Lecture 6
Infrared spectroscopy

February 4, 2016
$\text{D}_2\text{O} \text{ ice in H}_2\text{O}$

$\text{D}_2\text{O} \text{ ice in D}_2\text{O}$
Chemical Exchange

- Hydrogens on electronegative atoms such as Oxygen and Nitrogen
  - Undergo rapid “exchange” and often give only a relatively broad singlet due to “averaging”
  - These hydrogens also exchange (equilibrate) with Deuterium in D$_2$O and “disappear” from the spectrum

\[
\begin{align*}
&\text{O} &\text{O} \\
&\text{H}_3\text{C} = \text{C} - \text{CH}_3 &\text{H}_3\text{C} = \text{C} - \text{C}^- + \text{H}^+ \\
&D_2\text{O} &\text{DO}^- + \text{D}^+ \\
\end{align*}
\]
Common $^1\text{H}$-nmr Solvents

- DCCl$_3$
- CCl$_4$
- (CD$_3$)$_2$SO
- D$_2$O
- C$_6$D$_6$
Whats with what??

H₃C─O─Cl

What's with what??

Chemistry 328N
Coupling Constants

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\quad & \quad \text{Cl} \\
\quad & \quad \text{H} \\
\quad & \quad \text{H}
\end{align*}
\]
Chemical Shift additivity estimates

<table>
<thead>
<tr>
<th>Table structure</th>
<th>Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH₂-Cl</td>
<td>3.3</td>
</tr>
<tr>
<td>-CH₂-O-</td>
<td>3.6</td>
</tr>
<tr>
<td>total</td>
<td>6.9</td>
</tr>
<tr>
<td>Subtract -CH₂-CH₃</td>
<td>1.2</td>
</tr>
<tr>
<td>Crude Estimate</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Caution….estimates only!!
# Chemical Shift - $^1$H-NMR

<table>
<thead>
<tr>
<th>Type of H</th>
<th>$\delta$</th>
<th>Type of H</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{C}_3\text{H}_7)_4\text{Si}$</td>
<td>0</td>
<td>ROH</td>
<td>0.5-6.0</td>
</tr>
<tr>
<td>RCH$_3$</td>
<td>0.9</td>
<td>RCH$_2$ OR</td>
<td>3.3-4.0</td>
</tr>
<tr>
<td>RCH$_2$ R</td>
<td>1.2-1.4</td>
<td>R$_2$ NH</td>
<td>0.5-5.0</td>
</tr>
<tr>
<td>R$_3$ CH</td>
<td>1.4-1.7</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>R$_2$ C=CRC HR$_2$</td>
<td>1.6-2.6</td>
<td>RCCH$_3$</td>
<td>2.1-2.3</td>
</tr>
<tr>
<td>RC≡CH</td>
<td>2.0-3.0</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>ArC H$_3$</td>
<td>2.2-2.5</td>
<td>RCCH$_2$ R</td>
<td>2.2-2.6</td>
</tr>
<tr>
<td>ArC H$_2$ R</td>
<td>2.3-2.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
$^1$H Chemical Shifts
$^{13}\text{C}$ Chemical Shifts
### $^{13}\text{C}$-NMR chemical shifts

