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Structure 3.2 HL

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cis-trans isomerism

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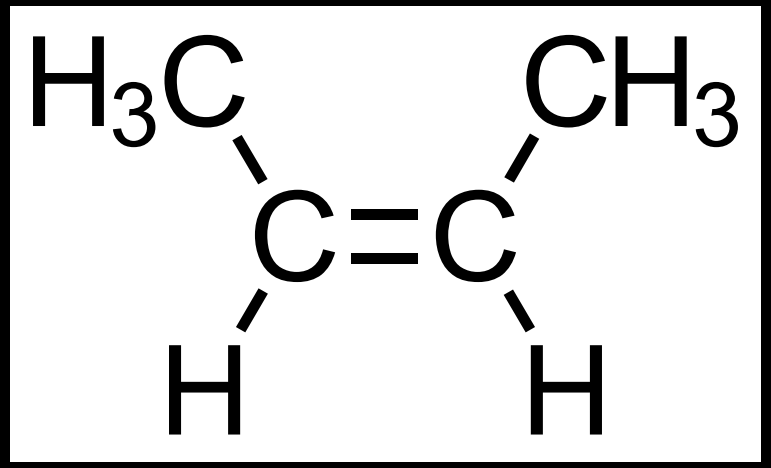
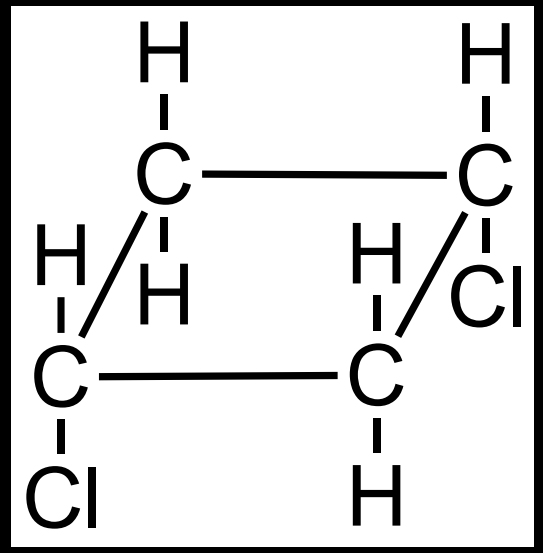
cis-trans isomerism

cis-trans **isomerism occurs where there is restricted rotation around a carbon to carbon bond.**



Restricted rotation around a C=C bond



Restricted rotation in a cyclic compound

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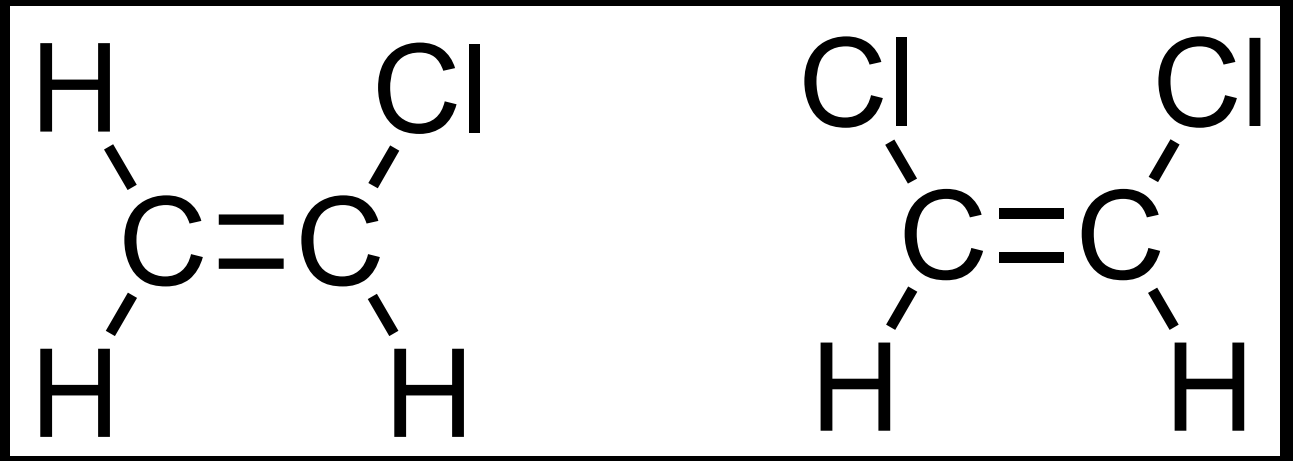
cis-trans isomerism

For *cis-trans* isomerism to occur, there must be two different groups on each of the carbon atoms of the C=C bond.



This molecule does not have *cis-trans* isomers

This molecule does have *cis-trans* isomers

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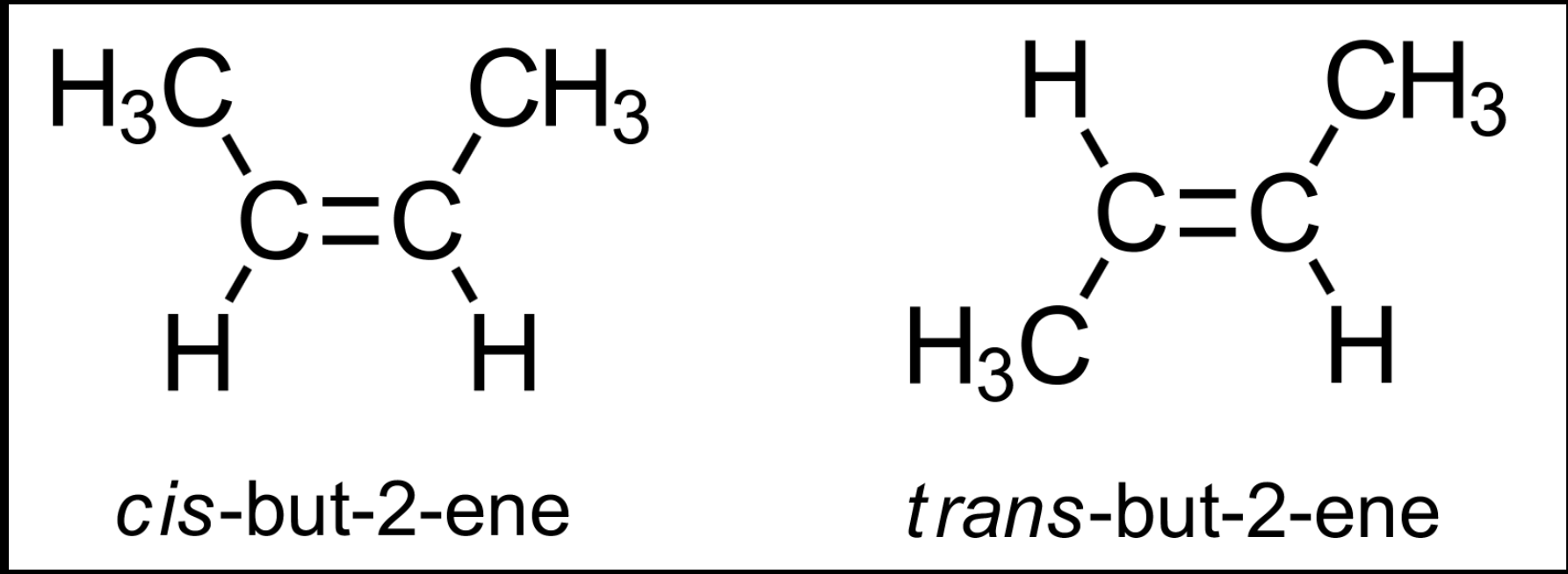
cis-trans isomerism

The π bond in the C=C bond restricts rotation, forming two different isomers.



cis **isomer – same groups on the same side of C=C bond.**

trans **isomer – same groups on opposite sides of C=C bond.**

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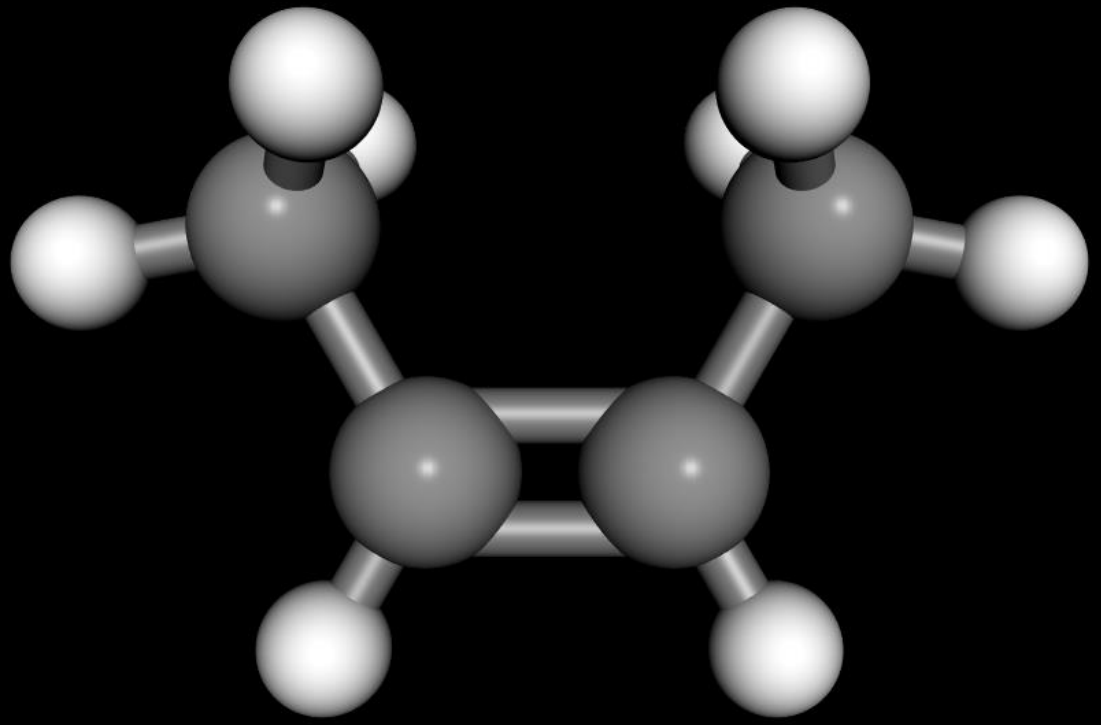
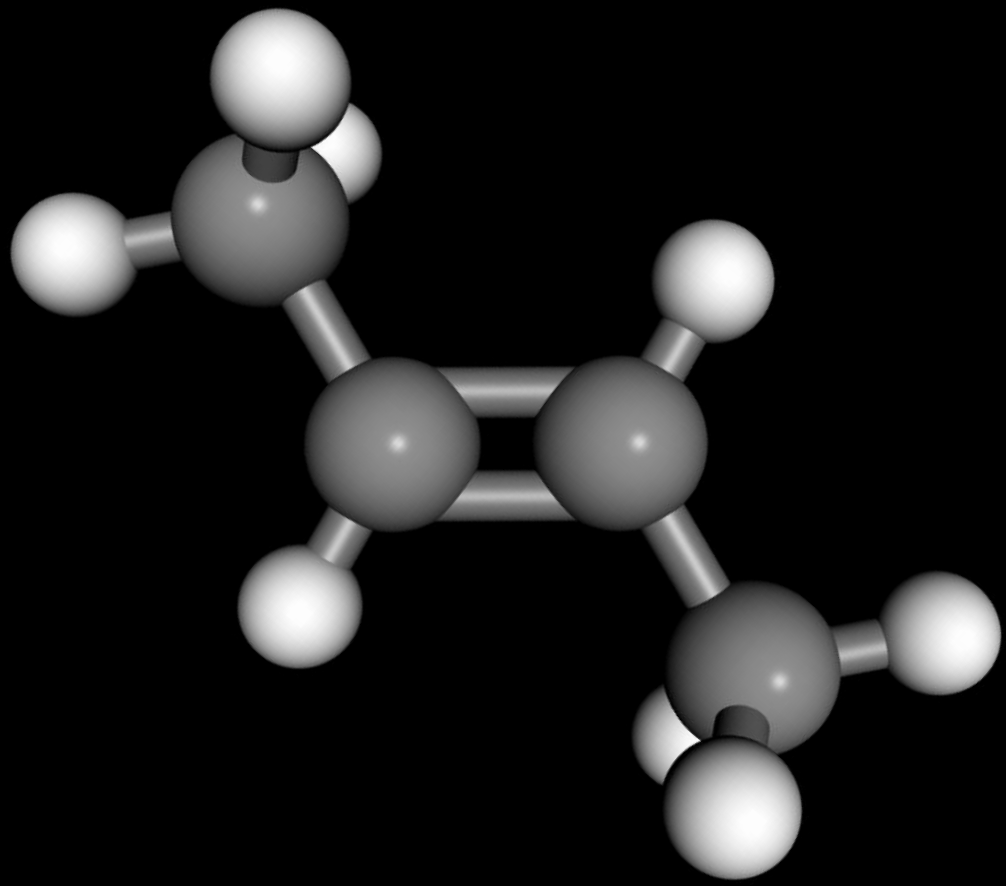
cis-trans isomerism



cis-but-2-ene



trans-but-2-ene

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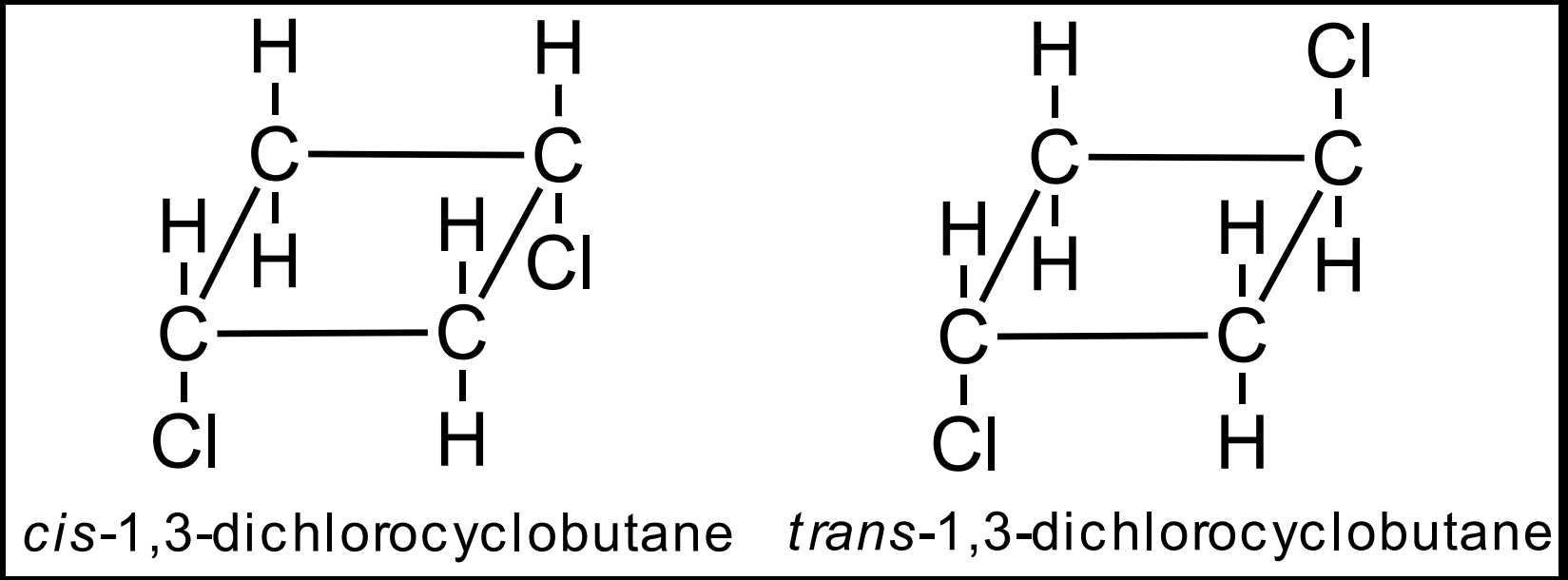
cis-trans isomerism

Cyclic compounds contain a ring structure that restricts rotation. When the molecule contains two or more different substituents attached to the ring, two different isomers are formed.



cis-1,3-dichlorocyclobutane

trans-1,3-dichlorocyclobutane

cis **isomer has the substituents on the same side of the ring,** ***trans*** **isomer has the substituents on opposite sides of the ring.**

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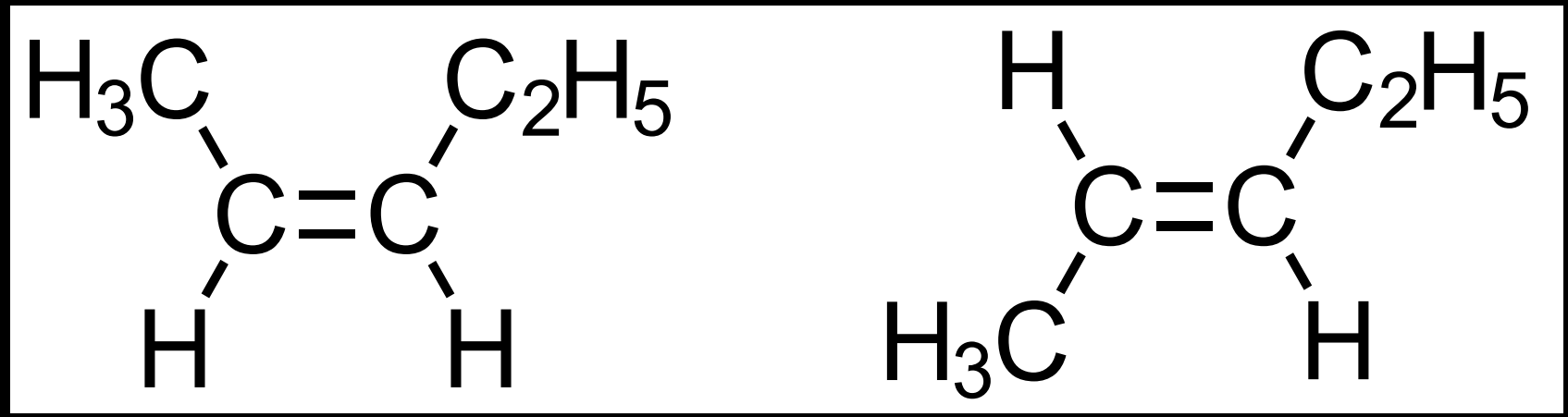
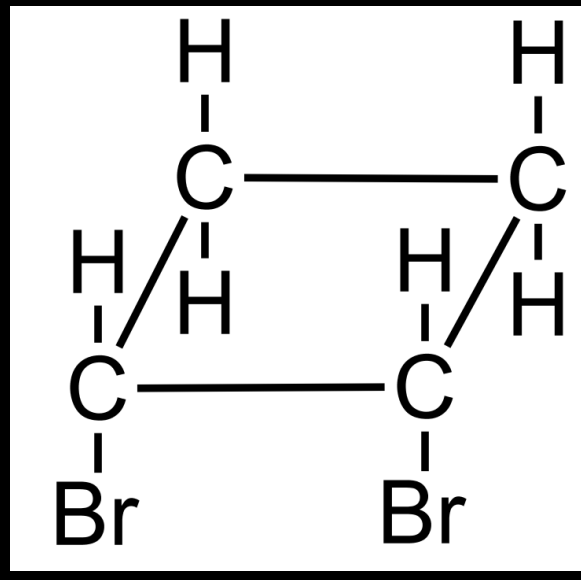
cis-trans isomerism

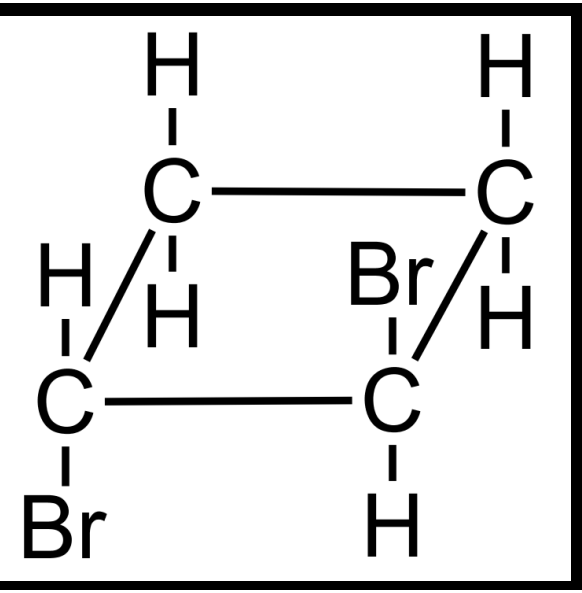


cis-pent-2-ene

trans-pent-2-ene



cis-1,2-dibromocyclobutane



trans-1,2-dibromocyclobutane

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Optical isomerism

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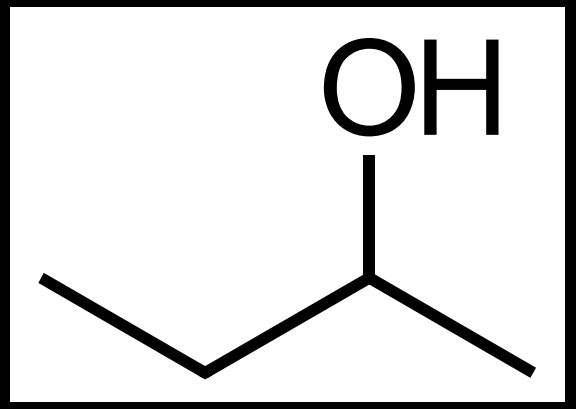
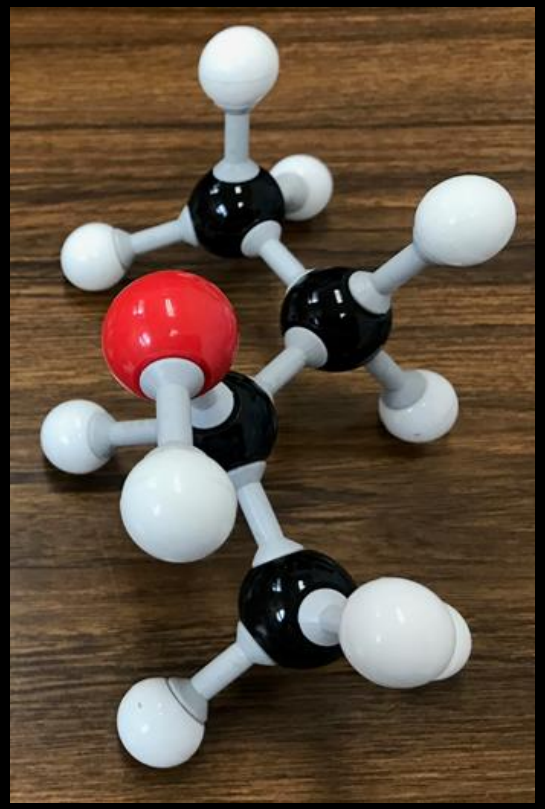
Optical isomerism

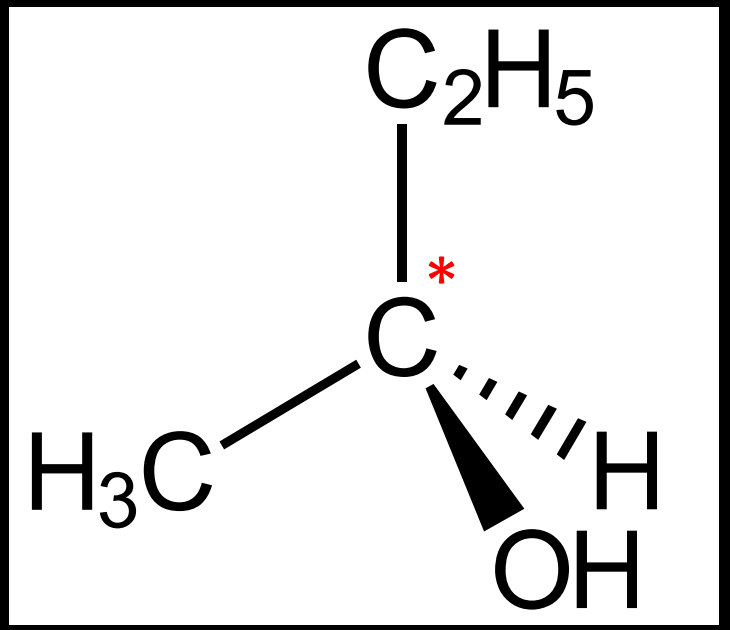
Optical isomerism is shown by chiral molecules that have a carbon atom bonded to four different atoms or groups (chiral center or asymmetric carbon).

butan-2-ol



$CH_3CH_2CH(OH)CH_3$





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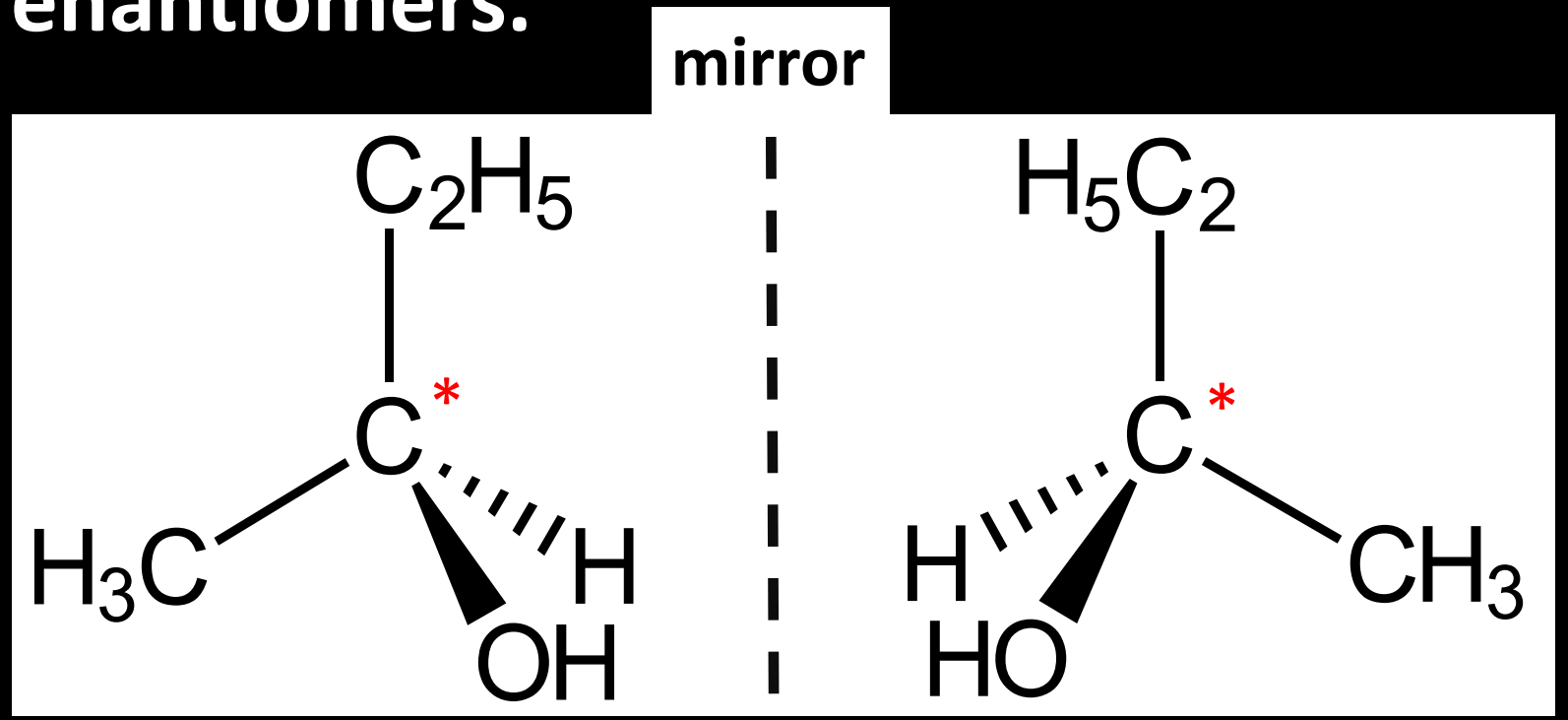
Optical isomerism

