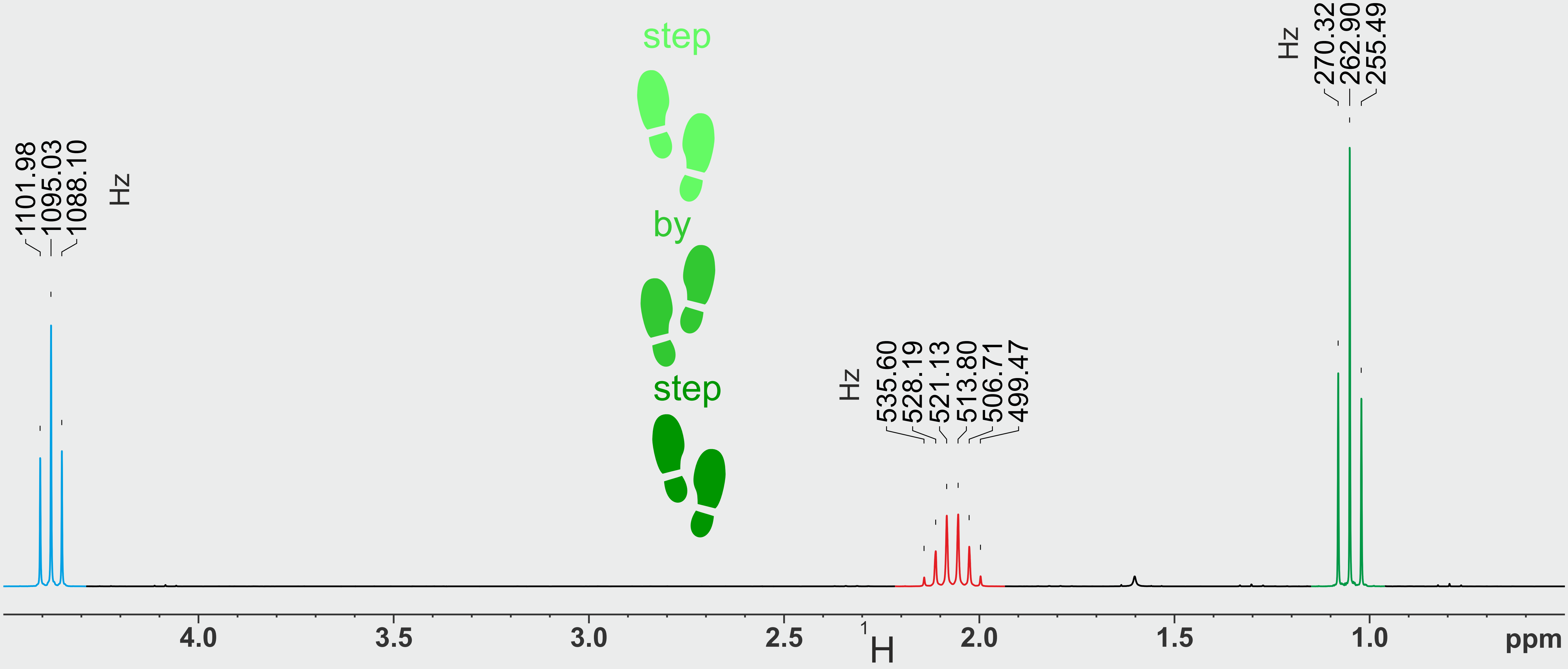
Exercise plus Solution – Quick PDF overview

It is recommended to use this PDF version only for a quick overview of the NMR challenge. All animations of the PowerPoint version are missing, under certain circumstances quality deficiencies may also occur.
The higher quality PowerPoint files are freely available for download at any time.



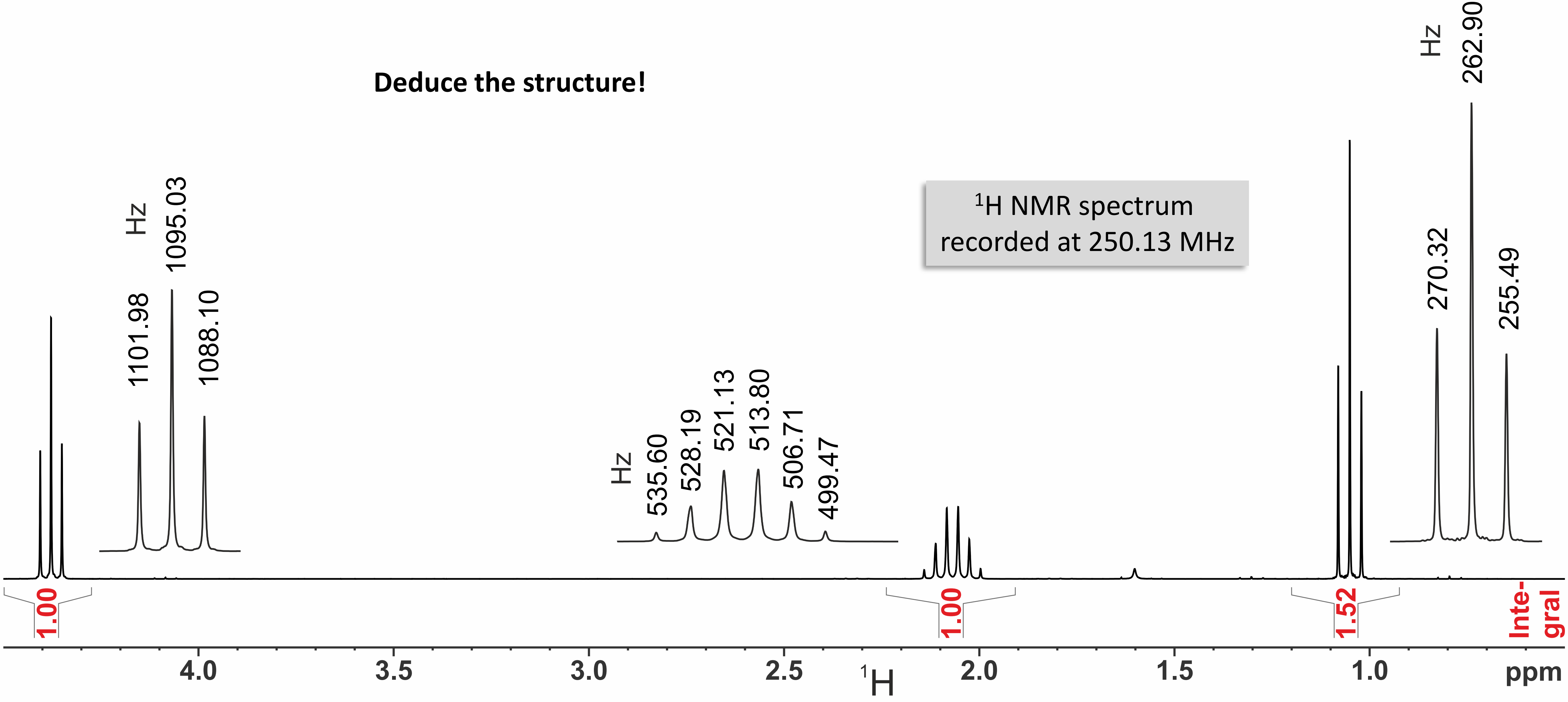
step

by

step

$C_3H_7NO_2$ measured in $CDCl_3$

Deduce the structure!



^1H NMR spectrum
recorded at 250.13 MHz

Basic considerations

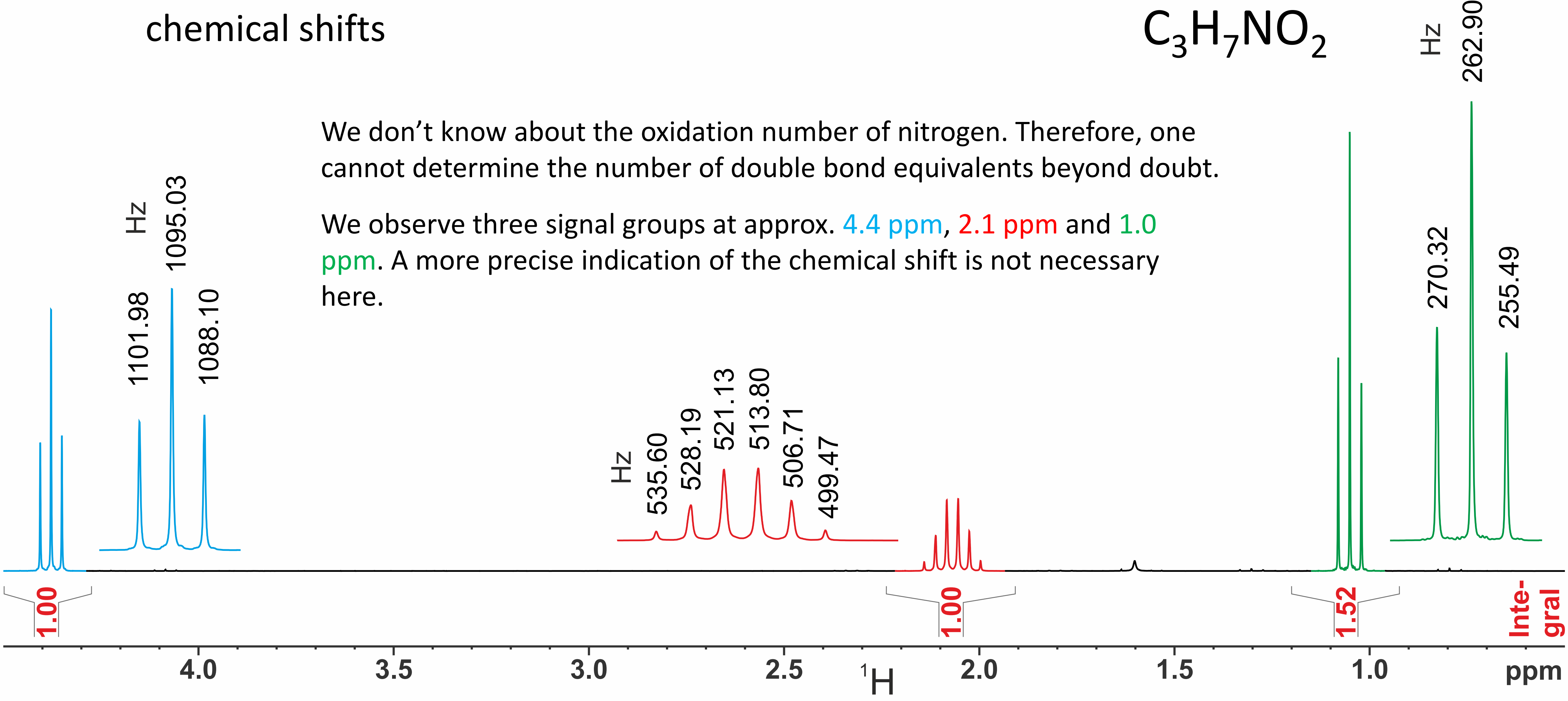
Double bond equivalents,
number of signal groups,
chemical shifts

Solution

$C_3H_7NO_2$

We don’t know about the oxidation number of nitrogen. Therefore, one cannot determine the number of double bond equivalents beyond doubt.

