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ADDED TO AND IMPROVED BY MR WILSON

NMR SPECTROSCOPY

1H NMR SPECTROSCOPY

Метод **я́дерного магни́тного резона́нса** (**ЯМР**) основан на взаимодействии внешнего магнитного поля) основан на взаимодействии внешнего магнитного поля сядрами) основан на взаимодействии внешнего магнитного поля сядрами, имеющими магнитный момент, т. е. для ядер с ненулевым спином. К ним относятся ^{1}H, ^{13}C, ^{15}N,^{35}P и другие. Спектроскопия ЯМР на ядрах ^{1}H в настоящее время наиболее развита и получила название протонный магнитный резонанс (ПМР).

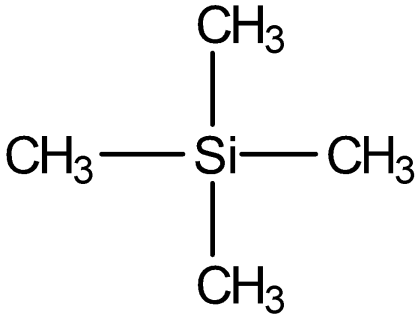
Ядролық магниттік резонанс (ЯМР) сыртқы магниттік өрістің магнитті моменті бар ядролармен өзара әрекетіне негізделген. Оларға ^{1}H, ^{13}C, ^{15}N,^{35}P және басқалар жатады. Ядросында ^{1}H бар спектроскопия қазір жақсы дамыған және ол протонды магнитті резонанс (ПМР) деп аталады.

Сабақтың мақсаты:
Ядролық магнитті резонанс әдісімен танысу
ЯМР қарапайым спектрлерімен танысу

Тілдік терминология
Ядролық магнитті резонанс
-magnetic nuclear resonance-
ядерно магнитный резонанс

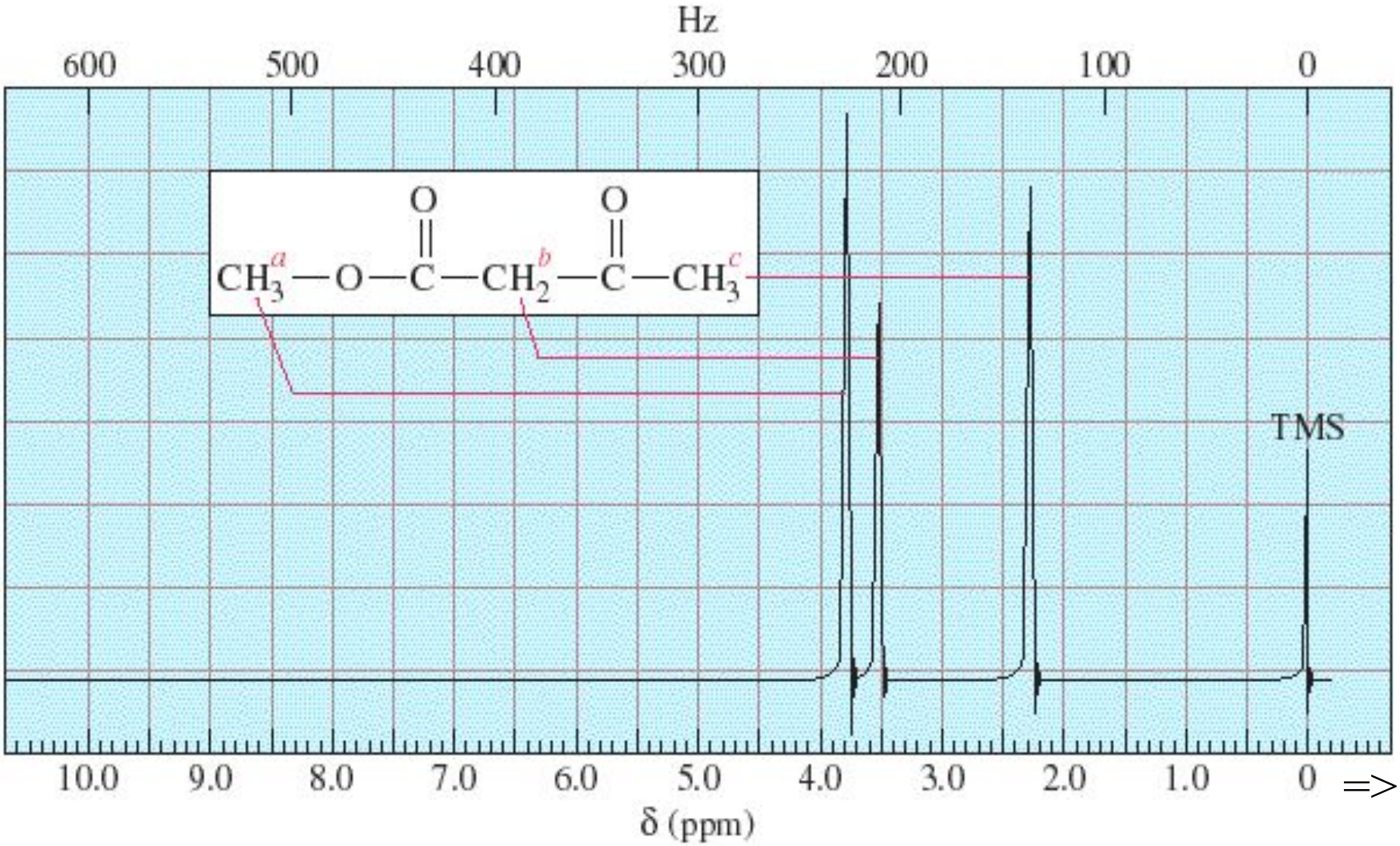
SOLVENTS & CALIBRATION

- Samples are dissolved in solvents free of ^{1}H atoms, e.g. CCl_4, $CDCl_3$.
- A small amount of TMS (tetramethylsilane) is added to calibrate the spectrum.



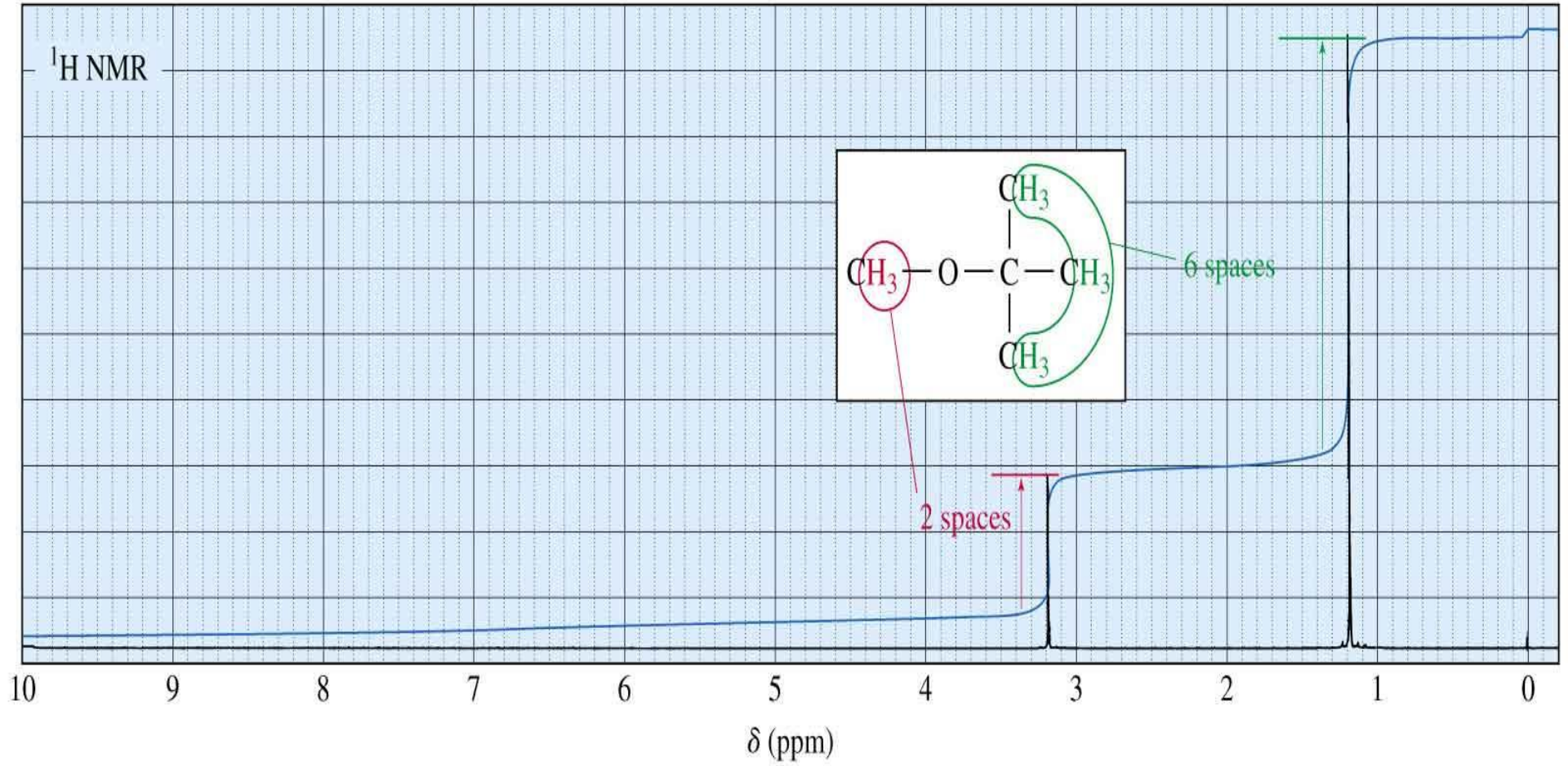
- It is used because:
  - its signal is away from all the others
  - it only gives one signal
  - it is non-toxic
  - it is inert
  - it has a low boiling point so is easy to remove

No. of Signals = No. of Environments



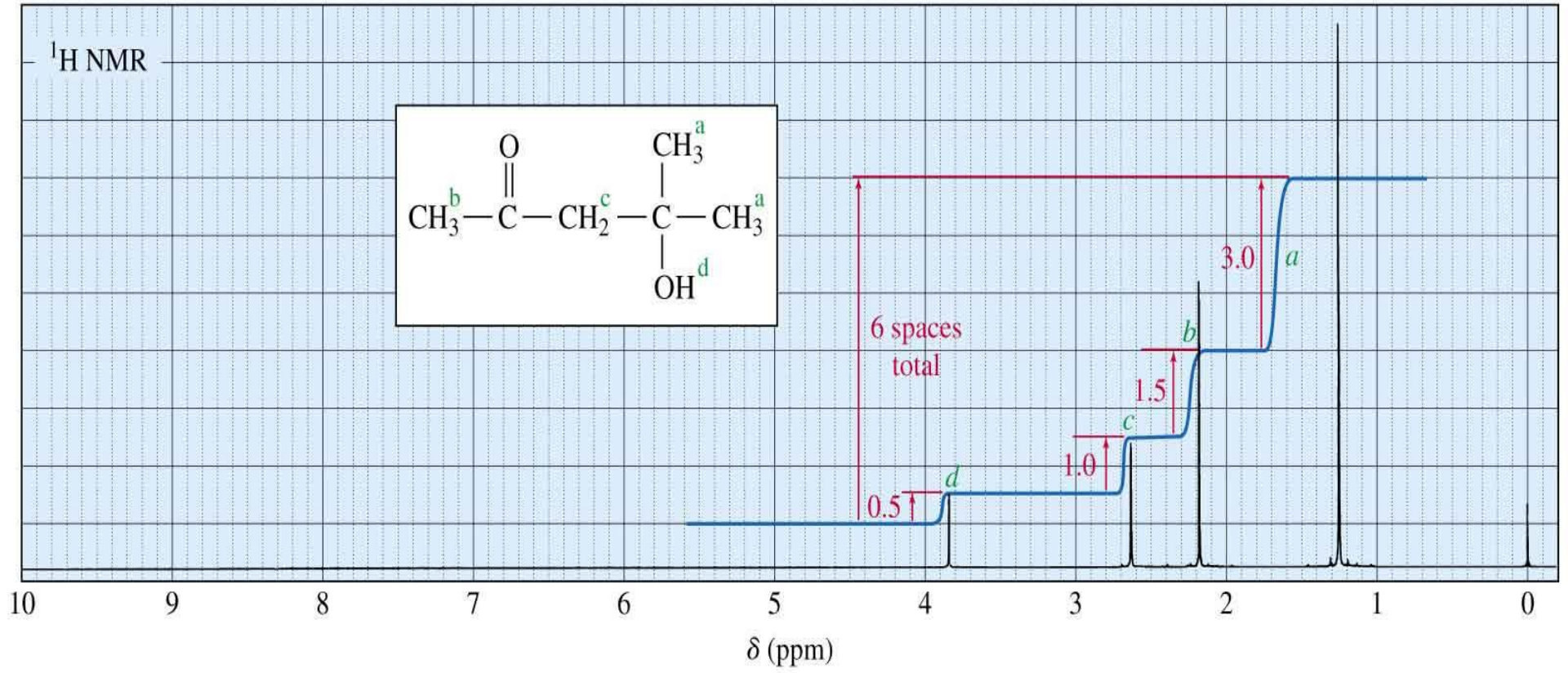
Intensity of Signals ∝ Number of H

- The area under each peak is proportional to the number of protons.
- Площадь под каждым пиком пропорциональна числу протонов
- Shown by integral trace. Показанный на интегральной кривой.



