E35 SPECTROSCOPIC TECHNIQUES
IN ORGANIC CHEMISTRY

THE TASK
To use mass spectrometry and IR, UV/vis and NMR spectroscopy to identify organic compounds.

THE SKILLS
By the end of the experiment you should be able to:
- explain how modern spectroscopic methods work,
- use a variety of complementary spectroscopic techniques to determine the structure of an unknown organic compound.

OTHER OUTCOMES
- You will develop generic scientific skills including using evidence to solve problems.
- You will develop an appreciation of the spectroscopic techniques used to identify organic and pharmaceutical compounds.

INTRODUCTION
These notes are designed to introduce you to the basic spectroscopic techniques which are used for the determination of the structure (constitution and stereochemistry) of organic compounds. Complementary material and problems in spectroscopy will be found in the relevant chapters of your textbook.

Mass Spectroscopy

Mass spectrometry is a technique by which the molecular weight of a compound may be determined. A small sample of the compound is vaporised in a mass spectrometer under high vacuum and then subjected to bombardment by a beam of high-energy electrons. The impact of the electrons on the molecule (M) causes the ejection of an electron from the molecule to form a positively charged ion called the *molecular ion* or parent ion ($M^{+\bullet}$). In principle, more than one electron can be removed from a molecule, so that the ion is characterised by its mass-to-charge ratio, m/z (or m/e). In practice multiply charged ions are rare in mass spectrometry.

$$M \quad + \quad e^- \quad \rightarrow \quad M^{+\bullet} \quad + \quad 2e^-$$
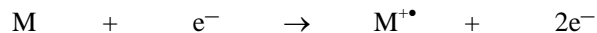
The positively charged ions are accelerated through an electric field before passing into a magnetic field. This causes the ions to travel a curved path whose curvature is dependent upon the m/z ratio and the speed at which the ions enter the magnetic field. Lighter ions have less momentum and are deflected more strongly than are heavier ions. The m/z ratio is calibrated in atomic mass units. Molecular ions arriving at the detector produce a peak in the mass spectrum at the molecular weight on the mass scale (horizontal axis). The peak height is proportional to the number of ions arriving in a given time. The symbol for the molecular ion (also called the parent ion) is M^+ or more exactly $M^{+\bullet}$ (since it also has an unpaired electron).

During the initial ionization process, some molecular ions are formed with an excess of internal energy. These ions break up in the ion chamber (see diagram on page E35-3) to produce *fragment ions* or *daughter ions* (m^+).

$$M^{+\bullet} \qquad \rightarrow \qquad m^+ \qquad + \qquad \text{neutral fragment}$$

Such ions appear in the mass spectrum as peaks at the relevant masses, with the peak heights corresponding to their relative populations. The most abundant ion, be it the parent or a fragment ion, produces the tallest peak in the spectrum. This peak is called the *base peak* and is arbitrarily assigned a relative intensity (height) of 100% on the vertical axis. Heights of all the other peaks are then expressed as percentages of the base peak.

The pattern of fragment peaks is characteristic of the original molecular constitution, because different kinds of bonds vary in strength; the weaker bonds break first during fragmentation. Different molecules have different weak spots, and so the molecular weight and fragmentation pattern give a lot of information on the structure of an unknown organic compound.

As most elements exist as more than one isotope, these will be resolved in a mass spectrum of a compound containing that element. Thus, the molecular weight of a compound as determined by mass spectrometry will correspond to the sum of the masses of the most abundant isotopes of the elements which constitute that compound. A table of isotopic abundances of elements common in organic compounds is given below.

Isotope	% Relative Abundance	Isotope	% Relative Abundance
^1H	100.00	^{35}Cl	100.00
^2H	0.016	^{37}Cl	32.5
^{12}C	100.00	^{79}Br	100.00
^{13}C	1.08	^{81}Br	98.0

Mass spectrometers can operate in either low or high resolution modes. In the low resolution mode, a mass spectrometer gives masses of ions to the nearest integral values. In high resolution mode, the mass of an ion can be determined to 0.0001 of a mass unit. Thus, whereas at low resolution, each of CO, N_2 and C_2H_4 has $M^{+\bullet}$ at m/z 28, a high resolution mass spectrum would distinguish each of the foregoing on the basis of their exact molecular weights. By using the accurate masses below, calculate the exact molecular weights of these compounds.

$$^1H = 1.0078, \qquad ^{12}C = 12.0000, \qquad ^{14}N = 14.0031, \qquad ^{16}O = 15.9949$$

Molecular formula	Molecular Weight
CO	
N_2	
C_2H_4	
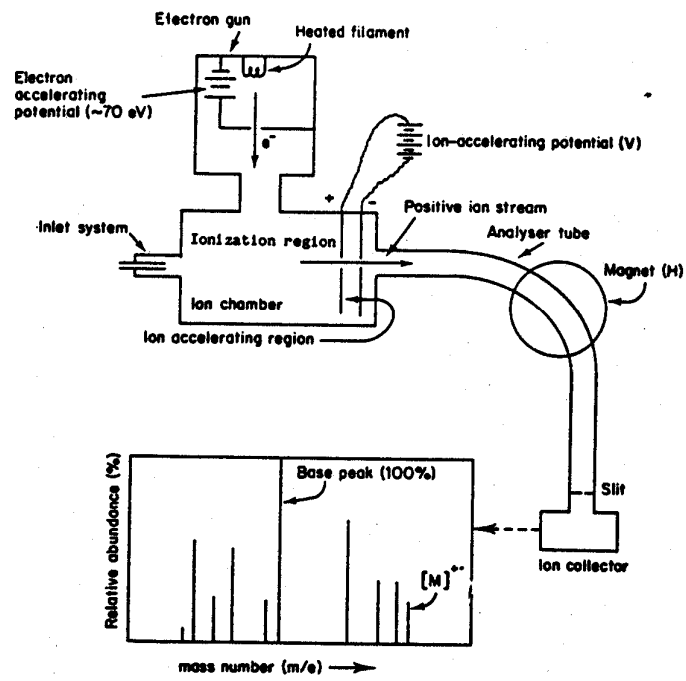
SCHEMATIC DIAGRAM OF AN ELECTRON-IMPACT MASS SPECTROMETER

Absorption Spectroscopy

Absorption spectroscopy measures the frequencies and intensities of electromagnetic radiation that are absorbed by a molecule. The electromagnetic spectrum spans the range of frequencies from about 10^6 Hz to about 10^{20} Hz. These frequencies correspond to the range of wavelengths from about 300 metres to about 3×10^{-12} metres, according to the relationship

$$v = c/\lambda$$ where v is the frequency of the radiation
c is the speed of light
λ is the wavelength of the radiation.

Electromagnetic radiation can be described in terms of its energy according to the relationship

$$E = hv$$ where v is the frequency of the radiation
h is the Planck constant
E is the energy of the radiation.

wavelength (m)	3	3×10^{-2}	3×10^{-4}	3×10^{-6}	3×10^{-8}	3×10^{-10}	3×10^{-12}
frequency (Hz)	10^8	10^{10}	10^{12}	10^{14}	10^{16}	10^{18}	10^{20}
energy (kJ)							

gamma rays

x-rays

ultraviolet light

visible light

infrared light

microwaves

television waves

radio waves

The Electromagnetic Spectrum
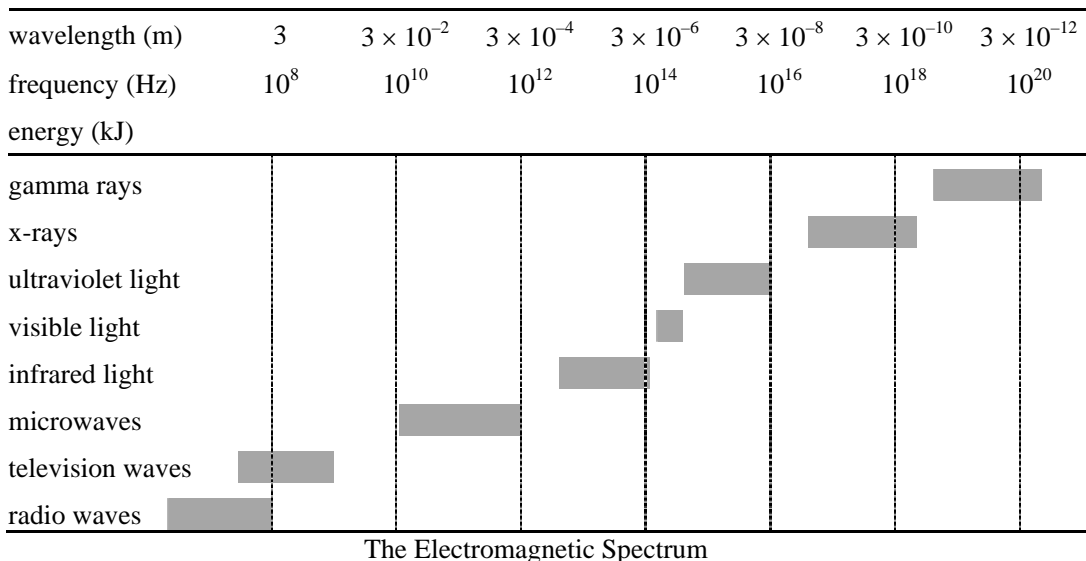
The absorption of electromagnetic radiation by a molecule excites the molecule from one energy state to a higher energy state. From experimental observations and from theories of molecular structure we know that the energy states of a molecule are sharply defined (quantised). The energy of radiation which is absorbed by a molecule corresponds to the energy difference between energy states of a molecule.

For organic compounds, the absorption of radiation is of most use in three main regions of the electromagnetic spectrum: the infrared (i.r.) region, the ultraviolet-visible (u.v.- vis.) region and the radiofrequency (r.f.) region.

Molecule in an excited
energy state

electromagnetic
radiation

$$\Delta E = hv$$

Molecule in a low
energy state
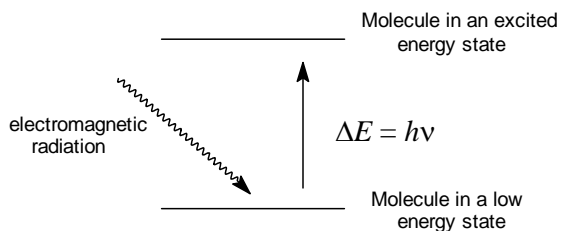
Infrared Spectroscopy

Radiation in the infrared region of the electromagnetic spectrum corresponds to the energy required to excite vibrations in covalent bonds. The absorption of infrared radiation causes the stretching and bending of bonds within a molecule. The stretching vibration occurs along the axis of the bond such that the bond length increases or decreases. The bending vibration involves a change in bond angle.

$$\leftrightarrow \leftrightarrow \qquad\qquad \uparrow \quad \uparrow$$
$$H–C\equiv N \qquad\qquad H–C\equiv N$$
$$\downarrow$$

Bond Stretching Bond Bending

The stretching or bending of each type of covalent bond (C–H, O–H, NH, C=O, *etc.*) requires absorption of radiation at a characteristic frequency in the infrared region of the electromagnetic spectrum. In general, the absorption of infrared radiation by a particular type of covalent bond is not greatly influenced by the rest of the molecule. This means that particular functional groups in a molecule can be detected by the absorption of infrared radiation at frequency ranges which are characteristic for the bonds contained in those particular groups.