We observe three signal groups at approx. 4.4 ppm, 2.1 ppm and 1.0 ppm. A more precise indication of the chemical shift is not necessary here.



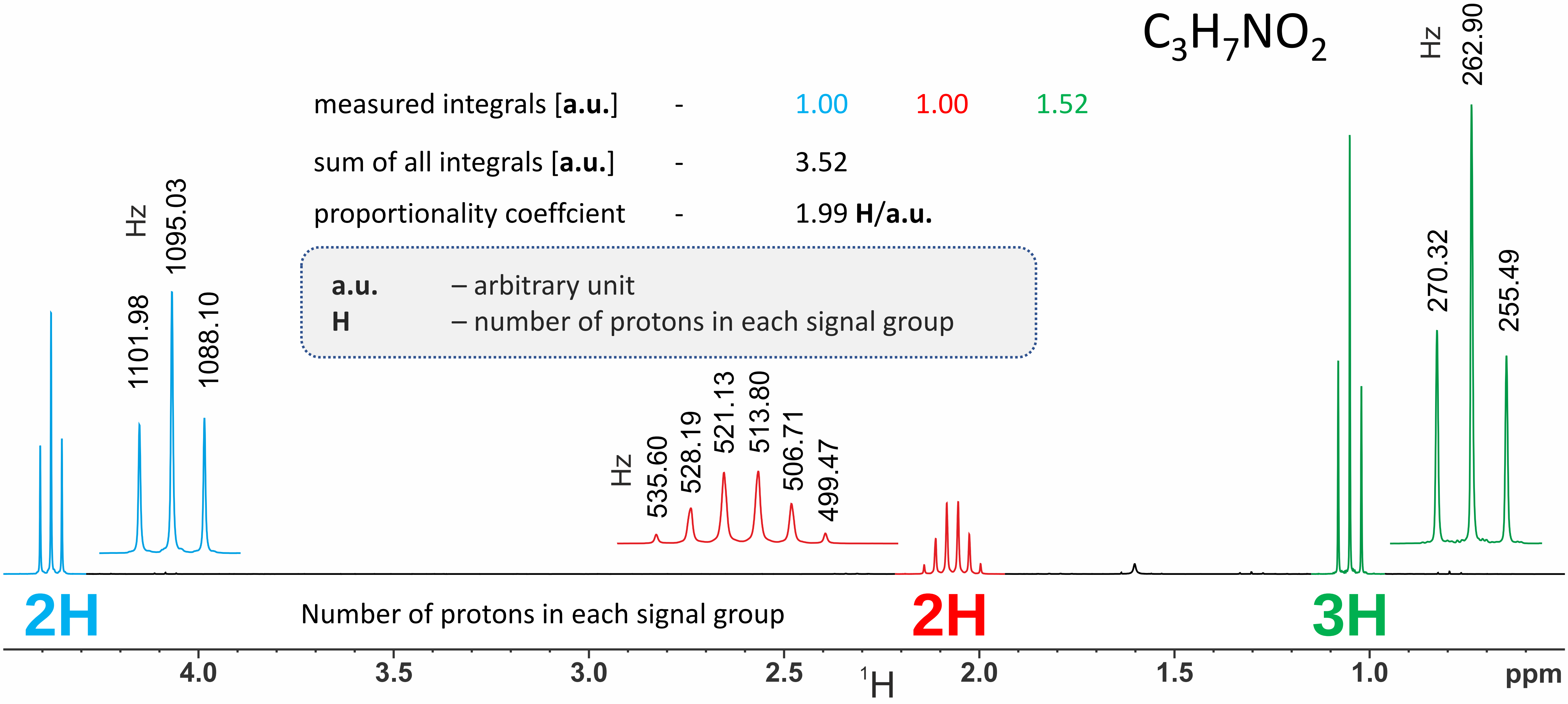
Basic considerations

Integration

$C_3H_7NO_2$

measured integrals [**a.u.**]	-	1.00	1.00	1.52
sum of all integrals [**a.u.**]	-	3.52		
proportionality coeffcient	-	1.99 **H/a.u.**		

a.u.	– arbitrary unit
H	– number of protons in each signal group



Number of protons in each signal group

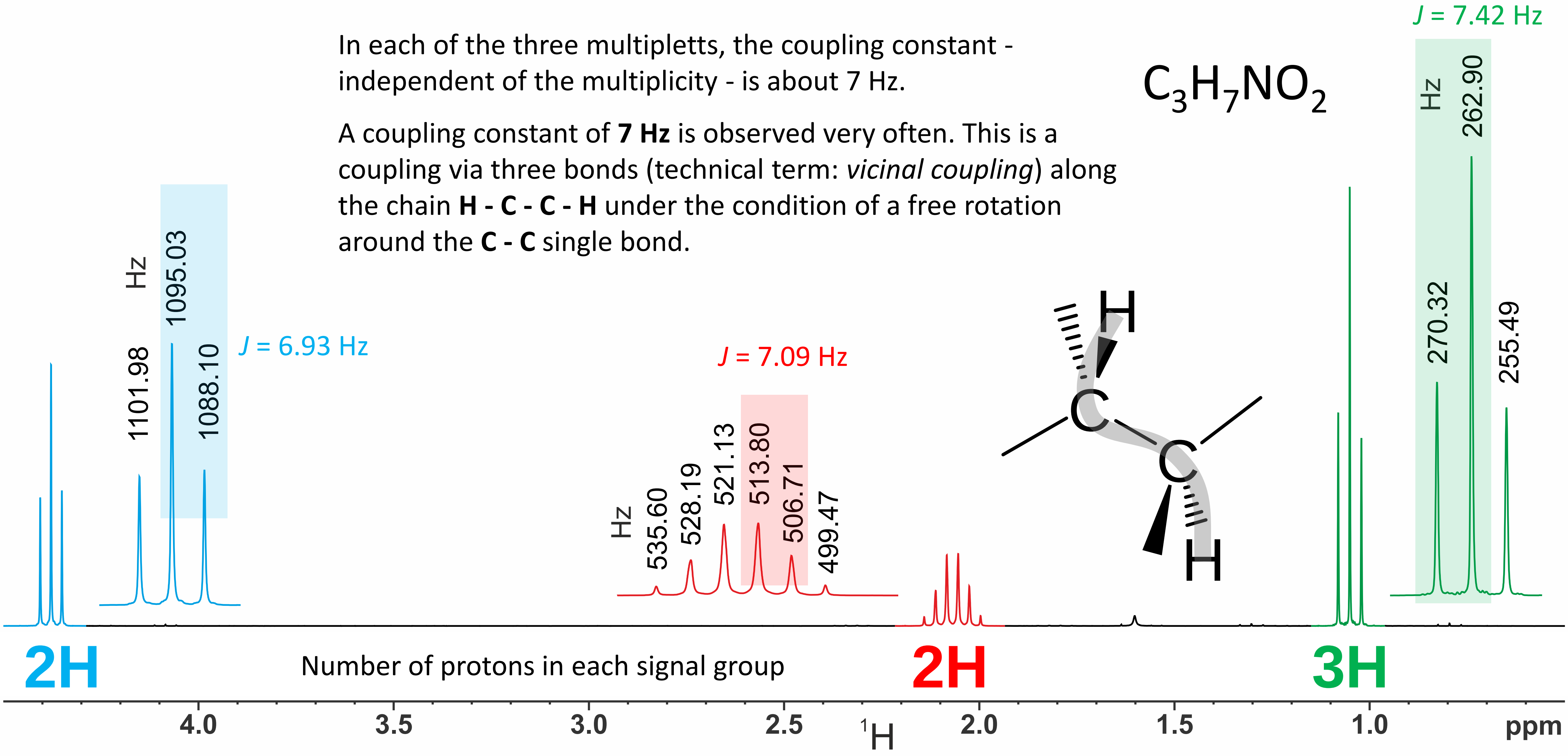
Basic considerations

Structural elements

In each of the three multipletts, the coupling constant - independent of the multiplicity - is about 7 Hz.

A coupling constant of **7 Hz** is observed very often. This is a coupling via three bonds (technical term: *vicinal coupling*) along the chain **H - C - C - H** under the condition of a free rotation around the **C - C** single bond.

$C_3H_7NO_2$

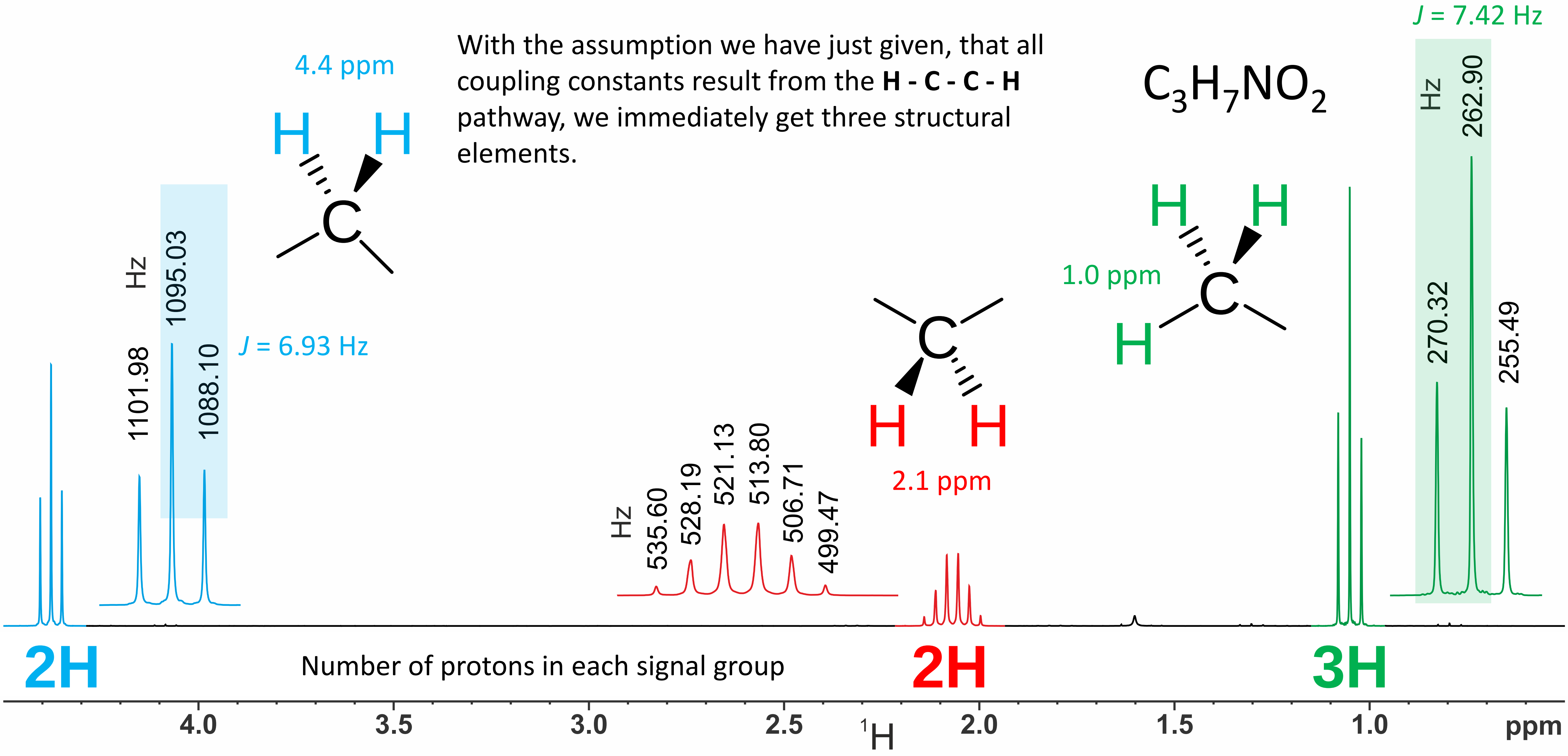


Basic considerations

Structural elements

With the assumption we have just given, that all coupling constants result from the **H - C - C - H** pathway, we immediately get three structural elements.