The four groups can be arranged in two three-dimensional configurations which are mirror images of each other. The two mirror images are non-superimposable and are known as enantiomers.



butan-2-ol

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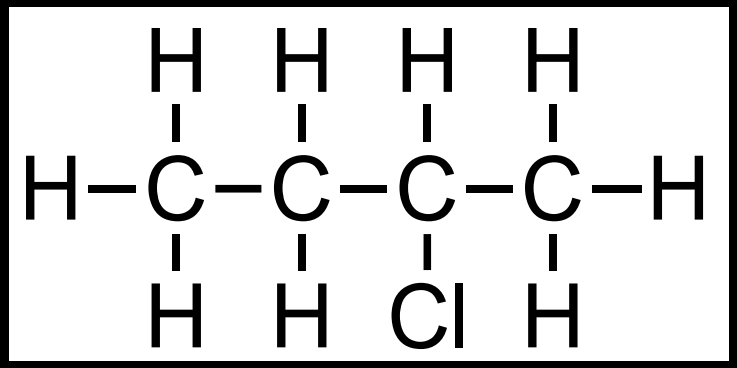
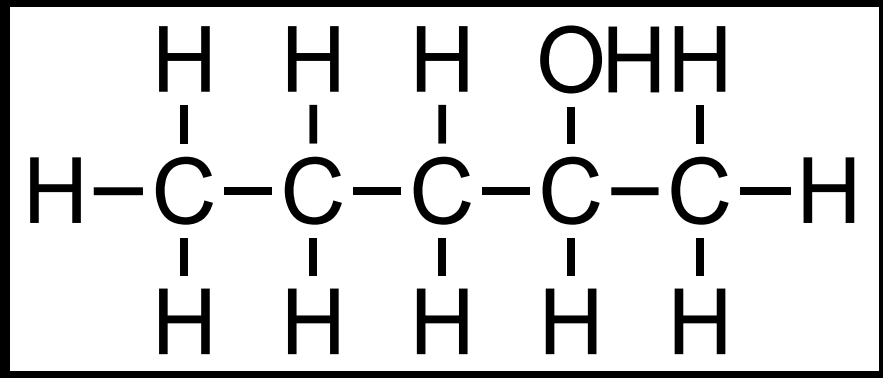
Optical isomerism

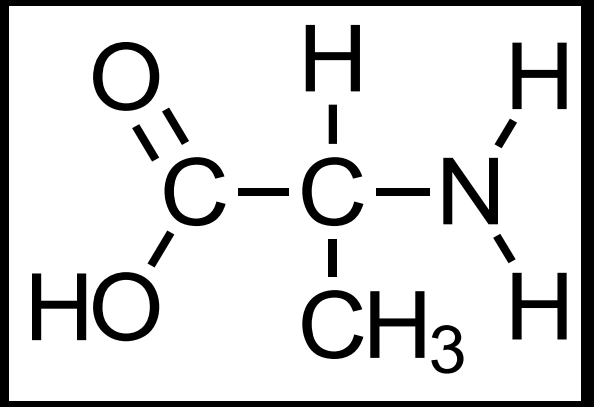
2-chlorobutane

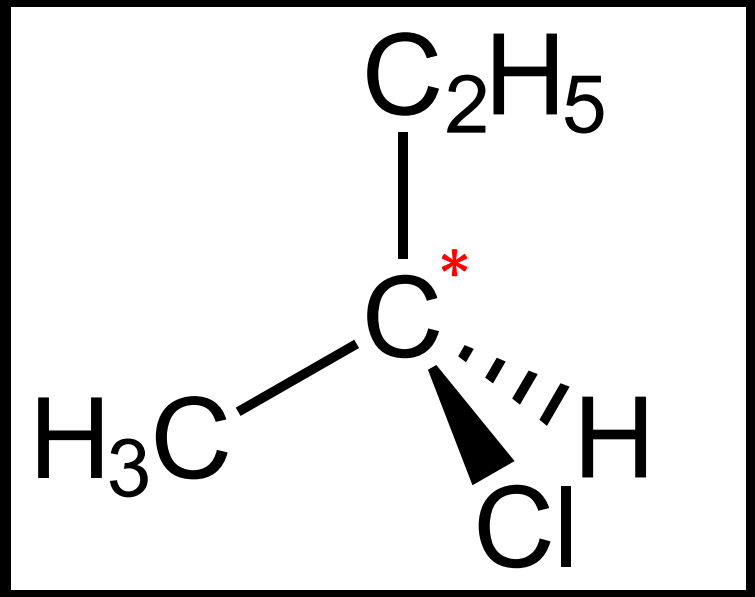


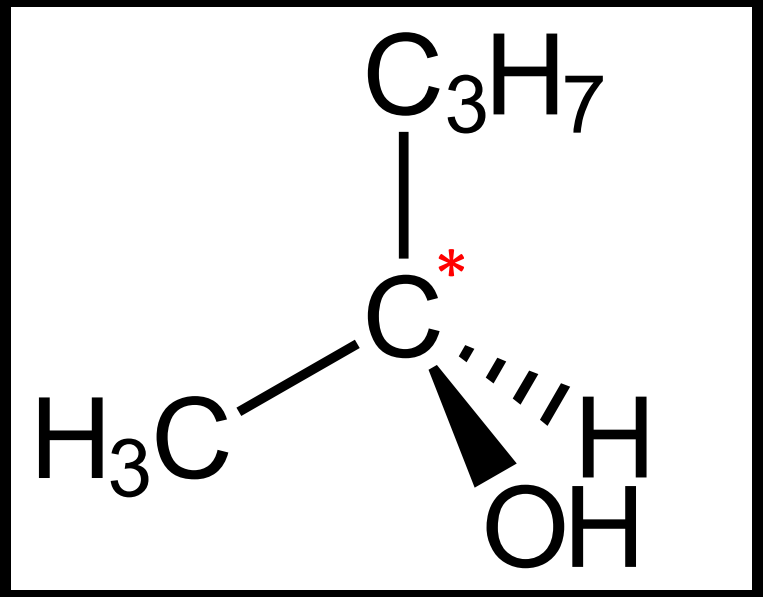
Pentan-2-ol

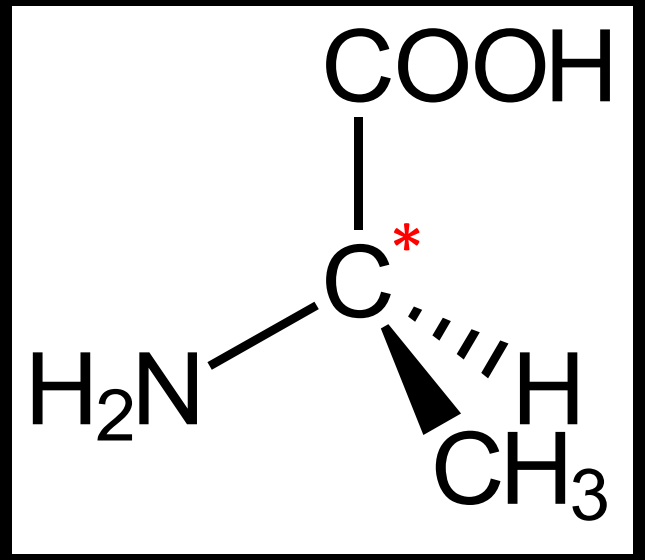


Alanine









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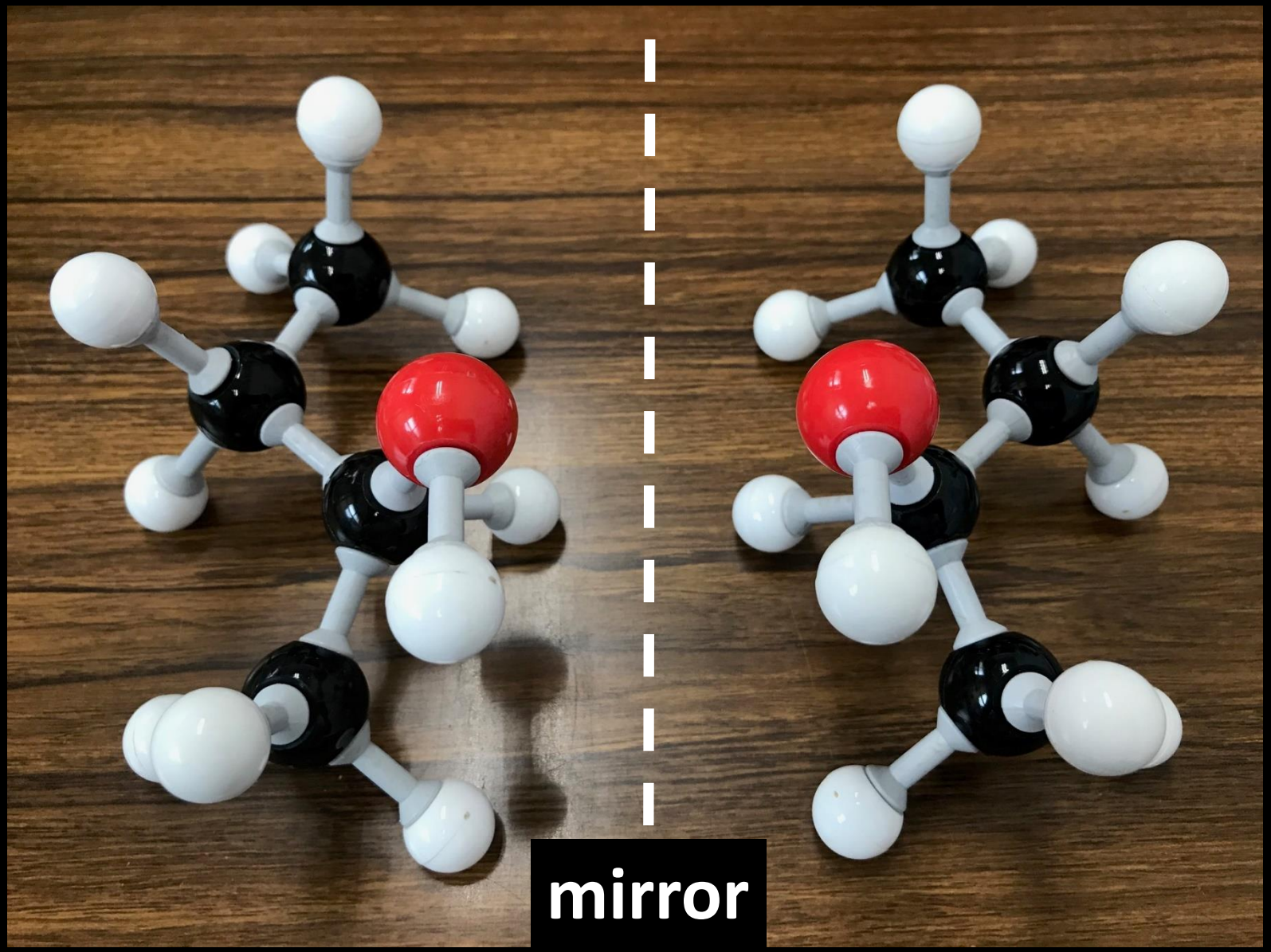
Optical isomerism



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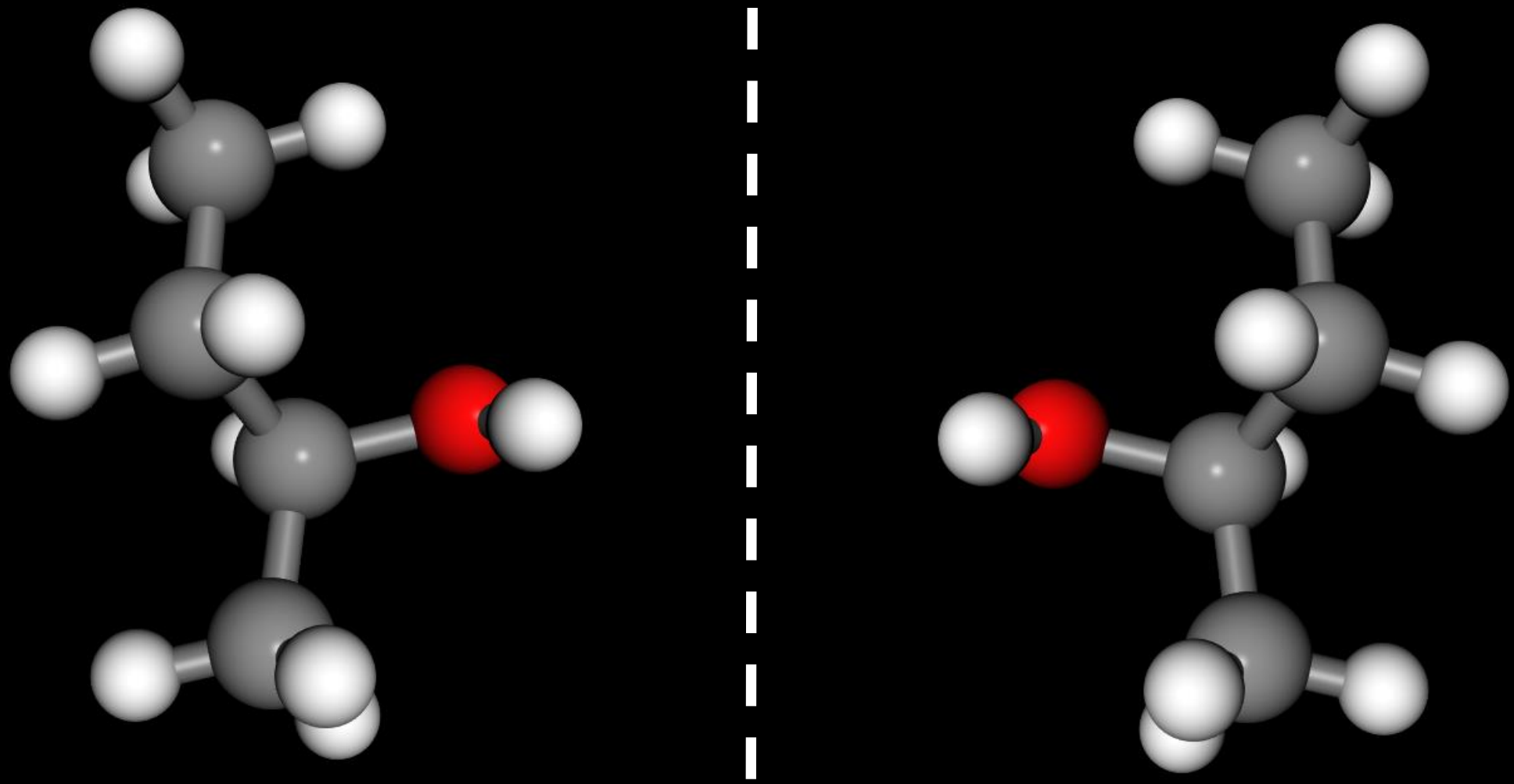
Optical isomerism



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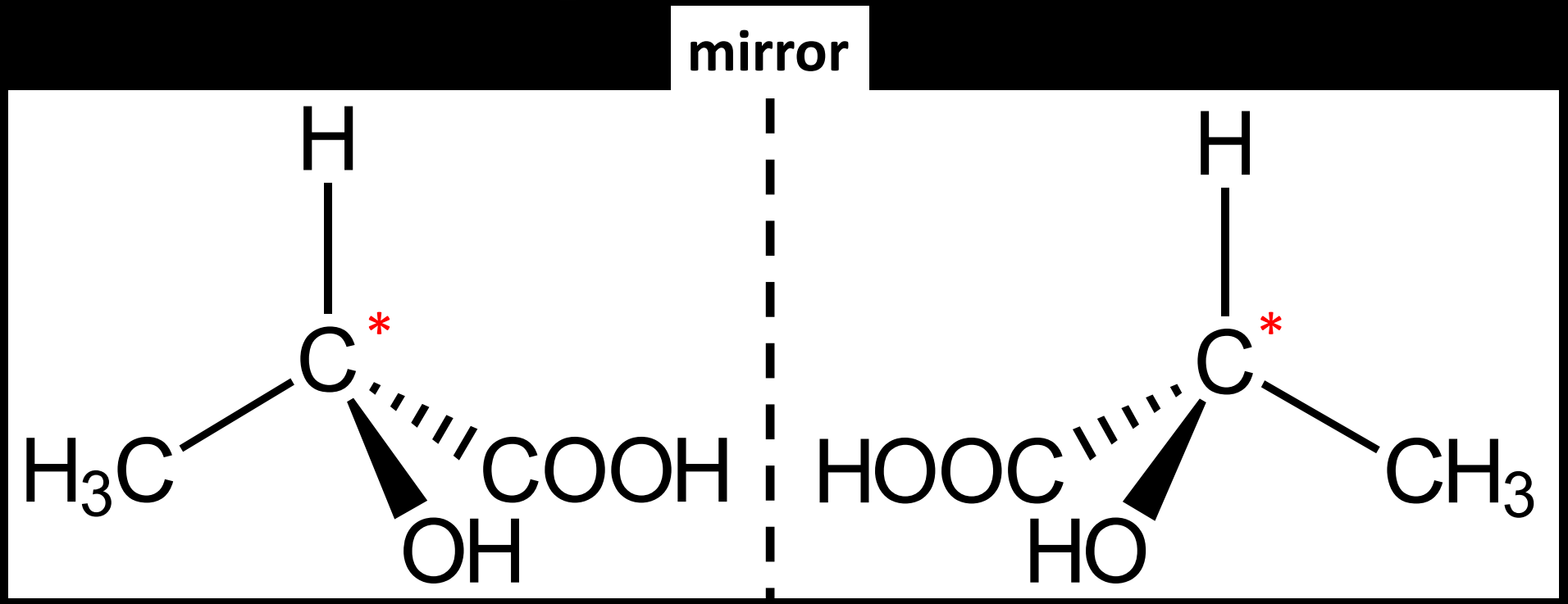
Optical isomerism



2-hydroxypropanoic acid (lactic acid)

The two optical isomers (enantiomers) are optically active with plane-polarised light.

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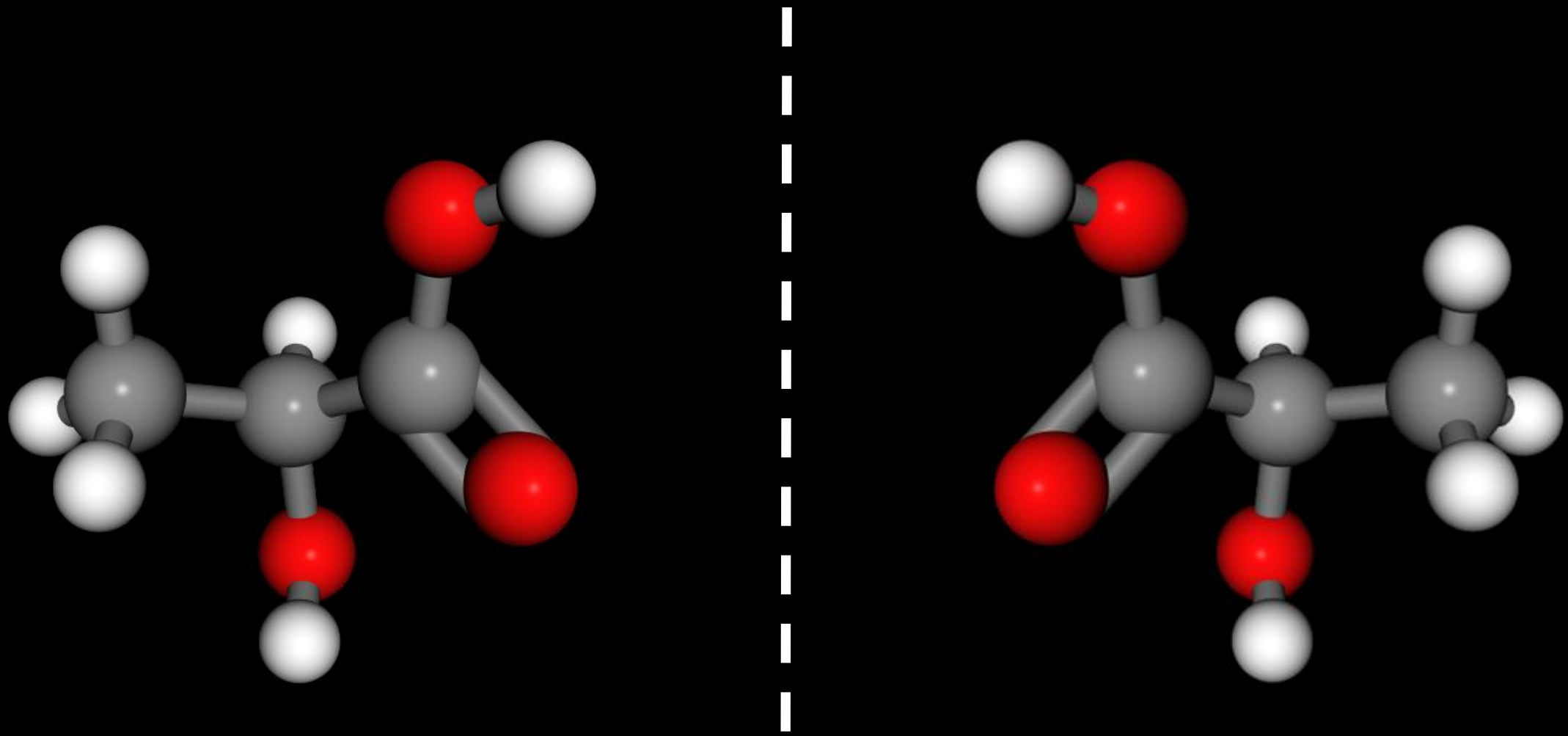
Optical isomerism



Optical isomerism

Enantiomers have identical physical properties, such as melting point and boiling point, except that they rotate the plane of plane-polarised light in opposite directions (optically active).

This property is used to distinguish between the two enantiomers of a chiral molecule.

The chemical properties of two enantiomers are also identical, except when they react with other chiral molecules (such as those found in the human body).

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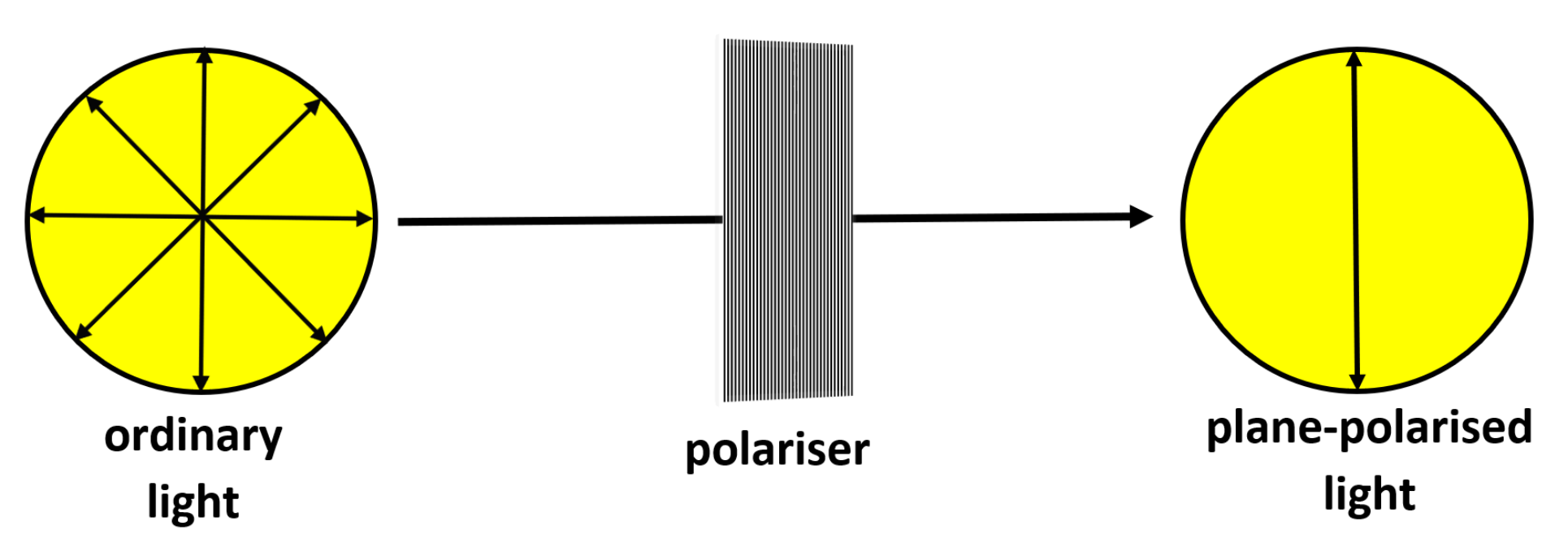
How to distinguish between enantiomers of a chiral compound

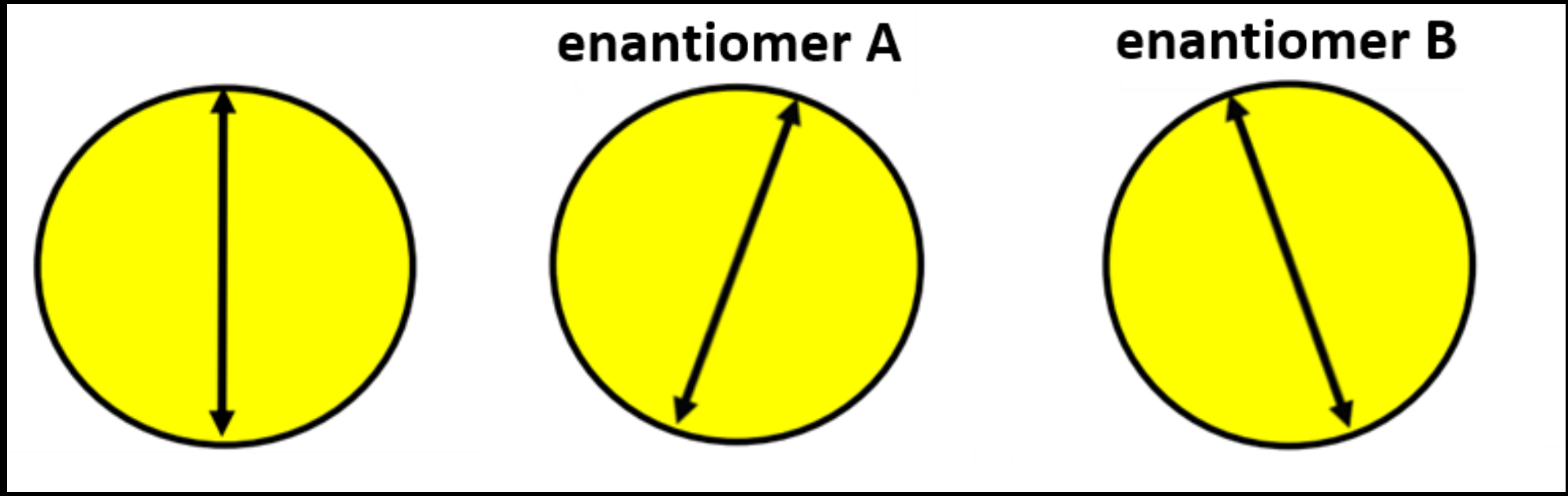
Optical isomerism

Ordinary light consists of waves that vibrate in all planes perpendicular to its direction of travel.
Plane-polarised light consists of waves vibrating in one plane only.



