NOTES ON THE INTERPRETATION OF NMR SPECTRA[1]

The nuclei of many elements give rise to NMR spectra but ^{1}H spectra are perhaps the most useful in elementary organic chemistry and so NMR interpretation for this year (Chemistry 2) will be limited to proton magnetic resonance spectra. This will be extended to ^{13}C spectra in the Chemistry 3 laboratory class.

The theory of NMR has been covered in the lecture course. These notes are intended to remind you of some of the ways in which structural information is derived from the spectra.

1. Peak Position - the Chemical Shift

The positions of the peaks in the spectrum - their chemical shifts - depend on the chemical environments of the hydrogen atoms. This is illustrated by the spectrum of methyl acetate (spectrum 1 of the set) in which the two methyl groups in different chemical environments give well separated peaks. Chemical shifts are expressed as δ_H (delta) units in parts per million (ppm) measured from the internal standard peak (tetramethylsilane - TMS) which is given a value of 0 δ_H.

$$\delta_H = \frac{\nu_{H} - \nu_{TMS}}{\nu_{TMS}} \times 10^6$$

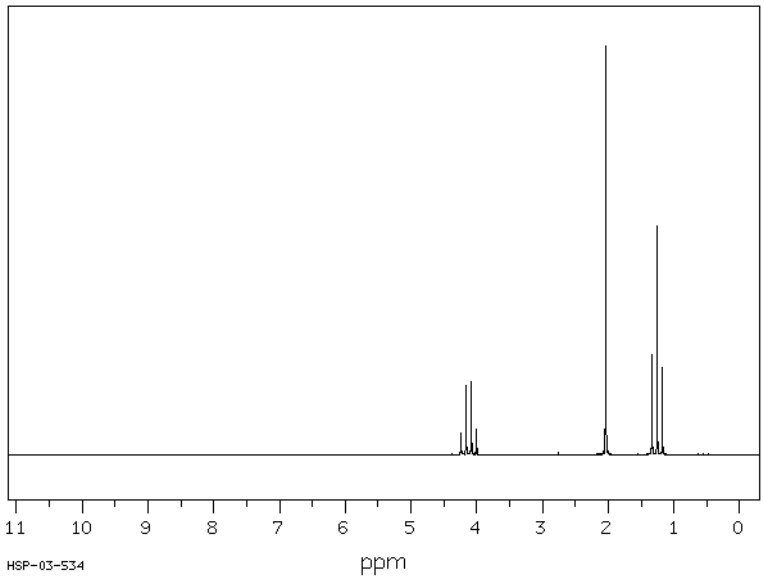
A correlation chart at the end of this appendix shows some typical δ_H values for common functional groups. Note that most protons in organic compounds absorb in the range δ_H 0-10 but very acidic protons have values >10 δ_H. Correlation charts must be used with some caution since in a complex molecule the chemical shift of a particular group of protons may be affected to some degree by several functional groups and thus may differ appreciably from the typical value given. Such effects can often by estimated from the known shielding or deshielding effects of substituents. In general electron withdrawing groups or electronegative atoms have a deshielding effect and cause the absorption to occur at *higher* frequency (= higher δ_H value). The CH_2 group in diethyl malonate $CH_2(CO_2Et)_2$ is subject to the combined deshielding effect of the two ester groups and absorbs at δ_H 3.37 whereas the CH_2 group of ethyl propionate $CH_3CH_2CO_2Et$ absorbs at δ_H 2.28.

2. Peak Intensity

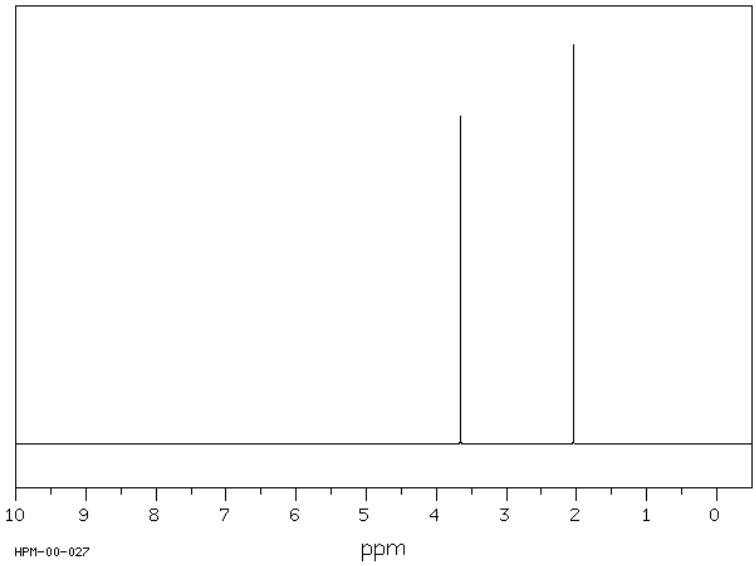
The intensity of each signal (*i.e.* the area under the peak) is proportional to the number of protons giving rise to that signal. The relative peak areas are derived from the integral trace where the height of each step is proportional to the peak area (see for example spectrum 2 of the set).