$C_3H_7NO_2$



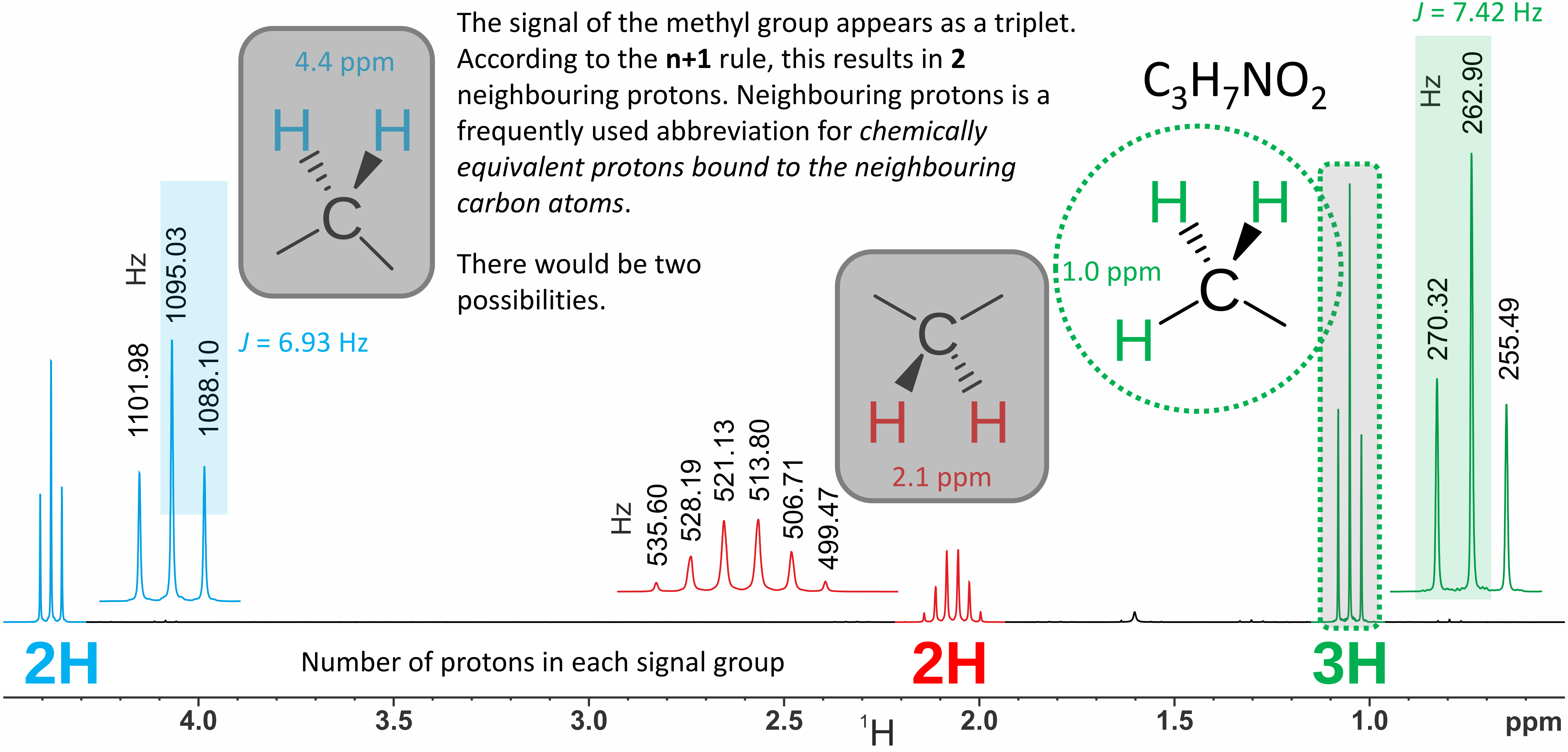
Basic considerations

Structural elements

The signal of the methyl group appears as a triplet. According to the **n+1** rule, this results in **2** neighbouring protons. Neighbouring protons is a frequently used abbreviation for *chemically equivalent protons bound to the neighbouring carbon atoms*.

There would be two possibilities.

$C_3H_7NO_2$

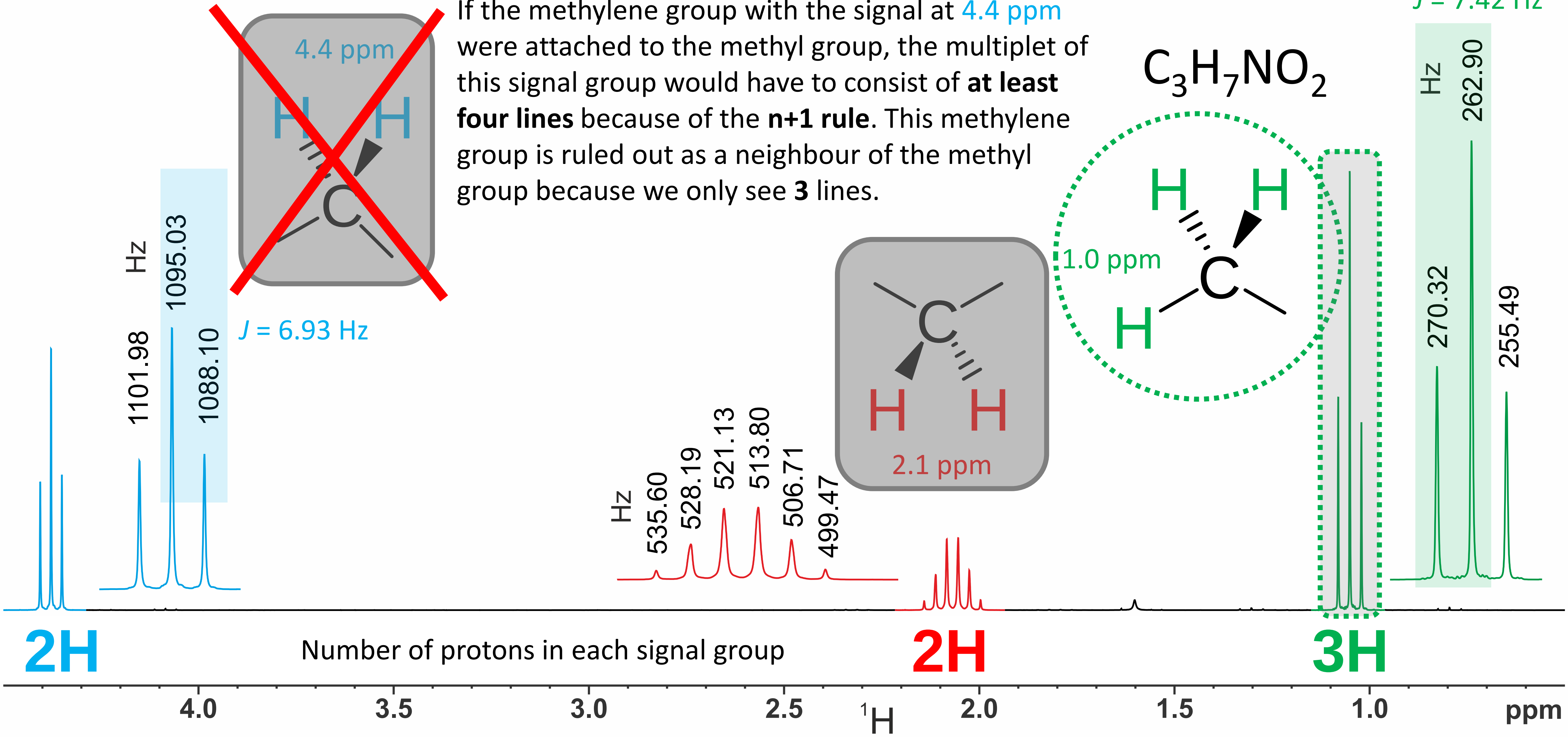


Basic considerations

Structural elements

If the methylene group with the signal at 4.4 ppm were attached to the methyl group, the multiplet of this signal group would have to consist of **at least four lines** because of the **n+1 rule**. This methylene group is ruled out as a neighbour of the methyl group because we only see **3** lines.

