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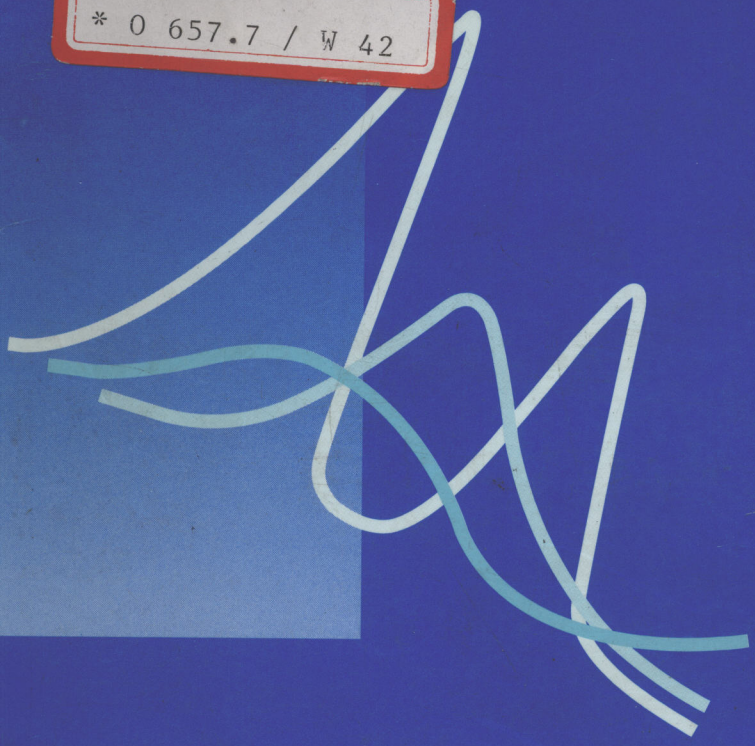

INTERPRETING *organic spectra*

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Interpreting Organic Spectra

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Preface

This book, like many other text-books, has its origins in a course given by the author. The course was for beginners in spectroscopy; it was a conventional series of lectures on techniques, with tutorials spent interpreting spectra. This quickly proved that while lecturing is a good way of teaching spectroscopy, lectures on how to interpret spectra have something in common with lectures on how to ride a bicycle. Since most organic chemists regard spectroscopy as a means of gaining structural information about compounds in which they are interested, the course was modified to become a series of workshops, in which a short lecture on a technique was followed by many examples to interpret, while post-graduate students helped with early difficulties. This resulted in a big improvement in the ability of students to get structural data out of spectra, and made the post-graduates wish that they had learned spectroscopy this way, but the exercises in combining the results of all the techniques were less successful. This book aims to correct this problem and is the course I would choose to teach if sufficient workshops were available. It tries to show that each technique has a particular speciality, and that these need to be combined to identify a structure which is consistent with all the spectra.

In a course like this, the question of how much to write about a technique is debatable. One extreme would be to consider only the spectra, and to ignore how they are produced; the other is to delve too deeply into the theory of the method, and leave the student uncertain what to look for in the actual spectrum. I have aimed to be closer to the first extreme than the second, since some excellent detailed books on spectroscopy are available. The theory parts of this book cover approximately the same ground as the video tapes on IR, MS, UV, ^{13}C and ^{1}H spectra which were made at the University of Liverpool and which are available from the Royal Society of Chemistry.

The spectra should also be useful to teachers who are not trying to teach all the areas of spectroscopy covered here. In many cases, the mass spectrum can be replaced by a molecular formula, though this substantially increases the difficulty of a few problems. Many ^{13}C problems can be solved without ^{1}H, and *vice versa*, though this will make a few problems too difficult for beginners.

Compiling a collection of spectra like this has required a lot of help, and I am particularly grateful for the help of Sandra Hedges, Ann Leyden, Steve Apter and Allan Mills in running most of them. Thanks are also due to Frank Doran, who discovered samples in remote corners of the Chemistry Department, and Dr. J. A. Race of Micromass, who was very helpful with mass spectrometry. Finally, I must thank Frances Poole, for typing the manuscript.

David Whittaker

Contents

CHAPTER 1

Infrared Spectroscopy

Infrared spectroscopy is the best means of identifying functional groups in a molecule. It involves measuring the absorption by a substance of radiation in the region from 4000 to 600 cm^{-1}. The range covers roughly 2.5–16 μm (1 $\mu m = 10^{-4}$ cm), but the frequency scale is now used universally.

Every bond in a molecule vibrates, resulting in a change in its dipole moment. This change in dipole moment provides a mechanism for the absorption of radiation. The energy of the vibration is such that the radiation absorbed is in the infrared region, which is of lower frequency, and hence lower energy, than visible light. Consequently, every bond in a molecule has an absorption peak in the infrared spectrum or the Raman spectrum of the molecule. Every substance therefore has its own unique infrared spectrum, so that we can identify any organic material by comparing its infrared spectrum with that of a known sample. In addition, each different functional group, such as O–H, C–H or C=C, absorbs within a narrow range of frequencies so that we can identify a functional group present in a molecule by the presence of an absorption band in a particular range of the infrared spectrum.

The frequency at which a bond absorbs radiation depends on the masses of the atoms forming the bond. The bonds which absorb radiation at the upper end of the frequency range are those which involve a light atom, hydrogen, with a heavier atom, such as nitrogen, oxygen or carbon. Hydrogen, being light, vibrates strongly and rapidly, so we see a strong, high energy absorption. As we move to lower frequencies, we come to the vibrations of two heavier atoms, such as C–N, C–O and C–C, and finally, at the lowest energies, we find the vibrations of the heavier atoms bonded to very heavy atoms, such as C–Cl, C–Br and C–I. Within this general trend, multiple bonds absorb higher energy radiation than single bonds, so the C≡C bond absorbs at higher frequency than the C=C bond.

Before we study an infrared spectrum, we should consider how it is obtained. The sample to be studied is usually examined in one of four ways:

(1) As a pure liquid.
(2) As a mull. This method is used for solids. The solid is ground finely using a pestle and mortar, and mixed with a small amount of a liquid hydrocarbon (liquid paraffin) and run as a liquid. This has the disadvantage that the spectrum of the liquid hydrocarbon is superimposed on the spectrum of the sample.
(3) The compound is finely ground, mixed with KBr, compressed and run as a disc. This avoids adding extra absorption, but is time consuming.
(4) The compound is dissolved in a suitable solvent, and run as a solution. The spectrum cannot be observed in regions where the solvent absorbs.

Now let us consider an infrared spectrum. The spectrum of phenylamine, $PhNH_2$ (also known as aniline), is shown in Figure 1.1.

