NMR
NMR is a nondestructive technique that gives exact positions of atoms in the molecule. Before NMR organic chemical structure was always ambiguous or inferred. NMR changes all that.

Order of topics
1. Practical NMR. How to use NMR to assign chemical structure.
2. How NMR works. In case you wanted to build an NMR spectrometer.
3. Modern NMR – 2D and DEPT.

1H NMR
1H is 99.99% abundant. What are the other forms of H?

A little bit of how NMR works:
When you put a molecule in an external magnetic field, the electrons around the 1H affect the way that the 1H aligns in the magnetic field, this alignment relates to energy in that there is an easy alignment and a hard alignment with the external magnetic field. Easy alignment is low energy and harder alignment is high energy. The NMR spectrum is split into regions corresponding to the energies created by the interactions of the orbitals surrounding the H.

The energies are plotted on a scale of about 0-10
0 relates to low energy and 12 relates to high energy transitions.
0 is called shielded and >10 is called deshielded meaning that the proton is less or more susceptible to the external magnetic field.
0 is called upfield and 10 is called downfield – this is historical when NMR was done on chart recorders.

<table>
<thead>
<tr>
<th>12</th>
<th>10</th>
<th>8</th>
<th>6</th>
<th>5</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deshielded</td>
<td>Shielded</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Downfield</td>
<td>Upfield</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

Chemical shift  The energy of the NMR absorption is related to functional group.

| 0-2 | H-C saturated | sp<sup>3</sup>C-H |
| 2-3 | H-C allyl | sp<sup>2</sup>C-sp<sup>3</sup>C-H |
| 3-4 | H-C-EN (EN=N,O,F,Cl,Br,I) | usually sp<sup>3</sup>C-H |
| 5-6 | H-C vinyl | sp<sup>2</sup>C-H |
| 6-8 | H-C aromatic | sp<sup>2</sup>C-H |

You can have multiple effects. CH<sub>3</sub>Cl | CH<sub>2</sub>Cl<sub>2</sub> | CHCl<sub>3</sub>
| 3-4 | 5-6 | 7-8 |

Every Cl exerts about a 2 ppm shift. Assumes that a normal proton in a completely saturated environment is about 1 ppm. (0-2 ppm).
Real NMR spectra

Note. Is the $^1$H NMR scale based on 0 being methane?

What would the $^1$H spectrum of CCl$_4$ look like?

**Organic Compounds with many $^1$H's.**

Integration = relative number of protons. Area under peaks. A ratio of number of protons.

Integration is not intensity, but might be for some resonances.
Predict the ratios of integration for these molecules:

CH₃CH₂Cl  CH₃CH₂OCH₂CH₃  (CH₃)₂CHOH

Spin-Spin Splitting – The interaction of local magnetic fields on H’s on neighboring C’s
Splitting = n + 1 nearest neighbors in a Pascal’s triangle intensity pattern:

<table>
<thead>
<tr>
<th># neighbors</th>
<th>lines</th>
<th>label</th>
<th>intensity ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 neighbors</td>
<td>1 line</td>
<td>singlet</td>
<td>1</td>
</tr>
<tr>
<td>1 neighbors</td>
<td>2 lines</td>
<td>doublet</td>
<td>1 1</td>
</tr>
<tr>
<td>2 neighbors</td>
<td>3 lines</td>
<td>triplet</td>
<td>1 2 1</td>
</tr>
<tr>
<td>3 neighbors</td>
<td>4 lines</td>
<td>quartet</td>
<td>1 3 3 1</td>
</tr>
<tr>
<td>4 neighbors</td>
<td>5 lines</td>
<td>pentet</td>
<td>1 4 6 4 1</td>
</tr>
<tr>
<td>5 neighbors</td>
<td>6 lines</td>
<td>sextet</td>
<td>1 5 10 10 5 1</td>
</tr>
<tr>
<td>6 neighbors</td>
<td>7 lines</td>
<td>septet</td>
<td>1 6 15 20 15 6 1</td>
</tr>
</tbody>
</table>

http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/nmr/nmr1.htm#nmr2
The coupling constant is called $J$. Note sets of coupled $H$'s will always have the same $J$.

$J$ values depend on hybridization, geometry and other electronic factors.

How many bonds is a normal $J$ coupling?

