37.4 Proton (1H) NMR spectroscopy

Name: _____ Class: _____ Date: _____ **Total: 28 marks**

KEY WORDS splitting • tetramethylsilane • chemical shift • chemical environment • proton

Objective

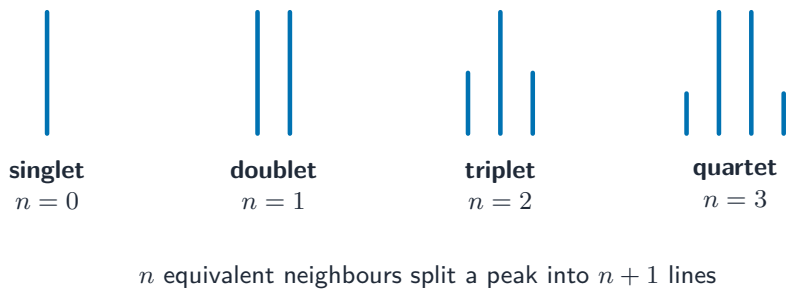
Build the skills to answer exam questions on **proton (^{1}H) NMR** – chemical environments, peak **area** ratios, **splitting** by the $n + 1$ rule, and the use of TMS and D_2O.

You must be able to:

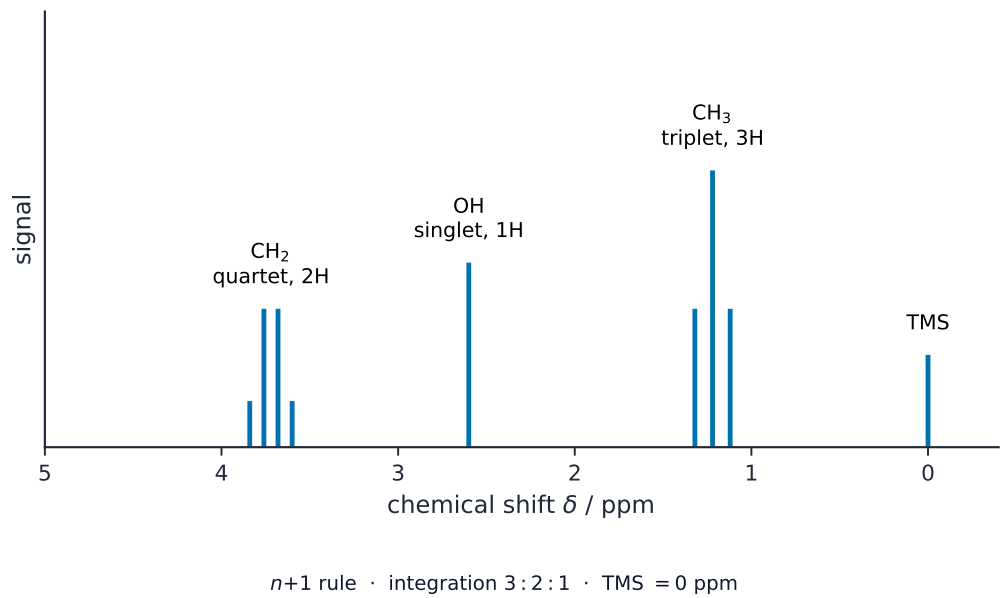
- count proton environments and use area ratios
- apply the $n + 1$ rule to predict splitting patterns
- explain the roles of TMS, a deuterated solvent and D_2O

1 Key knowledge and worked examples

Splitting and areas



The $n + 1$ rule: n equivalent neighbouring protons split a peak into $n + 1$ lines



Ethanol: three environments give a CH_3 triplet, a CH_2 quartet and an OH singlet, areas in ratio 3:2:1

- **number of peaks** = number of proton environments; **area ratio** = ratio of protons.
- $n + 1$ **rule:** n equivalent neighbours → $n + 1$ lines (0→singlet, 1→doublet, 2→triplet, 3→quartet).
- **TMS** sets the shift = 0; a **deuterated solvent** ($CDCl_3$) gives no signal; shaking with $\mathbf{D_2O}$ removes O–H/N–H peaks.