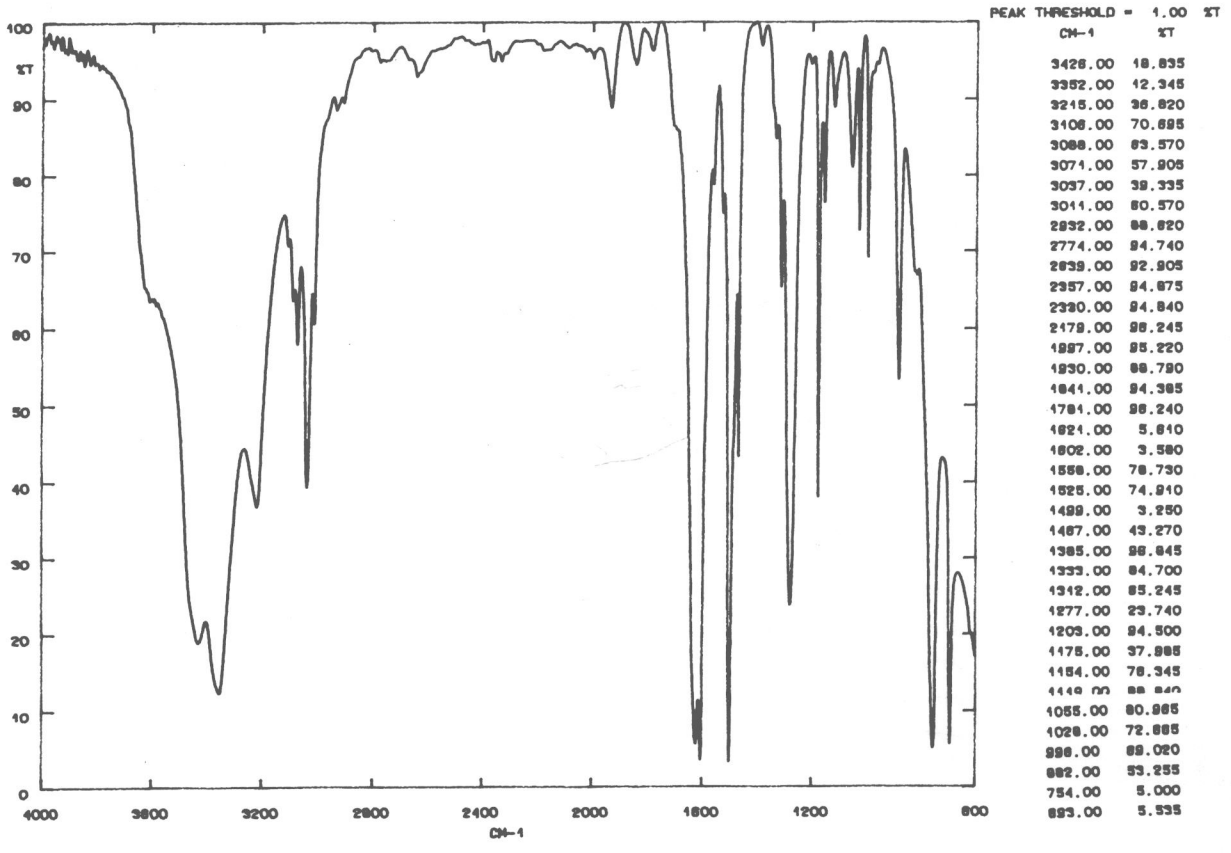
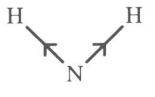


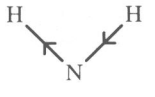
Figure 1.1

The spectrum records the amount of radiation transmitted at each frequency, so the maximum absorption occurs when the least light is transmitted, and the recorder line is closest to the bottom of the spectrum. Positions of maximum absorption are difficult to measure accurately from the spectrum, so most spectrometers record them automatically, and print them alongside the spectrum, giving the % of radiation transmitted (%T) alongside. The machine can be set to record frequencies of all or only the stronger peaks.

Phenylamine has an $-NH_2$ group, which characteristically absorbs in the region from 3500 to 3250 cm^{-1}. The spectrum actually has two peaks in this range, at 3426 and 3352 cm^{-1}. These do NOT represent a peak for each N–H bond (the bonds are indistinguishable so must have identical absorption frequencies): they result from the in-phase and out-of-phase vibrations of the N–H bonds:



In-phase, or
symmetric vibration



Out-of-phase, or
antisymmetric vibration

If the N–H bond is part of an amide, hydrogen bonding moves the absorption to lower frequency. If we have a secondary amine, with only one N–H bond, we obtain a single peak, which can easily be confused with the O–H bond.

A genuine O–H bond is shown in the next spectrum, that of butan-2-ol, $CH_3CH_2CH(OH)CH_3$. This is shown in Figure 1.2. The O–H bond absorbs

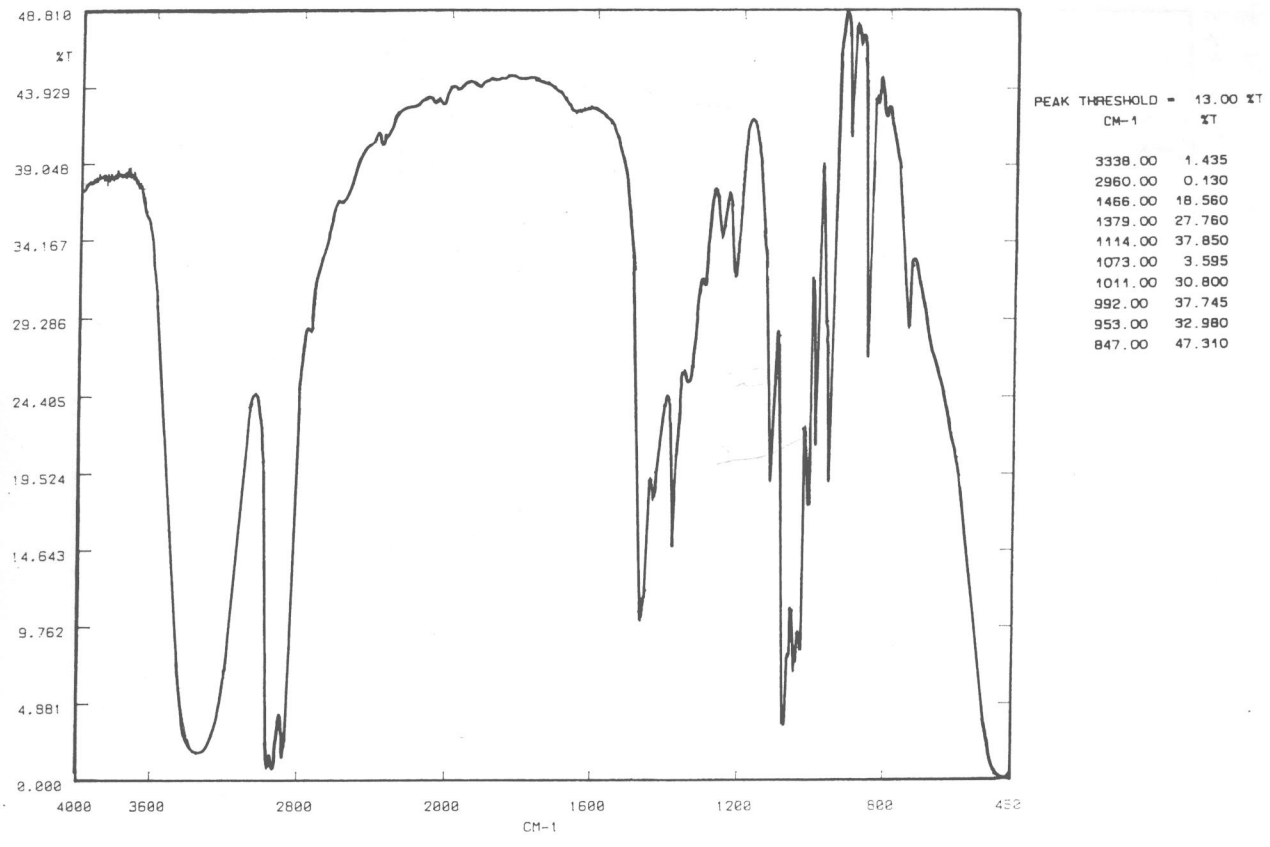
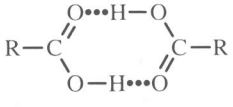


Figure 1.2

radiation in the range 3700–3200 cm^{-1}, and we find that butan-2-ol has a peak at 3338 cm^{-1}. The O–H peak, like the N–H peak but unlike other peaks in the spectrum, is a broad rounded peak rather than the usual sharp spiked peaks. This is a result of intermolecular hydrogen bonding. The hydrogen atom on any particular oxygen atom is probably attached to another oxygen atom by hydrogen bonding, so bond vibrations vary over a frequency range, and the broad peak which we see is an envelope covering many absorptions at slightly different frequencies. If we dilute the sample of butan-2-ol with solvent which cannot form a hydrogen bond, such as dichloromethane, we get the spectrum shown in Figure 1.3, in which the broad O–H bond peak is reduced, and a small sharp absorption peak has appeared at higher frequency, resulting from the non-hydrogen bonded O–H bond. At greater dilution of the alcohol dissolved in dichloromethane, the original O–H peak has almost vanished, and the non-hydrogen bonded peak has further increased in size, as shown in Figure 1.4.