Typically, infrared absorption frequencies are reported in wavenumbers (the number of complete wavecycles per centimetre). Wavenumbers ($\bar{\nu}$) are expressed in units of cm^{-1} (reciprocal centimetres) and are calculated from the wavelength (λ) of the radiation, according to the relationship

$$\bar{\nu} = \frac{1}{\lambda} \qquad \text{where } \lambda \text{ is expressed in centimetres.}$$

The bond stretching vibrations most useful from a diagnostic viewpoint fall approximately within the region of 3700-1500 cm^{-1}. The most important of these frequencies are the following.

Bond type	Frequency (cm^{-1})	Comments
C–H	2900-3000	sharp, intense, in most spectra
O–H or N–H	3200-3600	very broad
C=O	1650-1800	sharp, intense
C=C (aromatic)	≈ 1600	may be weak signal

Although the above values are good enough for most purposes, a slightly more accurate table is presented on the next page.

CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES

Functional Group	Bond	Stretching Absorptions (cm^{-1})	
Alkane	C–H	2960-2750	
Alkene	C–H	3090-3010	
	C=C	1680-1600	
Alkyne	C–H	3300	
	C≡C	2260-2100	
Arene	C–H	3100-2800	
	C=C	1600-1450	
Amine	N–H	3500-3200	1° two bands, 2° one band
Alcohol	O–H	3650-3590	
	O–H	3550-3450	hydrogen bonded
Aldehyde	C=O	1750-1640	
Ketone			
Carboxylic Acid	O–H	3000-2500	
	C=O	1740-1660	
Ester	C=O	1750-1670	
Amide 1°, 2°, 3°	C=O	1690-1630	
	N–H	3500-3140	1° two bands, 2° one band
Nitrile	C≡N	2260-2215	

The region from 1500-600 cm^{-1} contains absorptions due to complex vibrational energy changes involving motion of the molecule as a whole or combining bending, stretching and internal rotation. The bands in this region are complicated in appearance because there are many overlapping absorptions. This so-called "fingerprint" region can be used to check the identity of two samples by establishing that the same complex band pattern is shown by both.

Basic instrumentation for both infrared and ultraviolet spectroscopy (see next page) consists of an energy source, a sample cell, a dispersing device (prism or grating), a detector and a recorder. The solvent and the sample cell must be as transparent as possible in the relevant region of the electromagnetic spectrum because the amount of energy available for absorption by the sample must be maximised. In infrared spectroscopy sample cells are usually made of sodium chloride, and the solvent used is normally chloroform, carbon tetrachloride or carbon disulfide. For liquids, the neat sample as a liquid film between sodium chloride plates is often used.
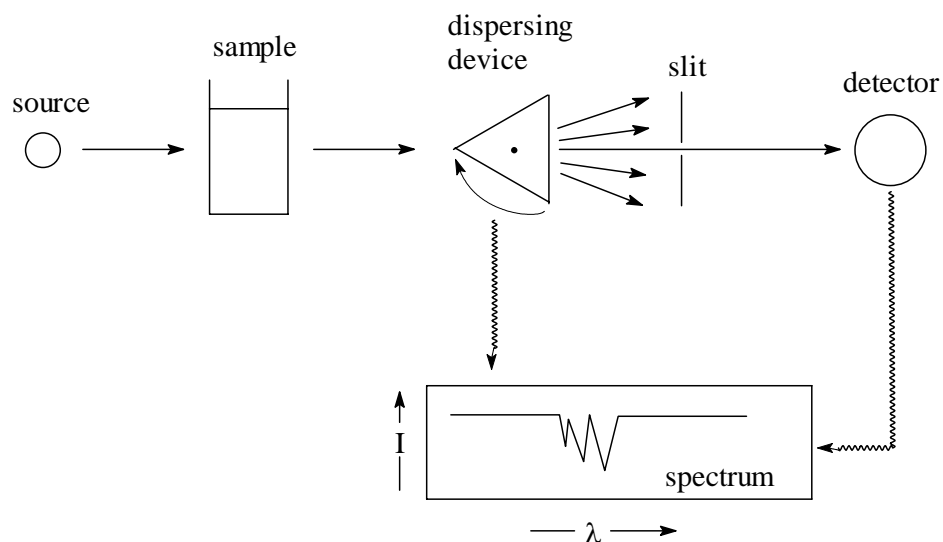
SCHEMATIC DIAGRAM OF A UV OR IR SPECTROMETER

The infrared spectrum of butanone is given below. Identify by the letters "a" and "b" in the spectrum the stretching absorptions due to the C–H and C=O bonds. Give $\bar{\nu}_{max}$ for the absorptions.

C–H	$\bar{\nu}_{max}$		C=O	$\bar{\nu}_{max}$
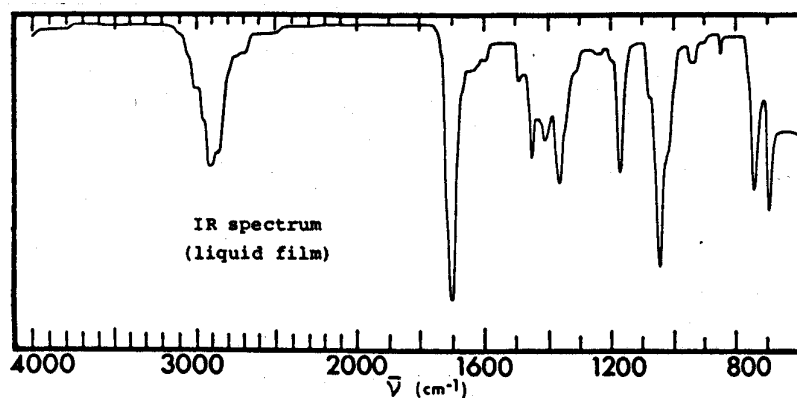
Ultraviolet-Visible Spectroscopy

> Ultraviolet radiation - 200 to 400 nm
> Visible radiation   - 400 to 800 nm

Ultraviolet radiation corresponds to the energy required to excite electrons in the bonds of organic molecules from a low energy level to a higher energy level. Electrons in σ-bonds are bound too tightly to be excited by radiation in the range of wavelengths from 200 to 400 nm. However, π-electrons in *conjugated* carbon-carbon and carbon-oxygen double bonds are easily excited to higher energy levels by ultraviolet radiation.   As in the case of infrared spectroscopy, an ultraviolet spectrometer records a plot of absorbance against wavelength. The spectra of organic compounds in solution are quite simple, consisting of broad regions of absorption.   The compound is dissolved in a solvent which is transparent to ultraviolet radiation - ethanol, water, cyclohexane and dioxan are commonly used, whilst the sample cell is usually made of quartz.

If the molecule absorbs strongly in the ultraviolet region in the range of wavelengths between 200 and 400 nm, then this indicates that the molecule contains a conjugated π-bond system within its structure. The greater the extent of conjugation within a molecule, the *less energy* required to excite the π-electrons and therefore the compound will absorb radiation at *longer wavelength*.   Extensively conjugated compounds such as β-carotene absorb blue light and consequently appear orange. (β-Carotene is the colouring pigment in carrots.)

λ_{max}

$CH_3\!-\!CH_3$	135 nm
$CH_2\!=\!CH_2$	167 nm
(acetone)	188 nm

outside normal u.v. range

(1,3-butadiene)	217 nm

β-carotene

λ_{max} 463 nm
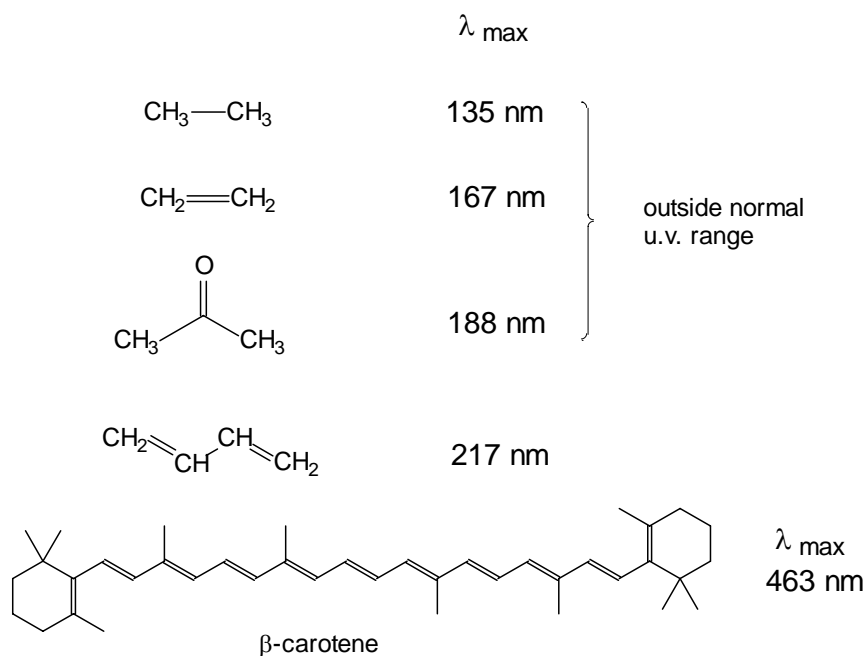
The intensity of the absorption of the ultraviolet radiation at a given wavelength is a characteristic property of a molecule, and can be used to determine *quantitatively* the amount of absorbing species in a solution.

Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance or n.m.r. spectroscopy involves the absorption of radiation in the radiofrequency range (1×10^6 to 8×10^8 Hz) of the electromagnetic spectrum. The nuclei of certain isotopes, for example ^1H, ^{13}C, ^{19}F, *etc.*, behave as if they were spinning charges. A spinning charge creates a magnetic field and thus acts as if it were a small bar magnet. When placed in a strong magnetic field, the spinning charge can adopt either one of two allowed orientations: with its "north" pole aligned with the direction of the strong magnetic field or against it.
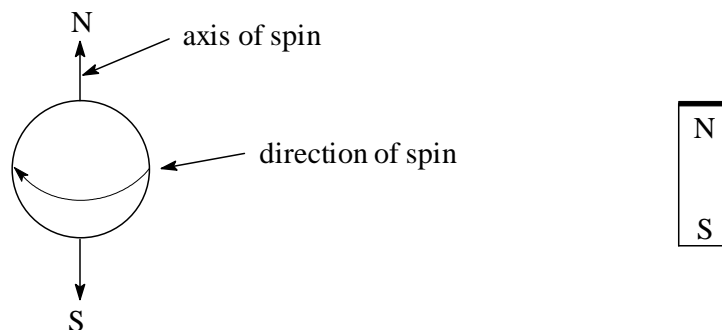
A spinning charge behaves like a small bar magnet.

Radiofrequency radiation corresponds to the energy required to flip a nucleus which is aligned in the direction of a strong magnetic field to the orientation opposed to the direction of the magnetic field. Nuclear magnetic resonance differs from other forms of spectroscopy in that an organic compound must be placed in a strong magnetic field before electromagnetic radiation can be absorbed. The sample is normally dissolved in a solvent, whose nuclei are not affected by the radiofrequency radiation, in a narrow glass tube which is placed between the poles of a large electromagnet and subjected to the radiofrequency radiation.

By far the most important nuclei which absorb radiofrequency radiation when placed in a magnetic field are ^1H (*i.e.* the proton) and ^{13}C.

^1H n.m.r. spectra are usually run in solution. Solvents that contain hydrogen are unsuitable as the signal from the solvent totally swamps all the signals from the compound being studied. Most n.m.r. solvents are simple organic liquids in which the usual ^1H isotope has been replaced with the ^2H isotope. ^2H is also known as deuterium (symbol D) and these deuterated solvents are commercially available. The most common n.m.r. solvents are:

$CDCl_3$	deuterated chlorform
CCl_4	carbon tetrachloride
D_2O	heavy water
C_6D_6	deuterated benzene
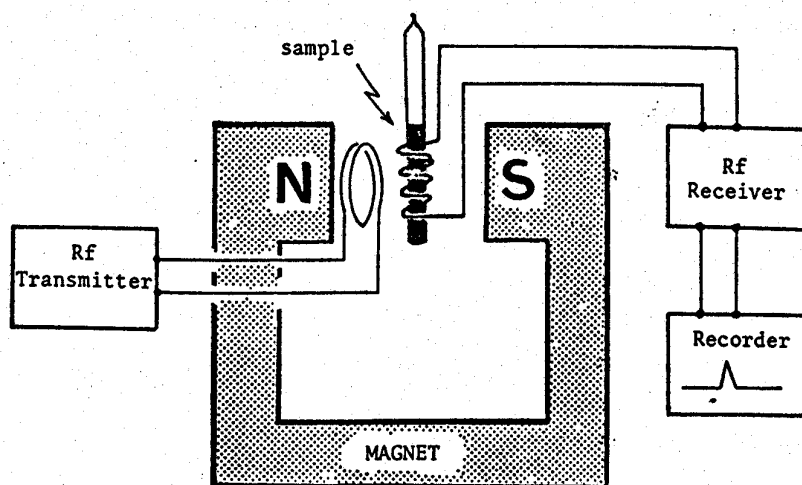
BASIC COMPONENTS OF AN NMR SPECTROMETER

The frequency (measured in MHz) at which nuclei absorb radiofrequency radiation depends mainly on the strength of the applied magnetic field as shown below. The magnetic field experienced by each nucleus, however, is not exactly the same as the applied magnetic field because the electrons in the bonds very slightly alter the magnetic field in their immediate vicinity. Nuclei in different environments thus absorb at different frequencies - an effect which is measured in Hz. Atoms (and therefore their nuclei) in exactly the same surroundings (by symmetry analysis) are called chemically equivalent. *All chemically equivalent atoms absorb at the same frequency in an n.m.r. spectrum.*
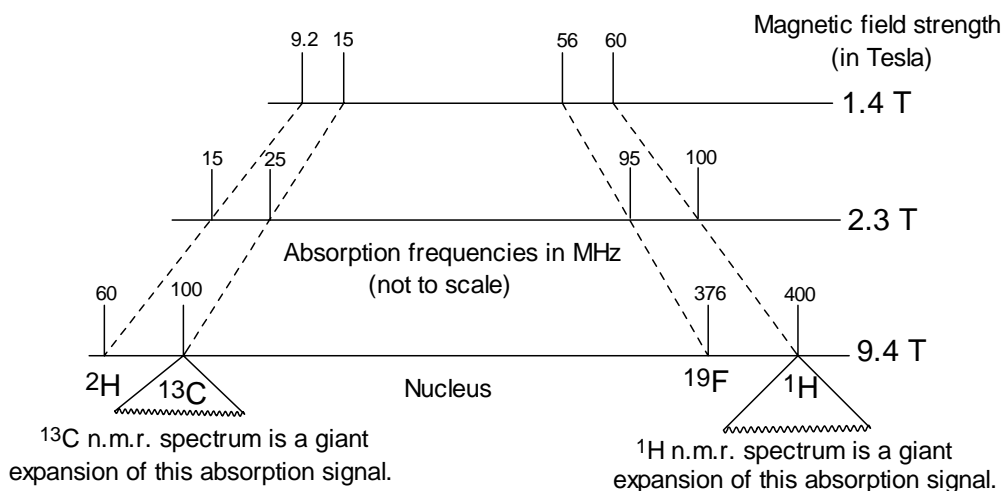
^{13}C n.m.r. spectrum is a giant expansion of this absorption signal.

^{1}H n.m.r. spectrum is a giant expansion of this absorption signal.

^{1}H NMR Spectroscopy

In reporting the frequencies where groups of chemically equivalent protons absorb, all signals are reported in terms of how far they are shifted from a reference signal. The difference between the reference signal and the signal of interest is termed the *chemical shift* and given the symbol δ. For ^{1}H n.m.r. spectroscopy, the reference signal is usually the single absorption of *tetramethylsilane* (TMS), $Si(CH_3)_4$. Chemical shifts are reported in dimensionless units of ppm (parts per million) which are independent of the magnetic field strength at which the spectrum is obtained. The signals from protons in organic compounds usually fall within the range of 0 to 13 ppm from TMS.

The chemical shifts (δ in ppm) of ^{1}H in common organic environments are as follows:

Tetramethylsilane $Si(CH_3)_4$	0 (By definition)
Protons attached to sp^3 hybridised carbon atoms (H–C)	0.8 - 1.8
Protons attached to sp hybridised carbon atoms (H–C≡C–)	2 - 3
Protons attached to sp^2 hybridised carbon atoms (H–C=C)	5 - 8
Protons attached to aromatic rings	6 - 9
Aldehydic protons (H–C=O)	9 - 10
Protons attached to an oxygen-bound carbon (H–C–O)	3.4 - 4.0
Protons attached to a carbonyl-bound carbon (CH_3–C=O)	≈ 2.1

Labile protons (–OH, –NH$_2$, –SH, –COOH *etc.*) have variable chemical shift ranges, depending upon the exact experimental conditions of concentration, temperature *etc.*, which influence the amount of hydrogen-bonding.

The ^{1}H n.m.r. spectrum of a mixture composed of differing concentrations of acetone (a), benzene (b), dimethyl ether (d), 1,1-dichloroethylene (e) and tetramethylsilane (t) is given below. Use the above list of chemical shifts to identify and label the signals due to each component of the mixture.
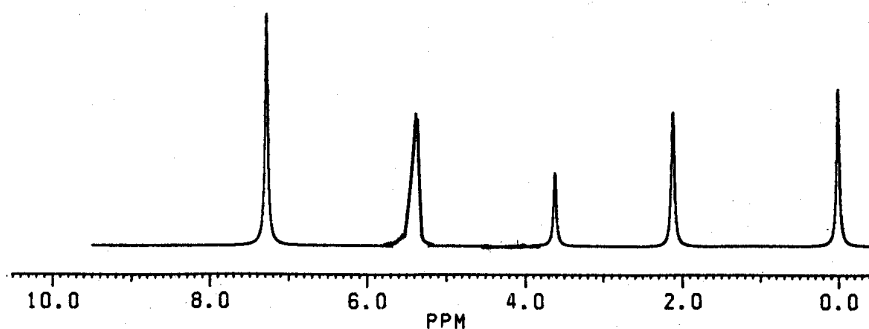
Fine structure is evident in many n.m.r. signals. This fine structure or splitting pattern of each signal is due to the presence of other protons in the vicinity (*i.e.* those which are attached to adjacent atoms) of the proton giving rise to the signal. The degree of signal splitting (or multiplicity) is given by the "n + 1 rule". *The signal from a proton with "n" chemically equivalent neighbours will be split into "n + 1" peaks. Note, however, that chemically equivalent protons do not split each other.*

Neighbours	Peaks	Multiplicity	Internal Intensities
0	1	singlet	1
1	2	doublet	1 1
2	3	triplet	1 2 1
3	4	quartet	1 3 3 1
4	5	quintet	1 4 6 4 1
5	6	sextet	1 5 10 10 5 1
6	7	septet	1 6 15 20 15 6 1

The relative intensity of each signal (as measured by its relative area) is directly proportional to the number of protons giving rise to that signal.

An example of a ^{1}H n.m.r. spectrum illustrating all these points is given below.
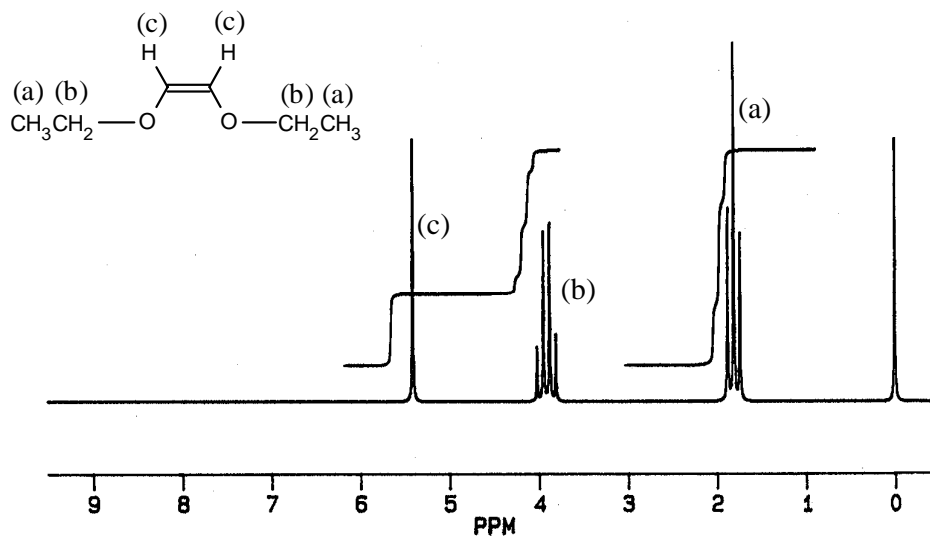
(a) These protons have two neighbours and thus appear as a triplet.
(b) These protons have three neighbours and thus appear as a quartet.
(c) These protons are chemically equivalent. Although they are neighbours, they do not split each other. This signal will appear as a singlet.

