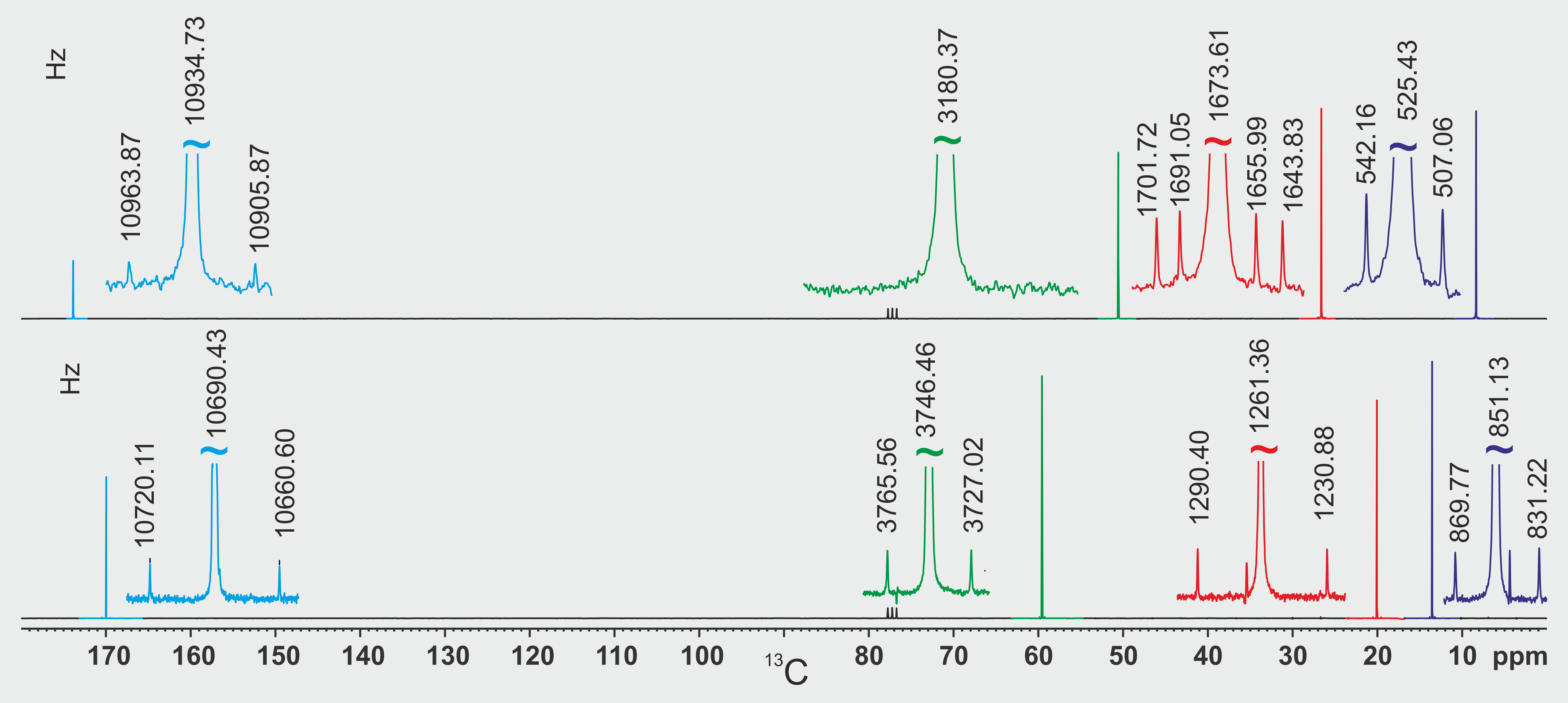
Übung plus Lösung – Schnellüberblick

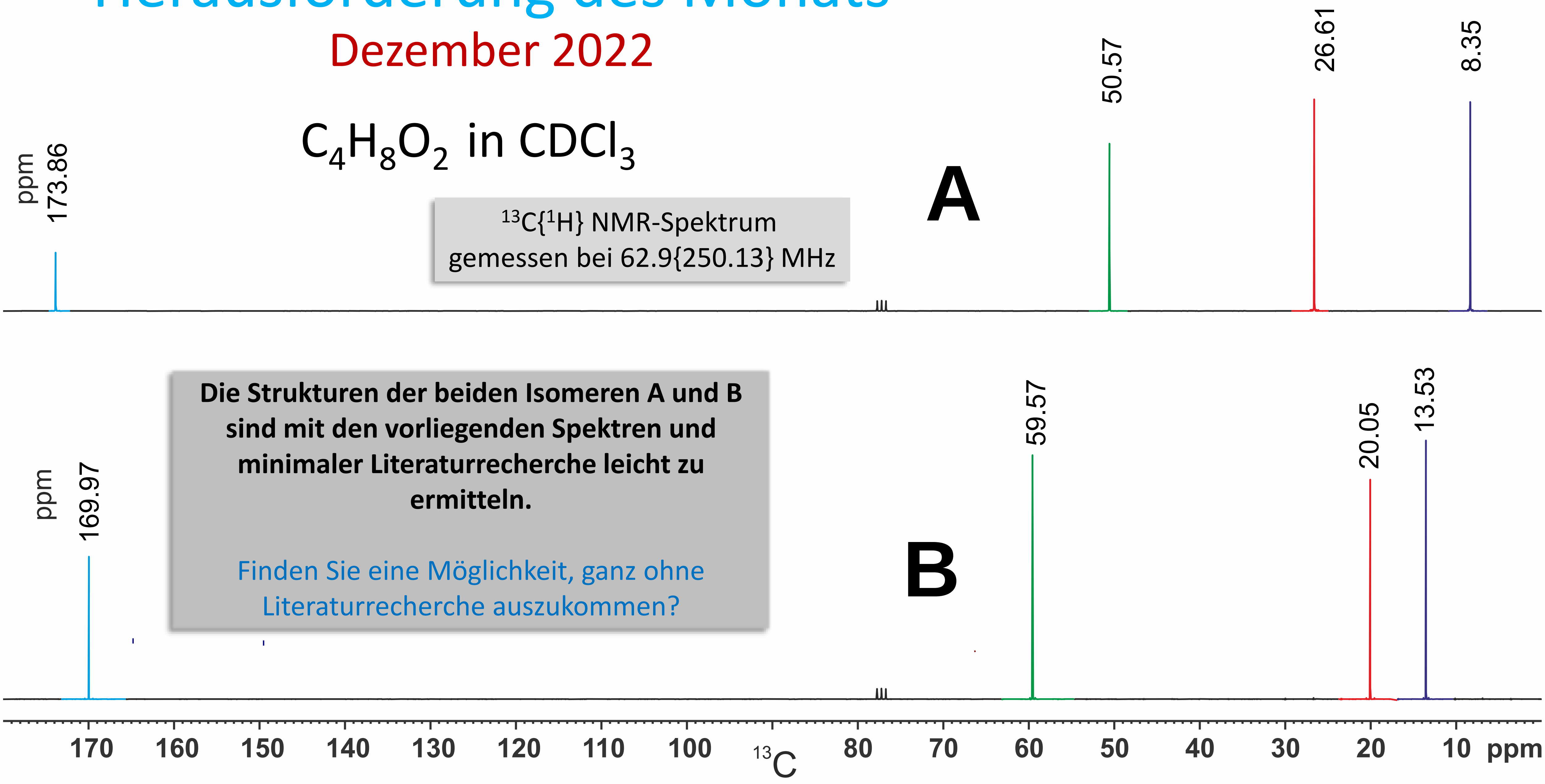
Diese Version soll nur dem schnellen Überblick über die Fragestellung dienen. Sämtliche PowerPoint-Animationen fehlen, in einigen Fällen könnte die Umsetzung von PowerPoint auf PDF merkwürdig aussehen.
Die qualitativ hochwertigen PowerPoint-Originale stehen jederzeit zum freien Download zur Verfügung.



