Lecture Notes for Organic Chemistry © 2007

Chapter 5 13-15 Spectroscopy

Much of what is known about organic chemistry comes from spectroscopy which is the study of light, or electromagnetic radiation (EM) as it interacts with matter.

The wavelength and frequency, which are inversely proportional, are related by the equation

\[ \nu \lambda = c \quad \text{or} \quad \lambda = \frac{c}{\nu} \]

where:

- \( c \) = speed of light \( (3 \times 10^{10} \text{ cm/sec}) \)
- \( \nu \) = frequency in hertz
- \( \lambda \) = wavelength in centimeters

Infrared frequencies are about \( 10^{14} \) Hz. IR spectra are measured in % transmittance vs cm⁻¹.

If a molecule is polar, its vibrating dipoles will absorb energy when they interact with the electric field of EM at resonance. No dipole = no IR absorption.

Stretching frequencies depend on:

- Bond strength and atomic mass
  - \( C=O > C=O > C-C \)
  - \( C-H > C-D > C-C \)
  - \( 3000 \ 2100 \ 1200 \)
Important stretching frequencies (cm⁻¹)

- **C-C**: 1200
- **C=C**: 1660
- **C=C**: 2200
- **C=C Isolated**: 1645
- **C=C Conjugated**: 1620
- **Aromatic**: 1600

C-H stretching
- \( \text{SP}^3 \) less than 3000 (to the right of 3000)
- \( \text{SP}^2 \) greater than 3000 (to the left of 3000)
- **SP**: 3300

Alcohols and amines

- **R-OH**: 3300, broad
- **R-NH**\(_{\text{H}}\): 3300, broad, with spikes (1 for 2°, 2 for 1°)
- **R-\( \text{O}^{-}\)OH**: 3000, broad

'Arboryls' - A very strong peak

'entered at 1710'

Aldehydes are distinguished by 2 C-H stretches at 2700, 2800

Acids are distinguished by broad OH, 3000

Conjugation lowers the C=O stretch to the 1620 region

Amides are the lowest frequencies, 1650-1630

US C=C, amides have no \( \text{SP}^2 \) C-H (73000) and show strong, broad N-H 3000-3500

A few carboxylic acids absorb higher than 1710

Trapped ring ketones to 1790

-N bonds absorb more strongly than C-C bonds (more polar)

- **C=N**: 1660
- **CEN 72200**: Very strong and sharp

15N spectrometry

Molecules are fragmented by electron impact (one of many techniques)
The fragments are mass analyzed

Strongest peak is the base peak

Molecular ion is called the parent peak; molecular weight = M

Very high resolution mass spectrometers can give 'exact' mass

From which a unique molecular formula is obtained.
$n + 1 = \text{PARENT} + 1 \quad \{\text{COME FROM HEAVIER ISOTOPES}\}$

$1 + 2 = \text{PARENT} + 2$

This leads to a few recognizable patterns:

- $B_2 \quad m + 2 = 100\% \text{ of } M$
- $C_1 \quad m + 2 = 33\% \text{ of } M$
- $I \quad I^+ = 127, \text{ LARGE CAP}$
- $N \quad 000 \text{ of } M$
- $S \quad m + 2 \text{ SLIGHTLY LARGER (4% of } M)$

Fragmentation patterns:

Almost all possible fragments are created, but there are a few especially stable ones. These are often highly stable cations: allyl, benzyl $\geq 30\%$

Alcohols lose $H_2O$, look for an $m-18$ peak (even#)

Skills:
- Identify common IR peaks
- Explain why peaks are strong, weak, or absent
- Identify the various aromatic peaks (conjugation)
- Identify the $C=C$ peaks (conjugation)
- Use MS for MW
- Use MS for $B_2, C_1, S, I, N$
- Identify fragmentation patterns
- Use for structure

Problems:
- 3, 4, 11, 19a, 25
- 2, 14
- 31, 5, 52, 6
- 14, 15
- 7, 20
- 8, 9, 10, 11
- 180
<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Functional Group</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3300</td>
<td>alcohol</td>
<td>O—H</td>
</tr>
<tr>
<td></td>
<td>amine, amide</td>
<td>N—H</td>
</tr>
<tr>
<td></td>
<td>alkyne</td>
<td>≡C—H</td>
</tr>
<tr>
<td>3000</td>
<td>alkane</td>
<td>−C—H</td>
</tr>
<tr>
<td></td>
<td>alkene</td>
<td>≡=C&lt;H</td>
</tr>
<tr>
<td></td>
<td>acid</td>
<td>O—H</td>
</tr>
<tr>
<td>2200</td>
<td>alkyne</td>
<td>−C≡C—</td>
</tr>
<tr>
<td></td>
<td>nitrile</td>
<td>−C≡N</td>
</tr>
<tr>
<td>1710 (very strong)</td>
<td>carbonyl</td>
<td>≫C=O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1660</td>
<td>alkene</td>
<td>≫C=C&lt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>imine</td>
<td>≫C=N&lt;</td>
</tr>
<tr>
<td></td>
<td>amide</td>
<td>≫C=O</td>
</tr>
</tbody>
</table>

Ethers, esters, and alcohols also show C—O stretching between 1000 and 1200 cm\(^{-1}\).

