_4CL_2O$



1754,1783 cm^{-1}

3480	79	1662	84	1049	25
2984	32	1408	17	958	44
2939	21	1398	4	816	43
1789	42	1312	68	734	16
1754	16	1292	18	636	16
1715	74	1260	84	611	80
1660	84	1140	79	670	86



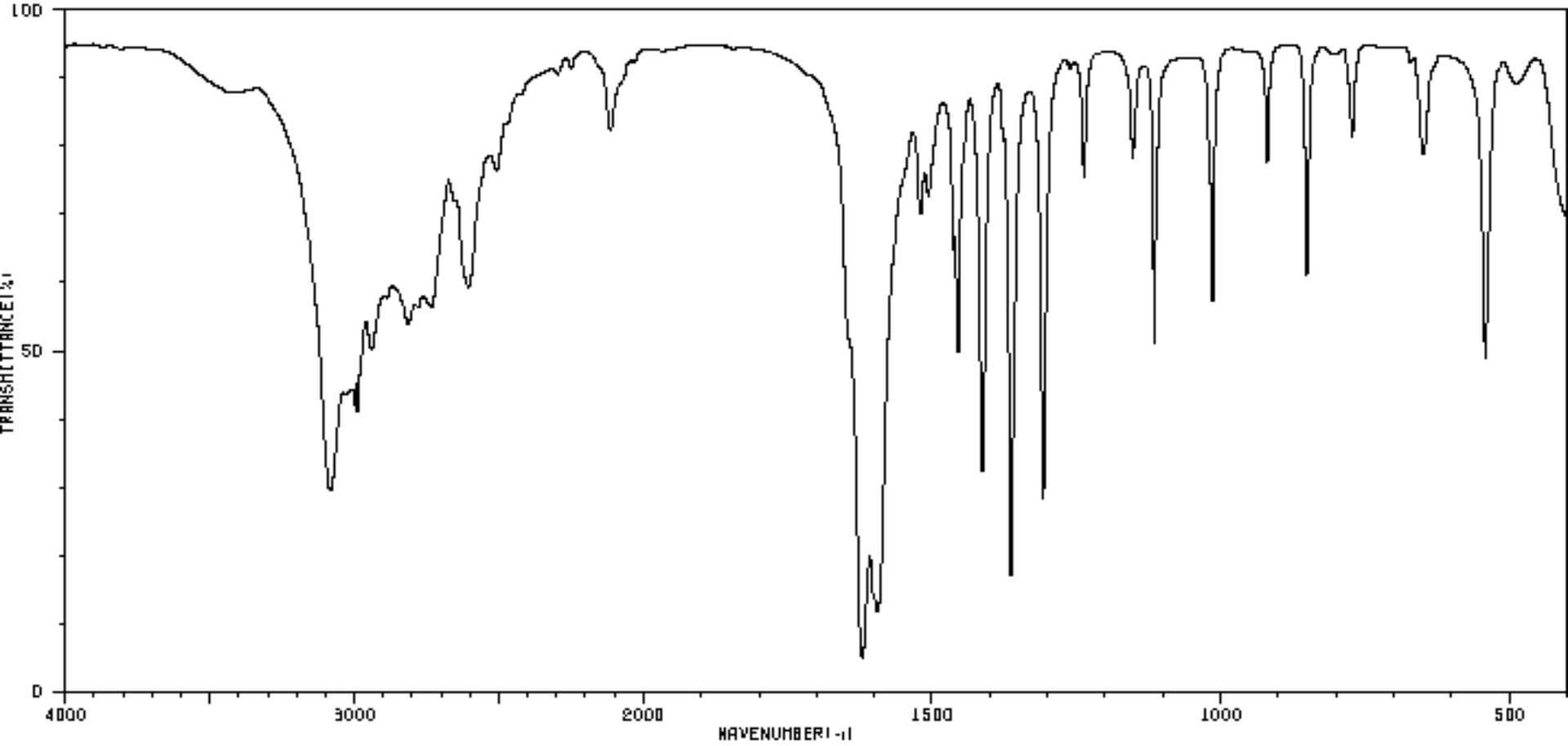
Factors affecting the frequency of infrared peaks

1. Resonance and conjugation
2. Ring strain:
    A: on carbonyl frequencies
    B. on C-H stretching frequencies
3. Halogens
    A: on carbonyl frequencies
    B. on C-H stretching frequencies
4. **Chirality**

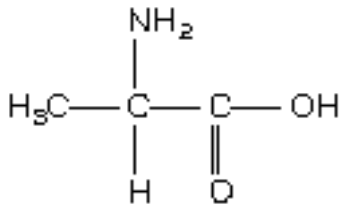
HIT-NO=1479	SCORE= ( )	SDBS-NO=1466	IR-NIDA-22117 : KBR DISC

D-ALANINE

$C_3H_7NO_2$



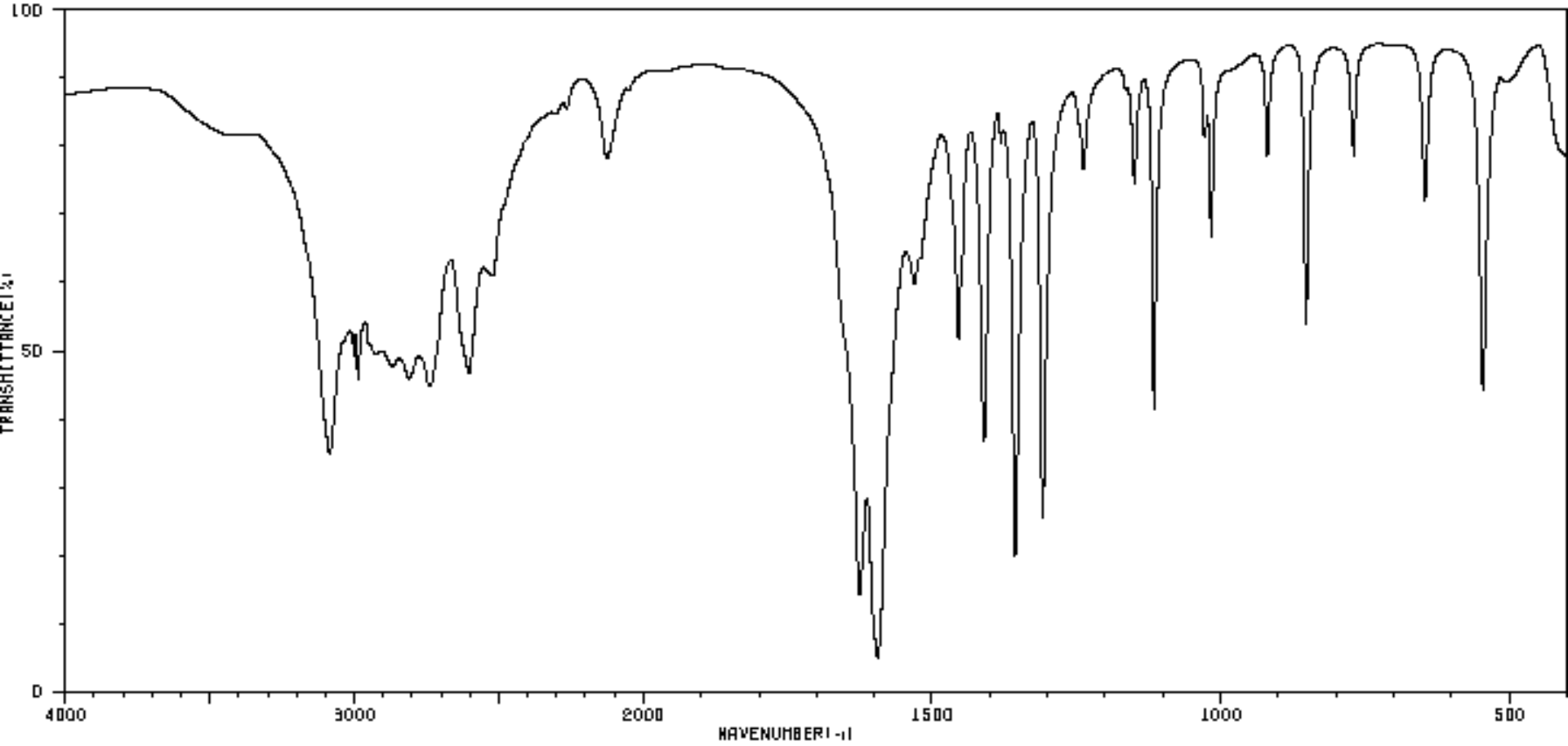
3082	26	2607	72	1466	47	1116	49	488	66
3000	41	2113	79	1413	31	1014	55
2989	39	1621	4	1378	77	919	74
2941	47	1594	11	1364	16	861	68
2816	52	1520	68	1308	26	773	79
2733	53	1505	70	1237	72	650	77
2604	67	1463	62	1163	74	542	47



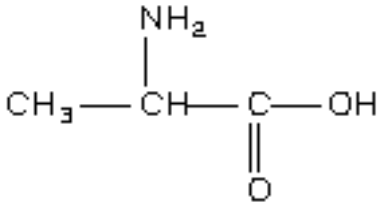
HIT-NO=1505	SCORE= ( )	SDBS-NO=1495	IR-NIDA-06483 : KBR DISC

DL-ALANINE

$C_3H_7NO_2$



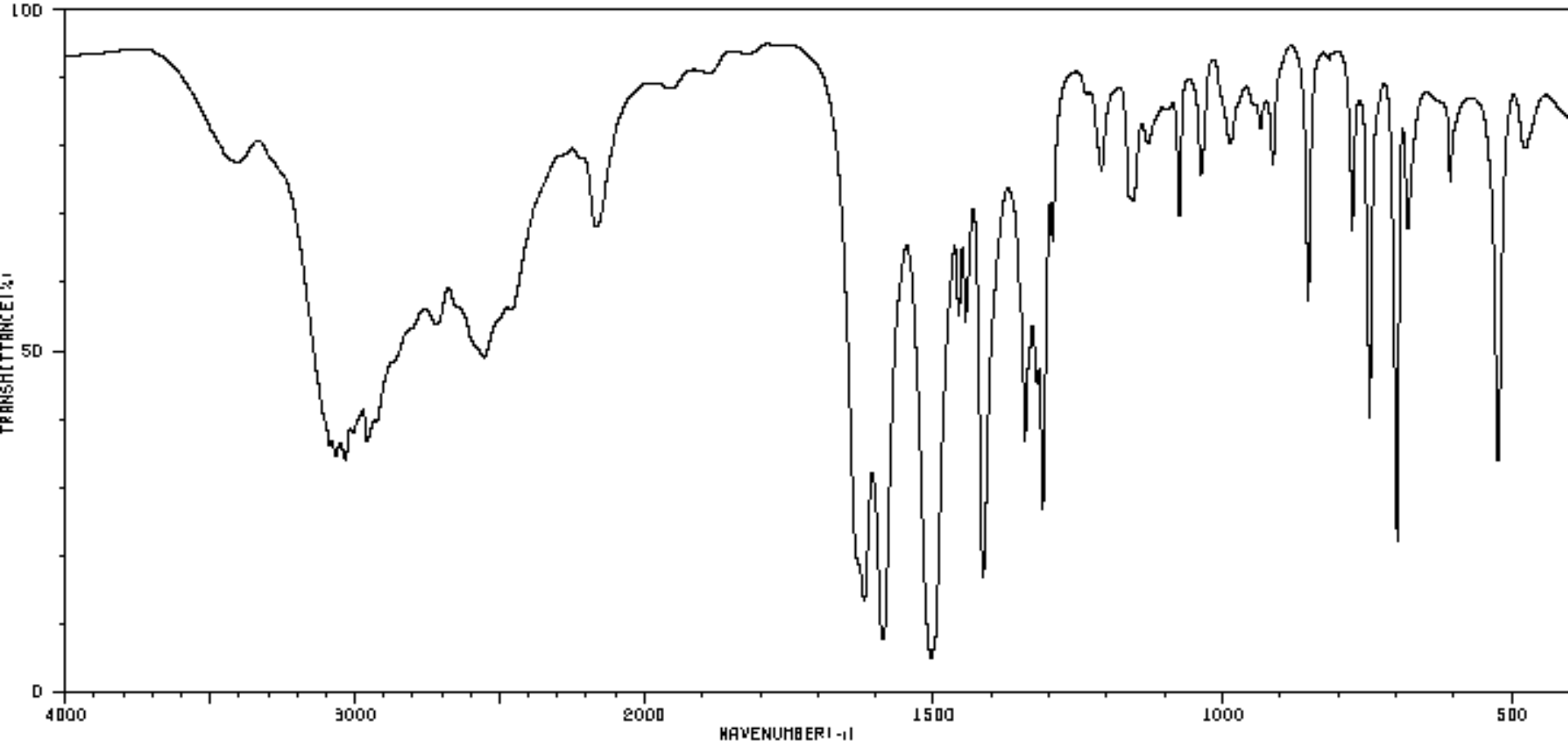
3086	33	2623	68	1381	77	1017	64
3003	47	2125	74	1357	19	919	77
2988	43	1628	15	1309	24	852	52
2866	46	1594	4	1238	74	770	77
2812	44	1531	57	1150	72	647	70
2736	43	1455	50	1116	39	546	42
2604	44	1410	36	1028	79		