$C_3H_7NO_2$



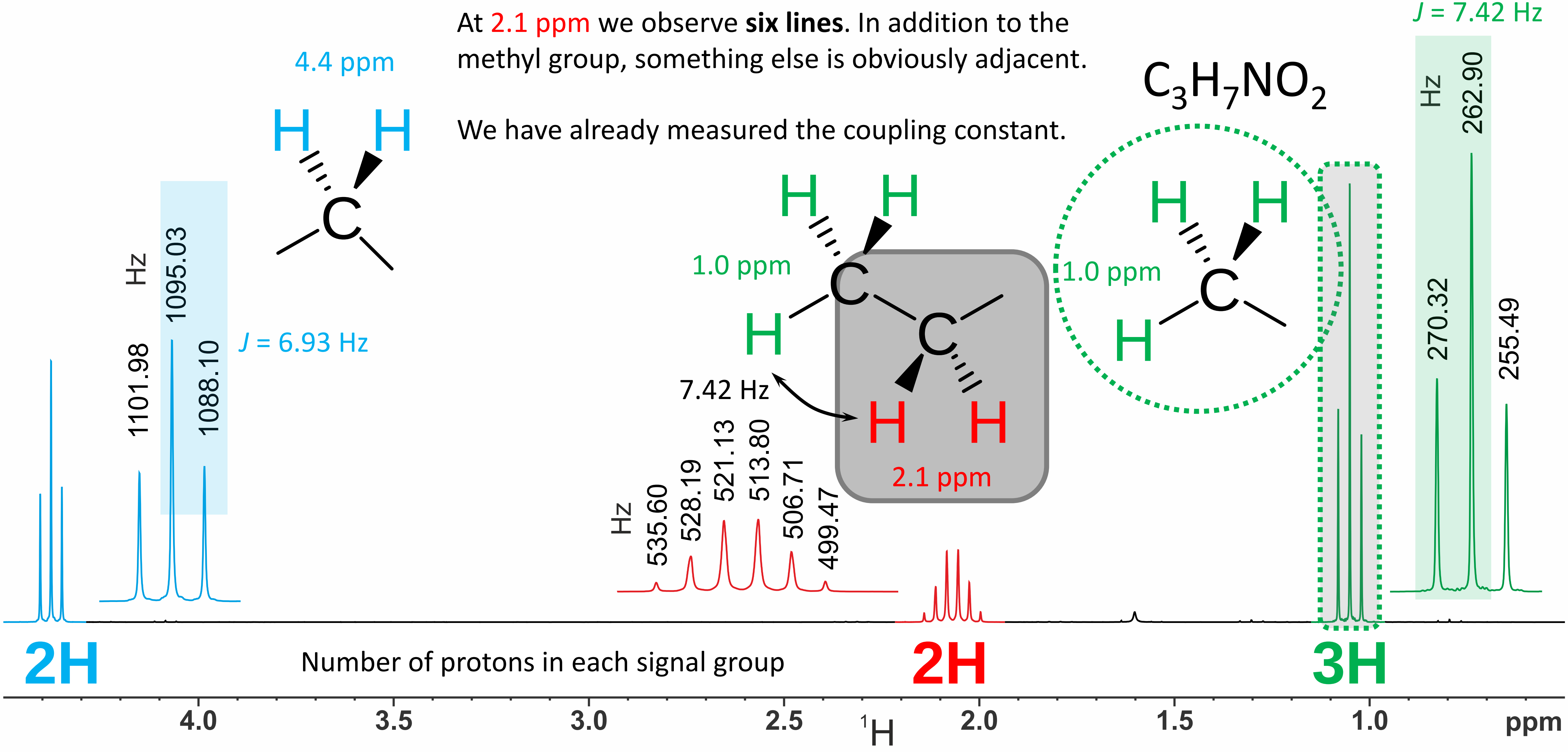
Basic considerations

Structural elements

At 2.1 ppm we observe **six lines**. In addition to the methyl group, something else is obviously adjacent.

We have already measured the coupling constant.

$C_3H_7NO_2$

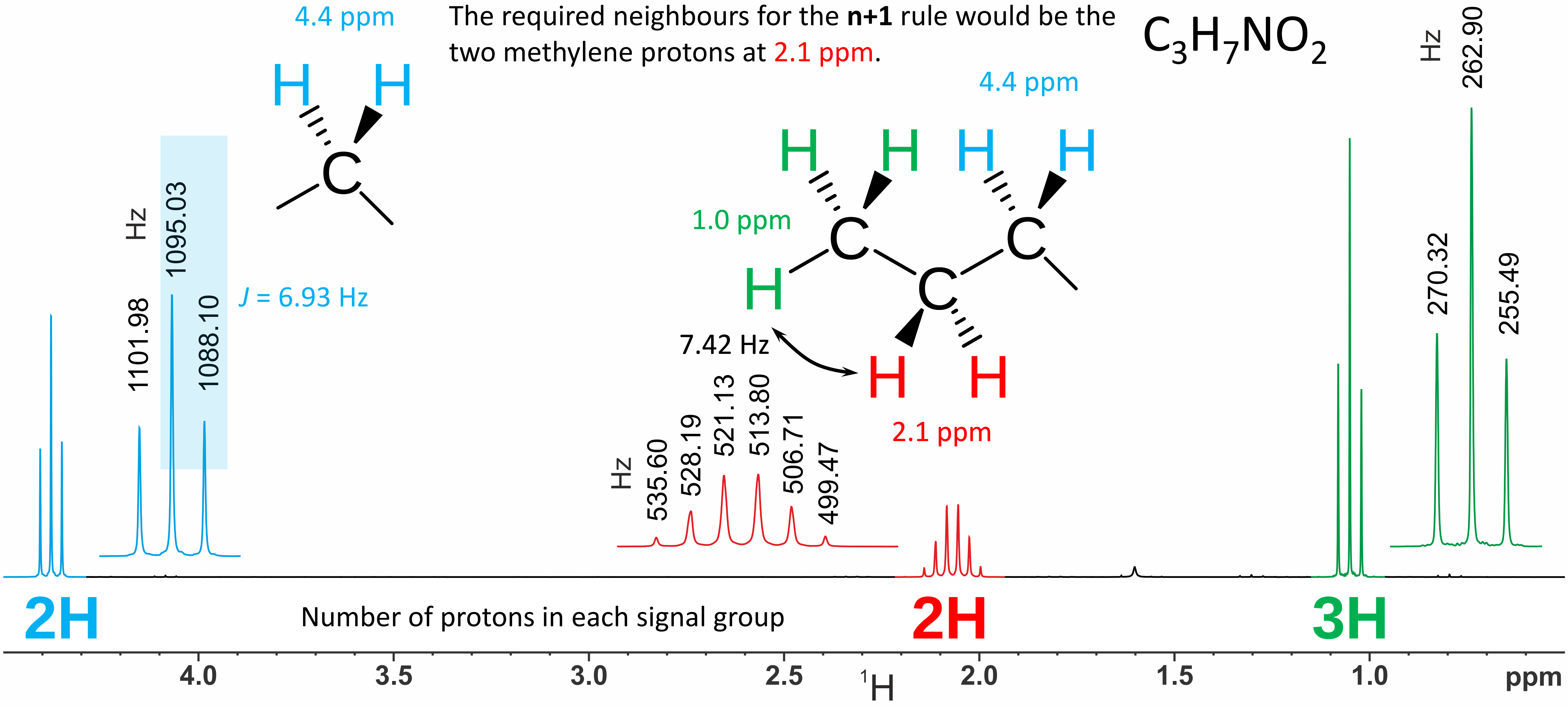


Basic considerations

Structural elements

We can explain the triplet at 4.4 ppm, if we attach the methylene group to the open bond of the ethyl group. The required neighbours for the **n+1** rule would be the two methylene protons at 2.1 ppm.

$C_3H_7NO_2$

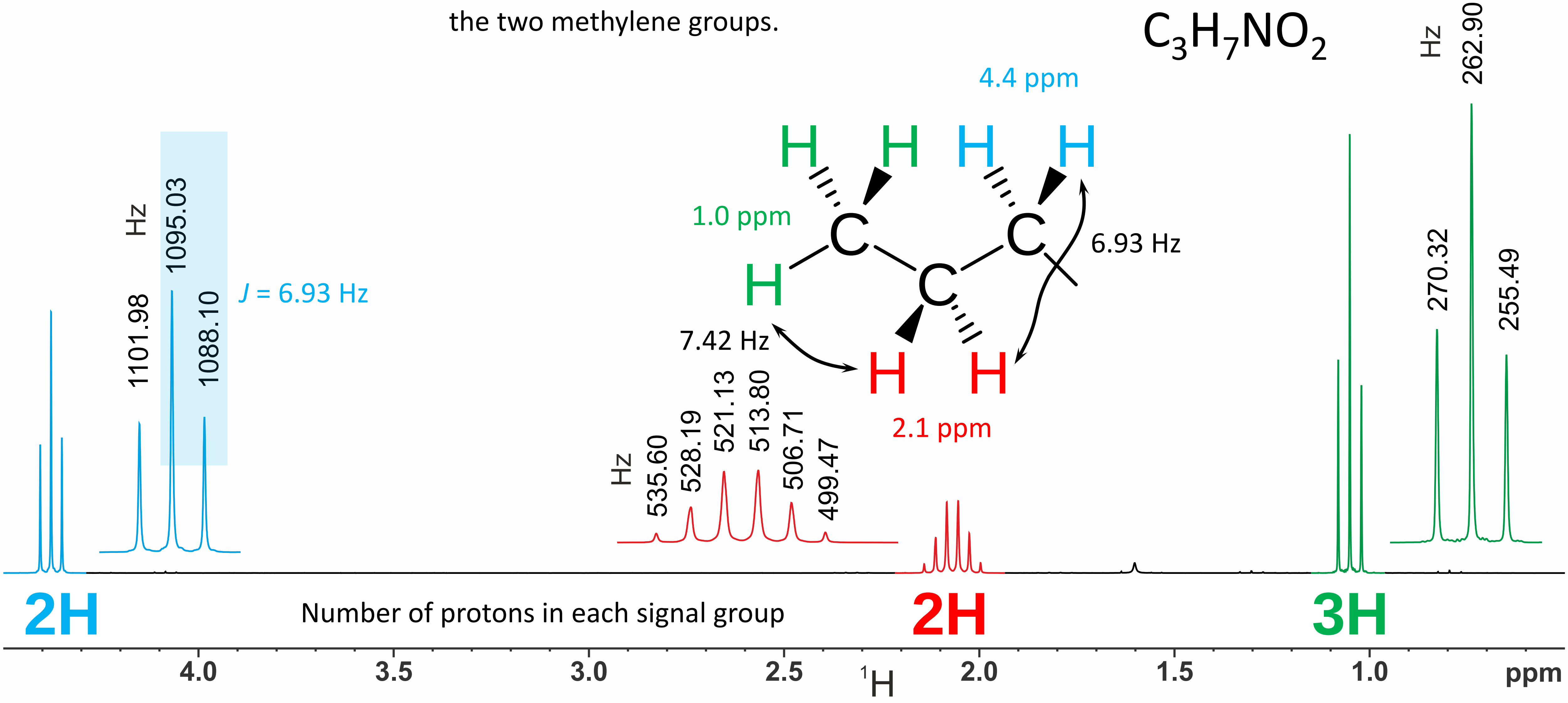


Basic considerations

Structural elements

We also already know the coupling constant between the two methylene groups.