Optical isomerism

The two enantiomers of a chiral compound rotate the plane of plane-polarised light by the same angle but in opposite directions.



plane-polarised light

20° clockwise rotation

20° anti-clockwise rotation

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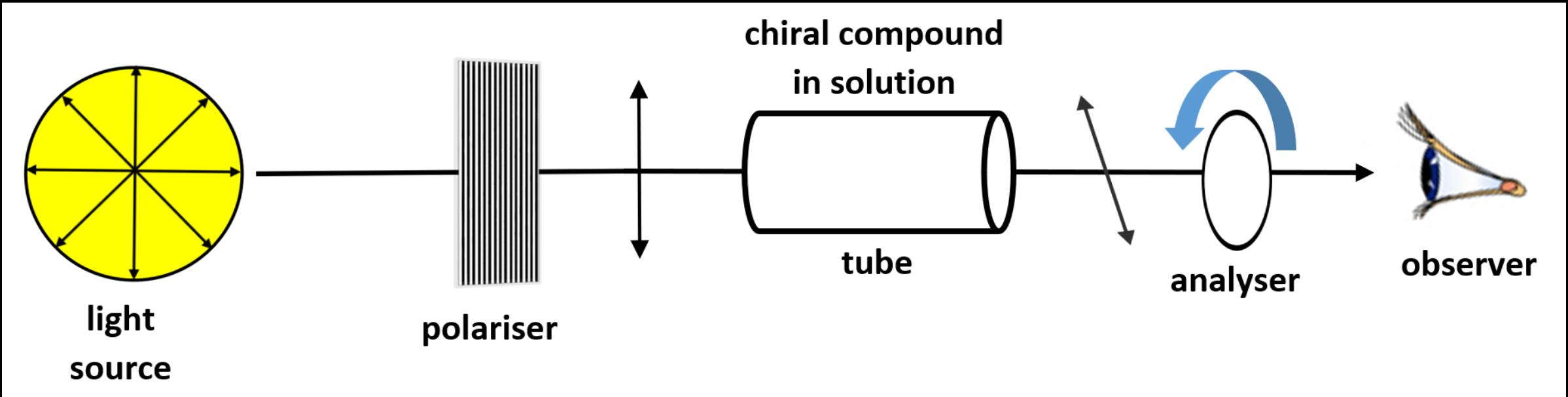
Optical isomerism



Plane-polarised light is passed through a tube containing a solution of the enantiomer.

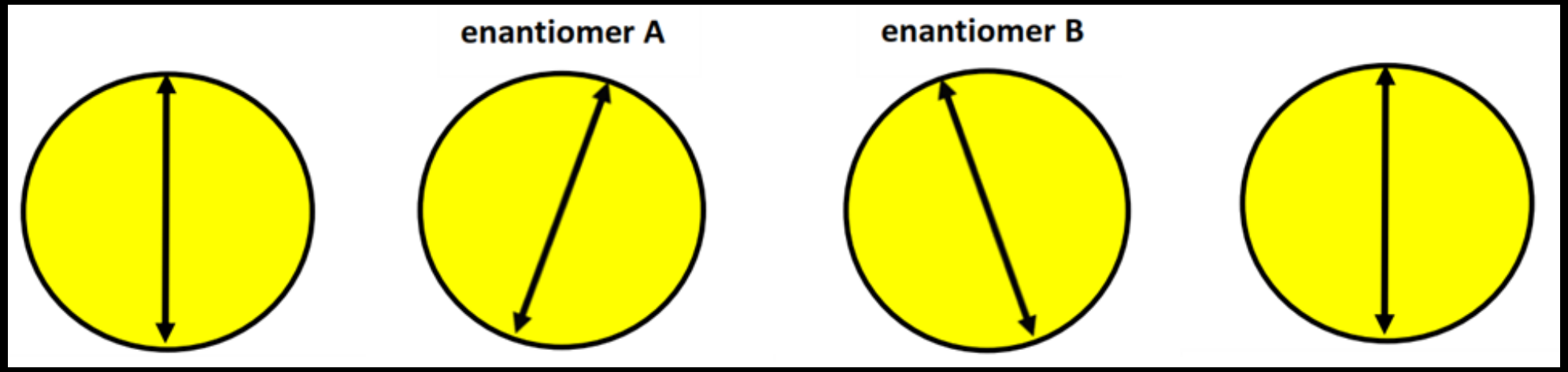
The plane of the plane-polarised light is rotated which then passes through the analyser.

The analyser is rotated until the light passes through and the angle and direction of rotation can be measured.

Optical isomerism

A solution containing equal amounts of both enantiomers is known as a racemic mixture (racemate).

If both enantiomers are present in equal amounts, the two rotations cancel out and the mixture is said to be optically inactive.



plane-polarised light

20° clockwise rotation

20° anti-clockwise rotation

no overall rotation

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Mass spectrometry

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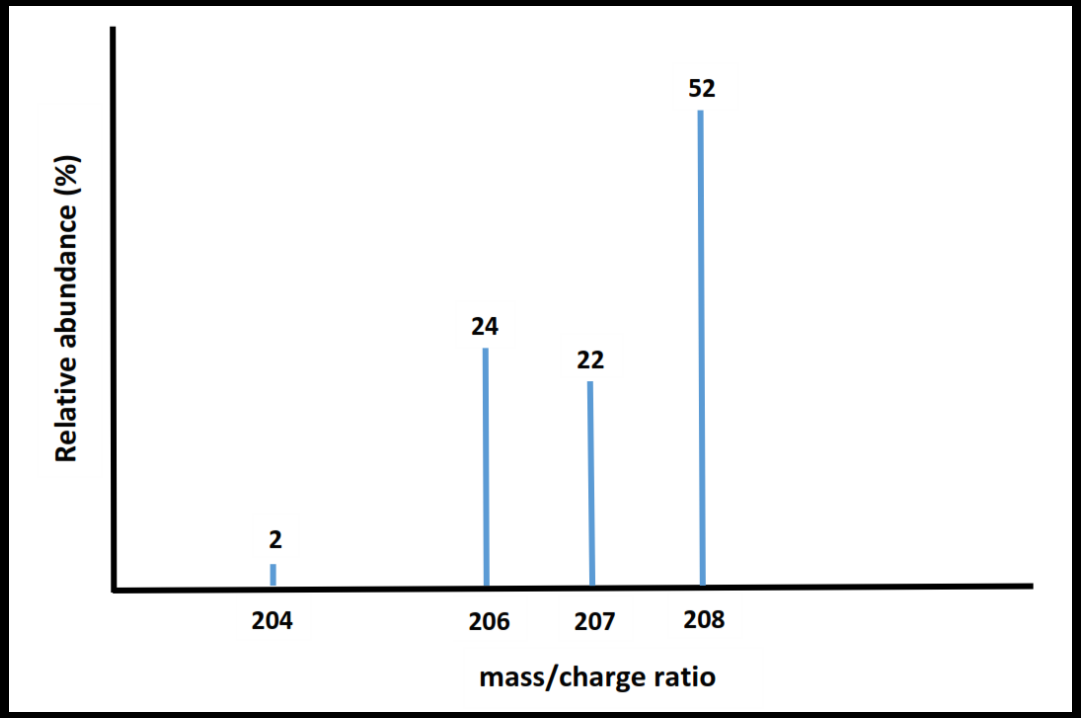
Mass spectrometry

Mass spectrometry is used to determine the relative atomic mass (A_r) of an element.



82
Pb
207.20

$$A_r = \frac{(2\times204)+(24\times206)+(22\times207)+(52\times208)}{100} = 207.2$$

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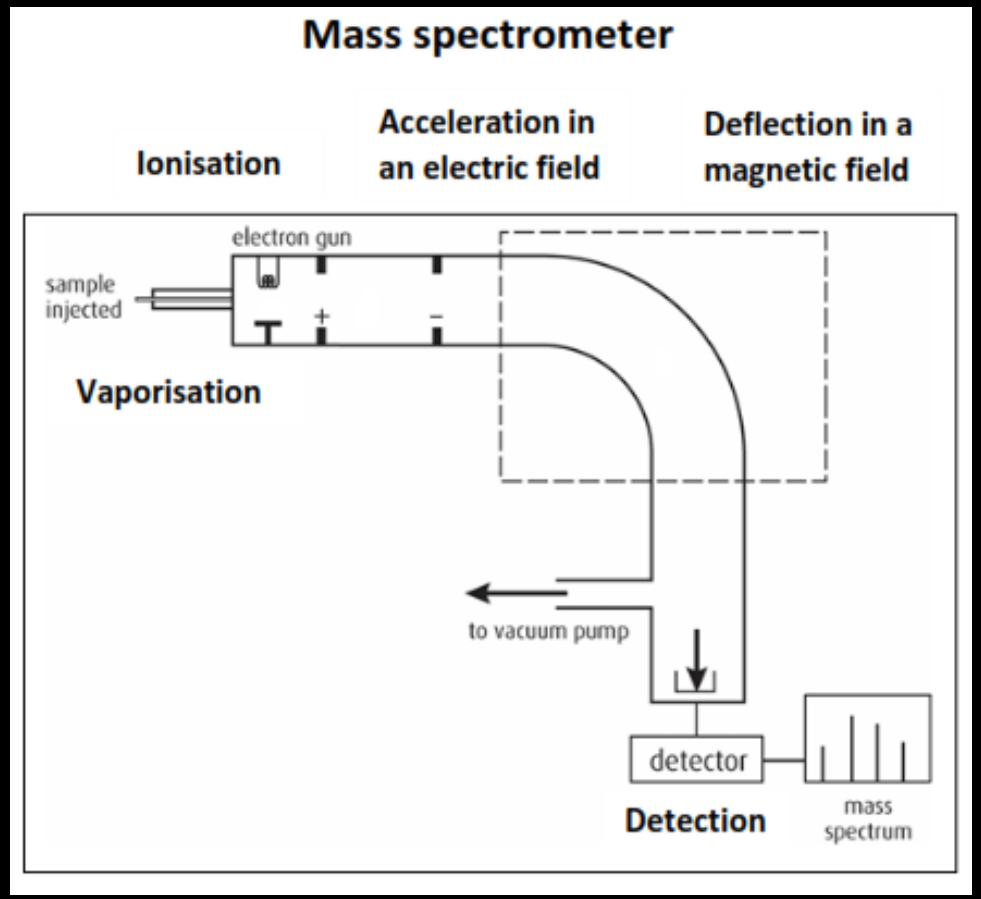
Mass spectrometry

Mass spectrometry can also be used to determine the structure of a compound.



When the vaporised organic sample passes into the ionisation chamber of a mass spectrometer, it is bombarded by a stream of electrons.

$$M_{(g)} + e^- \longrightarrow M^+_{(g)} + 2e^-$$

The $M^+_{(g)}$ ion is known as the molecular ion.

Mass spectrometry

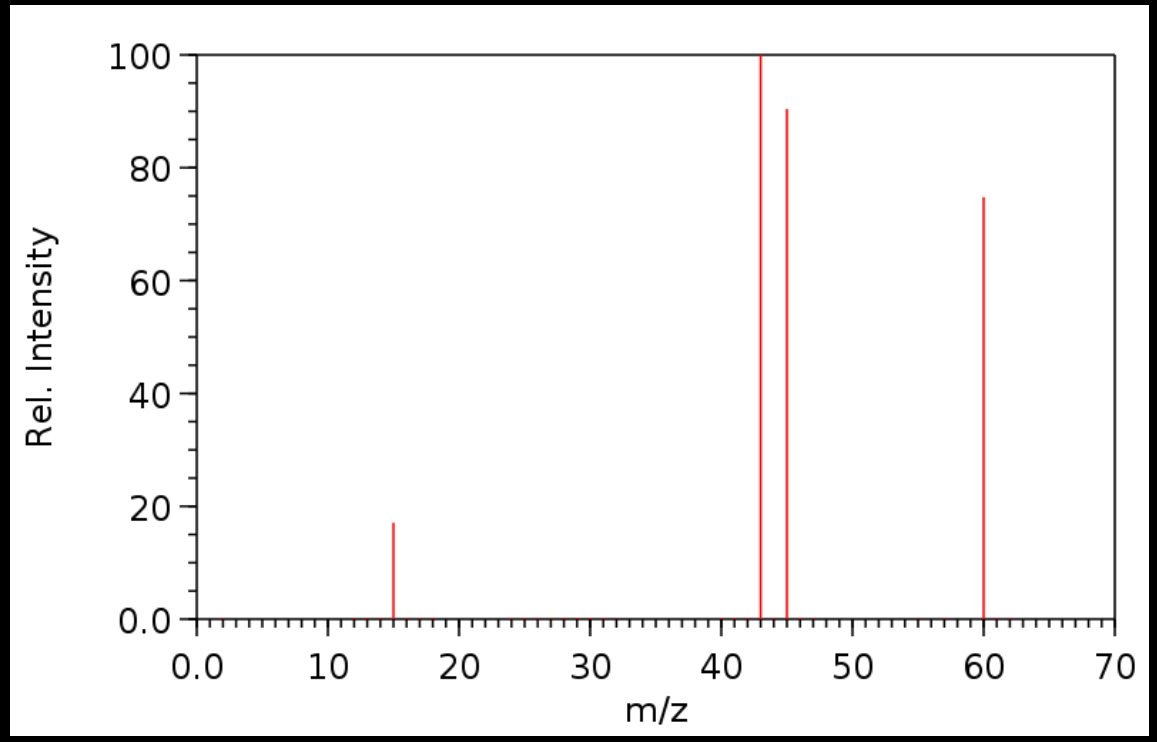
Inside the mass spectrometer, some of the molecular ions break down to produce fragments.

A fragmentation pattern is produced which gives useful information about the structure of the compound.

ethanoic acid

CH_3COOH

$M_r = 60.05$



Mass spectrometry

28. Mass spectral fragments lost

Mass lost	Fragment lost
15	CH_3
17	OH
18	H_2O
28	$CH_2{=}CH_2$, C=O
29	CH_3CH_2, CHO
31	CH_3O
45	COOH

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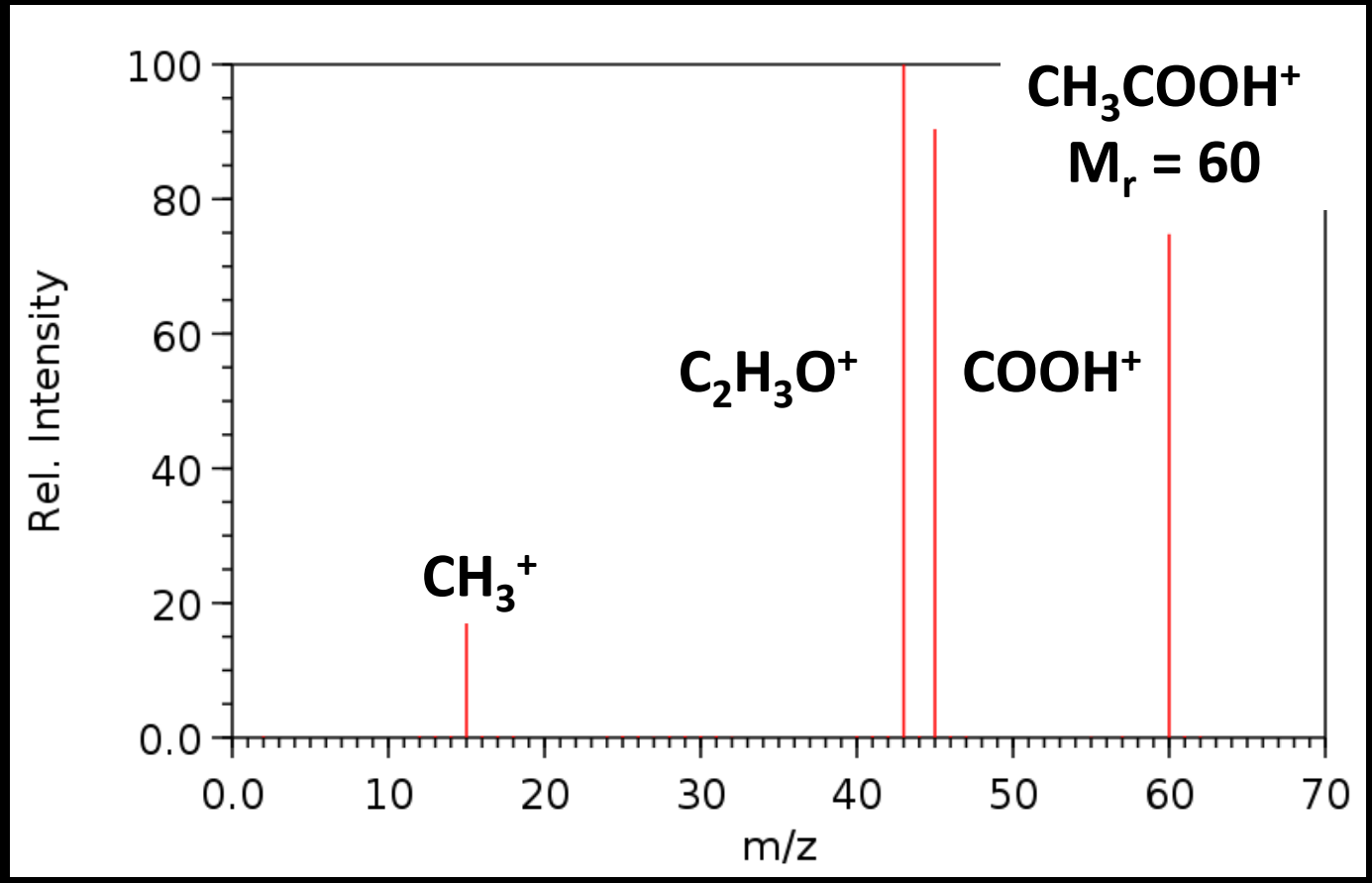
Mass spectrometry



The peak at m/z = 60 is produced by the molecular ion (M^+)

The peak at m/z = 45 loss of a CH_3 group (60 – 45 = 15)

The peak at m/z = 43 loss of a OH group (60 – 43 = 17)

The peak at m/z = 15 loss of a COOH group (60 – 15 = 45)

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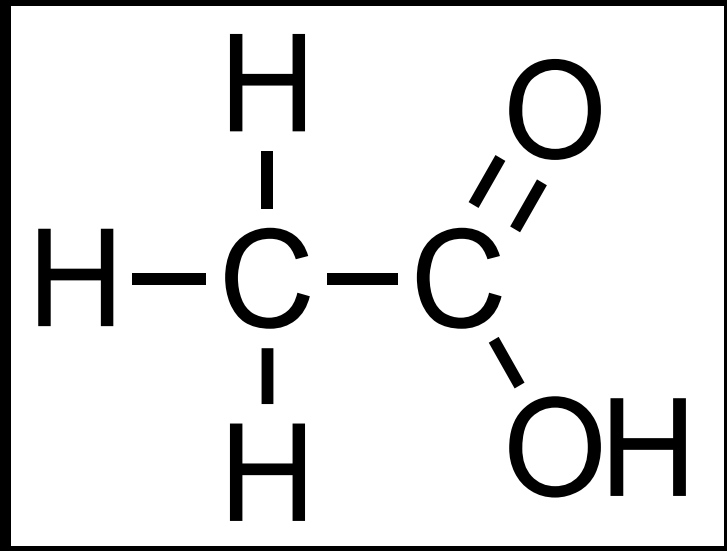
Mass spectrometry

Peak	Fragment
45 (60 – 45 = 15)	$COOH^+$ (loss of CH_3)
43 (60 – 43 = 17)	$C_2H_3O^+$ (loss of OH)
15 (60 – 15 = 45)	CH_3^+ (loss of COOH)

28. Mass spectral fragments lost

Mass lost	Fragment lost
15	CH_3
17	OH
18	H_2O
28	$CH_2=CH_2$, C=O
29	CH_3CH_2, CHO
31	CH_3O
45	COOH



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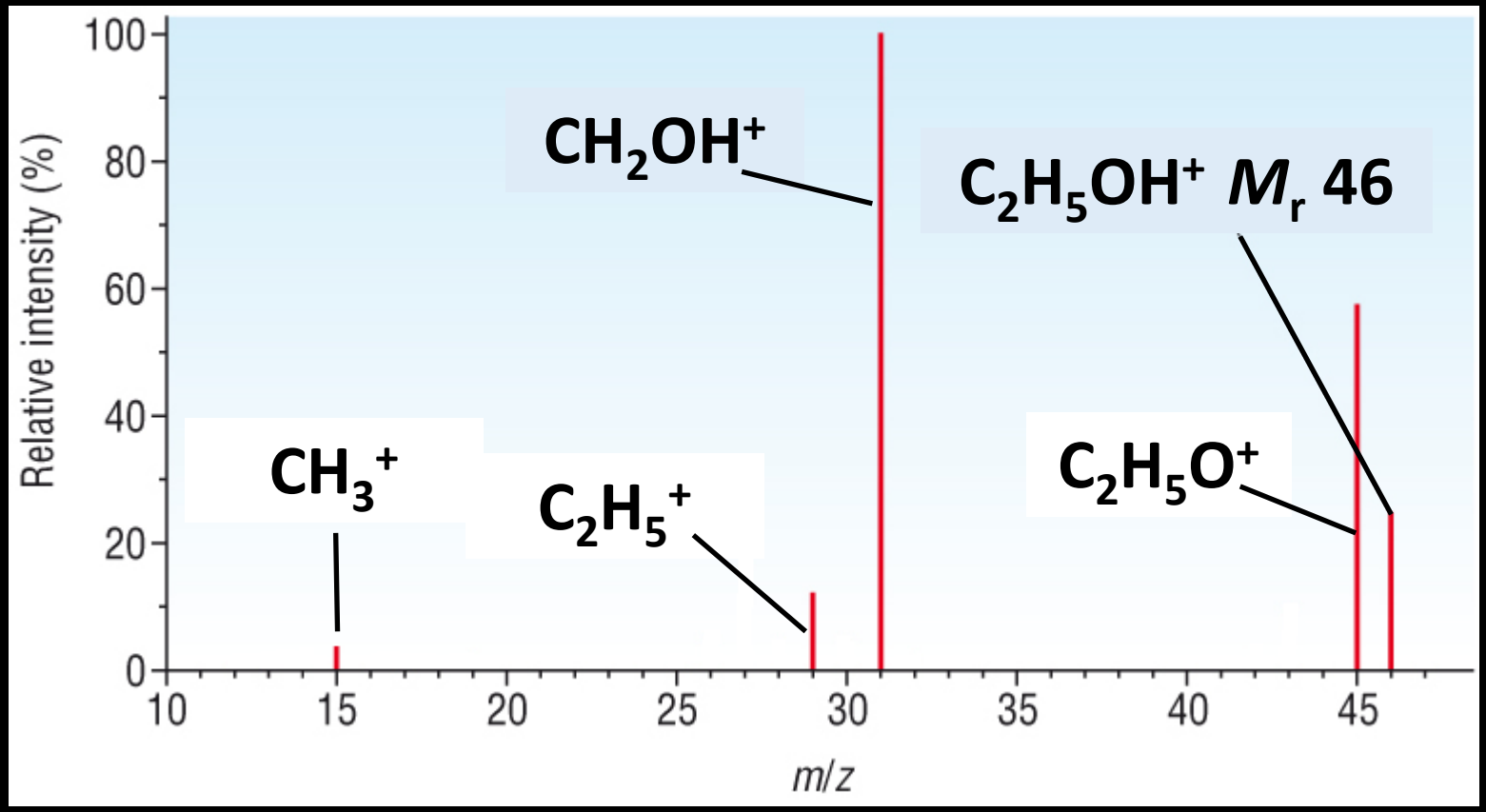
Mass spectrometry



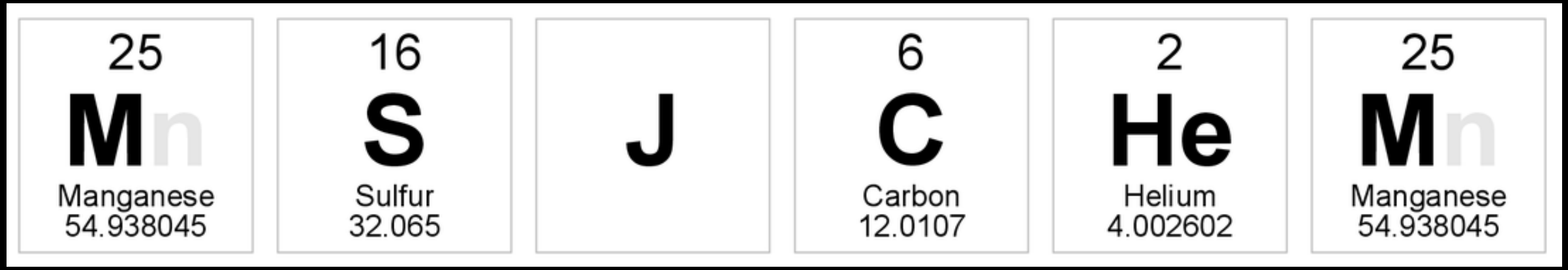
The peak at m/z = 46 is produced by the molecular ion (M^+)

The peak at m/z = 45 is produced by the M^+ losing a hydrogen atom (46 – 1 = 45)

The peak at m/z = 31 loss of a CH_3 group (46 – 15 = 31)

The peak at m/z = 29 loss of a OH group (46 – 17 = 29)

The peak at m/z = 15 loss of a CH_3O group (46 – 31 = 15)



Infrared spectroscopy

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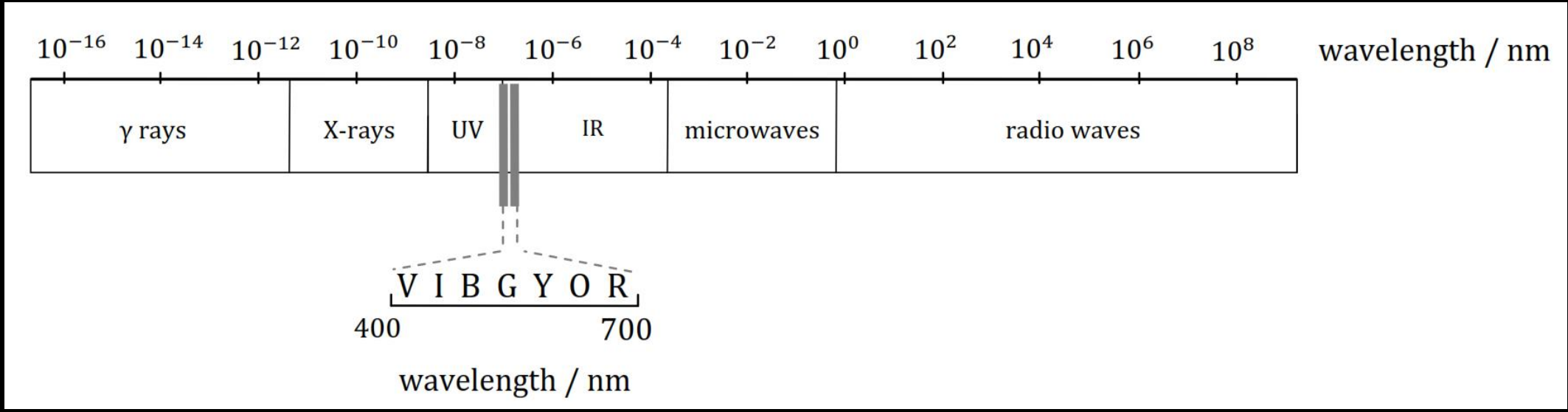
Infrared spectroscopy



When molecules absorb energy in the infrared region of the electromagnetic spectrum, it causes the bonds between the atoms to vibrate (the bonds stretch and bend).

The frequency of IR radiation that is absorbed is measured as the number of waves per centimeter (wavenumber cm^{-1})

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Infrared spectroscopy

26. Infrared data

Characteristic ranges for infrared absorption due to stretching vibrations in organic molecules.