Herausforderung des Monats

Dezember 2022

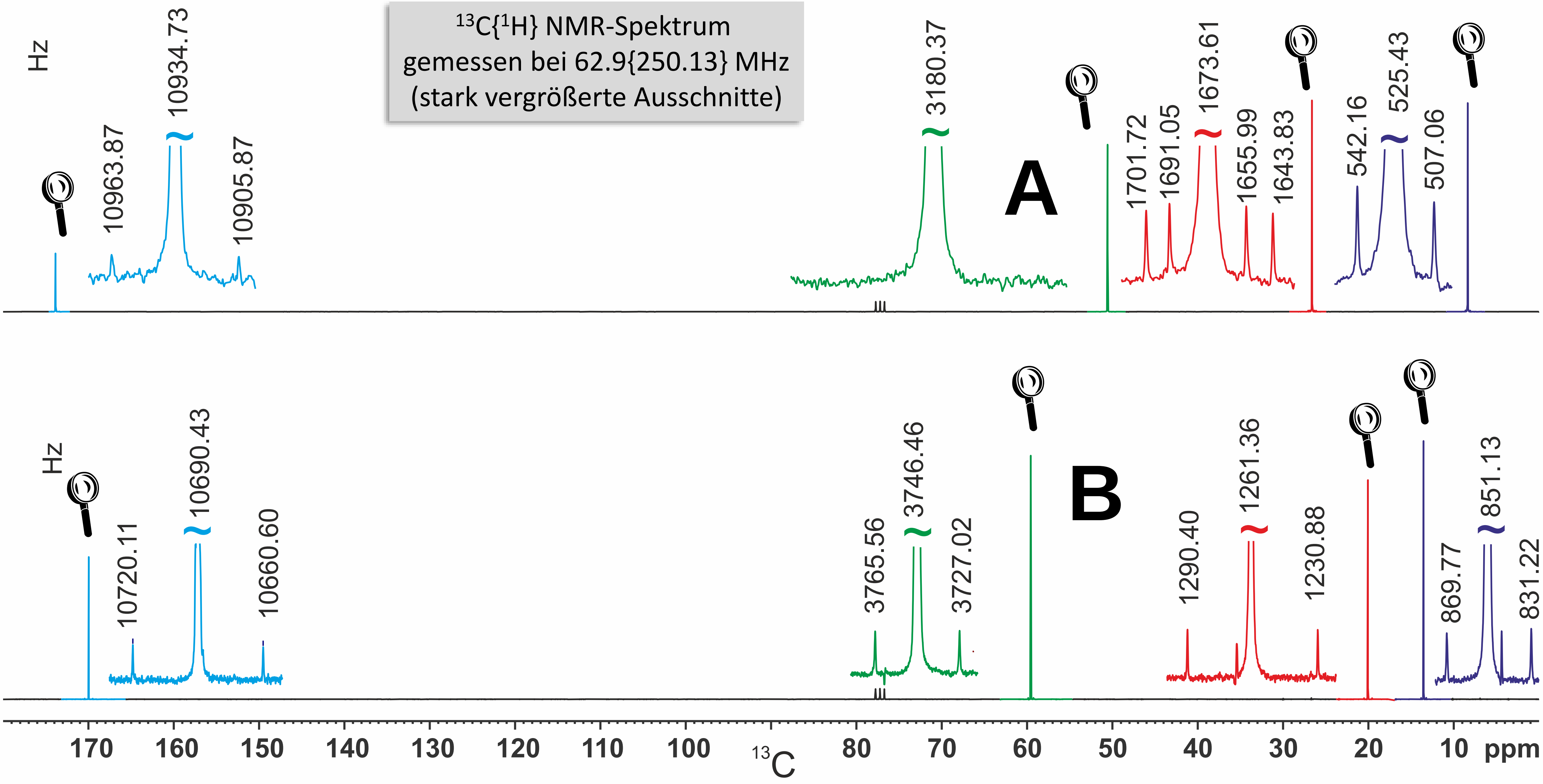
$C_4H_8O_2$ in $CDCl_3$

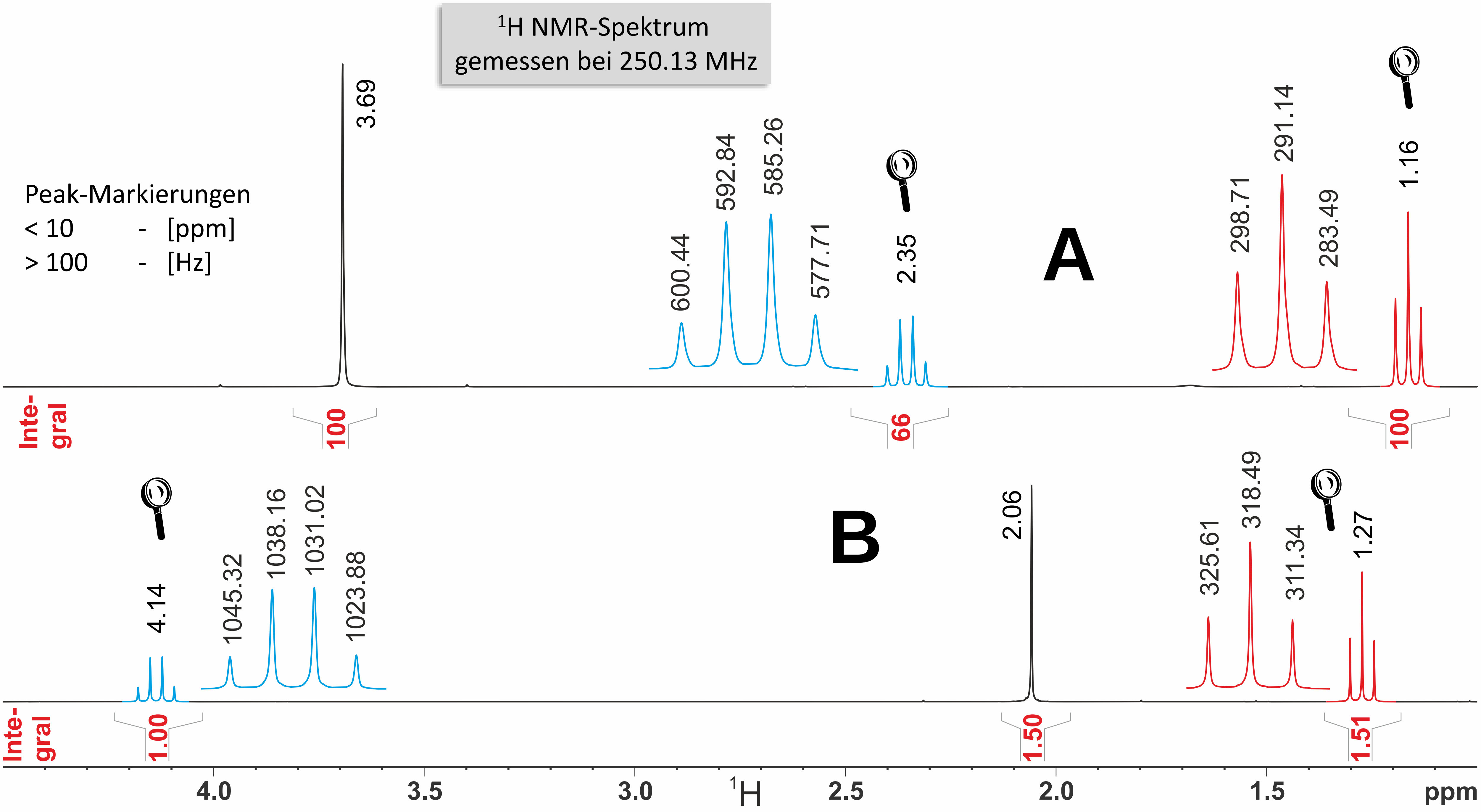


^{13}C{^{1}H} NMR-Spektrum
gemessen bei 62.9{250.13} MHz

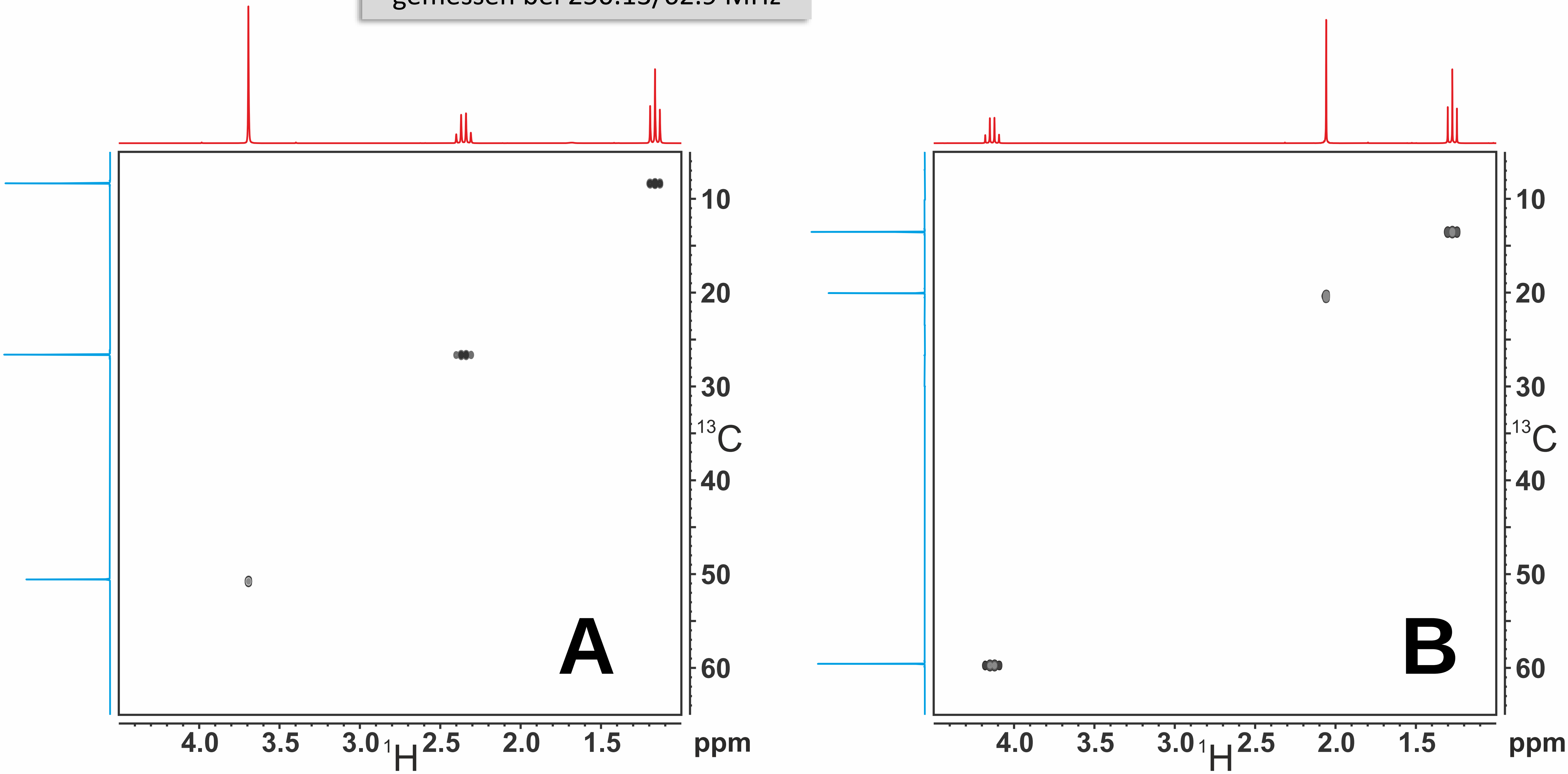
Die Strukturen der beiden Isomeren A und B sind mit den vorliegenden Spektren und minimaler Literaturrecherche leicht zu ermitteln.

Finden Sie eine Möglichkeit, ganz ohne Literaturrecherche auszukommen?

$^{13}C\{^1H\}$ NMR-Spektrum
gemessen bei 62.9{250.13} MHz
(stark vergrößerte Ausschnitte)
Hz
10963.87
10934.73
10905.87
3180.37
A
1701.72
1691.05
1673.61
1655.99
1643.83
542.16
525.43
507.06
Hz
10720.11
10690.43
10660.60
3765.56
3746.46
3727.02
B
1290.40
1261.36
1230.88
869.77
851.13
831.22
170
160
150
140
130
120
110
100
^{13}C
80
70
60
50
40
30
20
10
ppm


1H NMR-Spektrum
gemessen bei 250.13 MHz
Peak-Markierungen
< 10 - [ppm]
> 100 - [Hz]
A
3.69
600.44
592.84
585.26
577.71
2.35
298.71
291.14
283.49
1.16
Inte-
gral
100
66
100
B
4.14
1045.32
1038.16
1031.02
1023.88
2.06
325.61
318.49
311.34
1.27
Inte-
gral
1.00
1.50
1.51
4.0
3.5
3.0
1H
2.5
2.0
1.5
ppm

$^{1}H/^{13}C$ HSQC
gemessen bei 250.13/62.9 MHz



Herausforderung des Monats

Dezember 2022

Lösung

Grundlagen

Integration,Doppelbindungsäquivalente, Symmetrie

$C_4H_8O_2$ in $CDCl_3$

Als Beispiel der Strukturaufklärung soll Isomer **B** dienen. Alle nötigen Schritte sind für Isomer **A** völlig identisch.

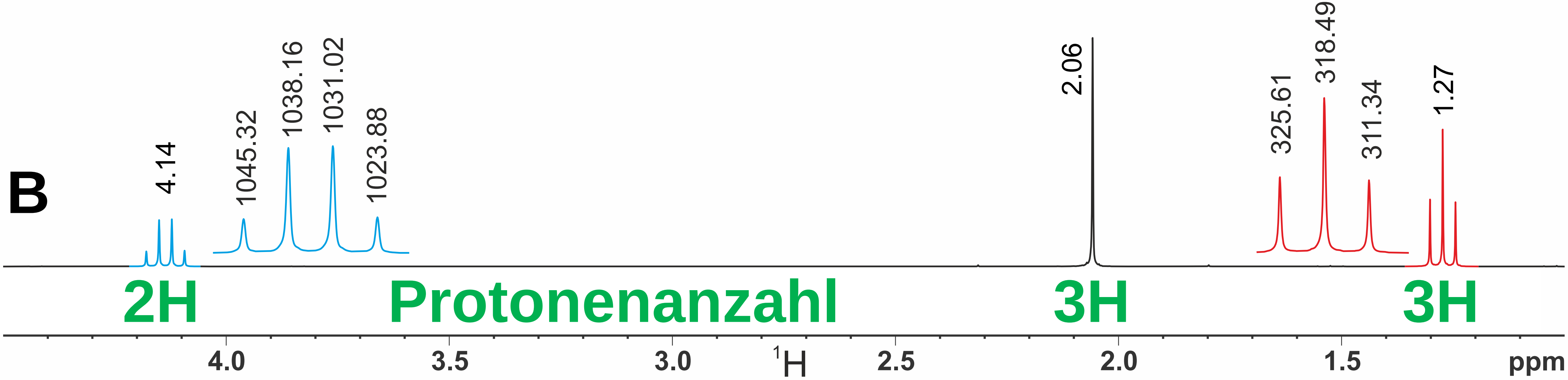
In beiden Isomeren beobachten wir zusätzlich zur identischen Summenformel:

- die gleiche Zahl an Kohlenstoffsignalen und
- die gleichen Protonenmultipletts mit jeweils korrespondierenden gleichen Integralen.

Der Hauptunterschied besteht in

- der chemischen Verschiebung des Quartetts.

Isomer **B** lässt sich sehr einfach integrieren. Es sind lediglich die gegebenen Integrale mit dem Faktor 2 zu multiplizieren.

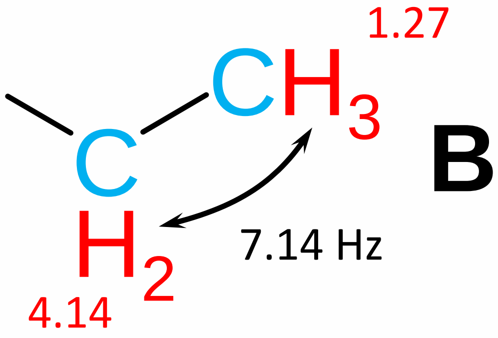


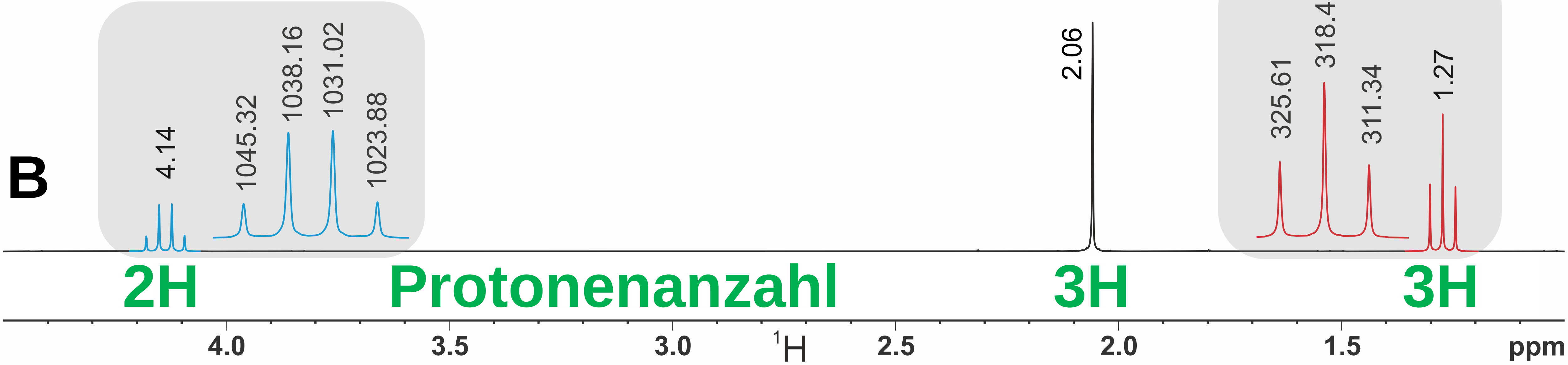
Grundlagen

Integration,Doppelbindungs-äquivalente, Symmetrie

$C_4H_8O_2$ in $CDCl_3$

Es gibt nur zwei Multipletts, beide mit den identischen, sehr typischen Koplungskonstante von **7.14 Hz**. Ein Quartett mit dem Integral 2 und ein Triplett mit dem Integral 3 lassen sich leicht durch eine Ethylgruppe erklären.



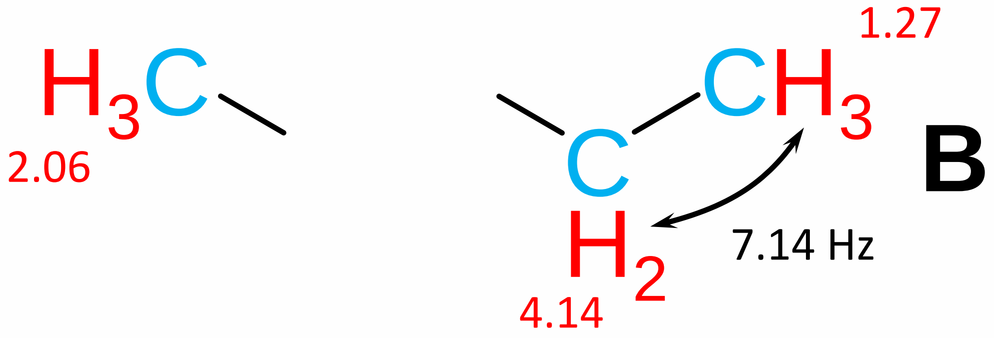


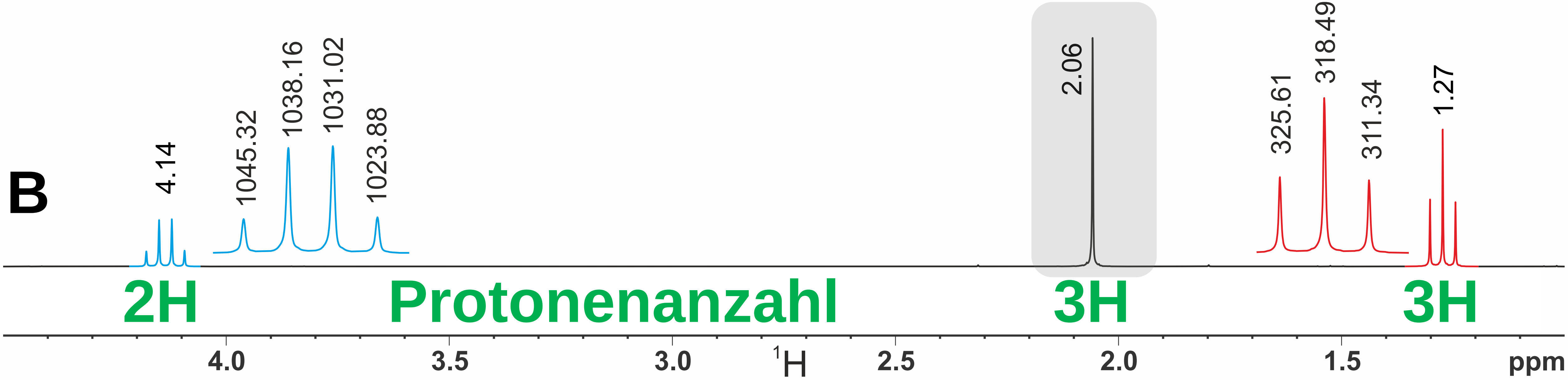
Grundlagen

Integration,Doppelbindungs-äquivalente, Symmetrie

$C_4H_8O_2$ in $CDCl_3$

Ein Singulett mit dem Integral entstammt einer Methylgruppe.