**Aldehyde 2700 + 2800**
CHAPTER 14: LECTURE NOTES FOR ORGANIC CHEMISTRY

INTERPRETATION OF NMR SPECTRA

Many nuclides are magnetic: \(^1H\) and \(^{13}C\) have magnetic nuclei. When a sample is placed in a strong magnetic field (\(B_0\)) these nuclei act as little bar magnets.

A nucleus aligned in the same direction as \(B_0\) is in a lower energy state, like a compass pointing north.

A nucleus aligned in the opposite direction is in a higher energy state.

NMR spectroscopy observes transitions between these two energy states.

The photon that is absorbed is of very low energy, with a frequency in the megahertz range (\(10^6\) Hz, or \(10^6\) cycles per second).

This is a type of absorption/emission spectroscopy, the nuclei are put into the higher energy state by absorbing a photon. As the nuclei return to the lower energy state they emit a photon that is the NMR signal.

The one crucial idea: frequency of the NMR signal depends on the magnetic field strength (\(B_0\)).

This is expressed by the Larmor equation:

\[ w = \gamma B_0 \]

Frequency (\(w\)) = Magnetogyric ratio \(\times\) field strength (\(\gamma \times B_0\)).

The magnetogyric ratio is unique for each isotope.

This means that all protons have the same frequency in a given field strength (as in MRI, magnetic resonance imaging).

Fortunately, each proton in a molecule finds itself in a slightly different magnetic environment, due to an effect called shielding.

Electrons in bonds produce magnetic fields that either oppose \(B_0\) (shield) or reinforce \(B_0\) (deshield).

So the effective magnetic field strength is slightly different for different types of protons (only a few parts per million, ppm).

This is called chemical shift.

From each proton spectrum we will get 4 pieces of information:

1) How many signals = How many different types of protons
2) How strong are the signals (integration) tells how many protons of each type
3) Chemical shift of each signal tells which types of functional group is present
4) Splitting pattern tells how many neighboring protons are present
HEMICAL SHIFT
- EXPRESSED IN ppm
- REFERENCED TO TETRAMETHYL SILANE (TMS) = 0

\[ \text{CH}_3 - \cdot \text{Si-CH}_3 \]
- DUE TO SHIELDING
ELECTRONS IN \\
BONDS "SHIELD" THE NUCLEUS FROM \( B_0 \), PRODUCE A LOWER EFFECTIVE FIELD AND LOWER FREQUENCY, LOWER CHEMICAL SHIFT. IF ELECTRONS SHIELD, ELECTRON WITHDRAWING GROUPS "DESHIELD" PRODUCING HIGHER FREQUENCIES, HIGHER CHEMICAL SHIFTS.

<table>
<thead>
<tr>
<th>( X ) in ( \text{CH}_3-X )</th>
<th>F</th>
<th>OH</th>
<th>Cl</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>electronegativity of ( X )</td>
<td>4.0</td>
<td>3.4</td>
<td>3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>chemical shift of ( \text{CH}_3-X )</td>
<td>84.3</td>
<td>83.4</td>
<td>83.0</td>
<td>82.7</td>
</tr>
</tbody>
</table>

THE EFFECT DIMINISHES WITH DISTANCE

THE EFFECT IS ADDITIVE (APPROXIMATELY)

\[
\begin{align*}
\text{CH}_4 & : 0.2 \\
\text{CH}_3-\text{Cl} & : 3.0 \\
\text{CH}_2\text{Cl}_2 & : 5.3 \\
\text{CHCl}_3 & : 7.3 \\
\end{align*}
\]

+2.8 +2.3 +2.5

VINYL AND AROMATIC PROTONS ARE ESPECIALLY DEShieldED BY A MAGNETIC FIELD PRODUCED BY \( \pi \) ELECTRONS

VINYL \( \rightarrow \) 5-6 ppm
AROMATIC \( \rightarrow \) 6-8 ppm

ALDEHYDE PROTONS EXPERIENCE SIMILAR \( \pi \)-DESHIELDING PLUS INDUCTIVE EFFECT OF \( \text{C}=\text{O} \) \( \rightarrow \) 9-10 ppm

CABOXYLIC ACID PROTONS \( \rightarrow \) 10 + ppm

NUMBER OF NMR SIGNALS

PROTONS IN IDENTICAL CHEMICAL ENVIRONMENTS WITH THE SAME SHIELDING ARE CALLED CHEMICALLY EQUIVALENT
ONLY 1 SIGNAL IS SEEN FOR "EQUIVALENT" PROTONS

\[
\begin{align*}
\text{CH}_3- & \text{1 TYPE OF PROTON 1 SIGNAL} \\
\text{CH}_3\text{CH}_2- & \text{2 TYPES OF PROTONS 2 SIGNALS} \\
\text{CH}_3-\text{C}- & \text{1 TYPE OF PROTON 1 SIGNAL} \\
\end{align*}
\]
THE STRENGTH OF THE NMR SIGNAL