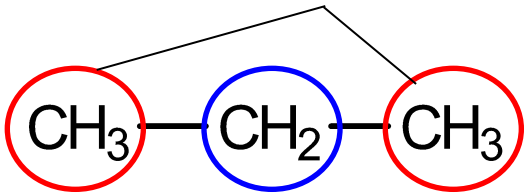
How Many Hydrogens?

When the molecular formula is known, each integral rise can be assigned to a particular number of hydrogens.

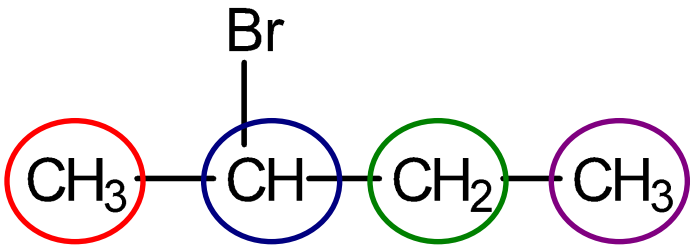


EQUIVALENT H's

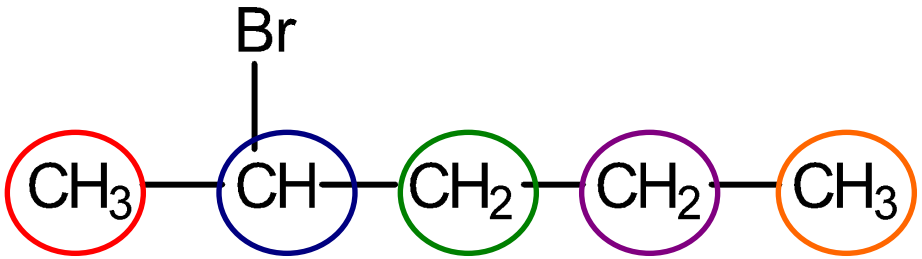
- In a spectrum, there is one signal for each set of equivalent H atoms. В спектре , есть один сигнал для каждого набора эквивалентных атомов H .
- The intensity of each signal being proportional to the number of equivalent H atoms it represents.
- Интенсивность каждого сигнала пропорциональна количеству эквивалентных атомов H он представляет.



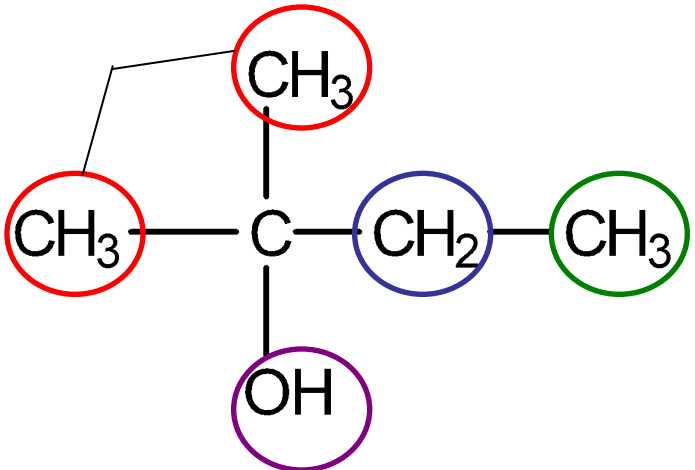
2 sets of equivalent H's: ratio 6:2 (3:1)



4 sets of equivalent H's: ratio 3:1:2:3



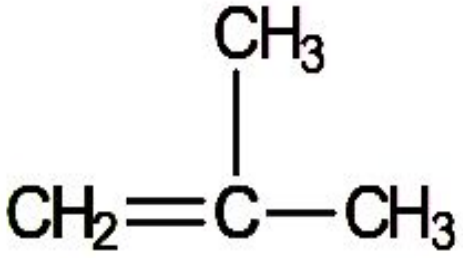
5 sets of equivalent H's: ratio 3:1:2:2:3



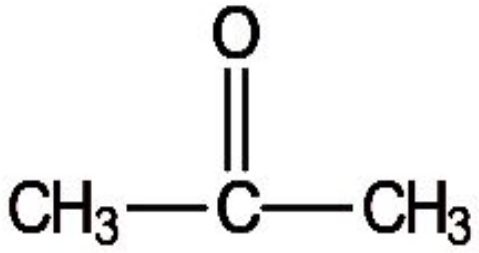
4 sets of equivalent H's: ratio 6:1:2:3

For each of the following compounds, predict the number of signals and the relative intensity of the signals.

a) methylpropene
b) propene
c) 2-chloropropane
d) propanone
e) methylamine
f) ethyl propanoate
g) 1,2-dibromopropane
h) dimethylethyl propanoate
i) but-2-ene



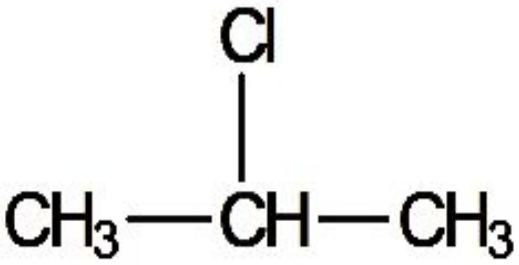
methylpropene



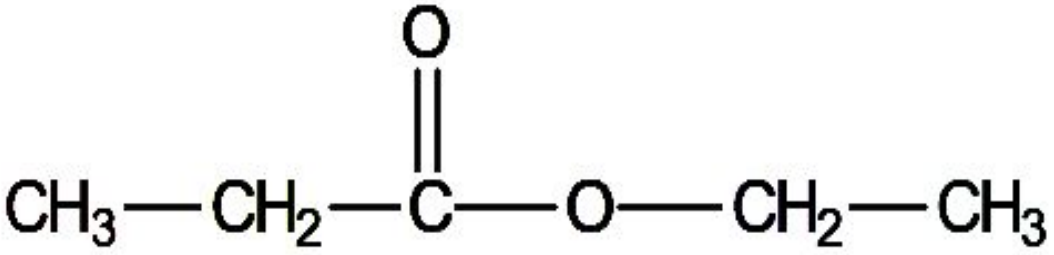
propanone

propene

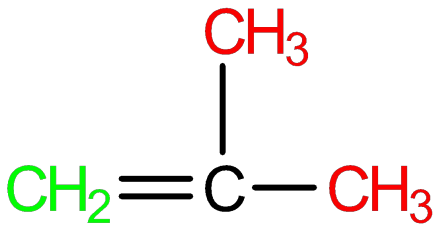
methylamine



2-chloropropane



ethyl propanoate

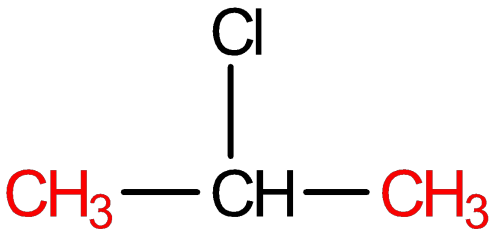


2 signals: ratio 6:2 (3:1)

methylpropene

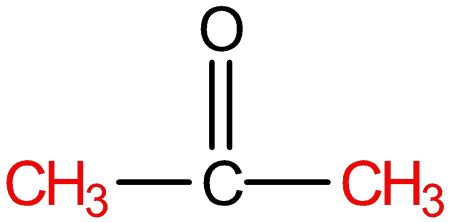
3 signals: ratio 2:1:3

propene



2 signals: ratio 6:1

2-chloropropane

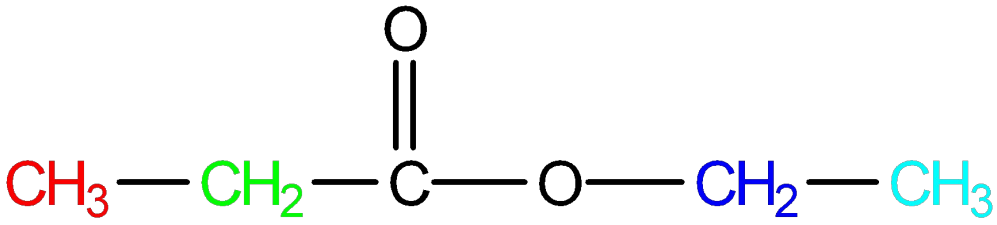


1 signal

propanone

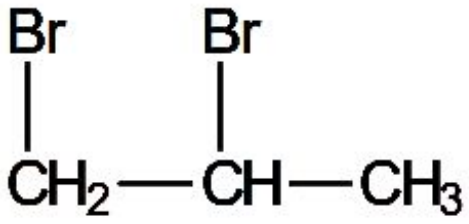
2 signals: ratio 3:2

methylamine

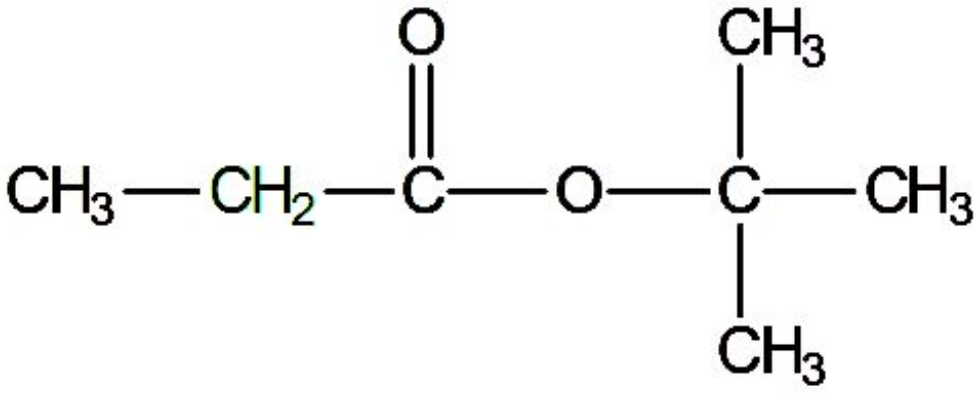


4 signals: ratio 3:2:2:3

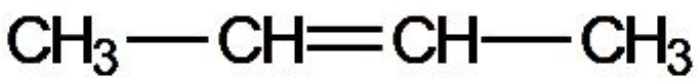
ethyl propanoate



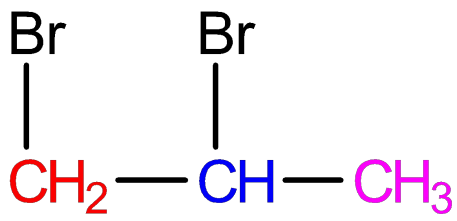
1,2-dibromopropane



dimethylethyl propanoate

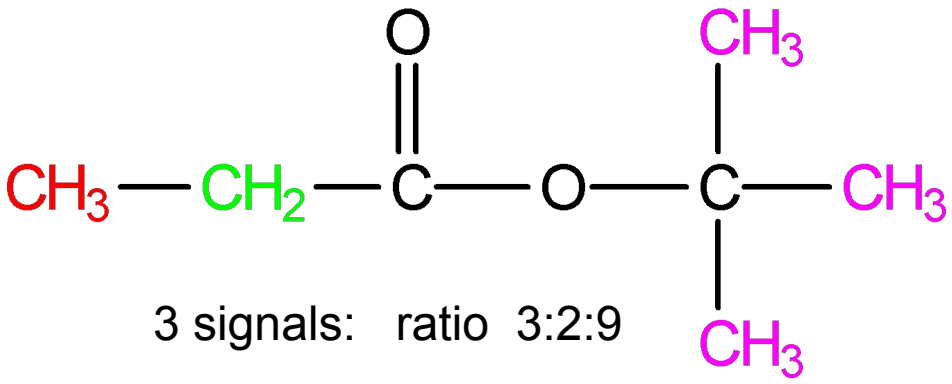


but-2-ene



3 signals: ratio 2:1:3

1,2-dibromopropane



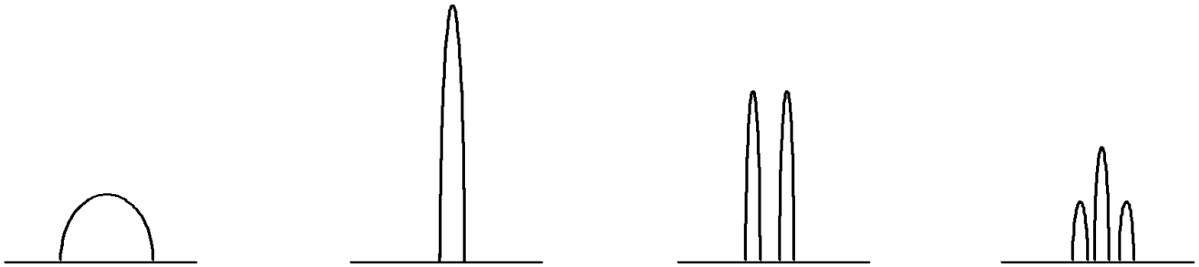
3 signals: ratio 3:2:9

dimethylethyl propanoate

2 signals: ratio 6:2 (3:1)