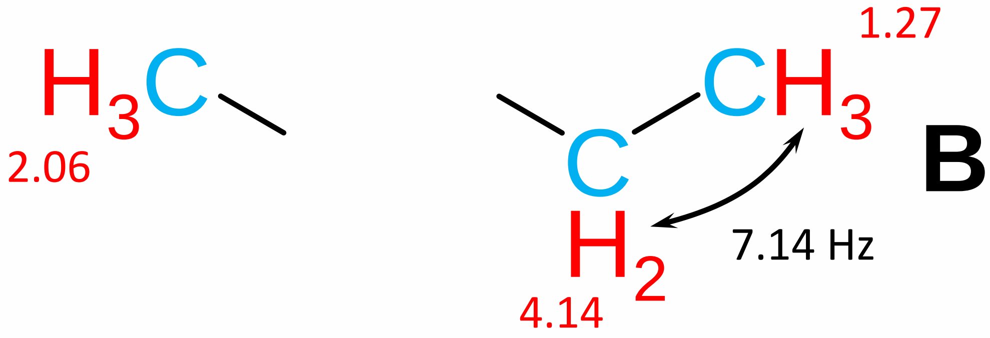
Grundlagen

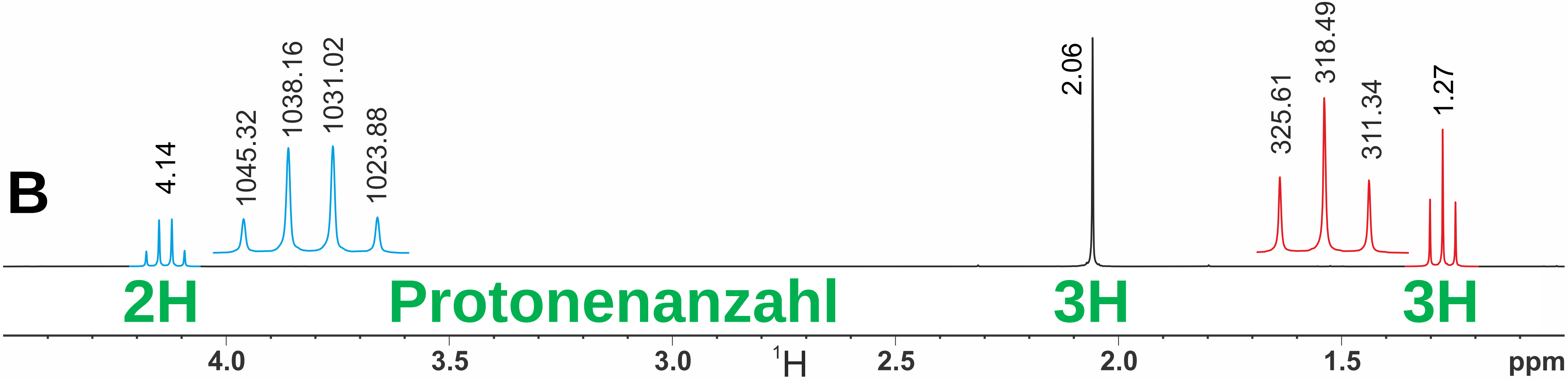
Integration,Doppelbindungsäquivalente, Symmetrie

$C_4H_8O_2$ in $CDCl_3$

Beide Fragmente summieren sich zu C_3H_8, womit noch die folgenden Teile fehlen:

- zwei Sauerstoffatome,
- ein Kohlenstoffatom und
- ein Doppelbindungsäquivalent.





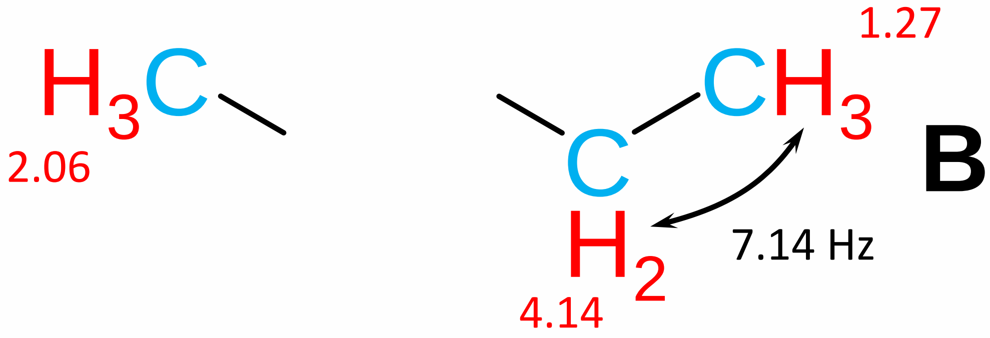
Grundlagen

Integration,Doppelbindungs-äquivalente, Symmetrie

$C_4H_8O_2$ in $CDCl_3$

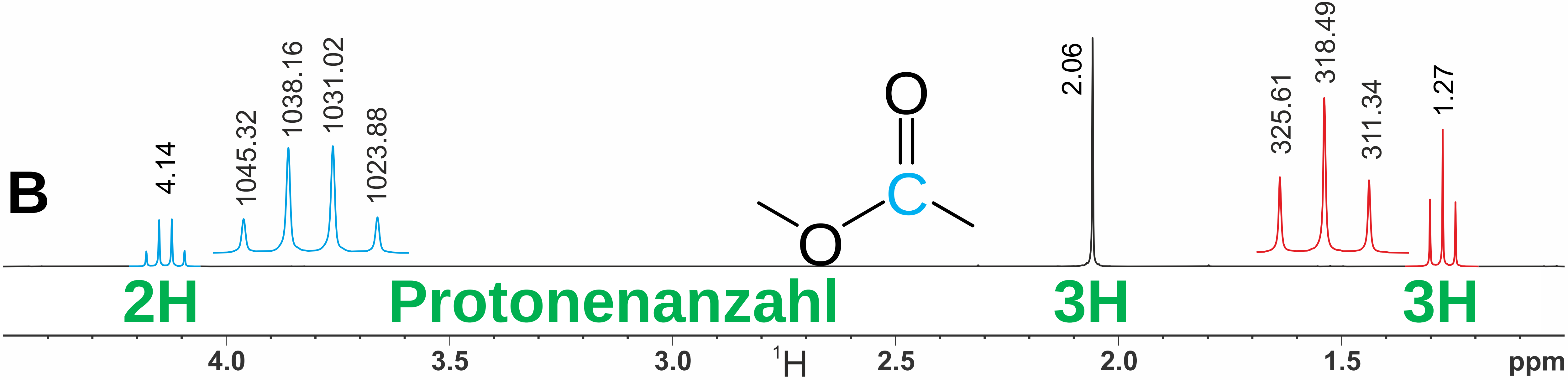
Beide Fragmente summieren sich zu C_3H_8, womit noch die folgenden Teile fehlen:

- zwei Sauerstoffatome,
- ein Kohlenstoffatom und
- ein Doppelbindungsäquivalent.



Daraus ergibt sich ein Baustein, der auf zwei verschiedene Arten zwischen die vorhandenen Fragmente eingefügt werden kann.

Probieren wir einfach Beide aus.



Übersetzung in Arbeit
Letzter Bearbeitungsstand: 7. 12. 2021

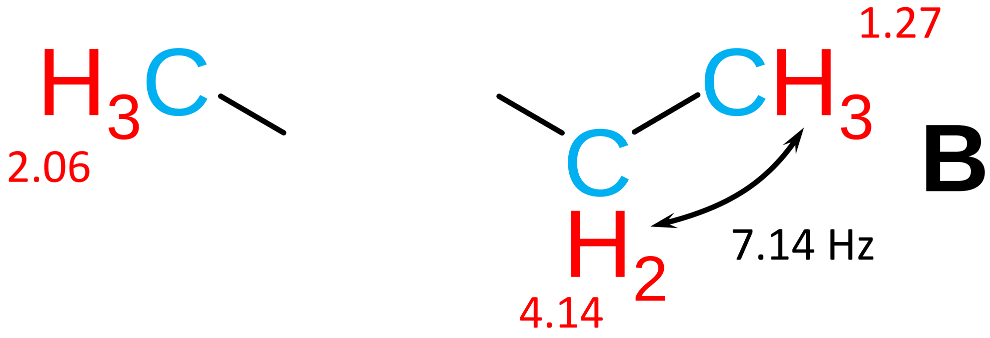
Grundlagen

Integration,Doppelbindungs-
äquivalente, Symmetrie

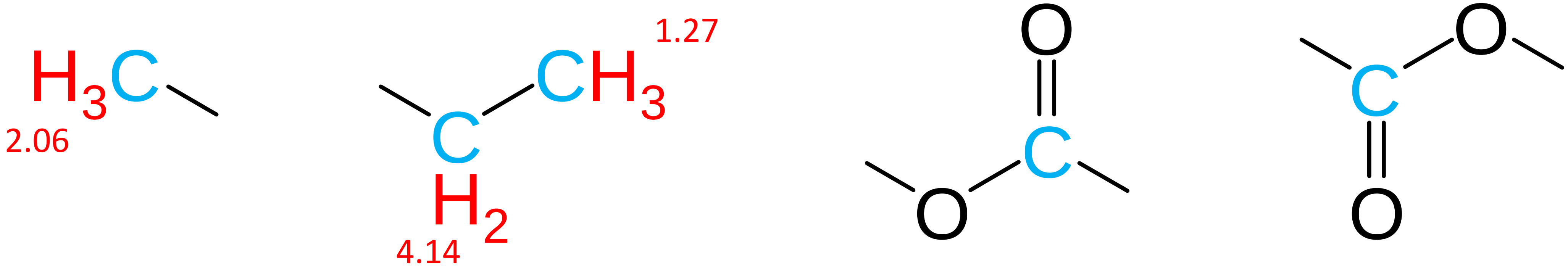
$C_4H_8O_2$ in $CDCl_3$

What we have to do is to create a copy of all already known pieces of information with a minor different geometric orientation of the –CO–O– group.

Now there are two possible final structures.



B



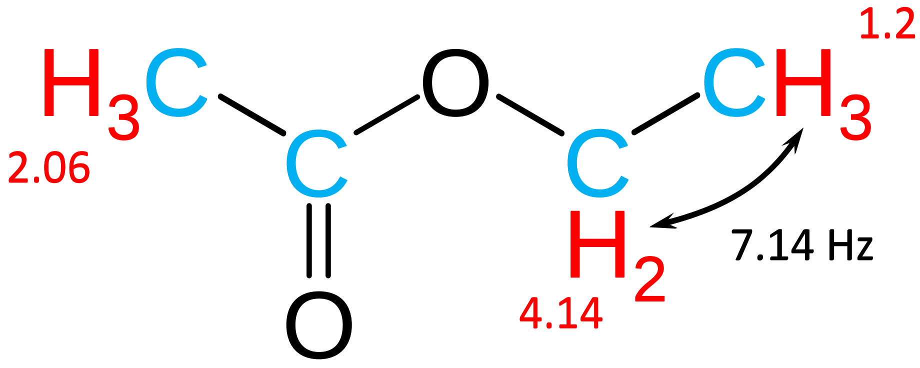
Grundlagen

Integration,Doppelbindungs-äquivalente, Symmetrie

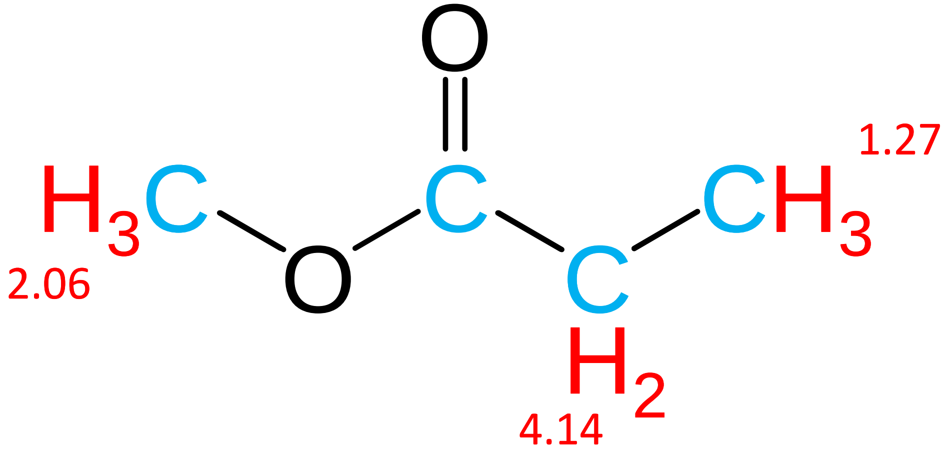
$C_4H_8O_2$ in $CDCl_3$

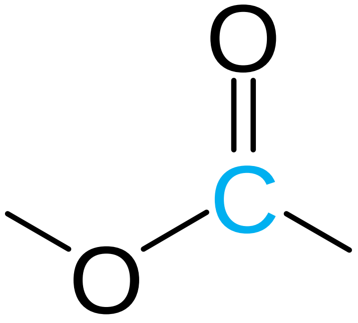
Now there are two possible final structures.

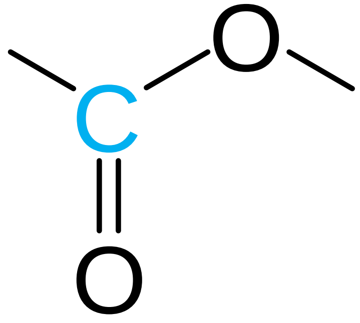
Now there are two possible final structures.



B



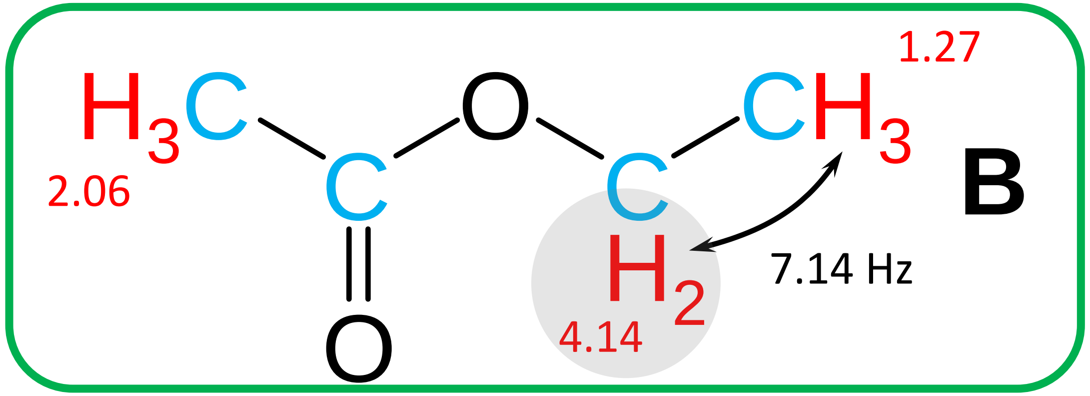




Easy solution

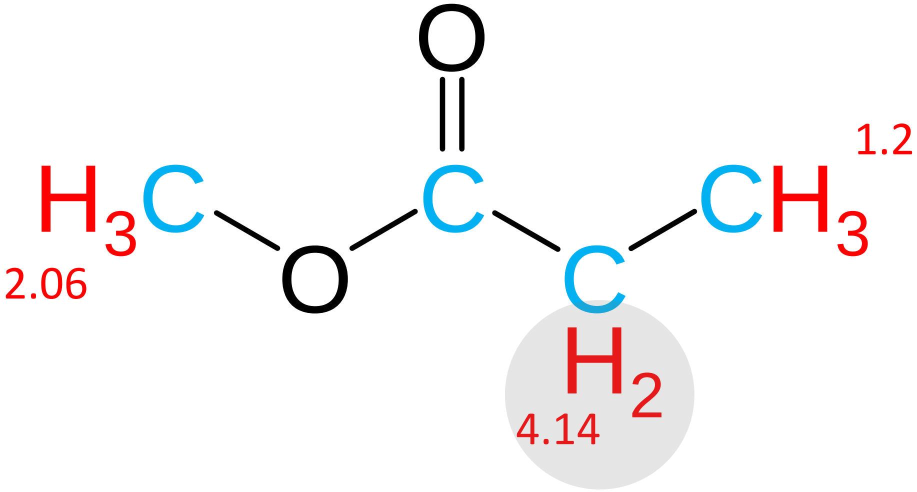
Now there are two possible final structures.