The relative intensities of the signals are calculated by determining the number of protons giving rise to each signal.

$$(a) : (b) : (c) \ = \ 6 : 4 : 2 \ = \ 3 : 2 : 1$$

^{13}C NMR Spectroscopy

In reporting the frequencies where groups of chemically equivalent carbons absorb, all signals are reported in terms of how far they are shifted from a reference signal. The difference between the reference signal and the signal of interest is termed the *chemical shift* and given the symbol δ. For ^{13}C n.m.r. spectroscopy, the reference signal is usually the single absorption of *tetramethylsilane* (TMS), $Si(CH_3)_4$ taken to be 0.0 ppm Chemical shifts are reported in dimensionless units of ppm (parts per million) which are independent of the magnetic field strength at which the spectrum is obtained.

In ^{13}C n.m.r. spectra there is one absorption for each different carbon environment in a molecule. If more than one carbon is in an identical environment within the molecule, the signals in the spectrum are coincident. For example, in the spectrum of propane ($CH_3CH_2CH_3$), the two CH_3 carbons appear as one line which is in a different place to the signal from the CH_2. In the ^{13}C n.m.r. spectrum the frequency of absorption is represented by the δ scale which runs from 0 to 200 with units of parts per million (ppm). A particular carbon environment results in a signal in a characteristic region of the spectrum, summarised below:

200	150	100	δ (ppm)	50	0

TMS

| C=O | C=C (aromatic rings) | C=C (alkenes) | | C—O | C—C C—H (alkanes) |
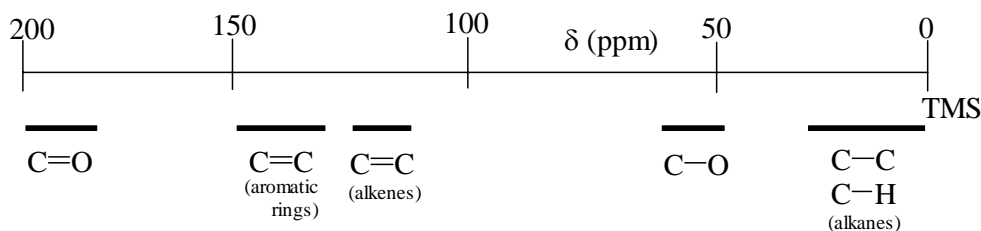
Demonstrator's Initials	

LABORATORY WORKSHOP : PROBLEMS IN SPECTROSCOPY

Mass Spectrometry

1.   What are the masses of the following ions?

$[CH_3]^+$		$[C_2H_5]^+$		$[C_6H_5]^+$		$[NH_2]^+$	

2.   At what *m/z* ratios would the parent ions derived from the following molecules appear in a mass spectrum?

CH_3—C(=O)—CH_3	(butadiene)	cyclohexanol OH

3.   A compound containing carbon, hydrogen and nitrogen displays a molecular ion peak in its mass spectrum at m/z 41 and a fragment ion at m/z 15. Give the structure of a compound which is consistent with these data.

4.   The mass spectrum of butanone is given below. On the diagram, identify (a) the parent peak and (b) the base peak. Give the formulas of the parent ion and the base peak ion.
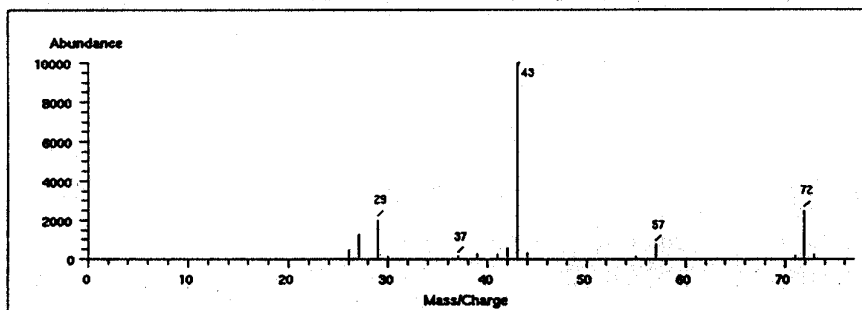
butanone
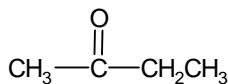
Parent Ion	Base Peak Ion

5.   The mass spectrum of chloroethane is given below. Give the molecular formulas of the ions at m/z 66 and 64.
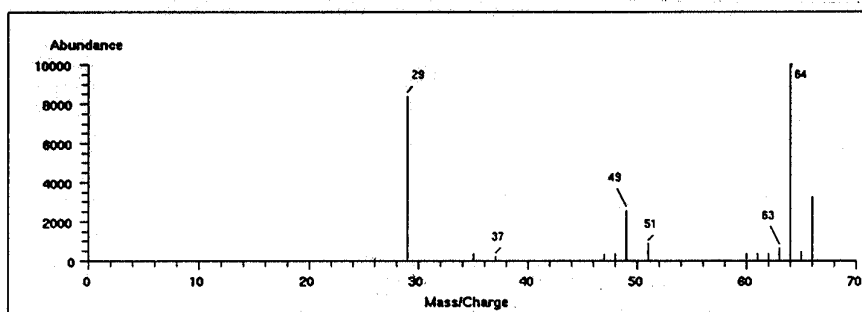
Molecular weight	Molecular formula
66	
64	

Why is the peak at m/z 64 approximately three times the height of the peak at 66?

Infrared and Ultraviolet-Visible Spectroscopy

1.   The infrared spectrum of 2-butanol is given below. Identify the stretching absorptions due to (a) the C–H and (b) the O–H bonds. Write the letters "a" and "b" next to the relevant absorptions in the spectrum. Give $\bar{v}_{max}$ for the absorptions.

IR spectrum
(liquid film)

$\bar{v}$ (cm^{-1})

C–H	$\bar{v}_{max}$		O–H	$\bar{v}_{max}$
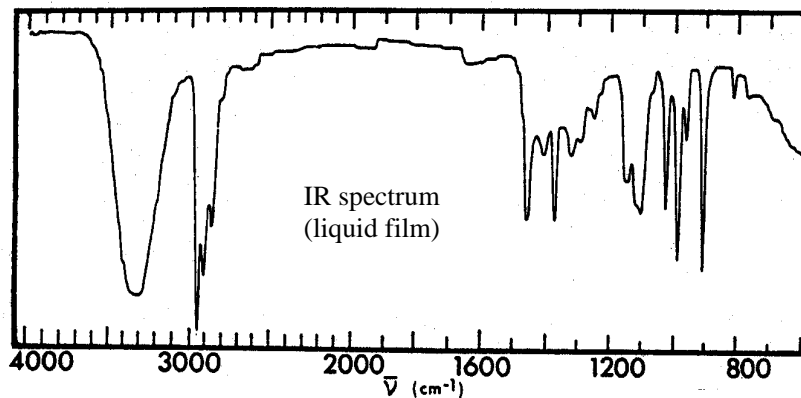
2.   The infrared spectrum of 2,6-dibromoaniline is given below. Identify with the letters "a" and "b" in the spectrum the stretching absorptions due to (a) the N–H and (b) the C=C bonds in the aromatic ring. Give $\bar{v}_{max}$ for the absorptions.

IR spectrum
(CHCl$_3$ solution)

$\bar{v}$ (cm^{-1})

N–H	$\bar{v}_{max}$		C=C	$\bar{v}_{max}$
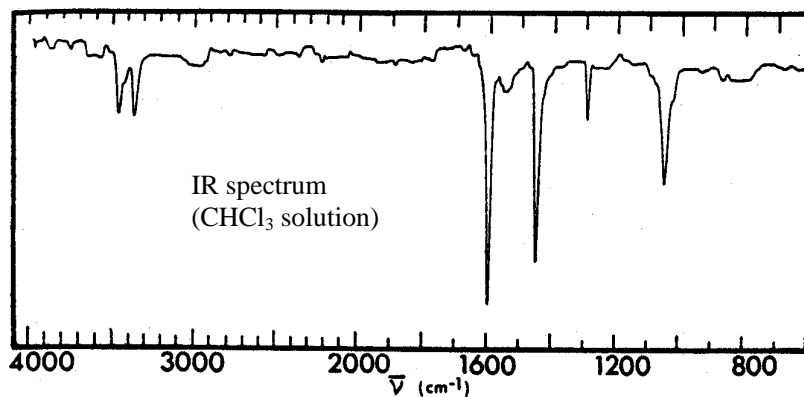
3.   The infrared spectrum of a carboxylic acid is given below. Identify with the letters "a" and "b" in the spectrum the stretching absorptions due to (a) the C=O and (b) the O–H bonds of the carboxyl group. Give $\bar{v}_{max}$ for the absorptions.

IR spectrum
(CHCl$_3$ solution)

4000   3000   2000   1600   1200   800
$\bar{v}$ (cm^{-1})

C=O	$\bar{v}_{max}$		O–H	$\bar{v}_{max}$
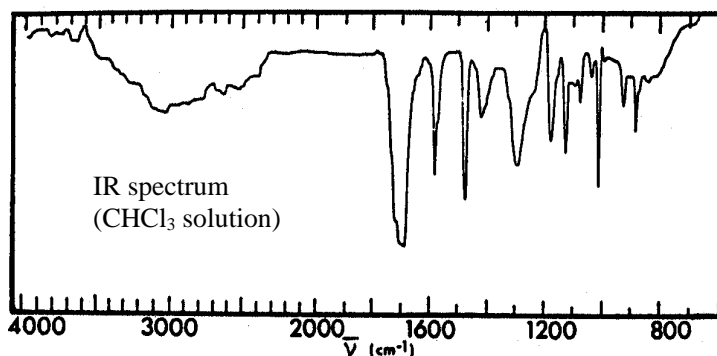
4.   A substance has a molecular formula of C_2H_5NO and has infrared absorptions at 3500, 3380, 2925 and 1675 cm^{-1}. Give a structure for the compound which is consistent with these data.