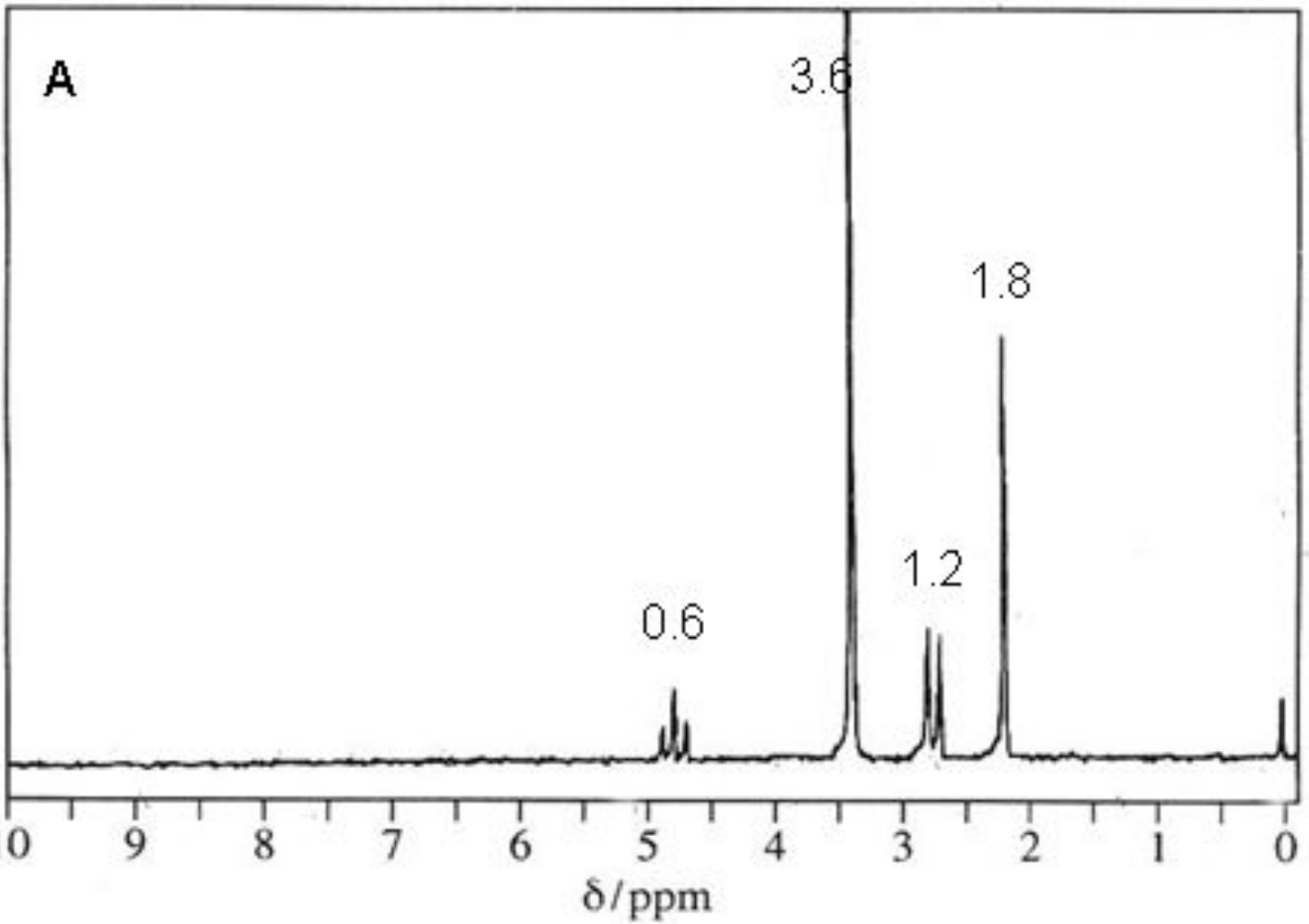
but-2-ene

RELATIVE INTENSITY

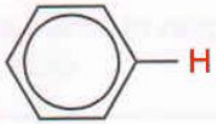
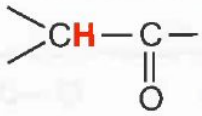
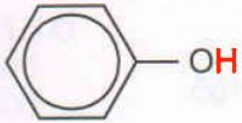


There are four signals here – each has the same area and so represents the same number of H atoms

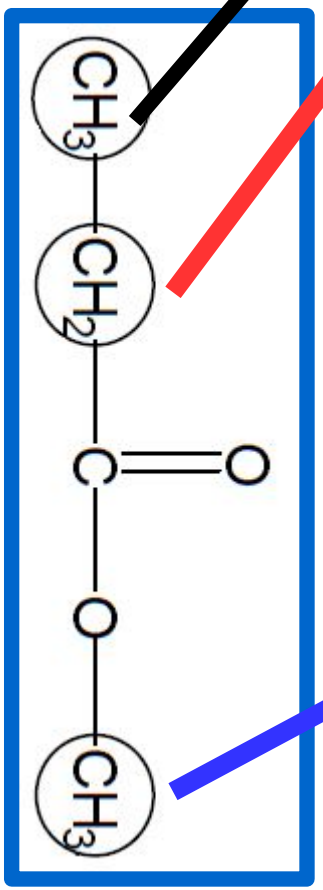
Integral given as number/ratio of H

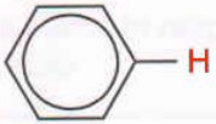
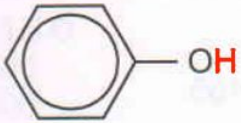


CHEMICAL SHIFT

type of proton	chemical shift, δ/ppm	type of proton	chemical shift, δ/ppm
CH_3—C	0.7–1.6		6.4–8.2
C—CH_2—C C—CH—C | C	1.4–2.3	—C—CHO	9.4–10.0
 carbonyls esters amides acids	2.0–2.7	—C—OH	0.5–4.5*
—CH—N amines amides	2.3–2.9		4.5–10.0*
	2.3–3.0	—C—NH	1.0–5.0*
—O—CH alcohols esters esthers	3.3–4.8	—CO—NH	5.0–12.0*
—CH—Cl or Br	3.0–4.2	—CO—OH	9.0–15.0*
—CH=CH—	4.5–6.0	*these signals are *very* variable (sometimes outside these limits) and often broad.	

What are the frequencies of these Hs?



type of proton	chemical shift, δ/ppm	type of proton	chemical shift, δ/ppm
CH_3—C	0.7–1.6		6.4–8.2
C—CH_2—C	1.4–2.3	—C—CHO	9.4–10.0
C—CH—C C			
CH—C(=O)— carbonyls, esters, amides, acids	2.0–2.7	—C—OH	0.5–4.5*
—CH—N amines, amides	2.3–2.9		4.5–10.0*
	2.3–3.0	—C—NH	1.0–5.0*
—O—CH alcohols, esters, esthers	3.3–4.8	—CO—NH	5.0–12.0*
—CH—Cl or Br	3.0–4.2	—CO—OH	9.0–15.0*
—CH=CH—	4.5–6.0	*these signals are *very* variable (sometimes outside these limits) and often broad.	

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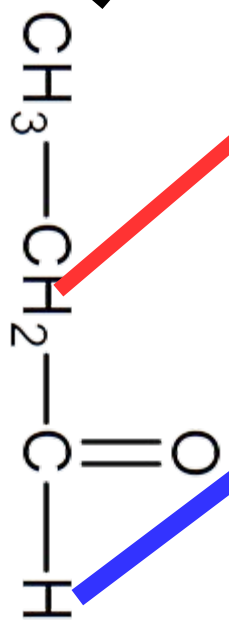
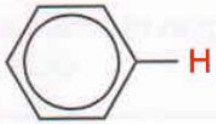
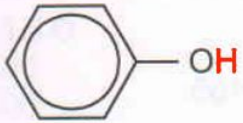
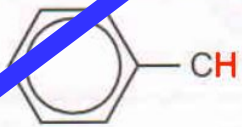


type of proton	chemical shift, δ/ppm	type of proton	chemical shift, δ/ppm
CH_3—C	0.7–1.6		6.4–8.2
C—CH_2—C	1.4–2.3	—C—CHO	9.4–10.0
C—CH—C			
C			
 carbonyls esters amides acids	2.0–2.7	—C—OH	0.5–4.5*
—CH—N amines amid	2.3–2.9		4.5–10.0*
	2.3–3.0	—C—NH	1.0–5.0*
—O—CH alcohols esters esthers	3.3–4.8	—CO—NH	5.0–12.0*
—CH—Cl or Br	3.0–4.2	—CO—OH	9.0–15.0*
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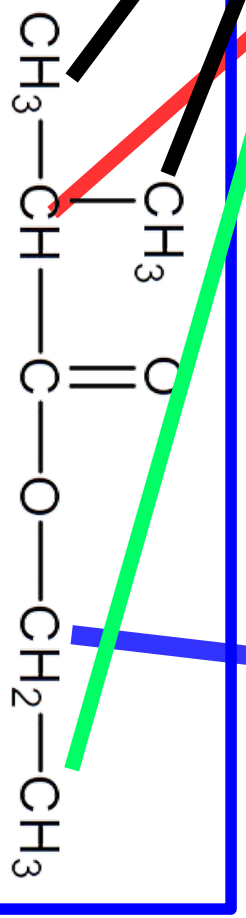
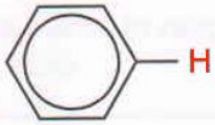
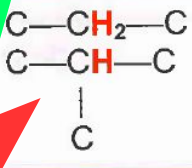
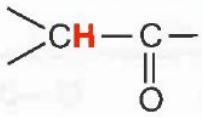
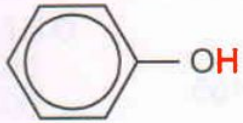
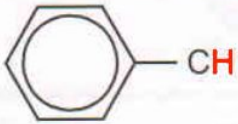
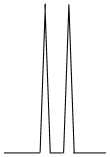


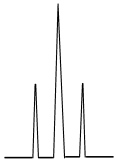
type of proton	chemical shift, δ/ppm	type of proton	chemical shift, δ/ppm
CH_3—C	0.7–1.6		6.4–8.2
	1.4–2.3	—C—CHO	9.4–10.0
 carbonyls esters amides acids	2.0–2.7	—C—OH	0.5–4.5*
—CH—N amines amides	2.3–2.9		4.5–10.0*
	2.3–3.0	—C—NH	1.0–5.0*
—O—CH alcohols esters esthers	3.3–4.8	—CO—NH	5.0–12.0*
—CH—Cl or Br	3.0–4.2	—CO—OH	9.0–15.0*
—CH=CH—	4.5–6.0	*these signals are *very* variable (sometimes outside these limits) and often broad.	

n+1

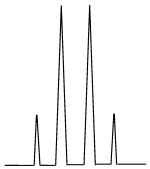
0 H next door
singlet (s)



1 H next door
doublet (d)

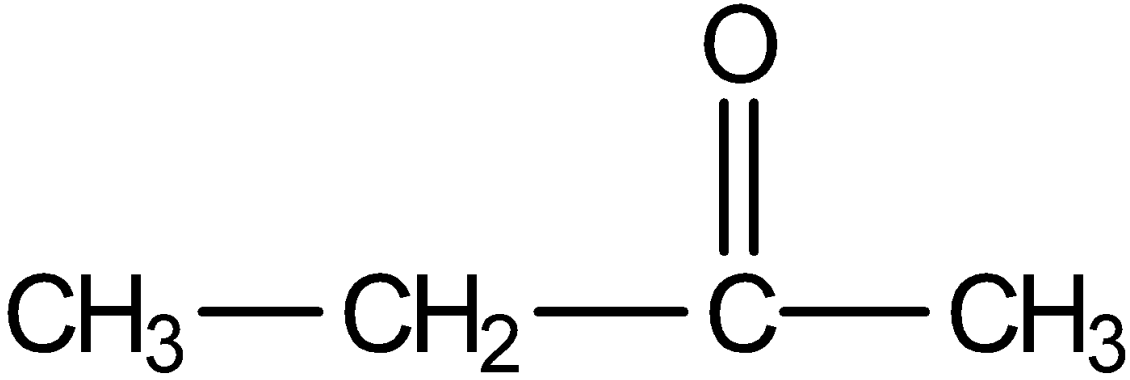


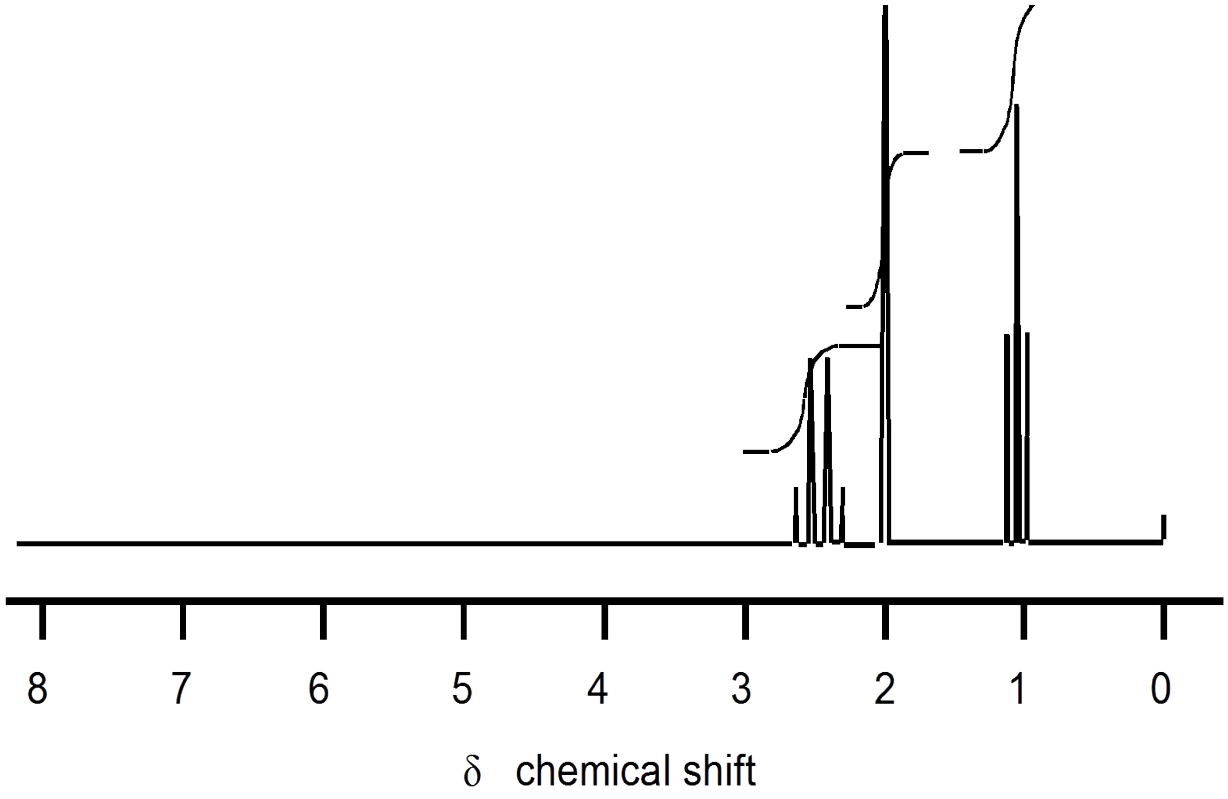
2 H next door
triplet (t)