The easiest way to select the correct one is the estimation of the chemical shifts of the methylene protons. That‘s possible using the good old Schoolery rules.



B

$\delta(CH_2) = (0.23 + 0.47 + 3.13)$ ppm = **3.83 ppm**



A

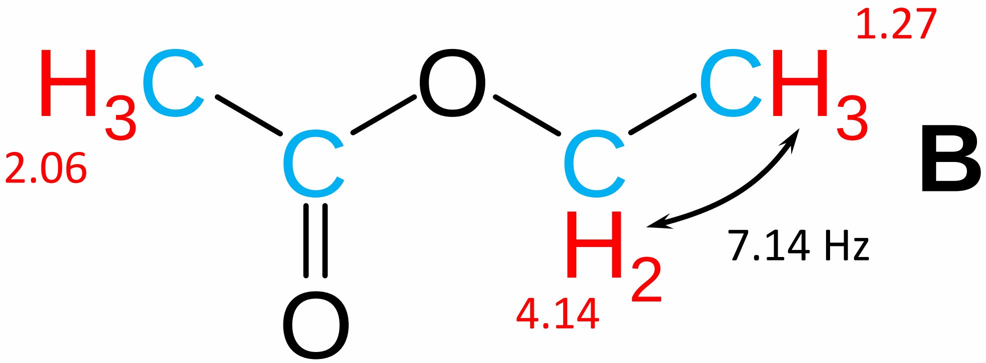
$\delta(CH_2) = (0.23 + 0.47 + 1.55)$ ppm = **2.25 ppm**

Apparently this estimation best fits to the upper structure. The lower structure appently belongs to isomer **A**, but of course all chemical shifts derived for isomer **B** are wrong. Let‘s remove all of them.

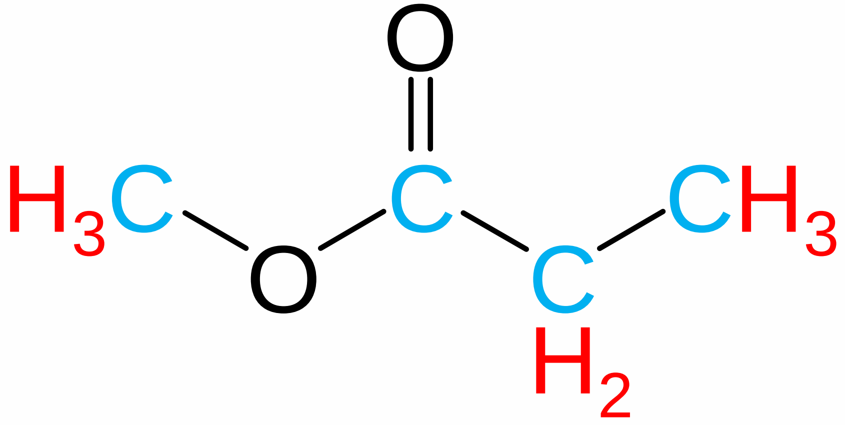
Full assignment

Carbon signals

We didn‘t assign the carbon chemical shifts so far. For this task, of course, our spectrum of choice is the HSQC.



B



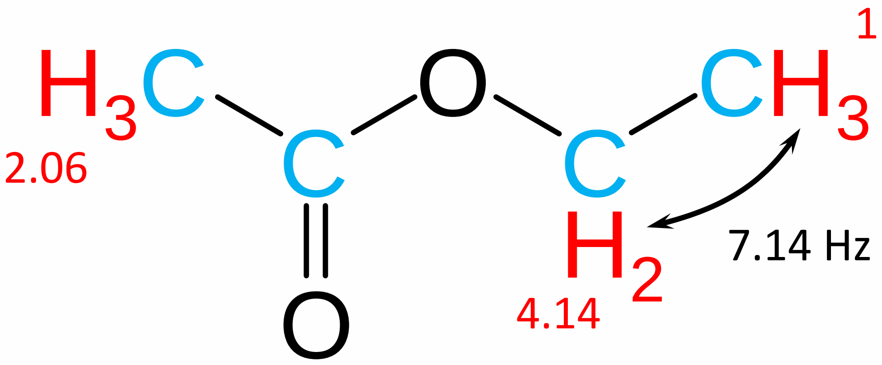
A

Full assignment

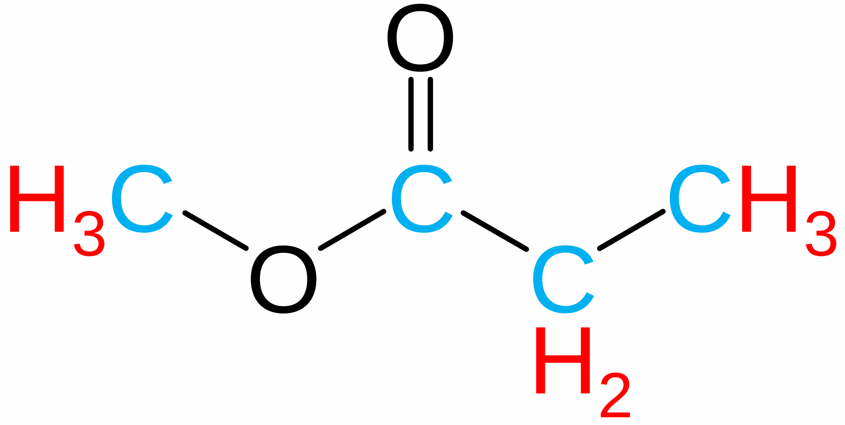
Carbon signals

We didn‘t assign the carbon chemical shifts so far. For this task, of course, our spectrum of choice is the HSQC.

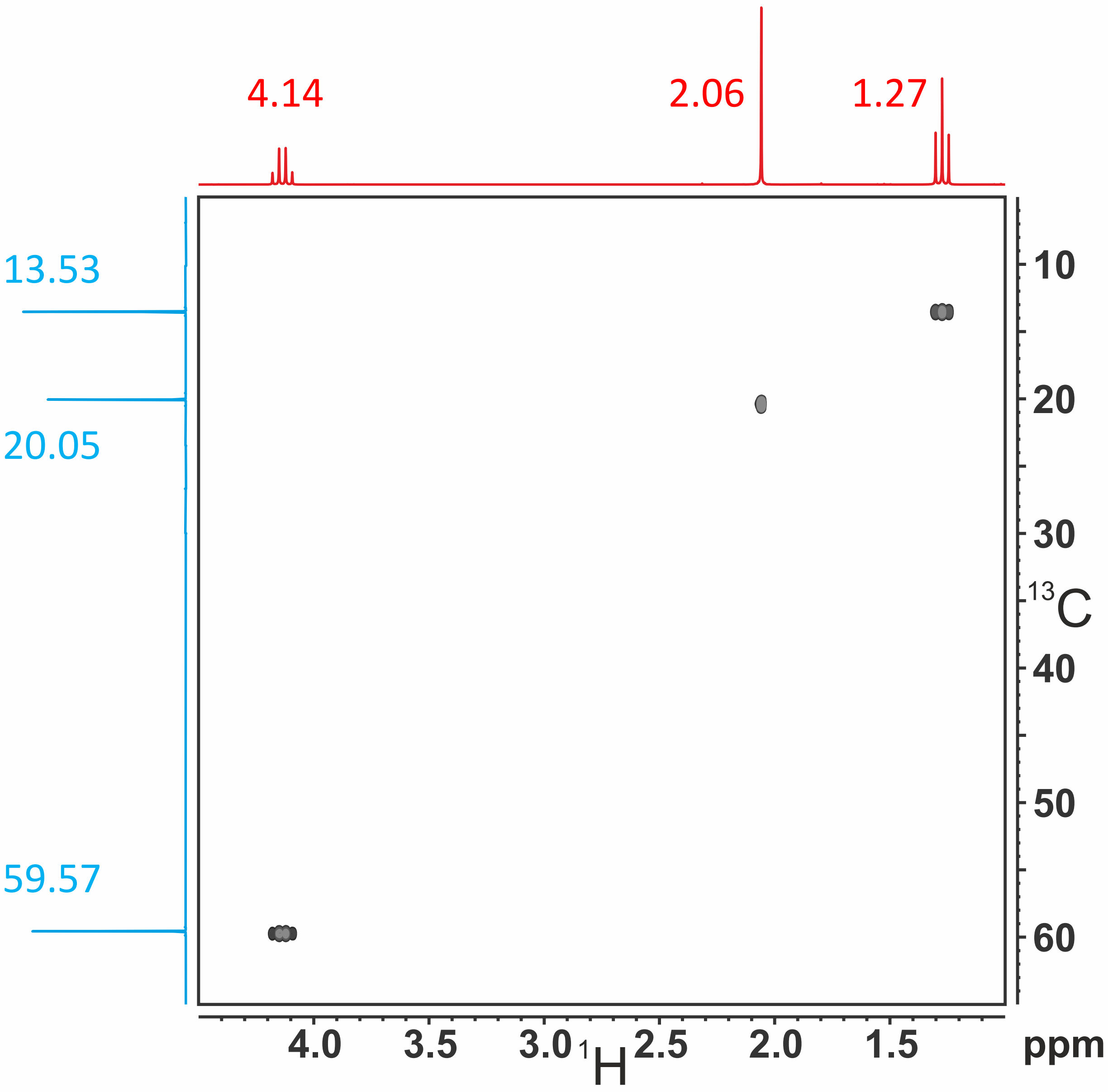
The chemical shifts for the pseudo projections come from the one dimensional proton and carbon spectra.



B

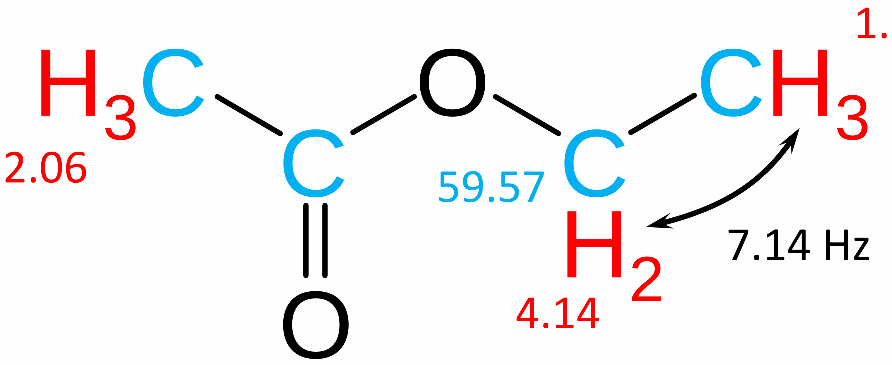


A

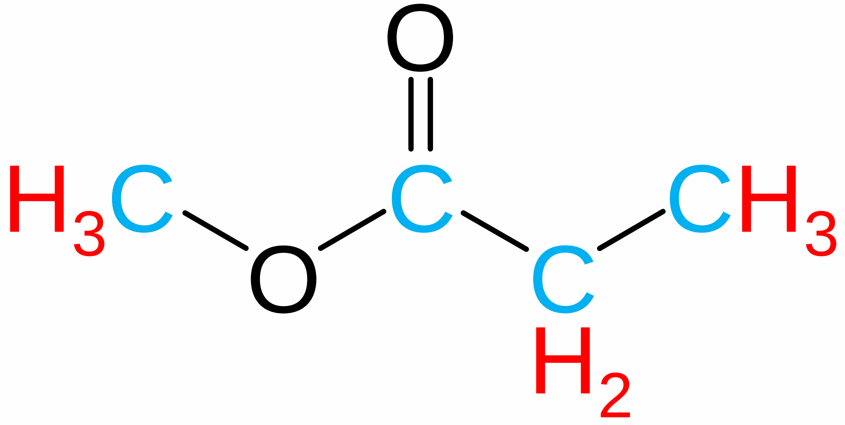


Let‘s select one cross peak to demonstrate the carbon signal assignment in detail.

The assignment procedure for both methyl groups is the same.



