NUCLEAR MAGNETIC RESONANCE AND INTRODUCTION TO MASS SPECTROMETRY

A STUDENT SHOULD BE ABLE TO:

1. Identify and explain the processes involved in proton and carbon-13 nuclear magnetic resonance (NMR) spectroscopy, and mass spectrometry (MS). Important factors include:

   The relationships between energy, frequency, and wavelength in the electromagnetic spectrum. From highest to lowest energy, important types of electromagnetic radiation are: x-rays, ultraviolet, visible, infrared, microwave, radio.
   Electron impact ionization, molecular ion, mass-to-charge (m/z) ratio.
   Chemical shift, integration, shielding and deshielding, signal splitting (spin-spin coupling) in NMR.

2. Explain and predict experimental results in nuclear magnetic resonance spectroscopy, including:

   The number of signals a compound has in its $^1$H-NMR or $^{13}$C-NMR spectrum, which is the number of sets of equivalent protons or carbons respectively. Diastereotopic groups can occur in molecules with a chirality center or in alkenes.
   Integration ratios: In $^1$H NMR, the signal area ratio is the same as the ratio of the protons giving rise to the signal.
   The relative chemical shift of given protons or carbons (from the effects of electronegativity and pi bonding).
   The splitting pattern (singlet, doublet, triplet, etc.) of a given $^1$H NMR signal in simple systems. In these, the number of peaks equals the number of neighbors plus one; neighbors may include $^{13}$C and $^{19}$F, as well as non-equivalent protons. Note: The term multiplet often indicates that the system involved is not simple. When splitting is caused by non-equivalent protons on two adjacent carbons, the approximation of counting the total number of neighbors plus one is often effective.

3. Fully analyze nuclear magnetic resonance spectra and identify unknown compounds from their NMR, MS, and/or infrared spectra. If the molecular formula is known, the hydrogen deficiency index may be helpful--see Module 1.

4. Predict $^1$H and $^{13}$C spectra for a given structure. The proton spectrum should include integration, chemical shift and splitting pattern. Also calculate m/z ratio for the molecular ion in MS.
$^{1}H$ Nuclear Magnetic Resonance Guide Sheet

$^{13}C$ NMR Guide Sheet

Revised April 2014
To best prepare for this module, please work Chapter 16 Skill Builder problems in the textbook. Also, all students should attend the NMR lab (Organic II lab) to work problems.

A STUDENT WHO HAS MASTERCED THE OBJECTIVES FOR THIS UNIT SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

1.1 a) Which of the following types of radiation has the longest wavelength? b) Which has the highest frequency? c) Which has the lowest energy?
   a) Microwaves  b) Infrared  c) Visible  d) Radio

1.2 Proton and carbon nuclear magnetic resonance spectra are produced by:
   a) Carbons and protons, respectively  b) Protons and carbons, respectively
   c) Oxygens attached to carbon  d) Multiple bonds between carbons

2.1 How many signals are present in the proton NMR spectra of each of the following compounds? In the $^{13}$C spectra? Count similar but theoretically different benzene ring protons as different.

2.2 a) Which of the following compounds has the protons with the highest chemical shift (value of delta) in this set? b) Which has the lowest chemical shift?

a) (CH$_3$)$_2$Mg  b) CH$_3$COH  c) CH$_3$CH  d) (CH$_3$)$_3$N
2.3  a) Which of the indicated proton(s) is (are) the most shielded (lowest value of \( \delta \))?
   b) Which is (are) the least shielded?

\[
\text{CH}_3\text{CH}_2\text{OCCH}_3
\]

A  B  C  D

2.4 What splitting pattern (singlet, doublet, triplet, quartet, quintet, etc.) is observed in the proton NMR spectrum of each of the indicated protons?

\[
\text{CH}_3\text{CH}_2\text{CHBr}_2
\]

A  B

\[
\text{CH}_3\text{CH}_2\text{OCCH}_3
\]

C  D  E  F

2. Identify each of the following unknowns from the given \( ^1\text{H} \) NMR and/or infrared spectroscopic information.