<table>
<thead>
<tr>
<th>Type of Carbon</th>
<th>Chemical Shift ($\delta$)</th>
<th>Type of Carbon</th>
<th>Chemical Shift ($\delta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{RCH}_3$</td>
<td>0–40</td>
<td>$\text{C} = \text{R}$</td>
<td>110–160</td>
</tr>
<tr>
<td>$\text{RCH}_2\text{R}$</td>
<td>15–55</td>
<td>$\text{O}$</td>
<td>160–180</td>
</tr>
<tr>
<td>$\text{R}_3\text{CH}$</td>
<td>20–60</td>
<td>$\text{RCOR}$</td>
<td>165–180</td>
</tr>
<tr>
<td>$\text{RCH}_2\text{I}$</td>
<td>0–40</td>
<td>$\text{RCNR}_2$</td>
<td>175–185</td>
</tr>
<tr>
<td>$\text{RCH}_2\text{Br}$</td>
<td>25–65</td>
<td>$\text{O}$</td>
<td>180–210</td>
</tr>
<tr>
<td>$\text{RCH}_2\text{Cl}$</td>
<td>35–80</td>
<td>$\text{RCOH}$</td>
<td></td>
</tr>
<tr>
<td>$\text{R}_3\text{COH}$</td>
<td>40–80</td>
<td>$\text{O}$</td>
<td></td>
</tr>
<tr>
<td>$\text{R}_3\text{COR}$</td>
<td>40–80</td>
<td>$\text{RCOH}$</td>
<td></td>
</tr>
<tr>
<td>$\text{RC} = \text{CR}$</td>
<td>65–85</td>
<td>$\text{O}$</td>
<td>180–210</td>
</tr>
<tr>
<td>$\text{R}_2\text{C} = \text{CR}_2$</td>
<td>100–150</td>
<td>$\text{RCH, RCR}$</td>
<td></td>
</tr>
</tbody>
</table>
$^{13}$C NMR Spectra

C-H: "coupled"

C-H: "decoupled"
Figure 6-1.2. 25 MHz $^{13}$C NMR spectrum of diphenyl selenide in CDCl$_3$. 
$^{13}$C-nmr Spectroscopy

- Each nonequivalent $^{13}$C gives a different, resolved signal.
The DEPT Experiment

- In the hydrogen-decoupled mode, information on spin-spin coupling between $^{13}\text{C}$ and attached hydrogens is lost.

- Distortionless Enhancement by Polarization Transfer (DEPT) is an NMR technique for determining whether $^{13}\text{C}$ signals are from CH$_3$, CH$_2$, CH, or quaternary carbons.

- DEPT is an instrumental trick that provides the means to acquire this information.
The DEPT method

- DEPT uses a complex series of pulses in both the $^1\text{H}$ and $^{13}\text{C}$ ranges, with the result that CH$_3$, CH$_2$, and CH signals exhibit different phases;
  - signals for CH$_3$ and CH carbons are recorded as positive signals (odd numbers of H)
  - signals for CH$_2$ carbons are recorded as negative signals (even numbers of H)
  - quaternary carbons give no signals in the DEPT method (zero H)
Broadband decoupled $^{13}$C nmr spectrum
$^{13}$C-NMR (a) and DEPT (b) spectra of isopentyl acetate
An Unknown 😊
Empirical formula C₄H₉, MW = 114

1³C-NMR chemical shifts

<table>
<thead>
<tr>
<th>Type of Carbon</th>
<th>Chemical Shift (δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCH₃</td>
<td>0–40</td>
</tr>
<tr>
<td>RCH₂R</td>
<td>15–55</td>
</tr>
<tr>
<td>R₃CH</td>
<td>20–60</td>
</tr>
<tr>
<td>RCH₂I</td>
<td>0–40</td>
</tr>
<tr>
<td>RCH₂Br</td>
<td>25–65</td>
</tr>
<tr>
<td>RCH₂Cl</td>
<td>35–80</td>
</tr>
<tr>
<td>R₃COH</td>
<td>40–80</td>
</tr>
<tr>
<td>R₃COR</td>
<td>40–80</td>
</tr>
<tr>
<td>R₃CR</td>
<td>65–85</td>
</tr>
<tr>
<td>R₂C═CR₂</td>
<td>100–150</td>
</tr>
</tbody>
</table>

Positive in DEPT
Disappears in DEPT

0.00 TMS
25.6
35.0

TMS
Whatzit??

T, C₅H₈O

δ<sub>c</sub> (ppm)

C

CDCl₃

CH₂

CH₂

TMS
$^{13}$C-NMR Spectroscopy review

- Each nonequivalent $^{13}$C gives a different signal
- Low abundance means weak signals
- C-C splitting is insignificant
- C-H splitting is big and complex so it is “turned off” by “decoupling”
- Range of Chemical Shifts is large compared to H
- Some Coupling info can be recovered by DEPT
- Integrals of $^{13}$C spectra are not useful except under very special circumstances
- Mnemonic device…. PONE???
NMR TUTOR(ek) ver. 2.2

by Darek Bogdal

Chemistry

Java applet for displaying molecular spectra by Guillaume Cottenceau.