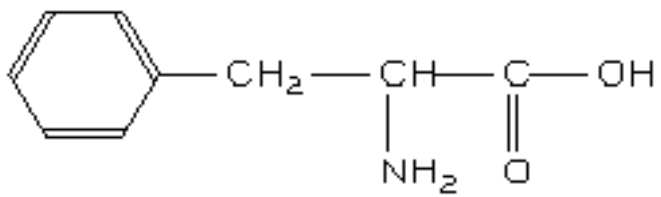
HIT-NO=2175	SCORE= ( )	SDBS-NO=2762	IR-NIDA-00479 : KBR DISC

DL-PHENYLALANINE

$C_9H_{11}NO_2$



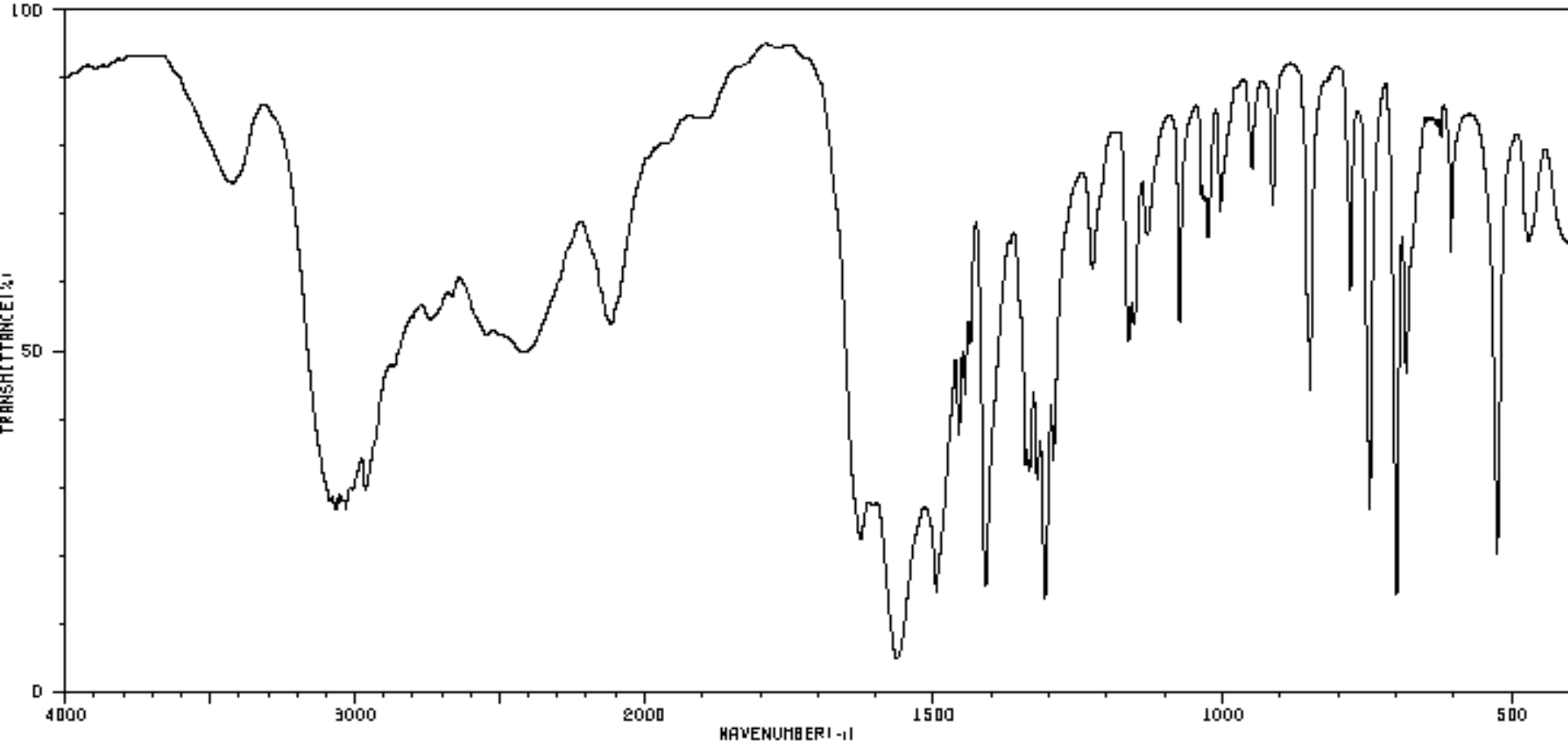
3412	74	2716	62	1444	62	1162	70	862	66
3401	74	2553	47	1414	16	1156	70	776	66
3066	33	2164	66	1342	35	1129	77	746	38
3062	36	1620	19	1321	43	1076	68	698	21
3032	33	1588	7	1311	26	1037	72	680	66
2956	35	1504	4	1295	64	986	77	607	72
2927	38	1466	59	1210	74	913	74	624	33



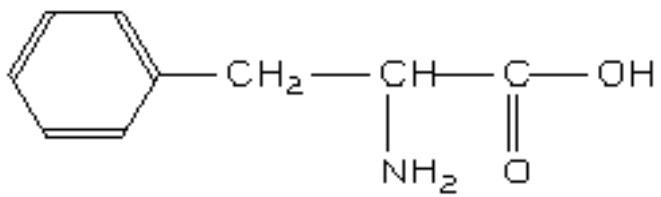
HIT-NO=1211	SCORE= ( )	SDBS-NO=994	IR-NIDA-24724 : KBR DISC

D-PHENYLALANINE

$C_9H_{11}NO_2$



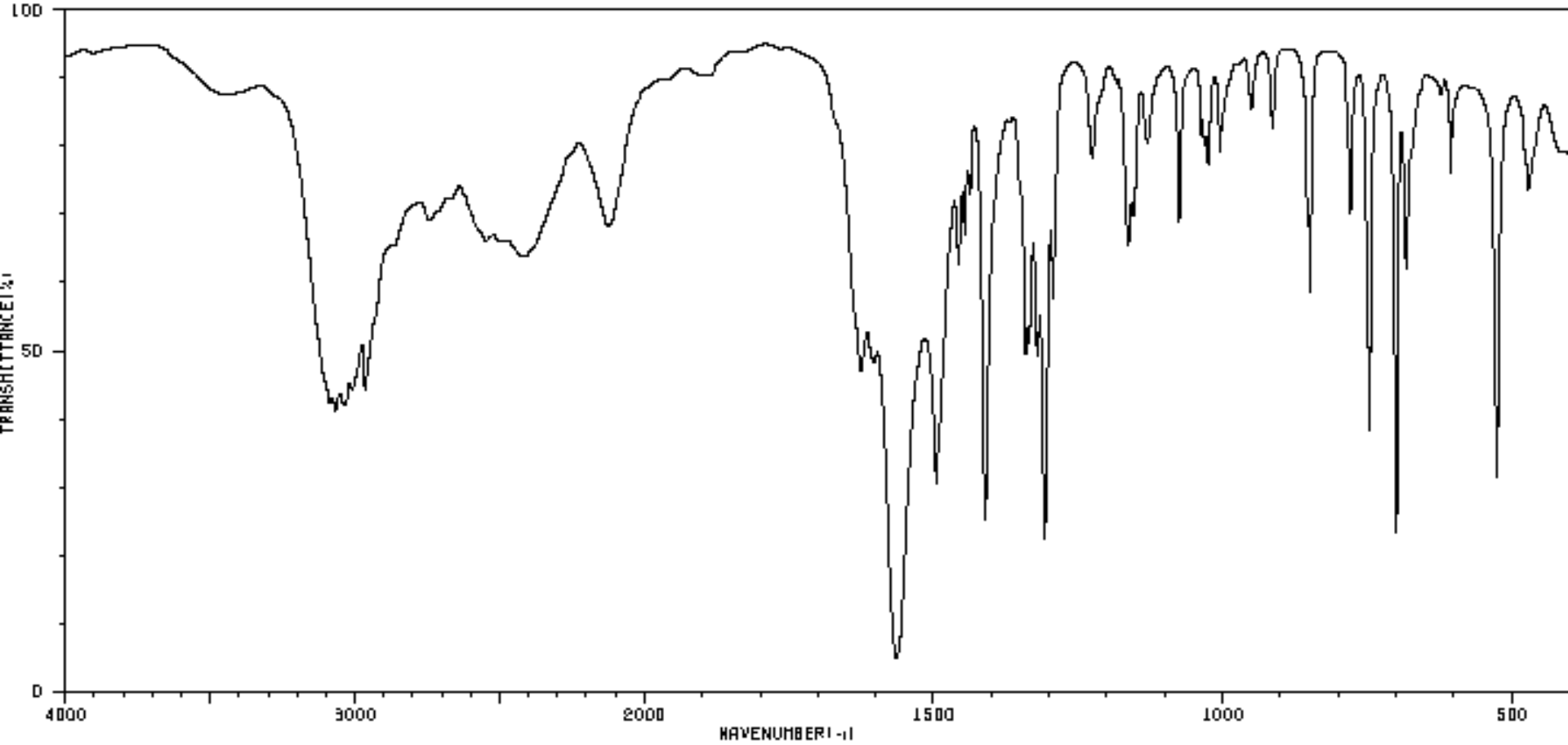
3067	26	1626	21	1341	32	1164	62	779	67
3056	27	1563	4	1335	31	1129	64	746	26
3031	26	1495	14	1321	30	1075	52	699	13
2964	28	1466	36	1307	13	1026	64	669	44
2741	53	1446	42	1293	33	1005	68	605	62
2416	47	1437	49	1226	60	913	68	525	20
2113	62	1410	16	1163	60	849	49	471	64