Bond	Organic molecules	Wavenumber (cm^{-1})	Intensity
C–I	iodoalkanes	490–620	strong
C–Br	bromoalkanes	500–600	strong
C–Cl	chloroalkanes	600–800	strong
C–F	fluoroalkanes	1000–1400	strong
C–O	alcohols, esters, ethers	1050–1410	strong
C=C	alkenes	1620–1680	medium-weak; multiple bands
C=O	aldehydes, ketones, carboxylic acids and esters	1700–1750	strong
C≡C	alkynes	2100–2260	variable
O–H	hydrogen bonding in carboxylic acids	2500–3000	strong, very broad
C–H	alkanes, alkenes, arenes	2850–3090	strong
O–H	hydrogen bonding in alcohols and phenols	3200–3600	strong, broad
N–H	primary amines	3300–3500	medium, two bands

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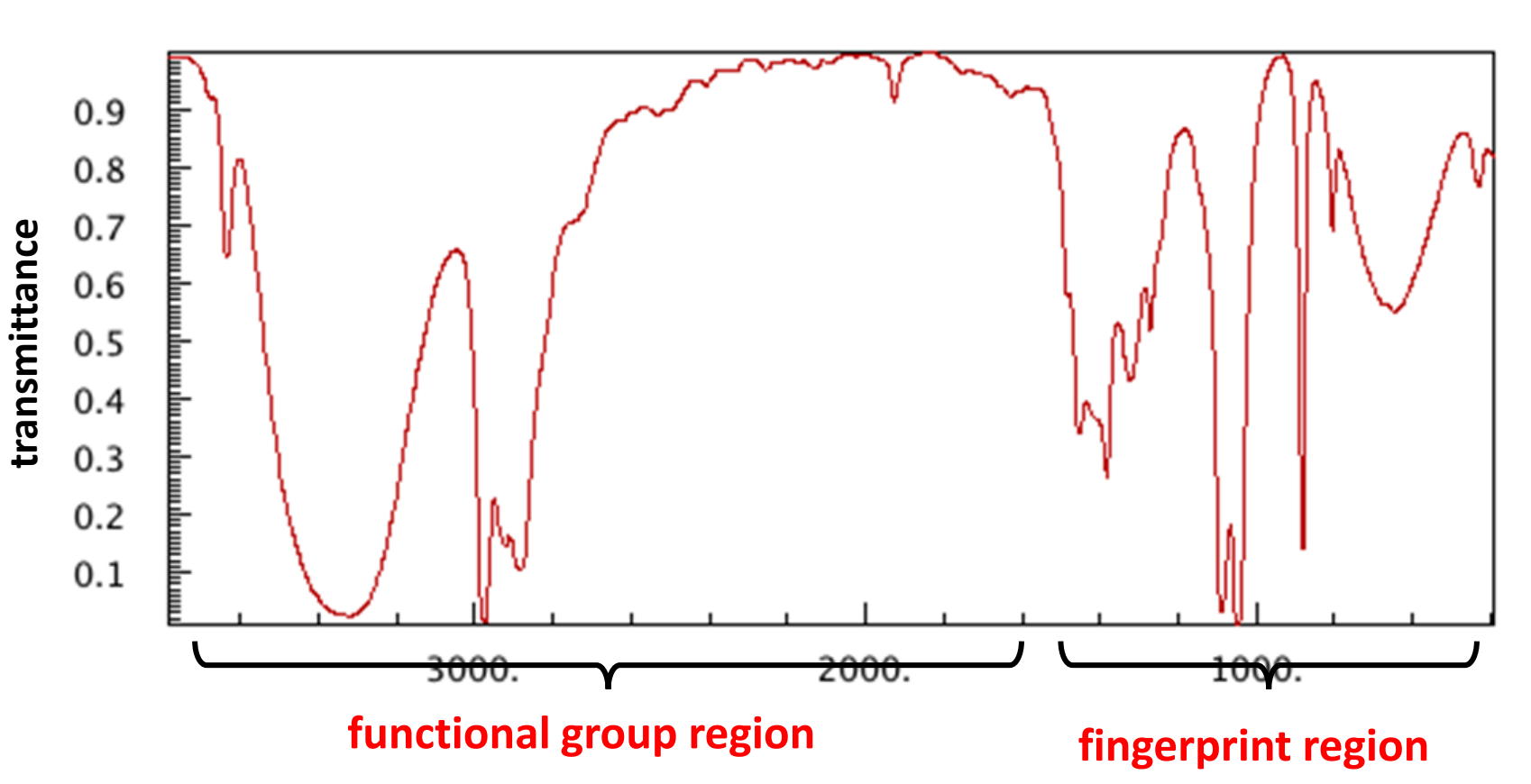
Infrared spectroscopy

IR spectrum for ethanol C_2H_5OH



The region of an infrared spectrum in the range of about 500 to 1500 cm^{-1}
This region of the spectrum is almost unique for any given compound.

The fingerprint region can be used to identify an unknown compound by comparing with the IR spectra of known compounds.

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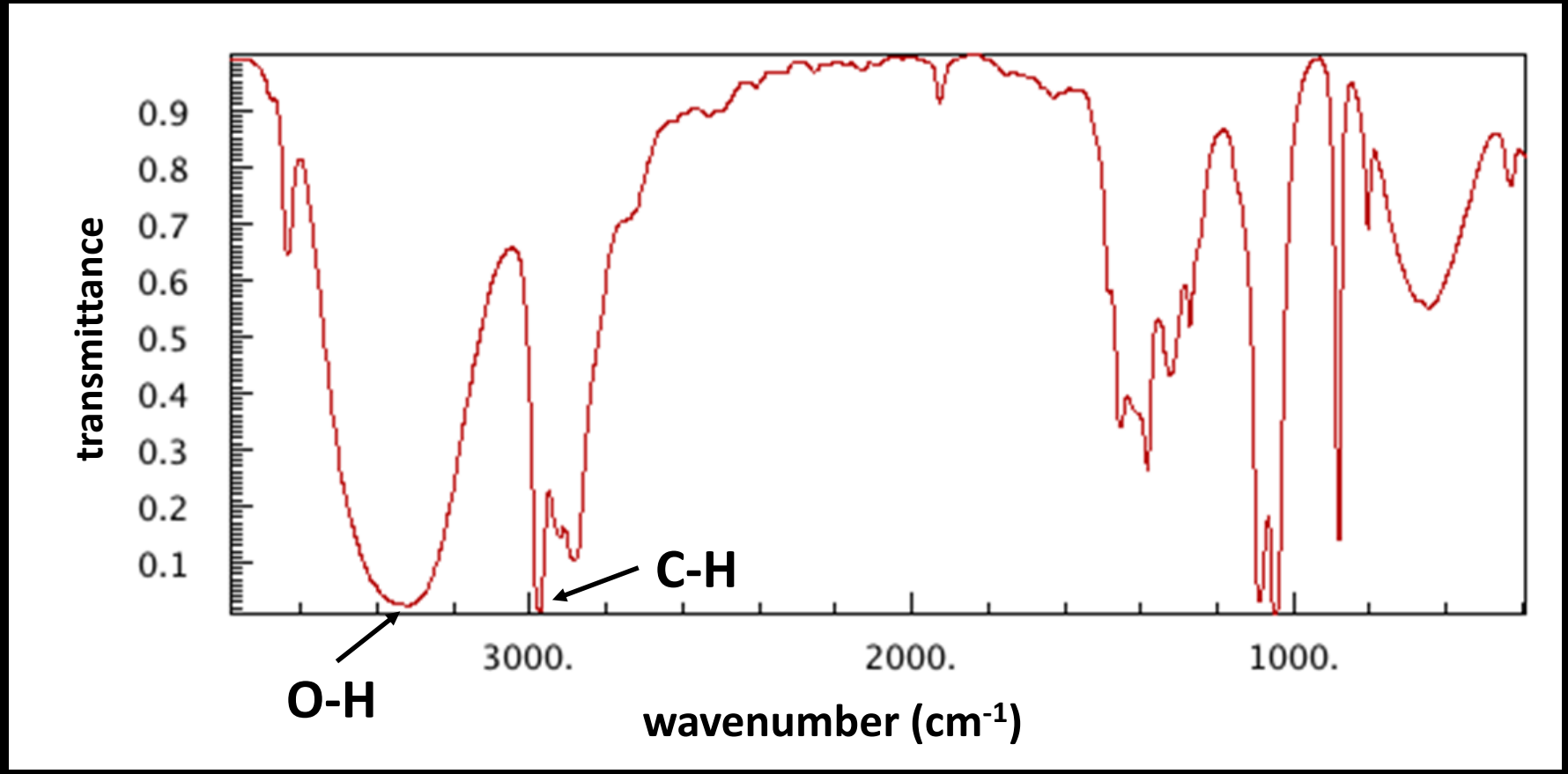
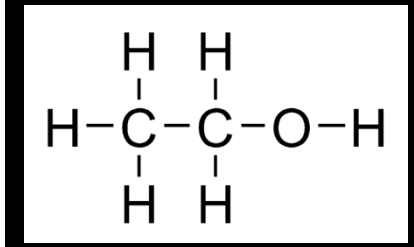
Infrared spectroscopy

IR spectrum for ethanol C_2H_5OH





Bond	Organic molecule	Wavenumber (cm^{-1})	Intensity
C-H	alkanes, alkenes, arenes	2850 – 3090	strong
O-H	hydrogen bonding in alcohols and phenols	3200 – 3600	strong, broad

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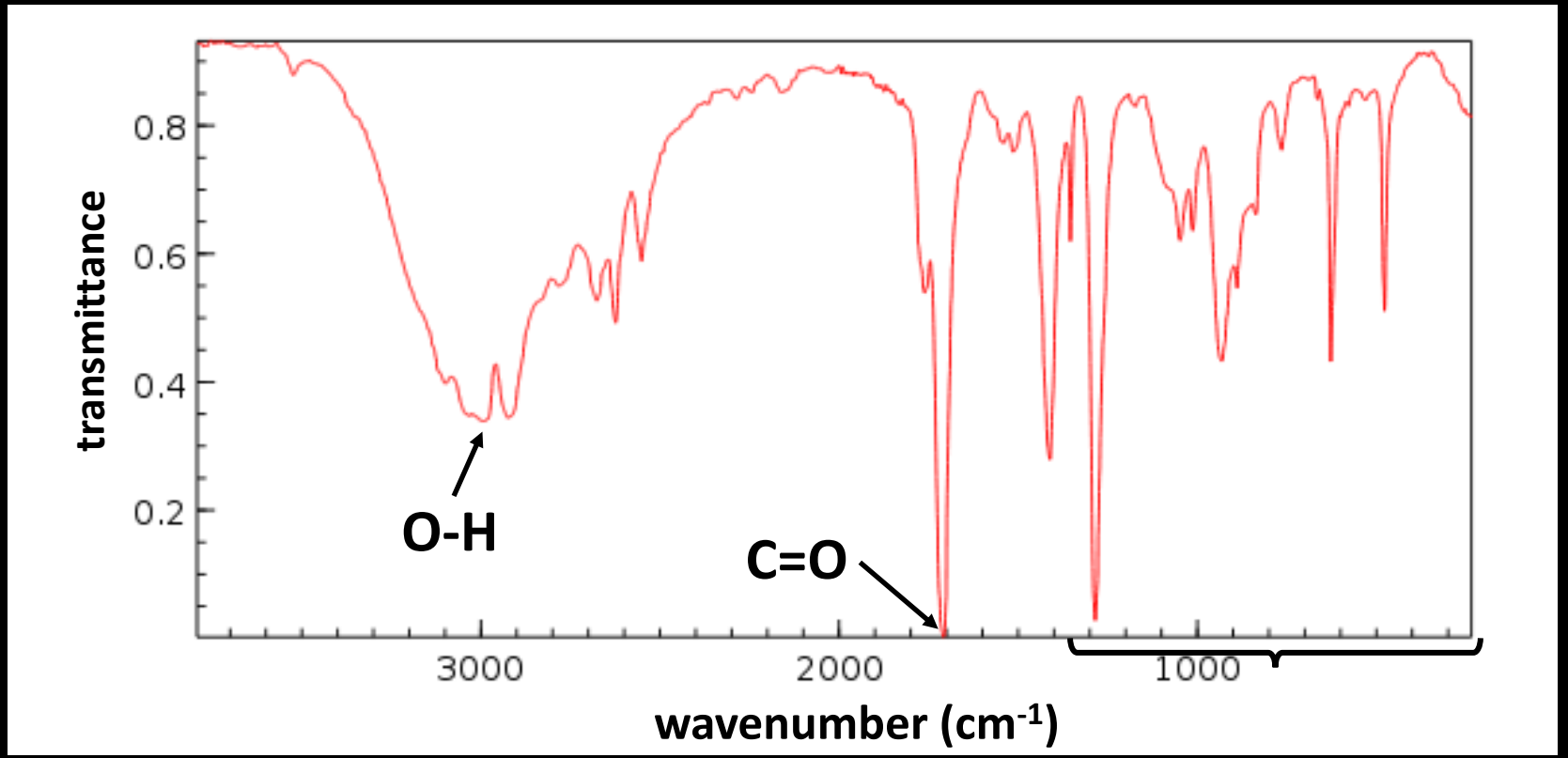
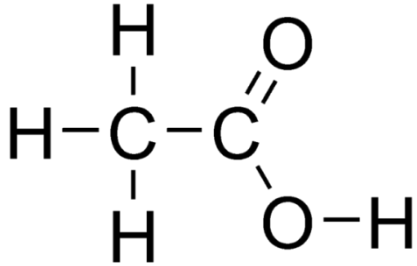
Infrared spectroscopy

IR spectrum for ethanoic acid CH_3COOH





Bond	Organic molecule	Wavenumber (cm^{-1})	Intensity
C=O	aldehydes, ketones, carboxylic acids and esters	1700 – 1750	strong
O-H	hydrogen bonding in carboxylic acids	2500 – 3000	strong, very broad

Infrared spectroscopy

A bond will only interact with IR radiation if it is a polar covalent bond (non-polar bonds do not absorb IR radiation).

Bond	Organic molecules	Wavenumber (cm^{-1})	Intensity
C–I	iodoalkanes	490–620	strong

The intensity of the band depends on the dipole moment of the bond:

- Strongly polar bonds produce strong bands
- Bonds with medium polarity produce medium bands
- Weakly polar bonds produce weak bands

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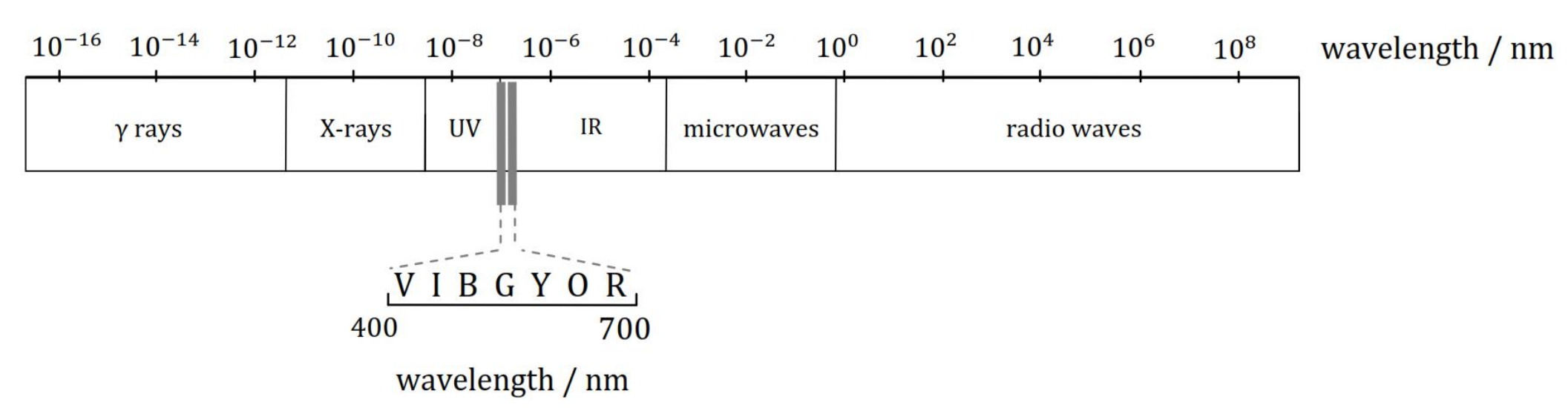
Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy

^{1}H NMR

Hydrogen nuclei behave as little magnets and a hydrogen nucleus can be aligned with an external magnetic field or opposed to it (which has higher energy).
The energy needed for the hydrogen nuclei to reverse their spin is very small and can be provided by radio waves.



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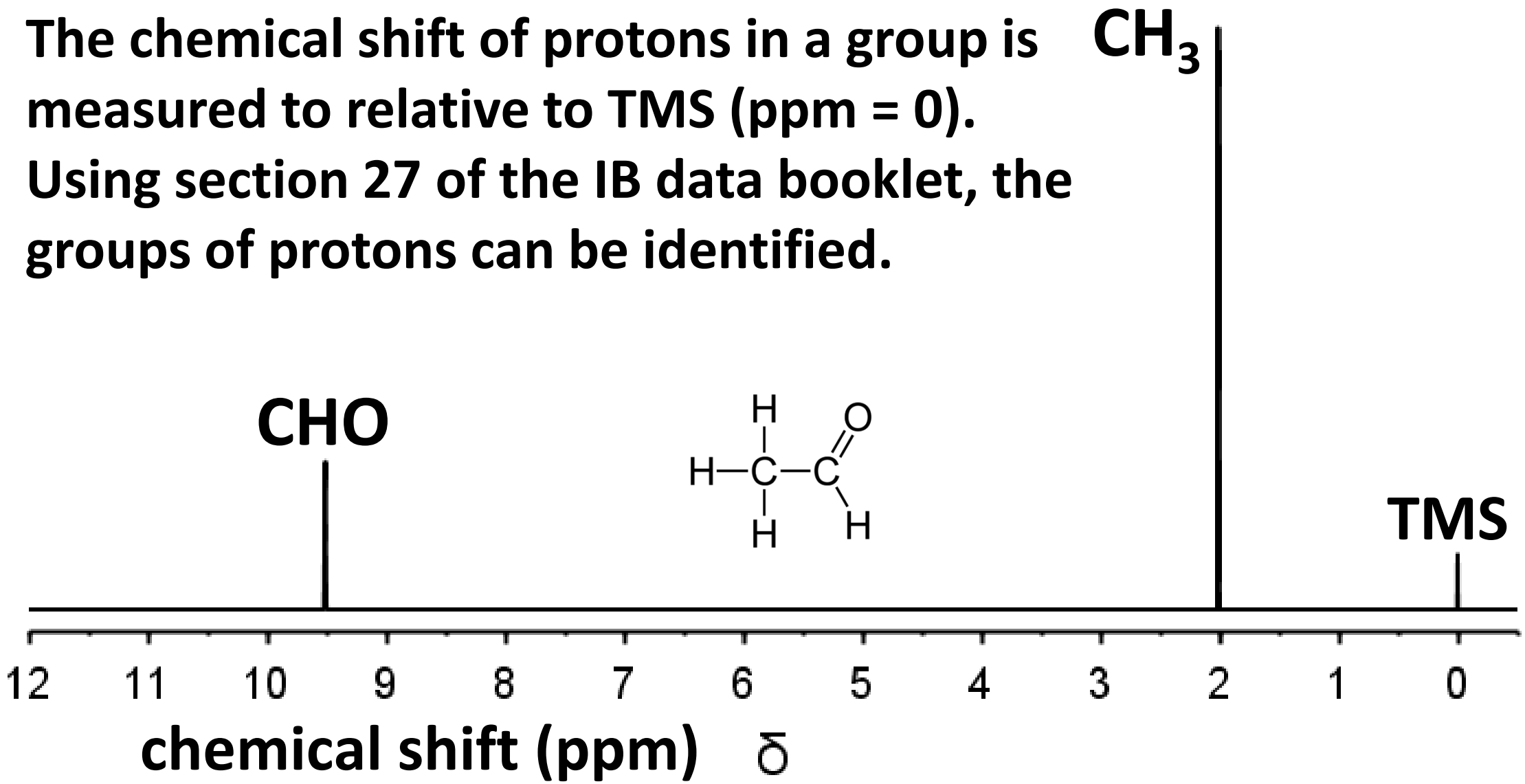
^{1}H NMR

The chemical shift of protons in a group is measured to relative to TMS (ppm = 0).
Using section 27 of the IB data booklet, the groups of protons can be identified.



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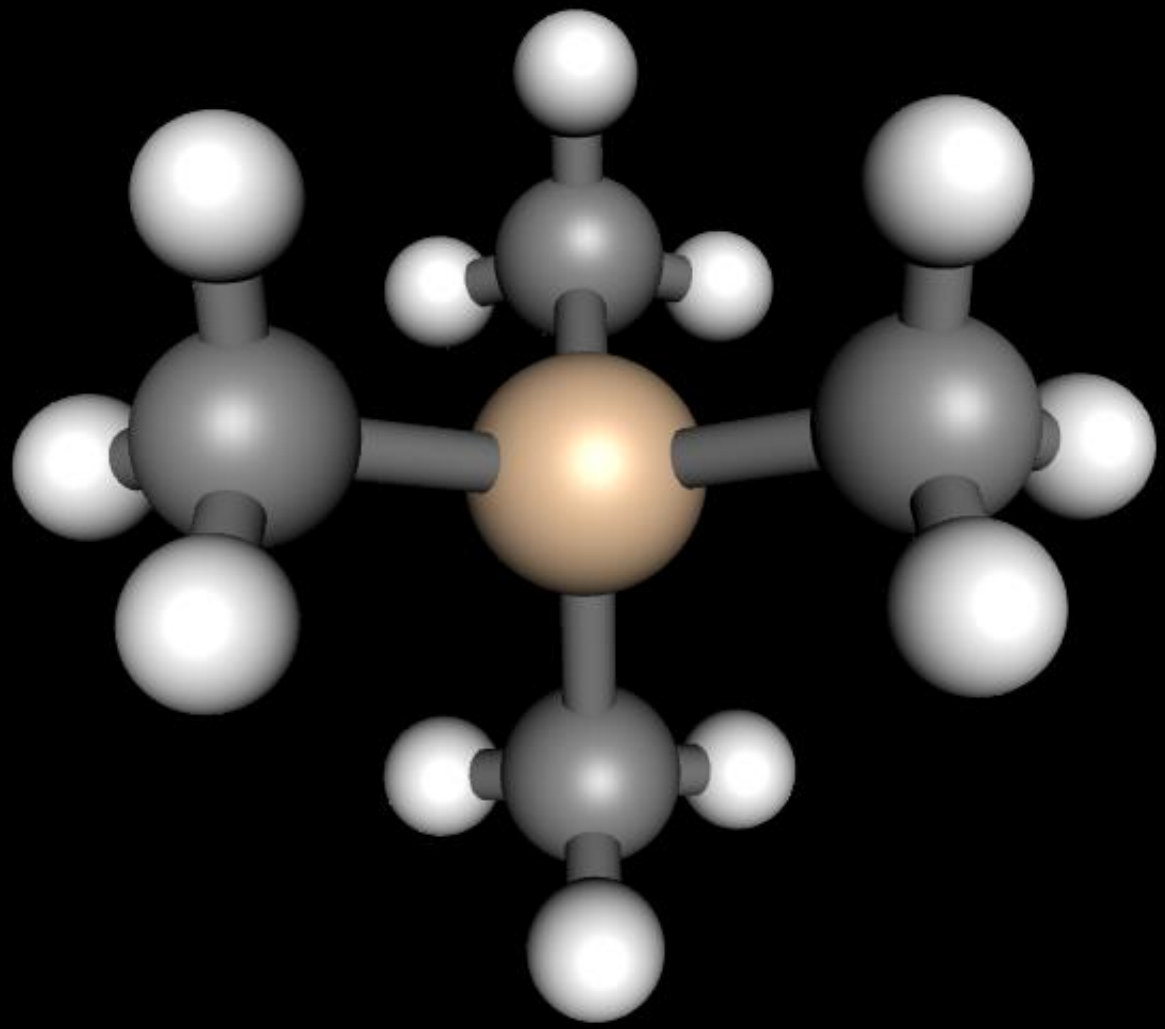
^{1}H NMR



The position of the NMR signal is measured relative to the signal produced by TMS tetramethylsilane $Si(CH_3)_4$

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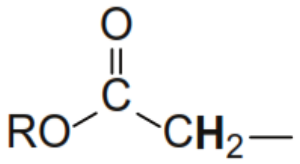
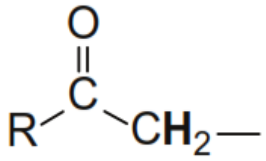
^{1}H NMR

27. ^{1}H NMR data

Typical proton chemical shift values (δ) relative to tetramethylsilane (TMS) = 0.

R represents an alkyl group, and Hal represents F, Cl, Br, or I.

These values may vary in different solvents and conditions.