The O–H bond of a carboxylic acid shows even stronger hydrogen bonding than that of an alcohol, since the acid is so strongly hydrogen bonded as to exist in the dimeric form in the pure liquid:



As a result, the carboxylic acid O–H group has an extremely broad absorption peak in the range 3200–2200 cm^{-1}. Combined with a carbonyl peak in the range 1725–1680 cm^{-1}, this makes identification of a carboxylic acid from its

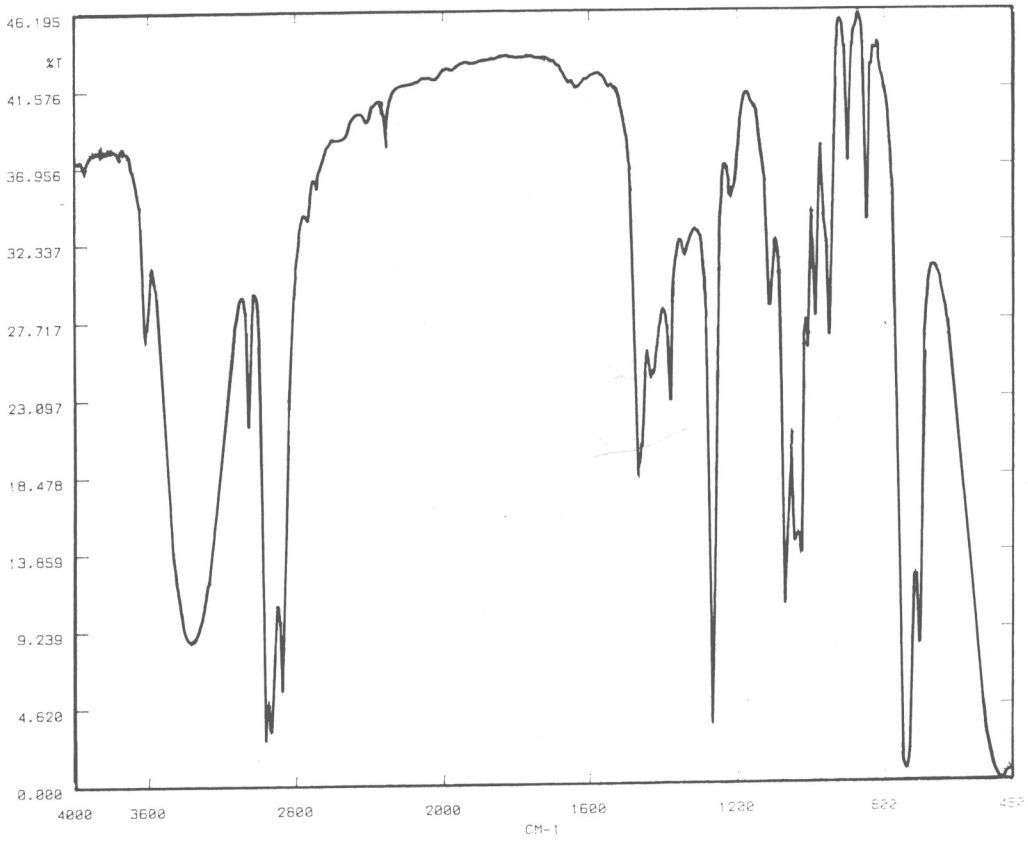


Figure 1.3

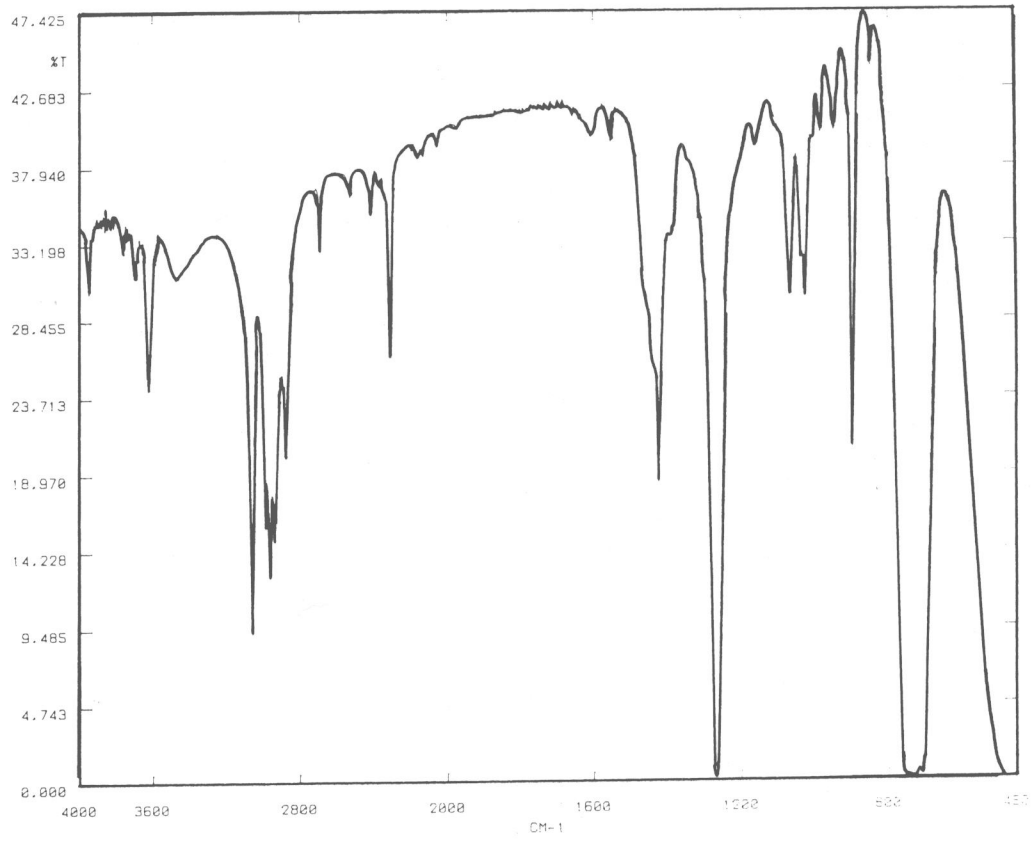


Figure 1.4

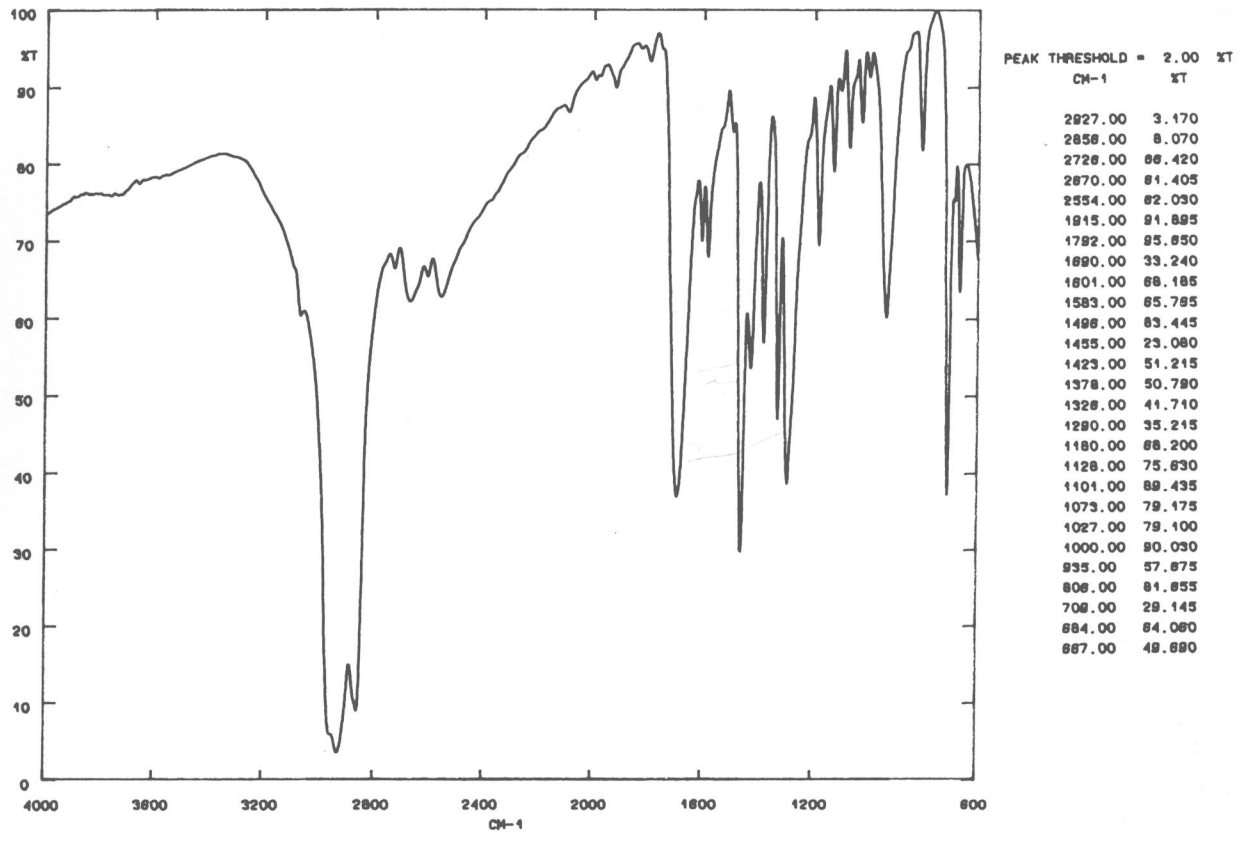


Figure 1.5

infrared spectrum an easy task. A typical carboxylic acid spectrum is that of benzoic acid, PhCOOH, which is shown in Figure 1.5.

As we move to lower frequencies in the infrared range, the next peak that we encounter is the C–H peak in the region 3100–2700 cm^{-1}. This supplies little useful structural information since almost all organic compounds contain hydrogen, and in the case of a solid run as a mull it will certainly be present in the liquid hydrocarbon used to make the mull. After the C–H absorption, we leave the high-frequency high-intensity X–H bonds, and, after a usually blank region of the spectrum, encounter the weaker triple bond absorption frequencies. The most common are the C≡N bond, which absorbs at 2300–2200 cm^{-1}, and the C≡C bond, which absorbs in the region from 2250 to 2100 cm^{-1}. This latter bond is particularly weak if neither carbon atom is bonded to hydrogen. The carbonyl group occurs next, absorbing over the unusually wide range of 1850–1640 cm^{-1}. However, the variation of the position of the C=O peak within this range is very valuable diagnostically, and will be considered separately.

As we further descend the frequency scale, we next come to the C=C bond region, which covers 1680–1620 cm^{-1} in unconjugated systems, and can go as low as 1590 cm^{-1} in conjugated systems. The C=C bond is often of low intensity, especially when fully substituted, and it is easily missed. In an aromatic system, the C–C bonds usually have two or three absorption peaks between approximately 1600 and 1500 cm^{-1}, usually with the strongest peak at about 1500 cm^{-1}. The spectrum of benzoic acid shown in Figure 1.5 illustrates this with weak peaks at 1601 cm^{-1} and 1583 cm^{-1}, and a stronger peak at 1496 cm^{-1}.

The region below about 1500 cm^{-1} is usually complex, and contains relatively little information about functional groups. It is often referred to as

Table 1.1 *Infrared absorption frequencies of common functional groups*

Functional group	*Absorption range* (cm^{-1})
N–H	3500–3250
CON–H	3500–3000
O–H	3700–3200
COO–H	3200–2200
C–H	3100–2700
C≡N	2300–2200
C≡C	2250–2100
C=O	1850–1640
C=C	1680–1590
Aromatic	1600–1500

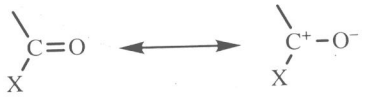