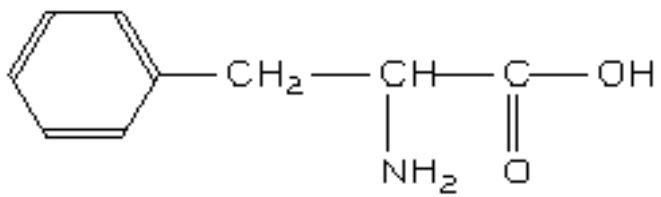
HIT-NO=1341	SCORE= ( )	SDBS-NO=1165	IR-NIDA-62222 : KBR DISC

L-PHENYLALANINE

$C_9H_{11}NO_2$



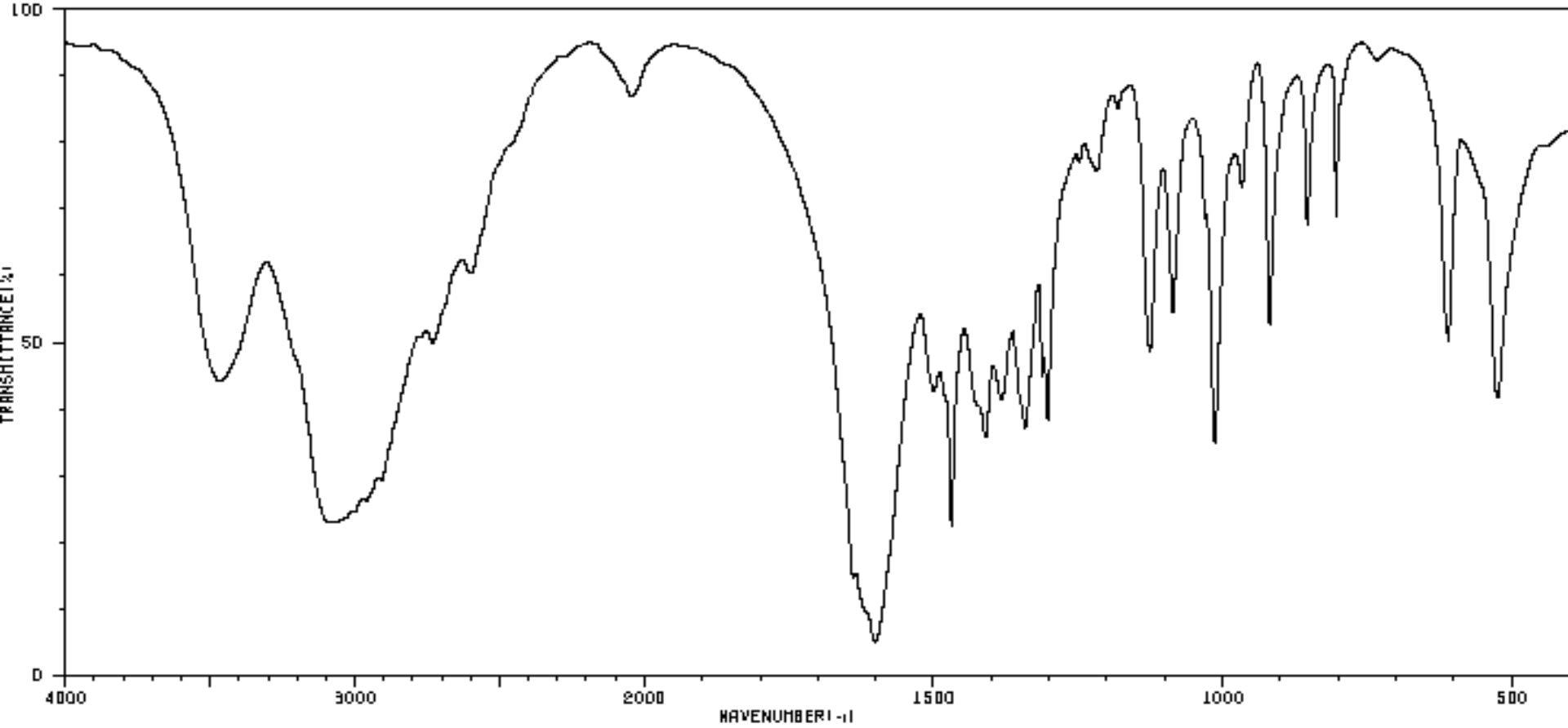
3088	41	2412	62	1446	64	1294	66	779	68
3067	39	2125	66	1437	70	1226	74	746	37
3053	42	1628	46	1411	24	1164	62	700	22
3036	41	1603	46	1341	47	1166	68	689	60
2964	43	1564	4	1336	49	1075	66	605	72
2740	66	1495	29	1321	47	1025	74	526	30
2728	68	1466	60	1308	21	849	67	471	70



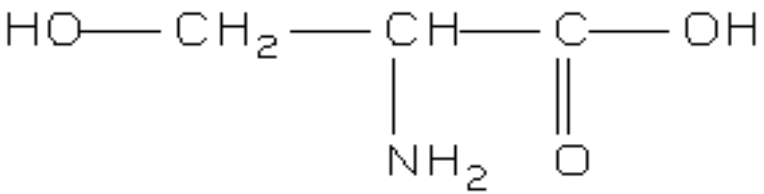
HIT-NO=1250	SCORE= ( )	SDBS-NO=1056	IR-NIDA-62992 : KBR DISC

L-SERINE

$C_3H_7NO_3$



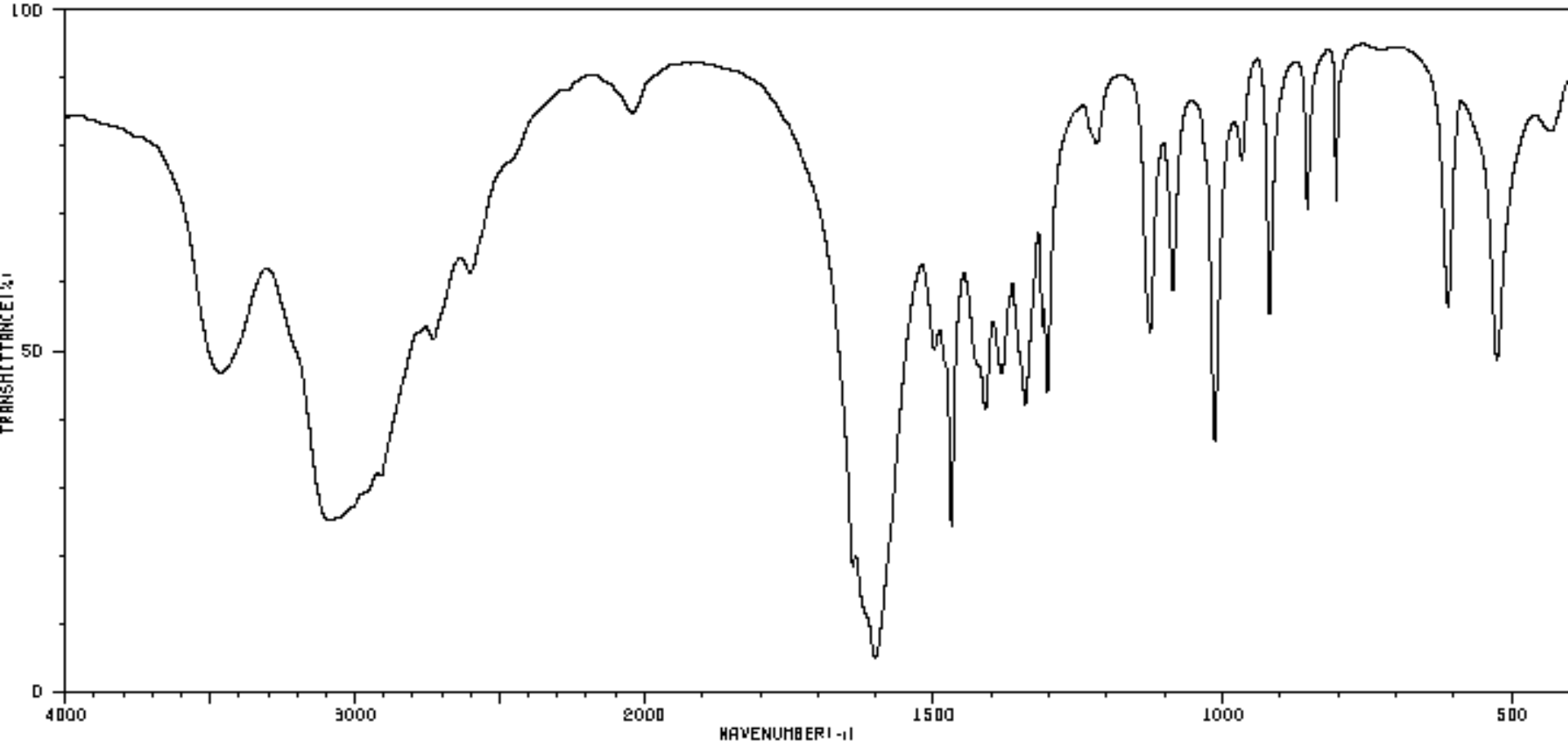
3466	42	1499	41	1303	37	967	70
3072	22	1470	21	1248	74	918	50
3062	22	1423	36	1216	72	854	64
2730	47	1411	34	1182	81	804	66
2600	58	1383	39	1126	46	610	47
2043	84	1342	35	1086	52	526	39
1601	4	1312	43	1013	33		



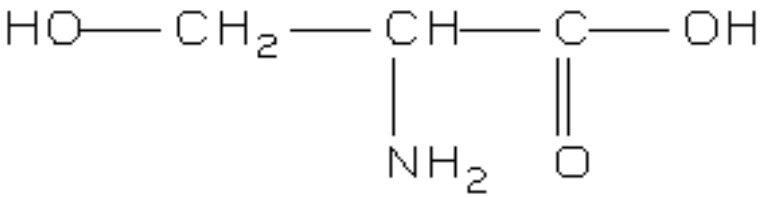
HIT-NO=2843	SCORE= ( )	SDBS-NO=3927	IR-NIDA-01554 : KBR DISC

D-SERINE

$C_3H_7NO_3$



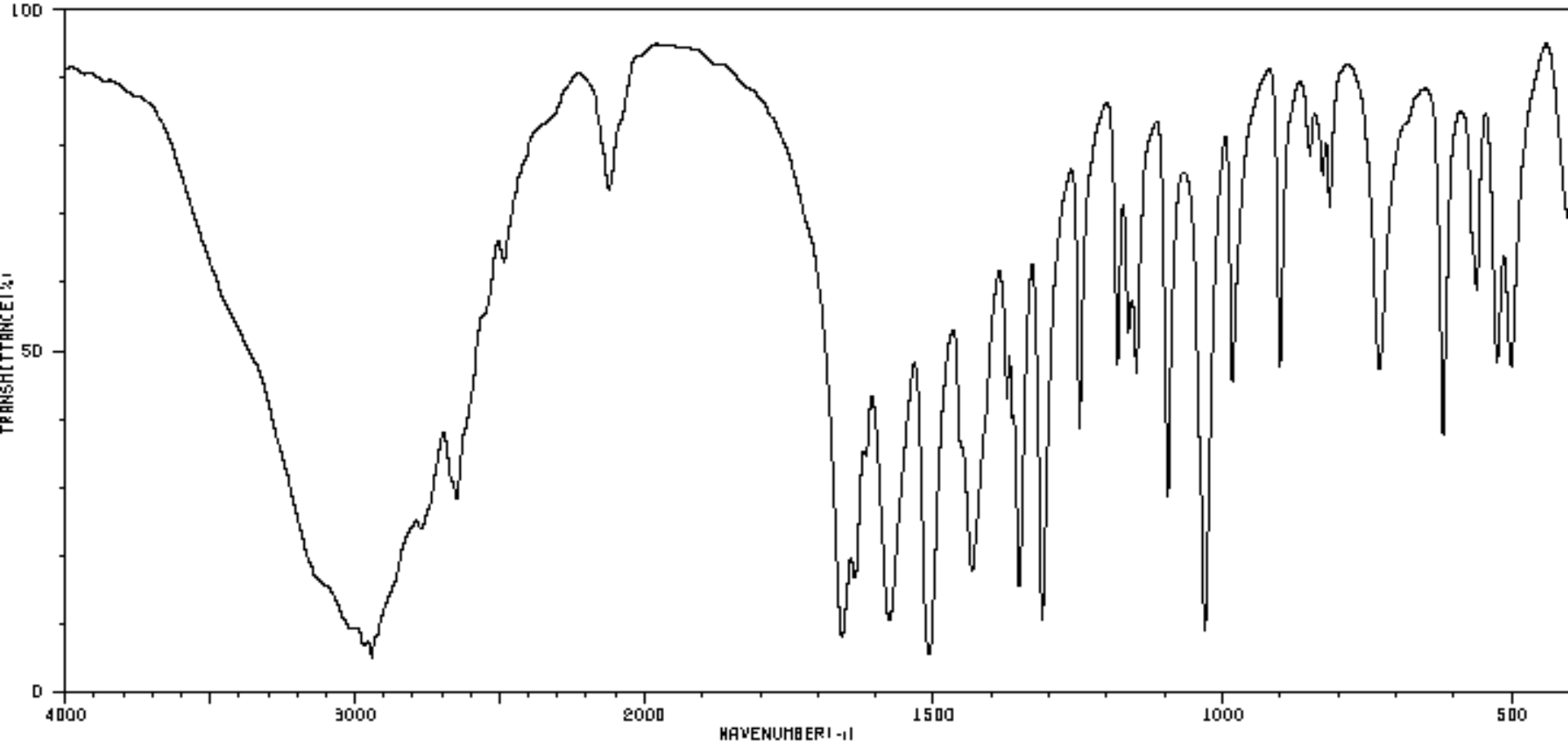
3466	44	1600	4	1303	42	863	68
3083	23	1499	49	1218	77	804	70
3072	24	1470	25	1126	50	611	59
2729	49	1411	39	1086	67	526	46
2601	58	1383	44	1014	35	434	79
2040	81	1342	41	967	74		
1640	17	1312	62	919	63		



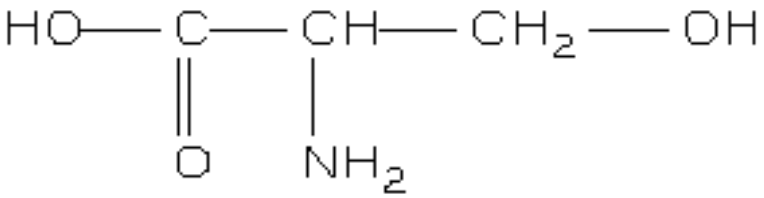
HIT-NO=1596	SCORE= ( )	SDBS-NO=1634	IR-NIDA-62972 : KBR DISC

DL-SERINE

$C_3H_7NO_3$



2970	6	2121	70	1364	38	1096	27	729	46
2956	7	1658	7	1352	14	1031	8	619	36
2942	4	1637	16	1312	10	983	45	561	57
2770	23	1577	10	1248	37	901	46	526	46
2665	29	1509	5	1182	46	849	77	501	46
2648	26	1434	17	1164	50	827	72		
2484	60	1373	41	1160	44	816	68		