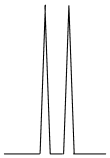
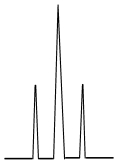
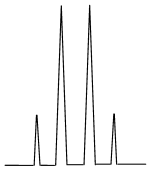
3 H next door
quartet (q)

more H next door
multiplet (m)

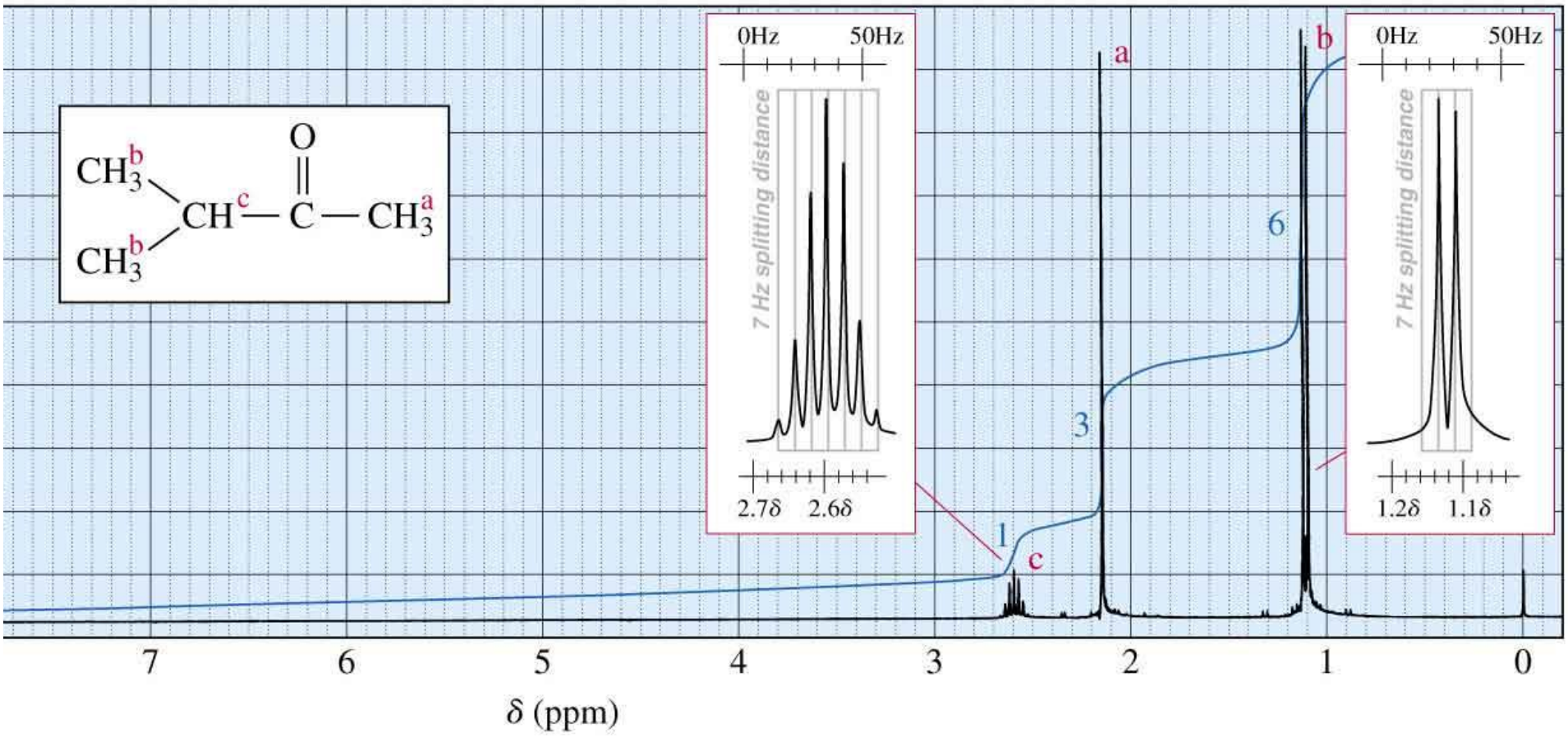




SPIN-SPIN COUPLING

signal	singlet	doublet	triplet	quartet
appearance				
number of lines	1	2	3	4
number of H's next door	0	1	2	3
relative size		1:1	1:2:1	1:3:3:1