3. Peak Multiplicity, Spin-Spin Coupling

The spectrum of ethyl acetate (next page) is more complex than that of methyl acetate (next page) in that it has 8 lines appearing in three groups (4,1,3) rather than the 3 lines which might be expected from the previous discussion. From the correlation chart and by comparison of the two spectra it can readily be deduced that the $\mathbf{H}_3CO_2CH_2CH_3$ protons correspond to the peak at about δ_H 1.9, the $\mathbf{CH}_2$ protons to the group at about δ_H 4 and the $CH_2C\mathbf{H}_3$ protons to the group at about δ_H 1.2. Thus it can be seen that the peaks due to the protons in the CH_2CH_3 group have been split into a quartet and a triplet respectively. This is due to magnetic interaction between the CH_3 and CH_2 groups. A



Ethyl Acetate



Methyl Acetate

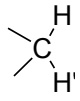
fuller discussion of spin-spin coupling is beyond the scope of these notes but the following generalisations will be found useful:

1. Protons in the same chemical and magnetic environment do not normally show coupling to each other.
2. In saturated acyclic systems, coupling is important only between protons on the same and on adjacent atoms, but longer range coupling can be observed in unsaturated and other more rigid systems, (see Table).
3. For spectra where the differences in the chemical shifts of the nuclei are large compared with the coupling constants, the multiplicity of a group equals (n + 1) where n is the number of protons on adjacent atoms.
4. Protons undergoing rapid chemical exchange do not normally couple with adjacent protons. Chemical exchange is most commonly encountered in the spectra of alcohols: in a given period of time any one hydroxyl proton may be attached to (and detached from) a number of alcohol molecules, especially if traces of acid or base are present. So the protons on the adjacent carbon are subjected to the effect of a rapid succession of hydroxyl protons, some of which have spins

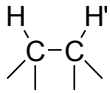
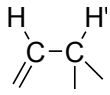
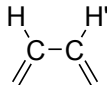
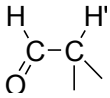
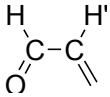
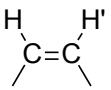
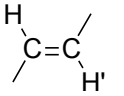
which are oriented with the field and others against it, and the net effect is that no splitting of the CH signal by the -OH proton and of the -OH signal by the CH proton(s) is observed.

A list of typical coupling constants is given in the Tables below:

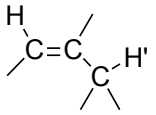
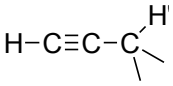
1. Geminal Coupling

Sub-structure	$^{2}J_{H,H}$ /Hz
	10-15
	0-3

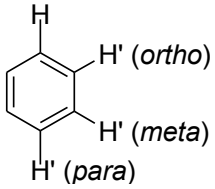
2. Vicinal Coupling

Sub-structure	$^{3}J_{H,H}$ /Hz
	5-8
	4-10
	6-13
 **(cont^{d})**	0-3
	5-8
 *cis*	6-12
 *trans*	12-18