NON-AROMATIC AMINO ACIDS

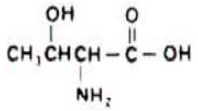
T3422-3 *CAS [6028-28-0]*
DL-Threonine

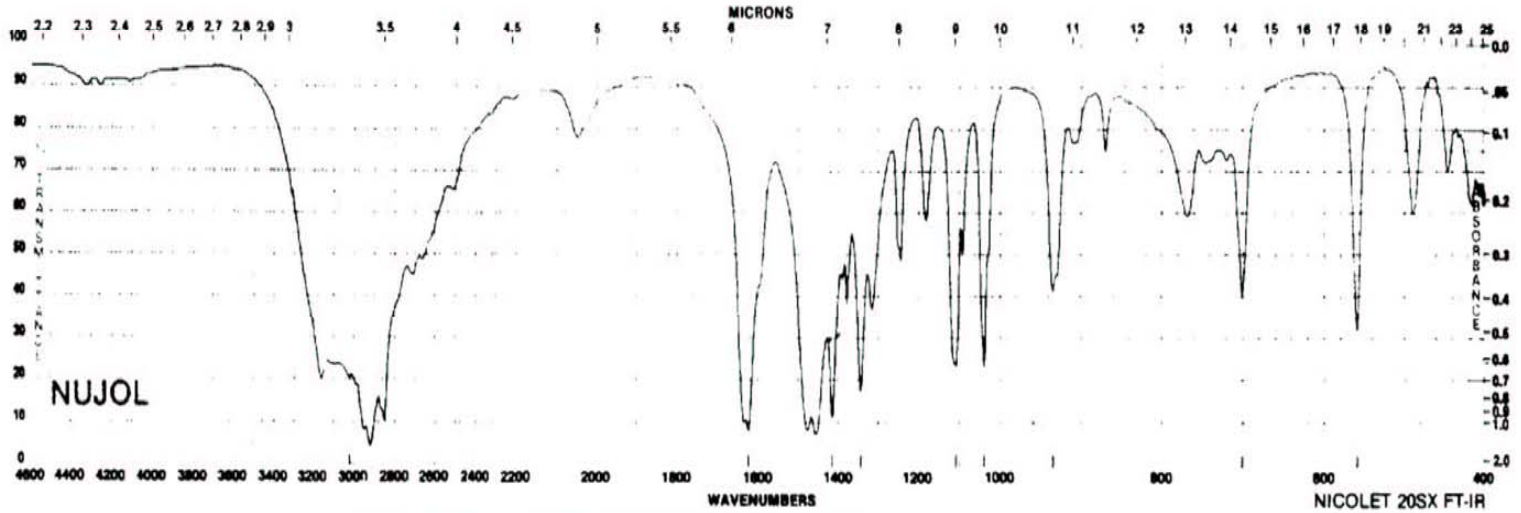
FW 119.12
mp 244°C (dec.)

IR III, 346G
NMR II, 1,492C
Merck 10,9229

3026.3 1347.4 936.3
1626.5 1111.6 702.9
1417.7 1041.3 560.9

A





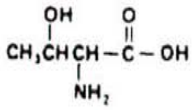
T3420-7 *CAS [72-19-5]*
L-Threonine, 98%

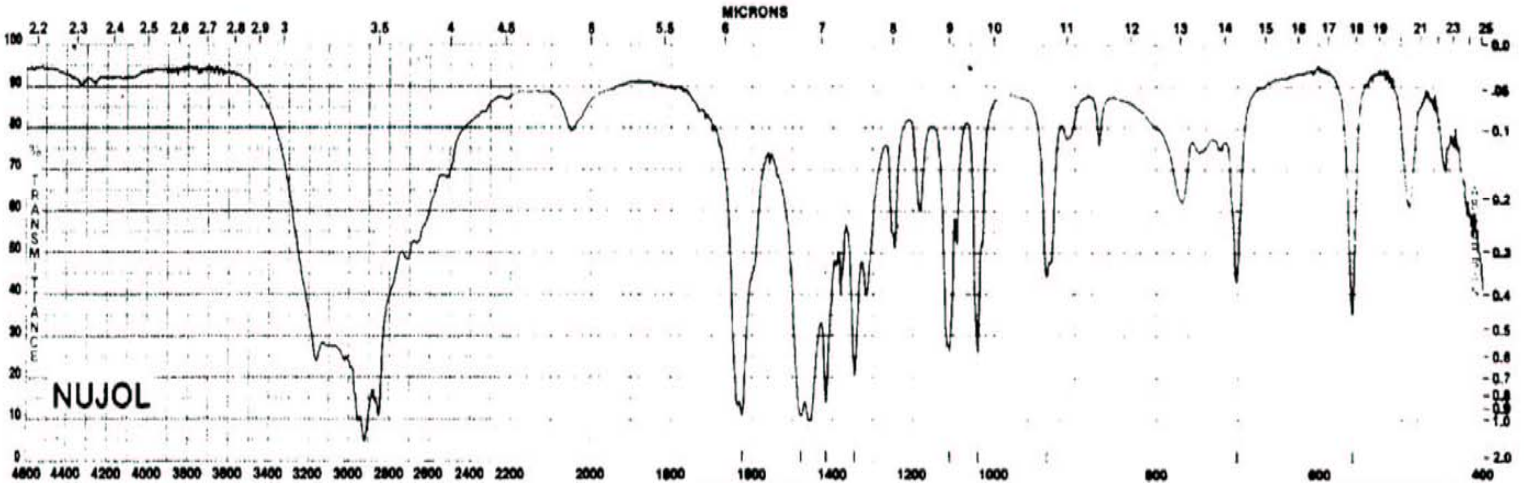
FW 119.12
mp 270°C (dec.)

IR III, 347C
NMR II, 1,492D
Merck 10,9229

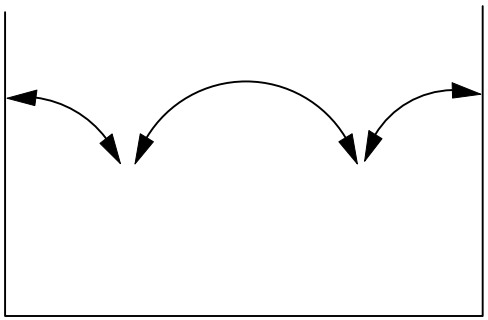
1626.4 1347.5 936.2
1480.1 1111.5 702.9
1417.8 1041.1 560.7

A

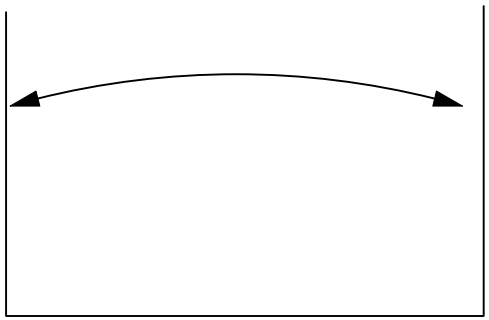




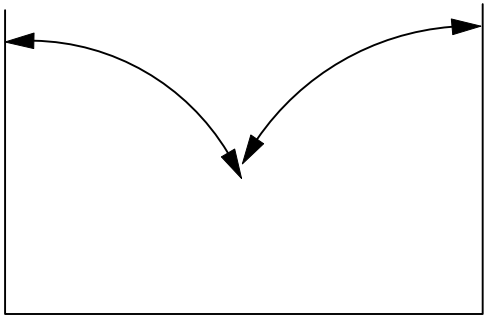
Why the big differences between D-serine and DL-serine?