the 'fingerprint region', since this is the region of greatest value when comparing the spectrum of an unknown compound with that of a known compound. At the lower frequency end of this region we come to the C–Cl bond absorption in the region 800–400 cm^{-1}. The C–Br and C–I bonds usually absorb at too low a frequency for most spectrometers. The halogens are more readily identified by mass spectrometry.

The absorbing frequencies discussed above have been collected together in Table 1.1.

The carbonyl absorption was referred to earlier as covering a very wide range of frequencies. The absorption frequency is unusually sensitive to substitution at the carbonyl carbon atom. The reason for this is that the carbonyl group exists as a resonance hybrid of two forms:

$$C{=}O \leftrightarrow C^{+}{-}O^{-}$$

The two forms absorb at different frequencies, the polar $C^{+}{-}O^{-}$ having the higher frequency absorption. If we now consider the hybrid



it is easy to see that electron withdrawing substituents will favour the $C^{+}{-}O^{-}$ form, and electron supplying substituents will favour the C=O form.

When the substituent X is a chlorine atom, this strongly electron withdrawing group favours the $C^{+}{-}O^{-}$ bond, so acid chlorides absorb in the region around 1815–1790 cm^{-1}. The carbonyl group is another electron withdrawing substituent, so that the anhydride absorbs in this region, but since we have two carbonyl groups close together we can have in-phase and out-of-phase vibrations, as with the NH_2 group. Saturated carboxylic acid anhydrides thus show two peaks, one in the region 1850–1800 cm^{-1} and the other in the region 1790–1740 cm^{-1}.

The position of the carbonyl peak, however, does not depend entirely on inductive effects. In esters, the overlap of the lone pair of electrons on X with the C=O bond reduces the double bond character of the C=O bond, so the ester carbonyl group absorbs in the range 1755–1735 cm^{-1}. Aldehydes and ketones come next at 1740–1700 cm^{-1}, then the carboxylic acid carbonyl absorbs at 1725–1700 cm^{-1}, which is lower than might have been expected, but its position is affected by the dimeric nature of the carboxylic acid group in solution.

All these examples have referred to the carbonyl carbon atom attached to a

Table 1.2 *Infrared absorption frequencies of substituted carbonyl groups*

	Absorption frequency range (cm^{-1})	
Functional group	*R = Aliphatic*	*R = Conjugated alkene or aromatic*
Anhydride, RCOOCOR	1850–1800 and 1790–1740	1830–1775 and 1770–1710
Acid chloride, RCOCl	1815–1790	1790–1750
Ester, RCOOR*	1800–1745	
Ester, RCOOAlkyl	1755–1730	1735–1710
Aldehyde, RCOH	1740–1715	1715–1680
Ketone, RCOAlkyl	1725–1700	1700–1665
Carboxylic acid, RCOOH	1725–1700	1715–1680
Amide, RCON	1680–1640	1695–1665

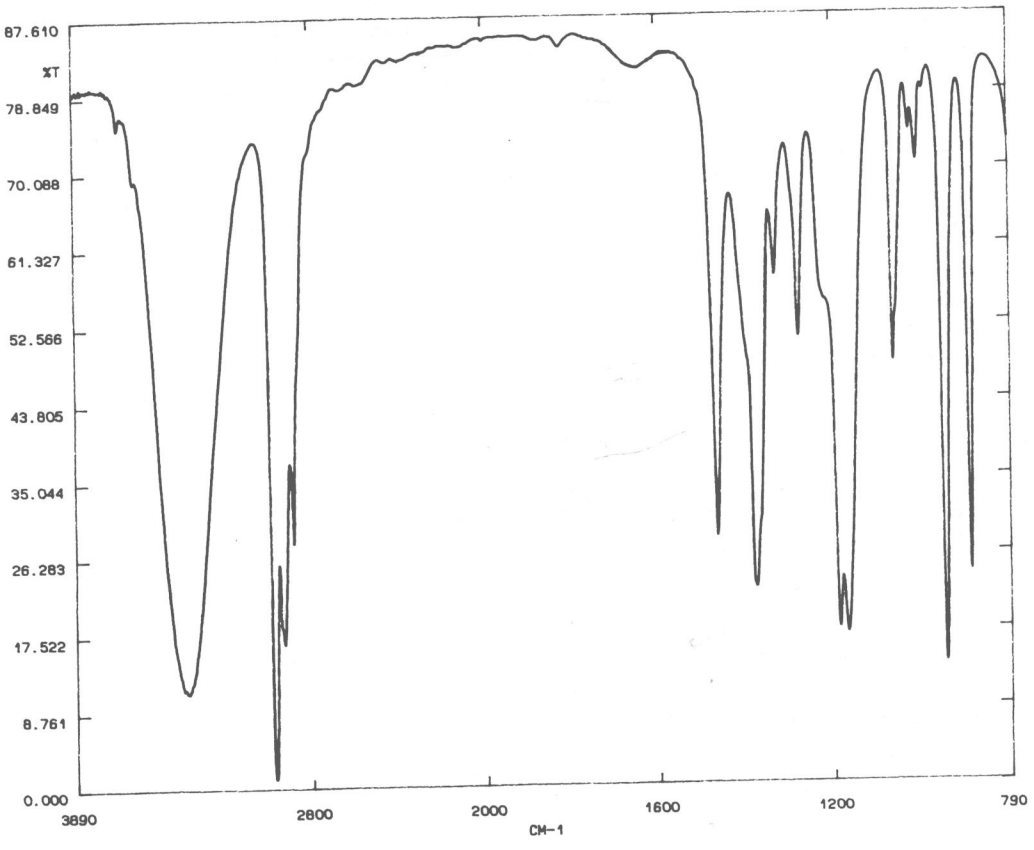
*R = aryl or vinyl.

