Nuclear magnetic resonance spectroscopy

II. ^{13}C NMR

Reading:
Pavia
Chapter 6.1-6.5, 6.7, 6.11, 6.13

1. General

- more/better/additional structural information for larger compounds
- problems:

a) C isotopes and their natural abundance

		^{1}H 99.95%
	^{12}C 98.9%	^{13}C 1.1%
nuclear spin I	0	$\frac{1}{2}$

b) gyromagnetic ratio

$$E = h\nu = \gamma \frac{h}{2\pi} B_0$$

^{1}H	γ 267.53	unit: radians/T
^{13}C	γ 67.28	

$\Rightarrow$ for B_0 1.41 T, $\omega(^{1}H)$ 60 MHz

$\omega(^{13}C)$ 15 MHz

$\Rightarrow$ much lower E needed for transition

$\Rightarrow$ even less nuclei in excess in the lower level

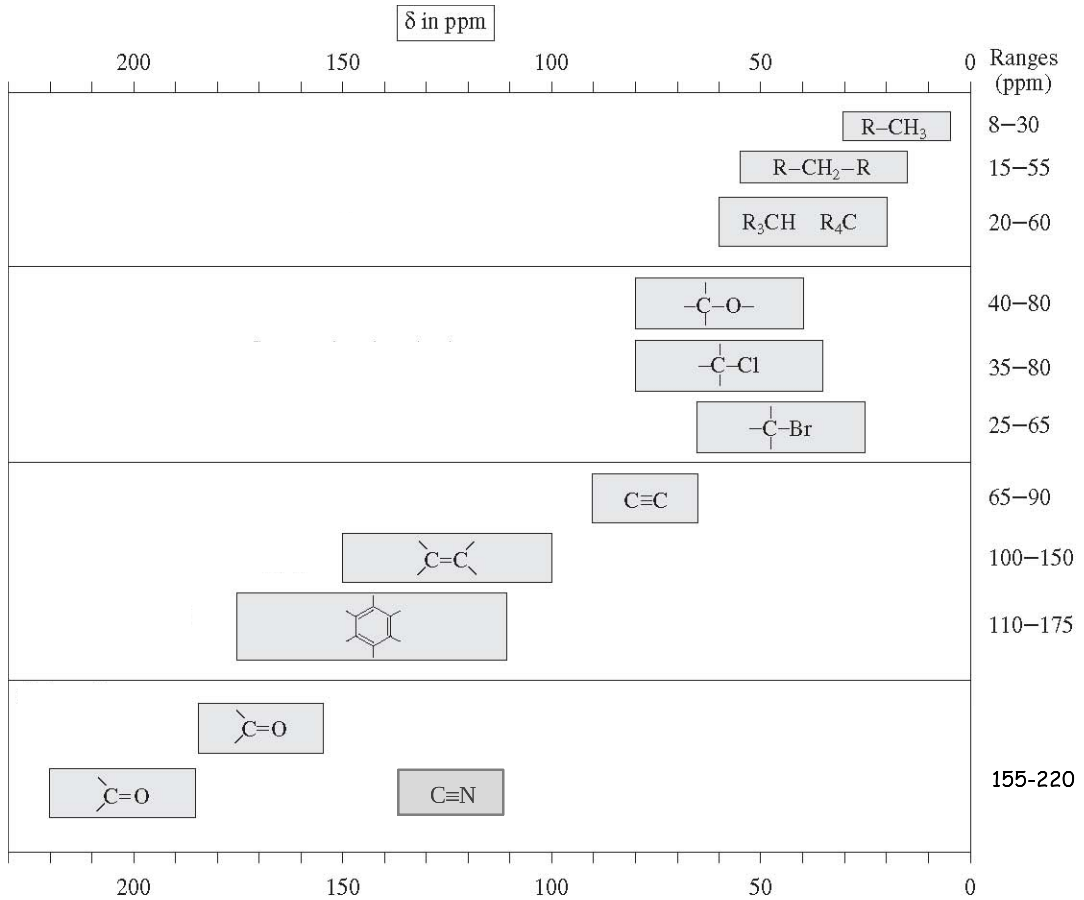
$\Rightarrow$ smaller signal

- solutions: sum up more scans, use more sample, use a stronger field

2. Chemical shift

- reference signal is from ^{13}C in TMS
- δ range is $\approx$ 200 ppm: advantage: - signals are spread out more
  - more detailed information possible
- order of deshielding follows that for ^{1}H:

Table 6.1



much detailed information provided:

you will need to provide this detail!