Structure

5.   A substance has a molecular formula of $C_3H_6O_2$. It has an infrared spectrum with a broad peak at 3000-2500 cm^{-1} and an intense sharp peak at 1715 cm^{-1}. Give a structure consistent with these data.

Demonstrator's Initials	

6.   Which of the following compounds would be expected to absorb radiation in the ultraviolet region (200 - 400 nm)?

(A)

(B)

(C)

(D)

H—C≡C—CH=CH₂

(E)

(F)

(G)

O=C=O

(H)

CH_3—CCl_3

(J)

(I)
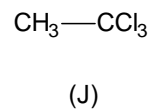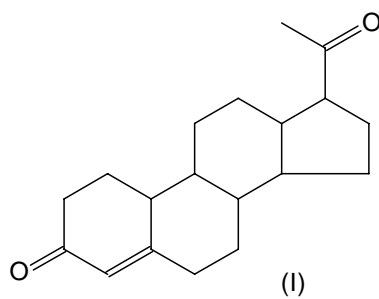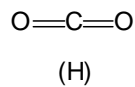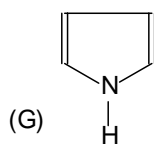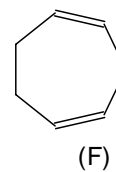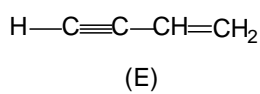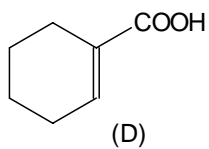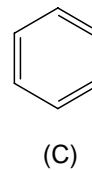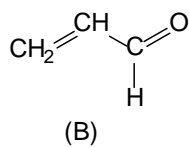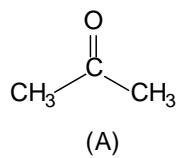
A	B	C	D	E	F	G	H	I	J

| Demonstrator's Initials | |

^{1}H NMR Spectroscopy

1.   By using the letters a, b, c, *etc.*, label the equivalent sets of protons in the following compounds. The first compound has been done as an example.
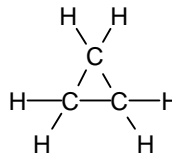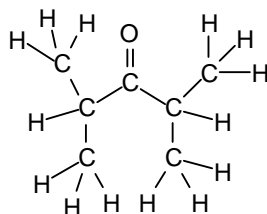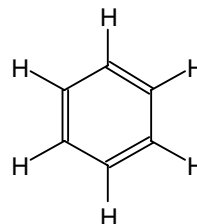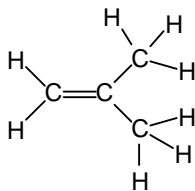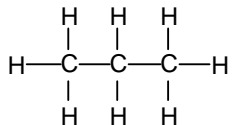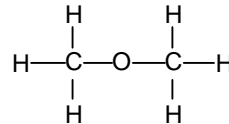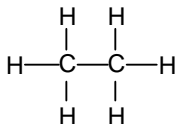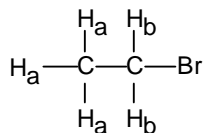
2.   How many signals would you expect to find in the ^{1}H n.m.r. spectrum of the following compounds?

CH_4
(a)

CH_3CH_3
(b)

$(CH_3)_3CBr$
(c)

CH_3CH_2OH
(d)

CH_3CCH_3
(e)

$CH_3C(OCH_3)_3$
(f)

$CH_3CH_2CHCH_2CH_3$
(g)

(h)
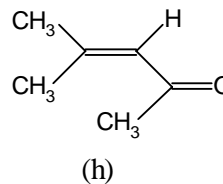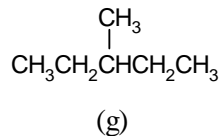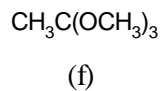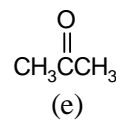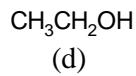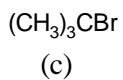
(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)

Demonstrator's Initials	

3.   The ^{1}H n.m.r. spectrum of acetone is given below. Give the chemical shifts of the signals due to (a) TMS and (b) acetone. Explain why the signals for each compound appear as singlets (single peaks).
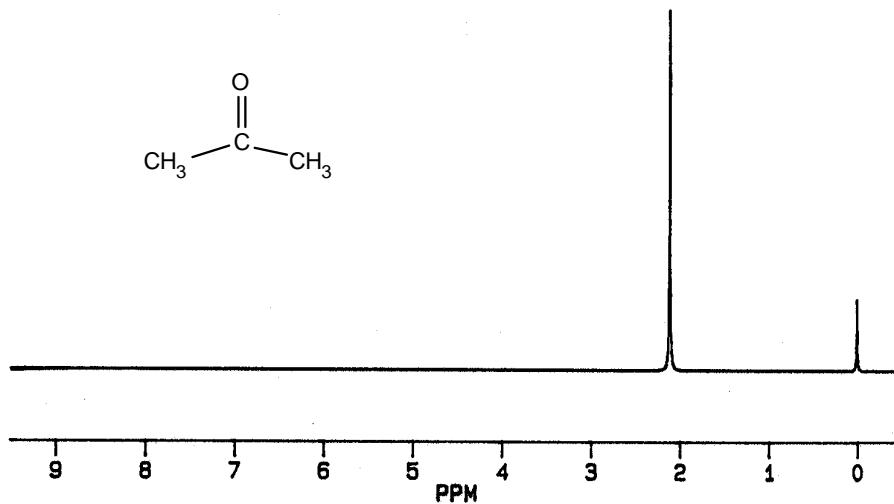
a: $\delta_{TMS} =$ ppm	b: $\delta_{acetone} =$ ppm

4.   The ^{1}H n.m.r. spectrum of methyl formate is given below. Give the chemical shifts of the signals due to (a) the CH_3 group and (b) the proton attached to the carbonyl group. Give the relative intensities of the signals.
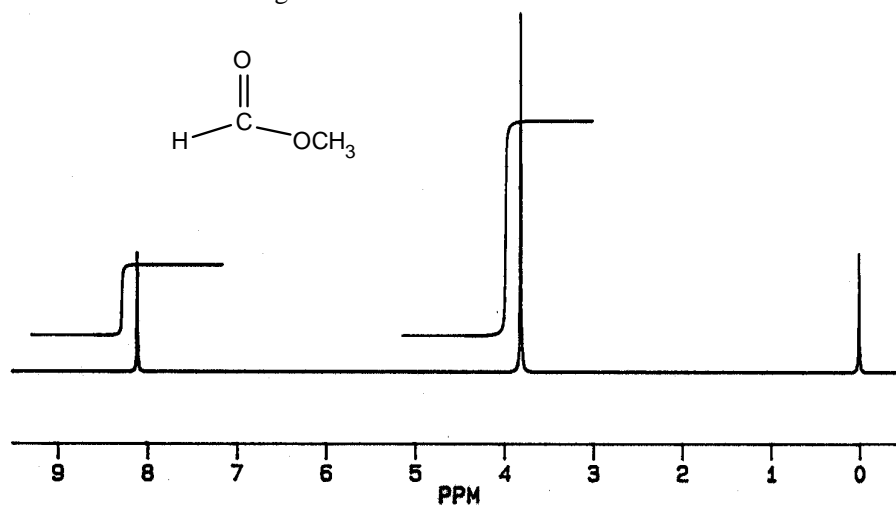
a = ppm; b = ppm	Relative Intensities a:b =

5.   The ^{1}H n.m.r. spectrum of butanone is given below. Using the letters "a", "b" and "c", identify the signals due to (a) the CH_3 group attached to the carbonyl group, (b) the CH_2 group and (c) the CH_3 group attached to the CH_2 group.
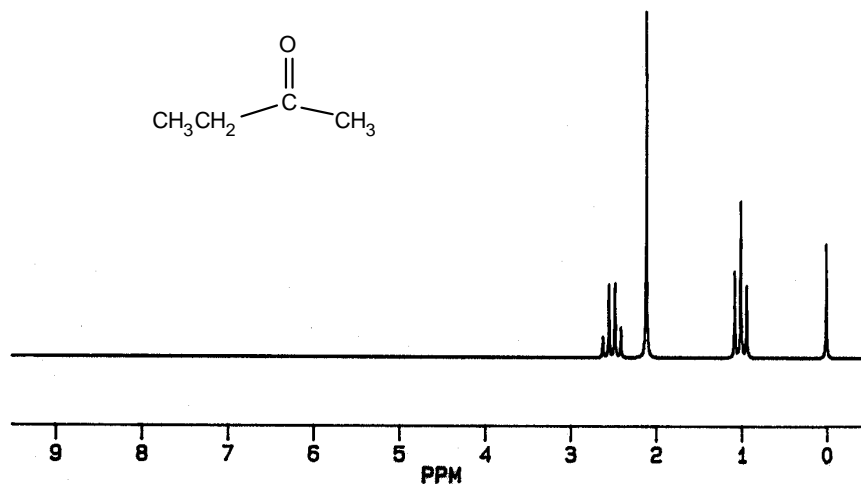
6.   Give the chemical shifts for and identify the signals in the ^{1}H n.m.r. spectrum of triethylamine. One of these signals is termed a triplet, the other a quartet. Explain the origin of the quartet.
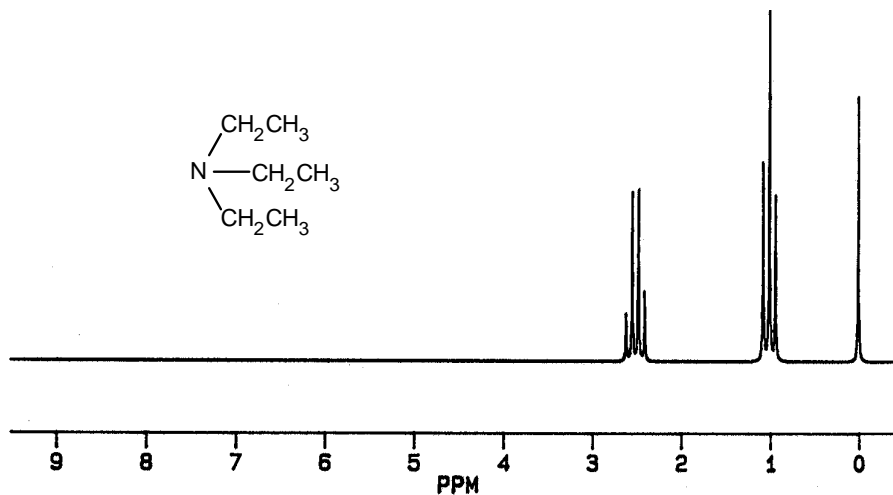
a = ppm;	b = ppm
a is due to	b is due to
Quartet is due to	