Splitting for 3,methylpropan-2-one

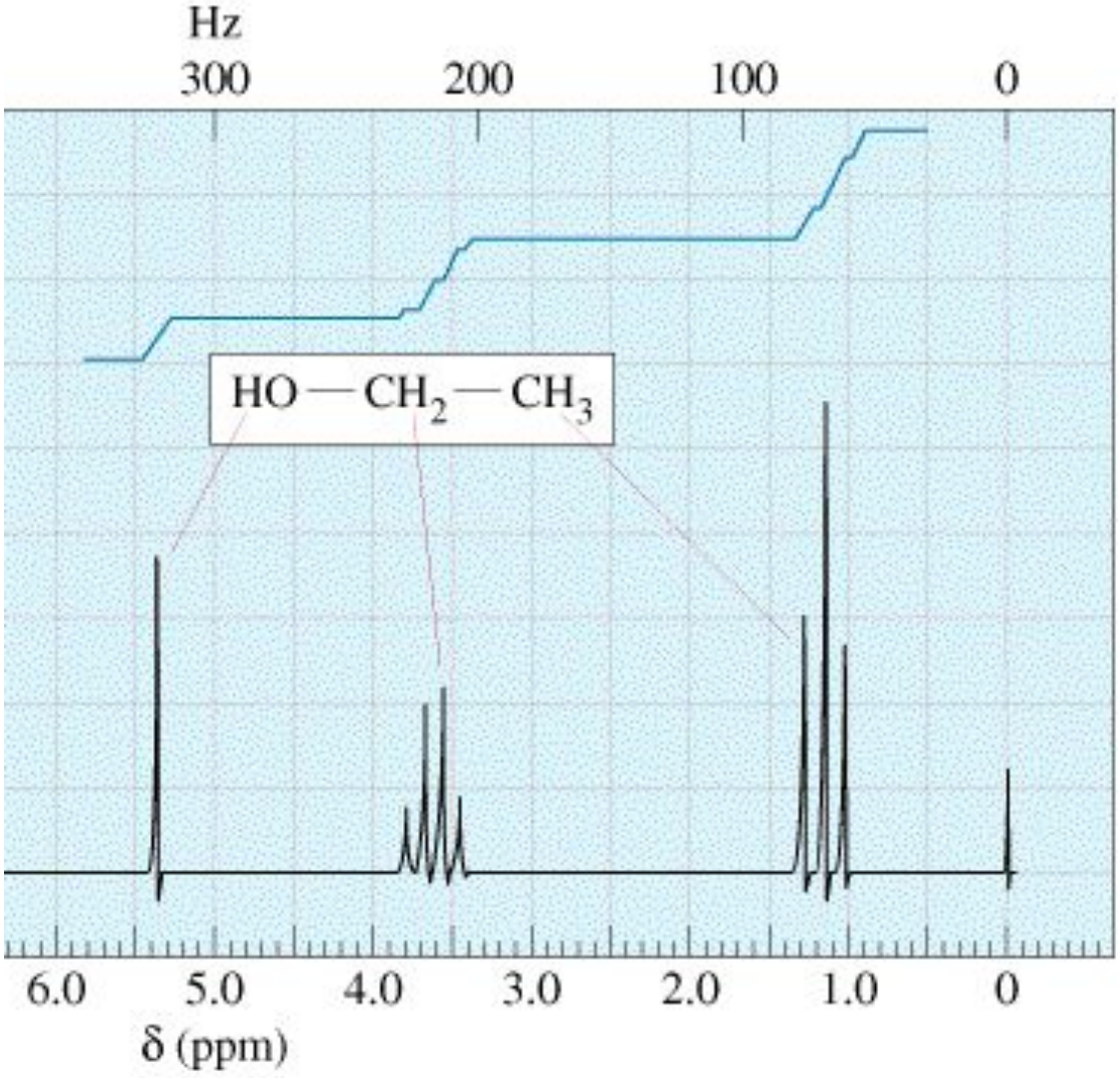


Number of H's next door +1

But you don't couple to

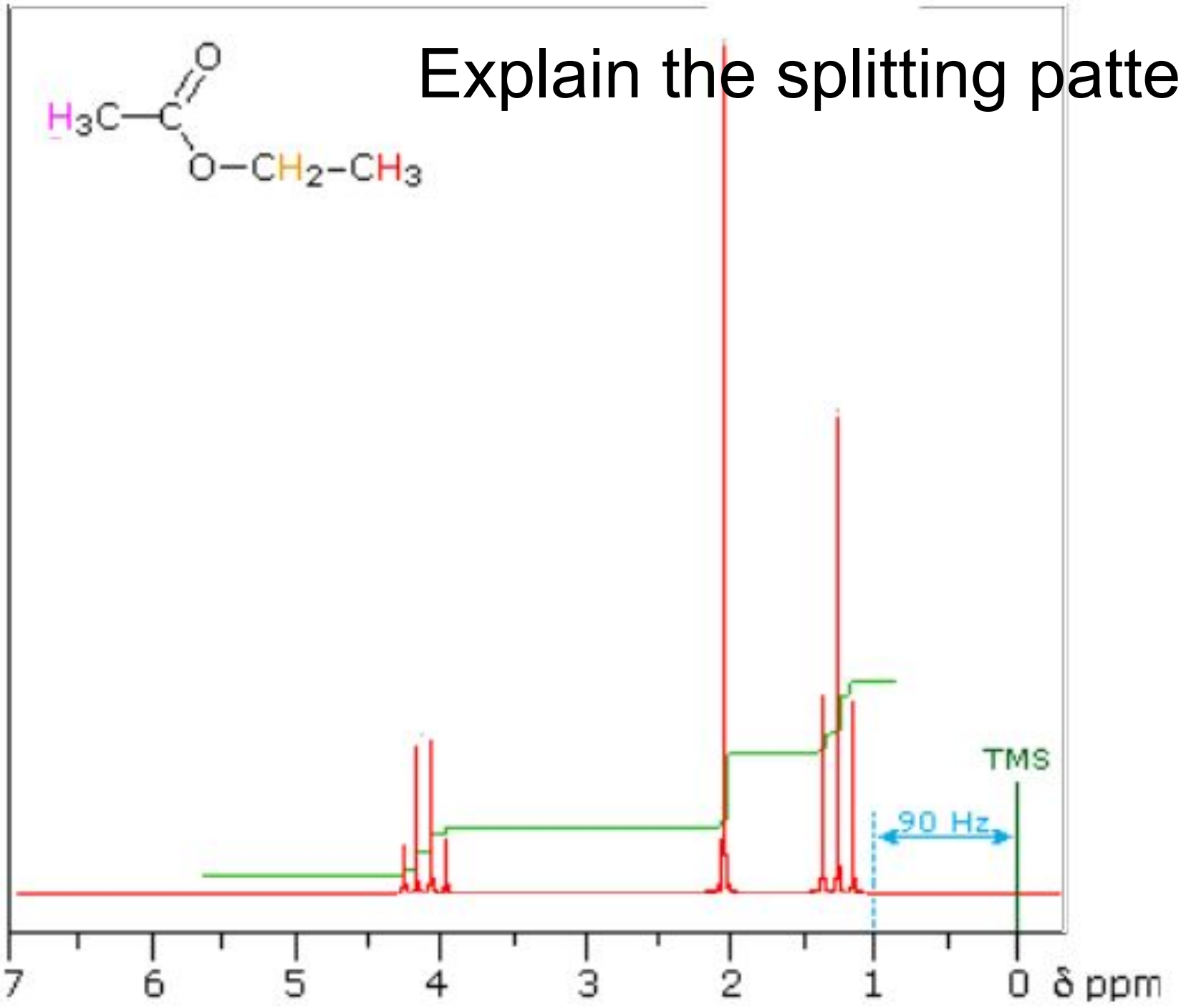
- H's that are equivalent
- H's on O's

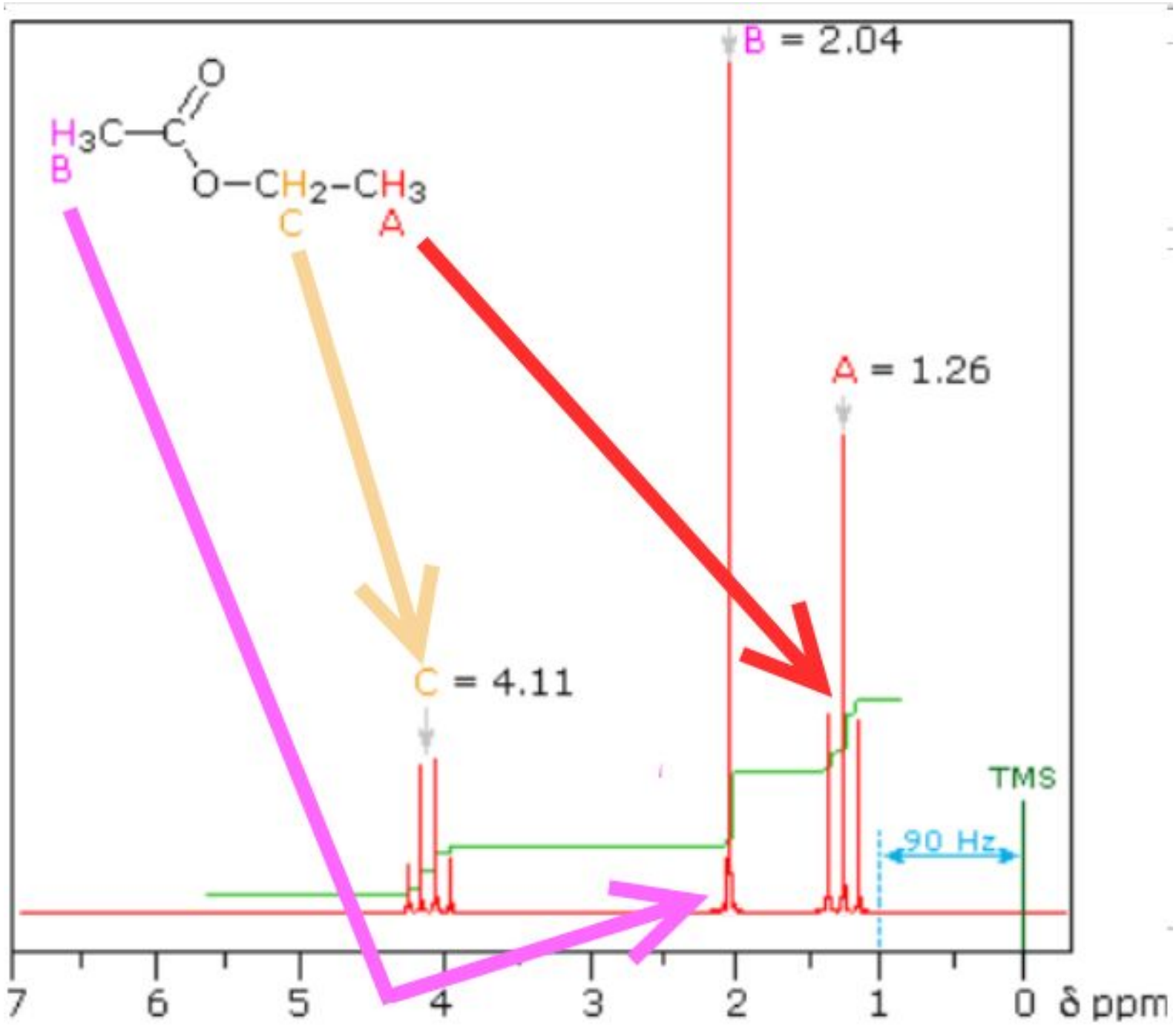
Hydroxyl Proton



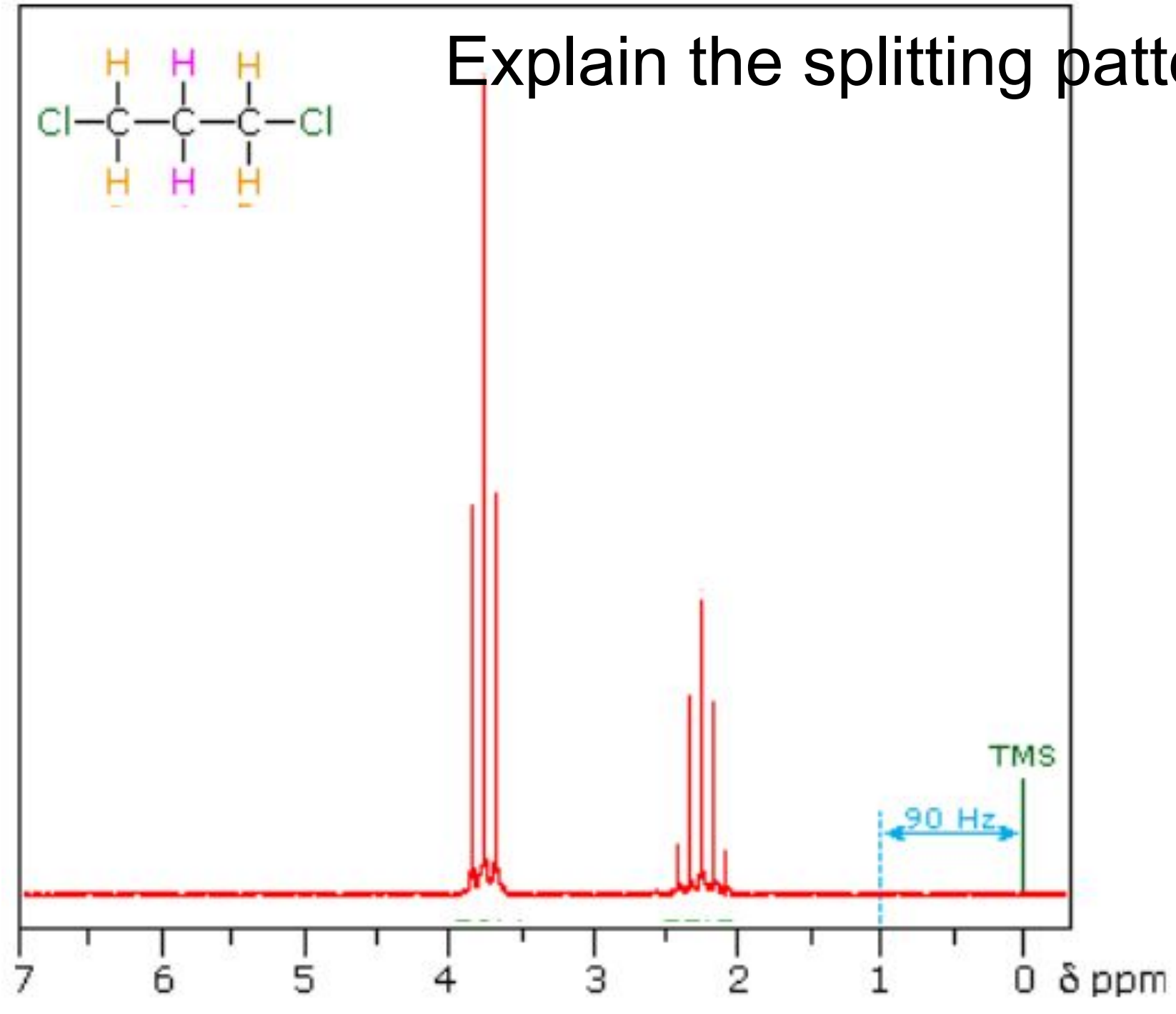
Ethanol with a small amount of acidic or basic impurities will not show splitting.