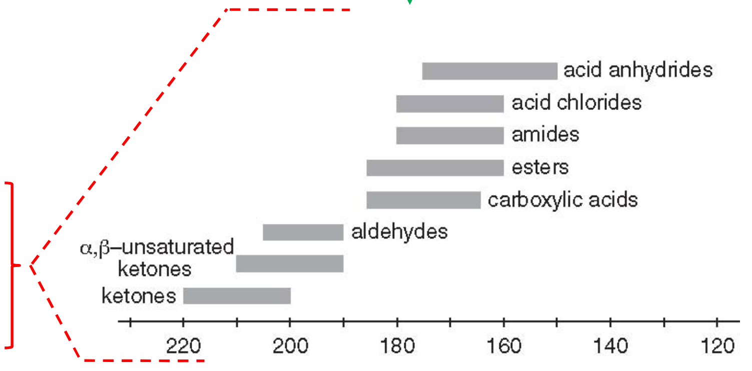


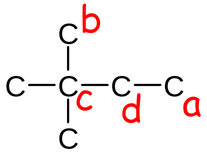
Fig. 6.2

3. Estimation of $\delta^{13}C$

- from increment systems
  - for alkanes

$\delta^{13}C$ (ppm) = -2.3 + increments for α, β… C atoms and steric corrections

see p. A-24



$\delta^{13}C_a = -2.3 + \underset{\alpha}{9.1} + \underset{\beta}{9.4} - \underset{\gamma}{3 \cdot 2.5} = 8.7$ ppm (exp. 8.9 ppm) ok

$\delta^{13}C_b = -2.3 + \underset{\alpha}{9.1} + \underset{\beta}{3 \cdot 9.4} - \underset{\gamma}{2.5} = 32.5$ ppm

$- 3.4$ steric: 1°, attached to 4°

$= 29.1$ ppm (exp. 29.1 ppm) ok

$\delta^{13}C_c = -2.3 + \underset{\alpha}{4 \cdot 9.1} + \underset{\beta}{9.4} = 43.5$ ppm

$- 3 \cdot 1.5 - 8.4$ steric: 4°, attached to 3 1° and 2°

$= 30.6$ ppm (exp. 30.6 ppm) ok

$\delta^{13}C_d = -2.3 + \underset{\alpha}{2 \cdot 9.1} + \underset{\beta}{3 \cdot 9.4} = 44.1$ ppm

$- 7.5$ steric: 2°, attached to 4° (and 1°)

$= 36.6$ ppm (exp. 36.9 ppm) ok

other substituents
alkenes
aromatic compounds

3. Estimation of δ^{13}C continued

- from increment systems

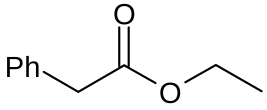
- for substituted alkanes	see Table A8.3, add to values from Table A8.2! (i.e., calculate from scratch!)
- for alkenes	see Tables A8.5 and A8.6
- for substituted benzenes	see Table A8.7

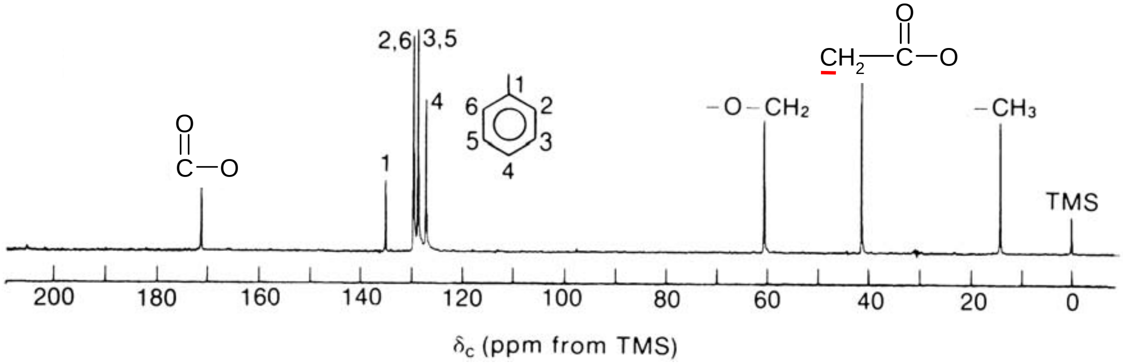
Work through these tables and examples on your own!

