

Exercise walk-through

37.4

Proton (^1H) NMR spectroscopy

A-Level Chemistry

NMR basics

carbon-13 NMR

each carbon **environment** gives one peak

proton NMR

chemical shift &
peak areas give the proton ratio

NMR

studies nuclei in a strong magnetic field; the number of peaks = the number of environments.

Splitting and the $n + 1$ rule



singlet

$$n = 0$$



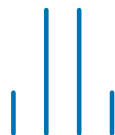
doublet

$$n = 1$$



triplet

$$n = 2$$



quartet

$$n = 3$$

n equivalent neighbours split a peak into $n + 1$ lines

Splitting : n equivalent neighbouring protons split a peak into $n + 1$ lines.

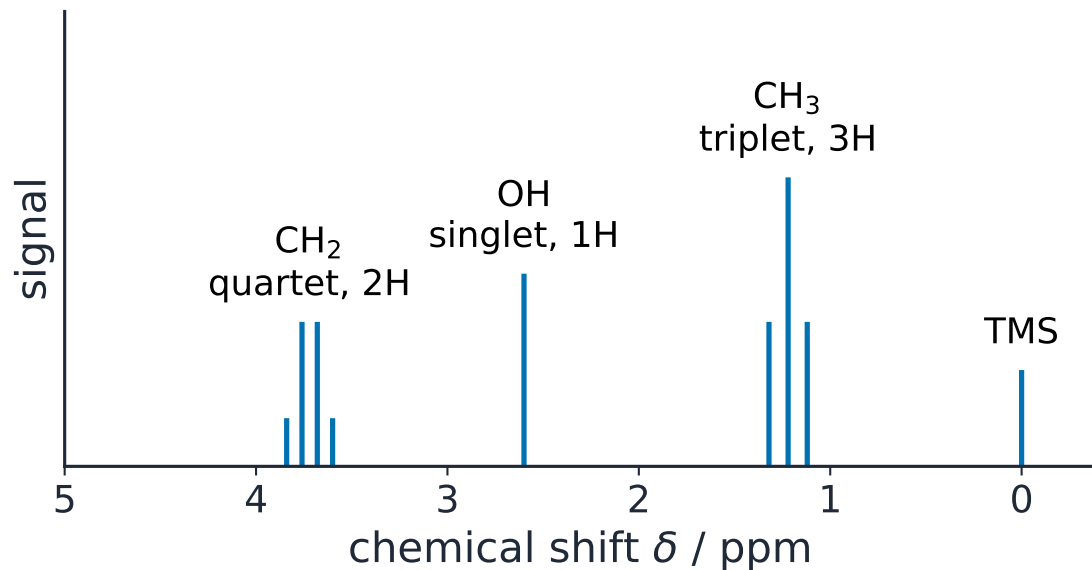
- $0 \rightarrow$ **singlet** ; $1 \rightarrow$ doublet
- $2 \rightarrow$ triplet; $3 \rightarrow$ quartet

A proton NMR spectrum

Ethanol: a CH_3 triplet, a CH_2 quartet & an OH singlet (areas 3:2:1).

- **TMS** is the zero reference
- a **deuterated solvent** gives no signal
- D_2O removes the O–H/N–H peak

A proton NMR spectrum, in detail



$n+1$ rule · integration 3 : 2 : 1 · TMS = 0 ppm

Ethanol: a CH_3 triplet, a CH_2 quartet & an OH singlet (areas 3:2:1).

Practical points

- **tetramethylsilane** (TMS) is the standard, set at a chemical shift of 0.
- a **deuterated solvent** (such as CDCl_3) is used so that the solvent itself gives no proton signal.
- shaking the sample with D_2O makes the O–H and N–H peaks disappear (their hydrogen is swapped for deuterium), which identifies those protons.

Exercises 2.1-2.3

2.1 State what the relative **areas** of ^1H NMR peaks tell you. [1]

2.2 Using the $n + 1$ rule, state the splitting of a CH_3 next to a CH_2 . [1]

2.3 State why a deuterated solvent is used, and name the compound used as the $\delta = 0$ reference. [2]

Exercises 2.1-2.3

2.1 State what the relative **areas** of ^1H NMR peaks tell you. [1]

2.1

- the ratio of the numbers of protons in each environment
-

2.2 Using the $n + 1$ rule, state the splitting of a CH_3 next to a CH_2 . [1]

2.2

- a triplet ($n = 2$ neighbours
 - $2 + 1 = 3$ lines)
-

2.3 State why a deuterated solvent is used, and name the compound used as the $\delta = 0$ reference. [2]

2.3

- A deuterated solvent contains no ^1H , so it adds no signals of its own to the spectrum; the reference is tetramethylsilane, TMS

