A-LEVEL CHEMISTRY • EXERCISE SHEET

37.4 Proton (1H) NMR spectroscopy

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

KEY WORDS splitting 裂分 • tetramethylsilane 四甲基硅烷 • chemical shift 化学位移 • chemical environment 化学环境 • proton 质子

Objective

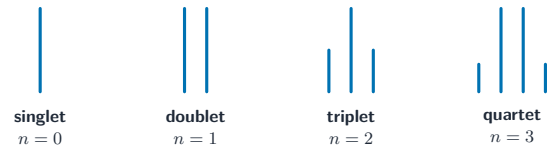
Build the skills to answer exam questions on **proton (^{1}H) NMR** 质子核磁共振 — chemical environments, peak **area** ratios, **splitting** 裂分 by the $n+1$ rule, and the use of TMS and D_2O.

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

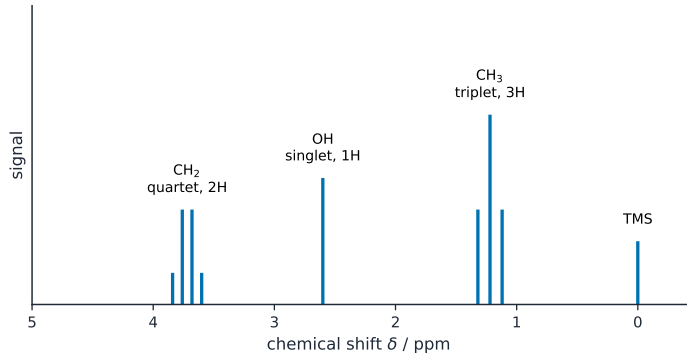
1 Worked examples

Splitting and areas



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

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



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

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 **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 ^{1}H 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 ^{1}H 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 ^{1}H 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 $\delta\,11.4$ that disappears when D_2O is added. Identify the group responsible and explain why the peak disappears. [3]

Solutions

2.1 the ratio of the numbers of protons in each environment.

2.2 a triplet ($n = 2$ neighbours $\rightarrow 2 + 1 = 3$ 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.