Type of proton	Chemical shift (ppm)
—C**H**$_3$	0.9–1.0
—C**H**$_2$R	1.3–1.4
—C**H**R$_2$	1.5
	2.0–2.5
	2.2–2.7

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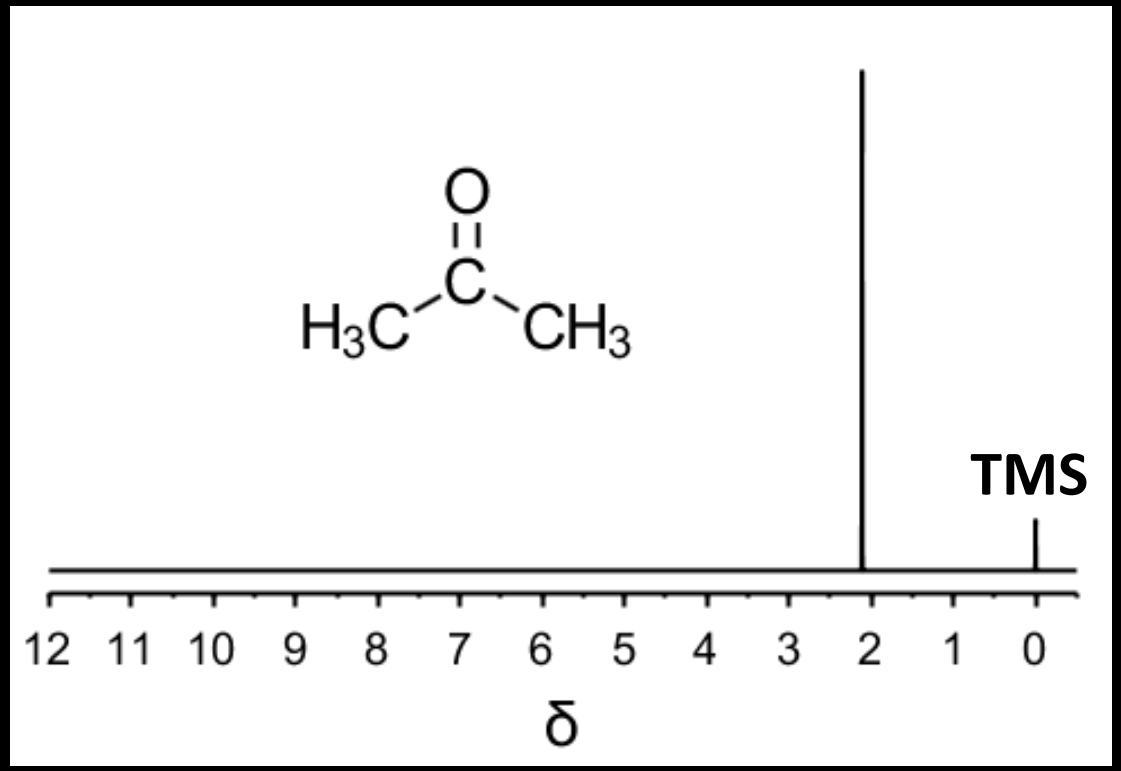
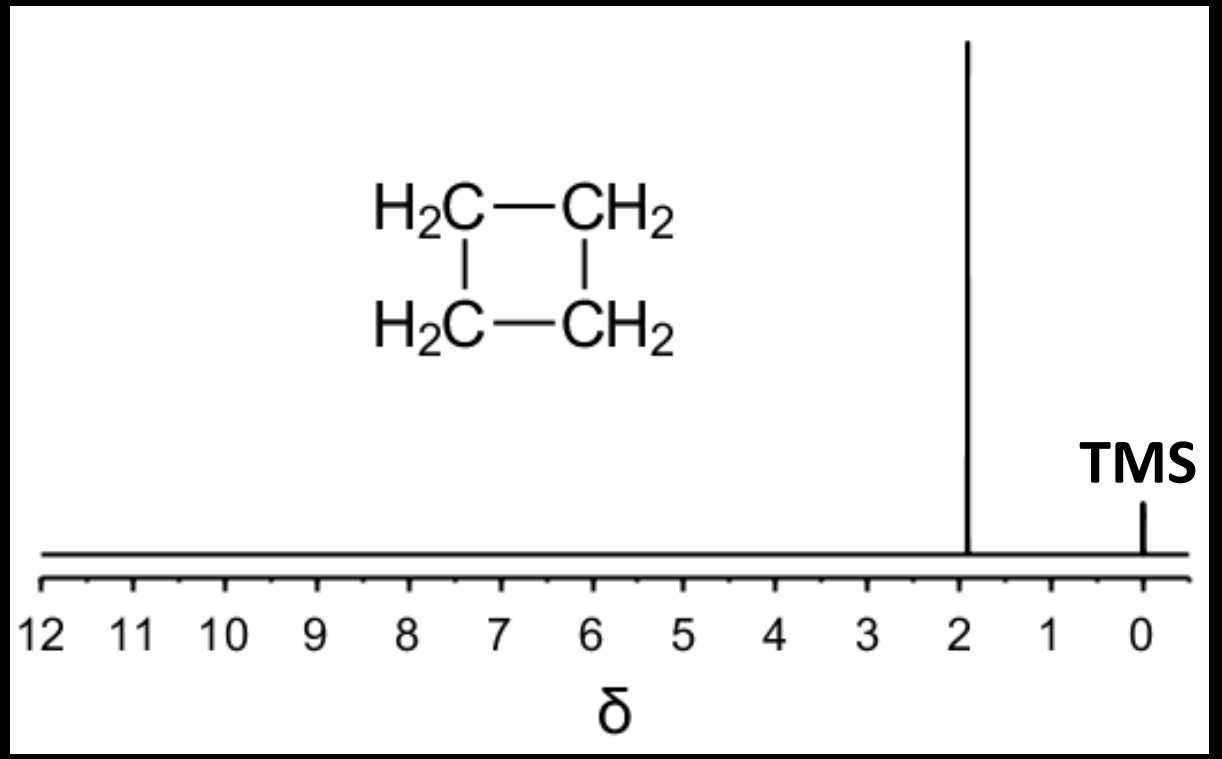
^{1}H NMR





Peak at 2.2 ppm –C**H**$_3$

Peak at 1.9 ppm –C**H**$_2$R

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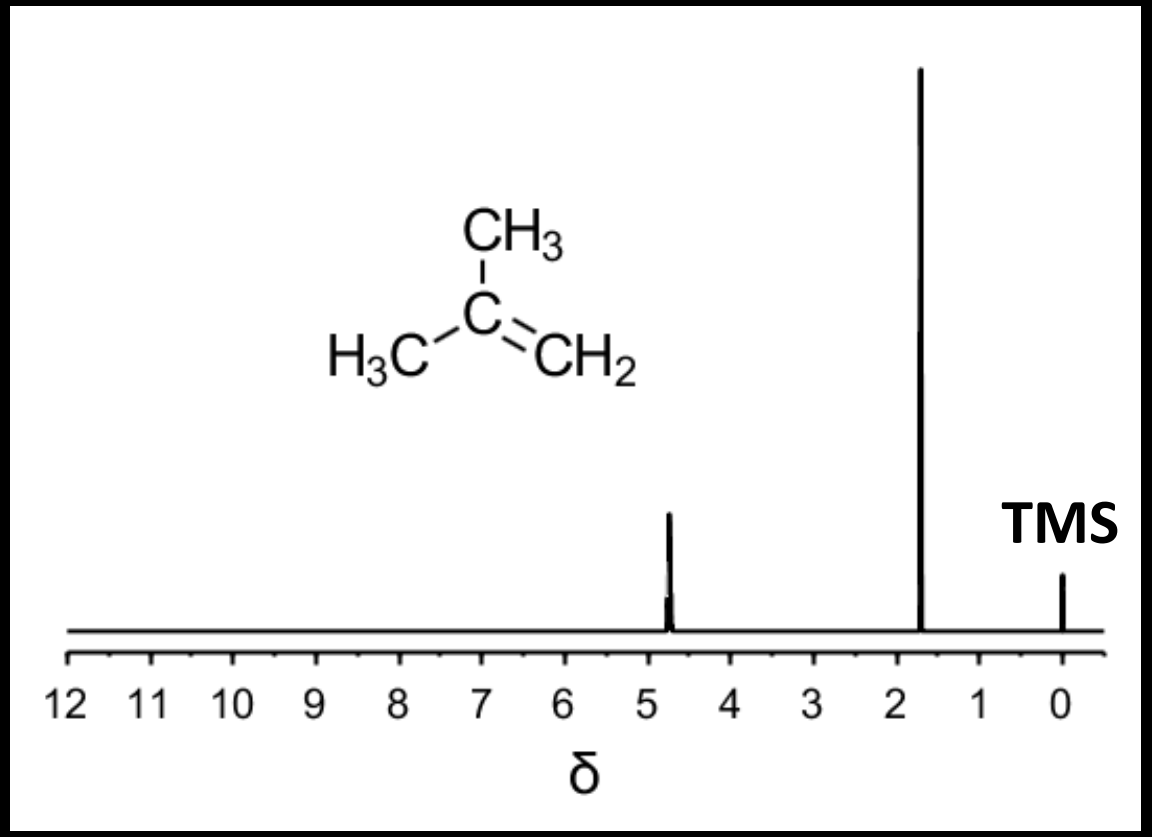
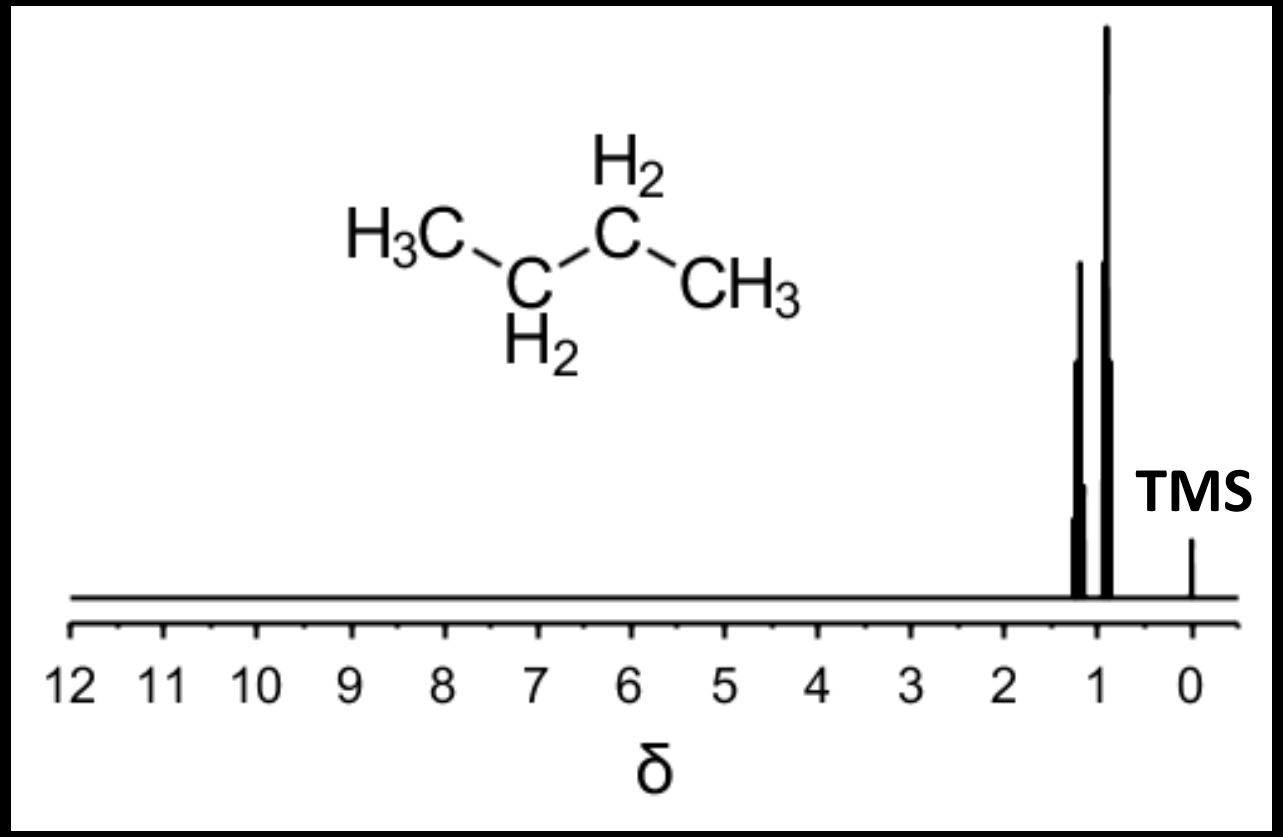
^{1}H NMR





Peak at 1.9 ppm –C**H**$_3$

Peak at 4.9 ppm C=C**H**$_2$

Peak at 0.9 ppm –C**H**$_3$

Peak at 1.3 ppm –C**H**$_2$R

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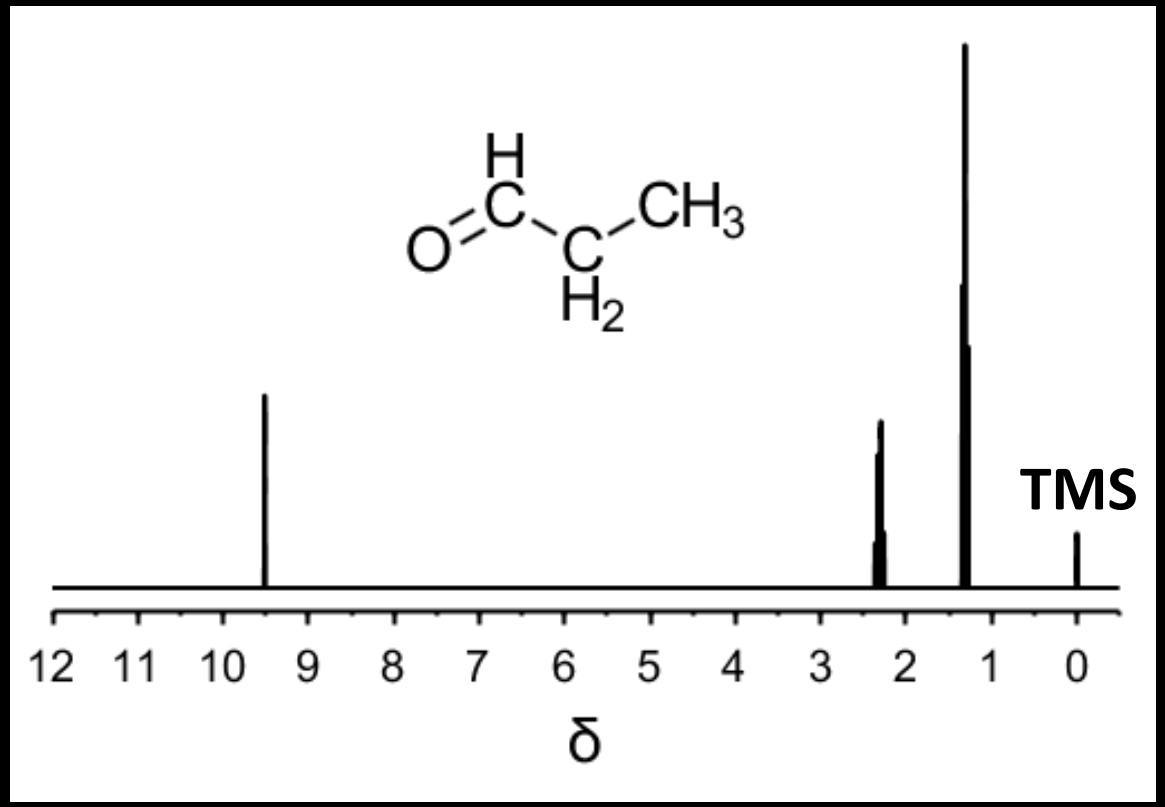
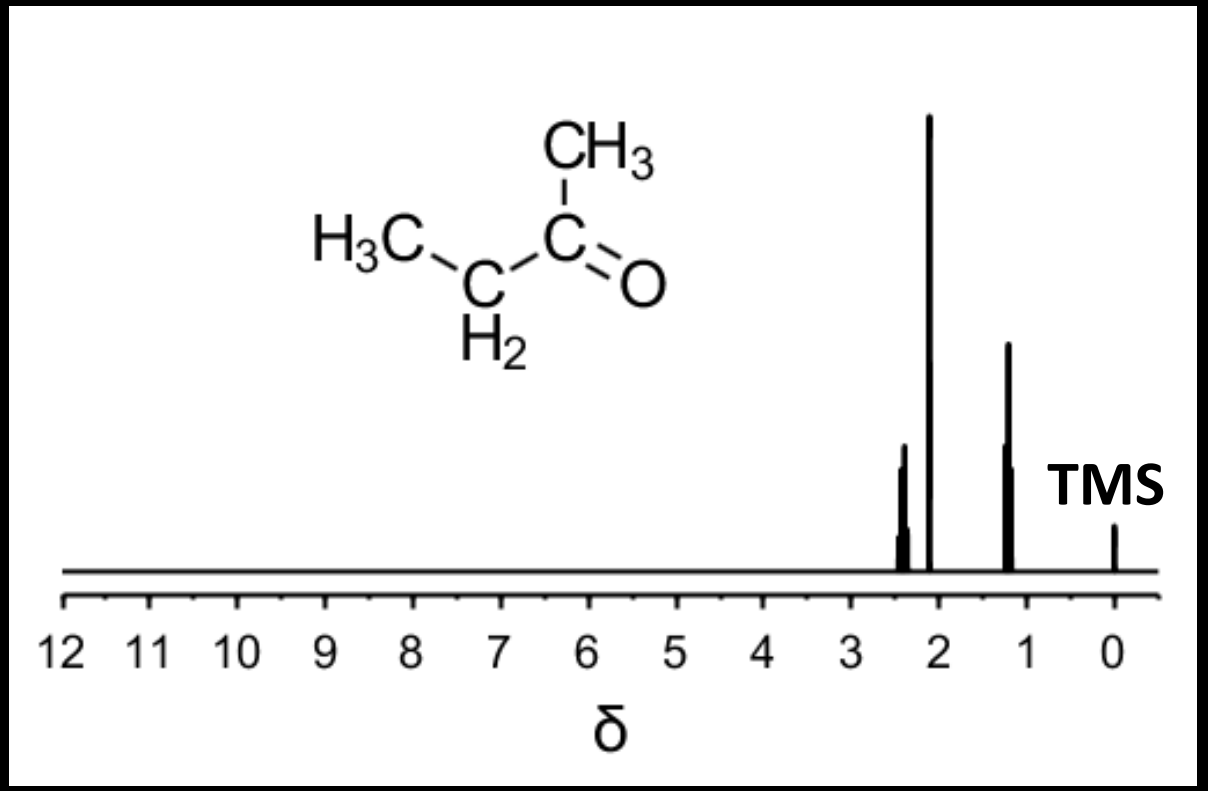
^{1}H NMR





Peak at 1.3 ppm –C**H**$_3$
Peak at 2.3 ppm –C**H**$_2$R
Peak at 9.5 ppm R–C**H**O

Peak at 1.2 ppm –C**H**$_3$
Peak at 2.1 ppm R–CO–C**H**$_3$
Peak at 2.4 ppm R–CO–C**H**$_2$–

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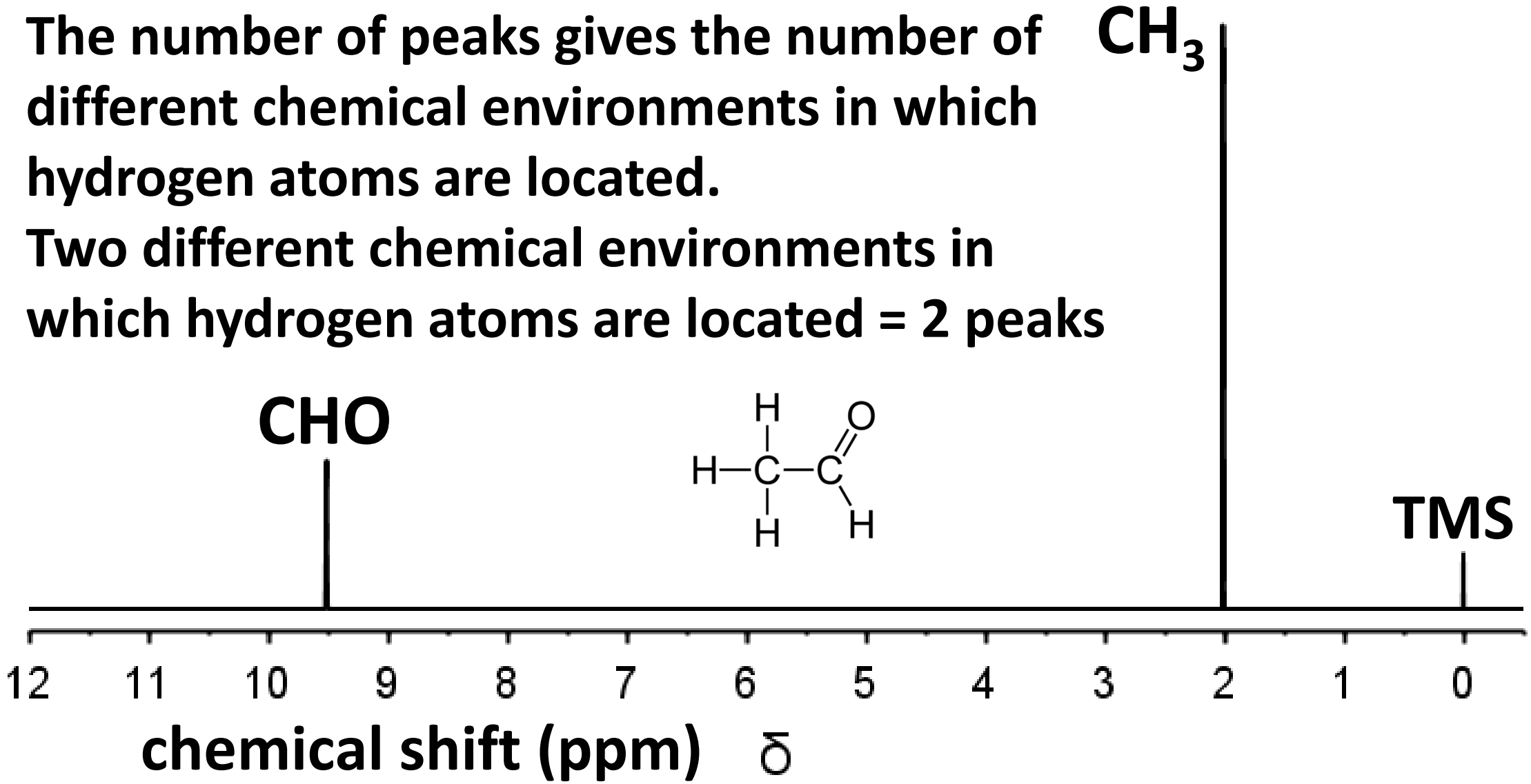
^{1}H NMR

The number of peaks gives the number of different chemical environments in which hydrogen atoms are located.

Two different chemical environments in which hydrogen atoms are located = 2 peaks



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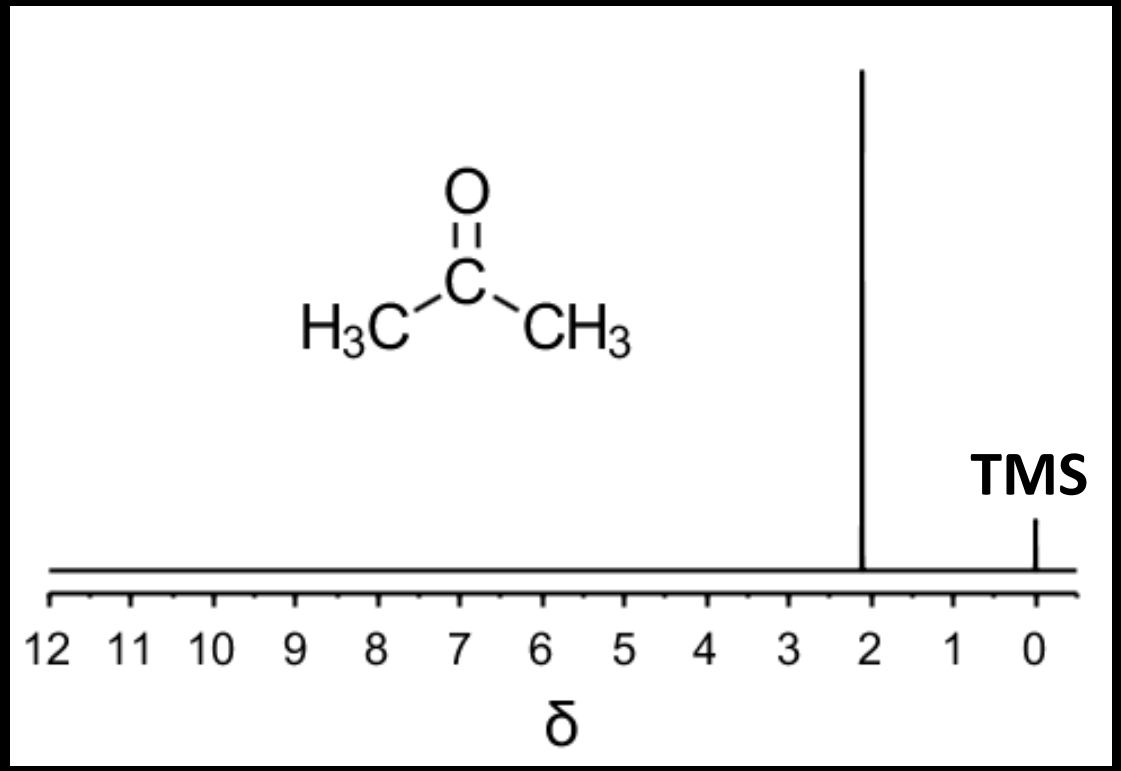
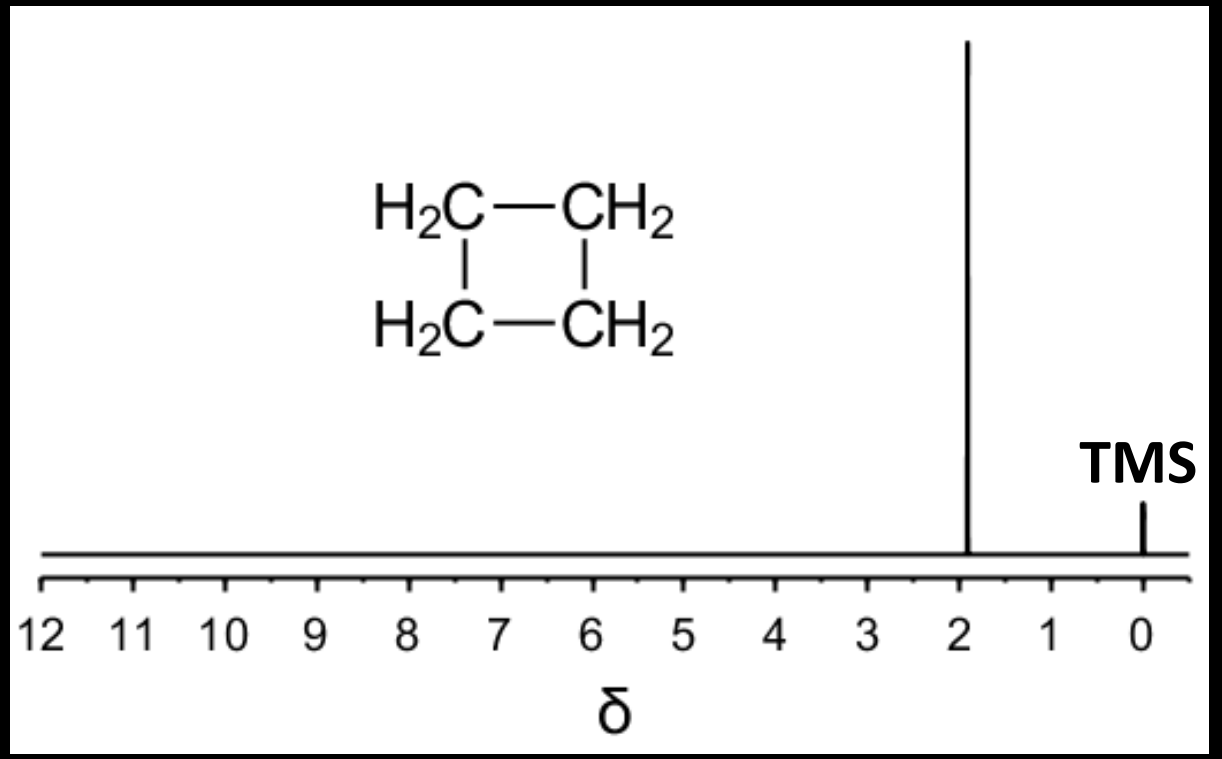
^{1}H NMR



Propanone: Only one type of chemical environment in which hydrogen atoms are located = 1 peak.



Cyclobutane: Only one type of chemical environment in which hydrogen atoms are located = 1 peak.