d *l*



d

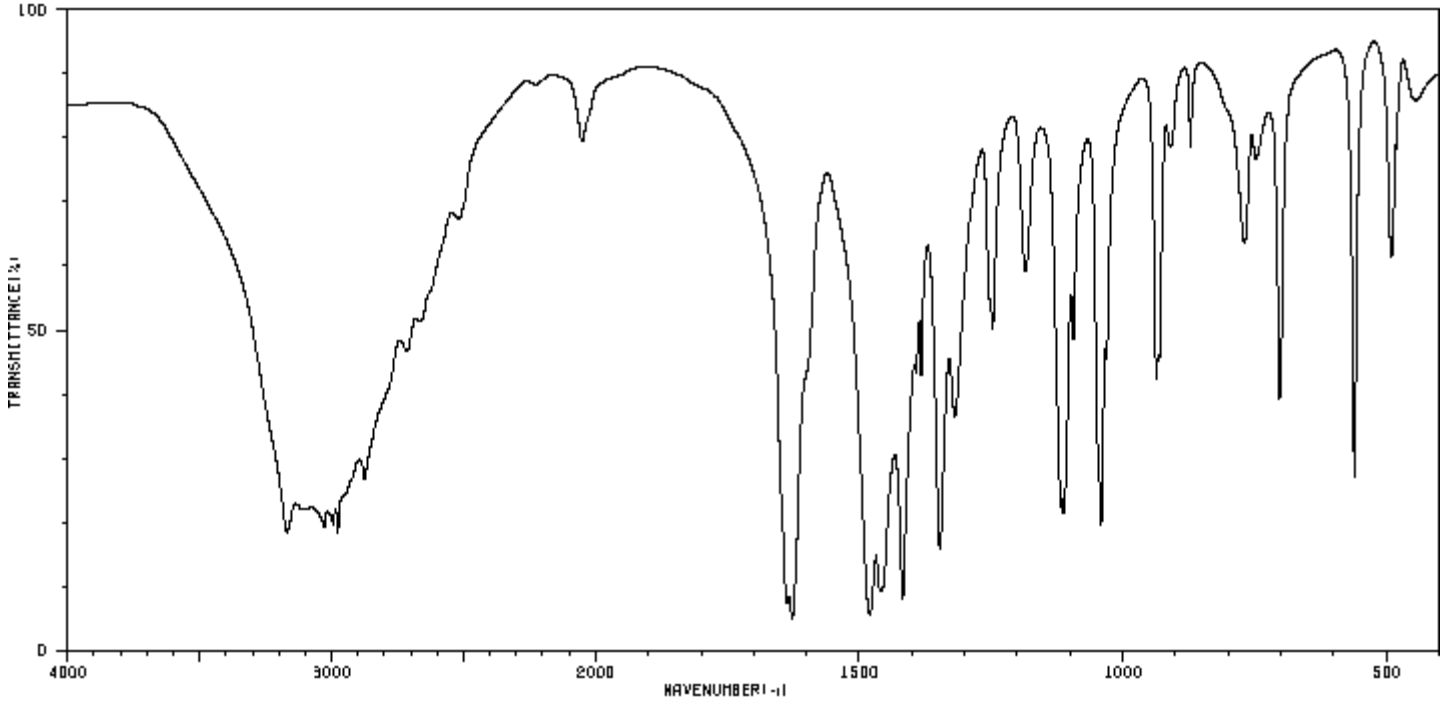


d *l*

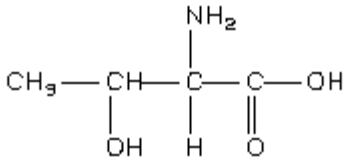
HIT-NO=1272	SCORE= ( )	SDBS-NO=1079	IR-NIDA-03957 : KBR DISC

L-THREONINE

$C_4H_9NO_3$



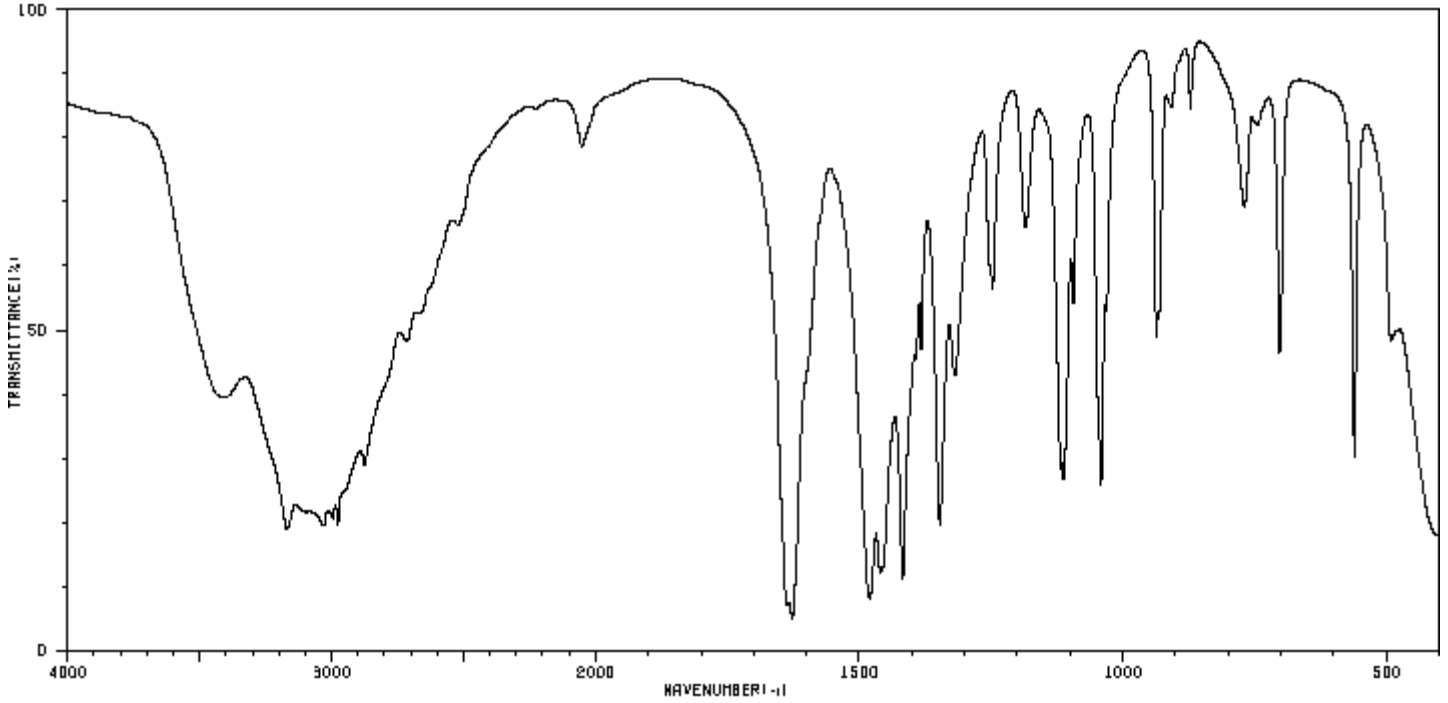
3168	17	2061	77	1382	41	1112	20	872	74
3027	18	1637	7	1348	15	1094	46	770	60
2996	16	1627	4	1319	35	1041	18	748	74
2976	17	1480	6	1264	62	1031	49	709	37
2874	25	1460	8	1247	47	937	41	561	26
2714	44	1418	7	1185	57	931	45	491	56
2617	64	1393	42	1118	21	909	77	481	74



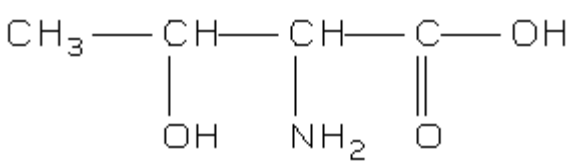
HIT-NO=2673	SCORE= ( )	SDBS-NO=3650	IR-NIDA-01286 : KBR DISC

D-THREONINE

$C_4H_9NO_3$



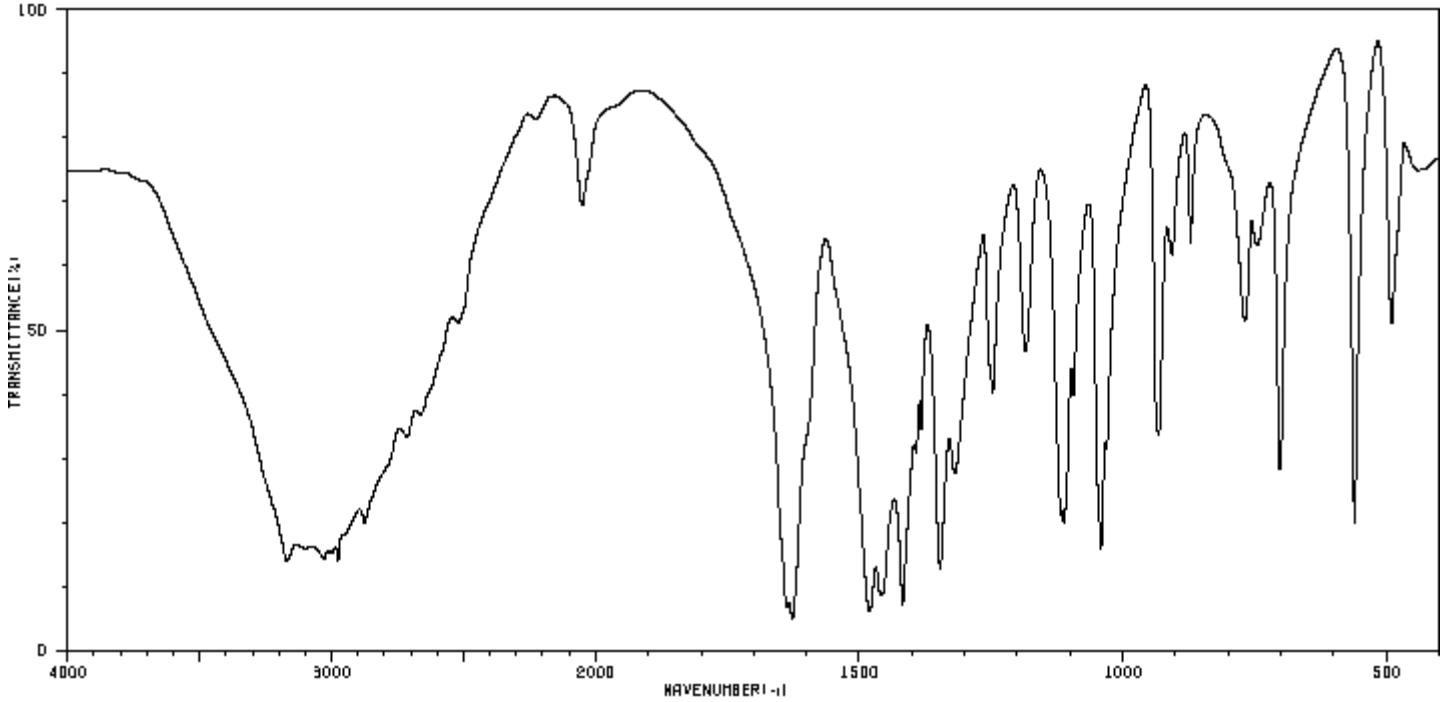
3415	37	2716	46	1382	44	1112	26	872	61
3405	37	2051	77	1348	18	1094	52	770	66
3169	16	1637	6	1319	41	1041	24	746	79
3029	18	1627	4	1263	67	1031	50	709	44
2995	20	1480	7	1247	53	937	47	561	28
2976	16	1459	11	1185	64	931	50	492	46
2874	27	1418	10	1118	26	908	81		



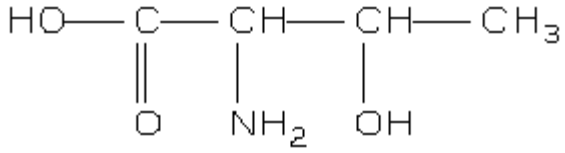
HIT-NO=1597	SCORE= ( )	SDBS-NO=1635	IR-NIDA-04373 : KBR DISC

DL-THREONINE

$C_4H_9NO_3$



3169	13	1627	4	1319	26	1031	30	661	19
3028	13	1480	6	1247	38	932	32	491	49
2976	13	1458	6	1185	44	907	58	461	60
2874	19	1418	6	1118	20	871	60	439	72
2713	32	1393	29	1112	19	769	49	434	72
2051	66	1382	33	1094	38	745	60	429	72
1637	6	1347	12	1041	15	703	26		



Some Examples of Conglomerates

Asparagine

Threonine

Glutamic Acid

Serine Anhydride

N-Acetylproline

Factors affecting the frequency of infrared peaks

1. Resonance and conjugation

2. Ring strain:

    A: on carbonyl frequencies

    B. on C-H stretching frequencies

3. Halogens

    A: on carbonyl frequencies

    B. on C-H stretching frequencies

4. Chirality

5. **Phase: solid, liquid and gas (fundamentals in the gas phase are shifted to higher frequencies) ie. solvent or solute interactions lead to weakening of force constants; effects of H-bonding.**

Effects of H-bonding

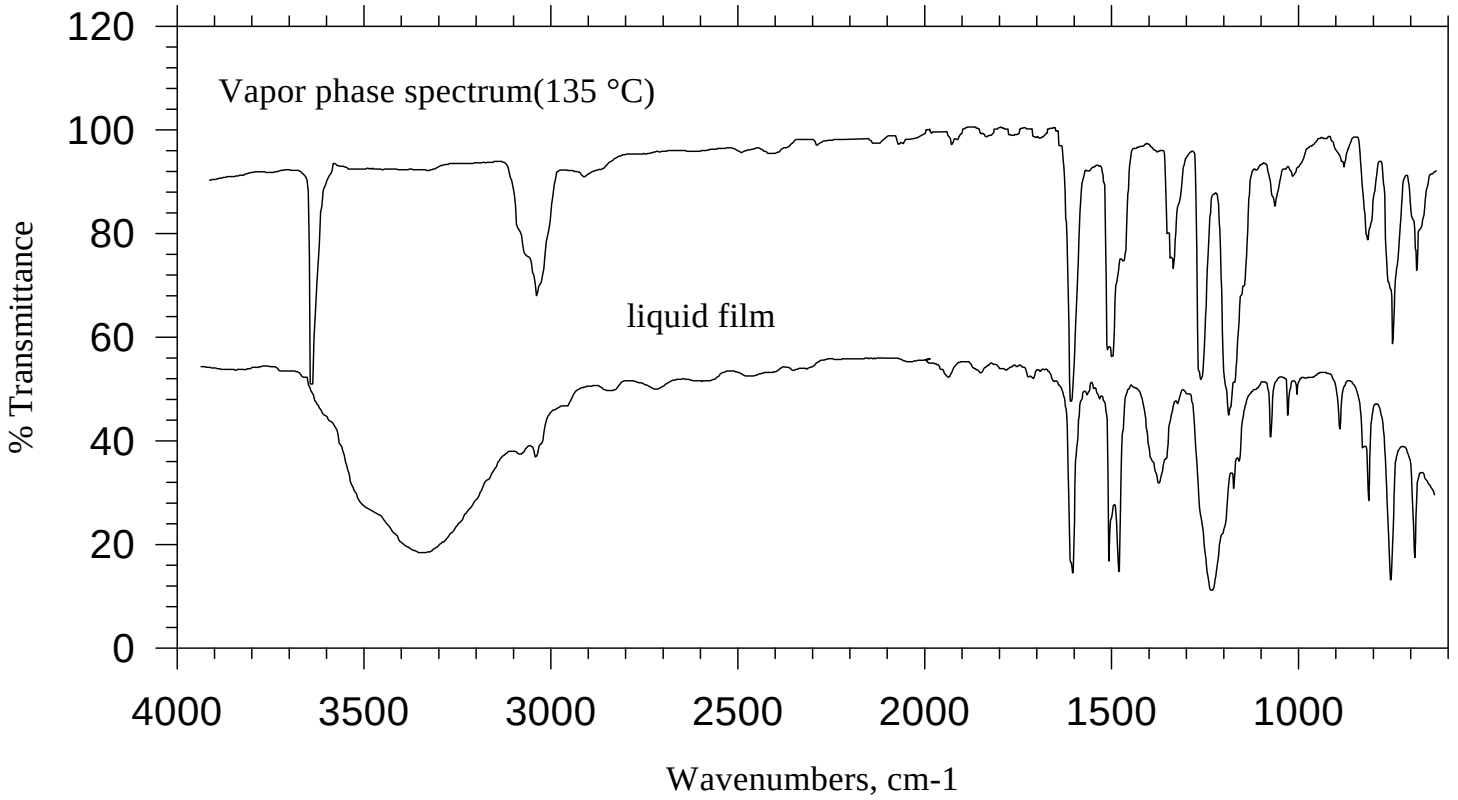
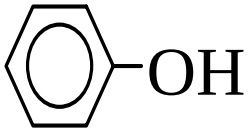
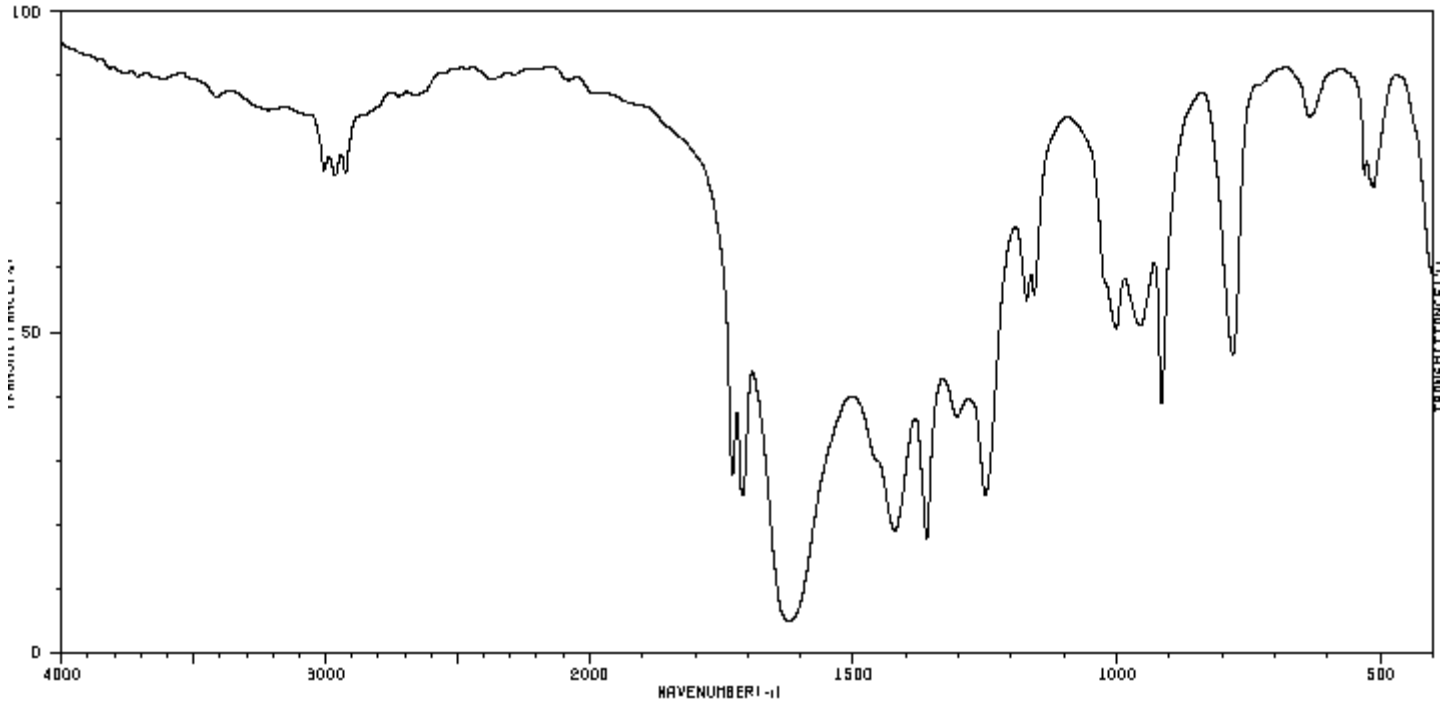