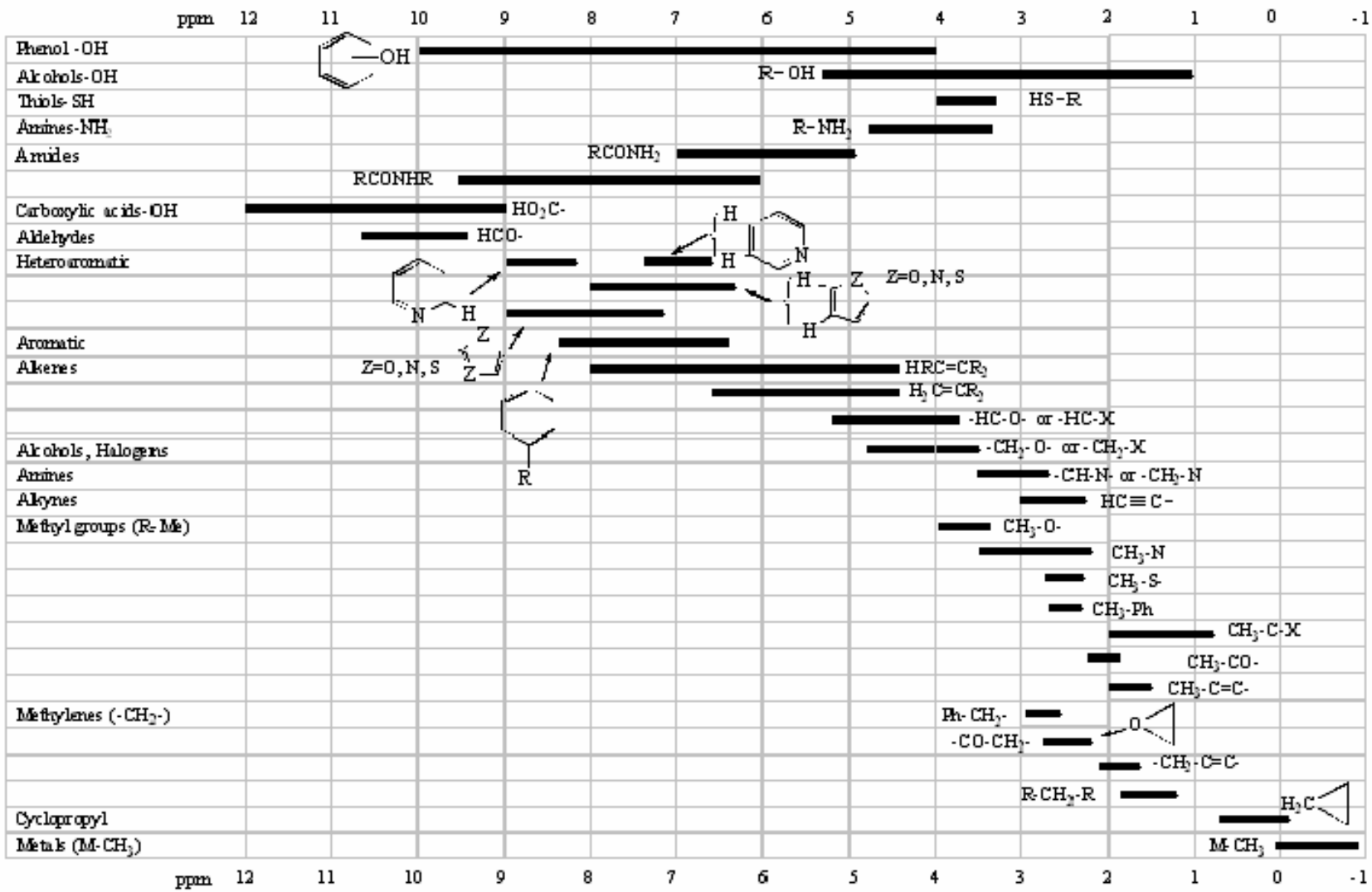
3. 1,3-Coupling

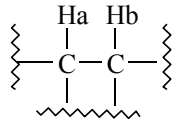
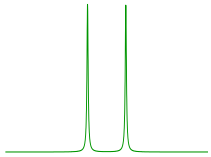
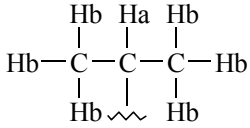
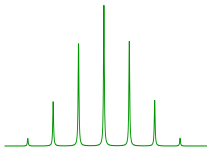
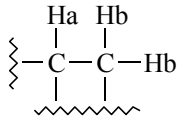
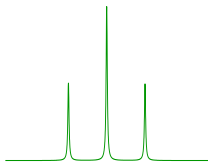
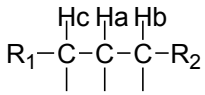
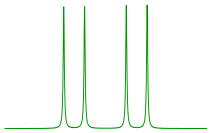
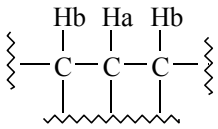
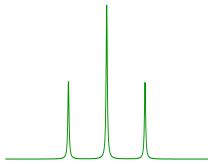
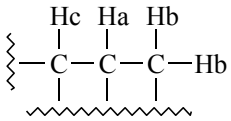
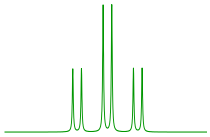
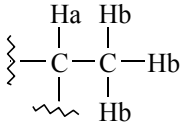
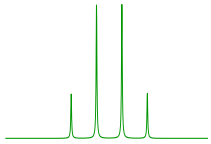
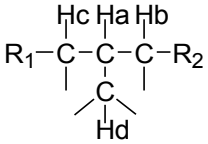
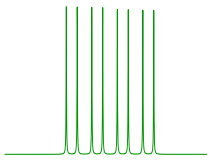
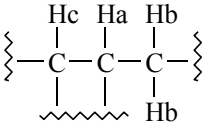
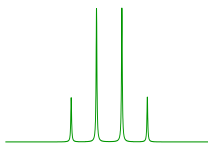
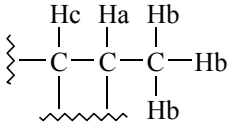
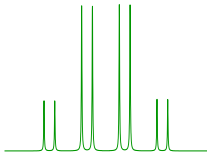
Sub-structure	$^4J_{H,H}$ /Hz
	0-3
	2-3

4. Aromatic

Sub-structure	$J_{H,H}$ /Hz
	*ortho* 6-9 *meta* 1-3 *para* 0-1

Summary of NMR chemical shifts for common functional groups



Entry	Structure	Notation and Pattern for Ha	Entry	Structure	Notation and Pattern for Ha
1		d 	6		sp 
2		t 	7		dd 
3		t 	8		dt 
4		q 	9	 $J_{ab} \neq J_{ac} \neq J_{ad}$	dddd 
5	 $J_{ab} = J_{ac}$	q 	10	 $J_{ab} \neq J_{ac}$	dq 

First order splitting patterns of some common spin systems

APPENDIX 2

NOTES ON THE INTERPRETATION OF INFRA-RED SPECTRA

The theory has been dealt with in your lecture course and these notes are concerned only with the interpretation of IR spectra.

Practical points: The preparation of samples for IR spectroscopy is discussed in "Practical Organic Chemistry" (pp 178-181) (EOC pp 280-287). There are two important points related to interpretation:

1. liquids are usually run as thin films so all the peaks in the spectrum come from the compound itself