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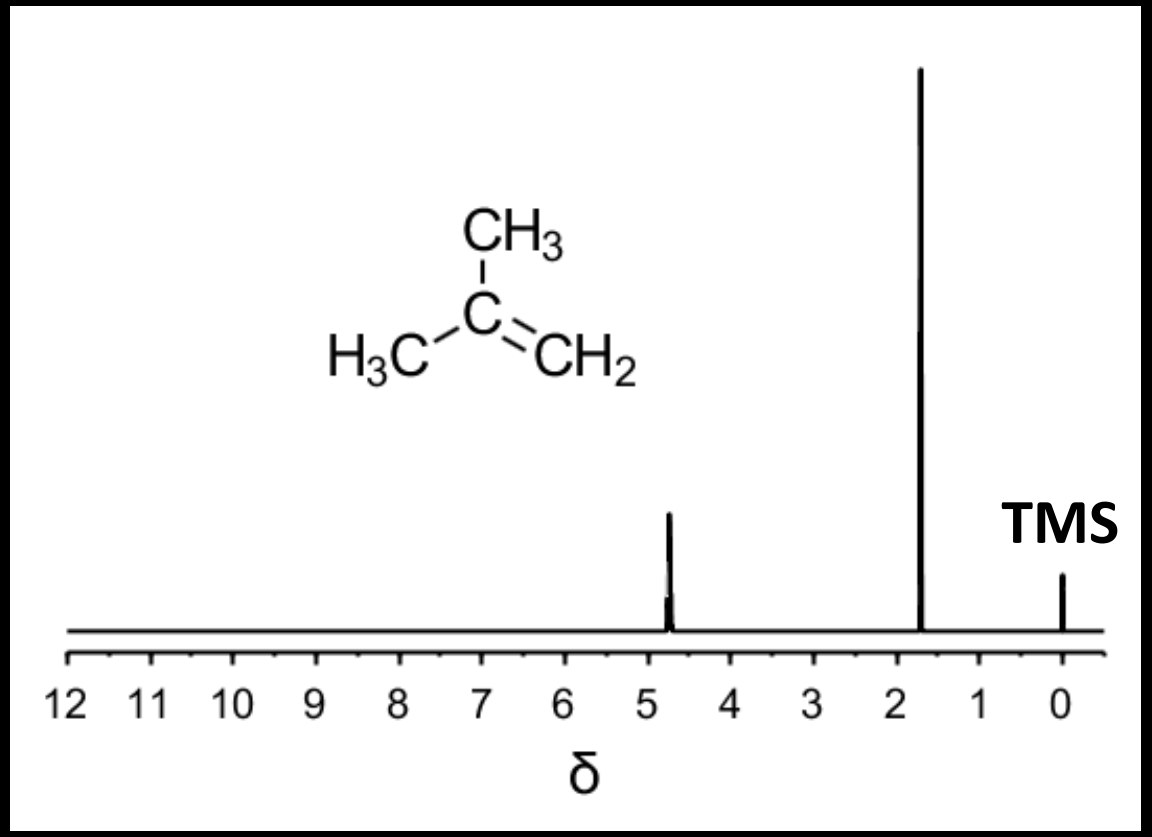
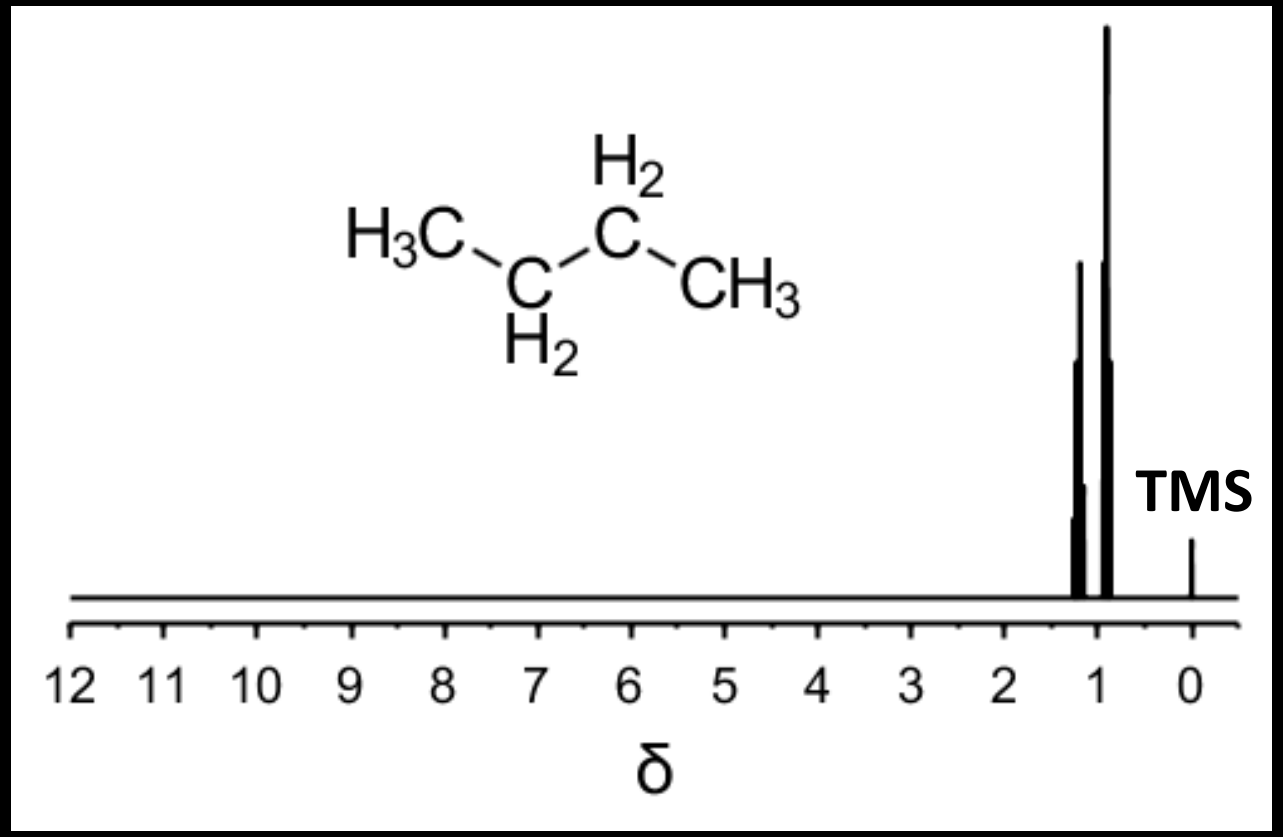
^{1}H NMR



2-methylpropene: two different chemical environments in which hydrogen atoms are located = 2 peaks.



Butane: two different chemical environments in which hydrogen atoms are located = 2 peaks.

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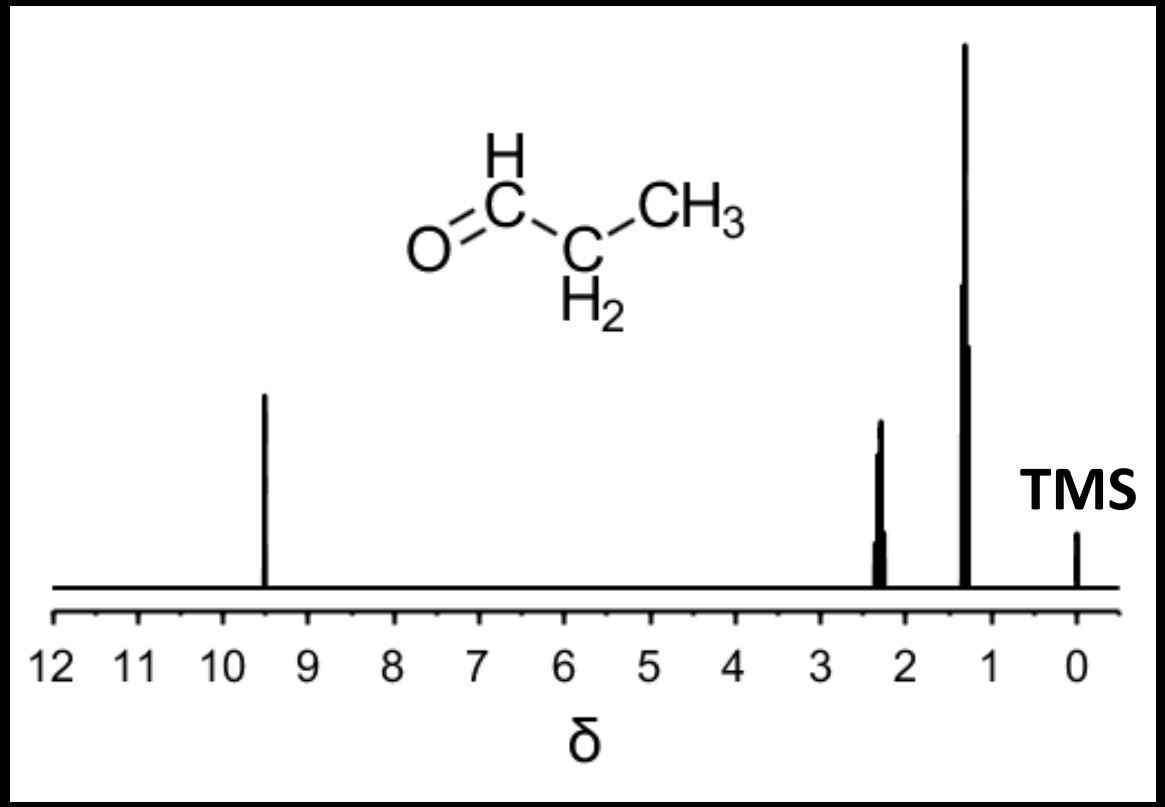
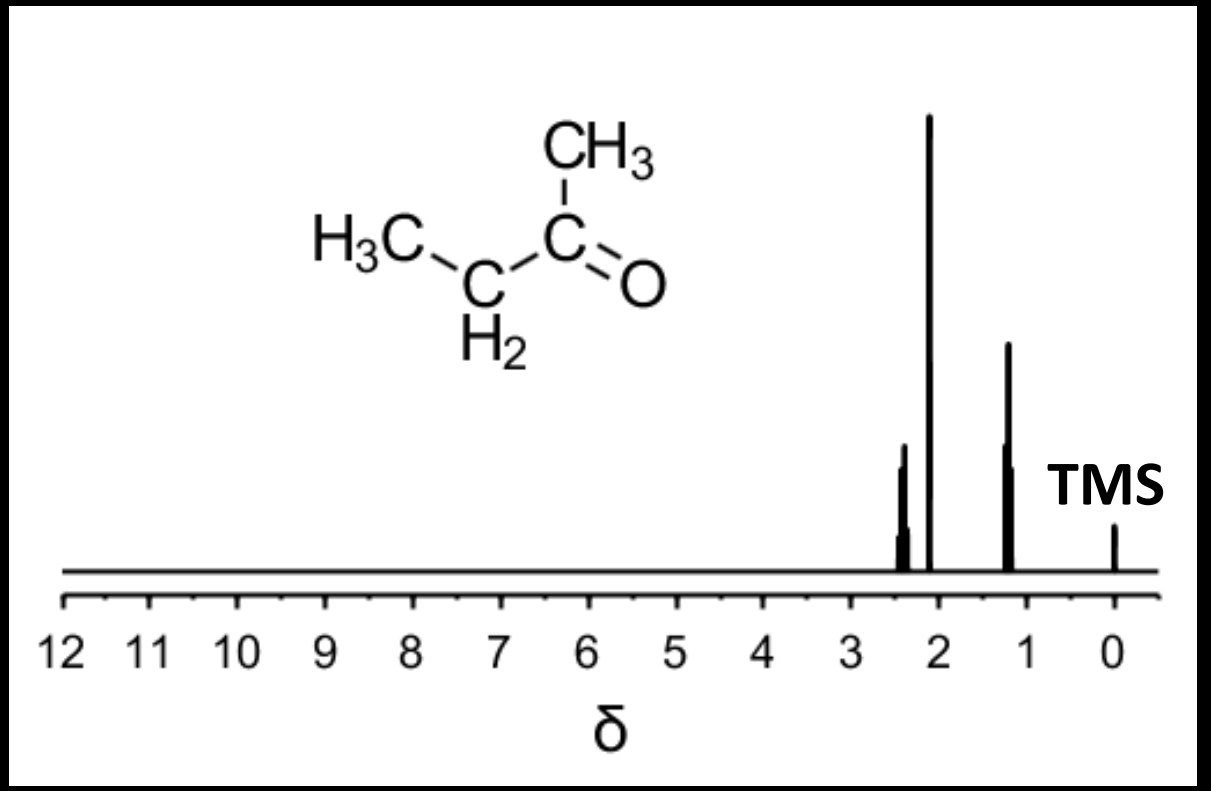
^{1}H NMR



Propanal: three different chemical environments in which hydrogen atoms are located = 3 peaks.



Butanone: three different chemical environments in which hydrogen atoms are located = 3 peaks.

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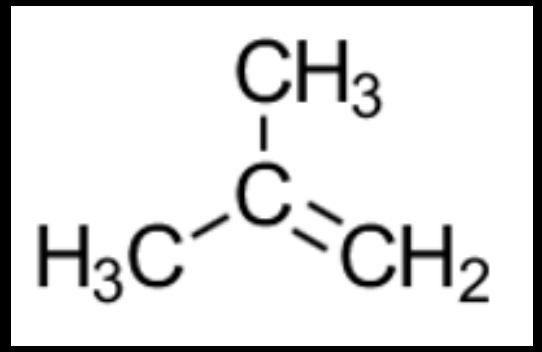
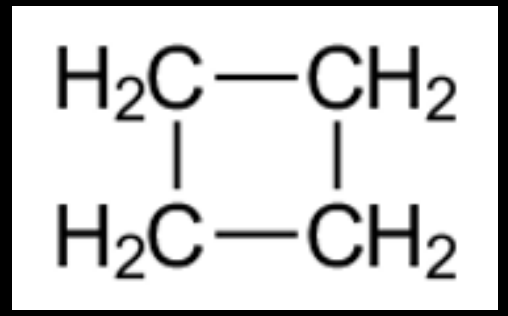
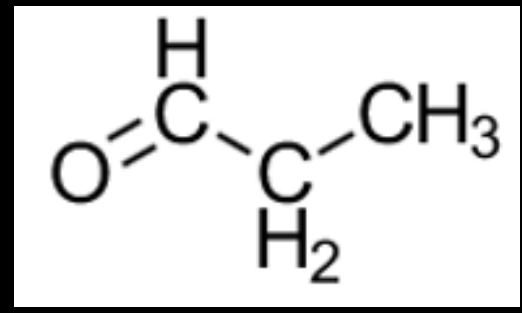
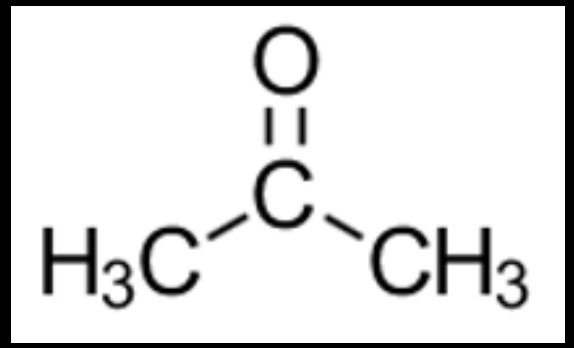
^{1}H NMR

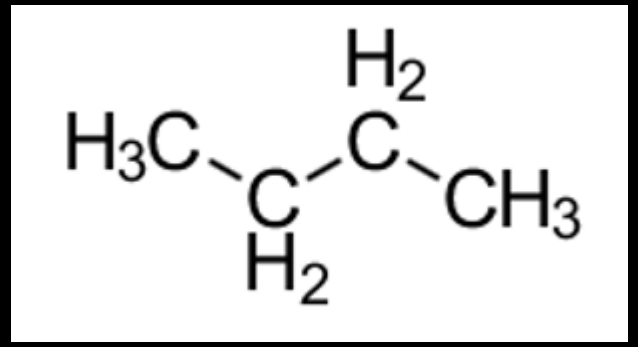
How to determine if hydrogen atoms (protons) are in different chemical environments.

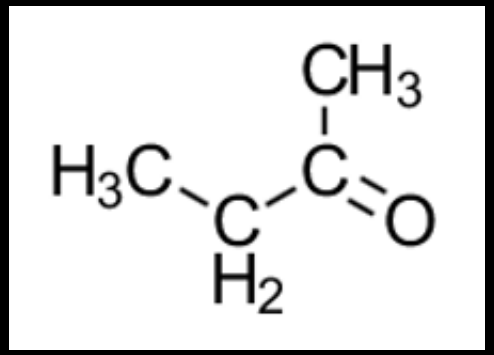












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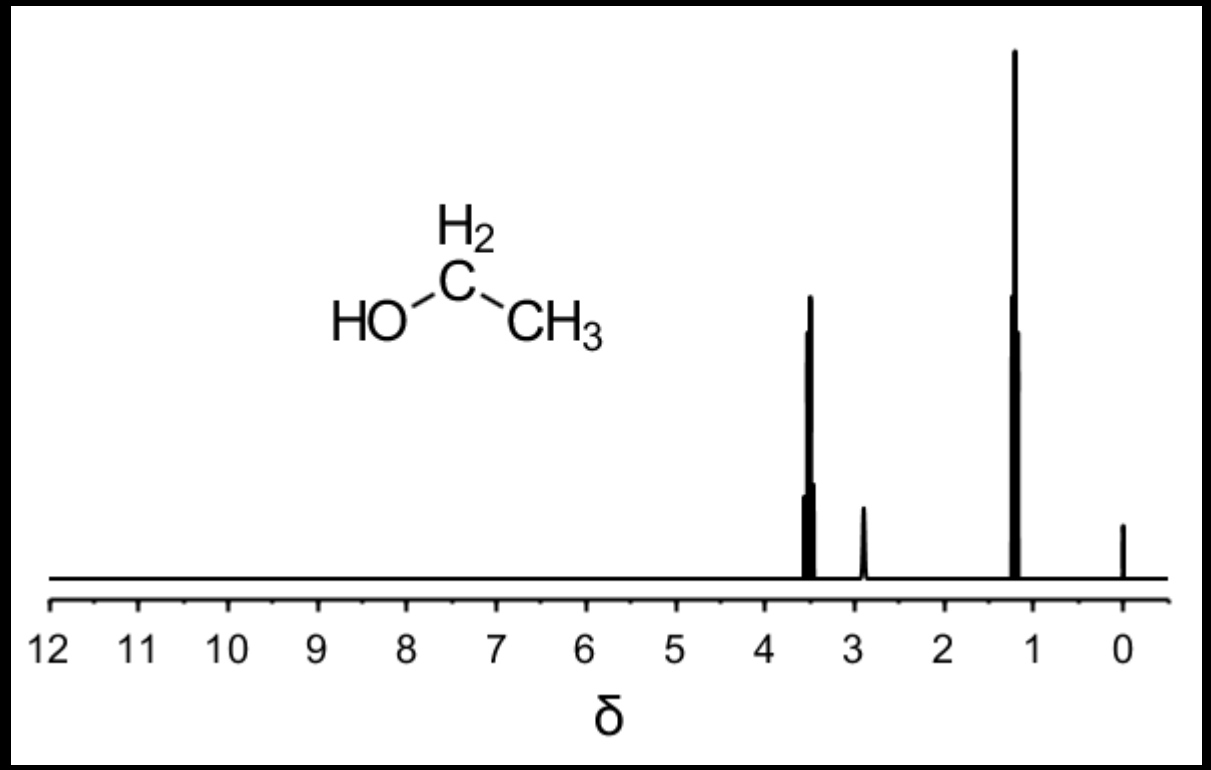
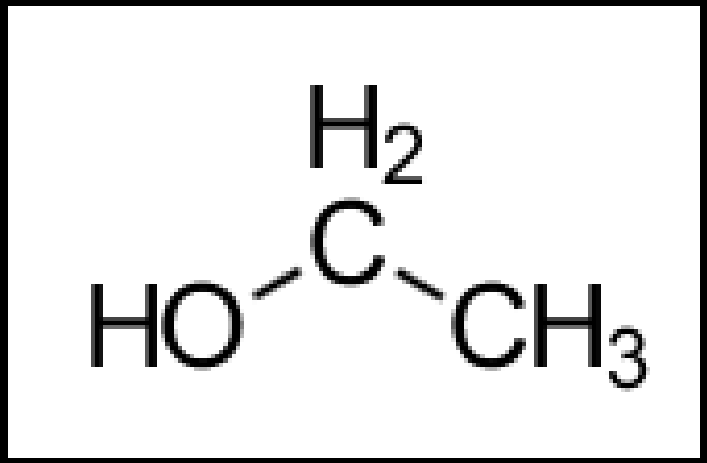
^{1}H NMR





Ethanol: three different chemical environments in which hydrogen atoms are located = 3 peaks.

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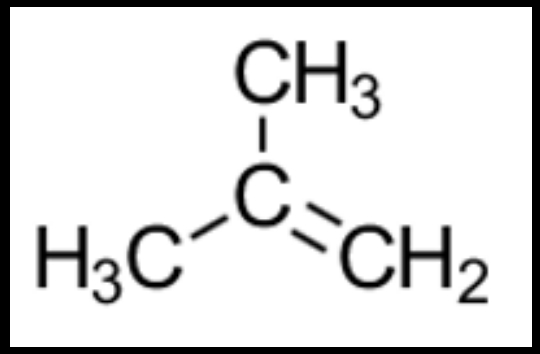
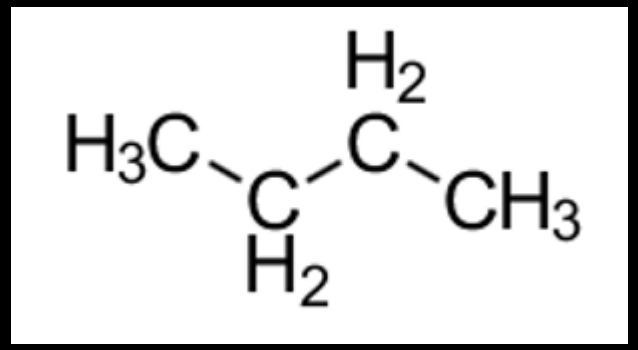
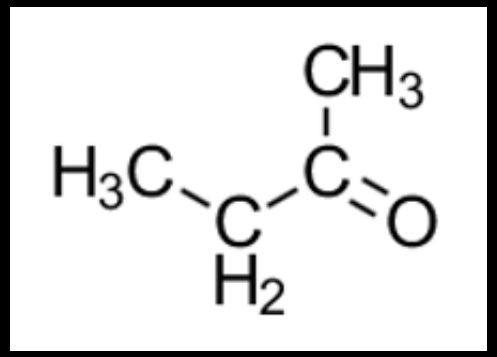
^{1}H NMR

Summary:

- If there are two of the same group (two CH_3 groups), look at the groups of atoms that those groups are bonded to; if they are the same, then the protons are in the same chemical environment, if not, they are in different chemical environments.

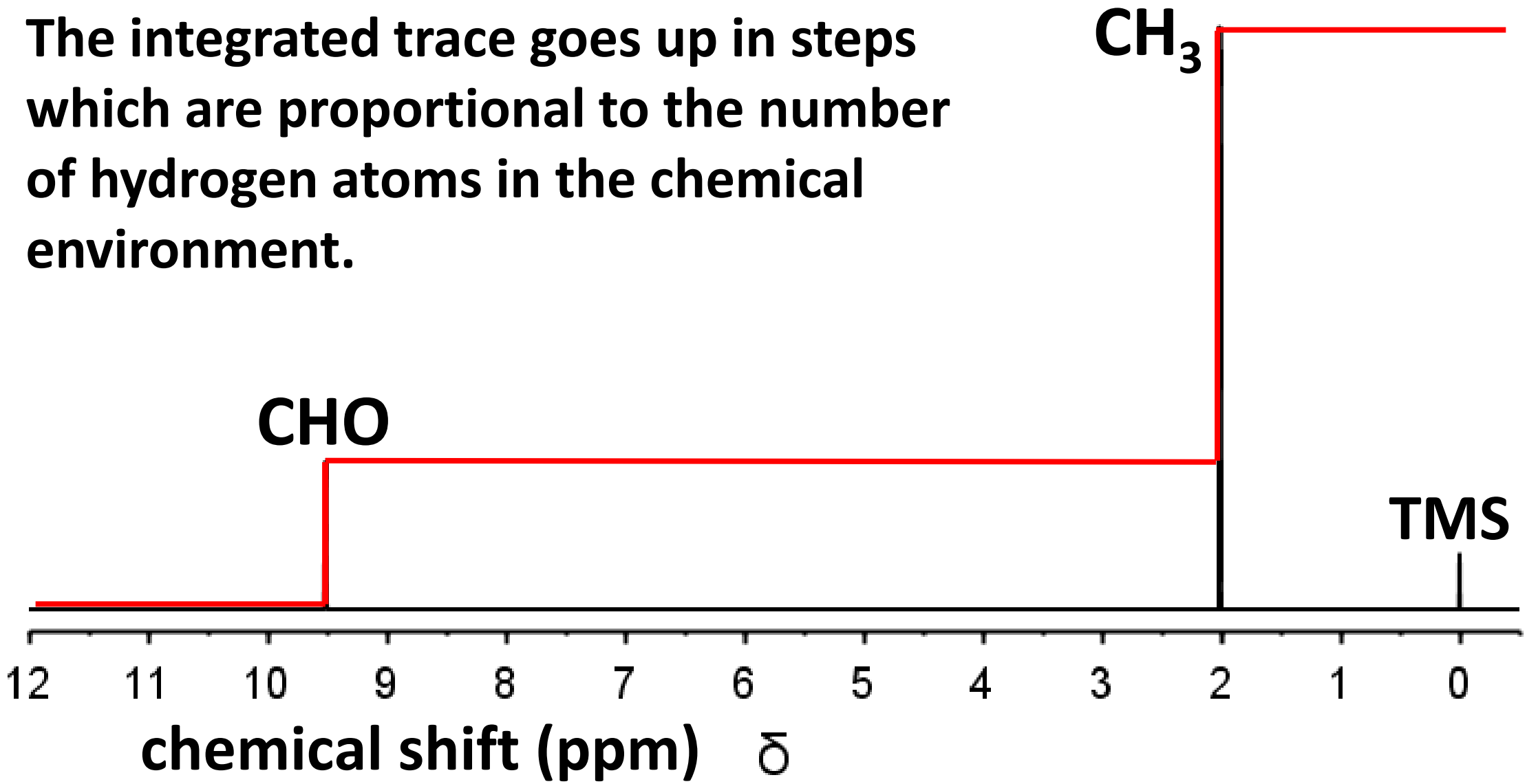






^{1}H NMR

The integrated trace goes up in steps which are proportional to the number of hydrogen atoms in the chemical environment.