$C_3H_7NO_2$

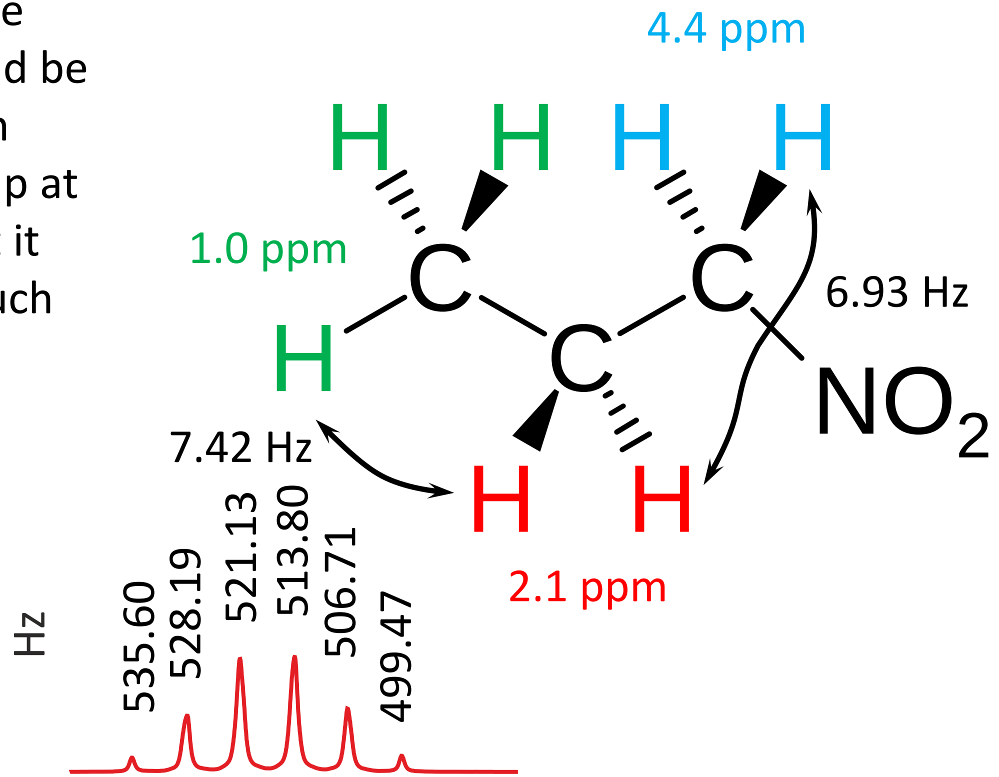


Final structure

Two choices

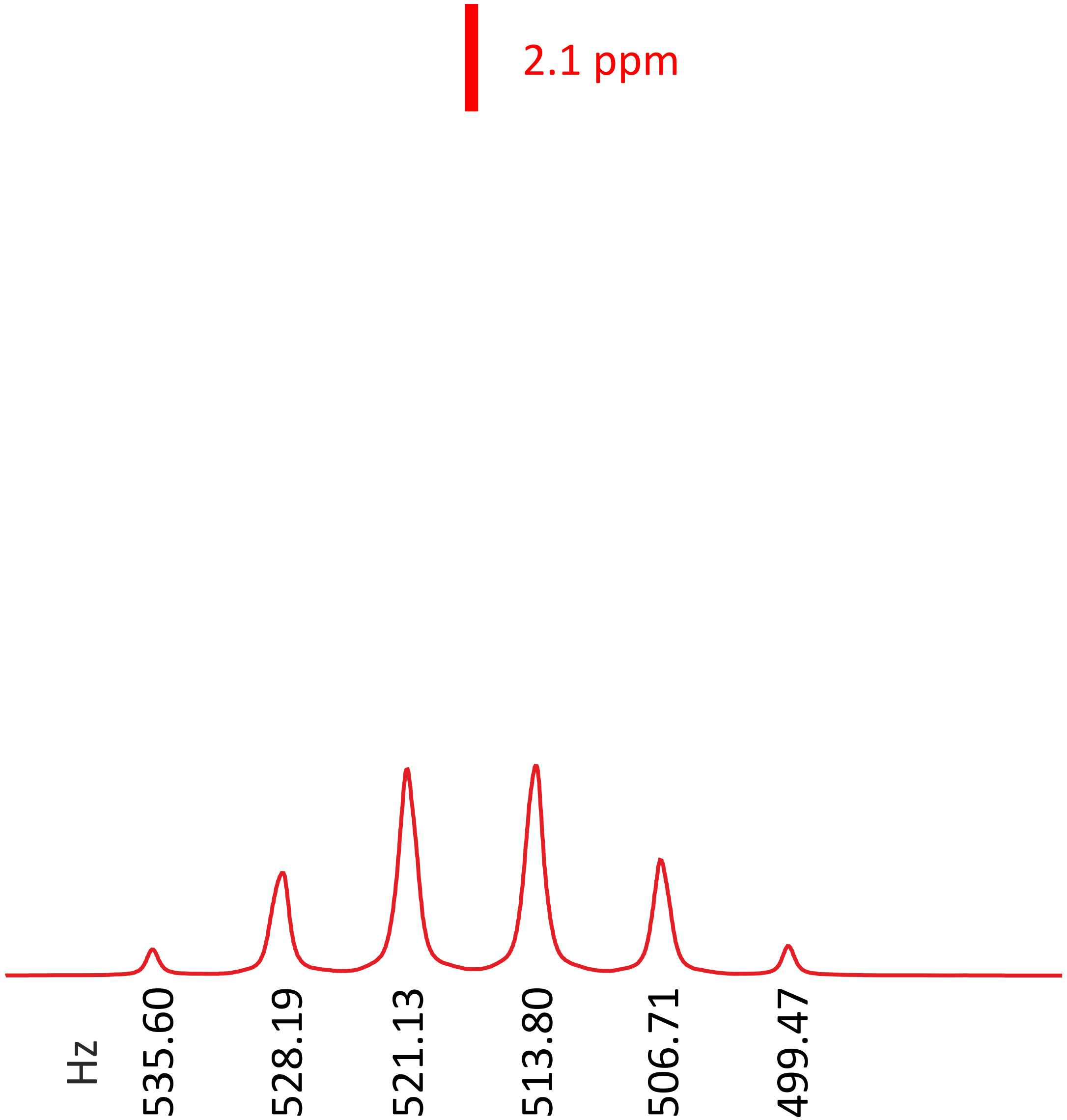
If we compare the fragment found with the molecular formula, **NO_2** remains. This could be a nitro group or a nitrite. Possibly, using an increment scheme for the methylene group at 4.4 ppm, a decision might be possible, but it will not be made here. Nitropropane is much more likely.

$C_3H_7NO_2$



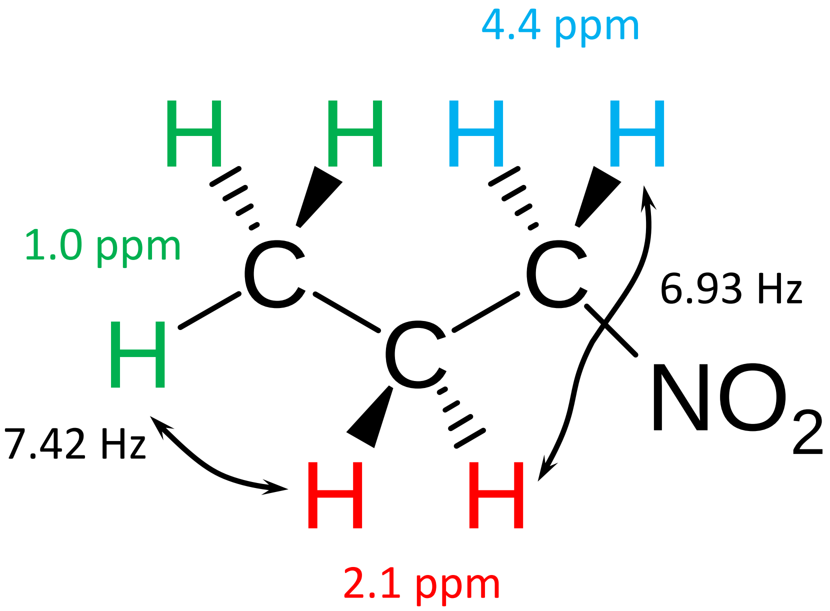
Multiplet structure

A pseudo sextet



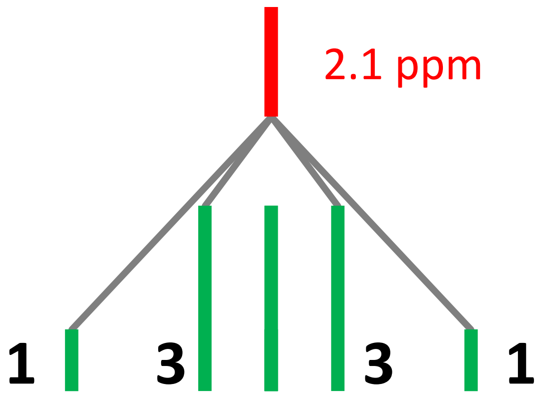
What is the correct explanation of the signal at 2.1 ppm?

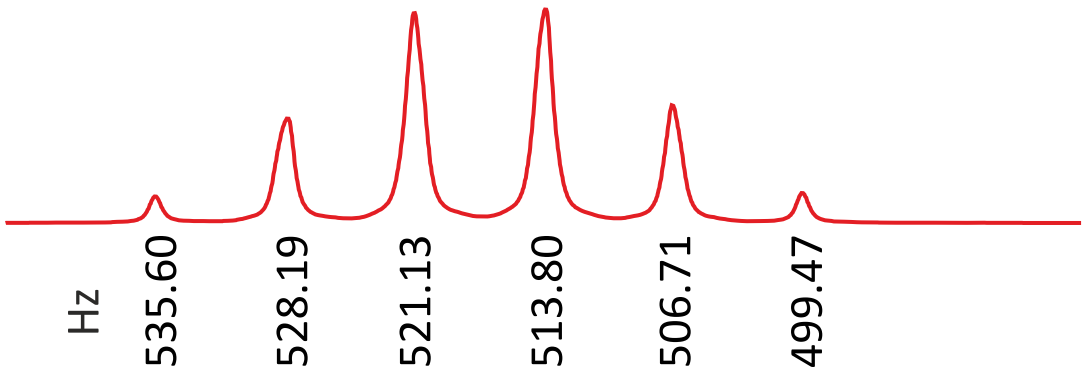
In a first step the neighbouring 3 equivalent protons of the methyl group cause a quartet splitting.