2. solids are usually run as Nujol mulls *i.e.* as dispersions in the viscous hydrocarbon oil Nujol (liquid paraffin), this means that the spectrum contains the three peaks due to Nujol (2900, 1461 and 1377 cm^{-1}) as well as those from the compound.

For the purpose of obtaining structural information from an IR spectrum, it is convenient to divide the spectrum into five regions as discussed below. The principal absorptions observed in these regions are indicated on the chart.

Region 1: 4000-2850 cm^{-1}
The principal absorptions in this region correspond to the stretching vibrations of single bonds to hydrogen: **C-H, O-H, N-H**.

C-H absorptions normally occur at the lower end of the range (below 3100 cm^{-1}). They are present in almost all organic IR spectra. In some cases it may be possible to distinguish H-C(sat.) (*ca* 2900 cm^{-1} *c.f.* Nujol,) from H-C (unsat.) (3100-3000 cm^{-1}). The only notable exceptions to this range are the C-H bonds of terminal alkynes (RC≡CH) which absorb at 3300 cm^{-1} and may therefore be confused with N-H; and aldehydes (RCH=O) which absorb at 2700-2800 cm^{-1}; but these absorptions are often weak and not easily recognised. If the spectrum shows **strong** absorptions above *ca* 3050 cm^{-1}, it almost certainly contains an O-H, N-H or NH_2 group.

O-H absorptions fall into three classes, depending on the environment of the OH group: (a) alcohols, (b) phenols, (c) carboxylic acids. As the acidity of the hydroxyl hydrogen increases (alcohol < phenol < acid) so the tendency to form intermolecular hydrogen bonds increases. This results in a decrease in the frequency of the O-H absorption and broadening of the peak. Thus alcohols usually absorb at 3400-3200 cm^{-1}, phenols at 3200 cm^{-1}, and carboxylic acids at 3000-2500 cm^{-1}. [NB Dilute *solutions* of alcohols and phenols, in which intermolecular hydrogen bonding is minimised, give O-H stretching absorptions as a sharp peak in the region of 3600 cm^{-1}].

