$^1$H Nuclear Magnetic Resonance
Gas Chromatograph of Molecular Hydrogen at –100 °C

Thermoconductivity Detector

Time

Intensity

1 2
What's going on?

Ortho Hydrogen              Para Hydrogen

O/P = 1:1 at 80 K
The magnetic moment of a spinning nucleus is colinear with the axis of spin.

For a nucleus with a spin of $\pm 1/2$, only two orientations in a magnetic field are allowed. Regardless of the strength of the magnetic fields currently available, only a very slight difference in population exist between the two orientations.
Processional frequency, $\nu$, is proportional to the magnetic field strength, $H$

$$\nu = \gamma H$$

$1 \text{ Hz} = 1 \text{ cycle/second}$

For $^1\text{H}$  

At 14,000 Gauss (1.4 Tesla)  
$\nu = 60 \text{ MHz}$

At 70,500 Gauss (7.05 Tesla)  
$\nu = 300 \text{ MHz}$

At 14,000 Gauss (14.1 Tesla)  
$\nu = 600 \text{ MHz}$

For $^{13}\text{C}$  

$\nu = 14 \text{ MHz}$  

$\nu = 70 \text{ MHz}$  

$\nu = 140 \text{ MHz}$

c = $\lambda \nu$;  
$\lambda = 3 \times 10^{10} \text{ cm sec}^{-1}/600 \times 10^{6} \text{ sec}^{-1} = 50 \text{ cm}$

The Electromagnetic Spectrum
If a nucleus experiences a different magnetic field it will precess at a different frequency and absorb at a different frequency \((E = hv)\).
A typical 1H NMR spectrum in frequency reported in parts per million

Since the frequency (cycles/sec) depends on the strength of the magnetic field, chemical shifts are reported relative to a standard, frequently tetramethylsilane (0 ppm). If the spectrum is run at a magnetic field strength that generates precessional frequencies of 300 MHz (300 million cycles per sec, 7.05 Tesla), 1 ppm is equal to 300 Hz (300 cycles per second). At 600MHz, 1 ppm = 600 Hz. Chemical shifts reported in ppm are independent of the field strength (or frequency)
Typical NMR Chemical Shifts

Tetramethylsilane = 0 ppm (standard)
Typical NMR Chemical Shifts
What causes the chemical shift?

The protons are immersed in a sea of electrons which are charged and have both an electric field and a magnetic field associated with their charge.
The nmr of 2,2, -dimethylpropanol

Figure NMR-2. The NMR spectrum of 2,2-dimethylpropanol
Why the multiplicity?
Consider the following:

If \( H_a \) has a different chemical shift from \( H_b \), roughly 50% of the nuclei of \( H_b \) will have one orientation of their magnetic moment and the other will have just the opposite.

The total field felt by \( H_a \) will be due to the external field, the local field due to electronic environment and the field due to the proton(s) three bonds removed. The field due to the local proton will either add or subtract to the total field experience by \( H_a \). Roughly 50% will have a neighbor with a ↑ and 50% with a neighbor ↓ resulting in two lines observed for \( H_a \).

\( J_{ab} \) is called the coupling constant.

With two identical neighbors:
With three identical neighbors:

n+1 rule = number of lines observed equals the number of nearest Hb neighbors + 1
neighbors are identical in the sense that the coupling constants are the same or very similar
Information obtained by a NMR spectrum

1. Chemical shift: indicates the type of proton
2. Relative areas: provide a ratio of the number of each type of H nucleus
3. Number of nearest neighbors (first order spectra)
The hydrogens are three bonds removed

The hydrogens are four or more bonds removed except for the OH
The nmr of 2,2-dimethylpropanol

Figure NMR-2. The NMR spectrum of 2,2-dimethylpropanol
One Criterium for First Order Spectra

The chemical shift difference between the hydrogens that are coupled to each other is greater than 10 times the magnitude of the coupling constant.