Multiplet structure

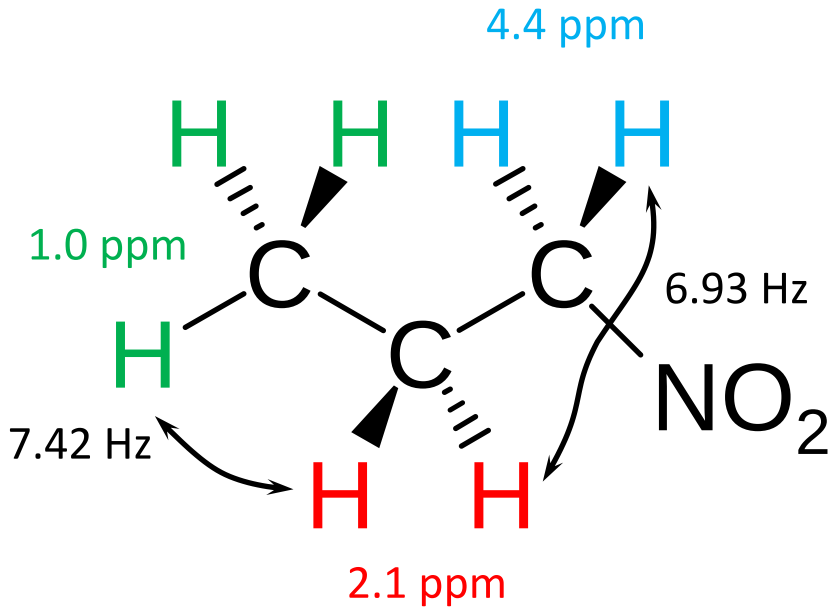
A pseudo sextet





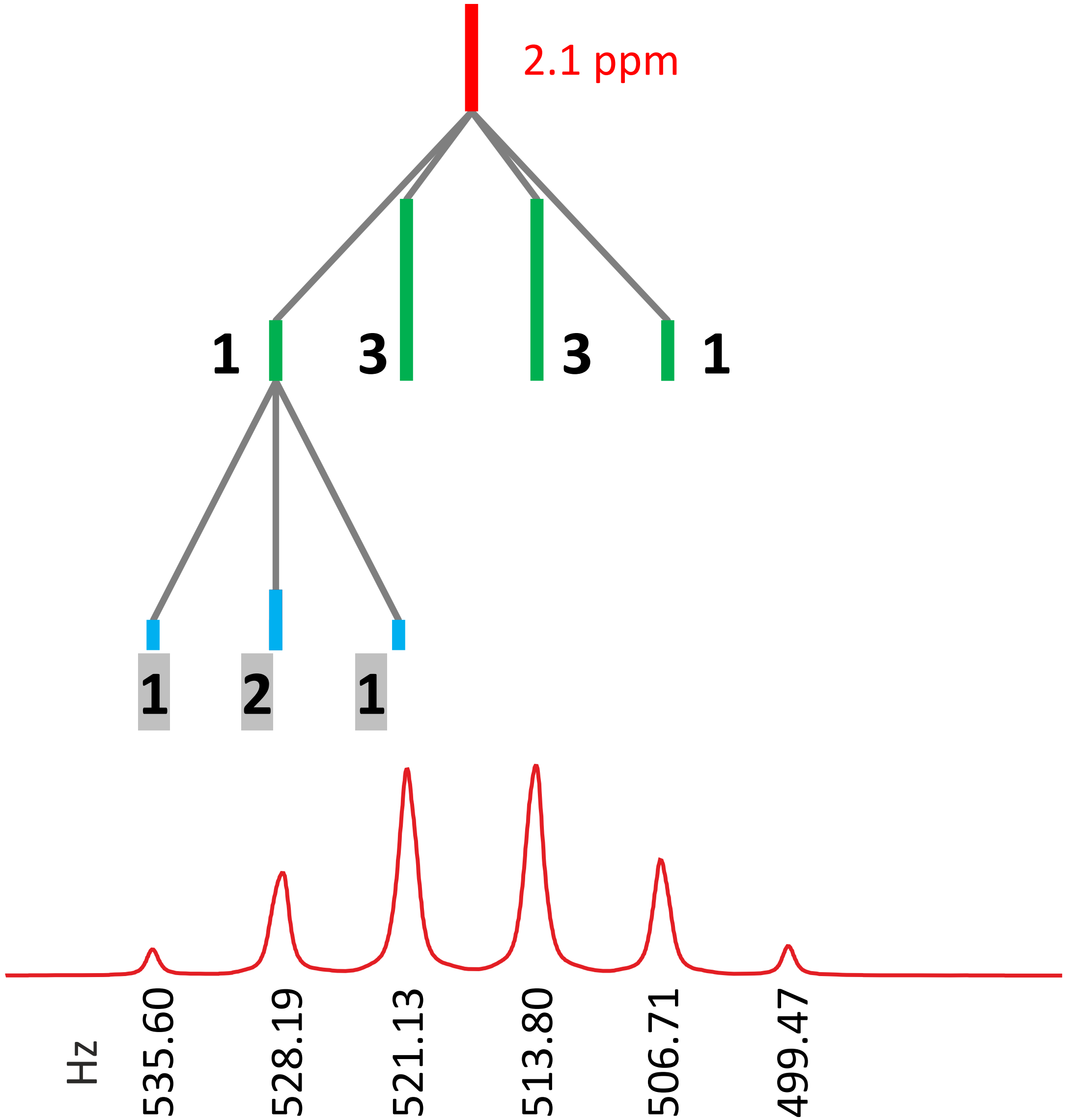
The integral ratio of the four quartet lines is **1 : 3 : 3 : 1**.

A triplet is formed from each of the four lines of the quartet by the two equivalent protons at 4.4 ppm. Let's start with the left line of the quartet.



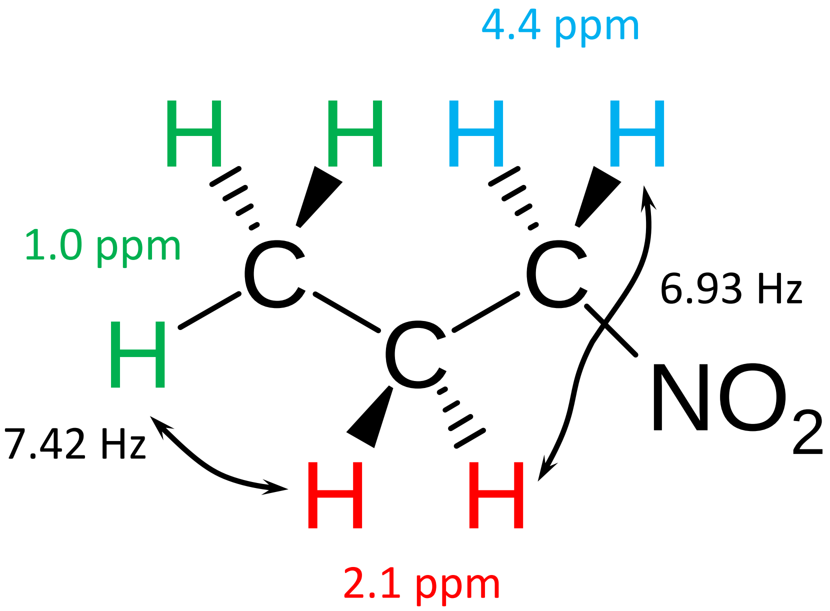
Multiplet structure

A pseudo sextet



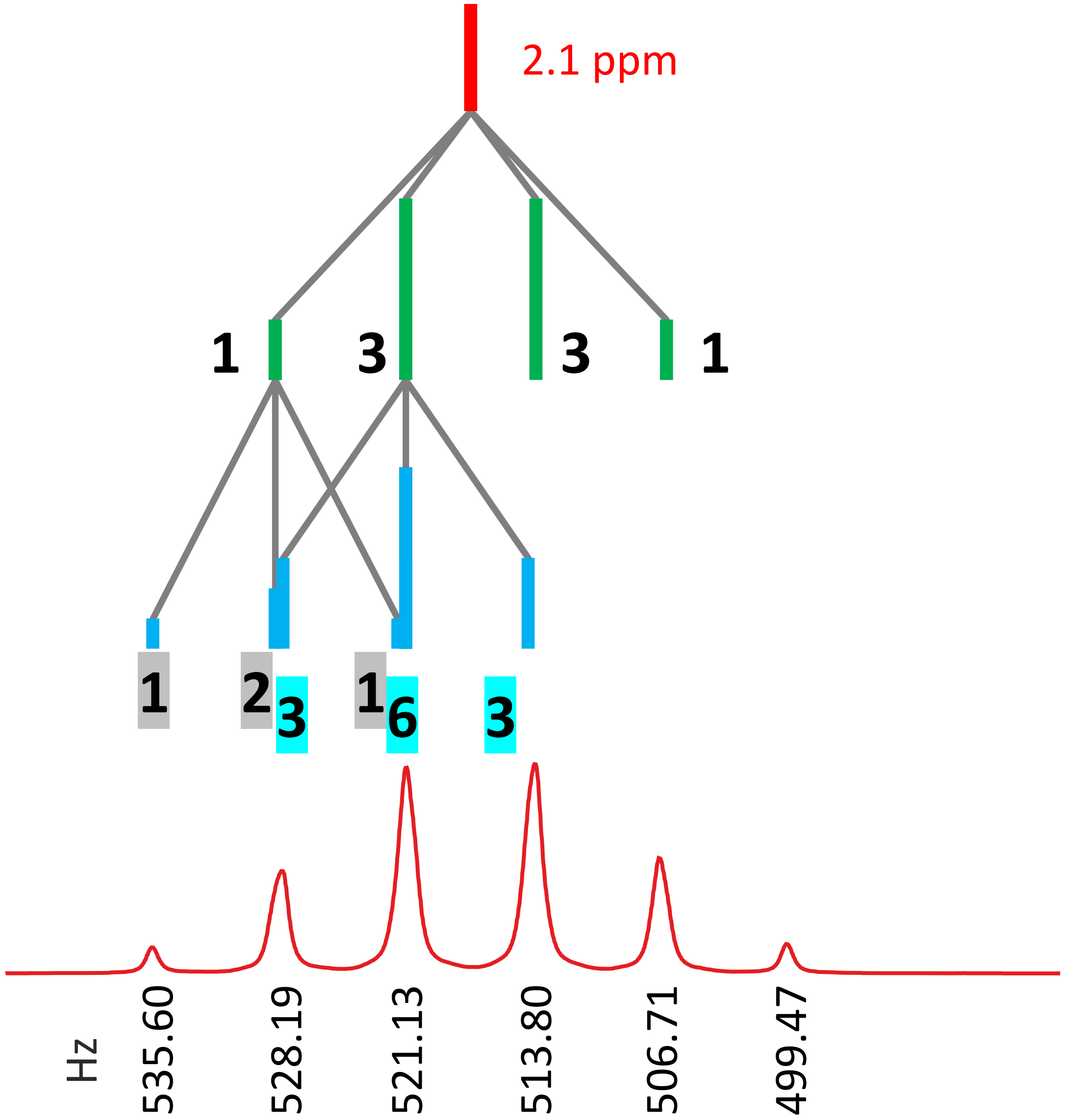
The integral ratio of the three triplet lines is **1 : 2 : 1**.

The second line of the quartet also forms a triplet in the integral ratio **1 : 2 : 1**.