saturated group; if it is attached to a multiple bond or an aromatic ring, then the carbonyl absorption frequency is lowered by 15–40 cm^{-1}. Thus, if we need to assign a carbonyl group, it is first necessary to see if the molecule shows signs of unsaturation; if this is next to the carbonyl carbon atom, then carbonyl frequencies will be lower than expected. Unexpectedly, conjugation shifts the amide carbonyl to higher frequency. It may be due to an inductive effect on the conjugated CO–N system.

The carbonyl absorption frequencies have been collected together in Table 1.2.

Problems in Interpreting Infrared Spectra

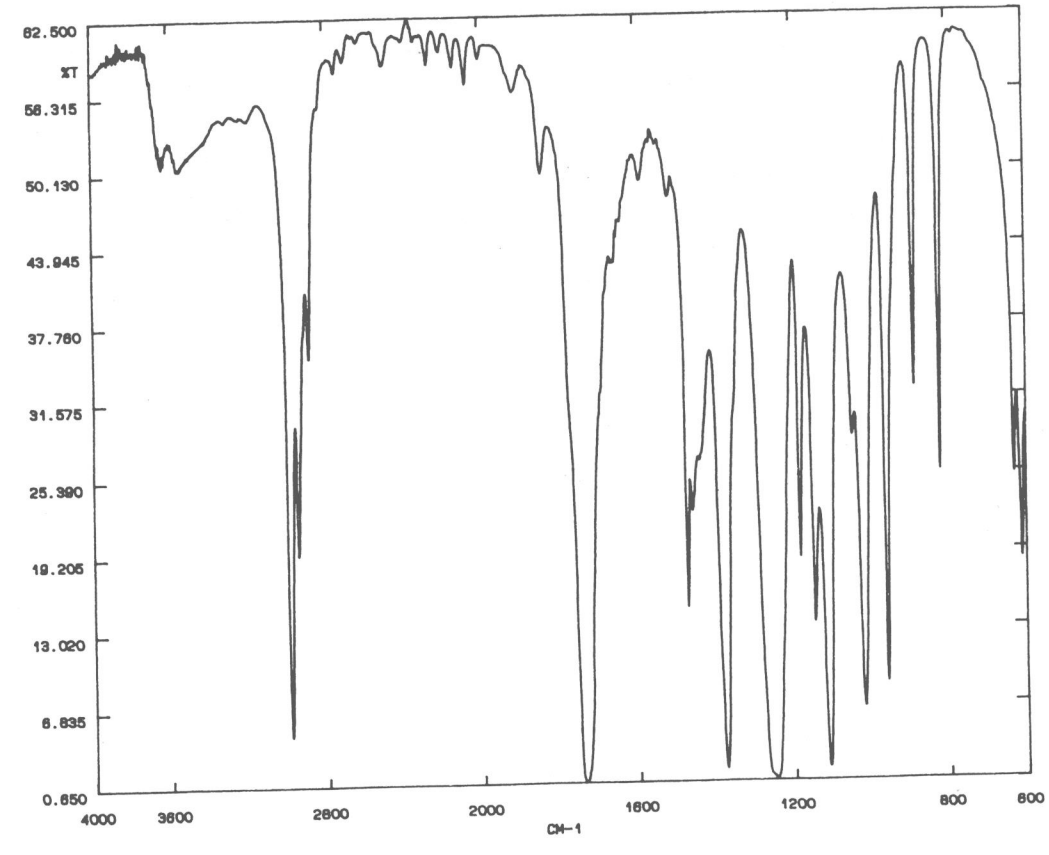
Using the data given in Tables 1.1 and 1.2, you should now be able to identify the common functional groups present in the compounds whose spectra comprise Samples 1 to 20. Remember that it is not sufficient to identify a compound as simply a carbonyl compound. If you observe a carbonyl peak, you should check for the presence of an aromatic ring or a double bond in the molecule, then use the data in Table 1.2 to say what type of carbonyl group (*e.g.* anhydride, ketone) is present in the sample. Note that some spectra are consistent with more than one structural type, since ranges of frequencies can overlap. All the spectra are run on pure liquids or nujol mulls.



PEAK THRESHOLD = 0.87 %T

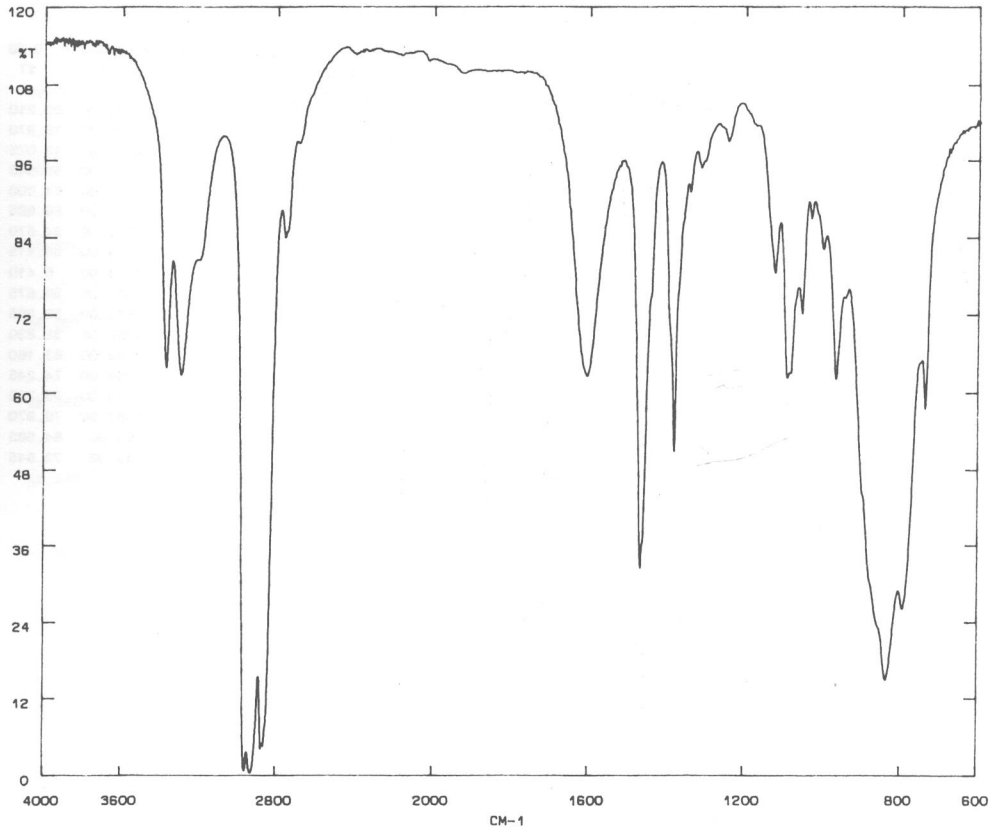
CM-1	%T
3682.00	75.375
3367.00	11.215
2971.00	1.285
2927.00	16.640
2883.00	28.145
2360.00	74.780
2342.00	77.010
1820.00	84.285
1646.00	78.275
1465.00	28.375
1376.00	22.375
1331.00	57.860
1277.00	50.920
1186.00	17.720
1167.00	17.155
1060.00	48.015
1020.00	74.275
1004.00	70.800
940.00	13.685
882.00	24.350