Exercises 2.4·2.5

2.4 Explain what happens to the spectrum of ethanol when a few drops of D_2O are added. [2]

2.5 Give the splitting pattern of the CH_2 signal in $\text{CH}_3\text{CH}_2\text{Br}$, with your reasoning. [2]

Exercises 2.4·2.5

2.4 Explain what happens to the spectrum of ethanol when a few drops of D_2O are added. [2]

2.4

- The $-\text{OH}$ peak disappears; the labile hydrogen is exchanged for deuterium, which does not appear in a ^1H spectrum

2.5 Give the splitting pattern of the CH_2 signal in $\text{CH}_3\text{CH}_2\text{Br}$, with your reasoning. [2]

2.5

- A quartet; the adjacent CH_3 has three protons, and $n + 1 = 4$

Exercises 3.1-3.2

3.1 A proton with **two** equivalent neighbours appears as a:

[1]

☐

A singlet

B doublet

C triplet

D quartet

3.2 Shaking a sample with D₂O causes a peak to **disappear**. This peak is due to: [1]

☐

A a CH₃ group

B an O-H or N-H proton

C a CH₂ group

D the TMS reference

Exercises 3.1·3.2

3.1 A proton with **two** equivalent neighbours appears as a:

[1]

☐

A singlet

B doublet

C triplet

D quartet

3.1 C

- Two equivalent neighbours give $2 + 1 = 3$ lines – a triplet

3.2 Shaking a sample with D₂O causes a peak to **disappear**. This peak is due to:

[1]

☐

A a CH₃ group

B an O–H or N–H proton

C a CH₂ group

D the TMS reference

3.2 B

- D₂O exchange removes the O–H / N–H peak

Exercise 3.3 (a)

3.3 The ^1H NMR spectrum of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, has three groups of peaks.

(a) Give the splitting pattern of the CH_3 and the CH_2 peaks, with reasons. [2]

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(a) Give the splitting pattern of the CH_3 and the CH_2 peaks, with reasons. [2]

(a)

- the CH_3 is a triplet (its 2 CH_2 neighbours give $2 + 1 = 3$); the CH_2 is a quartet (its 3 CH_3 neighbours give $3 + 1 = 4$)

Exercise 3.3 (b)

3.3 The ^1H NMR spectrum of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, has three groups of peaks.

(b) State the ratio of the peak areas.

[1]

Exercise 3.3 (b)

3.3 The ^1H NMR spectrum of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, has three groups of peaks.

(b) State the ratio of the peak areas.

[1]

(b)

- $\text{CH}_3 : \text{CH}_2 : \text{OH} = 3 : 2 : 1$

Exercise 3.4

3.4 A compound has two ^1H environments with area ratio 3:2; the larger peak is a triplet and the smaller a quartet. Deduce the two groups present and explain the splitting. [3]

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- the triplet (area 3) is a CH_3 with 2 neighbours, and the quartet (area 2) is a CH_2 with 3 neighbours; so the groups are CH_3 and CH_2 next to each other, i.e. an ethyl group; each splits the other by the $n + 1$ rule

Exercise 3.5 (a)

3.5 Compound X has the molecular formula $\text{C}_4\text{H}_8\text{O}_2$. Its proton NMR spectrum shows four signals.

δ	relative area	splitting
4.1	2	quartet
2.0	3	singlet
1.3	3	triplet

(a) State what the number of signals tells you about compound X.

[1]

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(a)

- X has three chemical environments for its protons – one for each signal

Exercise 3.5 (b)

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(b) Explain what the relative areas represent, and give the total number of hydrogen atoms they account for. [2]

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(b) Explain what the relative areas represent, and give the total number of hydrogen atoms they account for. [2]

(b)

- The areas are in the ratio of the numbers of protons in each environment; $2 + 3 + 3 = 8$ hydrogen atoms, which matches $\text{C}_4\text{H}_8\text{O}_2$

Exercise 3.5 (c)

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(c) Use the splitting patterns to deduce which groups are adjacent to each other. [3]

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- The quartet at δ 4.1 has three neighbours, so it is a CH_2 next to a CH_3 ; the triplet at δ 1.3 has two neighbours, so it is that CH_3 next to the CH_2 ; the singlet at δ 2.0 has no neighbours, so its CH_3 is attached to a carbon carrying no hydrogens, the $\text{C} = \text{O}$

Exercise 3.5 (d)

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(d) Deduce the structure of X and name it.

[3]

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[3]

(d)

- The δ 4.1 shift shows the CH_2 is attached to oxygen; so X is $\text{CH}_3\text{COOCH}_2\text{CH}_3$, ethyl ethanoate

Exercise 3.5 (e)

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(e) A different compound Y, also $\text{C}_4\text{H}_8\text{O}_2$, gives a broad singlet at δ 11.4 that disappears when D_2O is added. Identify the group responsible and explain why the peak disappears.

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(e)

- A carboxylic acid $-\text{OH}$; the labile proton exchanges rapidly with deuterium from the D_2O , and deuterium gives no signal in a proton NMR spectrum, so the peak vanishes