Geminal Hydrogens

Vicinal Hydrogens

http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/nmr/nmr1.htm#nmr2

Coupling patterns for equivalent Hydrogens

- **No Coupled Hydrogens**
  - [Diagram of no coupled hydrogens]
  - A Singlet

- **One Coupled Hydrogen**
  - [Diagram of one coupled hydrogen]
  - A Doublet

- **Two Coupled Hydrogens**
  - [Diagram of two coupled hydrogens]
  - A Triplet

- **Three Coupled Hydrogens**
  - [Diagram of three coupled hydrogens]
  - A Quartet

http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/nmr/nmr1.htm#nmr2

Coupling Patterns for nonequivalent Hydrogens

- **No Coupled Hydrogens**
  - [Diagram of no coupled hydrogens]
  - A Singlet

- **One Coupled Hydrogen**
  - [Diagram of one coupled hydrogen]
  - A Doublet

- **Two Coupled Hydrogens**
  - [Diagram of two coupled hydrogens]
  - A Doublet of Doublets

- **Three Coupled Hydrogens**
  - [Diagram of three coupled hydrogens]
  - A Doublet of Doublets

http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/nmr/nmr1.htm#nmr2
Range of J couplings

<table>
<thead>
<tr>
<th>Compound</th>
<th>J Couplings</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0 Hz</td>
</tr>
<tr>
<td>H&lt;sub&gt;3&lt;/sub&gt;C - CH&lt;sub&gt;2&lt;/sub&gt;-R</td>
<td>6 - 8 Hz</td>
</tr>
<tr>
<td>H&lt;sub&gt;3&lt;/sub&gt;C - CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3 - 12 Hz</td>
</tr>
<tr>
<td>R&lt;sub&gt;2&lt;/sub&gt;C - H</td>
<td>3 - 8 Hz</td>
</tr>
<tr>
<td>H</td>
<td>1 - 3 Hz</td>
</tr>
</tbody>
</table>

Equivalence. Many times H's have degenerate energy transitions in the NMR. The analytical method is to identify symmetry elements. Or alternatively, replace an H with an X. If replacing various H's leads to the same isomer, then the H is called equivalent. This is a unique position. Equivalent H's do not couple each other.

http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/nmr/nmr1.htm#nmr2
Common $^1$H NMR Patterns: Match the groups and assign peaks. Ethyl, Propyl and Isopropyl:

- $\text{C}_2\text{H}_5\text{Br}$
  - 2H
  - 3H

- $\text{C}_3\text{H}_7\text{Br}$
  - 1H
  - 6H

- $\text{C}_3\text{H}_7\text{Br}$
  - 2H
  - 2H
  - 3H
The 4-carbon molecules:
C₄H₉Br: Butyl, Isobutyl, sec-Butyl, ter-Butyl

Which butyl is missing? What would the ¹H NMR of the missing group look like?
\(^{13}\text{C} \text{ NMR}\) Like proton NMR but different. \(^{13}\text{C} \text{ NMR}\) is based on 0 – 200 ppm. Since this is 20 times \(^1\text{H}\), just multiply by 20.

1. Chemical shifts are not as predictable as proton, but this is a guide.
   - 0-40 H-C saturated
   - 40-60 H-C allyl
   - 60-80 H-C-EN (EN=N,O,F,Cl,Br,I)
   - 100-120 H-C vinyl
   - 120-160 H-C aromatic with the bonus of C=O, around 200 ppm.

2. Integration = not used too much. It is difficult to integrate \(^{13}\text{C}\).

3. Splitting = we usually ignore splitting. We usually blast the splitting away with microwave energy. Most \(^{13}\text{C} \text{ NMR}\) spectra that you will see are a forest of lines. \(^{13}\text{C}\) is about 1.1% of the C in any molecule. Therefore, what are the chances of two \(^{13}\text{C}\) being next to each other?
   - What are the chances of two \(^1\text{H} – ^1\text{H}\) being near each other?

4. Equivalence. This is the main point of \(^{13}\text{C} \text{ NMR}\). You can tell at a glance the number of unique carbons that are present in a molecule. This is very useful indeed.
   - Here are some examples of what \(^{13}\text{C} \text{ NMR}\) look like. Consider \(\text{C}_2\text{H}_5\text{Br}\)

\[\text{C}_3\text{H}_7\text{Br} \text{ The two propyl spectra are clearly indicative of the actual structure.}\]
Notice how the top two spectra are ambiguous, but the bottom two are clearly indicative of the correct structure. What would you need to distinguish the top two?
Problem Solving H-NMR spectra
1. Take formula and derive the degrees of unsaturation.
2. Determine the number of H’s by integration and match the formula.
3. Determine the chemical shift regions of each H.
4. Create fragments ready to assemble.
5. Assemble fragments based on splittings.

C₉H₁₂O
Degrees of unsaturation
More C$_2$H$_2$O IR shows broad peak between 3300-3600
More C₆H₁₂O IR shows broad peak between 3300-3600
$C_6H_{10}O_2$ An IR peak at 1700 cm$^{-1}$

**NMR**

$^{13}$C NMR
An improvement on $^{13}$C NMR. Consider $\text{C}_8\text{H}_{10}$

spectrum of ethyl benzene

http://www.chem.ucla.edu/cgi-bin/webspectra.cgi?Problem=bp21&Type=D
In the DEPT spectra, the C with an odd number of attached H have a positive phase (up) and those with an even number of H have a negative phase (down).

2-D NMR

H-H COSY

MEK


http://www.cis.rit.edu/htbooks/nmr/chap-10/j4-1.htm
More H-H COSY

http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch13/ch13-2dnmr-1.html#hetcor