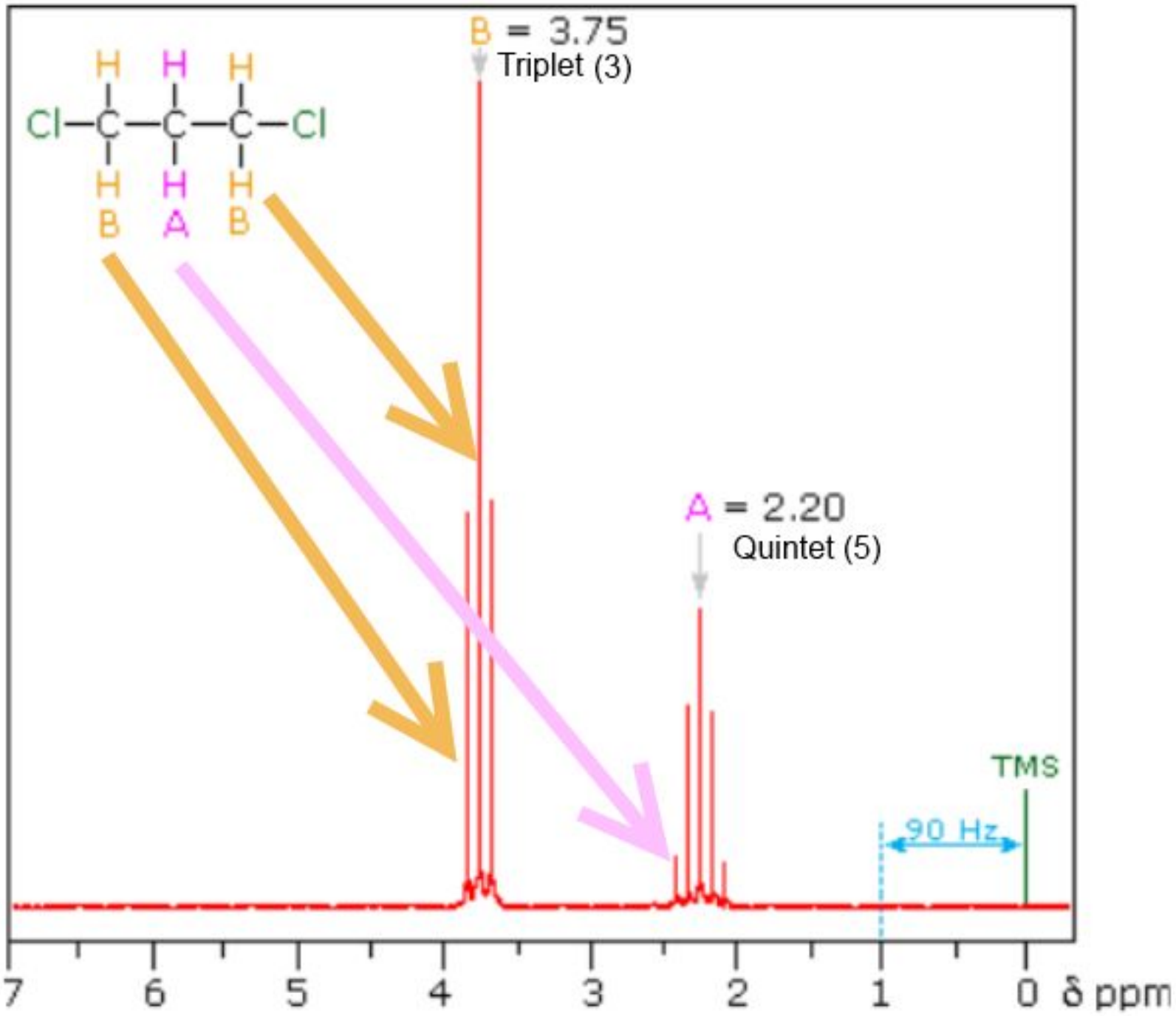
Explain the splitting patterns

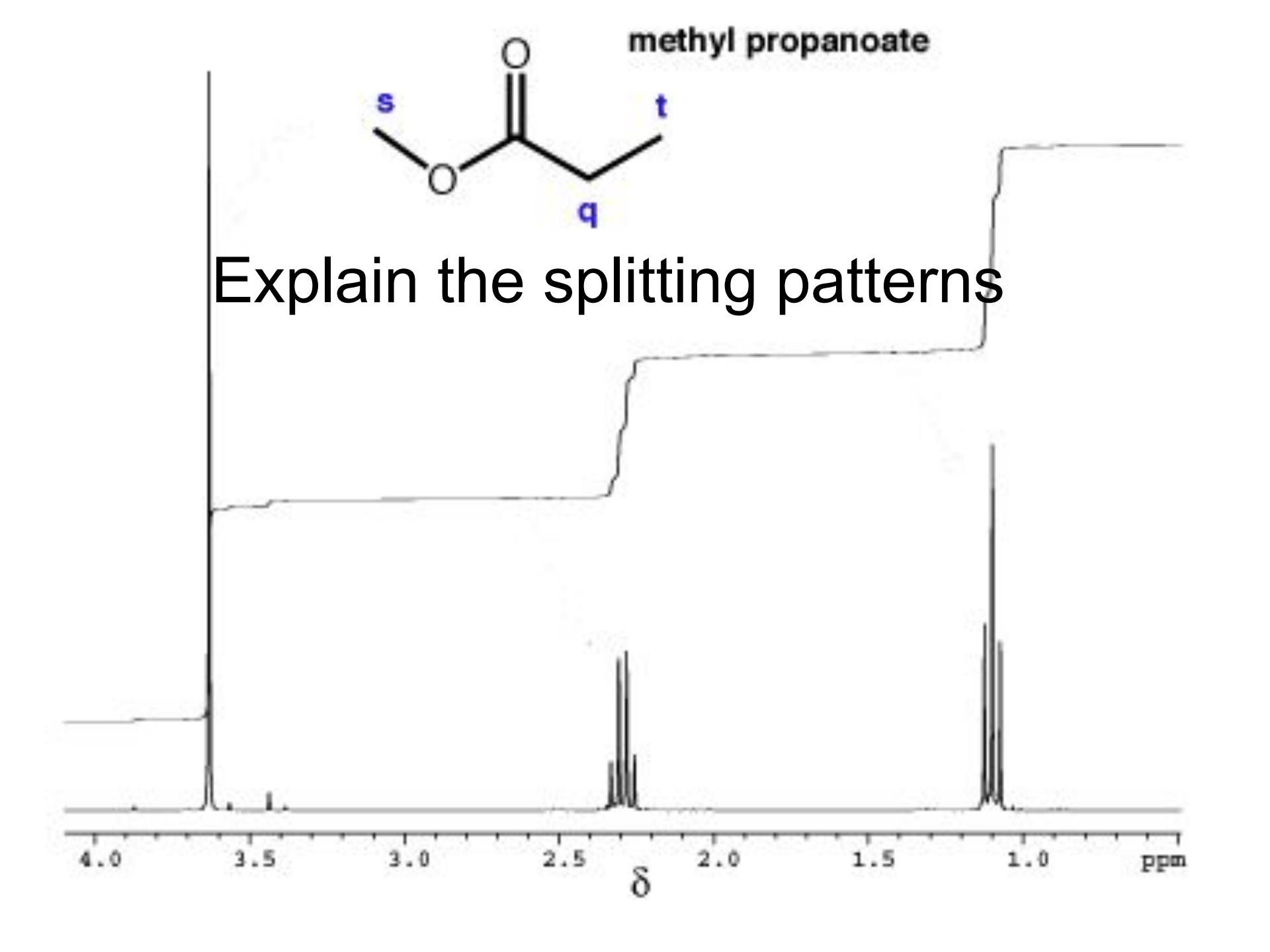


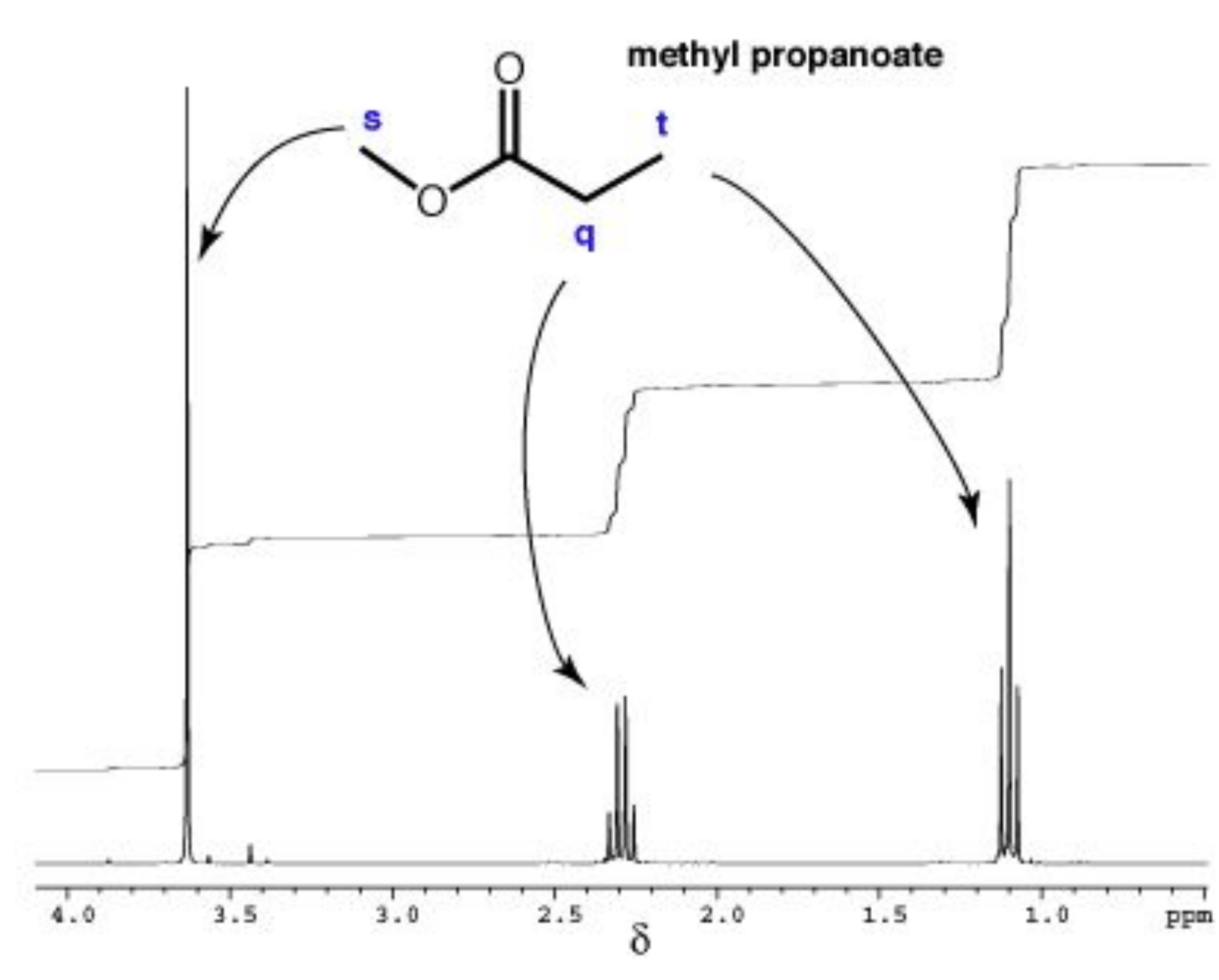

B = 2.04
A = 1.26
C = 4.11
TMS
90 Hz
7
6
5
4
3
2
1
0
δ ppm

Explain the splitting patterns



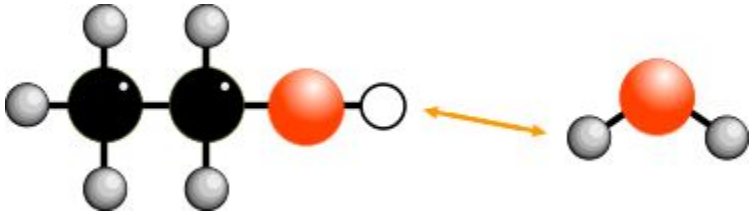

B = 3.75
Triplet (3)
A = 2.20
Quintet (5)
TMS
90 Hz
7
6
5
4
3
2
1
0
δ ppm

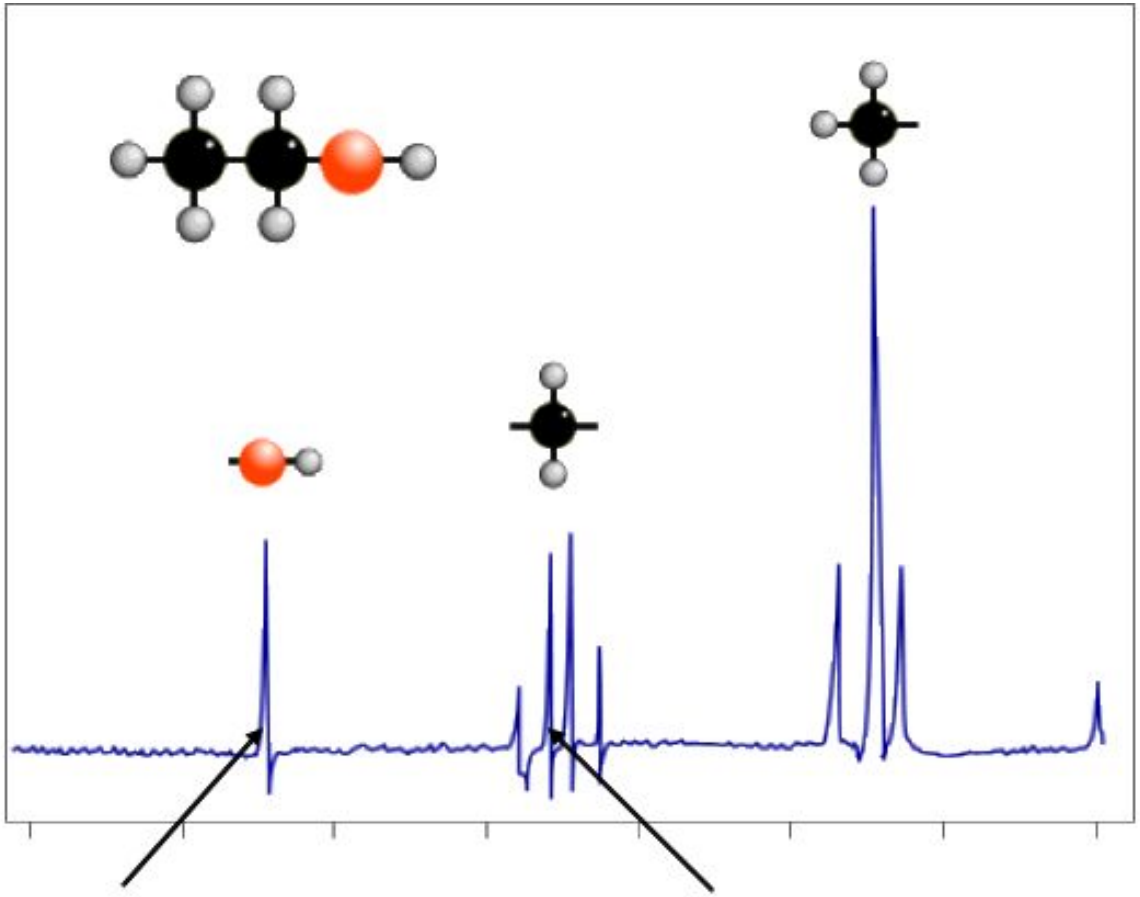

methyl propanoate
s
t
q
Explain the splitting patterns
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
δ


methyl propanoate
s
t
q
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
δ

Hydroxyl Proton

Arises because the H on the OH, rapidly exchanges with protons on other molecules (such as water or acids) and is not attached to any particular oxygen long enough to register a splitting signal.





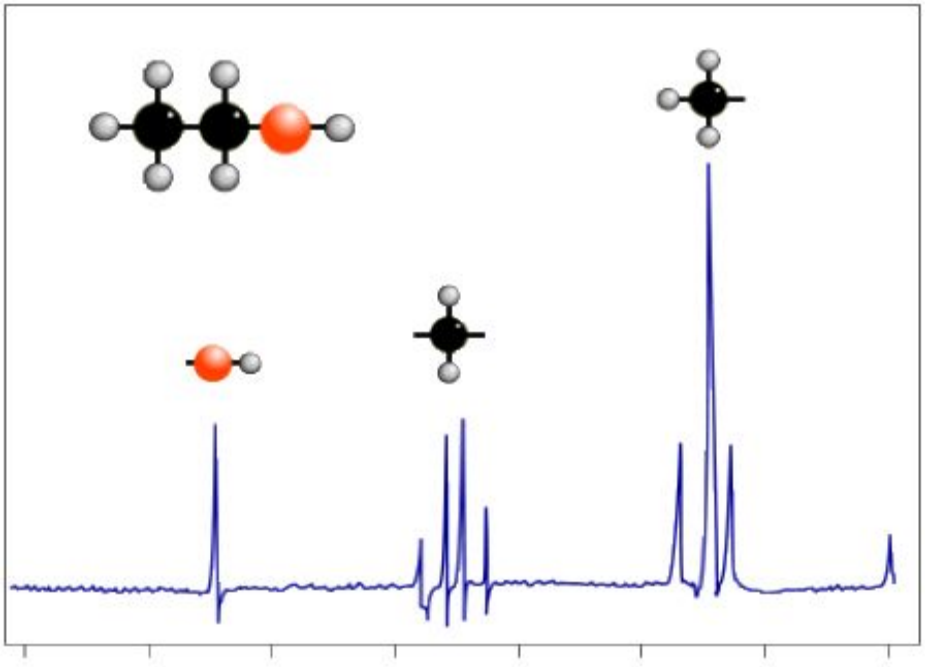
OH hydrogens are always seen as a singlet ... there is no splitting

This is a quartet despite the fact that there are 4 H's on adjacent atoms - the H on the OH doesn't couple