Sample 1.1



CM-1	%T
3454.00	46.852
2983.00	4.745
2942.00	19.302
2883.00	35.202
2067.00	57.147
1841.00	49.862
1741.00	0.852
1471.00	14.760
1375.00	1.692
1246.00	0.755
1183.00	18.652
1146.00	13.407
1111.00	1.730
1020.00	6.520
960.00	8.477
868.00	32.290
821.00	25.465
629.00	25.197
611.00	18.382

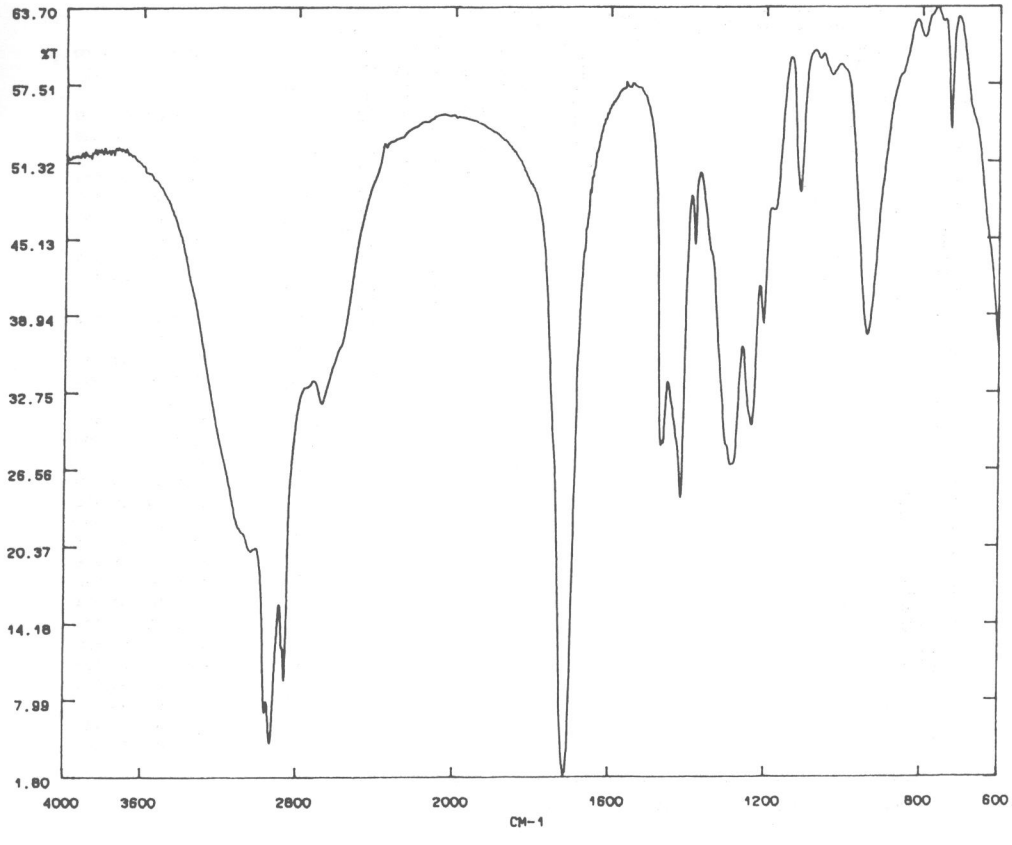
Sample 1.2



PEAK THRESHOLD = 12.00 %T

CM-1	%T
3367.00	63.705
3290.00	62.580
2924.00	0.300
1605.00	62.450
1465.00	32.335
1378.00	50.800
1090.00	62.150
967.00	62.030
837.00	14.860

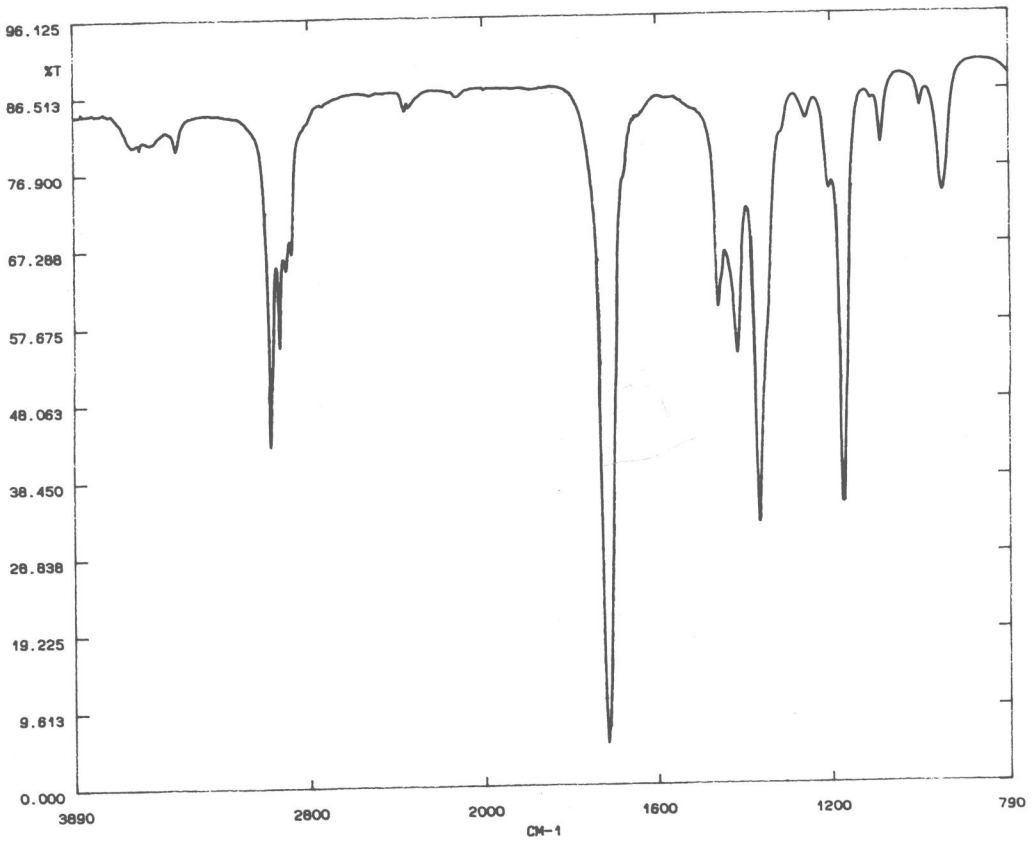
Sample 1.3



PEAK THRESHOLD = 6.19 %T

CM-1	%T
2928.00	4.512
2858.00	9.542
1713.00	1.802
1413.00	24.160
1285.00	26.767
1233.00	29.965
1110.00	48.802
939.00	37.175
725.00	53.837