\[ \text{X-CH}_2\text{CHY}_2 \]
$^{13}$ C NMR: natural abundance of 1%, spin of $\frac{1}{2}$ (like hydrogen)

The probability of finding 2 $^{13}$ C atoms next to each other is $0.01^2$ or $10^{-4}$

Hydrogen and carbon do couple to each other. However because the amount of $^{13}$ C is so small, spectra are generally decoupled during acquisition. This is done by irradiating all the hydrogens and causing them to rapidly change their spin orientation. It is somewhat analogous to the decoupling observed in alcohols where the hydrogens three bonds removed are decoupled to an OH hydrogen due to rapid chemical exchange

Information from $^{13}$C spectra

1. Number of chemically different carbons
2. Chemical shift information: the chemical environment of the carbon
13 C NMR Chemical Shifts

<table>
<thead>
<tr>
<th>Carbon Environment</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O (in ketones)</td>
<td>205 - 220</td>
</tr>
<tr>
<td>C=O (in aldehydes)</td>
<td>190 - 200</td>
</tr>
<tr>
<td>C=O (in acids and esters)</td>
<td>170 - 185</td>
</tr>
<tr>
<td>C in aromatic rings</td>
<td>125 - 150</td>
</tr>
<tr>
<td>C=C (in alkenes)</td>
<td>115 - 140</td>
</tr>
<tr>
<td>RCH2OH</td>
<td>50 - 65</td>
</tr>
<tr>
<td>RCH2Cl</td>
<td>40 - 45</td>
</tr>
<tr>
<td>RCH2NH2</td>
<td>37 - 45</td>
</tr>
<tr>
<td>R3CH</td>
<td>25 - 35</td>
</tr>
<tr>
<td>CH3CO-</td>
<td>20 - 30</td>
</tr>
<tr>
<td>R2CH2</td>
<td>16 - 25</td>
</tr>
<tr>
<td>RCH3</td>
<td>1</td>
</tr>
</tbody>
</table>

Information from 13 C NMR

Carbon count

Chemical Shift
Which of the following alcohols produced the $^{13}$ C NMR spectrum below?
\text{CH}_2=\text{CH-CO-CH}_3

\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \quad \text{O} \\
\text{O} & \quad \text{CH} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
Common NMR solvent: CDCl₃; CCl₄, CD₃SOCD₃; C₆D₆; CD₃COCD₃; D₂O

Deuterium ²H also has a spin; it has three orientation in a magnetic field

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Formula</th>
<th>H-NMR shift*</th>
<th>C-NMR shift</th>
<th>multiplet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform-d</td>
<td>CDCl₃</td>
<td>7.24 (singlet)</td>
<td>77.0</td>
<td>triplet</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>CCl₄</td>
<td>96.7</td>
<td></td>
<td>singlet</td>
</tr>
<tr>
<td>Dimethylsulfoxide-d₆</td>
<td>CD₃SOCD₃</td>
<td>2.49 (pentet)</td>
<td>39.7</td>
<td>septet</td>
</tr>
<tr>
<td>Benzene-d₆</td>
<td>C₆D₆</td>
<td>7.2 (singlet)</td>
<td>128.0</td>
<td>triplet</td>
</tr>
<tr>
<td>Acetone-d₆</td>
<td>CD₃COCD₃</td>
<td>2.04 (pentet)</td>
<td>29.8</td>
<td>septet</td>
</tr>
<tr>
<td>Water-d₂</td>
<td>D₂O</td>
<td>4.65 (singlet)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The H-NMR peak is due to a residual amount of ¹H in the deuterated solvent and is small
$^1$H NMR

25.16 MHz
0.75 ml : 1.5 ml CDCl$_3$

Acetone $^{13}$C NMR

http://www.orgchemboulder.com/Spectroscopy/Problems
Fig. 7.8 $\Lambda$-enaphthene. Same conditions as Fig. 7.7 but with decoupler ON only during acquisition time; number of transients, 150.