You're (probably) ok if you can do the following two examples. Do not look at the answers before you have tried them!

Example 1

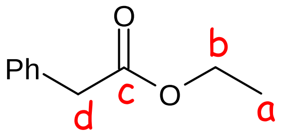
Are the assignments provided on the spectrum correct? (Calculate/estimate $\delta^{13}C$!)

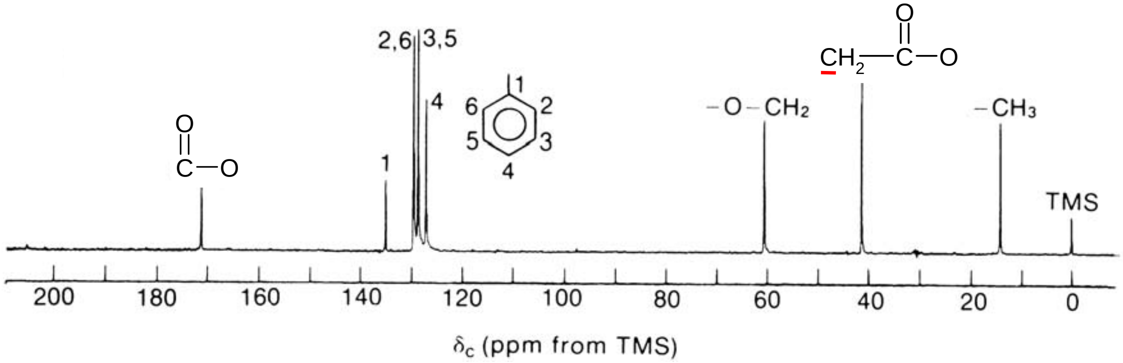




Example 1 answer

Are the assignments provided on the spectrum correct? (Calculate/estimate $\delta^{13}C$!)





$\delta^{13}C_a = -2.3 + \underset{\alpha}{9.1} + \underset{\beta\ OCOR}{6.5} = 13.3$ ppm (exp. 14 ppm) ok

$\delta^{13}C_b = -2.3 + \underset{\alpha}{9.1} + \underset{\alpha\ OCOR}{56.5} = 63.3$ ppm (exp. 61 ppm) ok

$\delta^{13}C_c$: ester: 160-190 ppm (exp. 171 ppm) ok

$\delta^{13}C_d = -2.3 + \underset{\alpha\ Ph}{22.1} + \underset{\alpha\ COOR}{22.6} = 42.4$ ppm (exp. 41 ppm) ok

Yes, all assignments are fine.

Ph:

$\delta^{13}C_1 = 128.5 + \underset{ipso\ CH_3}{9.3} \overset{?}{=} \overset{highest}{137.8}$ ppm $\overset{highest}{\text{(exp. 136 ppm)}}$

$\delta^{13}C_4 = 128.5 - \underset{para\ CH_3}{2.9} \overset{?}{=} \overset{lowest}{125.6}$ ppm $\overset{lowest}{\text{(exp. 127 ppm)}}$