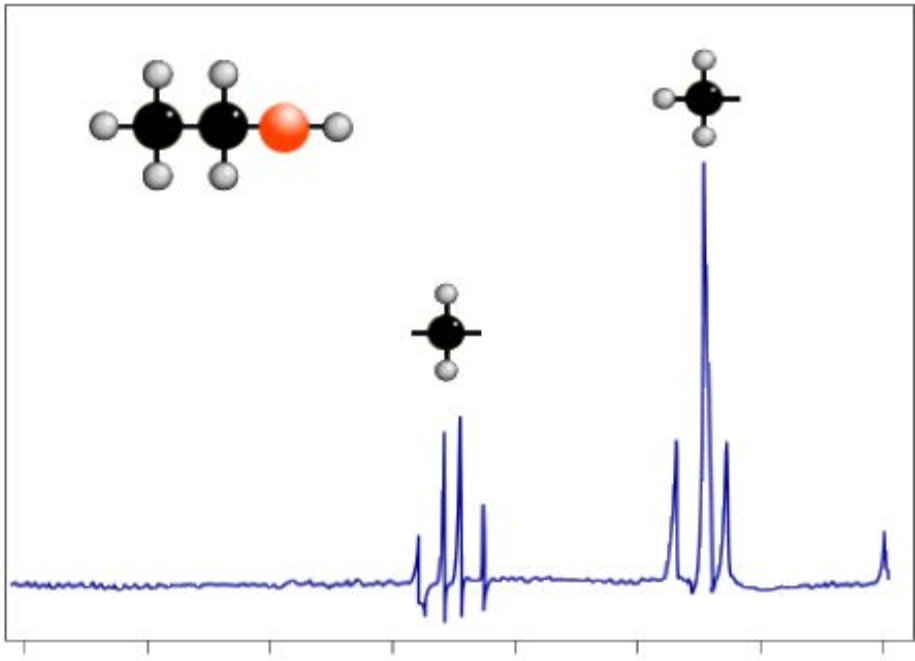
Identifying the O-H or N-H Peak

- Chemical shift will depend on concentration and solvent.
- To verify that a particular peak is due to O-H or N-H, shake the sample with D_2O
- Deuterium will exchange with the O-H or N-H protons.
- On a second NMR spectrum the peak will be absent, or much less intense.

before shaking with D_2O



after shaking with D_2O



H atoms attached to the N in amines also interchange with deuterium

SUMMARY

Number of signals how many different sets of equivalent H atoms there are

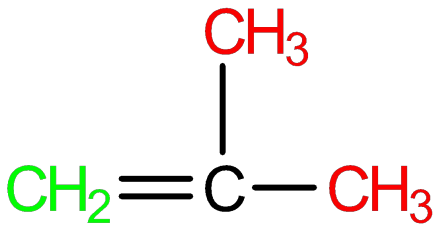
Position of signals information about chemical environment of H atom

Relative intensities gives ratio of H atoms for peaks

Splitting how many H atoms on adjacent C atoms

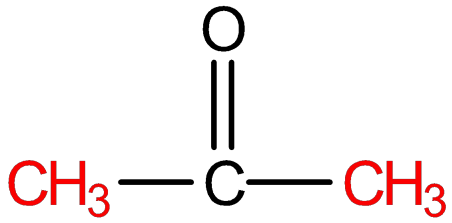
For each of the following compounds, predict the number of signals, the relative intensity of the signals, and the multiplicity of each signal.

a) methylpropene
b) propene
c) 2-chloropropane
d) propanone
e) methylamine
f) ethyl propanoate
g) 1,2-dibromopropane
h) dimethylethyl propanoate
i) but-2-ene



2 signals: ratio 6 : 2 (3 :1)

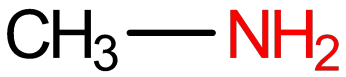
s s



1 signal

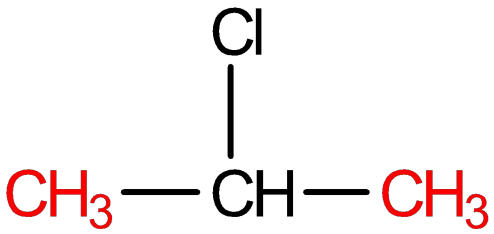
3 signals: ratio 2 : 1 : 3

d m d



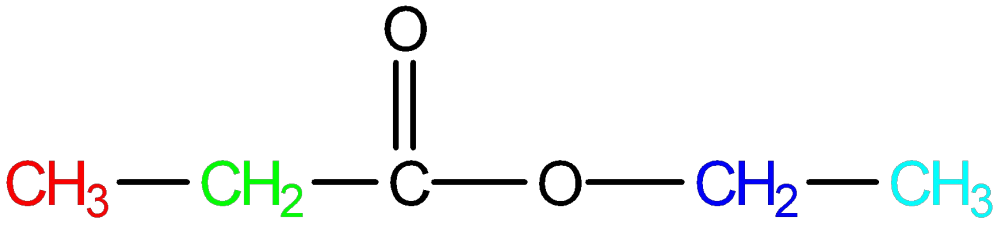
2 signals: ratio 3 : 2

t q



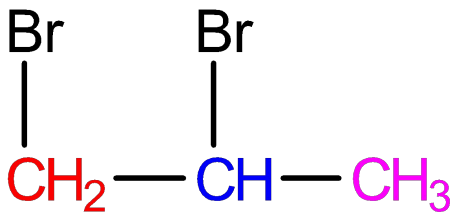
2 signals: ratio 6 : 1

d m



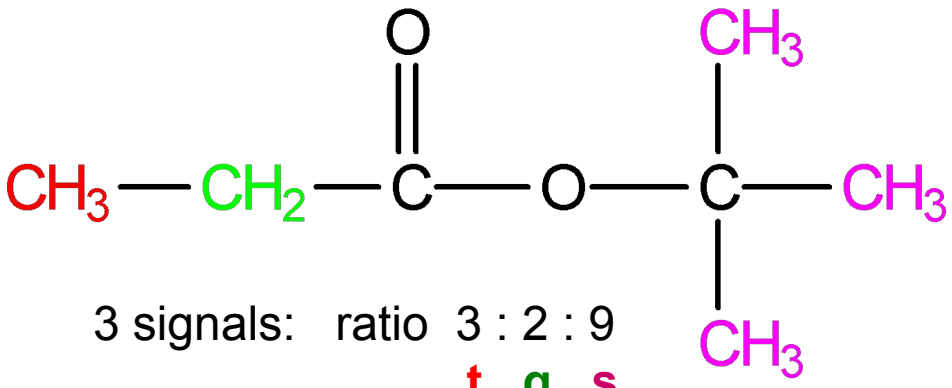
4 signals: ratio 3 : 2 : 2 : 3

t q q t



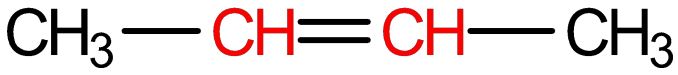
3 signals: ratio 2 : 1 : 3

d m d



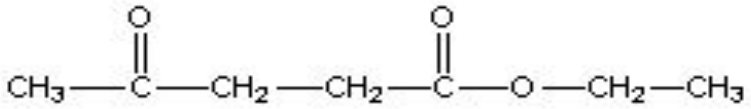
3 signals: ratio 3 : 2 : 9

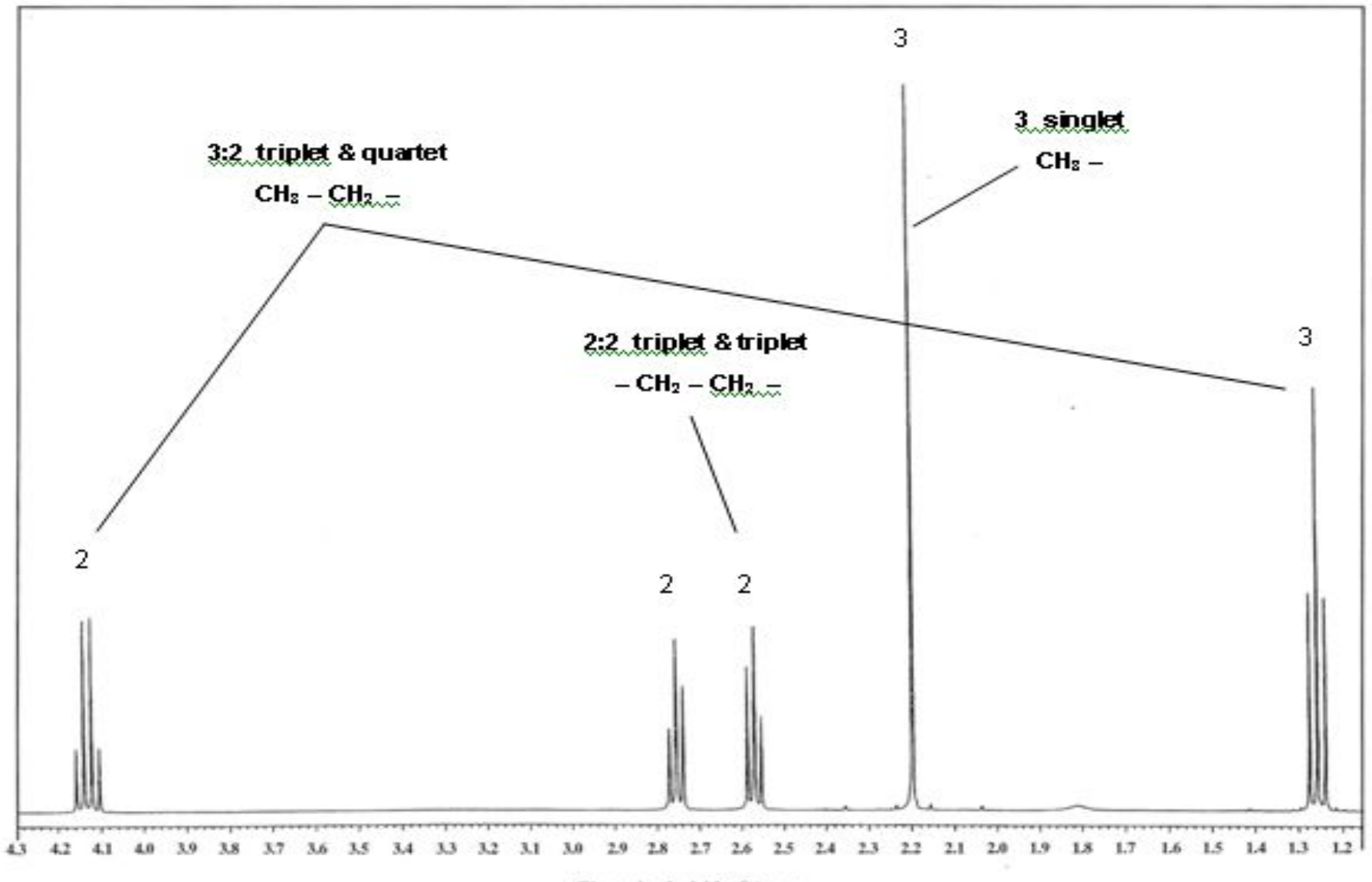
t q s



2 signals: ratio 6 : 2 (3 :1)

d q



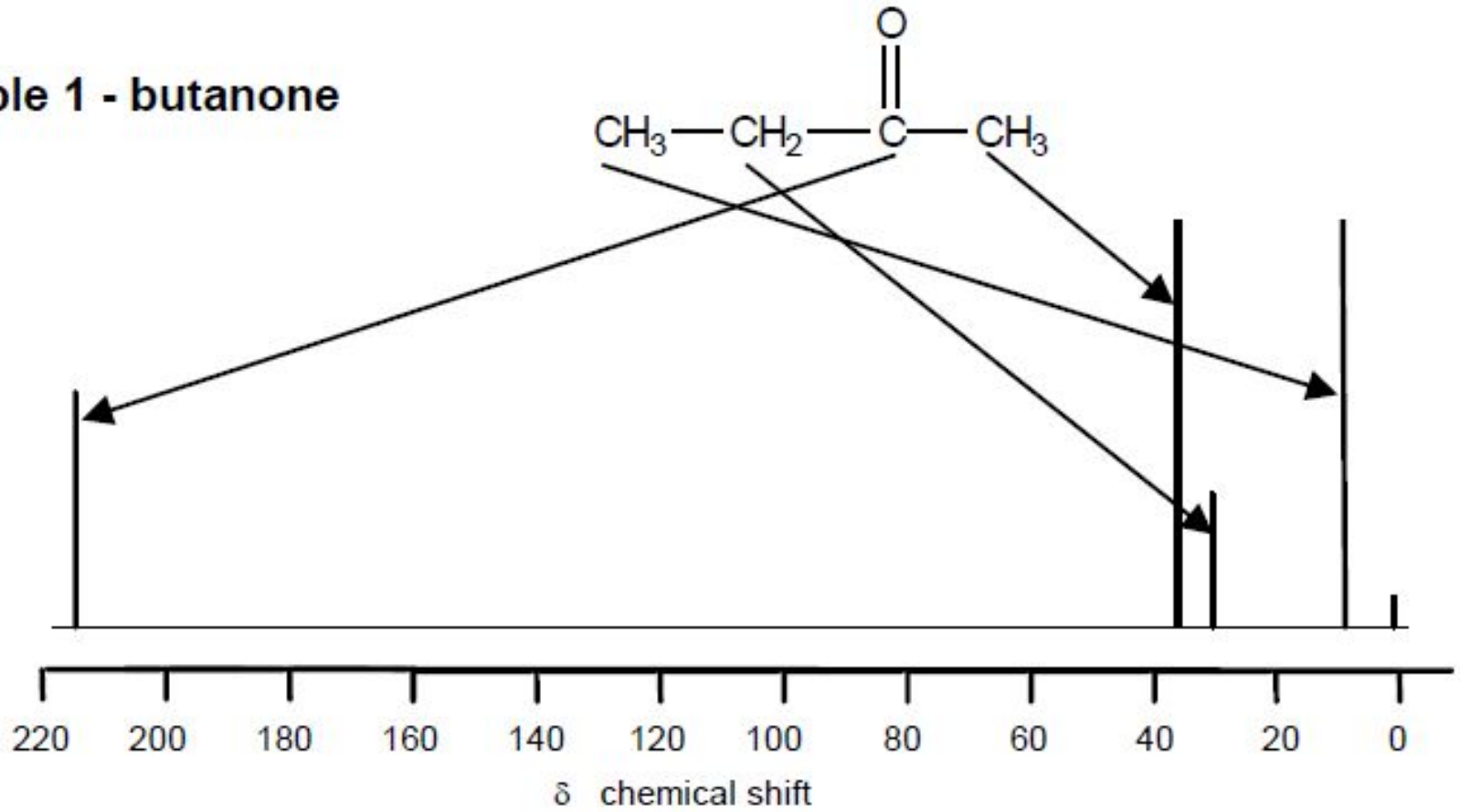

3
3 singlet
CH₃ –
3:2 triplet & quartet
CH₃ – CH₂ –
2:2 triplet & triplet
– CH₂ – CH₂ –
3
2
2
2
4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2
Chemical shift, δ/ppm