THE AREA UNDER A PEAK IS PROPORTIONAL TO THE NUMBER OF PROTONS

INTEGRATED AREAS WILL BE PROVIDED FOR ALL NMR PEAKS IN THIS COURSE
SOMETIMES THE AREAS WILL BE ABSOLUTE (AS IN "EQUALS 2 PROTONS")
SOMETIMES RELATIVE (AS IN 3:1 RATIO OF AREAS)

THE SPIN-SPIN SPLITTING PATTERN

DUE TO AN EFFECT CALLED "COUPLING"

LEADING TO THE N+1 RULE

IF A SIGNAL IS SPLIT BY N EQUIVALENT PROTONS, IT GIVES N+1 PEAKS

SO, 1 NEIGHBORING PROTON  \( \text{CH}_3 - \cdot \text{H} \rightarrow \text{M} \) DOUBLET, AREA 3
2 NEIGHBORING PROTONS  \( \text{CH}_3 - \cdot \cdot \text{H} \rightarrow \text{M} \) TRILET, AREA 5
3 NEIGHBORING PROTONS  \( \text{CH}_3 - \text{CH}_2 \rightarrow \text{M} \) QUARTET, AREA 2

SOME VERY COMMON PATTERNS

\[ \text{CH}_3\text{CH}_2 \rightarrow \text{M} \quad \text{M} \]
\[ \text{CH}_3 - \cdot \text{H} \rightarrow \text{M} \quad \text{M} \]

ETHYL

ISOPROPYL

SINGLETS MEAN NO NEIGHBORS

\[ \text{CH}_3 - \cdot \text{H} \rightarrow \text{M} \quad \text{M} \]
\[ \text{CH}_3 - \cdot \text{H} \rightarrow \cdot \text{O-CH}_3 \quad \cdot \text{CH}_2 - \cdot \text{H} \]

THE RANGE OF COUPLING

- USUALLY RESTRICTED TO 3 BONDS
- 4 AND 5 BOND COUPLING MAY BE SEEN, ESPECIALLY IN \( \Pi \) SYSTEMS
COUPLING

A single resonance line is decomposed into two lines by coupling with a neighboring nucleus.

This is because the resonance line experiences two different field strengths, one higher than $B_0$ and one lower, due to the two populations of the neighboring nucleus -- aligned either with or against $B_0$.

---

Points to Remember

- The strength of the interaction between coupled nuclei is expressed in Hz and is named $J$.
- The effect is transmitted through chemical bonds and decreases as the number of bonds between atoms increases.
- The coupling constant is independent of external field strength.
CARBON-13 SPECTRA
WE WILL TREAT THEM ALMOST THE SAME AS 'H SPECTRA
EXCEPT:
- THE CHEMICAL SHIFT IS LARGER, MORE THAN 200 ppm
- THE SPECTRA ARE NOT USUALLY INTEGRATED
- FOR NOW, WE WILL NOT LOOK AT COUPLING PATTERNS

THIS LEAVES US WITH:

1) THE NUMBER OF SIGNALS
   - REFLECTS THE NUMBER OF DIFFERENT TYPES OF CARBONS

2) THE CHEMICAL SHIFTS
   - USING THE USUAL ELECTRONEGATIVITY
   AND T' SHIELDING REASONING

SIMILAR TO 'H

<table>
<thead>
<tr>
<th>CH₄</th>
<th>CH₃Cl</th>
<th>CH₂Cl₂</th>
<th>CHCl₃</th>
<th>CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>-220</td>
<td>25</td>
<td>54</td>
<td>77</td>
<td>97</td>
</tr>
<tr>
<td>+27</td>
<td>+29</td>
<td>+23</td>
<td>+20</td>
<td></td>
</tr>
</tbody>
</table>

HOWEVER, THIS TREND DOES NOT HOLD FOR BROMIDES AND IODIDES

ALKENES AND AROMATICS STRONGLY DESHIELDED

ALKENES 100-150
AROMATICS 120-148 BENZENE = 128

ALKANES - SHIELDED $\approx 20$

C-O $\approx 50-60$

C=O 160-190

R-C-R $\geq 180$

C-X, HALOGENS $\approx 20-40$

C-N $\approx 30-50$
SKILL

PREDICT IR BANDS

DETERMINE FUNCTIONAL GROUPS
- FREQUENCY, MASS, BOND STRENGTH

PREDICT NMR SPECTRA,
- SHIFTS, INTEGRALS, COUPLING

DETERMINE STRUCTURES
- FROM SPECTRA

USE COMBINED IR, NMR

PROBLEM

13, 15, 24, 27, 21

14, 16, 17, 18

15, 16, 30

18, 19, 20

21, 22

18, 19

20, 21

23, 27

6, 17 (Chapter 5)