a) \( ^3\text{HCl}_3 \)
   \(^1\text{H} \) NMR:
   - singlet, \( \delta \) 2.2, 3H
   - singlet, \( \delta \) 4.0, 2H

b) \( ^2\text{H}_{10}\text{Br}_2 \)
   \(^1\text{H} \) NMR:
   - doublet, \( \delta \) 0.9, 6H
   - multiplet, \( \delta \) 1.5, 1H
   - triplet, \( \delta \) 1.85, 2H
   - triplet, \( \delta \) 5.3, 1H

c) \( ^3\text{H}_8\text{O} \) IR:
   - broad peak near 3400 cm\(^{-1}\)
   \(^1\text{H} \) NMR:
   - doublet, \( \delta \) 1.2, 6H
   - broad singlet, \( \delta \) 2.0, 1H
   - septet, \( \delta \) 4.0, 1H

\( ^1\text{H} \) NMR:
   - peak at 1710 cm\(^{-1}\)
   - singlet, \( \delta \) 2.1, 3H
   - multiplet, \( \delta \) 3.0, 4H
   - multiplet, \( \delta \) 7.1, 5H
3. e) C₅H₁₀
   ¹H NMR: triplet, δ 0.9, 3H
   multiplet, δ 1.5, 2H
   multiplet, δ 2.1, 2H
   multiplet, δ 4.8, 1H
   multiplet, δ 5.1, 1H
   multiplet, δ 5.8, 1H

Note: The chapter on spectroscopy in your textbook contains a number of unknown identification problems that require you to propose a structure for a compound when given spectral data and the formula for that compound. Other problems give the spectrum itself (not merely spectral data). Problems 16.55-16.58, 16.62 and 16.64 are recommended.

4. Predict ¹H and ¹³C NMR spectra for the following compounds. Also calculate m/z ratio for their molecular ions.

   a)  
   b)  
   c)  

Note: Additional problems to be considered in the textbook are 16.41 and 16.42

SOLUTIONS TO SAMPLE PROBLEMS:

1.1  a)  d  b)  c  c)  d
1.2  b
2.1 Signals in the $^1$H NMR:
   a) 3; b) 4; c) 2;  
d) 5; e) 5; f) 3; g) 2; h) 4; i) 4
In the $^{13}$C NMR:
   a) 2; b) 5; c) 3; d) 8; e) 4; f) 4; g) 2; h) 8; i) 3

2.2 a) b  
b) a

2.3 a) A  
b) C

2.4 a) triplet  b) triplet  c) triplet  
d) quartet  e) septet (7 peaks)  f) doublet  
g) doublet  h) doublet  i) triplet

3. a) CH$_3$CCl$_2$CH$_2$Cl  
b) (CH$_3$)$_2$CHCH$_2$CHBr$_2$  
c) (CH$_3$)$_2$CHOH  
d)  
\[
\begin{align*}
&\text{O} \\
&\text{H}_3\text{C} \quad \text{H} \quad 9.4 \text{ ppm, q, 1H} \\
&\text{H}_3\text{C} \\
\end{align*}
\]
e) CH$_3$CH$_2$CH$_2$CH=CH$_2$

4. a) m/z 44.05  
\[
\begin{align*}
&2 \text{ ppm, s, 1H} \\
&d, 3H \\
&\text{H}_3\text{C} \quad \text{H} \quad 9.4 \text{ ppm, q, 1H} \\
&\text{H}_3\text{C} \\
\end{align*}
\]
\[
\begin{align*}
&30 \text{ ppm (CH$_3$)} \\
&200 \text{ ppm (C=O)} \\
\end{align*}
\]
b) m/z 59.11  
\[
\begin{align*}
&0.9 \text{ ppm, t, 3H} \\
&2.6 \text{ ppm, t, 2H} \\
&\text{NH}_2 \\
&4.8 \text{ ppm, b, 2H} \\
&1.4 \text{ ppm, m, 2H} \\
\end{align*}
\]
\[
\begin{align*}
&15 \text{ ppm (CH$_3$)} \\
&25 \text{ ppm (CH$_2$)} \\
&45 \text{ ppm (CH$_2$-N)} \\
\end{align*}
\]
c) m/z 166.18  
\[
\begin{align*}
&7.8 \text{ ppm, d, 2H} \\
&7.0 \text{ ppm, d, 2H} \\
&\text{Br} \\
&\text{OCH}_2\text{CH}_3 \\
&1.4 \text{ ppm, t, 3H} \\
&4.4 \text{ ppm, q, 2H} \\
\end{align*}
\]
\[
\begin{align*}
&15 \text{ ppm (CH$_3$)} \\
&60 \text{ ppm (CH$_2$-O)} \\
&115 \text{ ppm (CH arom)} \\
&121 \text{ ppm (CH arom)} \\
&130 \text{ ppm (CH arom)} \\
&160 \text{ ppm (CH-Br ar)} \\
&170 \text{ ppm (C=O)} \\
\end{align*}
\]
1. a) How many signals are present in the $^1$H NMR spectrum of each of the following compounds? Count similar but theoretically different benzene ring protons as different. 
   b) How many signals are present in the $^{13}$C NMR spectrum of each?
   a) ______
   b) ______