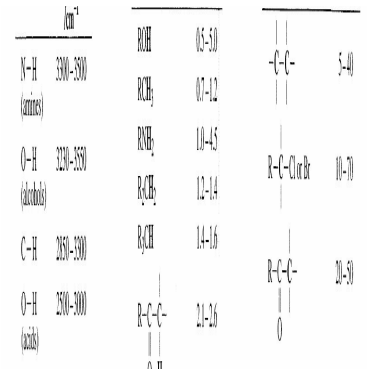
13C NMR SPECTROSCOPY

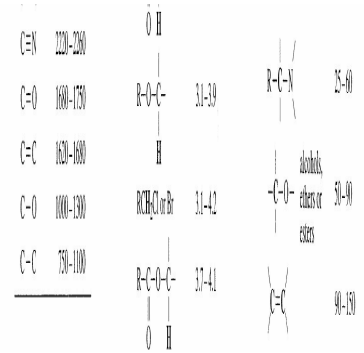
KEY POINTS

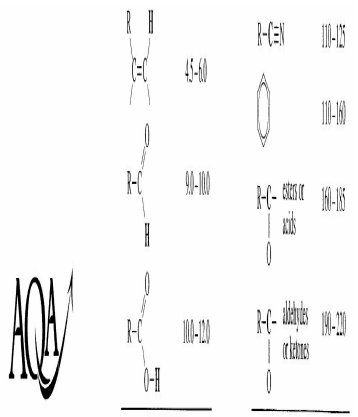
- ^{13}C NMR spectra are often simpler than ^{1}H NMR spectra.
- They give a lot of valuable information about the chemical environment of C atoms (e.g. the difference between C atoms in C=O, C-N, C≡N, C-C, C=C, etc.).
- There is one signal for each set of equivalent C atoms.
- There is no coupling (unlike ^{1}H NMR).
- The size of signal is not relative to the number of equivalent C atoms (unlike H atoms in ^{1}H NMR).
- As in ^{1}H NMR, the chemical shift (d) is measured relative to TMS.
- Although deuterated solvents are usually used, there will be a signal for any C atoms in the solvent.

Example 1 - butanone



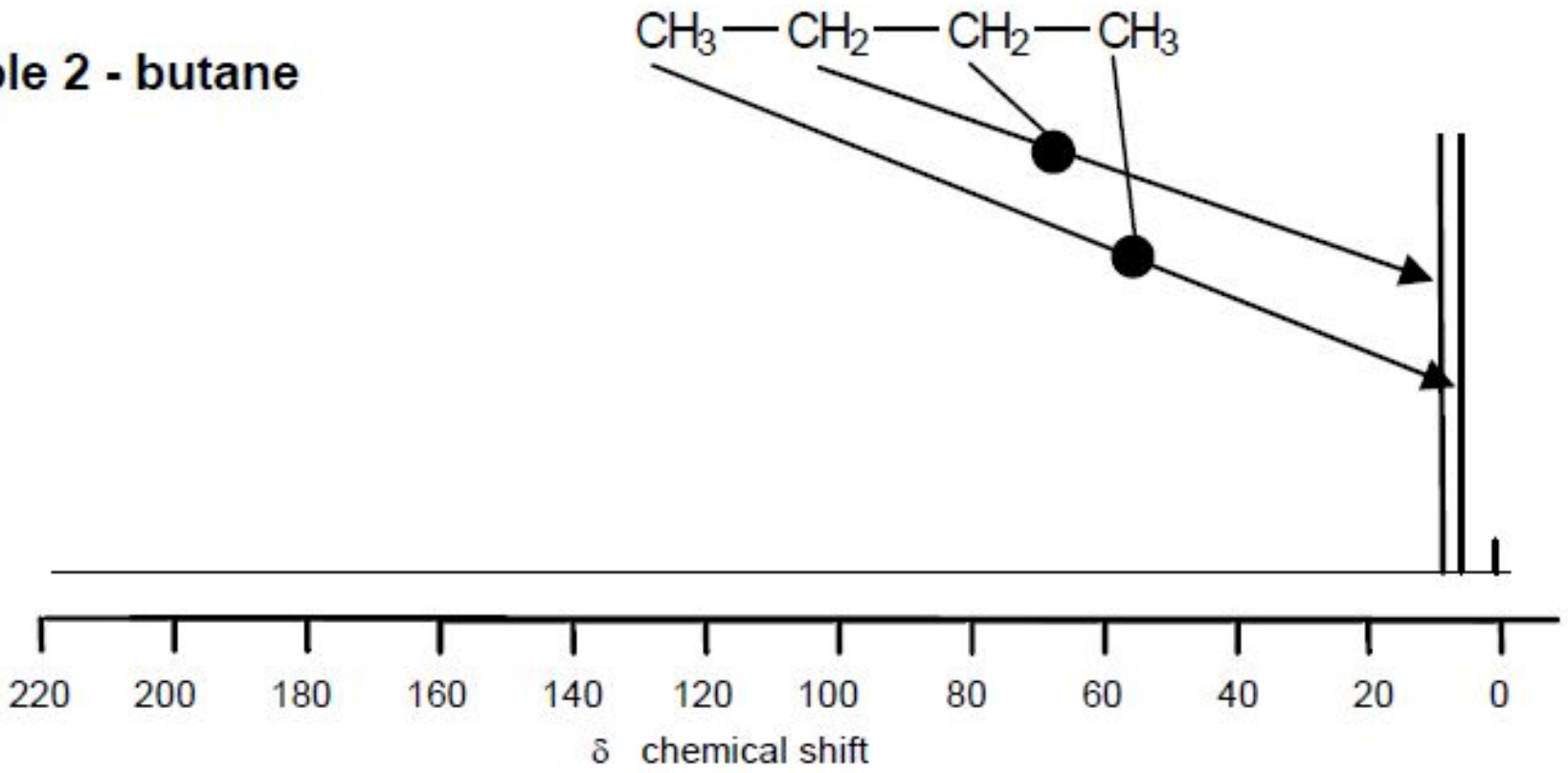


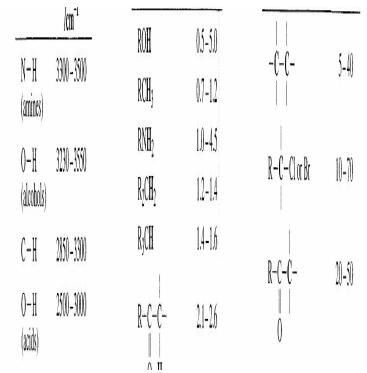


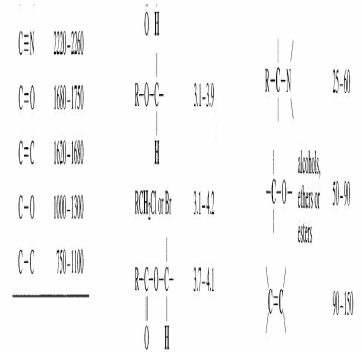


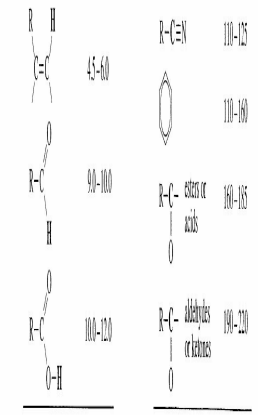
Data from AQA datasheet

Example 2 - butane



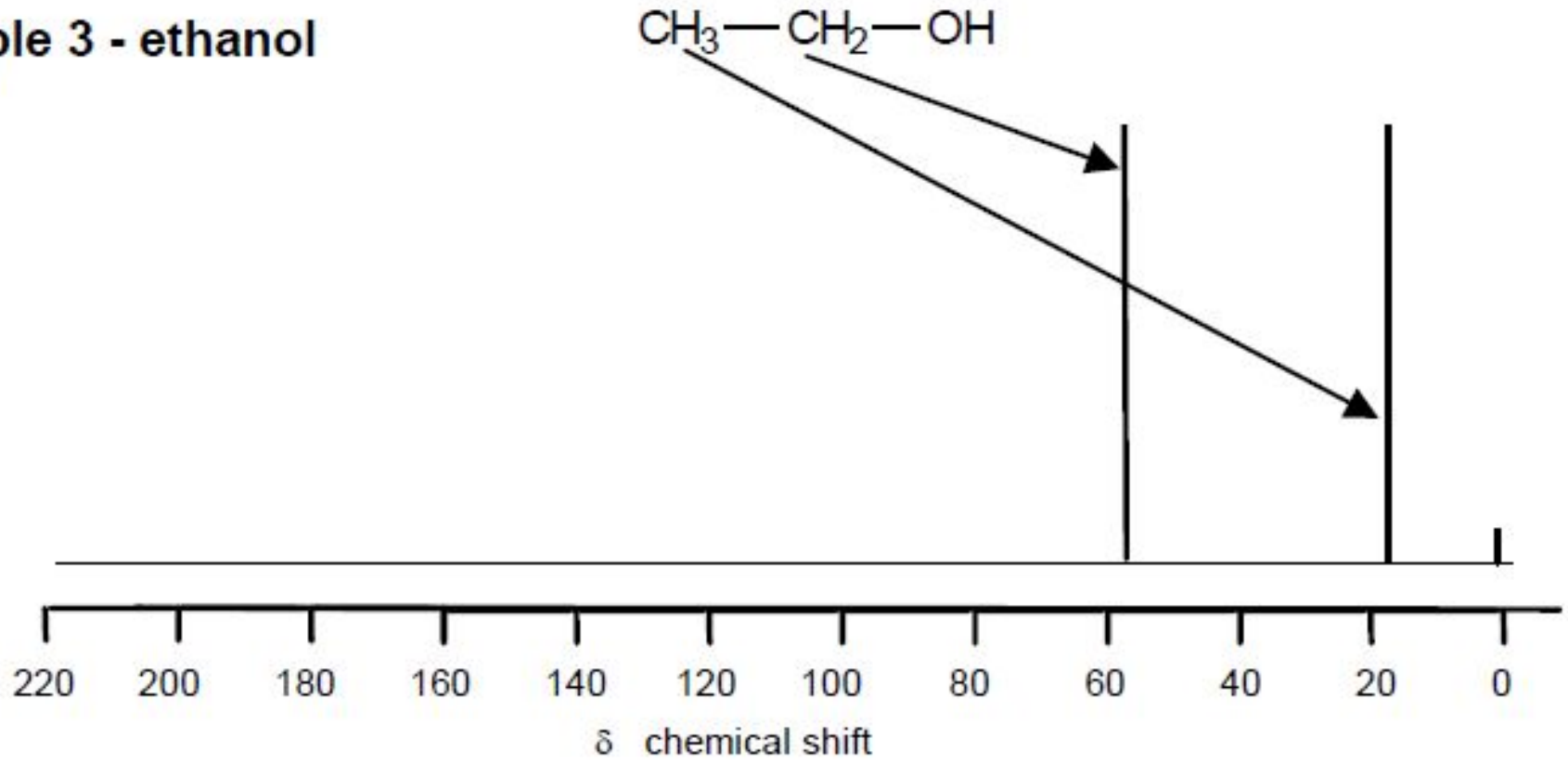


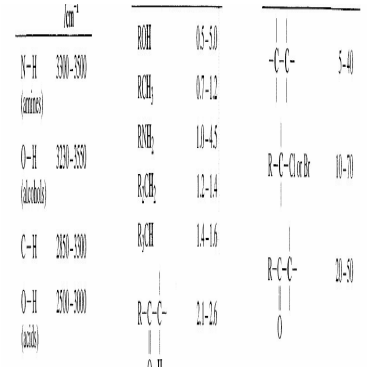


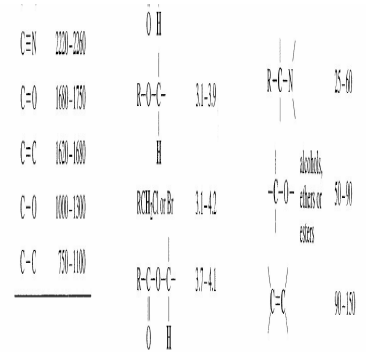


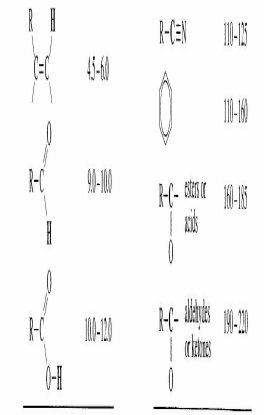
Data from AQA datasheet

Example 3 - ethanol









Data from AQA datasheet