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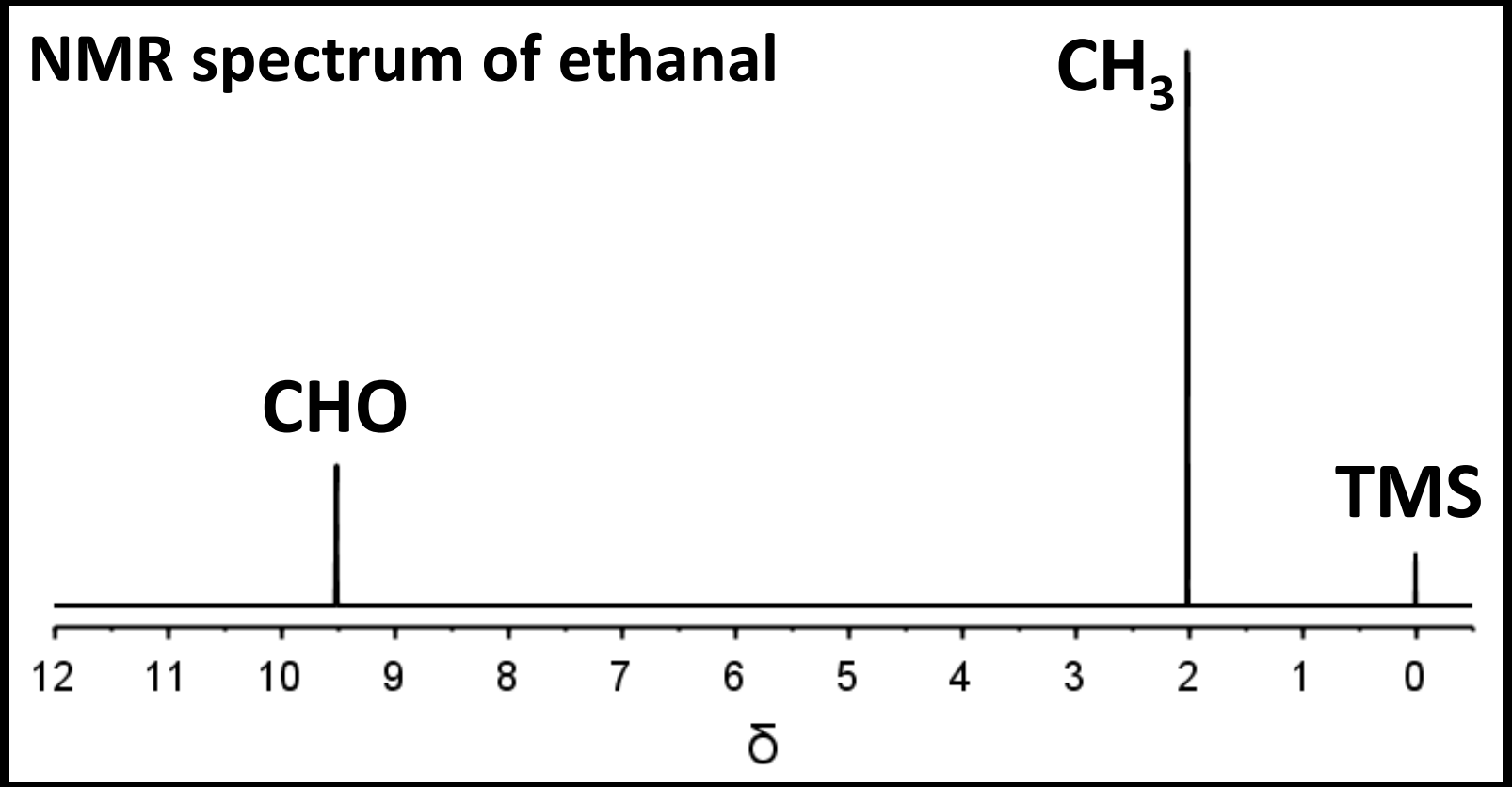
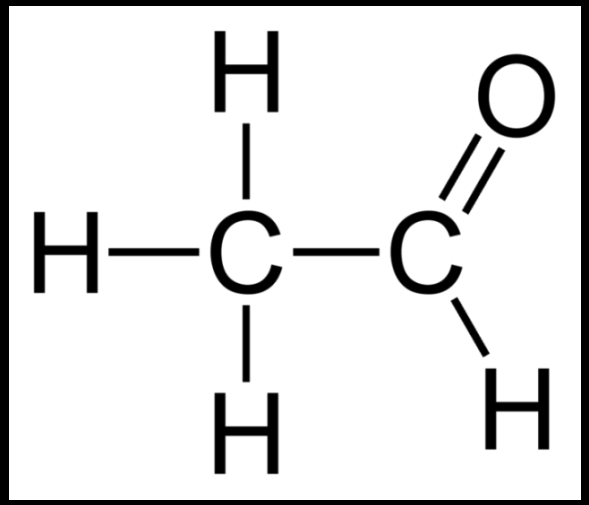
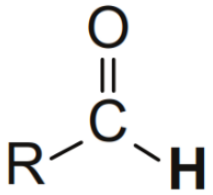
^{1}H NMR





Type of proton	Chemical shift (ppm)
– CH_3	0.9 – 1.0
	9.4 – 10.0

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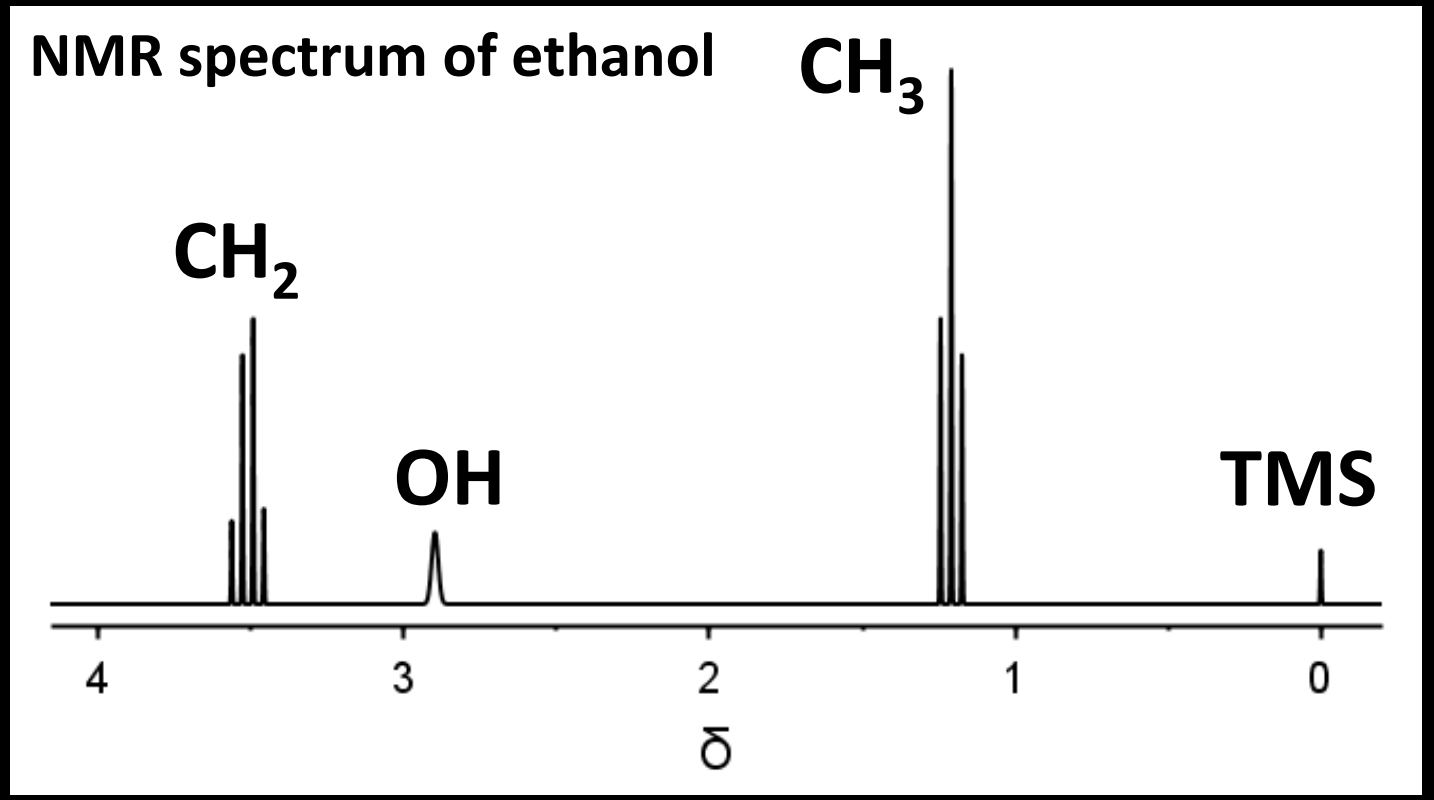
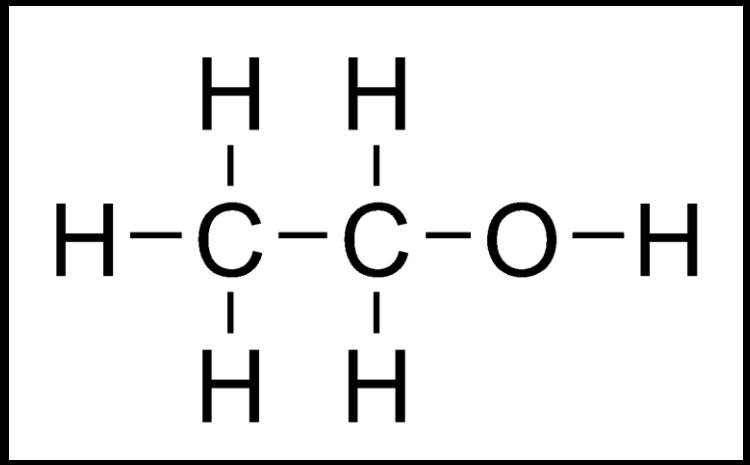
^{1}H NMR





Type of proton	Chemical shift (ppm)
– C**H**$_3$	0.9 – 1.0
R–O–C**H**$_2$ –	3.3 – 3.7
R–O–**H**	1.0 – 6.0

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TMS as the reference standard

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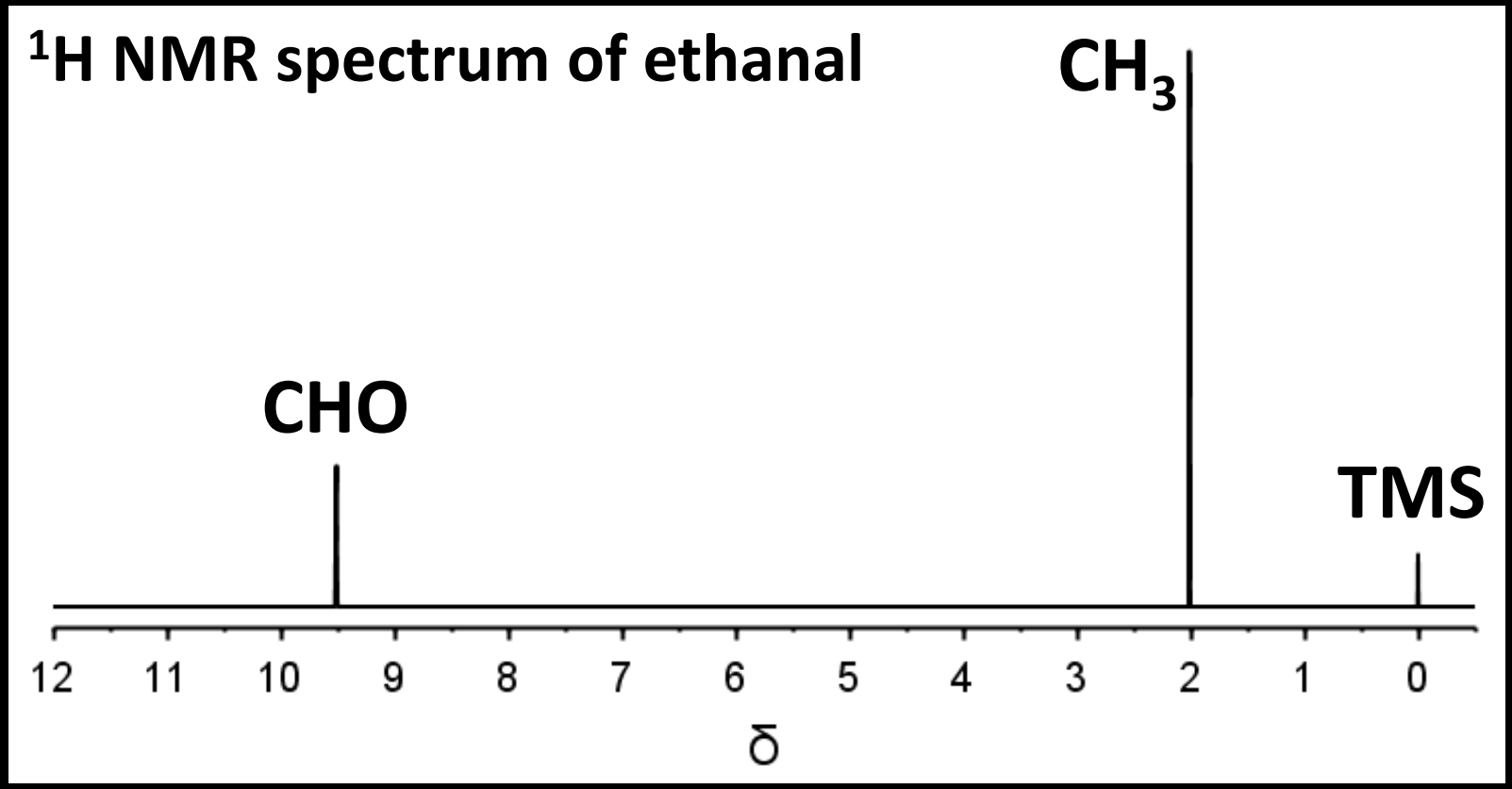
^{1}H NMR



The position of the NMR signal is measured relative to the signal produced by TMS tetramethylsilane $Si(CH_3)_4$

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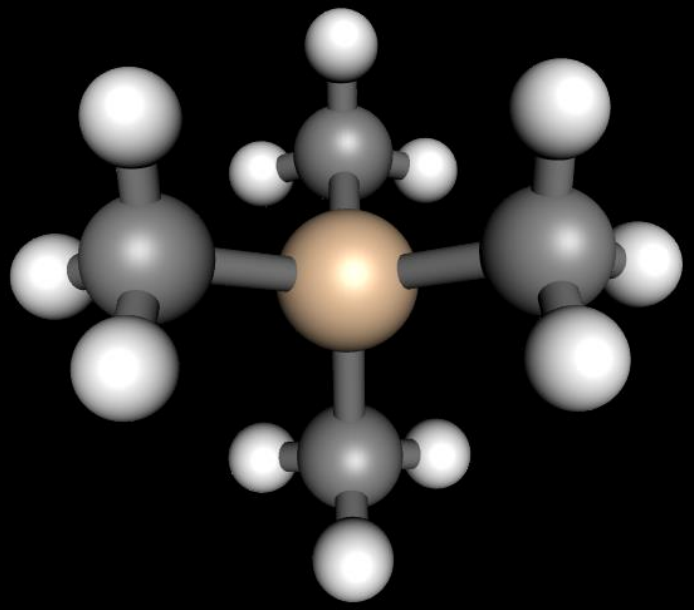
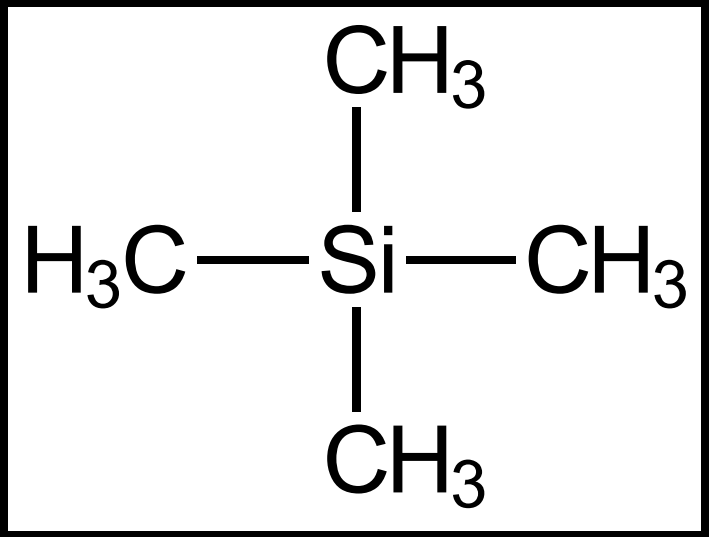
^{1}H NMR





All the protons are in the same chemical environment therefore it gives a strong single peak.

It is non-toxic and unreactive (does not interfere with sample).

It absorbs upfield, away from most other protons.

It is volatile (has a low boiling point) so can easily be removed from the sample.

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High resolution ^{1}H NMR

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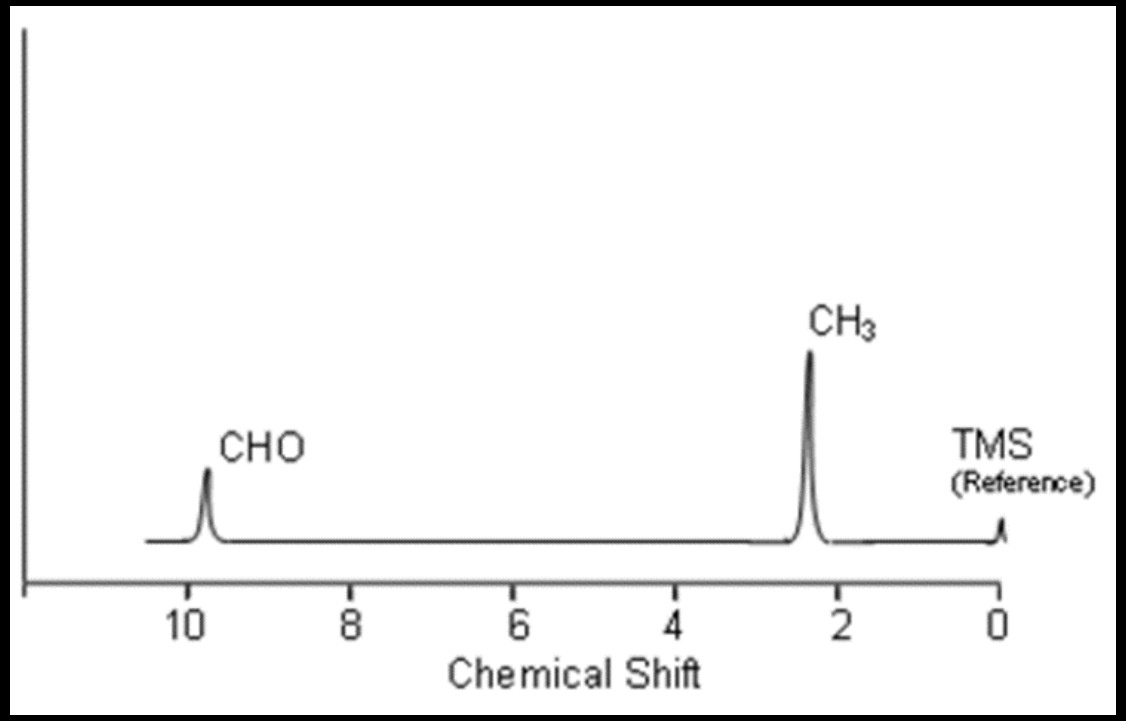
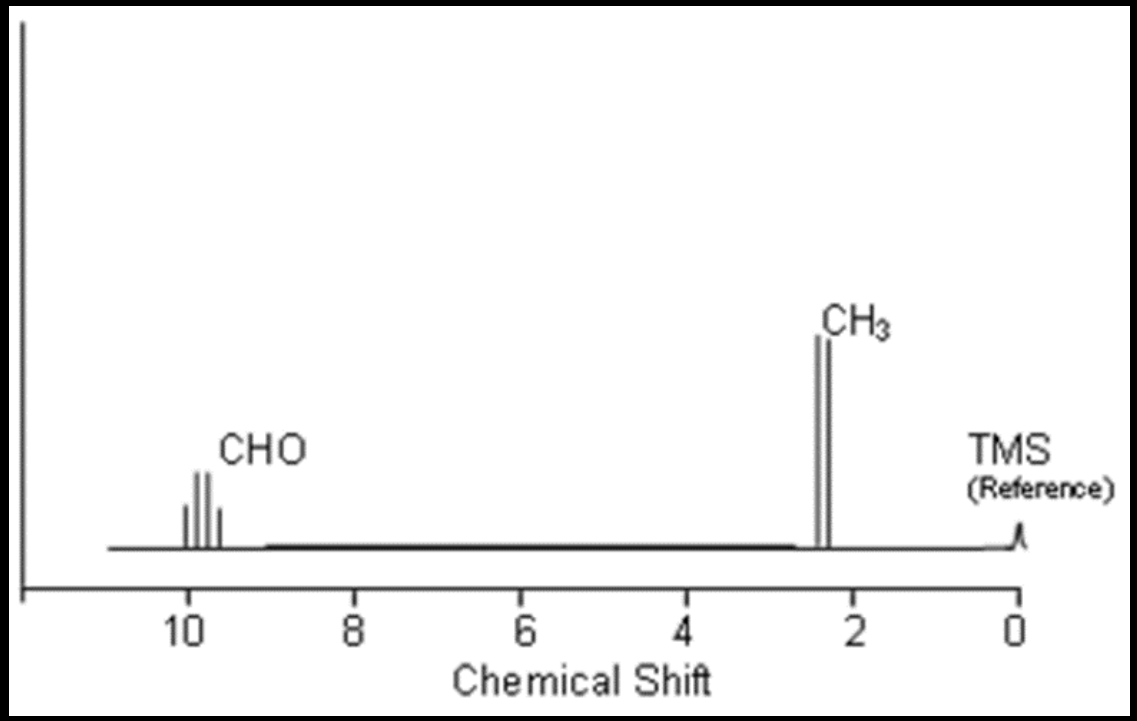
^{1}H NMR

low resolution ^{1}H NMR spectrum



high resolution ^{1}H NMR spectrum



In a high resolution ^{1}H NMR spectrum, what looked like single peaks in the low resolution spectrum are split into clusters of peaks.

^{1}H NMR

The number of peaks tells us about the number of protons attached to the adjacent carbon atom(s).

Number of adjacent protons	Number of peaks	Type of splitting	Relative intensities of peaks
0	1	singlet	1
1	2	doublet	1 1
2	3	triplet	1 2 1
3	4	quartet	1 3 3 1

The number of peaks is one more than the number of hydrogens (protons) attached to the adjacent carbon(s).

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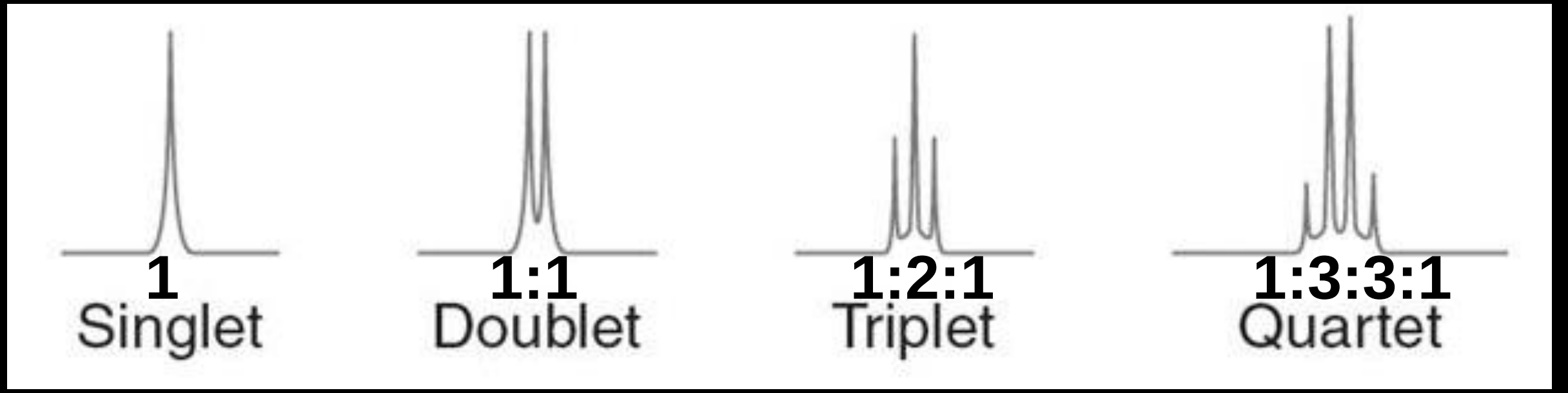
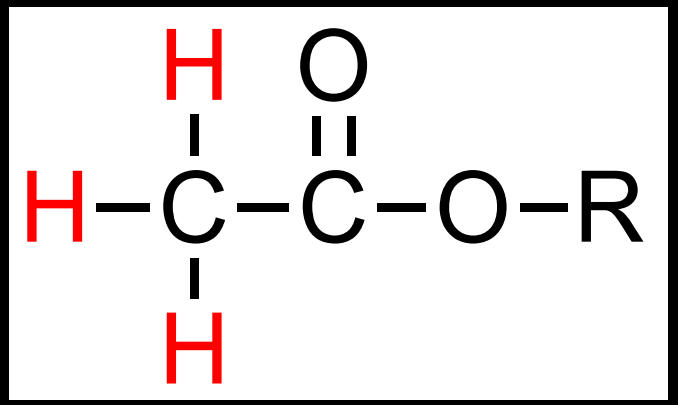
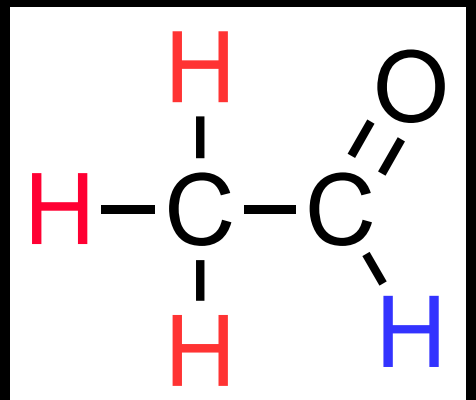
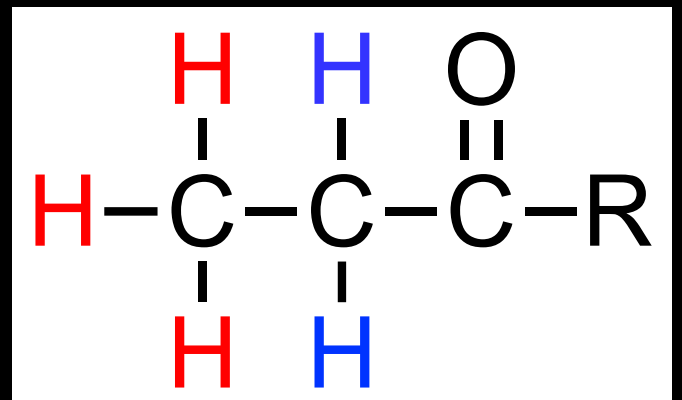
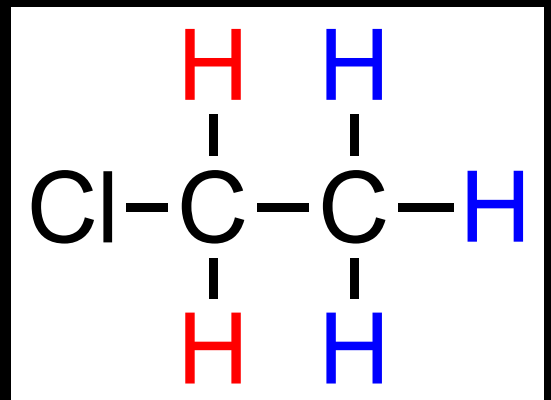
^{1}H NMR











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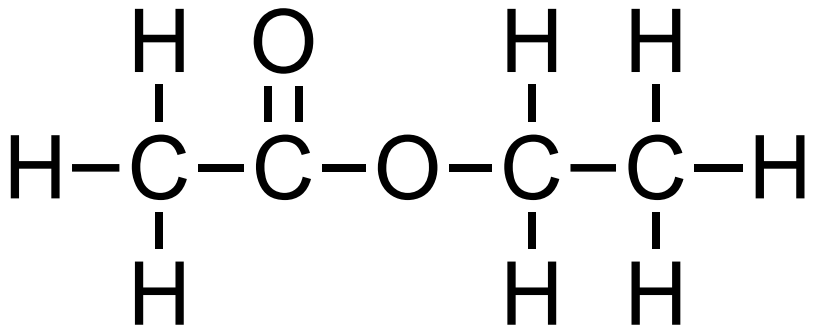
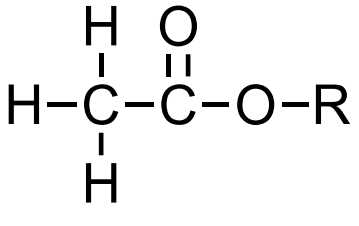
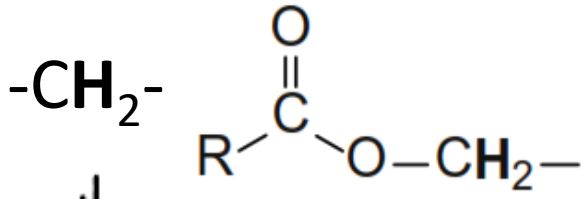
^{1}H NMR

ethyl ethanoate





2.0 ppm



4.0 ppm

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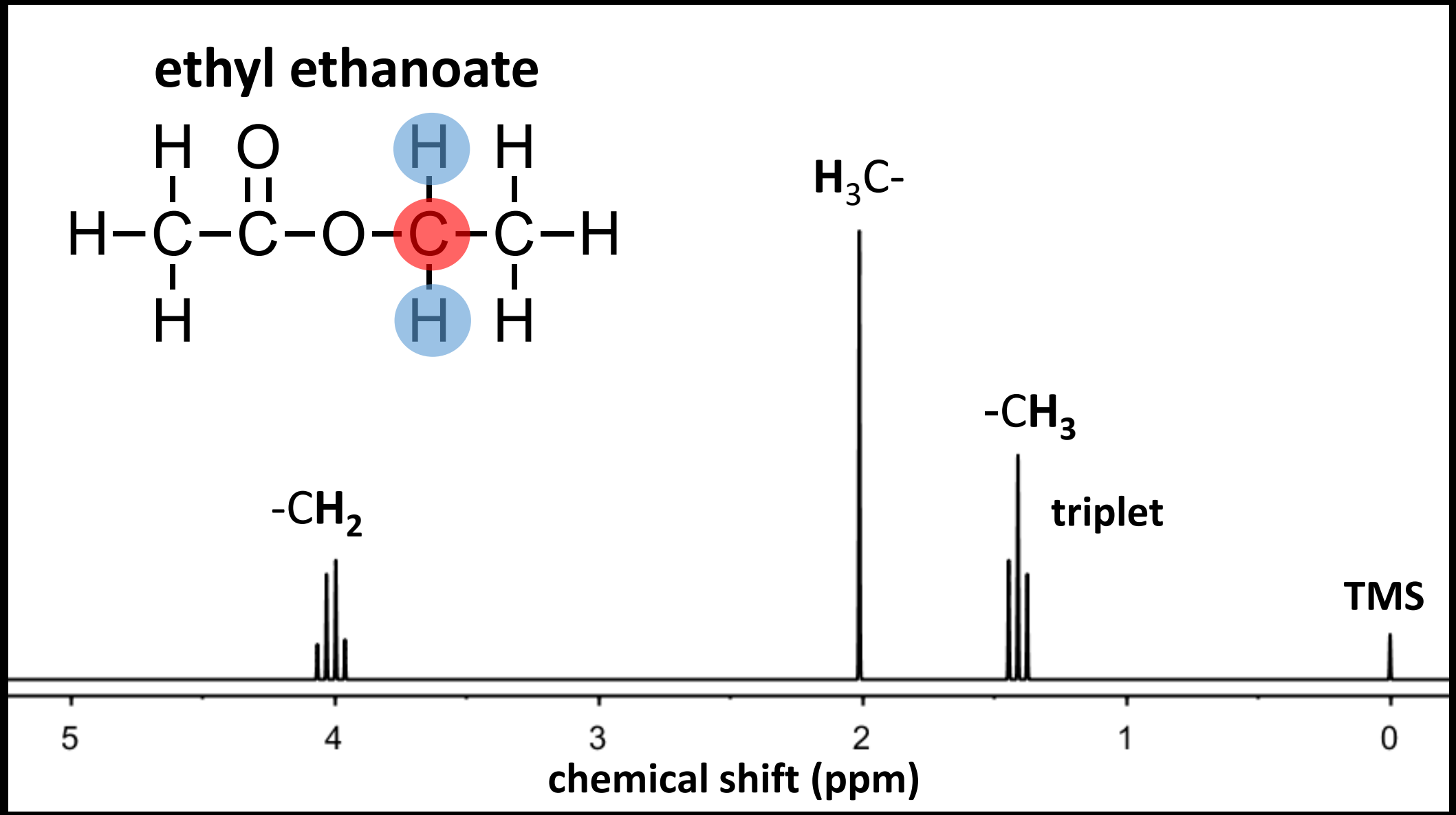
^{1}H NMR



