C1403 NMR Homework

The IR and proton (1H NMR) and carbon (13C NMR) spectra of the molecules of IR Tutor are given along with correlation tables.

This assignment will challenge you to interpret NMR spectra by correlating spectra data with molecular structure.
The following IR spectra that appear in IR Tutor are shown on the following slides together with the 1H NMR and the 13C NMR spectra of the same compounds. Correlation Tables for the IR, 1H NMR and 13C NMR are given. In this homework exercise you should try to make sense out of the 1H NMR and 13C NMR spectra based on the empirical approach that we used for the interpretation of IR spectra.

The different signals in the 1H NMR spectra correspond to signals for chemically different protons. The intensity of the signal is roughly proportional to the number of protons in the structure.

The different signals in the 13C NMR spectra correspond to signals for chemically different carbon atoms. The intensity of the signal is roughly proportional to the number of carbons in the structure.
Some Important and Characteristic Infrared Absorption Frequencies and Wavelengths for Some Common Stretching Motions

<table>
<thead>
<tr>
<th>Atom Group</th>
<th>Typical of</th>
<th>Frequency (cm(^{-1}))</th>
<th>Wavelength ((\mu))</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H (free)</td>
<td>Alcohols (dilute)</td>
<td>3550-3650 cm(^{-1})</td>
<td>2.8 (\mu)</td>
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<tr>
<td>O-H (H bonded)</td>
<td>Alcohols (concentrated)</td>
<td>3200-3400 cm(^{-1})</td>
<td>3.0 (\mu)</td>
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<tr>
<td>C(=)C(=)H</td>
<td>Acetylene (CH)</td>
<td>3300 cm(^{-1})</td>
<td>3.0 (\mu)</td>
</tr>
<tr>
<td>C(=)C(=)H</td>
<td>Benzene (CH), Ethylene (CH)</td>
<td>3010-3100 cm(^{-1})</td>
<td>3.3 (\mu)</td>
</tr>
<tr>
<td>C(\equiv)C(\equiv)H</td>
<td>Ethane (CH)</td>
<td>2950-3000 cm(^{-1})</td>
<td>3.5 (\mu)</td>
</tr>
<tr>
<td>C(\equiv)C</td>
<td>Acetylene</td>
<td>2100-2260 cm(^{-1})</td>
<td>4.5 (\mu)</td>
</tr>
<tr>
<td>C(\equiv)N</td>
<td>Nitriles</td>
<td>2000-2300 cm(^{-1})</td>
<td>4.5 (\mu)</td>
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<tr>
<td>C(\equiv)O</td>
<td>Carbonyl</td>
<td>1650-1750 cm(^{-1})</td>
<td>5.5- 6.0 (\mu)</td>
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<tr>
<td>C(\equiv)C</td>
<td>Alkene</td>
<td>1620-1680 cm(^{-1})</td>
<td>6.0 (\mu)</td>
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<tr>
<td>C(\equiv)C</td>
<td>Alkane</td>
<td>600-1500 cm(^{-1})</td>
<td>6.7-17 (\mu)</td>
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<tr>
<td>C(\equiv)O</td>
<td>Alcohols, Ethers</td>
<td>1000-1300 cm(^{-1})</td>
<td>10-7.7 (\mu)</td>
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</table>

In general we will only be using the data in an IR spectrum for stretching vibrations which have energies higher than 1620 cm\(^{-1}\). Although the bands at lower energy are known and assigned, the region below 1620 cm\(^{-1}\) is very congested with single bond stretches of two heavy atoms (see C-C and C-O in table) and C-H bends and are beyond the scope of what we want to do.
NMR units are ppm (parts per million). We discuss where this ppm unit comes from in class.

These are the signals of protons (1H NMR). We think of the position (in ppm) of the NMR signals in the same way we viewed the frequency of IR signals. The 1H NMR signals are characteristic of certain types of protons in molecules.
These are the position of the signals of carbon atoms (13C) in ppm. We think of the position of a NMR signal in ppm in the same way we viewed the frequency of IR signals. The 13C NMR signals are characteristic of certain types of carbon atoms in molecules.