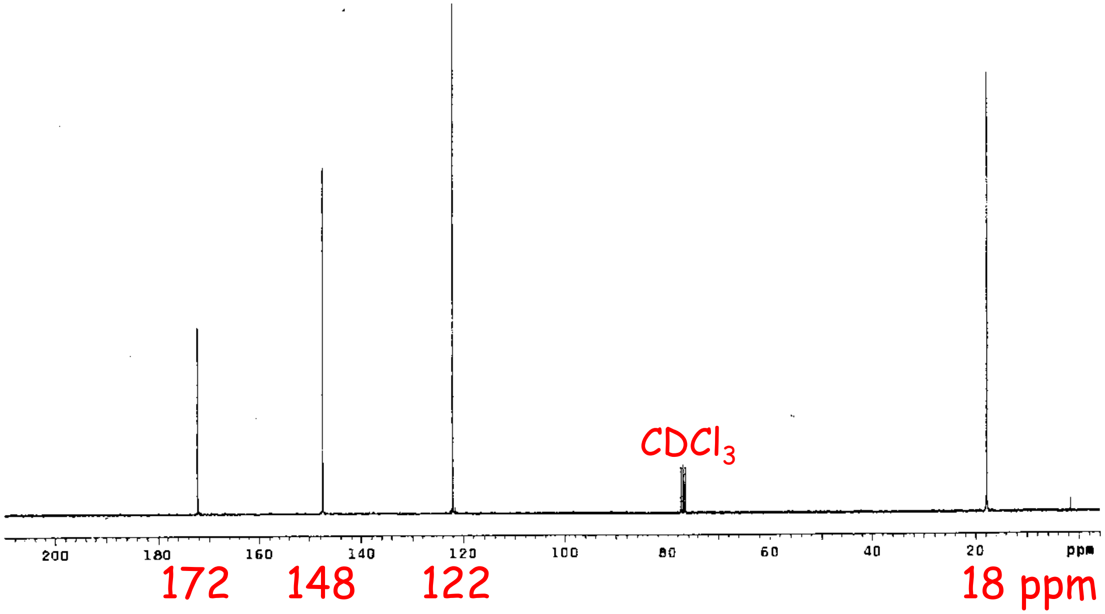
$\delta^{13}C_{2,6} = 128.5 + \underset{ortho\ CH_3}{0.7} \overset{?}{=} 129.2$ ppm (exp. 130 ppm)

$\delta^{13}C_{3,5} = 128.5 - \underset{meta\ CH_3}{0.1} \overset{?}{=} 128.4$ ppm (exp. 129 ppm)

all ok: CH_3 might be the wrong choice, but it's equally wrong for all positions: error cancels

Example 2

For this $C_4H_6O_2$, the ^1H NMR spectrum shows signals around 5 and 12 ppm. Which of the four possible isomers has the following spectrum? (Estimate $\delta^{13}C$!)



