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

<table>
<thead>
<tr>
<th>Isotope</th>
<th>% Abundance</th>
<th>Nuclear Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>99.95%</td>
<td>0</td>
</tr>
<tr>
<td>$^{12}$C</td>
<td>98.9%</td>
<td>0</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>1.1%</td>
<td>1/2</td>
</tr>
</tbody>
</table>

b) gyromagnetic ratio

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

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$\gamma$ (unit: radians/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>267.53</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>67.28</td>
</tr>
</tbody>
</table>

⇒ for $B_0$ 1.41 T, $\omega(1H)$ 60 MHz

⇒ much lower E needed for transition

⇒ even less nuclei in excess in the lower level

⇒ 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
- $\delta$ range is $\approx 200$ ppm: advantage: - signals are spread out more
  - more detailed information possible
- order of deshielding follows that for $^1$H:

![Diagram of chemical shifts with labels for various functional groups and ranges in ppm]

Table 6.1

much detailed information provided:

![Figure 6.2 showing ranges and corresponding functional groups]
3. Estimation of $\delta^{13}C$

- from increment systems
- for alkanes

$$\delta^{13}C \text{ (ppm)} = -2.3 + \text{ increments for } \alpha, \beta \ldots \text{ C atoms and steric corrections}$$

see p. A-24

$\delta^{13}C_{a} = -2.3 + 9.1 + 9.4 - 3 \cdot 2.5 = 8.7 \text{ ppm (exp. 8.9 ppm) } \text{ ok}$

$\delta^{13}C_{b} = -2.3 + 9.1 + 3 \cdot 9.4 - 2.5 = 32.5 \text{ ppm}$

- 3.4 steric: 1°, attached to 4°

= 29.1 ppm (exp. 29.1 ppm) \text{ ok}

$\delta^{13}C_{c} = -2.3 + 4 \cdot 9.1 + 9.4 = 43.5 \text{ ppm}$

- 3.15 - 8.4 steric: 4°, attached to 3 1° and 2°

= 30.6 ppm (exp. 30.6 ppm) \text{ ok}

$\delta^{13}C_{d} = -2.3 + 2 \cdot 9.1 + 3 \cdot 9.4 = 44.1 \text{ ppm}$

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

= 36.6 ppm (exp. 36.9 ppm) \text{ ok}

other substituents
alkenes
aromatic compounds
3. Estimation of $\delta^{13}C$ 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 $\delta^{13}C$!)

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

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

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

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

$\delta^{13}C_1 = 128.5 + 9.3 = 137.8$ ppm (exp. 136 ppm)

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

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

all ok: CH$_3$ might be the wrong choice, but it’s equally wrong for all positions: error cancels

Yes, all assignments are fine.
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

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 $\delta^{13}C$!)

\[ U = 2 \quad H-C=C \quad COOH \]

1. $\delta^{13}C(COOH)$: 165-185 ppm  \text{ok} \\ 2. $\delta^{13}C(CH_3)$: $-2.3 + 19.5 = 17.2$ ppm  \text{ok}

\[
\begin{align*}
\text{difference is 26 ppm} \\
\text{difference is 23.5 ppm  \text{ok}} \\
\text{difference is 13.5 ppm  \text{too far off}}
\end{align*}
\]
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:

\[
\begin{align*}
\text{---CH}_3 & \quad ^{13}\text{C signal split by }^1\text{H into q} \\
\text{\textbackslash CH}_2 & \quad \text{t} \\
\text{\textbackslash CH} & \quad \text{d} \\
\text{no proton: signal is not split,}\quad \text{s} & \quad (\text{quaternary C, R}_2\text{C}=\text{O, R-C≡N...})
\end{align*}
\]
4. Spin-spin coupling continued

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

⇒ 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-$^1$H) coupling are called “proton-decoupled”
  $\Rightarrow$ 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

- 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

Even more extreme example:
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 CH₃ grows most
      - signal for CH₂ 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"

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
    ⇒ 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
    ⇒ full signal is recorded

  - for a slow-relaxing nucleus, the FID is collected incompletely
    ⇒ only partial signal is recorded

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