Figure IR-25. The liquid and vapor spectra of phenol. 

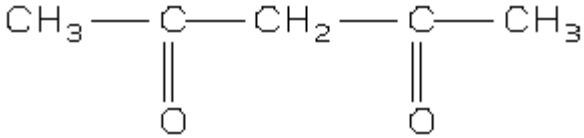
HIT-NO=1274	SCORE= ( )	SDBS-NO=1030	IR-NIDA-24815 : LIQUID FILM

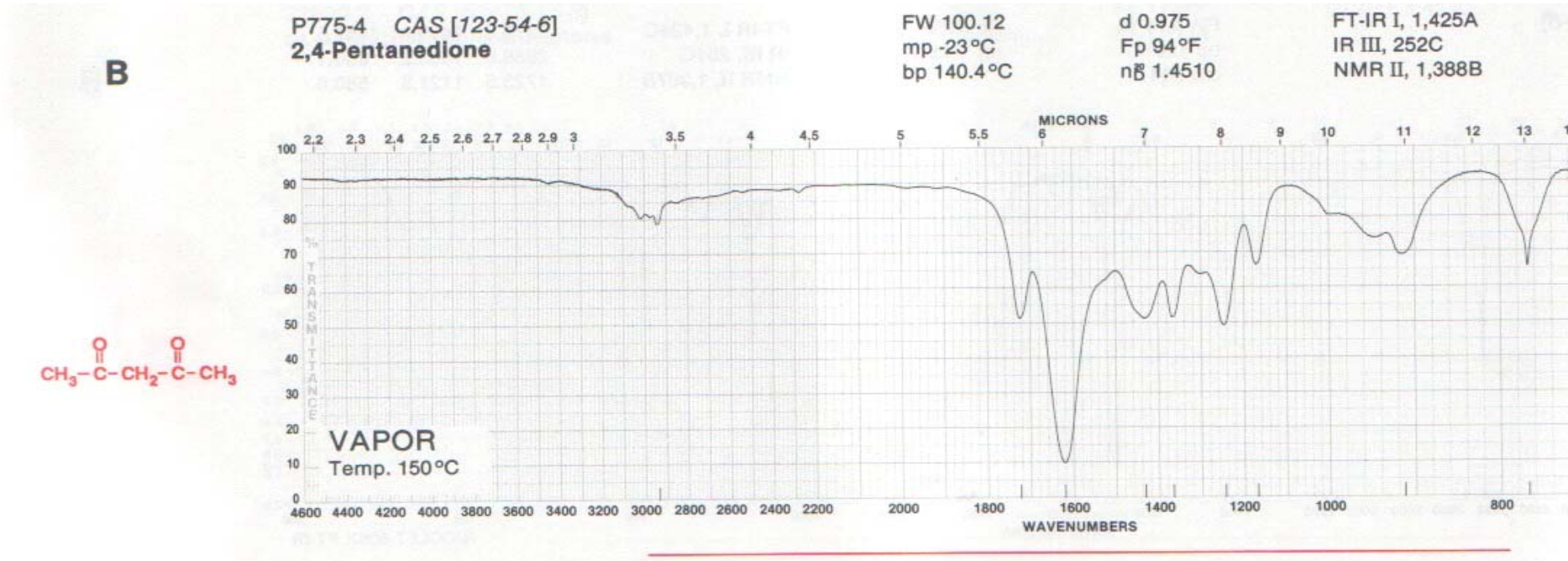
2,4-PENTANEDIONE

$C_5H_8O_2$



3006	72	1422	18	956	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	59	519	70
1622	4	1001	49	512	70





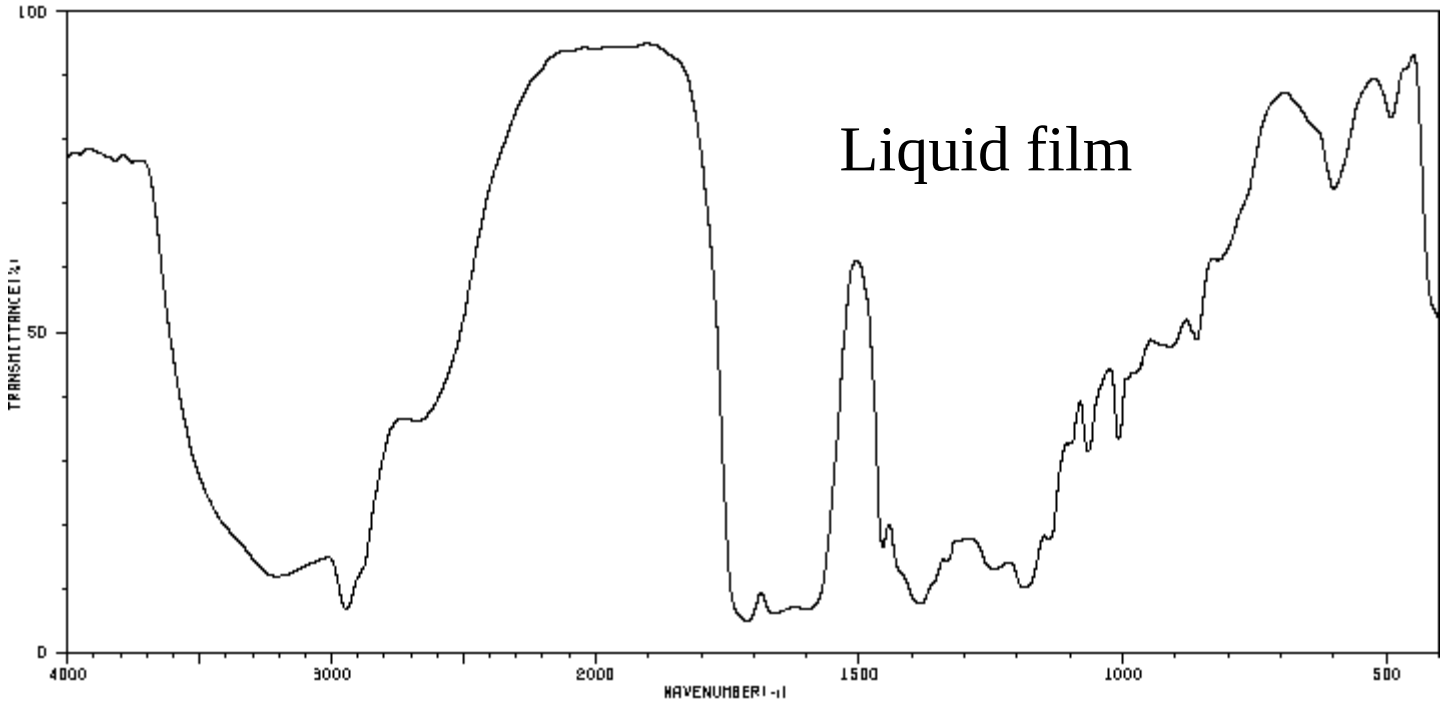
Gas Phase FT-IR spectrum of 2,4-pentanedione, Aldrich Chemical Co.

Effect of Phase

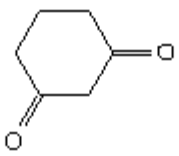
HIT-NO=4015	SCORE= ( )	SDBS-NO=10165	IR-NIDA-66083 : LIQUID FILM

1,3-CYCLOHEXANEDIONE

$C_6H_8O_2$



2946	6	1066	30
1711	4	1008	32
1455	16	860	47
1391	7	607	70
1385	7	602	70
1193	10	491	79
1186	10		

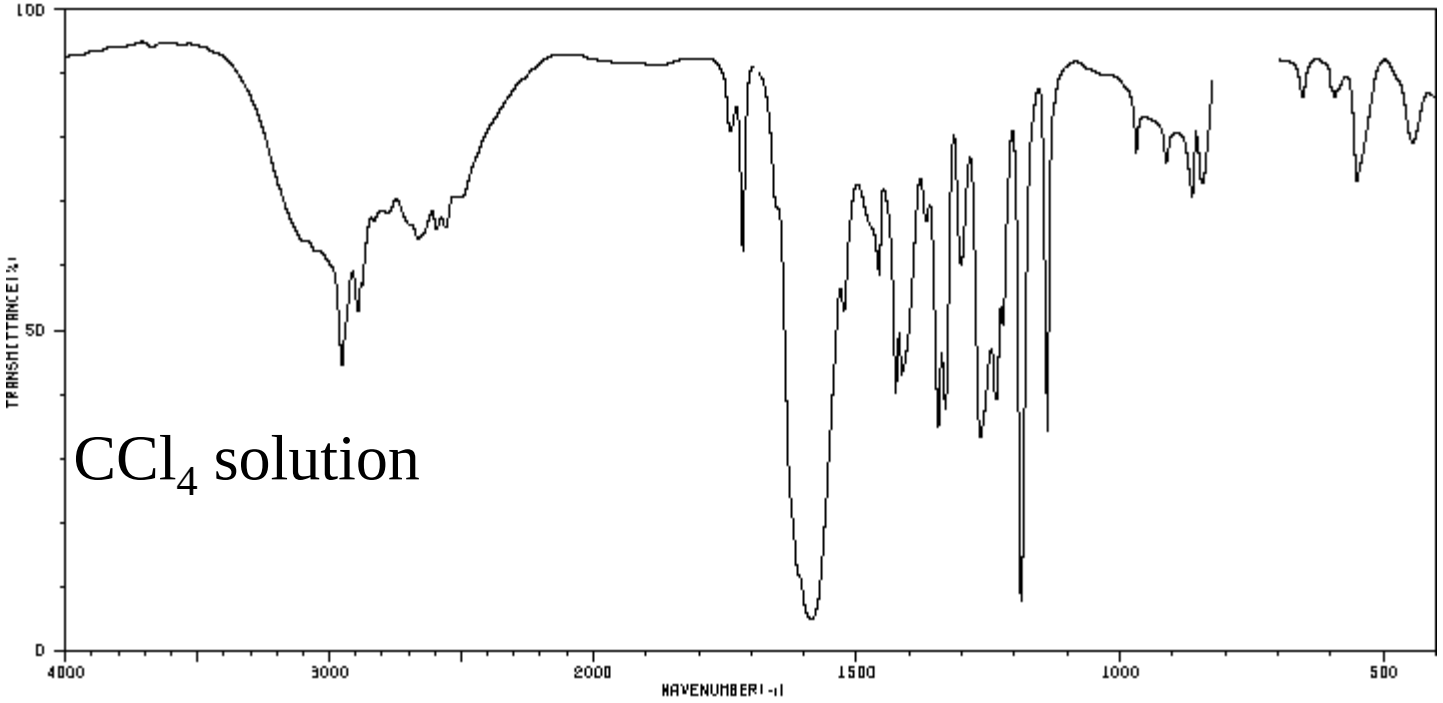


Effect of Phase

HIT-NO=597	SCORE= ( )	SDBS-NO=10165	IR-NIDA-07243 : CCL4 SOLUTION

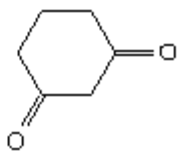
1,3-CYCLOHEXANEDIONE

$C_6H_8O_2$



CCl_4 solution

2962	43	1739	79	1426	38	1236	37	845	70
2893	50	1728	81	1415	42	1222	49	654	84
2874	55	1718	60	1369	64	1188	7	648	64
2665	62	1696	96	1346	34	1138	39	593	84
2592	64	1586	4	1332	36	970	74	551	70
2570	64	1524	50	1302	58	912	72	543	72
2559	64	1466	57	1265	32	863	68	445	77