7.   Assign the signals in the ^{1}H n.m.r. spectrum of 2-bromoethyl acetate.
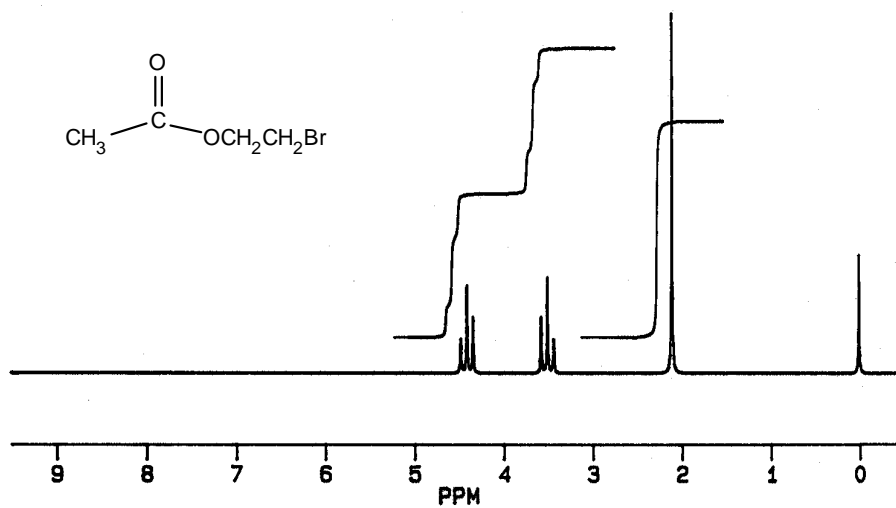
a is due to	b is due to	c is due to

8.   The compound A has a molecular formula of $C_4H_8O_2$ and its ^{1}H n.m.r. spectrum is given below. Give a structure of compound A consistent with these data.
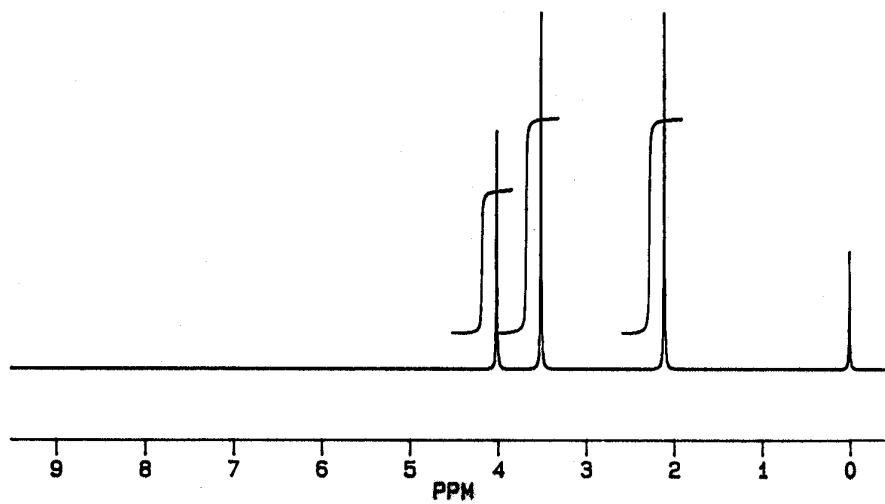
A:

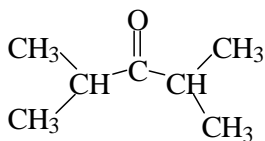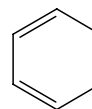9.   The ^{1}H n.m.r. spectrum of one of the isomers of trichloroethane is given below. Which isomer is it? What are the relative areas of the signals in the spectrum?
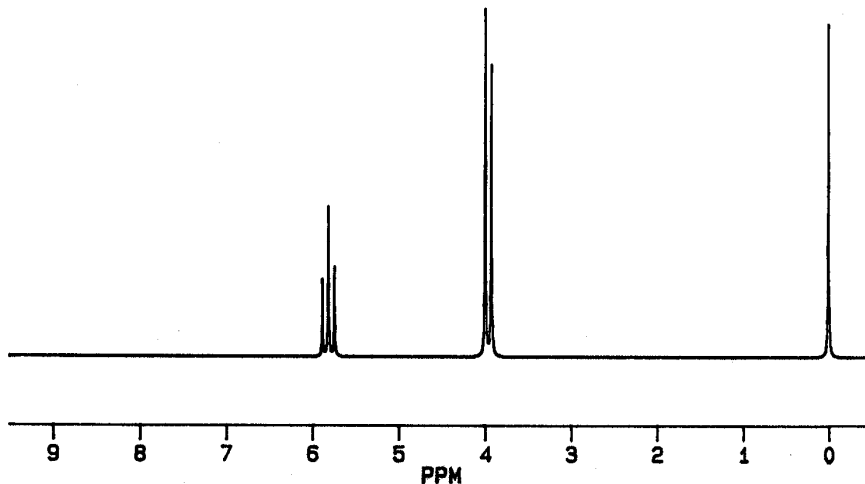
Isomer:	Relative Areas:

| Demonstrator's Initials	

^{13}C NMR Spectroscopy

1.   By using the letters a, b, c, *etc.*, label the equivalent sets of carbon atoms in the following compounds. The first compound has been done as an example.

a   b
CH$_3$—CH$_2$Br   CH$_3$—CH$_3$ CH$_3$—O—CH$_3$

CH$_3$—CH$_2$—CH$_3$ CH$_2$=C(CH$_3$)CH$_3$

CH$_3$CH(CH$_3$)—C(O)—CH(CH$_3$)CH$_3$ ⌇OH

2.   How many signals would you expect to find in the ^{13}C n.m.r. spectrum of the following compounds?

CH$_4$ CH$_3$CH$_3$ (CH$_3$)$_3$CBr   CH$_3$CH$_2$OH   CH$_3$CCH$_3$ (with =O)

(a)   (b)   (c)   (d)   (e)

CH$_3$C(OCH$_3$)$_3$ CH$_3$CH$_2$CHCH$_2$CH$_3$ (with CH$_3$)

(f)   (g)   (h)

CH$_3$—O—C(=O)—CH$_2$CH$_3$

(i)   (j)   (k)   (l)

(m)   (n)   (o)   (p)

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
(i)	(j)	(k)	(l)	(m)	(n)	(o)	(p)
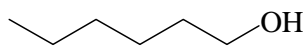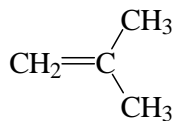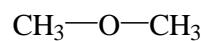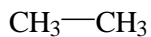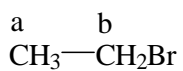
3.   The ^{13}C n.m.r. spectrum of acetone is given below. Give the chemical shifts of the signals due to (a) carbonyl carbon and (b) methyl groups.
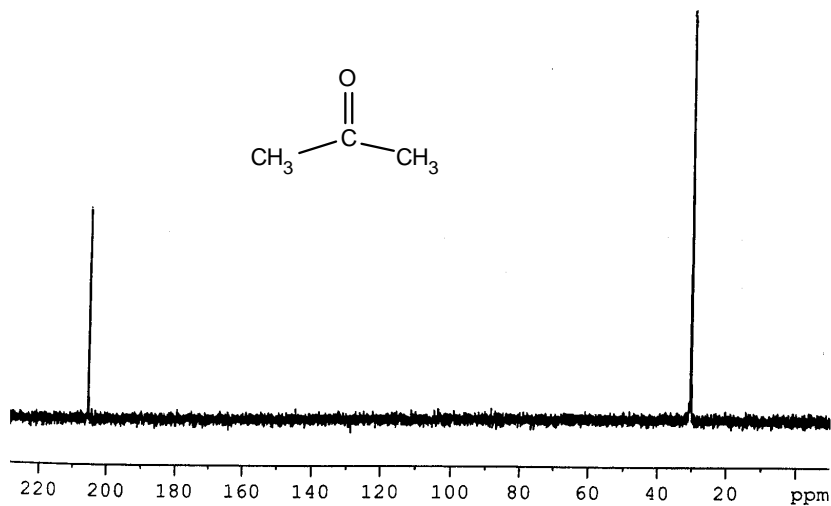
a) $\delta_{C=O}$ = ppm	b) δ_{methyl} = ppm

4.   The ^{13}C n.m.r. spectrum of diethyl ether ($CH_3CH_2OCH_2CH_3$) is given below. Give the chemical shifts of the signals due to (a) the CH_3 groups and (b) the CH_2 groups.
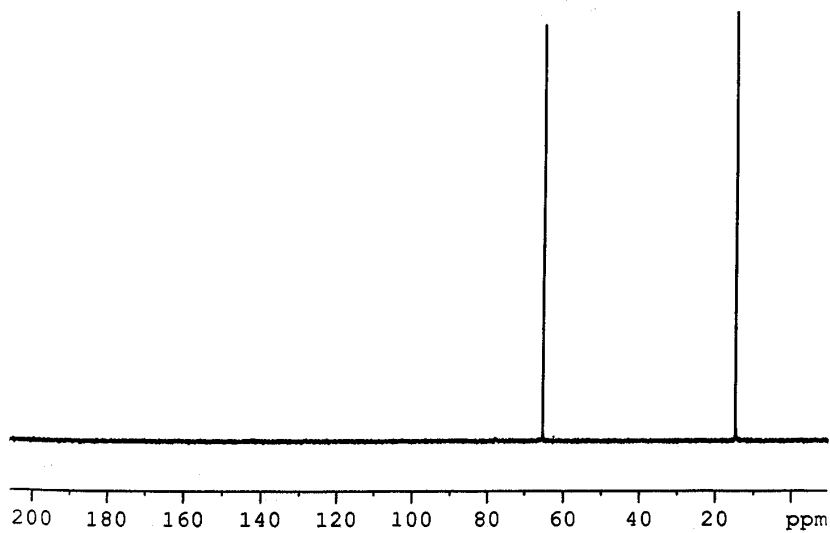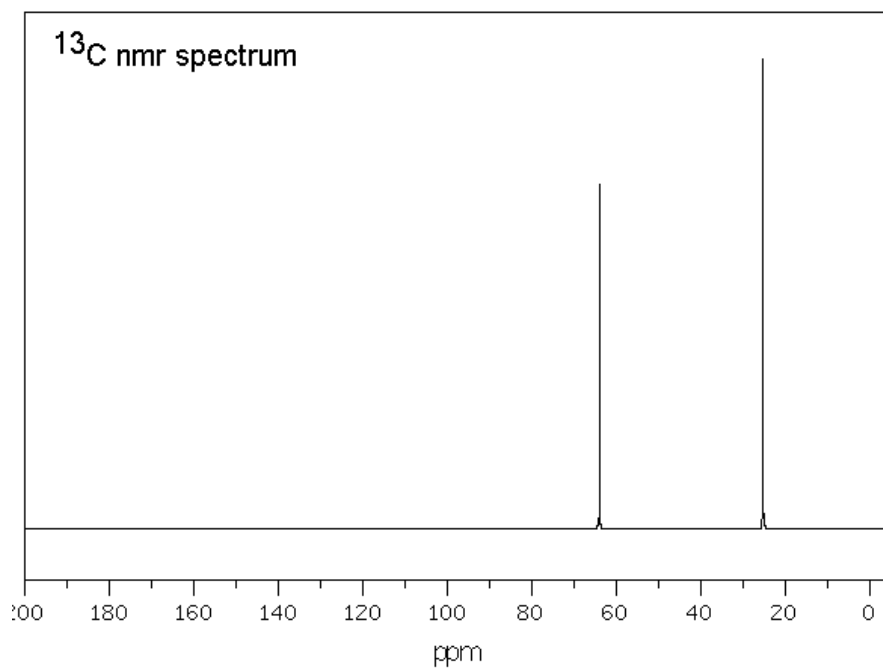