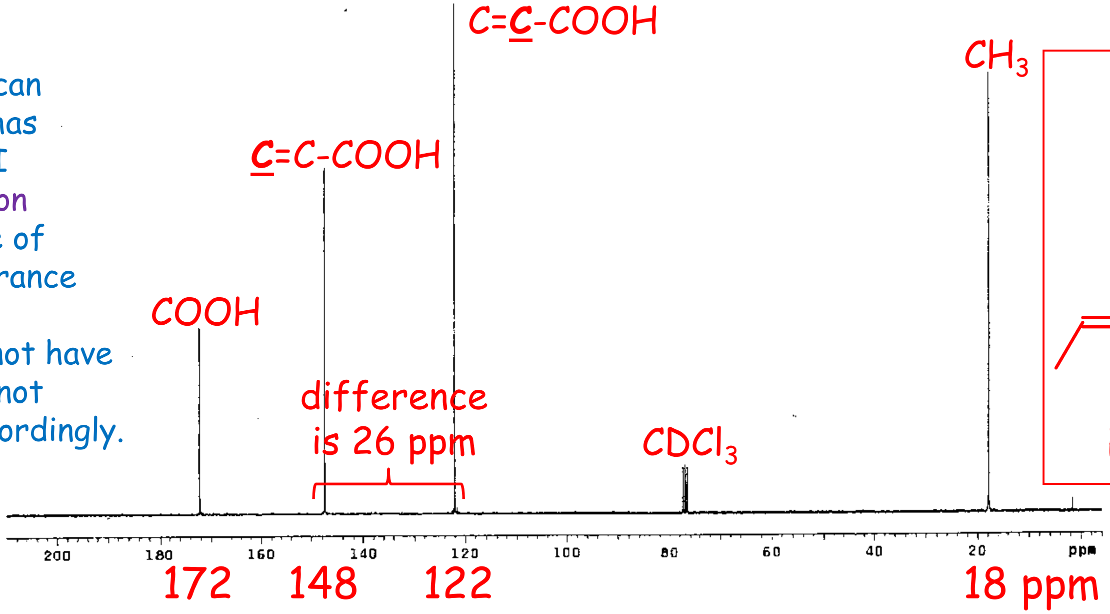
Example 2 answer

U = 2

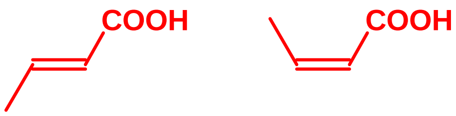
H-C=C COOH

For this $C_4H_6O_2$, the ^1H NMR spectrum shows signals around 5 and 12 ppm. Which of the four possible isomers has the following spectrum? (Estimate $\delta^{13}C$!)

I used Table A8.6; you can also use A8.4. Neither has steric corrections, yet I included the Z-correction for illustration: because of conjugation, steric hindrance is more than likely .
On an exam, you would not have to consider this if I do not phrase the question accordingly.



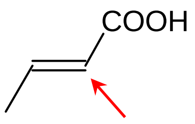
Can't decide: could be E or Z-crotonic acid:



E is a bit closer…

$\delta^{13}C(COOH)$: 165-185 ppm ok

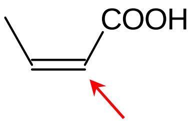
$\delta^{13}C(CH_3)$: -2.3 + 19.5 = 17.2 ppm ok



123.3
+ 10.6
+ 9
= 142.9

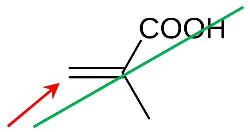
123.3
- 7.9
+ 4
= 119.4

difference is 23.5 ppm ok



123.3
+ 10.6
+ 9
-1.1
= 141.8

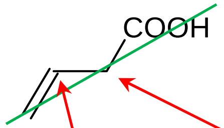
123.3
-7.9
+ 4
-1.1
= 118.3



123.3
- 7.9
+ 9
= 124.4

123.3
+ 10.6
+ 4
= 137.9

difference is 13.5 ppm too far off



123.3
- 7.9
= 115.4

123.3
+ 10.6
= 133.9

-2.3
+ 19.5
+ 20.1
= 37.3 too far off

4. Spin-spin coupling

- as in ^{1}H NMR, but in principle two situations:
  - ^{13}C coupling with ^{13}C

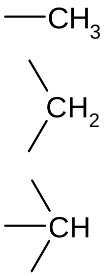
    ⇒ rare event: probability of 2 ^{13}C next to each other is very low

  - ^{13}C coupling with ^{1}H

    ⇒ “heteronuclear” coupling

    ⇒ follows the n+1 rule

    ⇒ ^{1}J coupling:



^{13}C signal split by ^{1}H into q

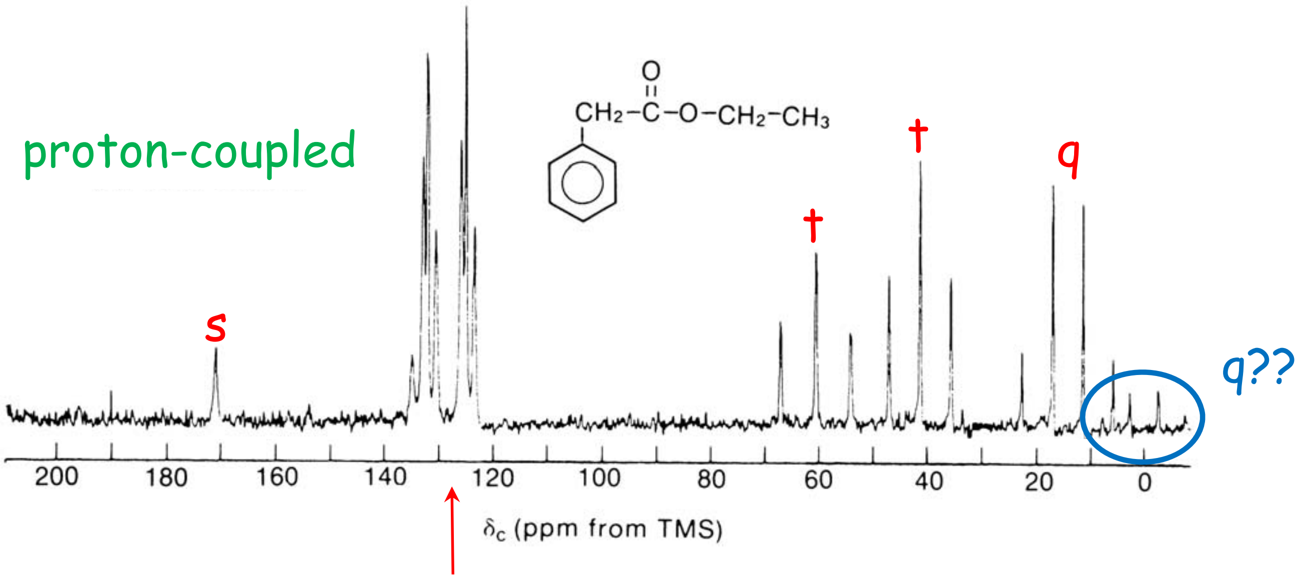
t

d

no proton: signal is not split, s (quaternary C, $R_2C{=}O$, $R{-}C{\equiv}N$…)

4. Spin-spin coupling continued

- ^{13}C spectra that show $^{1}J(^{13}C-^{1}H)$ coupling are called “proton-coupled” or “non-decoupled”