■ Reading a proton NMR spectrum, in four passes

Work through the spectrum in this order; each pass answers a different question and each carries its own marks.

1. **Number of signals = number of chemical environments.** Protons are equivalent if swapping them leaves the molecule identical. Ethanol, CH_3CH_2OH, has three environments, so three signals.
2. **Area (integration) ratio = ratio of the numbers of protons.** Ethanol integrates 3 : 2 : 1.
3. **Chemical shift δ says which environment**, read off the data booklet. Roughly: CH_3 next to carbon 0.9; next to C = O 2.2; CH next to O 3.5; aromatic H 7.0; aldehyde H 9.5; carboxylic acid H 11.5.
4. **Splitting = the $n + 1$ rule.** A signal is split into $n + 1$ peaks by n protons on the **adjacent** carbon: 0 neighbours → singlet, 1 → doublet, 2 → triplet, 3 → quartet.

Two things the exam tests every session.

- **–OH and –NH protons do not split and are not split**, because they exchange rapidly. They give a broad singlet at a variable shift.

- **Adding D_2O makes that peak disappear**, because the labile H is exchanged for D, which does not appear in a ^1H spectrum. That is how an –OH or –NH is identified, and it is a favourite one-mark question.

Worked example. A compound $C_3H_6O_2$ gives three signals: δ 11.5 (1H, singlet, lost on shaking with D_2O), δ 2.4 (2H, quartet), δ 1.1 (3H, triplet). Deduce its structure.

1. The δ 11.5 singlet lost with D_2O is a carboxylic acid –OH.
2. The 3H triplet at δ 1.1 is a CH_3 with two neighbours, so CH_3CH_2–.
3. The 2H quartet at δ 2.4 is that CH_2, with three neighbours, next to the C = O.
4. Assembling: CH_3CH_2COOH, propanoic acid, which matches $C_3H_6O_2$.

The solvent is usually $CDCl_3$ or another deuterated solvent, chosen because it contains **no ^{1}H** and so adds no signals of its own. **TMS** is the reference at $\delta = 0$: inert, volatile, and its twelve equivalent protons give one strong sharp peak away from everything else.

2 Practice

2.1 State what the relative **areas** of ^{1}H 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]

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 CH_3CH_2Br, with your reasoning. [2]

3 Exam-style questions

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 D_2O causes a peak to **disappear**. This peak is due to: [1]

- ☐ **A** a CH_3 group
- **B** an O–H or N–H proton
- **C** a CH_2 group
- **D** the TMS reference

3.3 The ^1H NMR spectrum of ethanol, CH_3CH_2OH, has three groups of peaks.

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

(b) State the ratio of the peak areas. [1]

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]

3.5 Compound X has the molecular formula $C_4H_8O_2$. 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]

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

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

(d) Deduce the structure of X and name it. [3]

(e) A different compound Y, also $C_4H_8O_2$, 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. [3]

Solutions

Each answer shows the steps, then the **result**.

2.1

- the ratio of the numbers of protons in each environment

2.2

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

2.3

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

2.4

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

2.5

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

3.1 C

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

3.2 B

- D_2O exchange removes the O–H / N–H peak

3.3

(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 $3 + 1 = 4$)

(b)

- $CH_3 : CH_2 : OH = 3 : 2 : 1$

3.4

- 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

3.5

(a)

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

(b)

- The areas are in the ratio of the numbers of protons in each environment; $2+3+3=8$ hydrogen atoms, which matches $C_4H_8O_2$

(c)

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

(d)

- The $\delta\,4.1$ shift shows the CH_2 is attached to oxygen; so X is $CH_3COOCH_2CH_3$, ethyl ethanoate

(e)

- A carboxylic acid –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