<table>
<thead>
<tr>
<th>Type of carbon</th>
<th>Chemical shift (δ) ppm*</th>
<th>Type of carbon</th>
<th>Chemical shift (δ) ppm*</th>
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</thead>
<tbody>
<tr>
<td>RCH₃</td>
<td>0–35</td>
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<tr>
<td>R₂CH₂</td>
<td>15–40</td>
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<tr>
<td>RCH₂Br</td>
<td>20–40</td>
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<tr>
<td>R₃CH</td>
<td>25–50</td>
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<td>RCH₂Cl</td>
<td>25–50</td>
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<tr>
<td>RCH₂NH₂</td>
<td>35–50</td>
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<tr>
<td>RCH₂OH</td>
<td>50–65</td>
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<tr>
<td>—C≡C—</td>
<td>65–90</td>
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</table>
1H NMR

1H range = 0 to ~ 10 ppm

Increasing magnetic field, $H_0$

13C NMR

13C range = 0 to ~ 200 ppm

Use the correlation tables and note scale of x-axis
Example: n-hexane. You’ve seen the IR and have considered the C-H stretches. C-H stretches at ~ 2900 cm$^{-1}$.
Now let’s consider the 1H (proton) and 13C (carbon) NMR spectra of n-hexane (next slide).

The 1H NMR shows the signals of ALL of the protons of which a molecular structure is composed. The position of the signal depends on the chemical environments of the electrons so 1H NMR provides information on molecular structure of any molecules containing X-H bonds.

The 13 C NMR shows the signals of ALL of the carbons of which a molecular structure is composed. The position of the signal depends on the chemical environments of the carbon atoms so 13C NMR provides information on organic molecules.
Now consider the structure of n-hexane below. How many different kinds of protons and carbon atoms does the structure suggest?

First consider the protons: there are three different kinds of protons: the CH₃ protons on C₁, the CH₂ protons on C₂ and the CH₂ protons on C₃. We note that C₁ is equivalent to C₆, C₂ is equivalent to C₅ and C₃ is equivalent to C₄.

We expect to see three signals in the 1H NMR of n-hexane (next slide) for the three different types of protons. We can’t predict where they will be but we will empirically try to correlate them with the structure of n-hexane.

The intensity of the signals in a 1H NMR are proportional to the relative number of protons in a structure. This will make the assignments easier.
Next let’s consider the *carbon* atoms of n-hexane.

There are only three different kinds of carbon atoms in n-hexane: $C_1 = C_6$, $C_2 = C_5$, and $C_3 = C_4$.

We therefore expect three signals for the three different carbon atoms.

The signals in a 13C NMR are proportional to the relative number of carbon atoms in a structure. This will make the assignments easier.
Use the correlation tables and note scale of x-axis.
Assign the $1^H$ signals to the protons of n-hexane.

Assign the $13^C$ signals to the carbon atoms of n-hexane.

$n$-hexane
2,3-dimethyl butane
Assign the signals in the NMR spectra to the H and C in the structures.

Use the correlation tables and note scale of x-axis.
1-hexene
Use the correlation tables and note scale of x-axis.

Assign the signals at ~5 ppm and ~5.7.

Assign the signals at ~115 ppm and ~140 ppm.
Toluene
methyl benzene
Use the correlation tables and note scale of x-axis

Assign the signal at ~ 2.3 ppm.

Assign the signal at ~ 20 ppm.

toluene
1-heptyl cyanide

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}≡\text{N} \]
Use the correlation tables and note scale of x-axis.

Assign the 1H signals

1H NMR

Assign the 13C signals

13C NMR

1-heptylcyanide
HC≡CCH₂CH₂CH₂CH₂CH₃

1-heptyne

4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 cm⁻¹ 400
Can you find the C-H signal associated with the triple bond?

Which signals are due to the triple bond carbons?

Use the correlation tables and note scale of x-axis
Can you find the C-H signal associated with the triple bond?

$\text{HC}≡\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

Which signals are due to the triple bond carbons?

$\text{HC}≡\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
24-Heptanone

CH₃CH₂CCH₂CH₂CH₂CH₂CH₃

3-heptanone
1H: How many signals can you assign?

3-heptanone

1H: Which signal is associated with this signal in the IR of 3-heptanone?
What is the signal at \(~ 4.2\) ppm due to? The signal at \(~ 2.0\) ppm?

What are the peaks at \(~ 170\) ppm and \(~ 60\) ppm due to?

Use the correlation tables and note scale of x-axis.
CH₃CH₂CH₂CH₂CH₂CH₂CH₂CHO

1-heptanal
What is the signal at ~10 ppm due to? Can you find the analogous signal in the IR?

What is the signal at ~200 ppm due to?

Use the correlation tables and note scale of x-axis
What is the signal at ~ 3.5 ppm due to?

HO
1-hexanol

What is the signal ~63 ppm due to?

CH₃CH₂CH₂CH₂CH₂CH₂OH

Use the correlation tables and note scale of x-axis
CH₃CH₂CH₂CH₂CH₂CH₂CH₂COH
1-Heptanolic Acid
What is the signal at ~11 ppm due to?

What is the signal at ~180 ppm due to?

Use the correlation tables and note scale of x-axis