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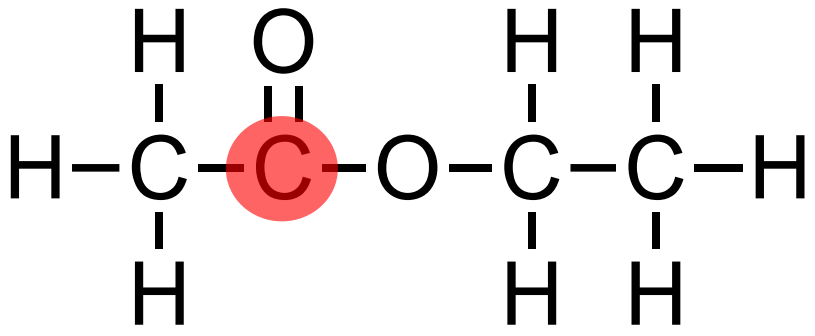
^{1}H NMR

ethyl ethanoate



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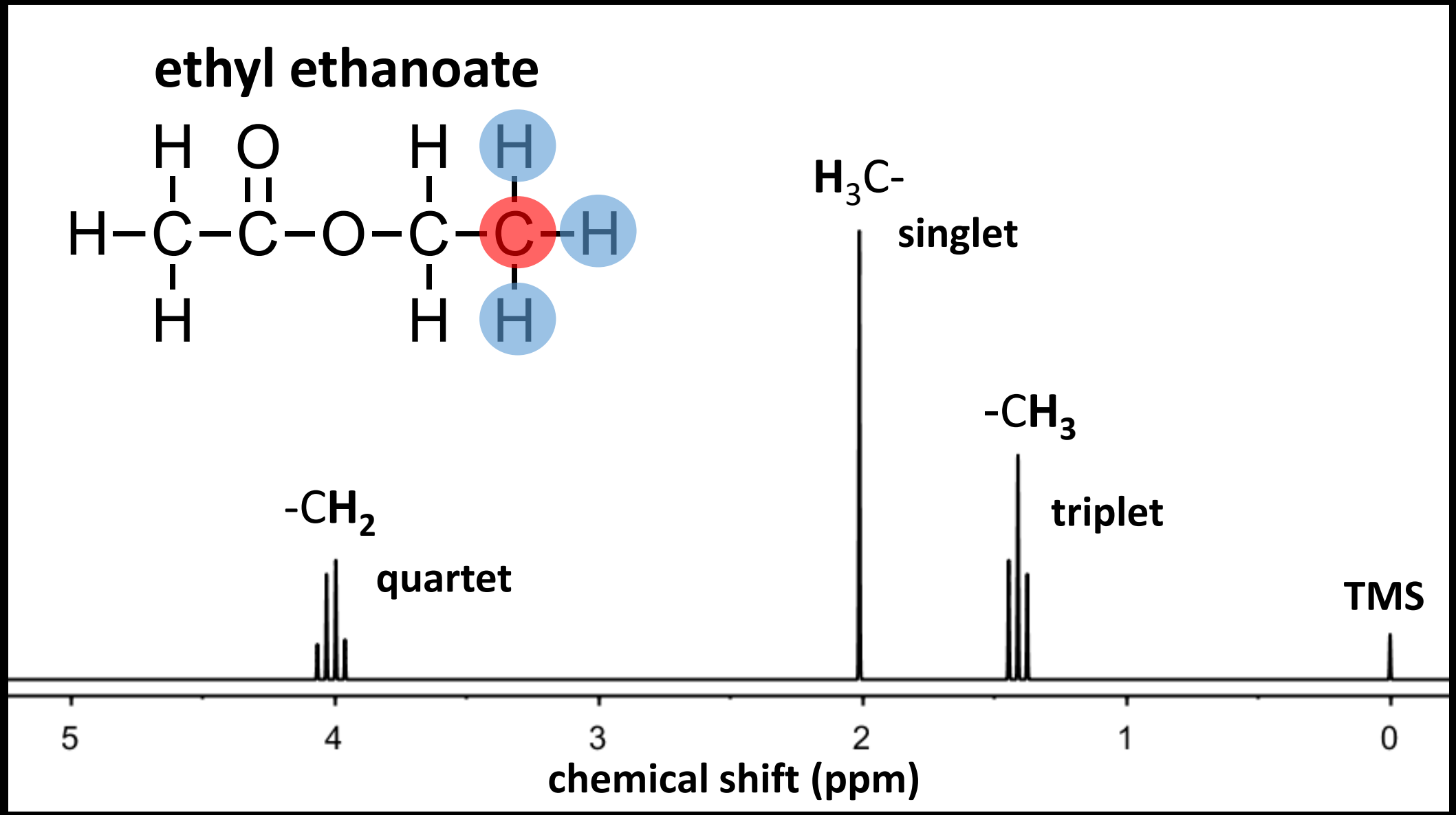
^{1}H NMR



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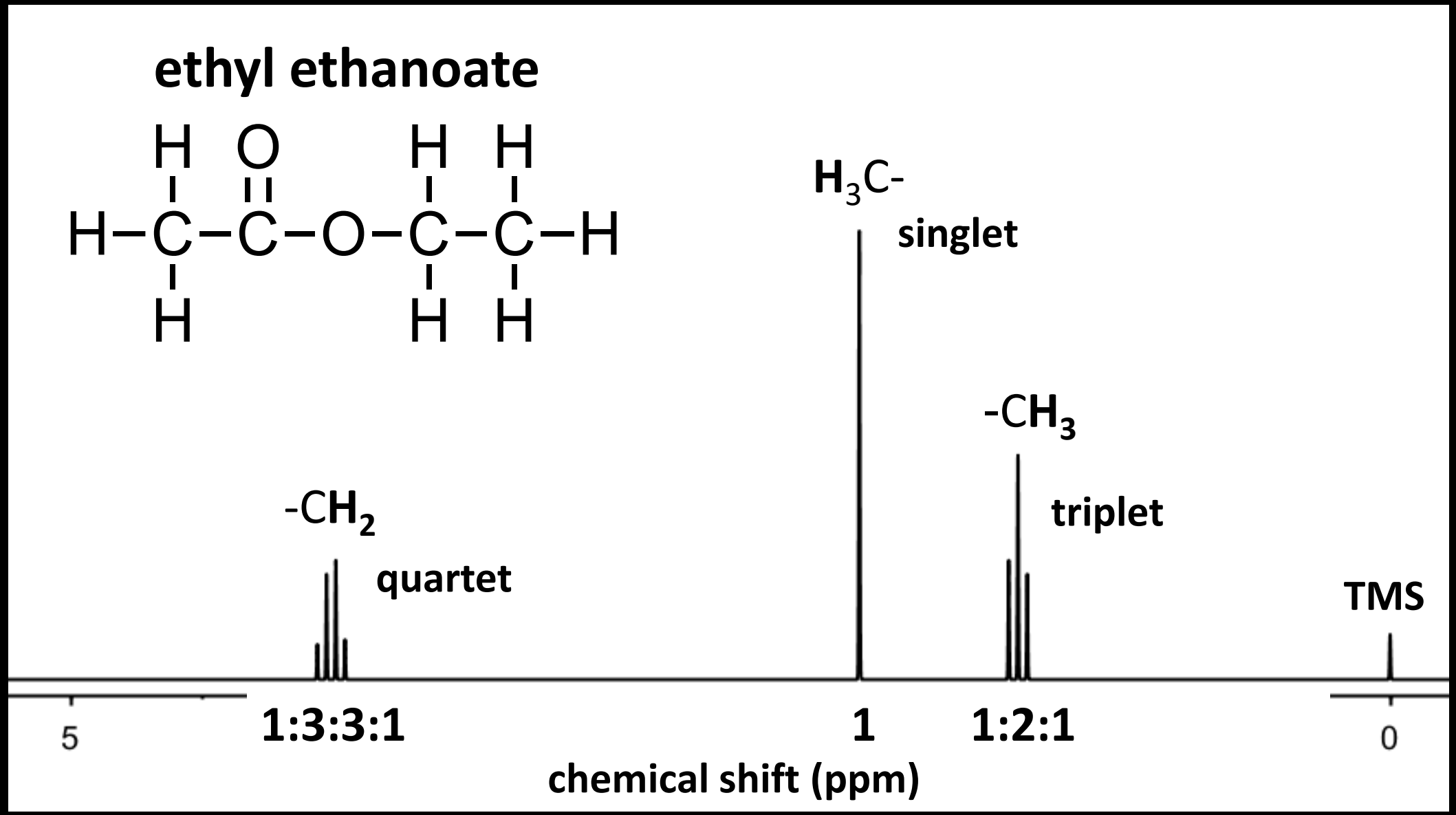
^{1}H NMR



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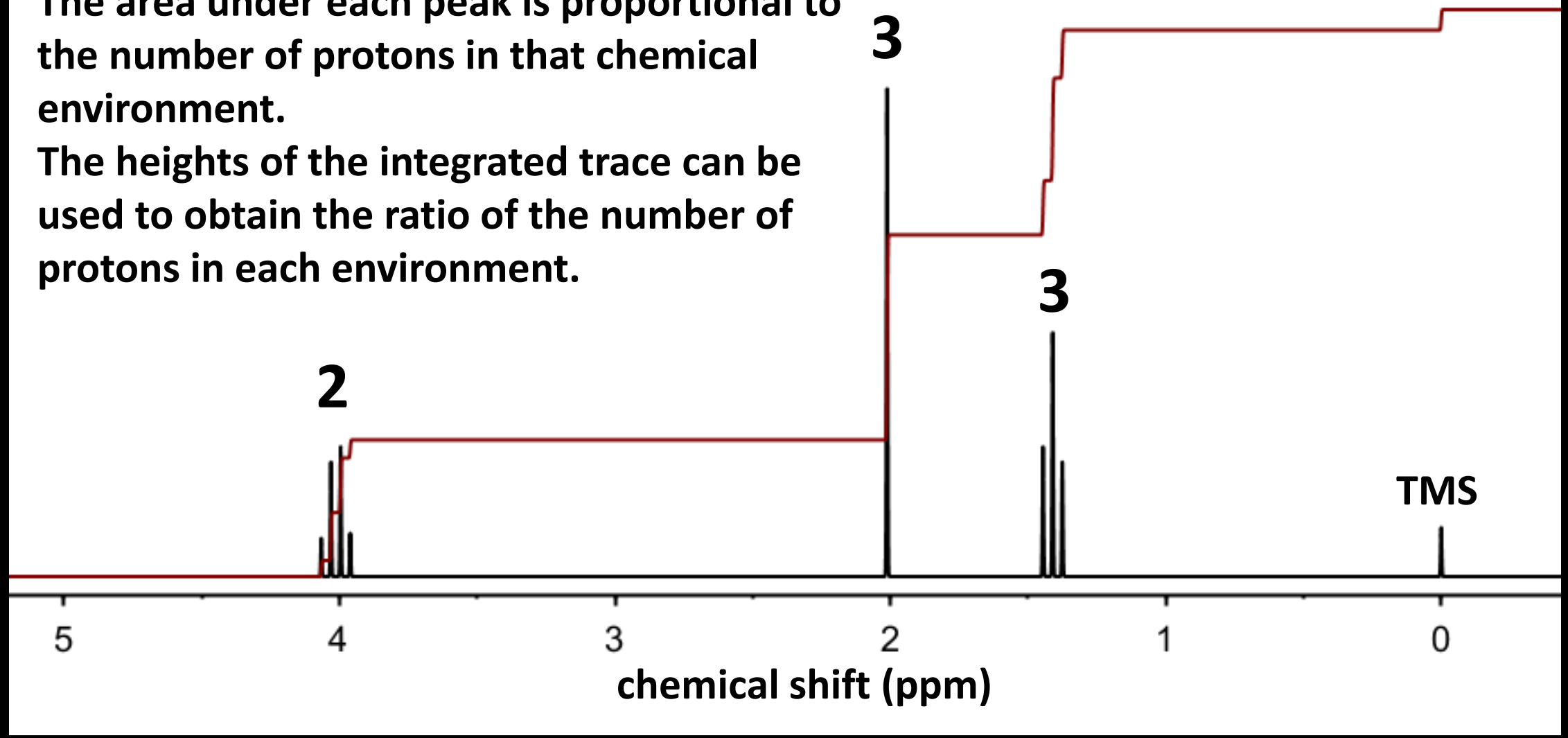
^{1}H NMR

The area under each peak is proportional to the number of protons in that chemical environment.

The heights of the integrated trace can be used to obtain the ratio of the number of protons in each environment.



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Determining the structure of a compound using analytical techniques

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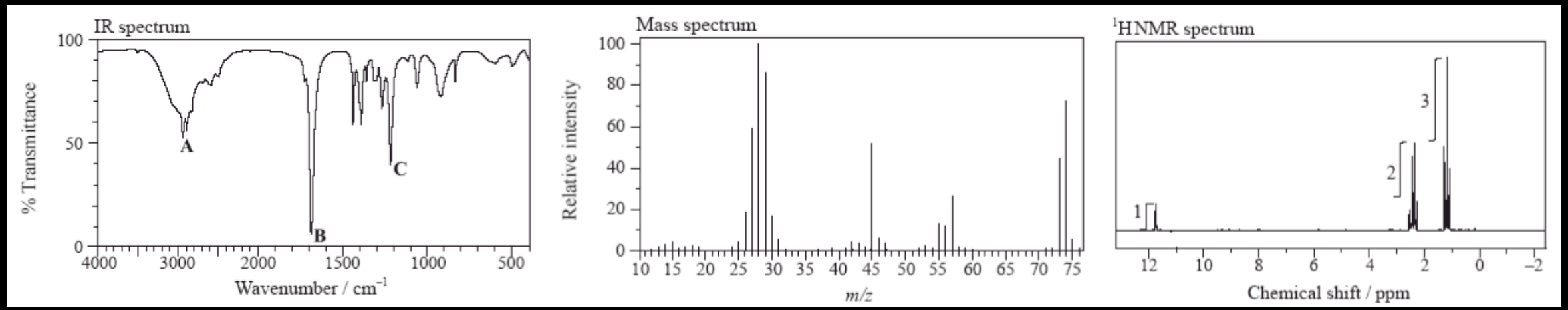
Analytic techniques

The determination of the structure of an unknown compound usually involves combining the information from different analytical techniques.

Deduce the structure of an unknown compound, X, which has the molecular formula $C_3H_6O_2$.



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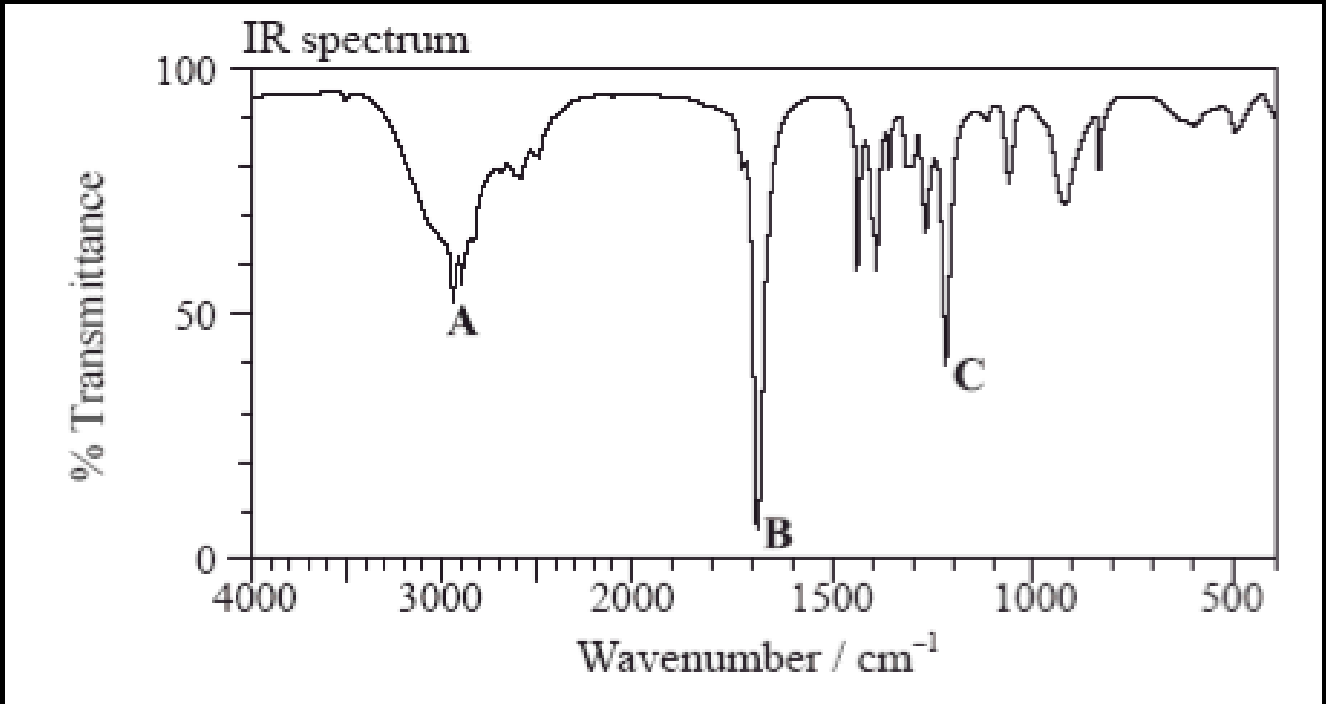
IR spectroscopy



26. Infrared data

Characteristic ranges for infrared absorption due to stretching vibrations in organic molecules.

Bond	Organic molecules	Wavenumber (cm^{-1})	Intensity
C–I	iodoalkanes	490–620	strong
C–Br	bromoalkanes	500–600	strong
C–Cl	chloroalkanes	600–800	strong
C–F	fluoroalkanes	1000–1400	strong
C–O	alcohols, esters, ethers	1050–1410	strong
C=C	alkenes	1620–1680	medium-weak; multiple bands
C=O	aldehydes, ketones, carboxylic acids and esters	1700–1750	strong
C≡C	alkynes	2100–2260	variable
O–H	carboxylic acids (with hydrogen bonding)	2500–3000	strong, very broad
C–H	alkanes, alkenes, arenes	2850–3090	strong
O–H	alcohols and phenols (with hydrogen bonding)	3200–3600	strong, broad
N–H	primary amines	3300–3500	medium, two bands

Peak A: O-H carboxylic acids (with hydrogen bonding)

Peak B: C=O aldehydes, ketones, carboxylic acids, esters

Peak C: C-O alcohols, esters, ethers

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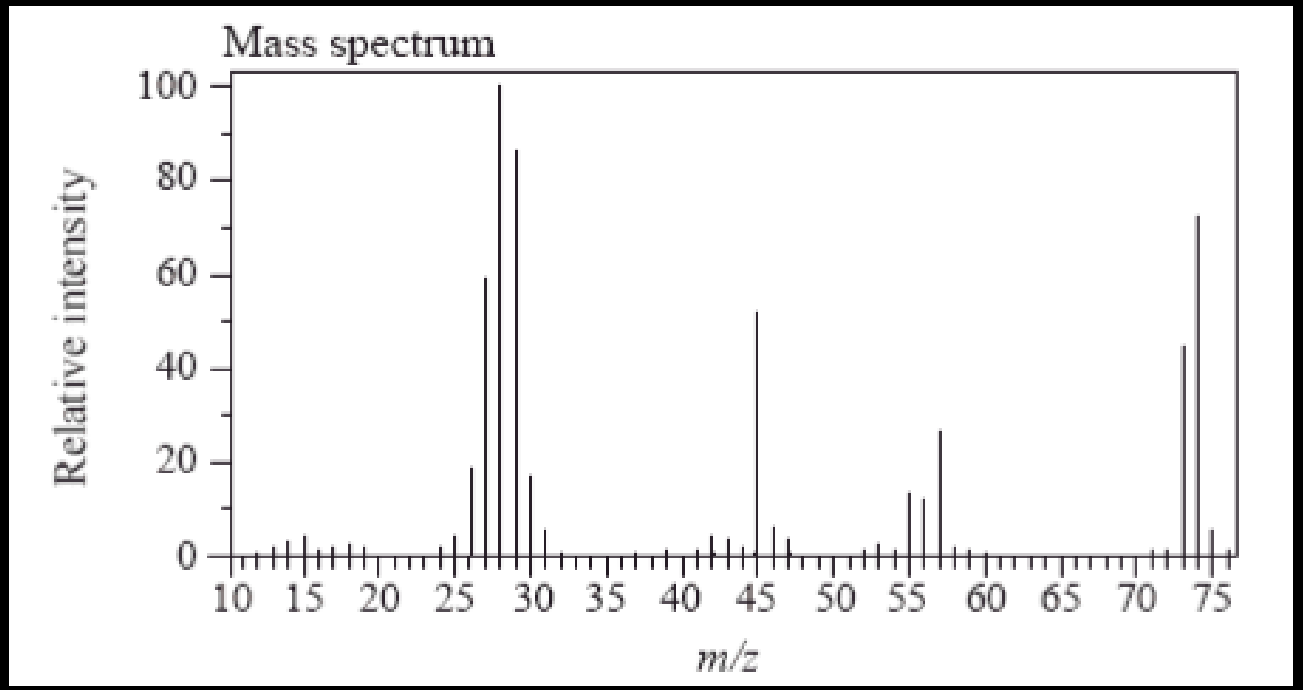
Mass spectrometry



28. Mass spectral fragments lost

Mass lost	Fragment lost
15	CH_3
17	OH
18	H_2O
28	$CH_2{=}CH_2$, C=O
29	CH_3CH_2, CHO
31	CH_3O
45	COOH

m/z = 74: $C_2H_5COOH^+$ (mass of molecular ion)

m/z = 45: $COOH^+$ (loss of CH_3CH_2)

m/z = 29: $C_2H_5^+$ (loss of COOH)

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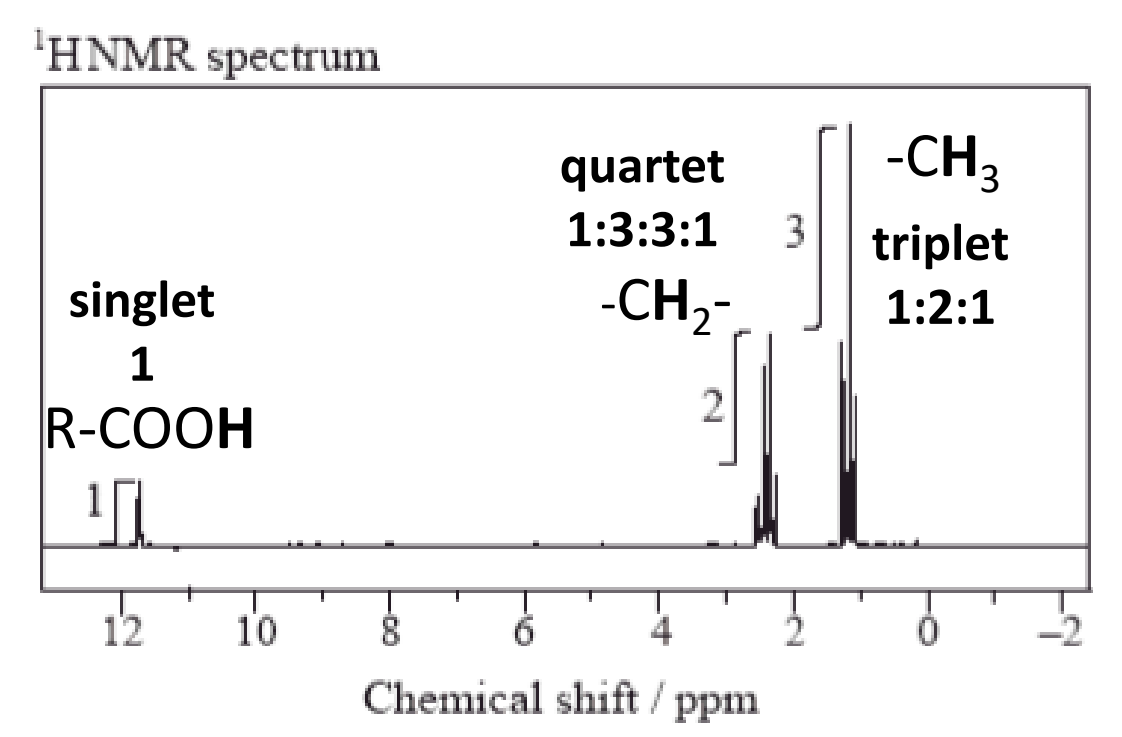
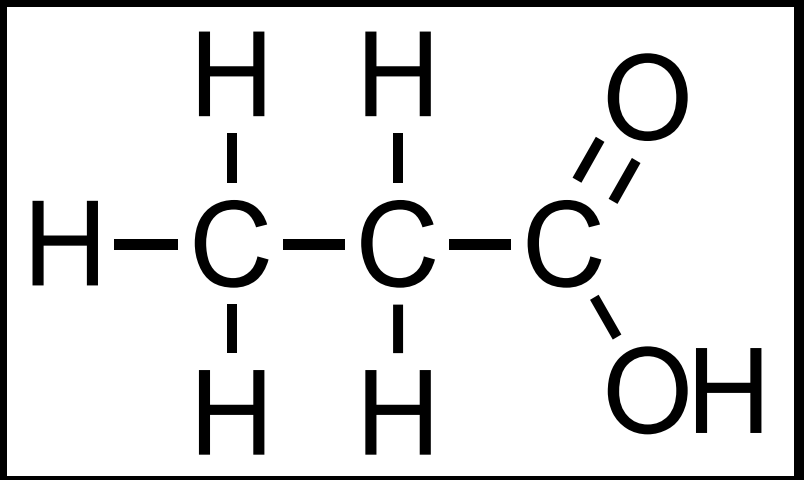
^{1}H NMR spectroscopy



27. ^{1}H NMR data

Type of proton	Chemical shift (ppm)
-CH$_3$	0.9-1.0
R-CH$_2$-CO-	2.0-2.9
-COOH	9.0-13.0



Three main clusters of peaks shows there are three different chemical environments that contain protons.

Ratio of protons = 1:2:3