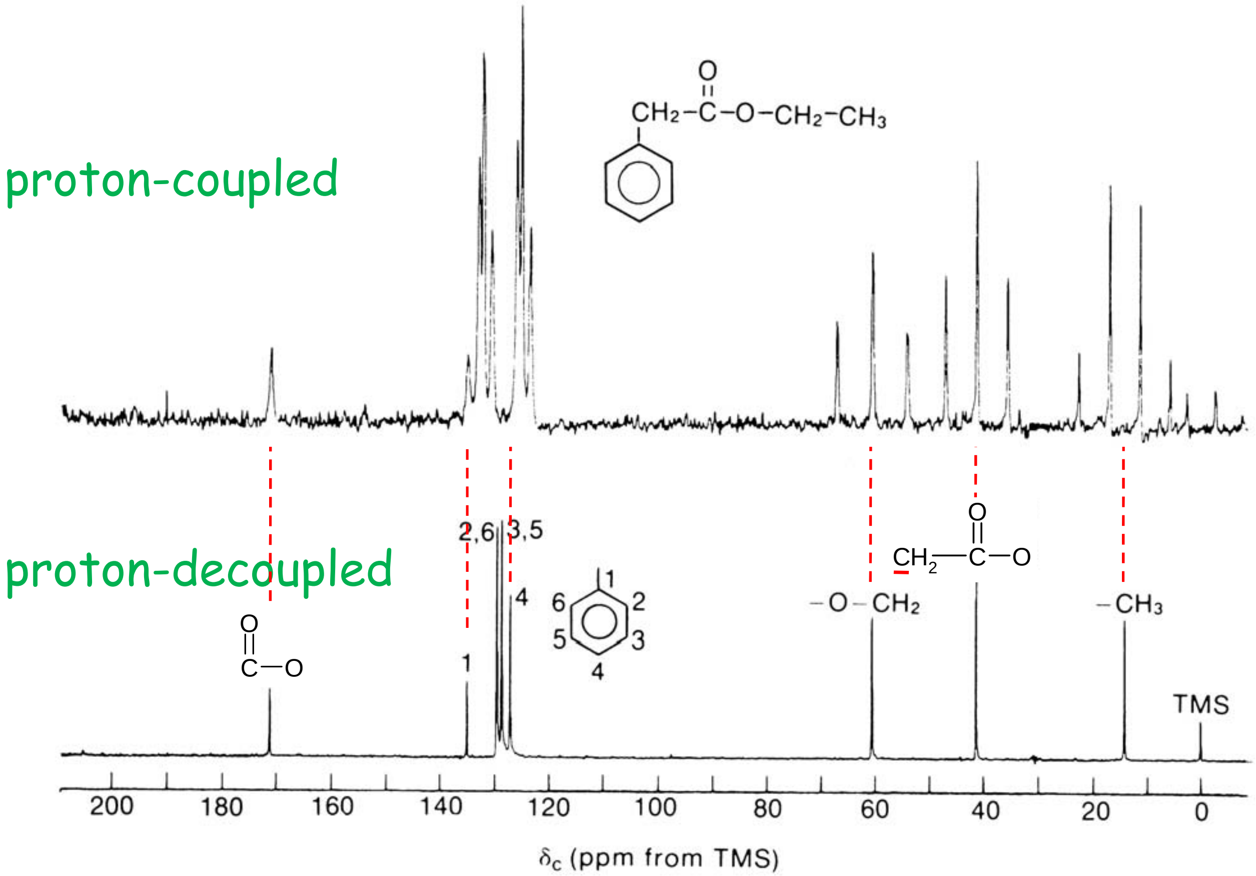


4 signals in here!
What are they?

⇒ not often recorded, because of frequent overlap between multiplets, especially if the molecule contains many (sp^3) C atoms

4. Spin-spin coupling continued

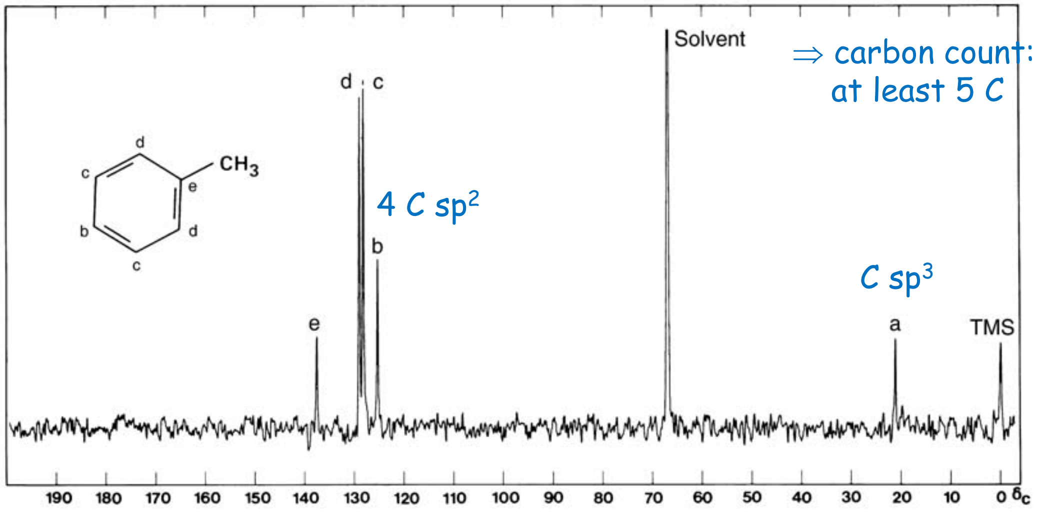
- ^{13}C spectra that ***do not*** show $^1J(^{13}C\text{-}^1H)$ coupling are called "proton-decoupled"
  ⇒ only singlets are observed



- advantage: simpler spectra
- disadvantage: important information on C-H connectivity is lost