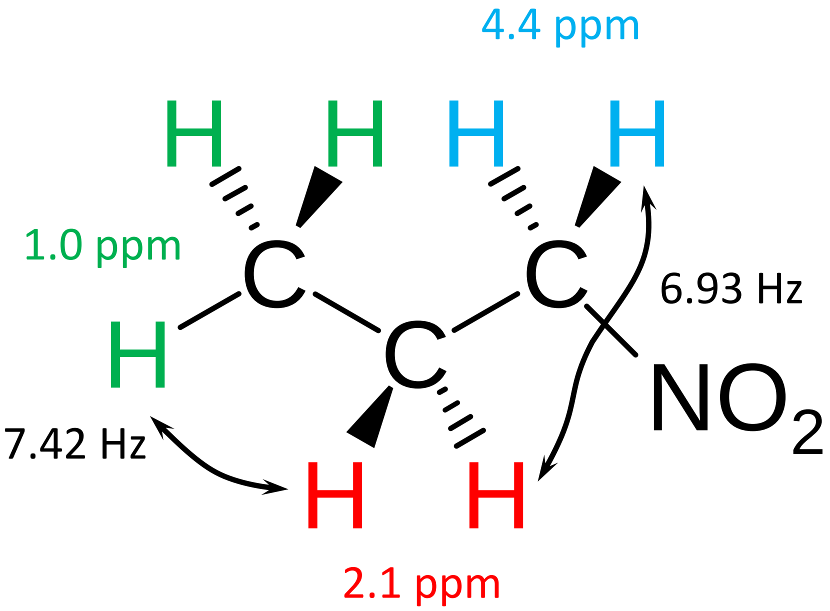
Multiplet structure

A pseudo sextet



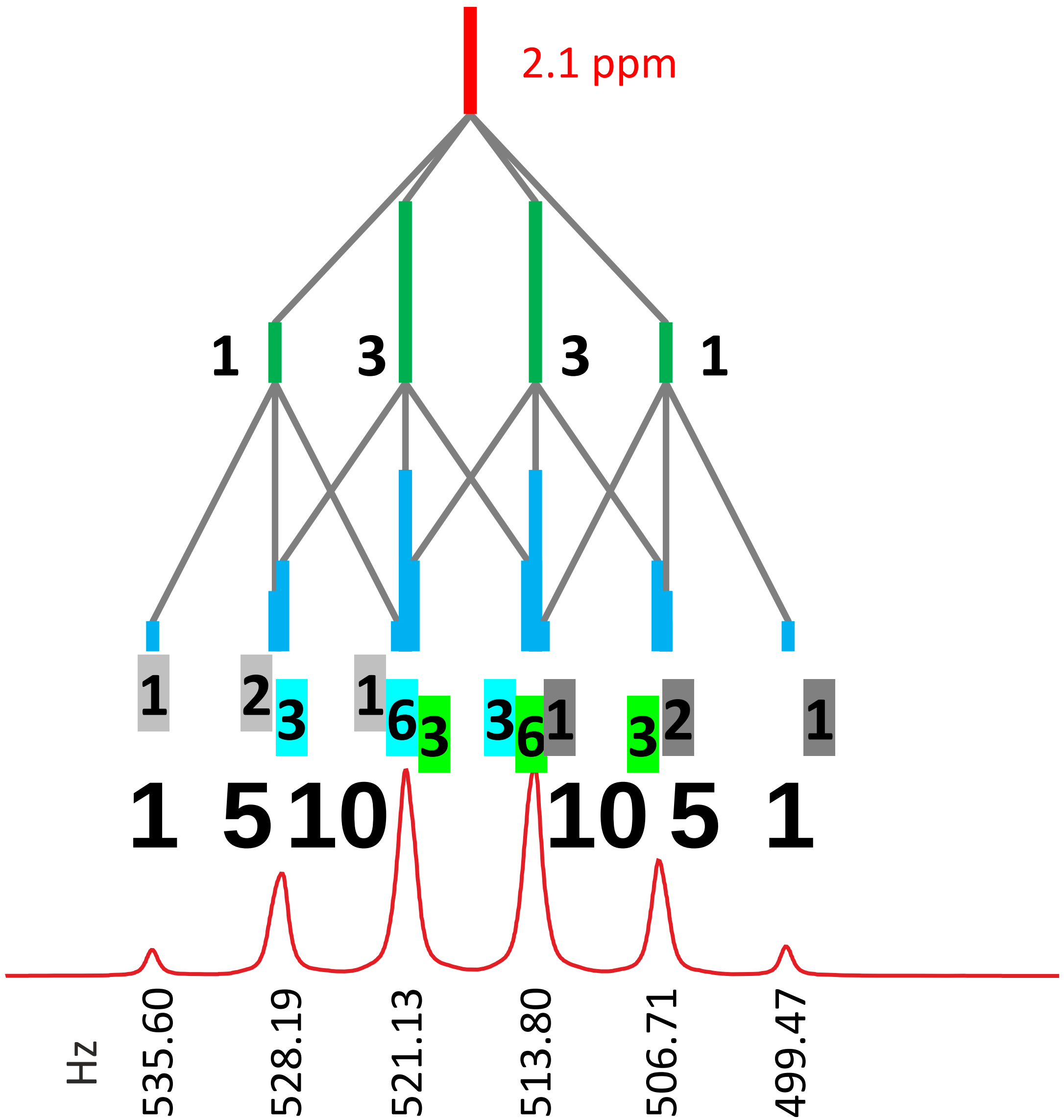
But since we startet from a triple-intensity line of the quartet we also have to triple the ratio from **1 : 2 : 1** to **3 : 6 : 3**.

We can proceed analogously with the two other lines of the quartet.

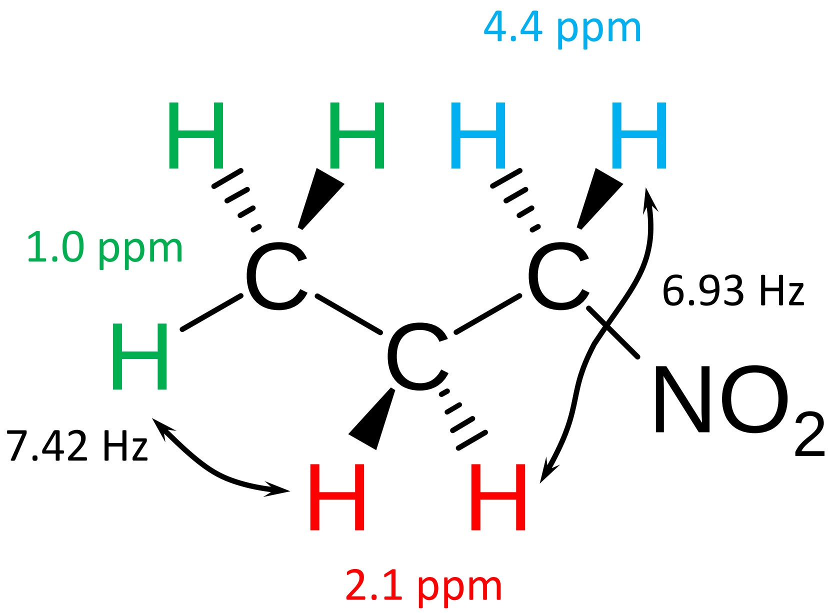


Multiplet structure

A pseudo sextet

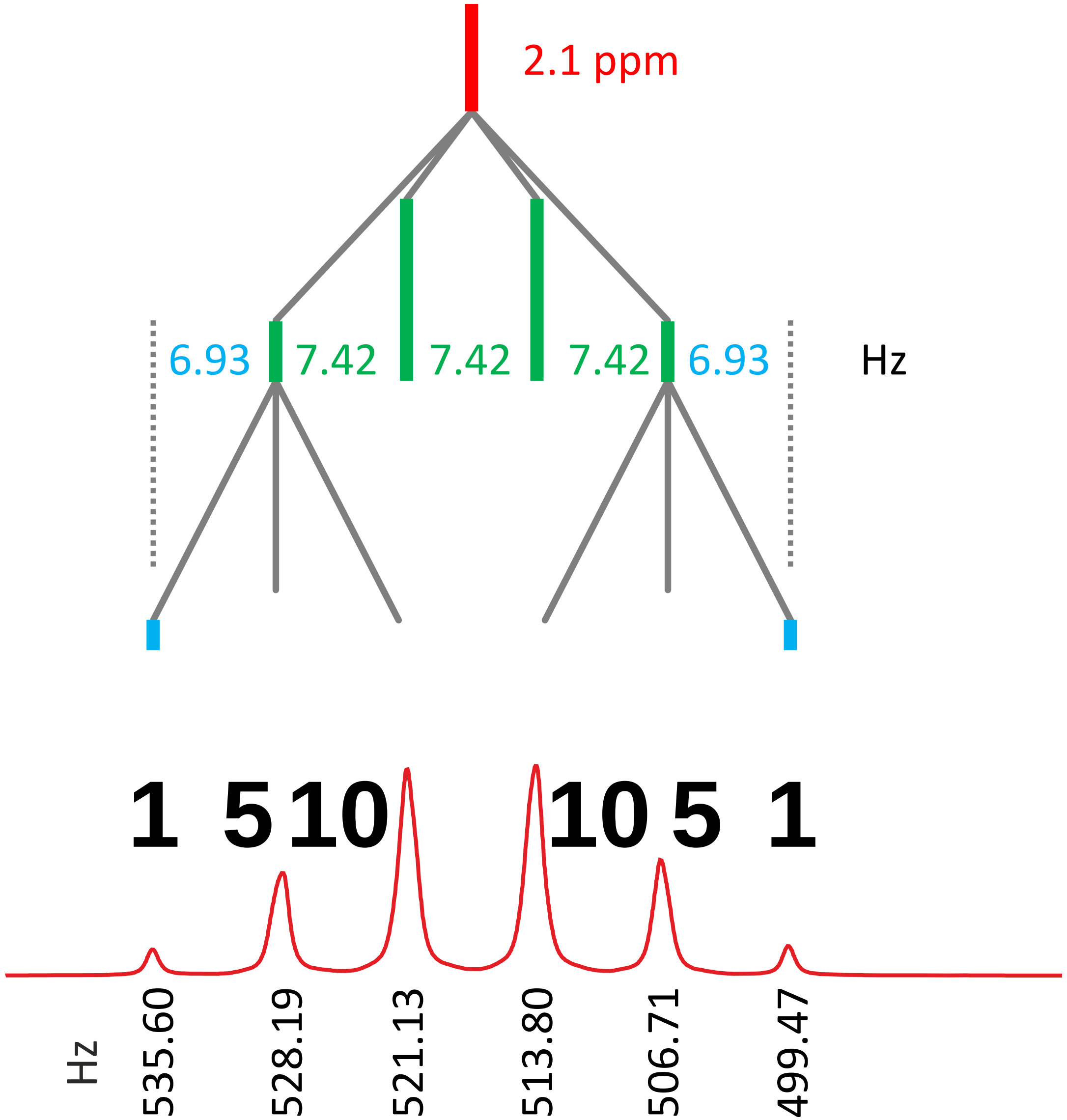


Because of the very similar coupling constants, some of the **12** lines almost coincide. Because of the natural linewidth of the NMR signals, these superimposed lines cannot be observed separately. But we can sum the integrals of the overlapping lines and get an integral ratio of **1 : 5 : 10 : 10 : 5 : 1**.