Project supervisor Henry Rzepa.

Imperial College of Science Technology and Medicine.
Molecular Vibrations

- For a molecule to absorb IR radiation, the bond undergoing vibration
  - must be polar (change dipole moment)

- Covalent bonds that do not meet this criterion are said to be IR inactive
  - the C-C double and triple bonds of symmetrically substituted alkenes and alkynes, for example, do not absorb IR radiation because they are not polar bonds

\[ \text{H}_2 \quad \text{N}_2 \quad \text{CO}_2 \quad ?????
\]
THE ENERGY OF ELECTROMAGNETIC WAVES

\[ c = \lambda \nu \]

\[ \bar{\nu} = \frac{1}{\lambda} \]

- (nu-bar) represents wavenumber, the number of wavelengths in 1 cm
- This is a unit of frequency!
- units are 1/cm or cm\(^{-1}\) (Kaysers)

\[ E = h \nu = h \frac{c}{\lambda} = hc \bar{\nu} \]

10 microns (micrometers) = 1000 cm\(^{-1}\)
Harmonic Oscillator Model

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \]
\[ \mu = \frac{(m_1)(m_2)}{m_1 + m_2} \]

\[ E_{\nu} = \hbar \nu_o (\nu + 1/2) \]

- \( \hbar = \) Planck’s constant
- \( \nu_o = \) characteristic frequency
- \( \nu = 0, 1, 2, 3, \ldots \)
- quantized
- vibrational
- energy

x=0 represents the equilibrium separation between the nuclei.
Energy quantization of the oscillator

classical and quantum behavior are very different:

- Classical: all possible values of total energy are allowed.
- Quantum: only certain 'energy levels' are allowed.

Note that although the energy levels are equally spaced for the harmonic oscillator, this is not true for all QM systems.

Note also that it is not possible for the quantum harmonic oscillator to have zero energy – it must have some energy even at 0 K.
Functional group absorptions

The diagram illustrates the percent transmittance of various functional groups across different wavelengths (µm) and wavenumbers (cm⁻¹). Key functional groups and their corresponding regions are highlighted:

- N–H
- O–H
- C–H
- C≡C
- C≡N
- C=O
- C=N

The fingerprint region is marked around 1000 cm⁻¹.
Infrared Absorption Frequencies

<table>
<thead>
<tr>
<th>Structural unit</th>
<th>Frequency, cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretching vibrations (single bonds)</td>
<td></td>
</tr>
<tr>
<td>(sp) C—H</td>
<td>3310-3320</td>
</tr>
<tr>
<td>(sp^2) C—H</td>
<td>3000-3100</td>
</tr>
<tr>
<td>(sp^3) C—H</td>
<td>2850-2950</td>
</tr>
<tr>
<td>(sp^2) C—O</td>
<td>1200</td>
</tr>
<tr>
<td>(sp^3) C—O</td>
<td>1025-1200</td>
</tr>
</tbody>
</table>
Infrared Absorption Frequencies

Stretching vibrations (multiple bonds)

<table>
<thead>
<tr>
<th>Structural unit</th>
<th>Frequency, cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C} = \text{C} )</td>
<td>1620-1680</td>
</tr>
<tr>
<td>( \text{C} \equiv \text{C} )</td>
<td>2100-2200</td>
</tr>
<tr>
<td>( \text{C} \equiv \text{N} )</td>
<td>2240-2280</td>
</tr>
</tbody>
</table>
IR Spectra of chloroform and deuterochloroform

Mode of vibration | $\text{CHCl}_3$ | $\text{CDCl}_3$
--- | --- | ---
C-H stretching | 3020 | 2256
C-H bending | 1219 | 912
C-Cl stretching | 773 | 737
C-Cl bending | 671 | 652

* Spartan '02 AM1 minimization

Shift of peak due to replacement of H with D (2x mass)
IR Group Correlation Tables