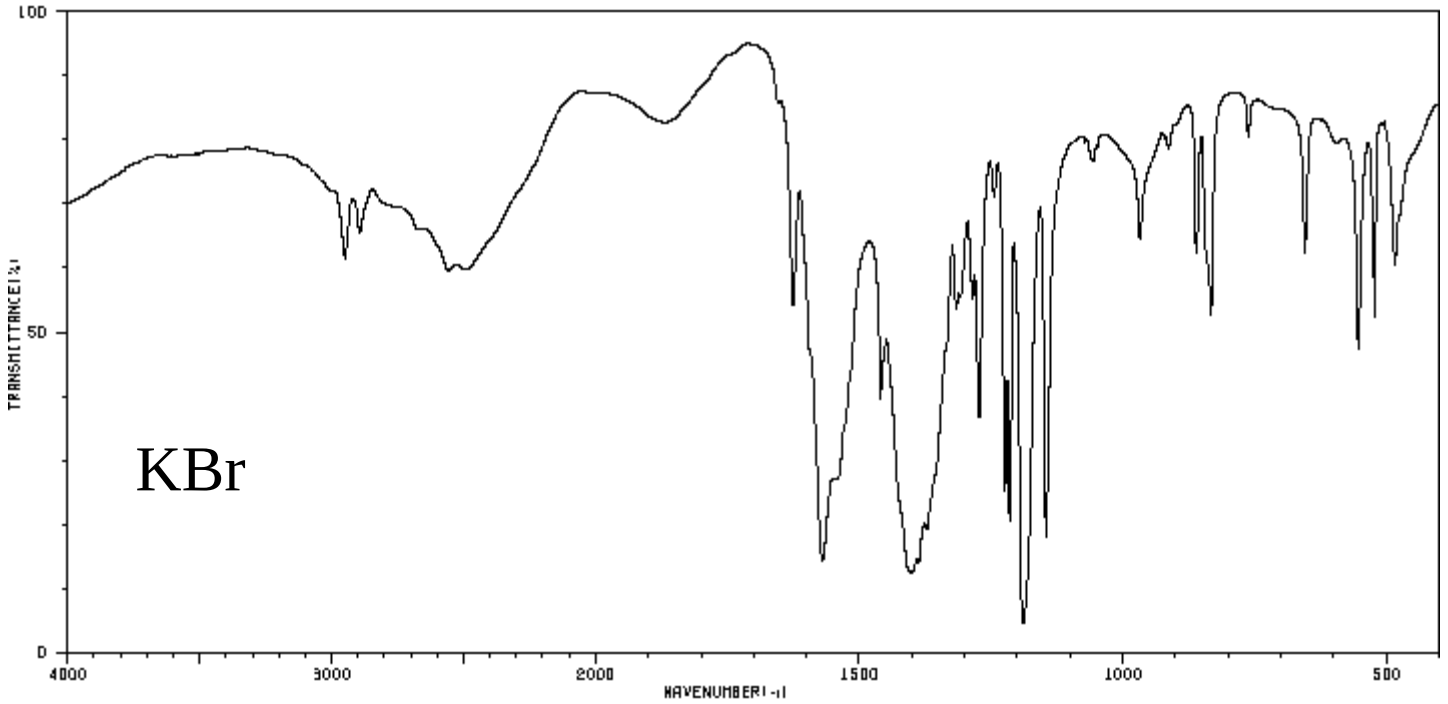


Effect of Phase

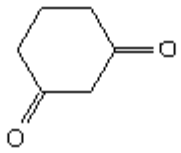
HIT-NO=5280	SCORE= ( )	SDBS-NO=10165	IR-NIDA-02351 : KBR DISC

1,3-CYCLOHEXANEDIONE

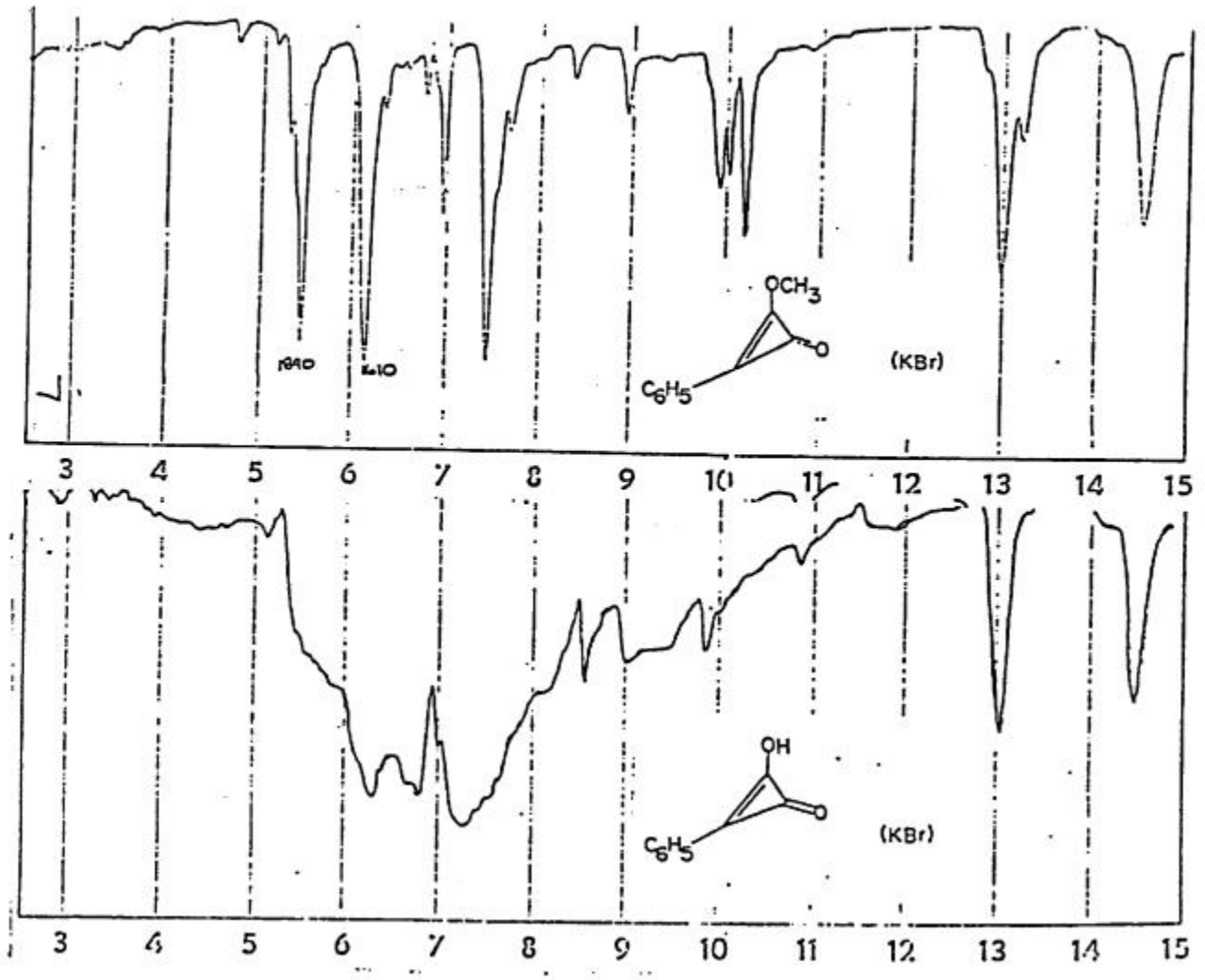
$C_6H_8O_2$



2949	60	1387	14	1224	25	968	62	623	60
2894	64	1371	19	1215	20	913	77	485	58
2557	56	1317	52	1190	4	861	60		
1625	63	1308	69	1146	18	833	52		
1570	14	1285	53	1063	77	762	77		
1460	36	1273	36	1056	74	655	60		
1402	12	1244	68	1048	77	564	46		



Effects of H-bonding



2000 1000

cm^{-1}

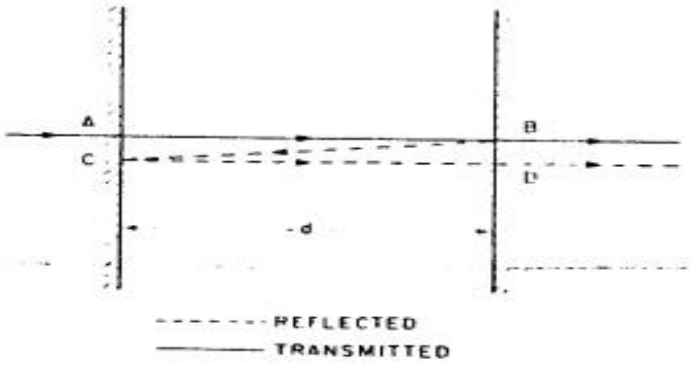


Fig. 3-1 - Path of radiation between the inner surfaces of a film or cell. Path of reflected radiation is drawn at an angle to separate it from that transmitted.

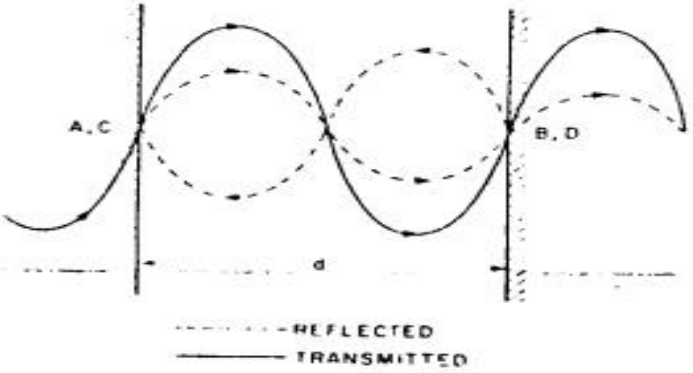


Fig. 3-2 - Wave patterns for transmitted and reflected portions of radiation when cell thickness, d, is such that 2d = m λ, the in-phase condition for a fringe maximum. The reflected radiation, as finally transmitted, is in phase with that transmitted directly.

