

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 (^1H) 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

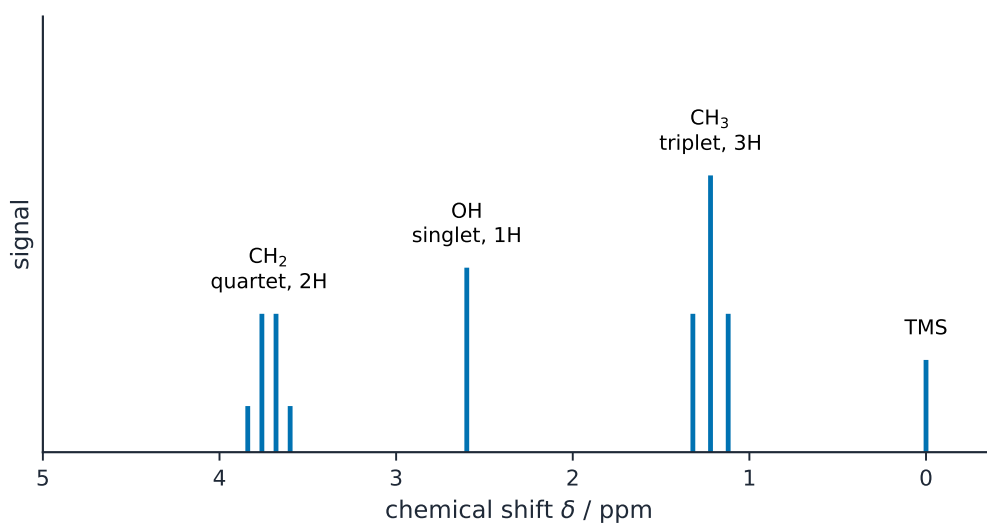
1 Worked examples

■ 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 $\rightarrow n + 1$ lines (0 $\rightarrow$ singlet, 1 $\rightarrow$ doublet, 2 $\rightarrow$ triplet, 3 $\rightarrow$ 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, $\text{CH}_3\text{CH}_2\text{OH}$, 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 $\text{C}=\text{O}$ 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 $\rightarrow$ singlet, 1 $\rightarrow$ doublet, 2 $\rightarrow$ triplet, 3 $\rightarrow$ 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 D₂O 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 C₃H₆O₂ gives three signals: δ 11.5 (1H, singlet, lost on shaking with D₂O), δ 2.4 (2H, quartet), δ 1.1 (3H, triplet). Deduce its structure.

1. The δ 11.5 singlet lost with D₂O is a carboxylic acid –OH.
2. The 3H triplet at δ 1.1 is a CH₃ with two neighbours, so CH₃CH₂–.
3. The 2H quartet at δ 2.4 is that CH₂, with three neighbours, next to the C = O.
4. Assembling: CH₃CH₂COOH, propanoic acid, which matches C₃H₆O₂.

The solvent is usually CDCl₃ or another deuterated solvent, chosen because it contains **no** ¹H 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 ¹H NMR peaks tell you. [1]

2.2 Using the $n + 1$ rule, state the splitting of a CH₃ next to a CH₂. [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 D₂O are added. [2]

2.5 Give the splitting pattern of the CH₂ signal in CH₃CH₂Br, with your reasoning. [2]

3 Exam-style questions

3.1 A proton with **two** equivalent neighbours appears as a: [1]

A	B
C	D

- 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	B
C	D

- A** a CH₃ group
B an O–H or N–H proton
C a CH₂ group
D the TMS reference

3.3 The ¹H NMR spectrum of ethanol, CH₃CH₂OH, has three groups of peaks.

(a) Give the splitting pattern of the CH₃ and the CH₂ 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 C₄H₈O₂. 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 $\text{C}_4\text{H}_8\text{O}_2$, 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. [3]