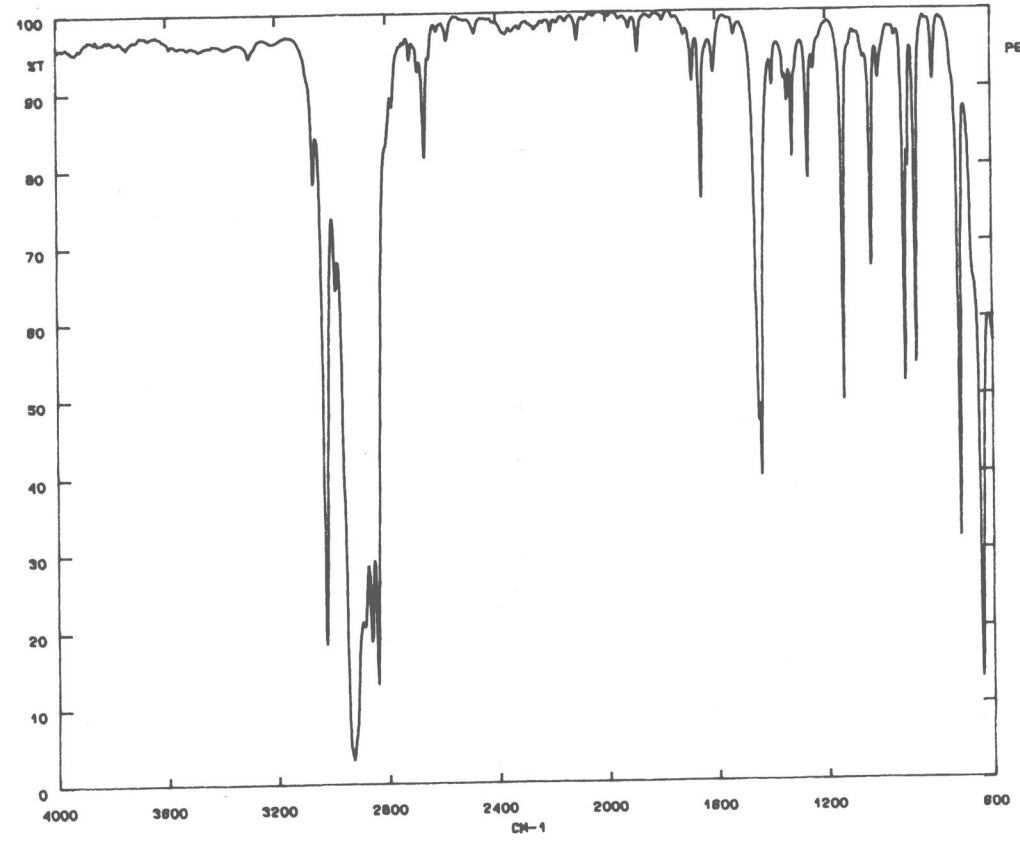
Sample 1.4



PEAK THRESHOLD = 0.96 %T

CM-1	%T
3584.00	80.210
3416.00	79.970
2980.00	43.075
2940.00	55.345
2910.00	64.900
2883.00	66.895
2360.00	84.670
2123.00	86.415
1718.00	5.410
1461.00	59.675
1417.00	53.885
1366.00	32.830
1258.00	83.160
1206.00	74.245
1173.00	35.205
1087.00	79.970
996.00	84.585
946.00	73.845

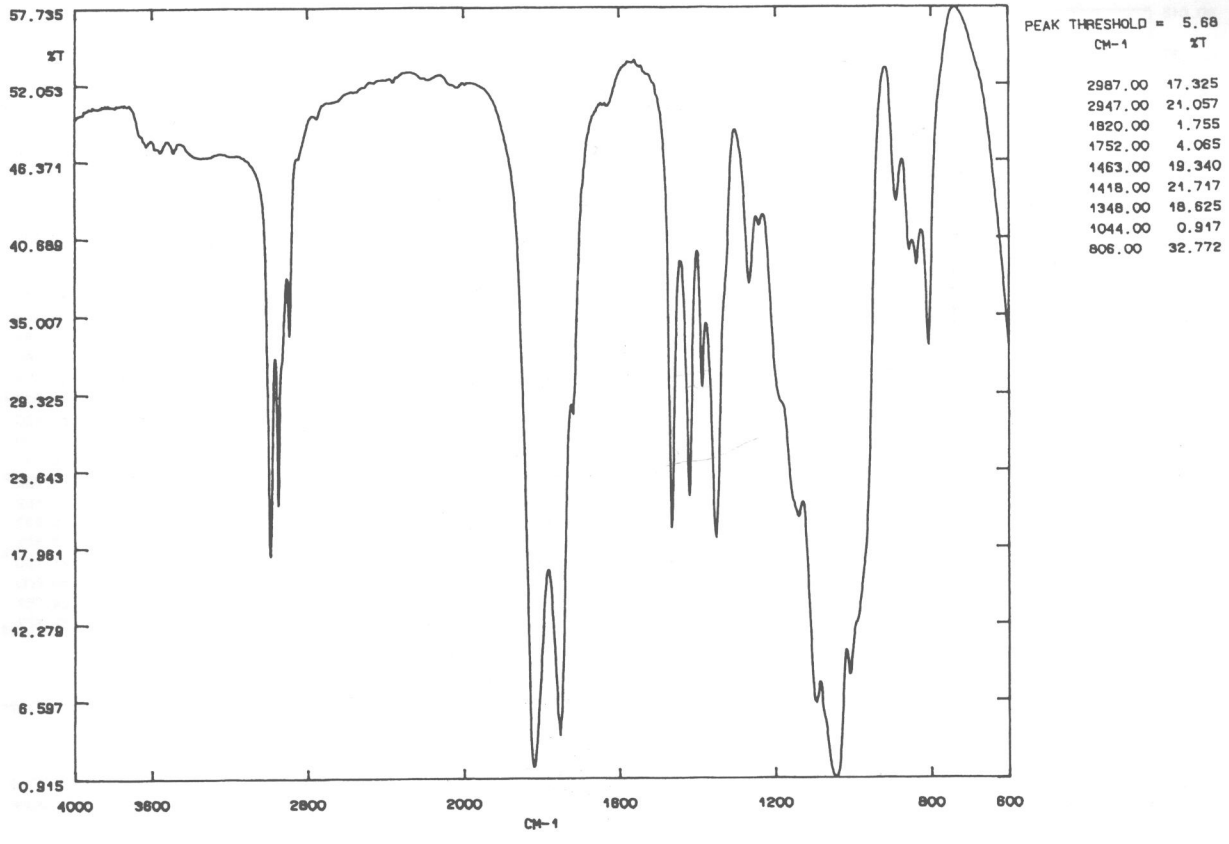
Sample 1.5



PEAK THRESHOLD = 2.00 %T

CM-1	%T
3293.00	94.470
3083.00	78.000
3023.00	18.275
2984.00	84.185
2927.00	3.170
2859.00	18.630
2838.00	13.010
2711.00	93.950
2659.00	81.375
2575.00	96.470
2474.00	97.340
2361.00	97.205
2101.00	96.315
1881.00	94.690
1682.00	90.825
1653.00	75.665
1605.00	91.980
1447.00	46.695
1438.00	39.650
1393.00	90.300
1339.00	88.290
1322.00	81.115
1285.00	78.235
1138.00	49.265
1037.00	88.695
1008.00	91.035
917.00	51.650
905.00	79.595
877.00	54.010
810.00	90.800
719.00	31.430
640.00	13.075