5. Integration

- ^{13}C spectra are not usually integrated

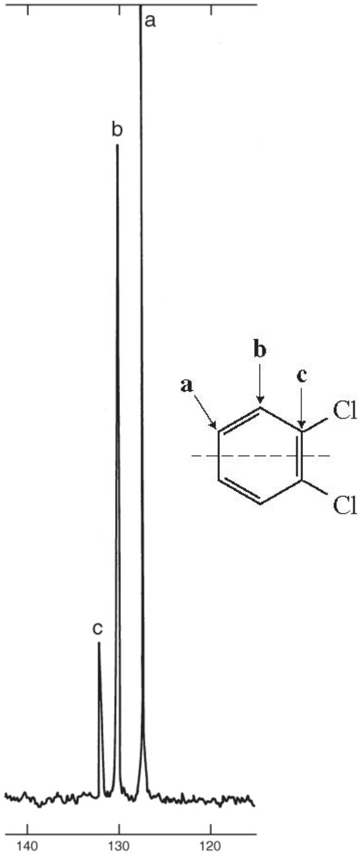


⇒ carbon count: at least 5 C

4 C sp^2

C sp^3

even more extreme example:



- 2 ortho, 2 meta C: spectrum shows 2 large peaks
- 1 ipso, 1 para C: spectrum shows 2 small peaks, but certainly not of the same area

- make sure you always know the solvent peak, and do not count it as part of the molecule!

5. Integration continued

- two problems are the reason:

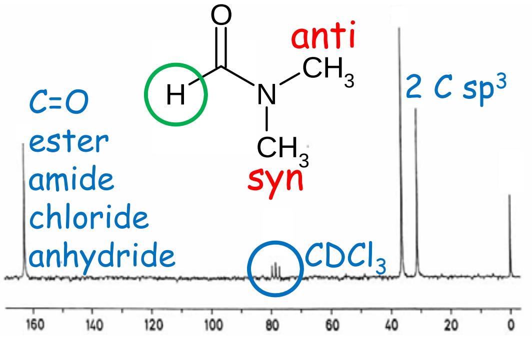
a) NOE (nuclear Overhauser enhancement)

- in proton-decoupled spectra
- intensity of a signal increases upon decoupling
    - signal for CH_3 grows most
    - signal for CH_2 grows less …
    - C=O, ipso-C or quaternary C signal ends up being tiny
- reason lies in the decoupling experiment

Example application

NOE usage for peak assignment

- NOE also works "through space"



⇒ at least 3 C

syn signal gets enhanced more: is closer to H

http://131.104.156.23/Lectures/CHEM_207/CHM_207_NMR.htm

5. Integration continued

- two problems are the reason:

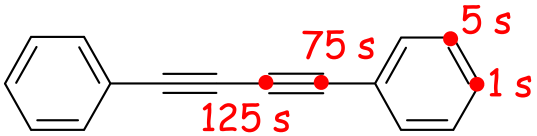
b) relaxation of a nucleus

- FT-NMR records the FID signal

$\Rightarrow$ follows the excited nucleus as it relaxes to the ground state

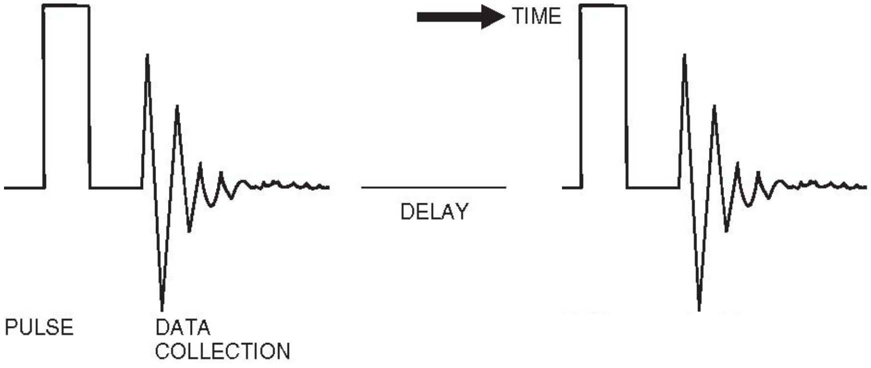
de-excitation is – fast for ^{1}H

- variable for ^{13}C, depending on the environment



- for a fast-relaxing nucleus, the FID is collected completely

$\Rightarrow$ full signal is recorded



- for a slow-relaxing nucleus, the FID is collected incompletely

$\Rightarrow$ only partial signal is recorded

Why don't we just wait longer between pulses???