2. a) What splitting pattern (singlet, doublet, triplet, etc.) is observed for each of the underlined proton(s)? b) What is the m/z ratio for the molecular ion for each of the compounds? (Atomic masses: H, 1; C, 12; F, 19; Br, 80)
   a) ______
   b) ______

3. a) Which of the following compounds gives a signal with the highest delta value (most deshielded) in the proton NMR? b) Which gives a signal with the lowest delta value?
   a) ______

4. Identify each of the following unknown compounds.
   a) C$_8$H$_{10}$O
      IR: no peaks near 1700 or 3400 cm$^{-1}$
      $^1$H NMR: singlet, δ2.3, 3H
                             singlet, δ3.8, 3H
                             doublet, δ6.8, 2H
                             doublet, δ7.1, 2H
   b) C$_{10}$H$_{14}$O
      IR: peak at 3400 cm$^{-1}$
      $^1$H NMR: singlet, δ1.3, 9H
                             singlet, δ4.9, 1H
                             multiplet, δ7.0, 4H
c) C_5H_{10}O
IR: peak at 1710 cm^{-1}
^1H NMR: doublet, δ 1.1, 6H
    singlet, δ 2.1, 3H
    septet, δ 2.6, 1H

d) C_4H_7N
IR: peak at 2250 cm^{-1}
^1H NMR: triplet, δ 1.07, 3H
    multiplet, δ 1.67, 2H
    triplet, δ 2.27, 2H

e) C_3H_5ClO_2
IR: broad peak at 2500-3000 cm^{-1}
    peak at 1715 cm^{-1}
^1H NMR: triplet, δ 2.8, 2H
    triplet, δ 3.8, 2H
    singlet, δ 11.6, 1H

5. Predict proton and ^13C NMR spectra for the following compound. Also calculate m/z ratio for the molecular ion (radical cation). Atomic masses: H=1, C=12, O=16.
Name ____________________________   First Drill Test (Sample B)
Organic Chemistry 2220D     Answer All Questions

1. a) How many signals are present in the proton NMR spectrum of each of the following compounds? Count similar but theoretically different benzene ring protons as different. b) How many signals are present in the $^{13}$C NMR spectrum of each?

- a) ______
- b) ______

2. a) What splitting pattern (singlet, doublet, triplet, etc.) is observed for each of the underlined proton(s)? b) What is the m/z ratio for the molecular ion for each of the compounds? (Atomic masses: H, 1; C, 12; O, 16; Br, 80)

- a) ______
- b) ______

3. Which of the following indicated protons gives a signal with the highest δ value (most deshielded)? Which gives a signal with the lowest δ value? What is the m/z ratio for the molecular ion?

- ______ highest δ value
- ______ lowest δ value
- ______ m/z ratio

4. Identify each of the following compounds from the given IR and proton NMR spectra (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet).

- a) C$_3$H$_7$Br
  $^1$H NMR: doublet, δ 1.7, 6H
  septet (7 peaks), δ 4.3, 1H

- b) C$_7$H$_8$O
  IR: broad peak at ~3200-3550 cm$^{-1}$
  $^1$H NMR: s, δ 2.4, 1H
  s, δ 4.6, 2H
  m, δ 7.3, 5H

- c) C$_3$H$_6$Br
  $^1$H NMR: d, δ 2.0, 3H
  q, δ 5.2, 1H
  m, δ 7.4, 5H
d) C₄H₈O₂

IR: strong peak near 1710 cm⁻¹
    broad peak near 3400 cm⁻¹

¹H NMR:  d, δ 1.4, 3H
         s, δ 2.2, 3H
         s, δ 4.0, 1H
         q, δ 4.3, 1H

5. Predict ¹H NMR and ¹³C NMR spectra for the following compound. Also calculate m/z ratio for its molecular ion (radical cation). Atomic masses: H=1, C=12, N=14, O=16.