N-H absorptions in amines and amides normally occur within the range 3500-3150 cm^{-1}. Hydrogen bonding affects the frequency much less than for the O-H absorptions. N-H peaks are usually sharper but weaker in intensity than O-H peaks. It is possible to distinguish between primary and secondary amines and amides on the basis of these N-H absorptions. Ths -NH- group (secondary) gives rise to a single peak and the $-NH_2$ group (primary) to a multiplet. In dilute *solutions*, where hydrogen bonding is at a minimum, $-NH_2$ absorptions appear as a sharp doublet, but otherwise the usual absorption pattern is as shown in the figure 'typical absorptions for NH groups' below. It should be noted that tertiary amines and amides, which do not contain an N-H bond, do not absorb in this region.

Region 2: 2850-1850 cm^{-1}

Although strongly hydrogen bonded OH absorptions extend down to *ca* 2500 cm^{-1} (*e.g.* in carboxylic acids) in general this is a region in which few molecules absorb at all. The only common functional groups which have characteristic absorptions in this region are triple bonds, **alkynes** (acetylenes) and **nitriles**, which absorb between 2300 and 2100 cm^{-1}. These absorptions are often of low intensity except for terminal acetylenes and when the triple bond is conjugated.

Thiols absorb (S-H stretching) at 2600-2500 cm^{-1}; and **cumulated double bond systems** (X=C=Y) absorb in the range 2300-1900 cm^{-1}.

Some spectra may show a small broad peak at *ca* 2300 cm^{-1} due to atmospheric carbon dioxide.

Region 3: 1850-1600 cm^{-1}

This narrow range is of great importance because it contains double-bond stretching vibrations the most important of which are **C=O, C=N and C=C.**

By far the most useful of these is the **carbonyl group** absorption. This is almost invariably a very strong absorption occurring in the range 1850-1650 cm^{-1} where no other groups absorb with comparable intensity. The exact frequency depends on the molecular environment of the carbonyl group, and it is thus often possible to determine which kind of carbonyl group is present. The Table below gives the approximate ranges for different types of carbonyl group.

Carbonyl compound	ν_{max}/cm^{-1}	Comments
Anhydrides	1850-1740	2 peaks *ca* 60 cm^{-1} apart
Acyl halides	1815-1750	(1 peak)
Esters	1750-1710	
Aldehydes	1740-1680	
Ketones	1725-1660	
Carboxylic acids	1720-1660	
Amides	1680-1630	

Conjugation of the carbonyl group with a π-electron system lowers the carbonyl absorption frequency; α,β-unsaturated and aromatic carbonyls thus absorb towards the lower end of the ranges given in the Table. Hydrogen bonding (especially intramolecular) also lowers the frequency, in some cases appreciably (*c.f.* ethyl *o*-aminobenzoate, 1680 cm^{-1}). On the other hand, incorporation of the carbonyl group into a strained ring increases the frequency, so cyclohexanone absorbs at 1710 cm^{-1}, the frequency expected for an acyclic ketone, whereas cyclopentanone absorbs at 1740 cm^{-1}, cyclobutanone at 1780 cm^{-1} and cyclopropanone at *ca.* 1810 cm^{-1}.

Some, although not all, aromatic compounds show a very sharp absorption at *ca.* 1600 cm^{-1}. This absorption in polystyrene (1603 cm^{-1}) is often used to calibrate the spectrometer chart.

Care must be exercised in interpreting absorptions in the 1650-1600 cm^{-1} range if the N-H stretching peak has been observed in Region 1, since the N-H bending vibration falls within this range.

Region 4: 1600-1000 cm^{-1}

Both this region and Region 5 often contain a complicated absorption pattern, only a few of the absorptions being of diagnostic significance. Outstanding among these are the absorptions of the **nitro group** (two peaks, 1560-1500 and 1360-1320 cm^{-1}) and the **sulfonyl group** (two peaks, 1350-1300 and 1160-1140 cm^{-1}), and further sharp aromatic absorption, in some compounds, at *ca* 1500 cm^{-1}. C-H bending (*c.f.* Nujol) and C-O and C-N single bond stretching vibrations fall within this region but are not generally useful for identification purposes.