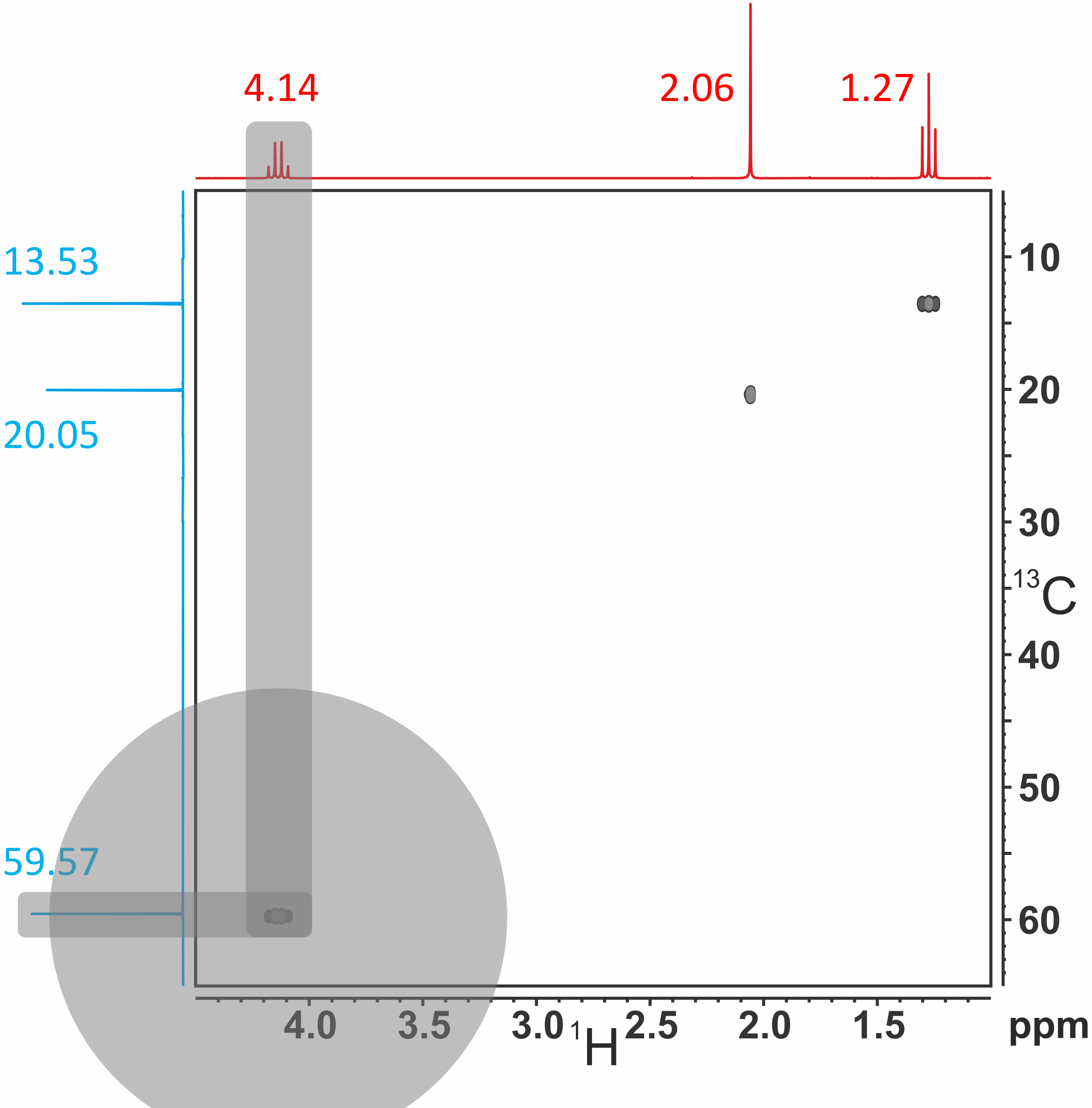
B



A

Full assignment

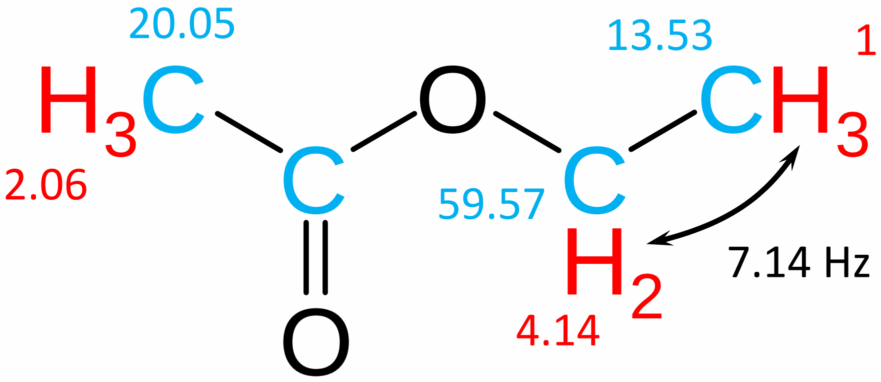
Carbon signals



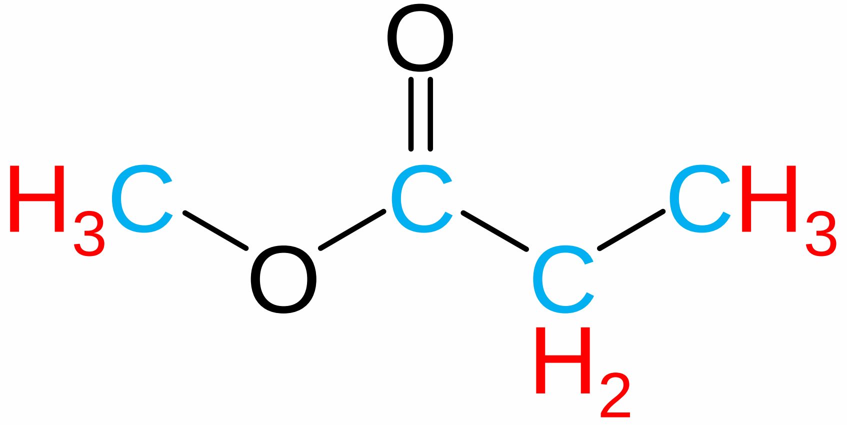
Full assignment

Carbon signals

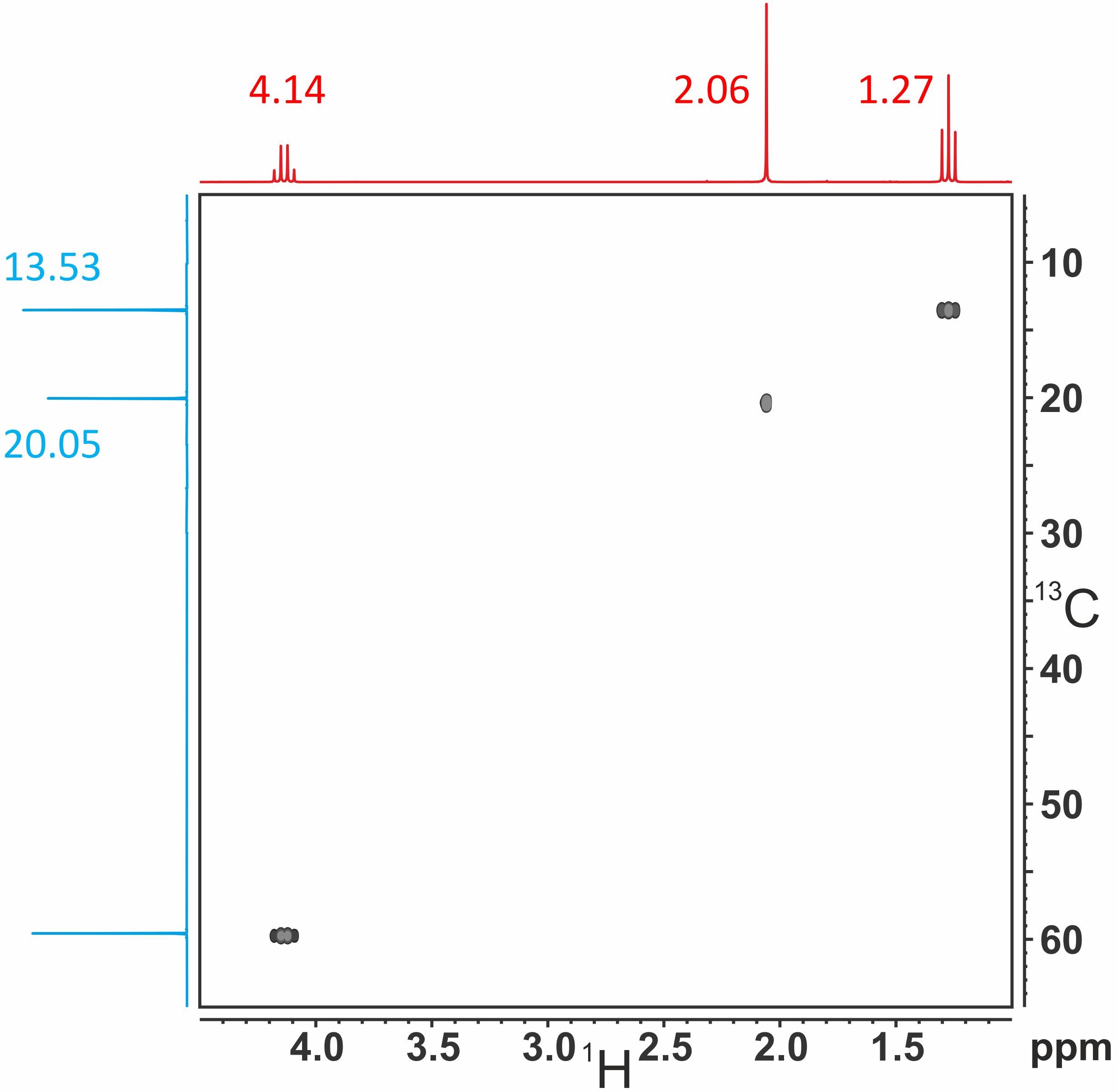
The assignment procedure for both methyl groups is the same.



B



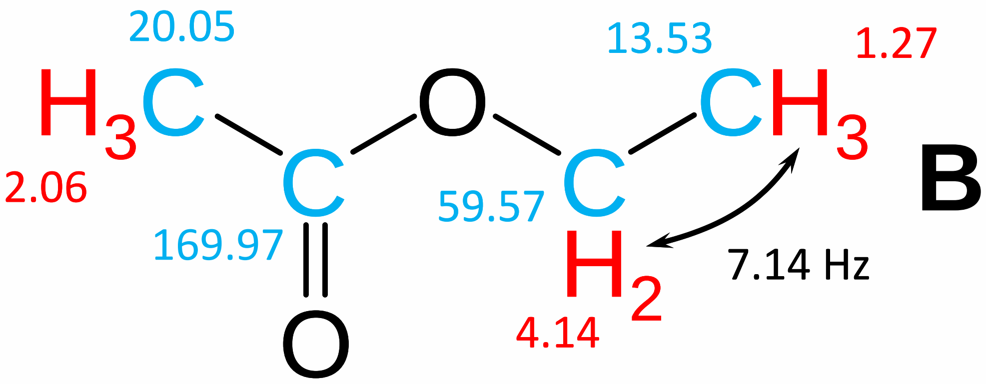
A



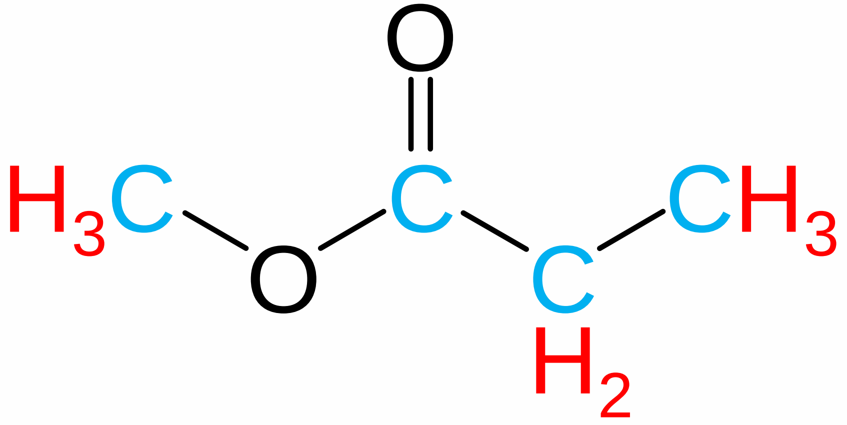
Full assignment

Carbon signals

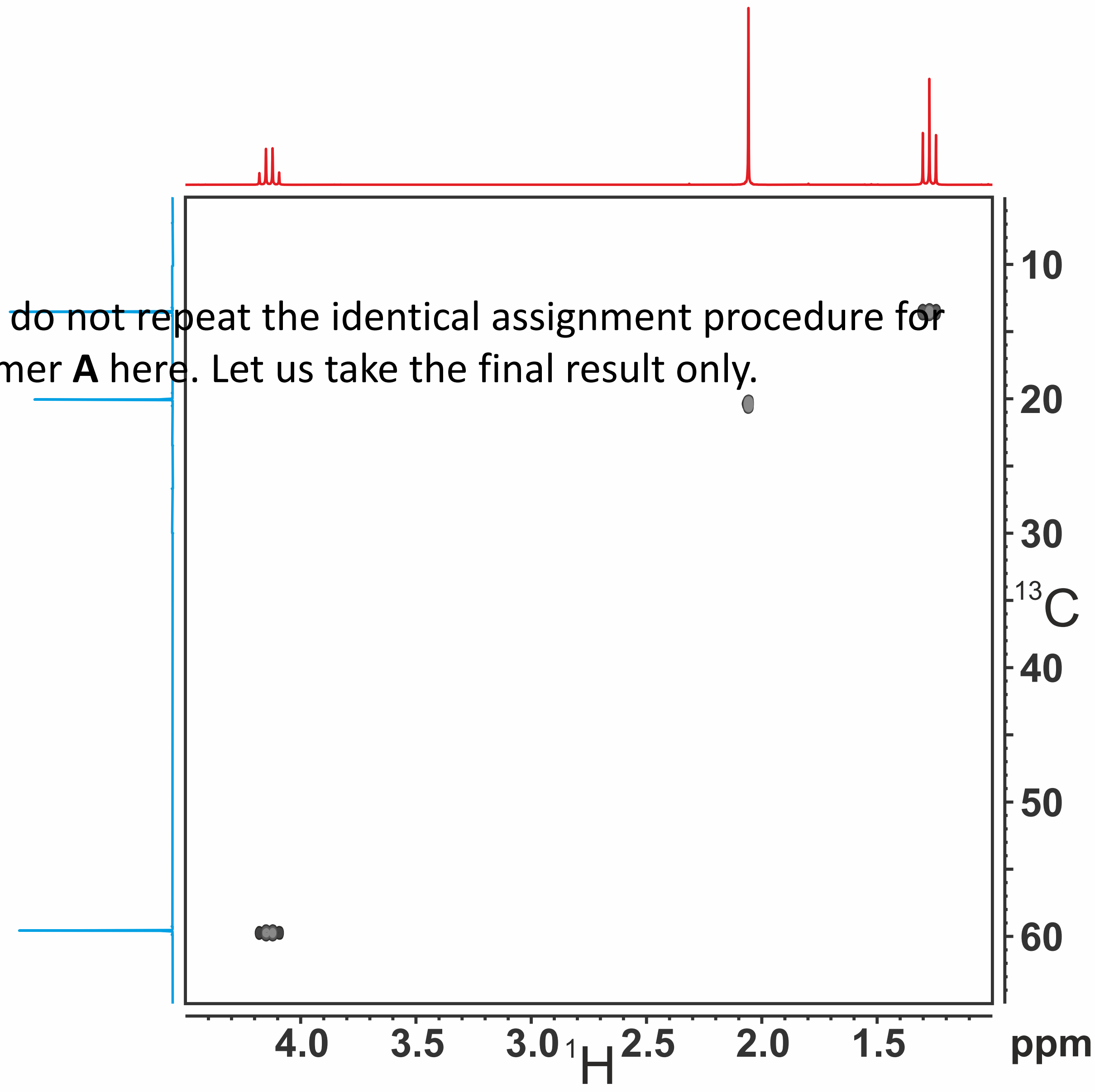
The chemical shift for the carbonyl group carbon atom comes from the one dimensional carbon spectrum.