Sample 1.6



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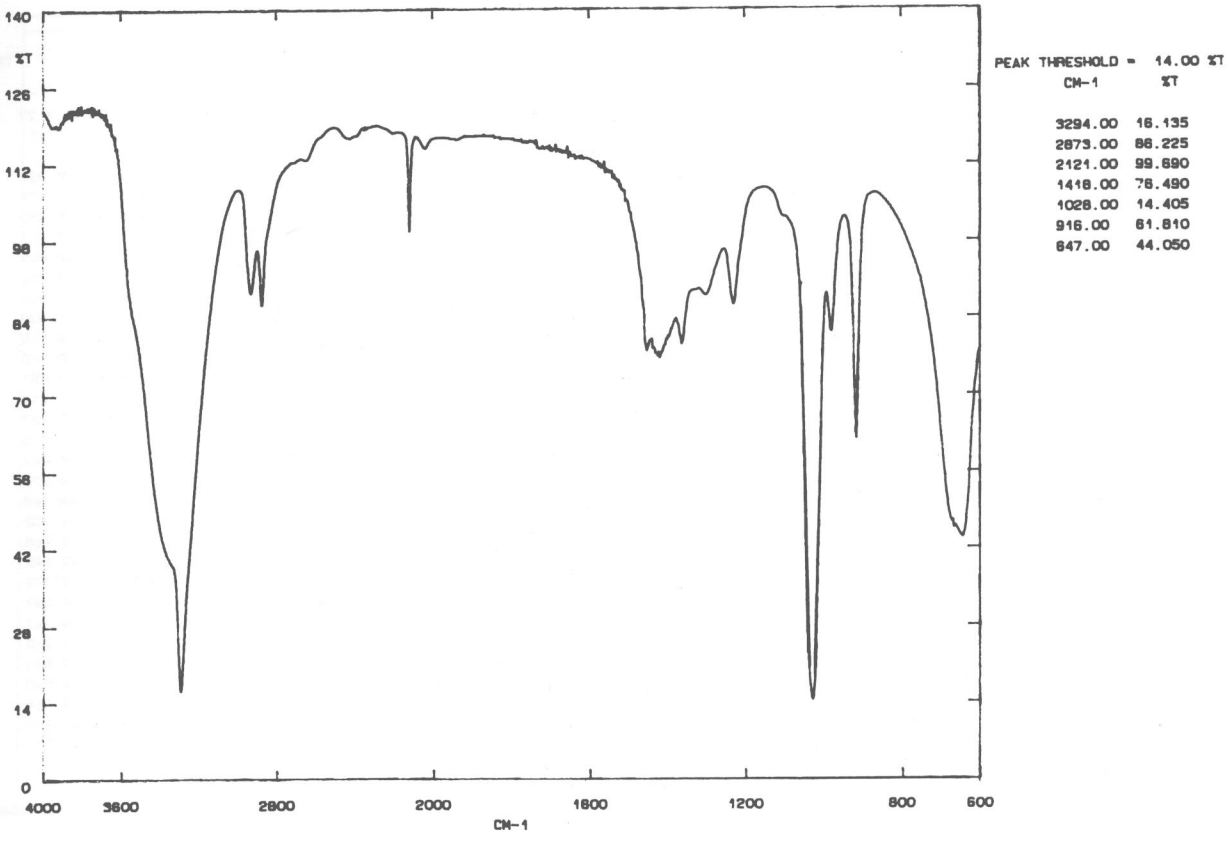
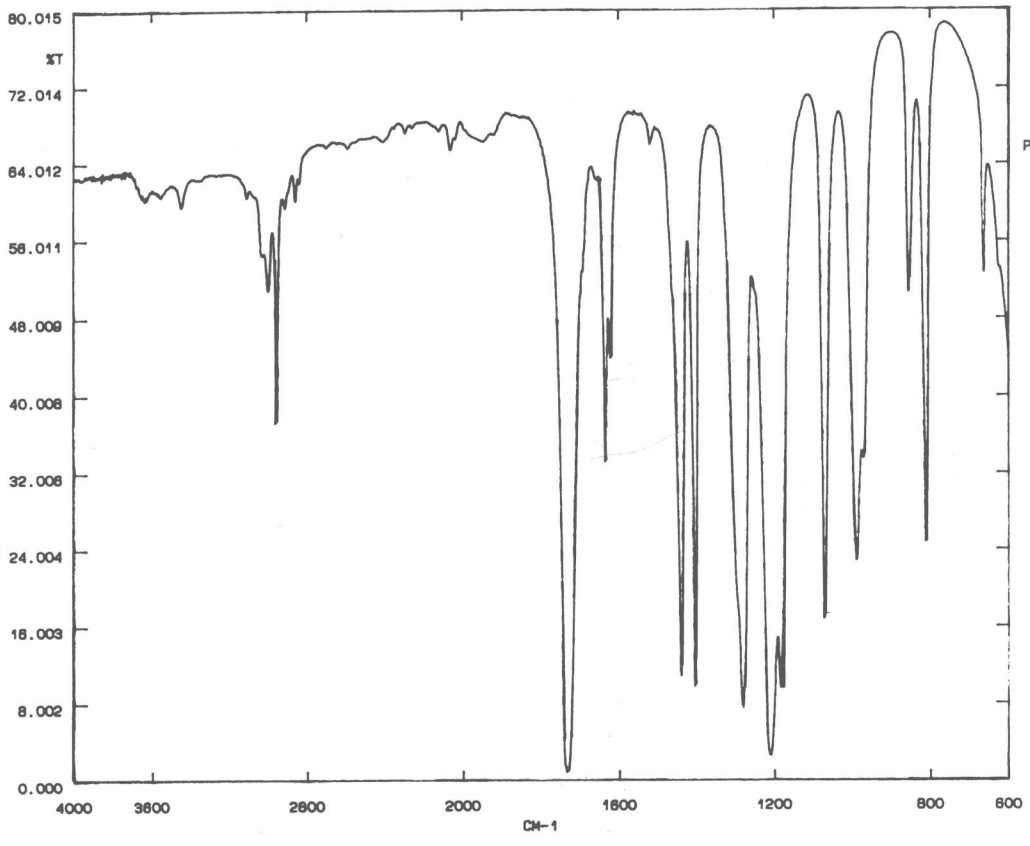


Sample 1.8



PEAK THRESHOLD = 1.60 %T

CM-1	%T
3632.00	60.207
3446.00	59.610
2999.00	50.890
2955.00	37.537
2856.00	60.270
2083.00	65.490
1945.00	66.382
1734.00	0.860
1635.00	33.122
1621.00	43.870
1518.00	65.995
1439.00	11.192
1404.00	9.717
1279.00	7.522
1208.00	2.582
1183.00	9.537
1070.00	16.832
989.00	22.790
855.00	50.600
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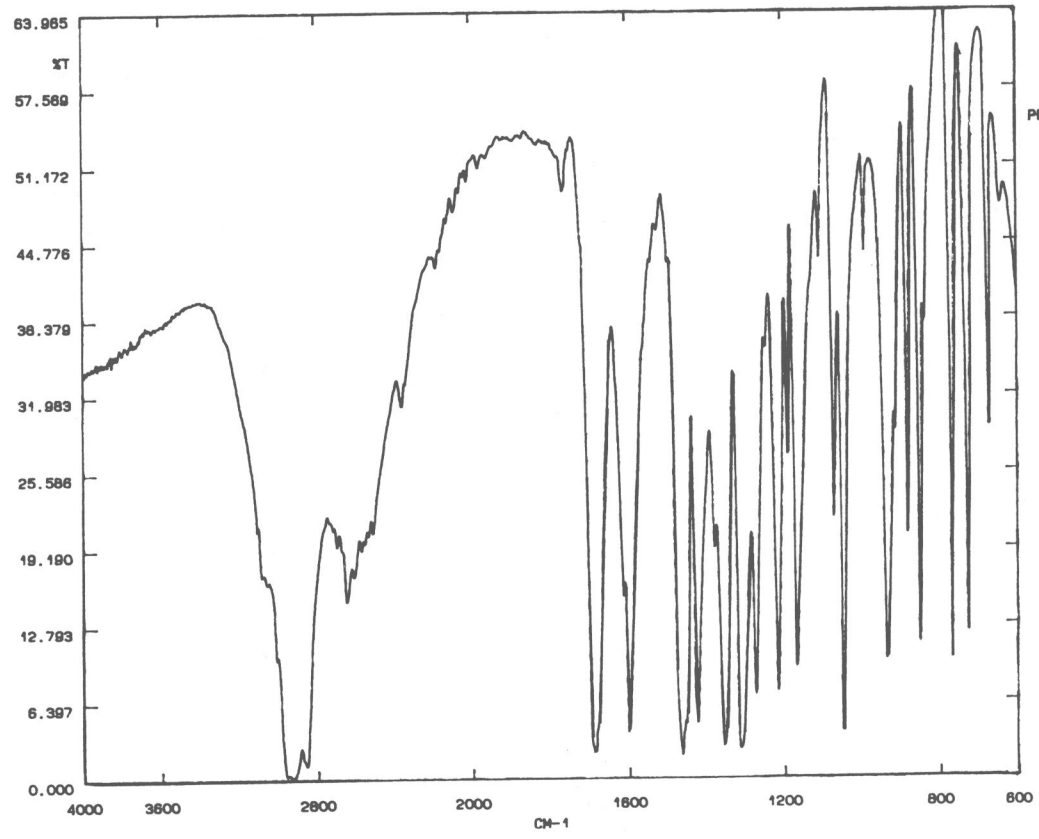
663.00	52.577

Sample 1.9



PEAK THRESHOLD = 1.27 %T

CM-1	%T
2927.00	0.097
2856.00	1.177
2646.00	14.910
2363.00	31.127
1764.00	49.055
1689.00	2.162
1600.00	3.832
1462.00	1.900
1422.00	4.575
1376.00	19.220
1353.00	2.657
1311.00	2.412
1272.00	6.927
1214.00	7.170
1190.00	26.897
1168.00	9.225
1107.00	43.365
1071.00	21.702
1049.00	3.905
991.00	43.892
935.00	9.772
914.00	28.897
882.00	20.347
851.00	11.242
839.00	37.885
769.00	9.890
728.00	12.155
674.00	29.310
641.00	47.787

Sample 1.10