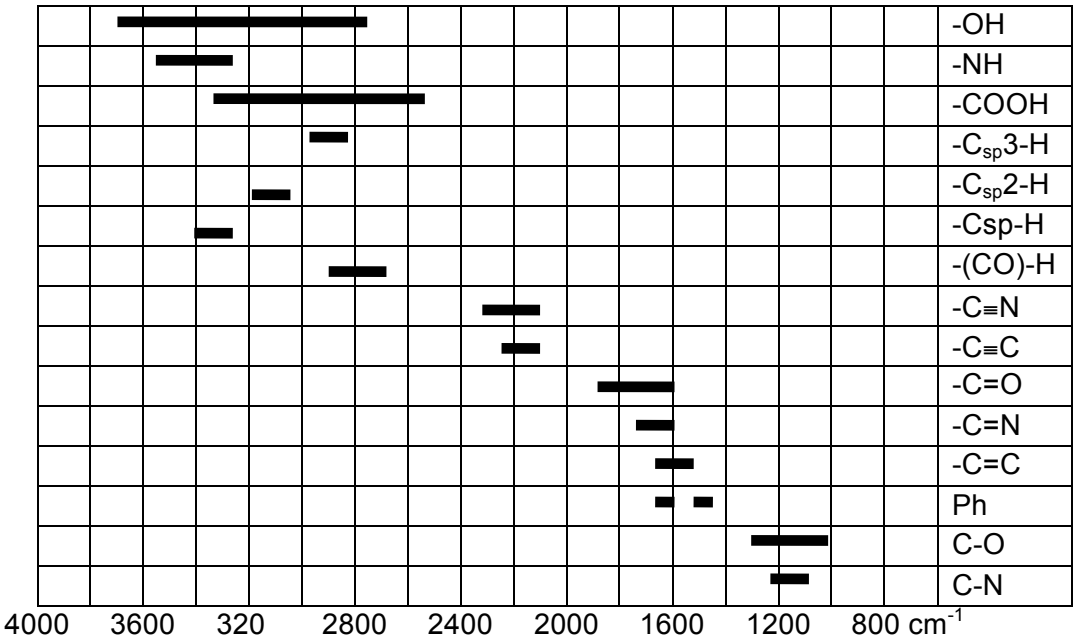
Region 5: 1000-667 cm^{-1}

The most significant absorptions here are those of the (unsat.) C-H bending vibrations and the C-halogen (especially C-Cl) stretching vibrations. Aliphatic compounds which contain neither multiple bonds nor halogens exhibit little absorption in this region; on the other hand aromatic compounds absorb strongly. It may be possible to recognise particular kinds of =CH-, see Table below, however this kind of information is often more easily obtained from ^{1}H NMR spectra (see later). In elementary identification work it is usually sufficient to use this region to distinguish qualitatively between aromatic and aliphatic compounds rather than to attempt a detailed analysis of the absorption pattern.

Alkenes	**ν_{max}/cm^{-1}**	**Aromatics**	**ν_{max}/cm^{-1}**
$RCH=CH_2$	*ca.* 990 and 910	5 adjacent H	770-730 and *ca.* 700
RCH=CHR (*Z*)	*ca.* 690	4 adjacent H	770-735
RCH=CHR (*E*)	980-960	3 adjacent H	810-750
$R_2C=CH_2$	*ca.* 890	2 adjacent H	860-800
$R_2C=CHR$	840-810	1 isolated H	*ca.* 880

Carbon-chlorine vibrations occur in the 800-600 cm^{-1} region but these are of no value for detecting chlorine in the molecule; this is better done by other methods.

The spectrum as a whole: - However complicated the absorption pattern of a particular compound, it is completely characteristic of that compound and will serve as a **fingerprint** for identification purposes. The region of the spectrum below 1500 cm^{-1}, which is often very complex is referred to as the **fingerprint region**. Although two compounds containing the same functional groups may show very similar absorptions above 1500 cm^{-1}, even small structural differences will give rise to major differences in the absorptions in the fingerprint region. Confirmation of the identity of an unknown compound may thus be obtained by comparison of the IR spectrum of the unknown with that of an authentic sample (or its spectrum in one of the catalogues of IR spectra).



Summary of IR bands for common functional groups.