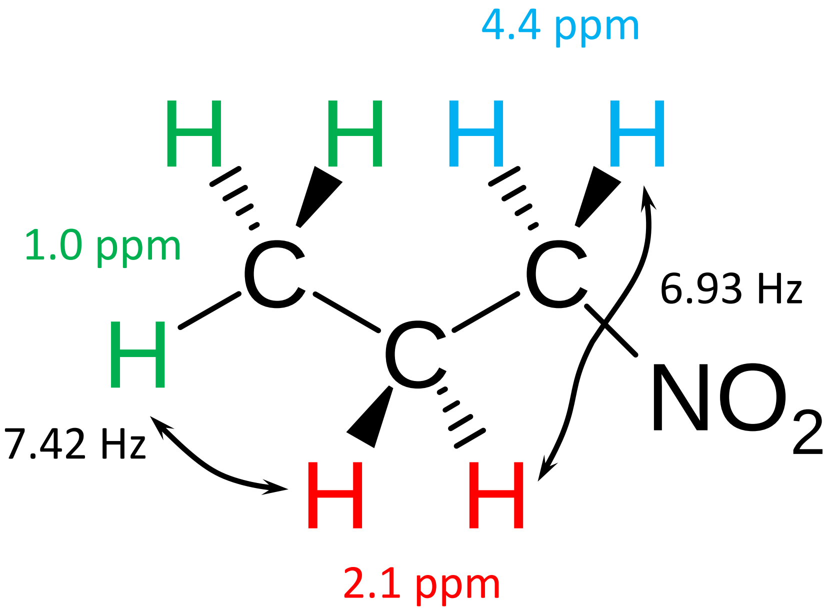
Multiplet structure

A pseudo sextet



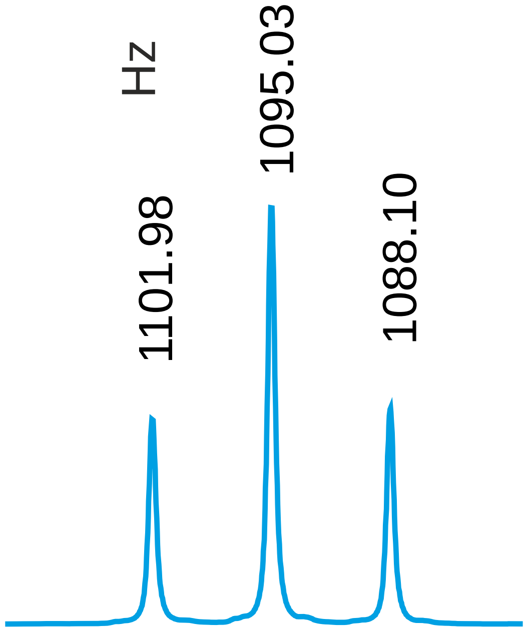
Only the two outermost lines of this pseudo sextet are not superimposed. The frequency difference of these two lines should be 3 * 7.42 + 2 * 6.93 Hz = 36.12 Hz.

The measured frequency difference is 36.13 Hz (535.60 Hz - 499.47 Hz). The distances between the inner lines are linear combinations of 6.93 Hz and 7.42 Hz because of the superposition.



Final remark

The symmetry is tricky

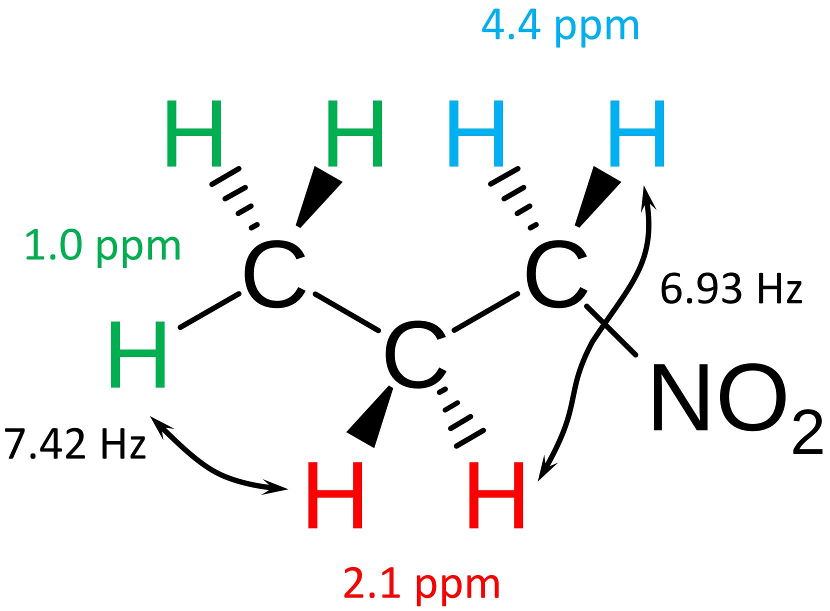


One addition remark for – really very advanced – readers:

The multiplet at 4.4 ppm looks like a perfect triplet.

In fact, the symmetry of the molecule is more subtle than is apparent at first (and even the second, third, …) sight. The explanation, which is by no means simple, is not to be given here.

An example of how much the multiplet in unsymmeric achiral compounds with -CH_2-CH_2- substructure can deviate from the expected triplet structure is 1-Br-2-Cl-ethane (next page).

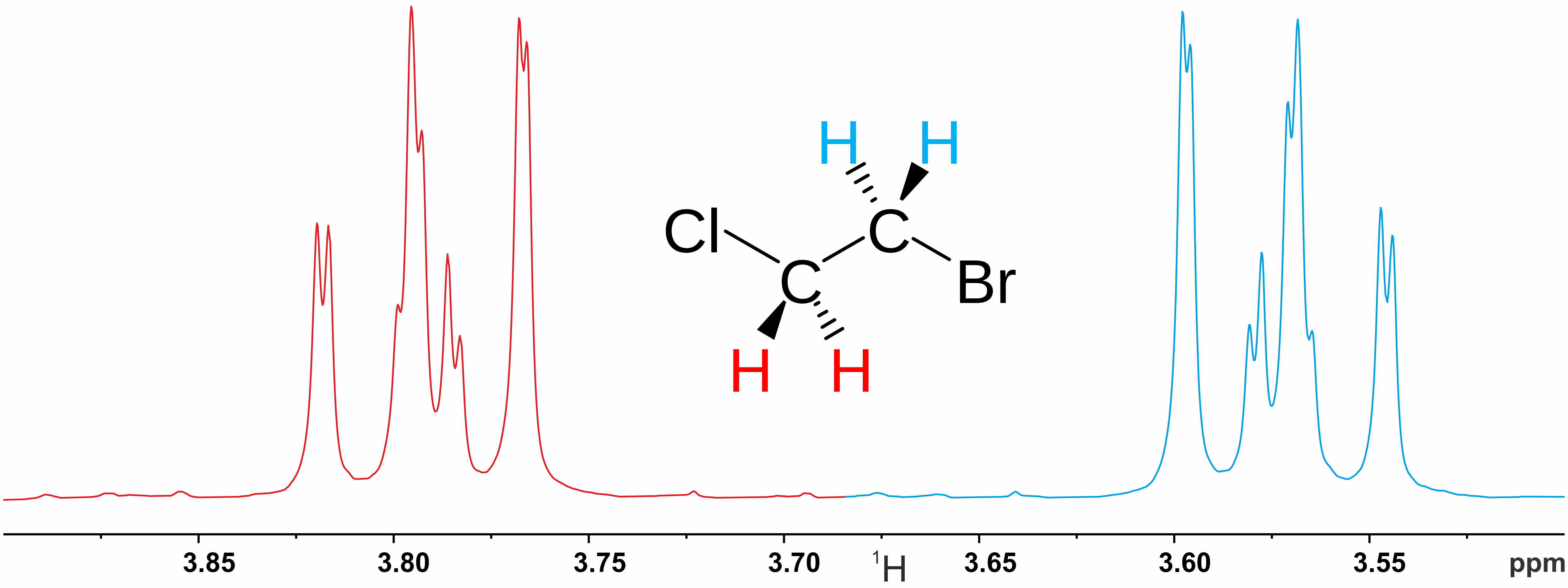


Final remark

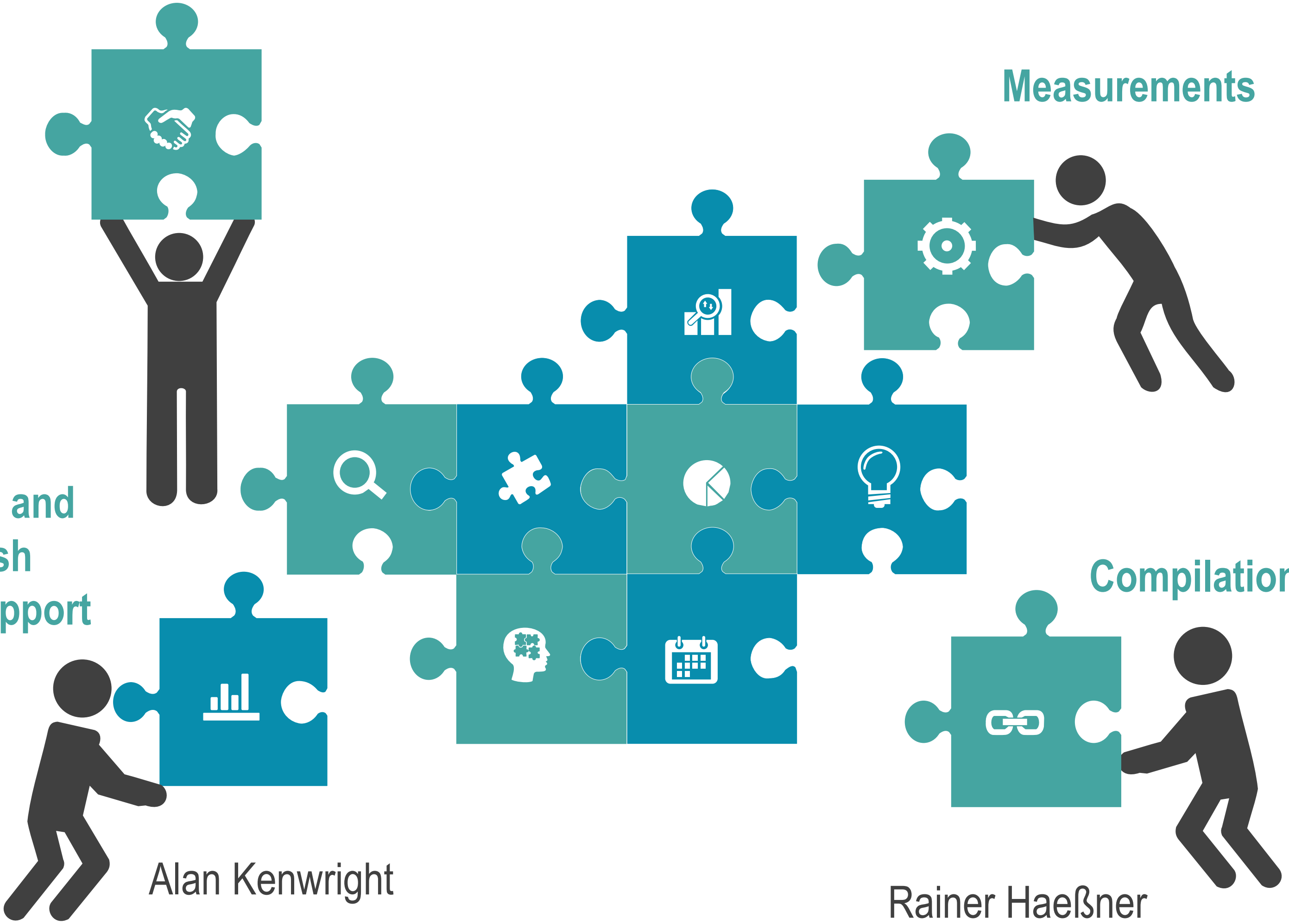
The symmetry is tricky

300.08 MHz

Source: Maik Icker, University Leipzig



Contributions



Spectrometer time

TU Munich
University Leipzig

Measurements

Rainer Haeßner
Maik Icker

Discussions and native English language support

Alan Kenwright

Compilation

Rainer Haeßner

[More exercises …]