B



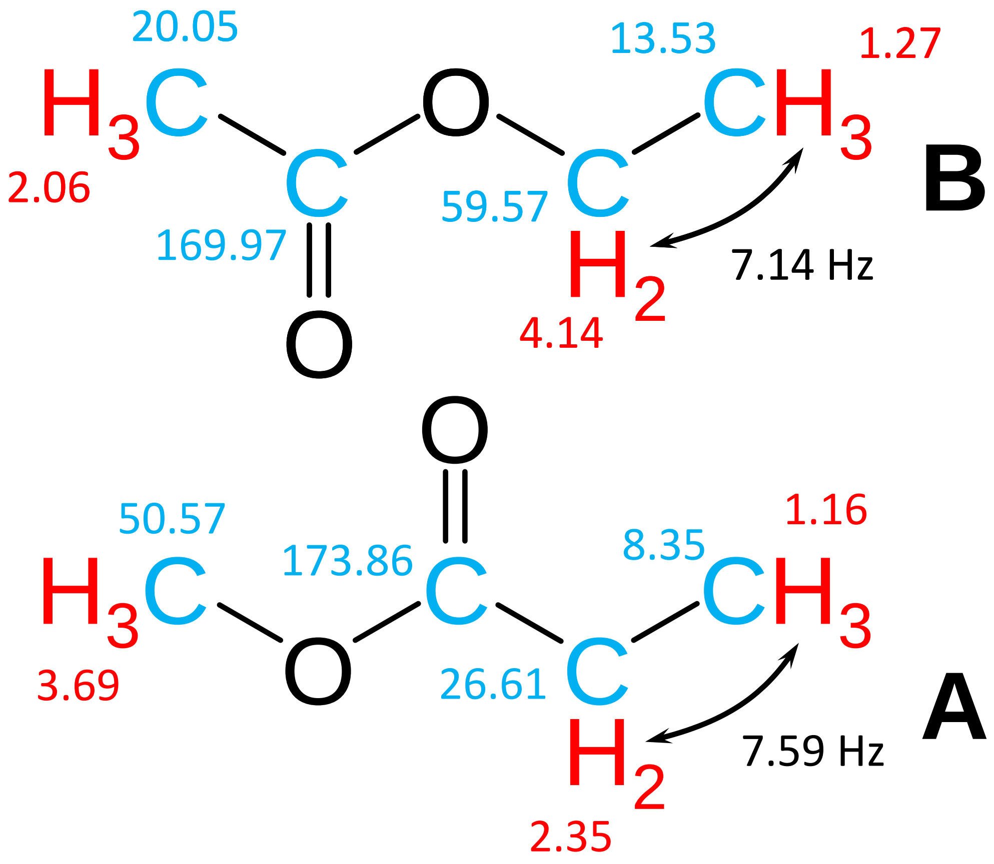
A



We do not repeat the identical assignment procedure for isomer **A** here. Let us take the final result only.

The alternative way

Don‘t use a textbook

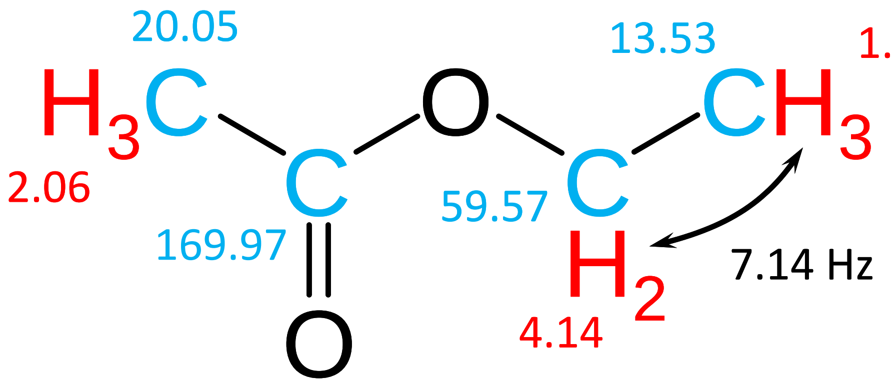


But how can we distinguish between isomer **A** and isomer **B** without using Schoolery‘s rule?

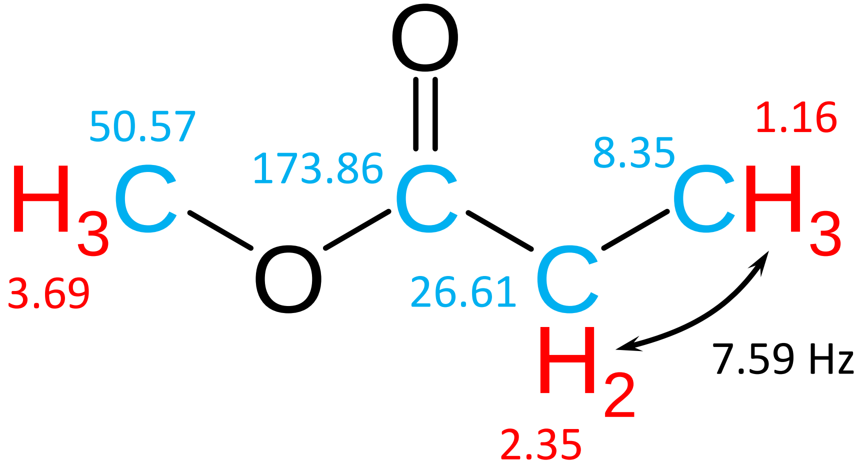
There has to be a way to differentiate between the two isomers using the carbon-carbon coupling pattern. The signal-to-noise ratio of the carbon spectrum is good enough to show these couplings.
But how to use these couplings without refering to a textbook about the typical size of such coupling constants?

The alternative way

Don‘t use a textbook



B



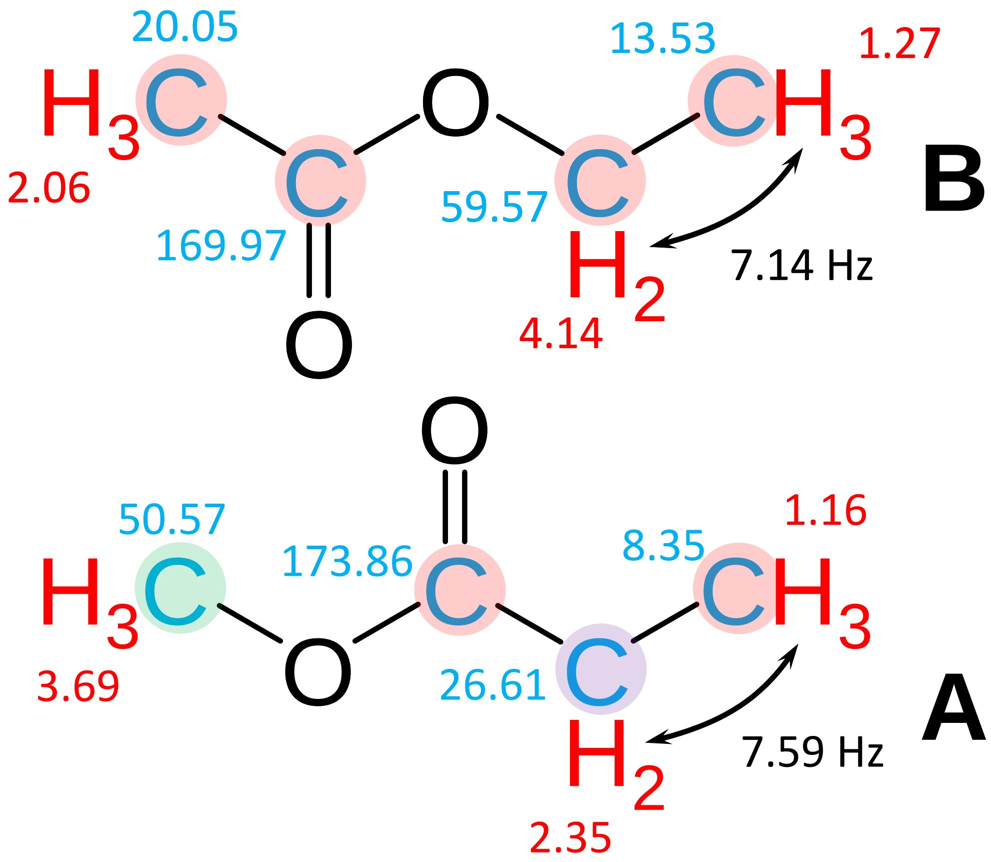
A

Do you see any difference between the isomers, which might be helpful in using the carbon-carbon satellites without any prior knowledge?

It is a question of pattern recognition. But, what on earth might be the pattern?

The alternative way

Don‘t use a textbook



Do you see any difference between the isomers, which might be helpful in using the carbon-carbon satellites without any prior knowledge?

It is a question of pattern recognition. But, what on earth might be the pattern?

Let us label the eight carbon atoms using three different colours. What could distinguish carbon atoms that have been marked with the same colour?

And now?

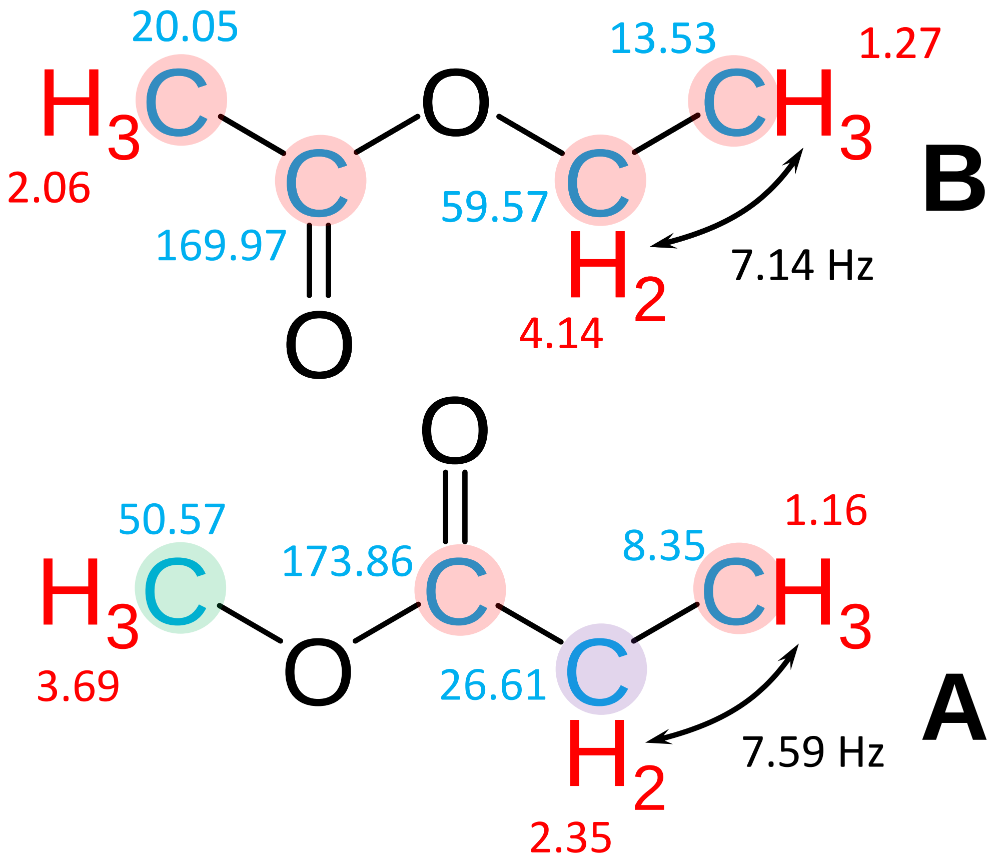
The alternative way

Don‘t use a textbook

🟢 **no** neighbouring carbon atom with a distance of one bond

🔴 **one** neighbouring carbon atom with a distance of one bond

🟣 **two** neighbouring carbon atom with a distance of one bond



It is a reasonable assumption, that all one bond carbon-carbon coupling constants are of comparable size.

Each of the three cases results in a different pattern for the satellite signals due to carbon-carbon coupling.
Let us assume a model compund and think about what the pattern might look like.

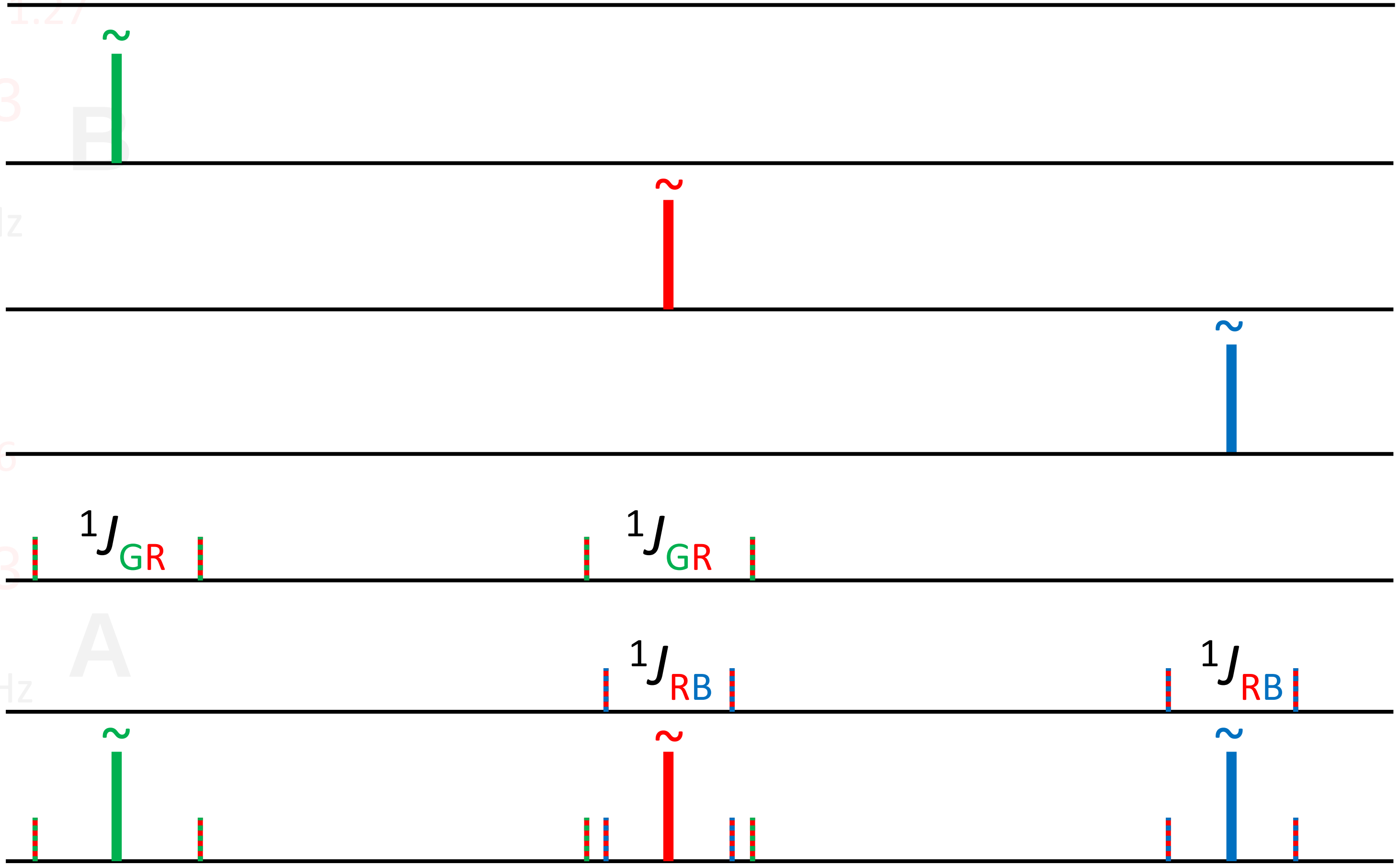
Carbon-carbon couplings

Probability and spectra

We should remember, that **every** NMR spectrum is **not** the result of **one molecule**, but of a huge ensemble of molecules.