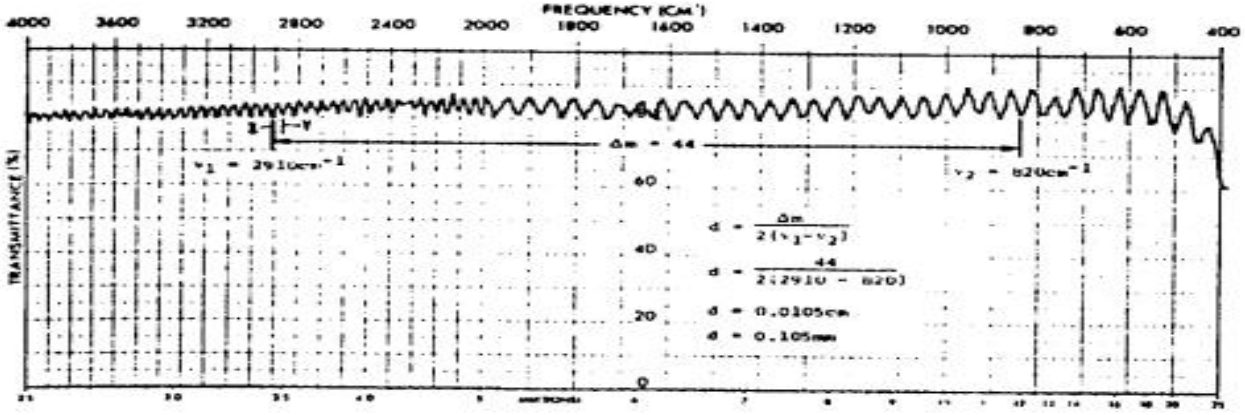
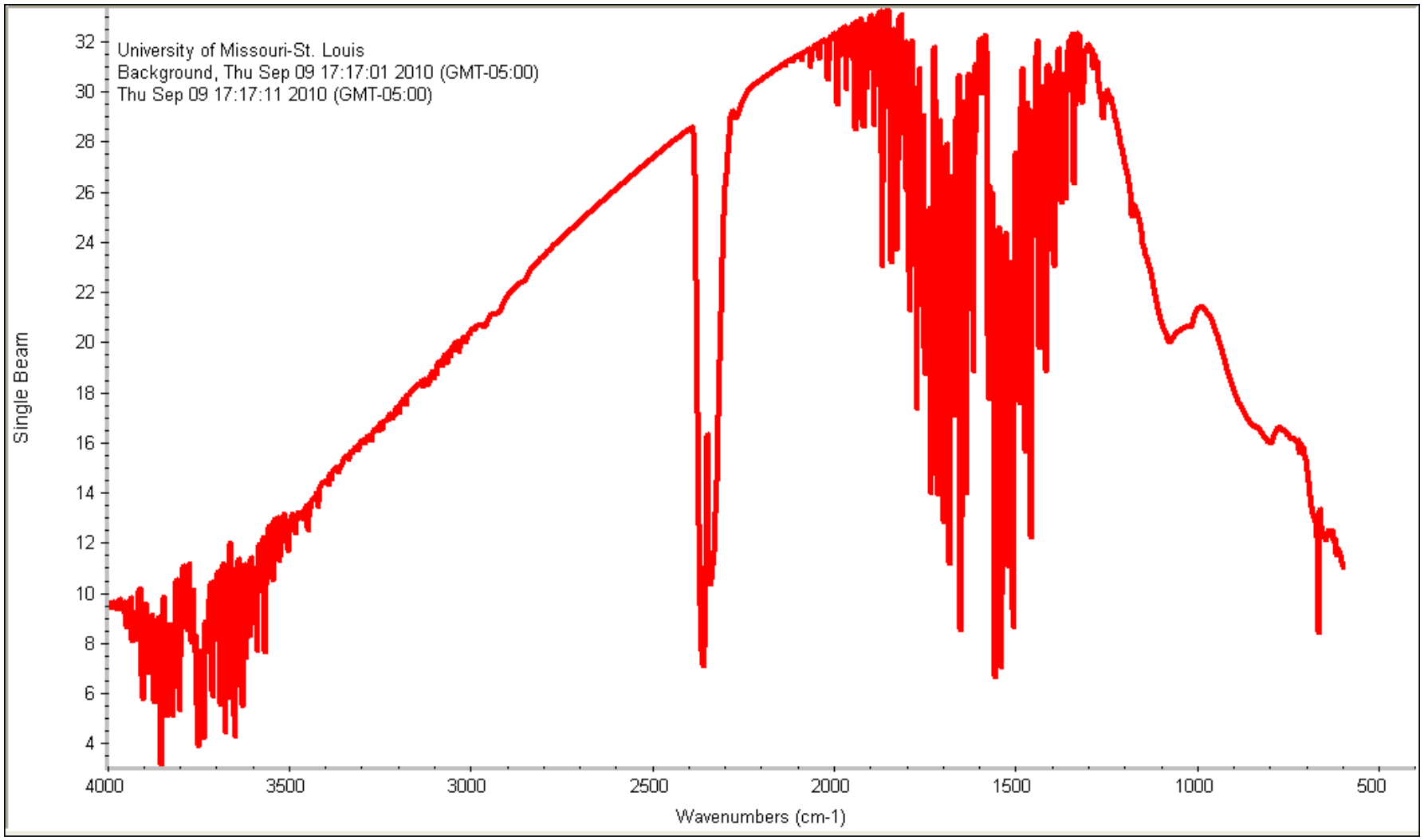


Fig. 3-3 - Fringe pattern obtained for an empty 0.1 mm thick sealed KBr cell

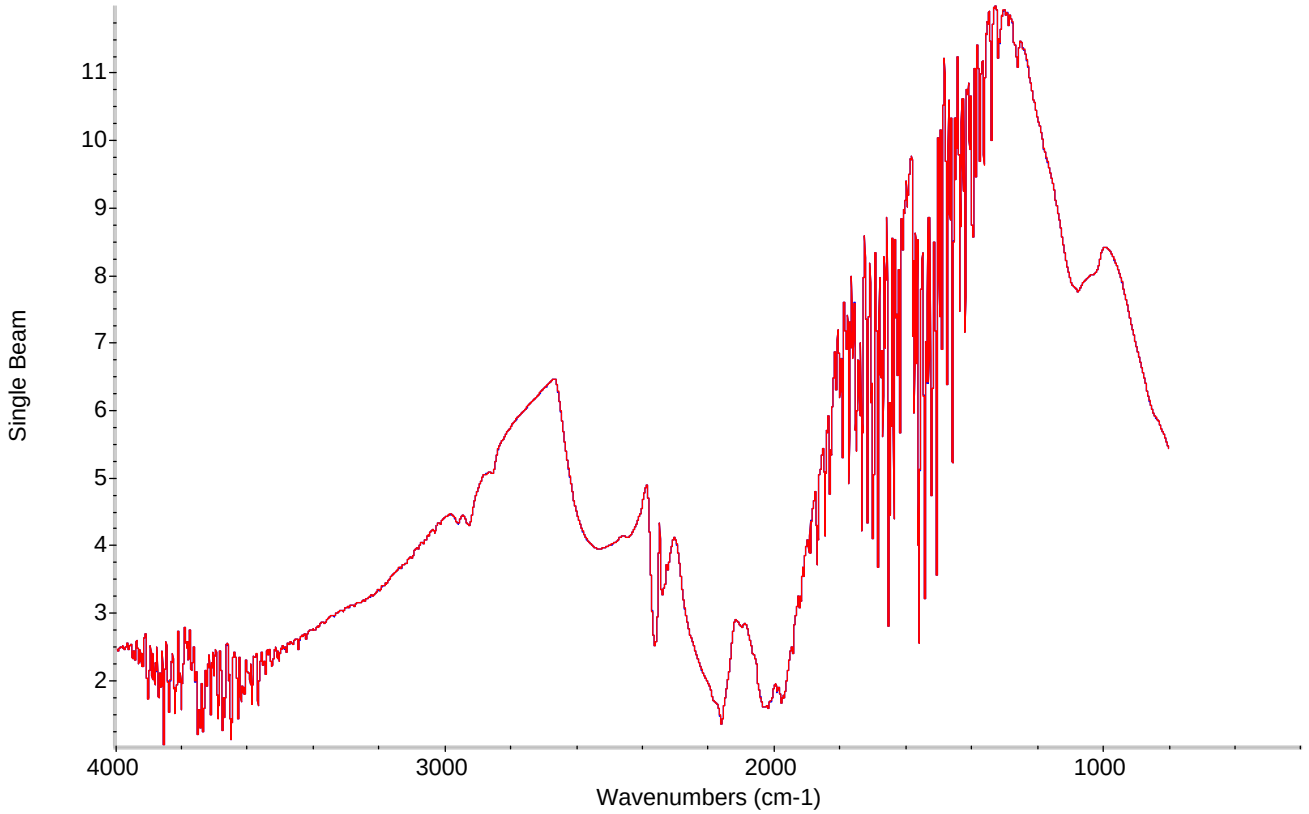
FT IR


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)

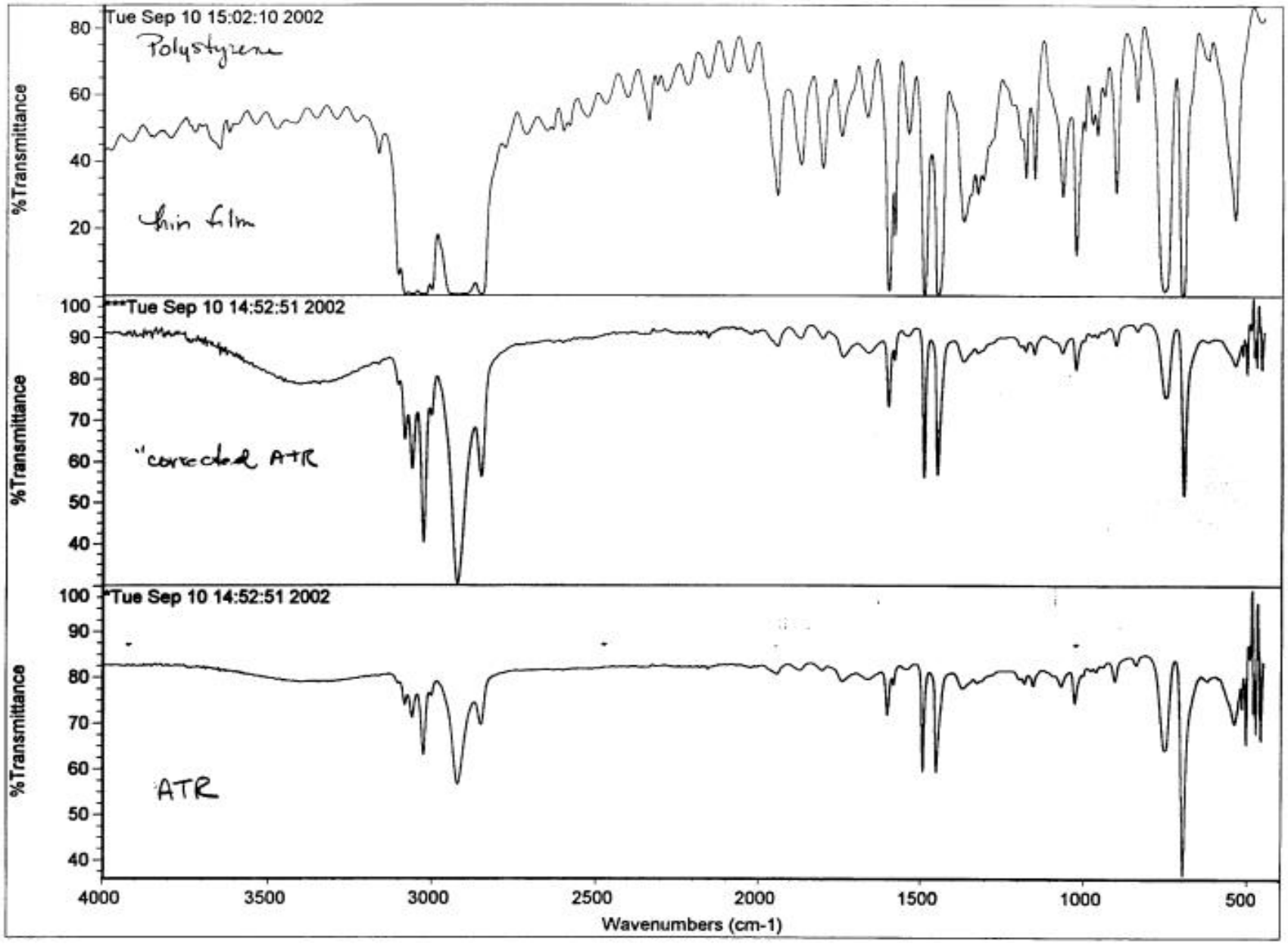
ATR: attenuated total reflectance; when a beam of electromagnetic radiation is reflected off an object, it actually penetrates of the order of one wavelength.

In IR, this is of the order of microns which is sufficient to obtain a spectrum of the material provided it is poly-dispersed.

The depth of penetration is wavelength dependent, it is therefore necessary to compensate for this dependency.



Infrared spectrum of ATR and of the background CO_2 and H_2O vapor.


Tue Sep 10 15:02:10 2002
Polystyrene
thin film
%Transmittance
***Tue Sep 10 14:52:51 2002
"corrected ATR
%Transmittance
*Tue Sep 10 14:52:51 2002
ATR
%Transmittance
Wavenumbers (cm-1)