a) δ_{methyl} = ppm	b) $\delta_{methylene}$ = ppm

5.   The ^{13}C n.m.r. spectrum of ethyl acetate is given below. Mark clearly on the spectrum which carbon is assigned to each signal. (Hint: compare this spectrum with that of acetone and diethyl ether.)
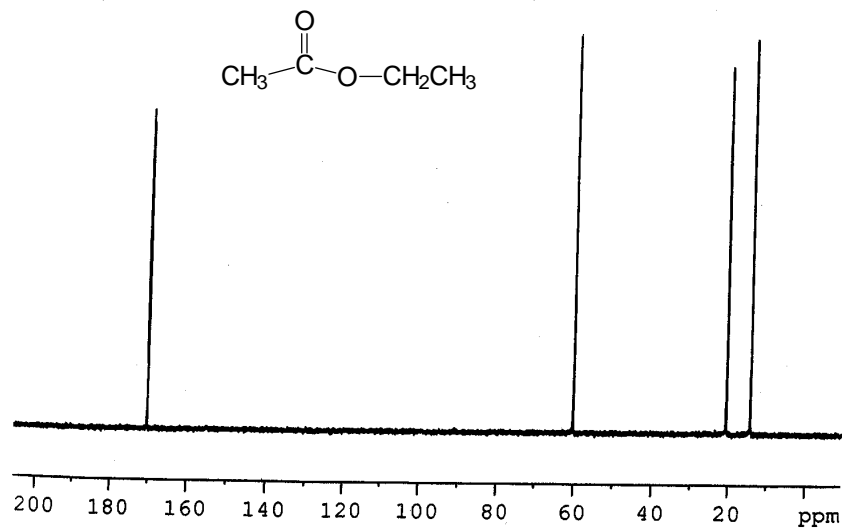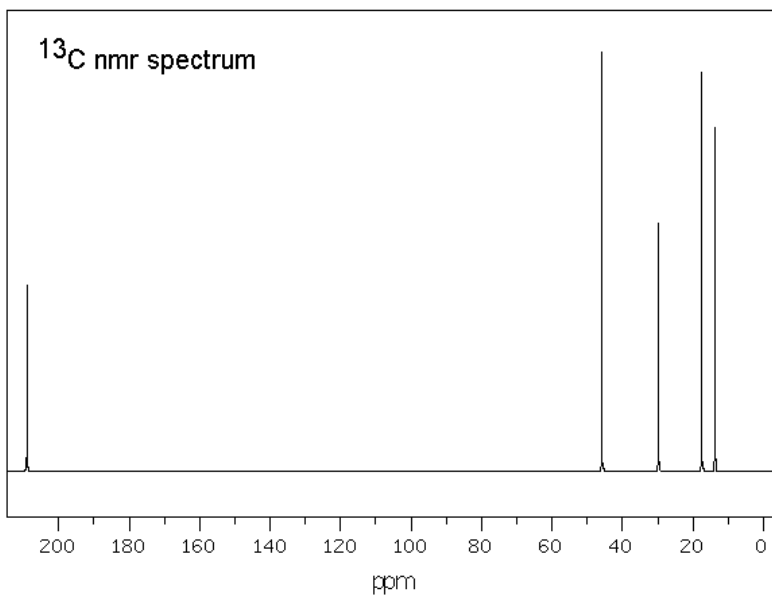

6.   A compound has the molecular formula C_3H_8O and has the ^{13}C n.m.r. spectrum given below. Give a structure for this molecule.

7.   A compound has the molecular formula C_3H_8O and has the [13]C n.m.r. spectrum given below. Give a structure for this molecule.
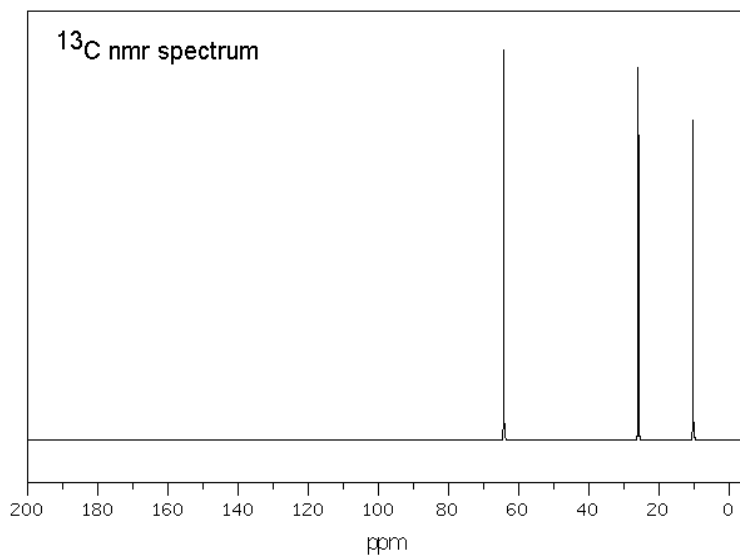
8.   The [13]C n.m.r. spectrum of one of the isomers of pentanone, $C_5H_{10}O$, is given below. Give a structure for this molecule.

9.   Anisol is an aromatic ether. Is the ^{13}C n.m.r. spectrum below, what you would predict for this molecule? Justify your answer.
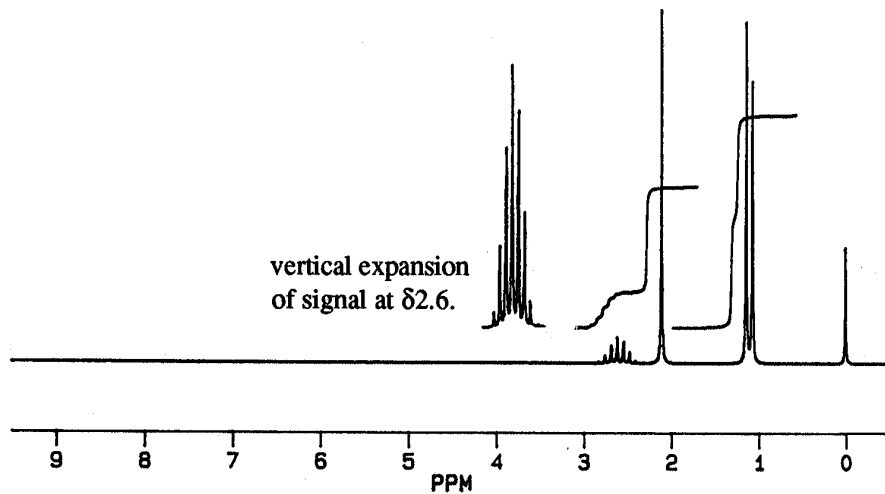
OCH$_3$

220   200   180   160   140   120   100   80   60   40   20   ppm
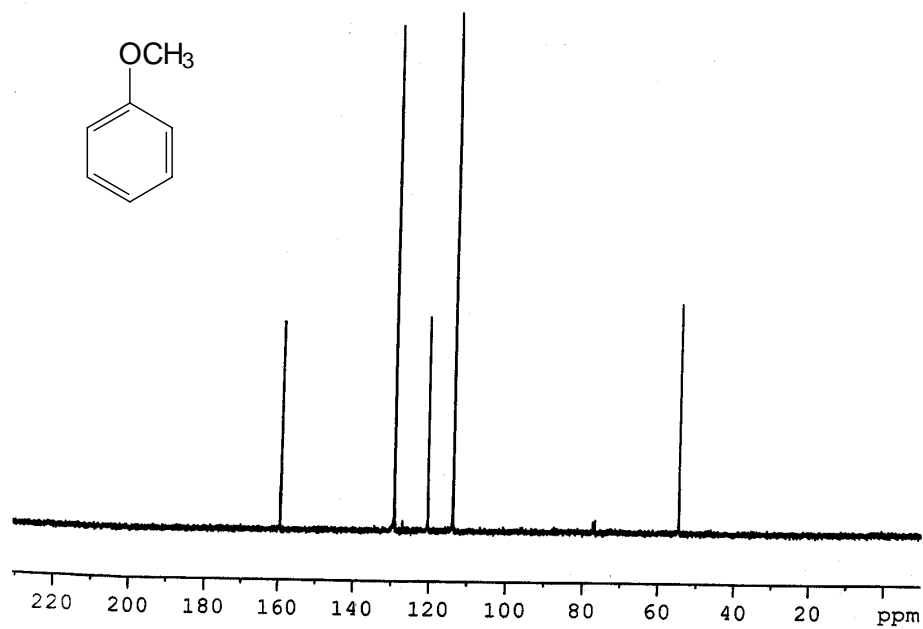
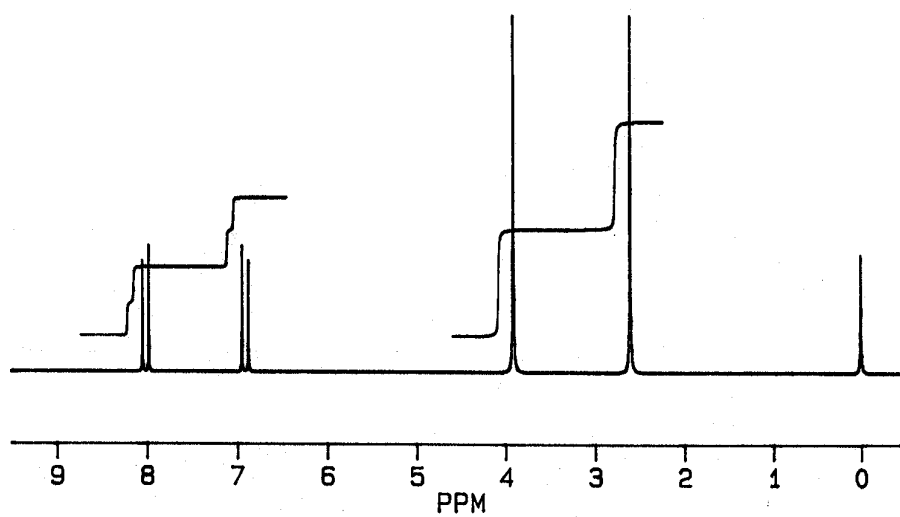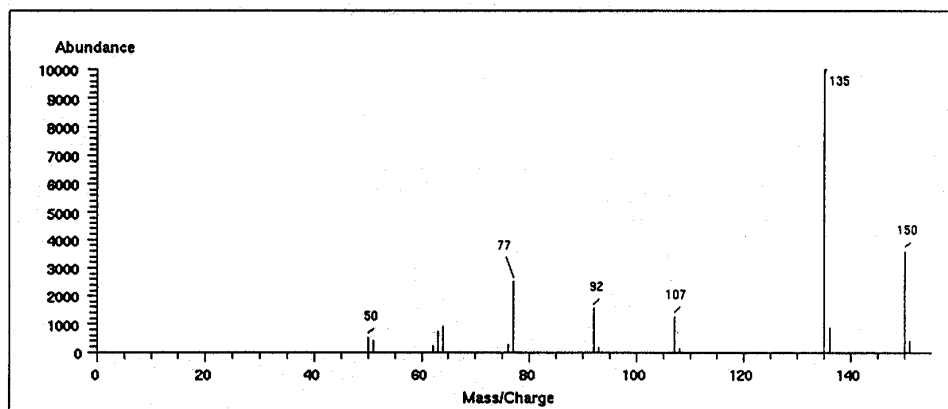Answer:

Demonstrator's Initials	

The Combined Use of Spectroscopic Techniques (including ^{1}H NMR).

1.   A compound has a strong absorption near 1720 cm^{-1} in its infrared spectrum and a parent ion at *m/z* 86 in its mass spectrum. Its ^{1}H n.m.r. spectrum is given below. Give a structure consistent with these data.

vertical expansion
of signal at δ2.6.

Structure:

2.   A compound of molecular formula $C_9H_{10}O_2$ has a strong absorption in the ultraviolet spectrum around 265 nm, and strong absorptions in the infrared spectrum at 1670 cm^{-1} and 2900 cm^{-1}. The mass spectrum and ^1H n.m.r. spectrum are given below. Give a structure consistent with these data.
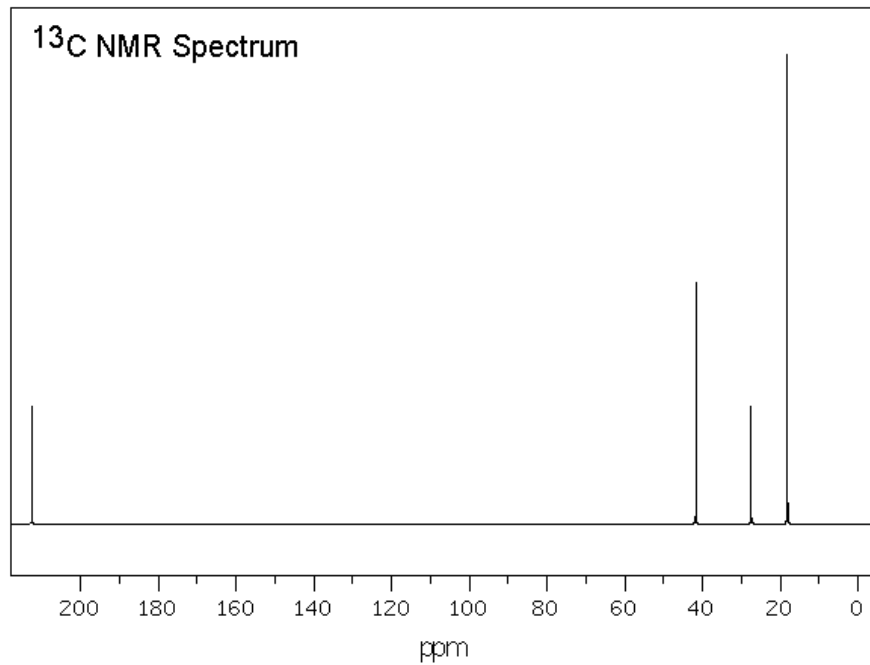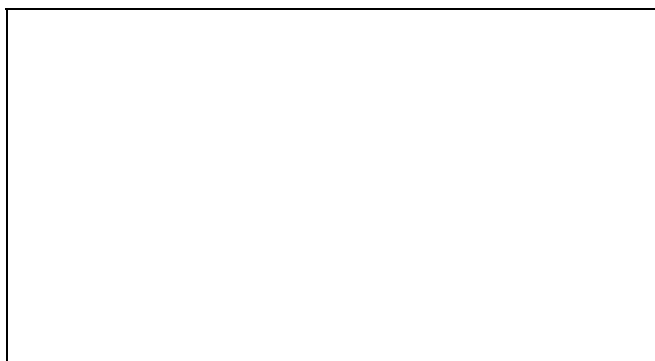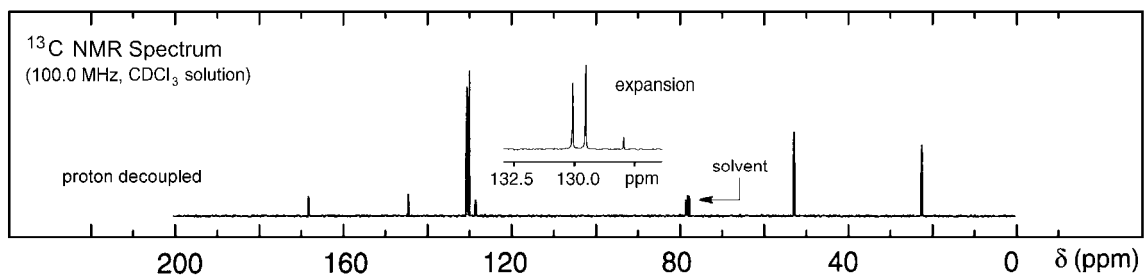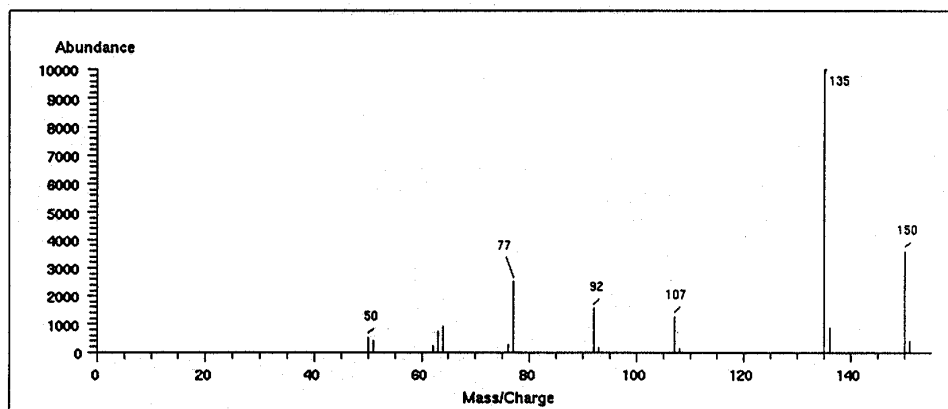

Structure:

Demonstrator's Initials	

The Combined Use of Spectroscopic Techniques (including ^{13}C NMR).

1.   A compound has a strong absorption near 1720 cm^{-1}, but no absorptions above 3000 cm^{-1} in its infrared spectrum. It has a parent ion at *m/z* 86 in its mass spectrum and its ^{13}C n.m.r. spectrum is given below. Give a structure consistent with these data.
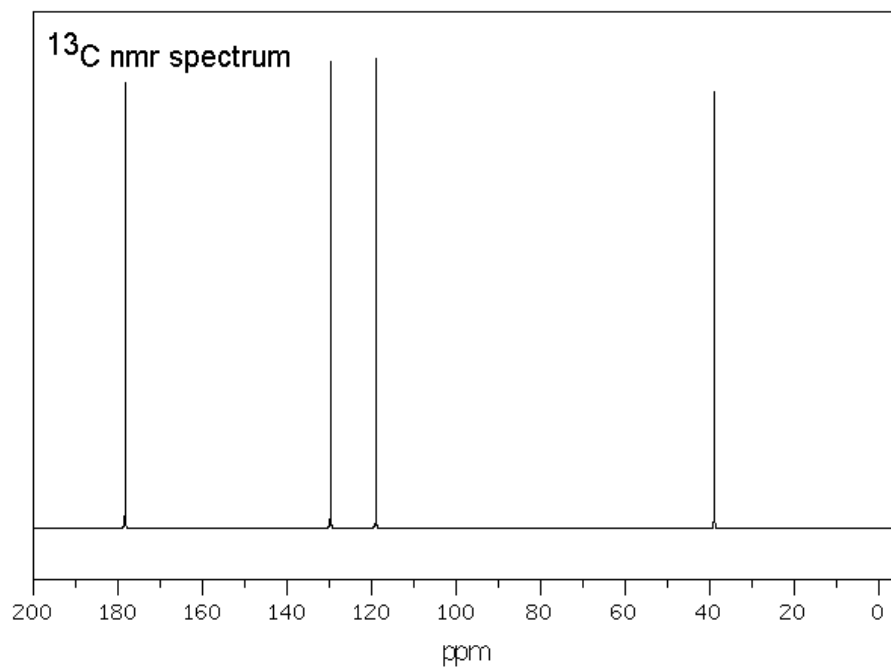

^{13}C NMR Spectrum

ppm

2.   A compound of molecular formula $C_9H_{10}O_2$ has a strong absorption in the ultraviolet spectrum around 265 nm, and strong absorptions in the infrared spectrum at 1670 cm^{-1} and 2900 cm^{-1}. The mass spectrum and ^{13}C n.m.r. spectrum are given below. Give a structure consistent with these data.

3.   A compound of molecular formula $C_4H_6O_2$ has strong absorptions in the infrared spectrum at 1670 cm^{-1} and 3400 cm^{-1}.   The ^{13}C n.m.r. spectrum is given below.   Give a structure consistent with these data.

Demonstrator's Initials	