Let‘s simulate the carbon spectrum of the single (asymmetric) model compound (equivalent to the right part of isomer **A**)

— C — C — C —



≈ 97% — $^{12}\mathrm{C}$ — $^{12}\mathrm{C}$ — $^{12}\mathrm{C}$ — **(no signal at all)**

≈ 1% — $^{13}\mathrm{C}$ — $^{12}\mathrm{C}$ — $^{12}\mathrm{C}$ —

≈ 1% — $^{12}\mathrm{C}$ — $^{13}\mathrm{C}$ — $^{12}\mathrm{C}$ —

≈ 1% — $^{12}\mathrm{C}$ — $^{12}\mathrm{C}$ — $^{13}\mathrm{C}$ —

≈ 0.01% — $^{13}\mathrm{C}$ $\overset{^1J_{GR}}{—}$ $^{13}\mathrm{C}$ — $^{12}\mathrm{C}$ —

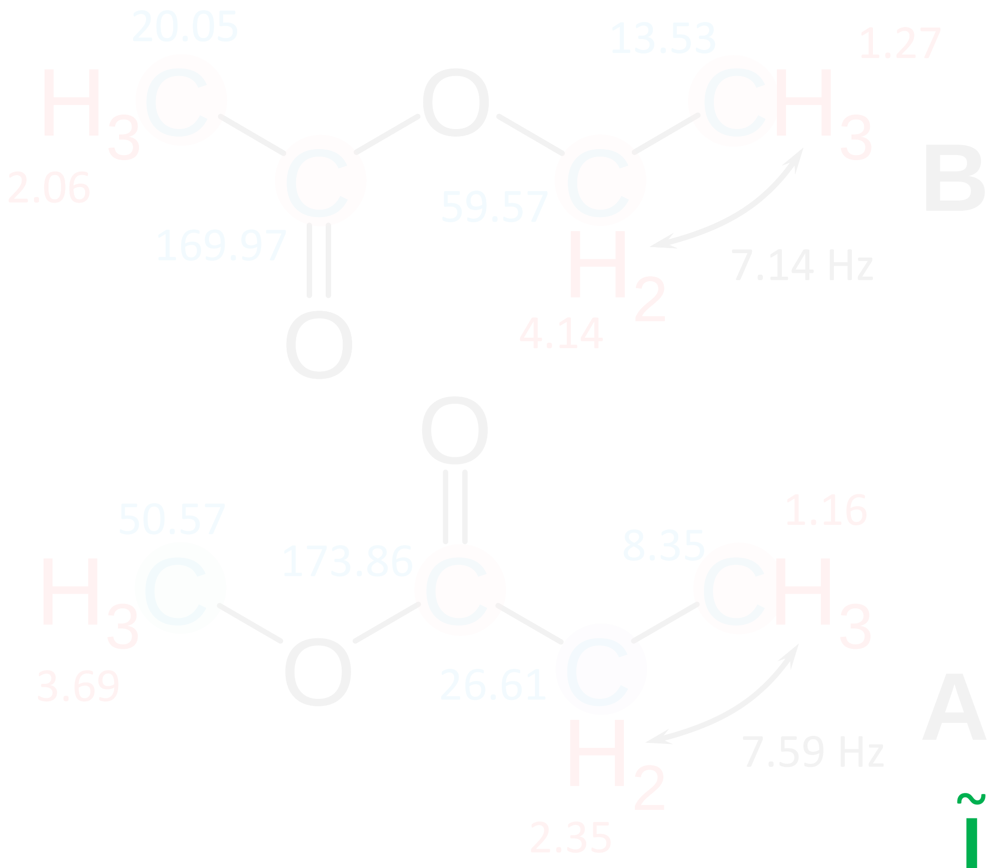
≈ 0.01% — $^{12}\mathrm{C}$ — $^{13}\mathrm{C}$ $\overset{^1J_{RB}}{—}$ $^{13}\mathrm{C}$ —

Sum of all components

Carbon-carbon couplings

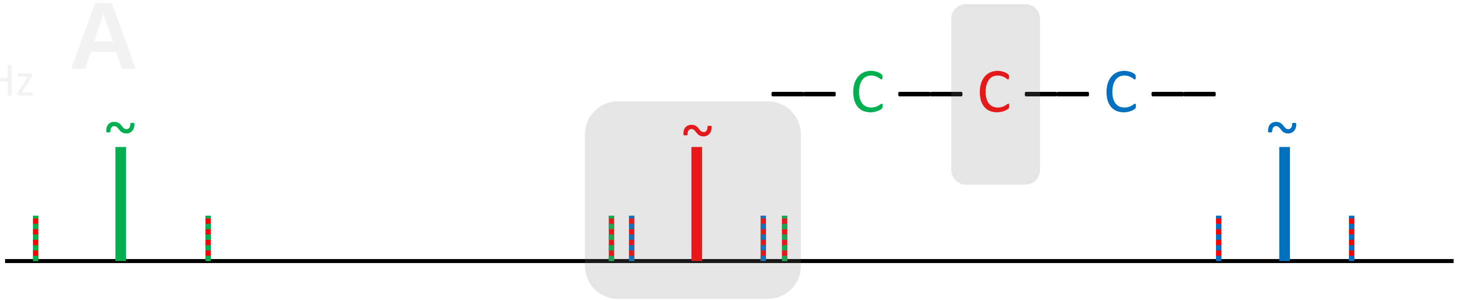
Probability and spectra

— C — C — C —



Please note, that the carbon-carbon multiplet pattern for the red carbon atom is neither a triplet nor a doublet of doublets. Rather, it is two nested independent doublets.

For a triplet or a doublet of doublets we would need three ^{13}C atoms within the same molecule. The probability is very, very low: about 0,0001%



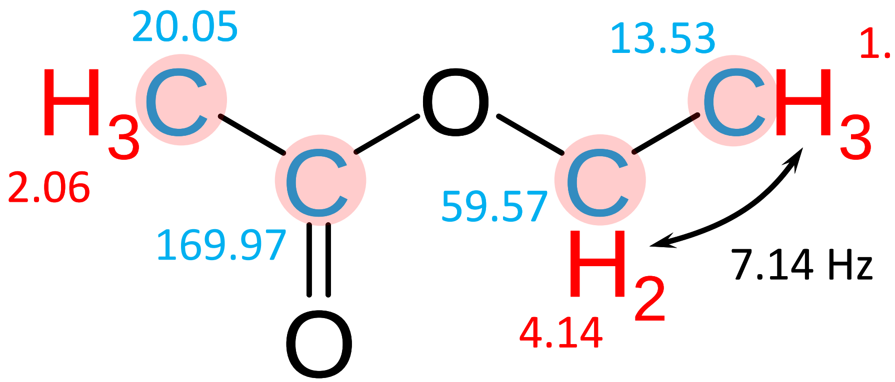
Carbon-carbon couplings

Practical use

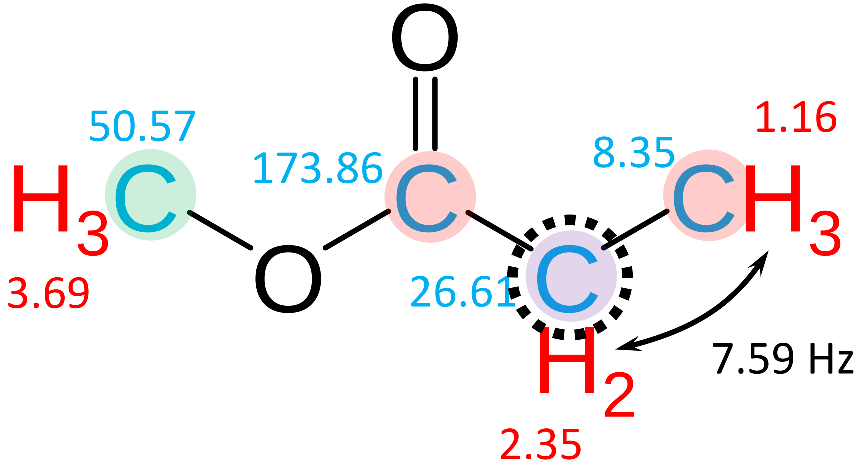
🟢 **no** satellites due to carbon-carbon coupling

🔴 **one** doublet due to carbon-carbon coupling

🟣 **two** nested doublets due to carbon-carbon coupling



B

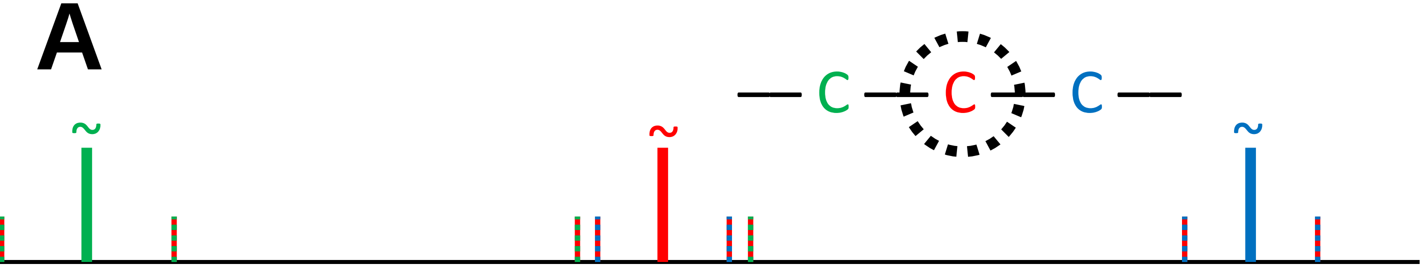


A

Which satellite pattern due to carbon-carbon coupling do we expect for the three types of carbon atoms shown before?

Apparently the coupling pattern for the carbon atom marked in mauve is unique and we have to look wether this pattern is visible in the carbon spectra of isomer **A** or isomer **B**.

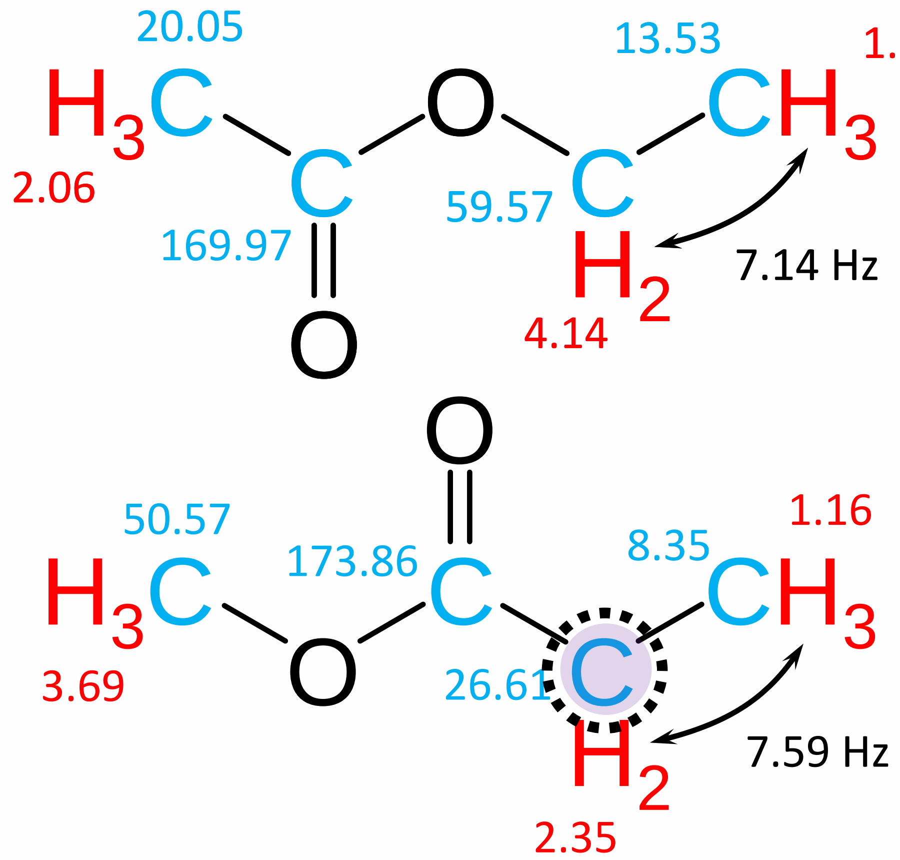
Due to the use of Schoolery‘s rule we already know the solution. Let us forget this solution to demonstrate the use of the carbon-carbon coupling pattern.

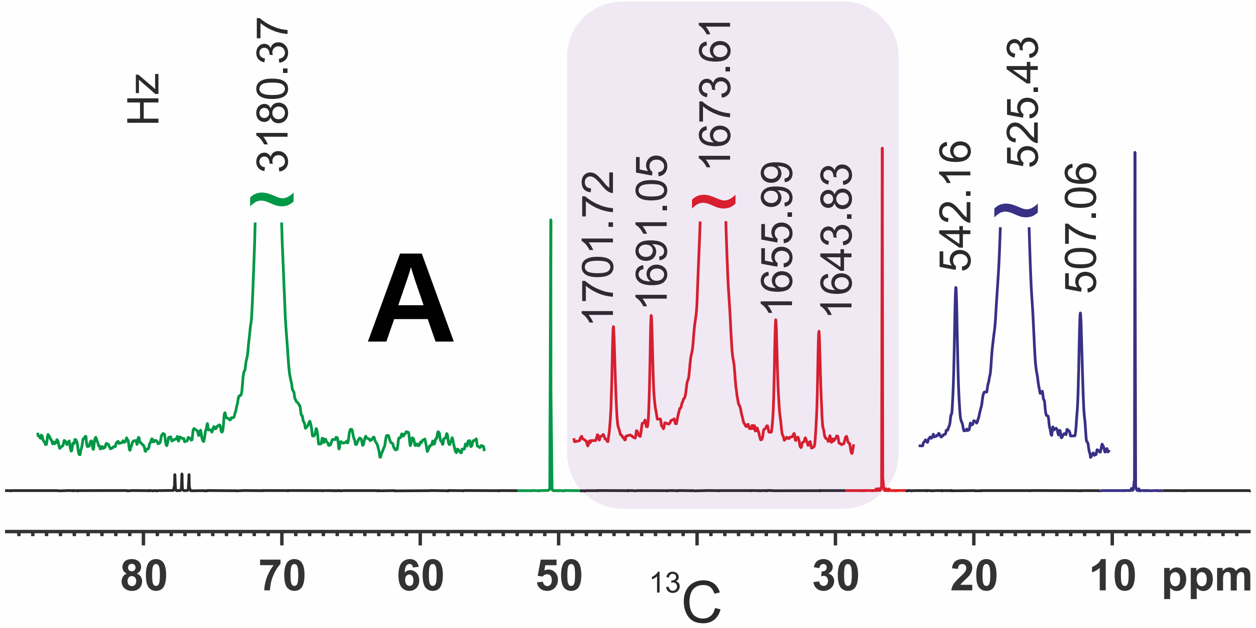


Carbon-carbon couplings

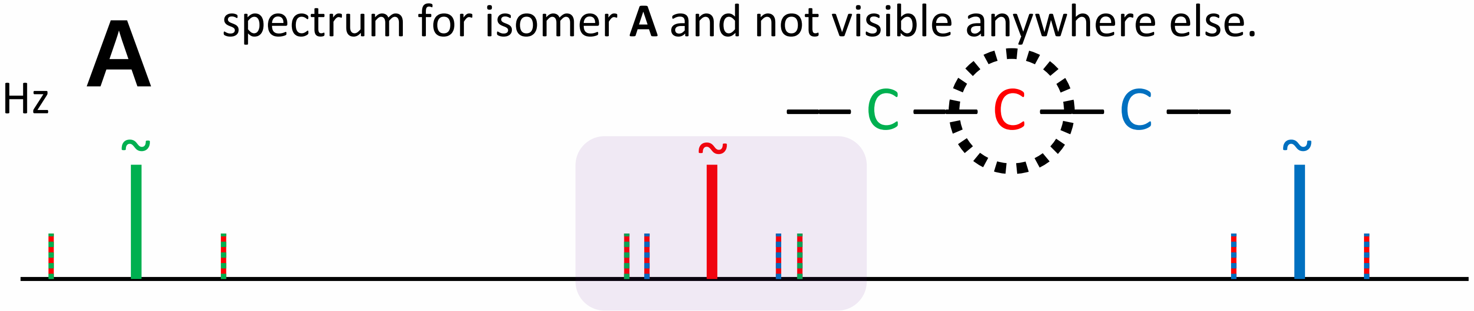
Practical use

● **two** nested doublets due to carbon-carbon coupling





The pattern we are looking for is part of the carbon spectrum for isomer **A** and not visible anywhere else.

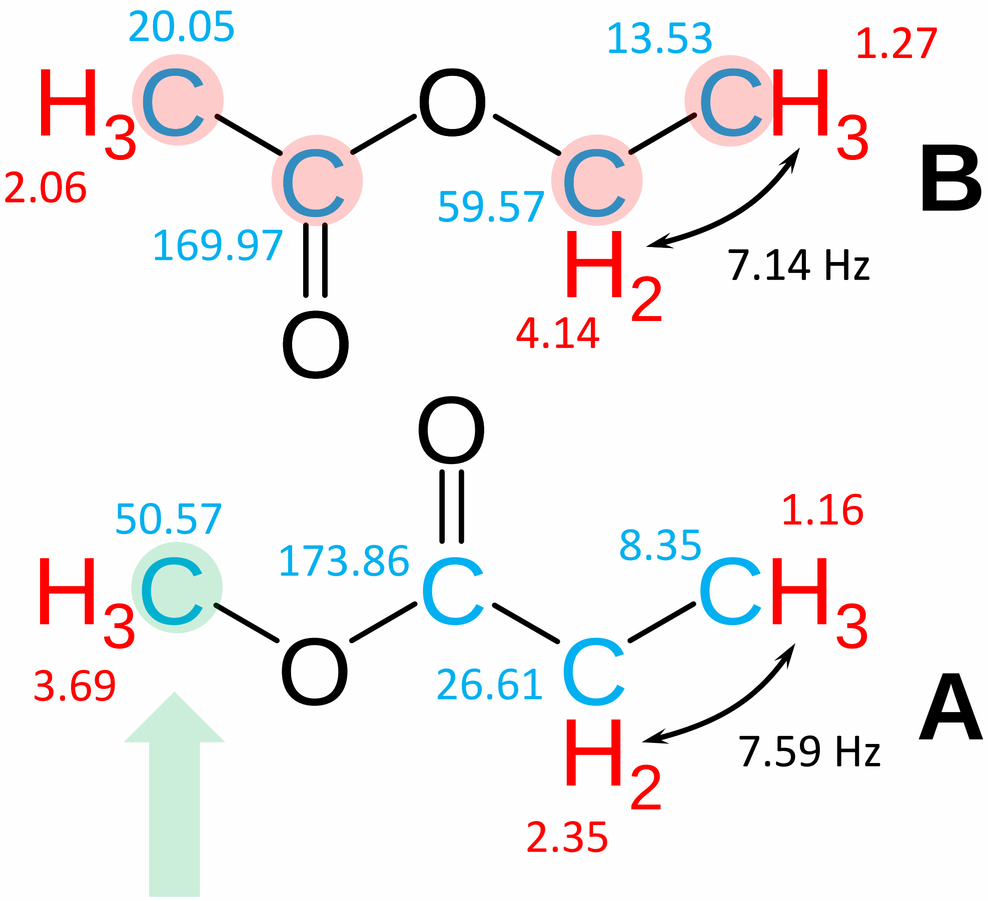


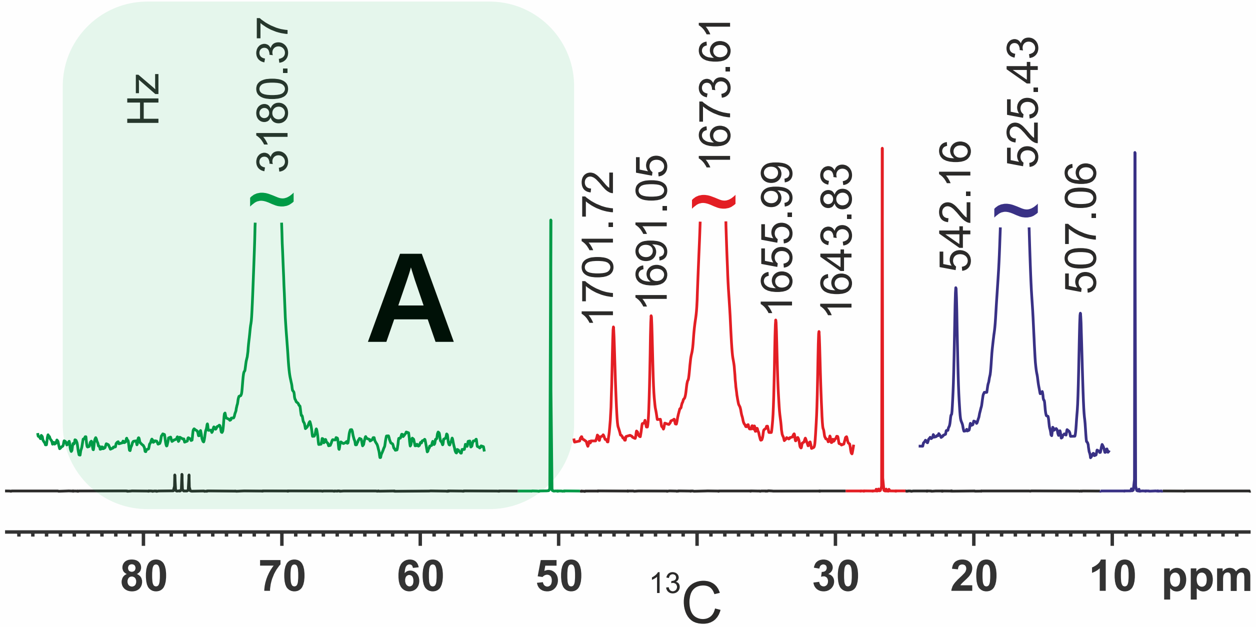
Carbon-carbon couplings

Practical use

🟢 **no** satellites due to carbon-carbon coupling

🔴 **one** doublet due to carbon-carbon coupling





The pattern we are looking for is part of the carbon spectrum for isomer **A** and not visible anywhere else.

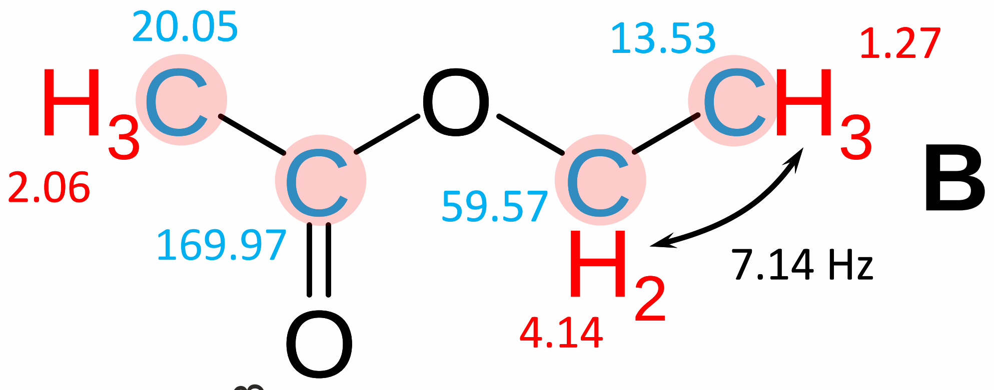
And there is no carbon-carbon splitting here.

In the case of isomer **B** we should see only doublets as satellites due to carbon-carbon coupling.
Let‘s check.

Carbon-carbon couplings

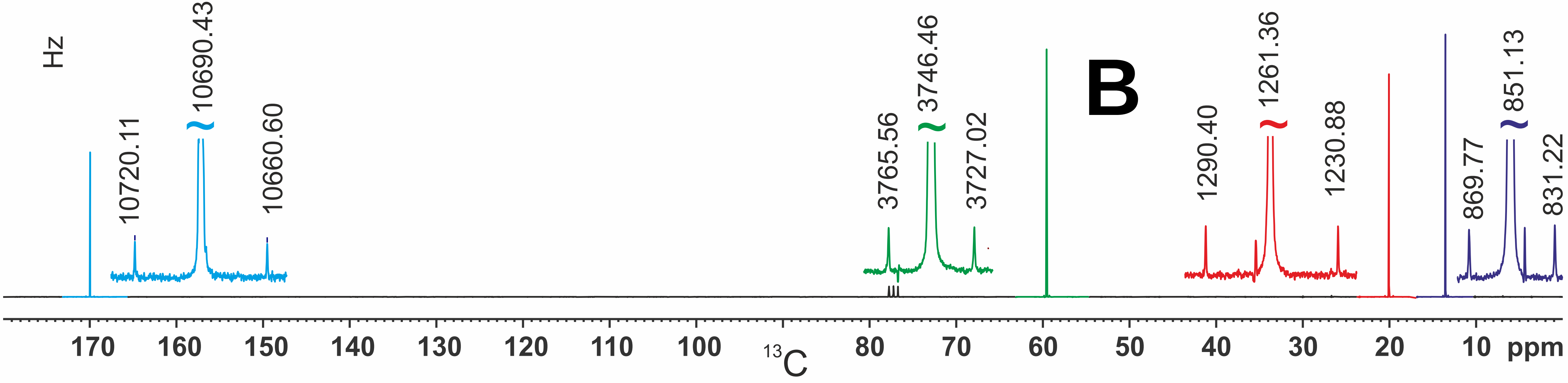
Practical use

● **one** doublet due to carbon-carbon coupling

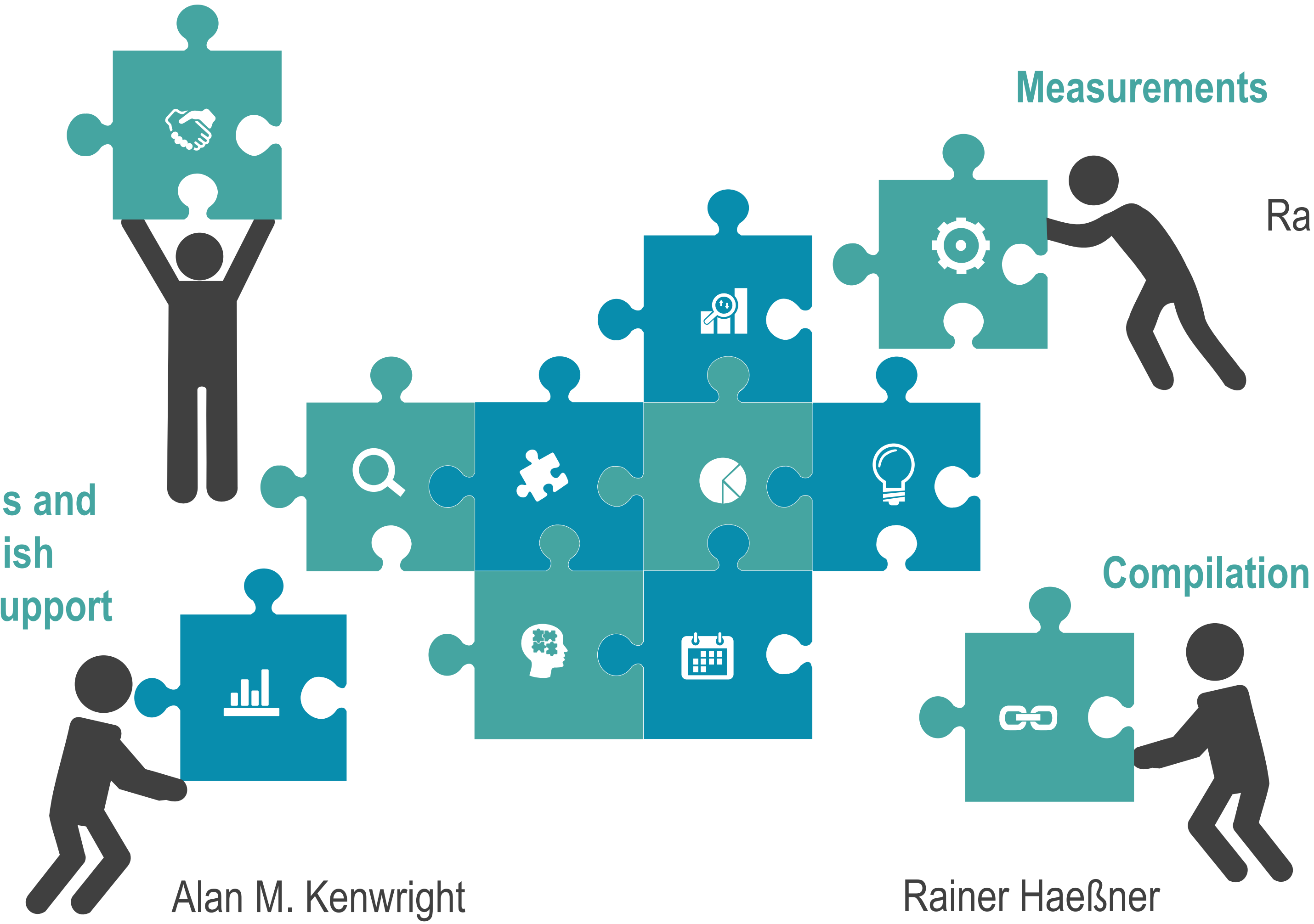


Apart from three spikes of unknown source, we see exactly the four expected doublets.

Of course, in practice, one would not solve this simple question with this enormous measurement effort. The objective here was to motivate the search for solutions off the beaten track.



Contributions



Spectrometer time

TU Munich

Measurements

Rainer Haeßner

Discussions and native English language support

Alan M. Kenwright

Compilation

Rainer Haeßner