Spectroscopy in Inorganic Chemistry

Nuclear Magnetic Resonance Spectroscopy
• spin

dehuterium

helium

NMR
The neutron has 2 quarks with a $-\frac{e}{3}$ charge and one quark with a $+\frac{2e}{3}$ charge resulting in a total charge of 0. The proton however, has 2 quarks with $+\frac{2e}{3}$ charge and only one quark with a $-\frac{e}{3}$ charge giving it a net positive charge. Both protons and neutrons are spin=$\frac{1}{2}$.
I > 0 the nucleus has spin (I = 1/2, 1, 3/2, 2, etc) and a magnetic dipole μ, and thus may be suitable for NMR observation.

Number of spin states = 2I + 1

<table>
<thead>
<tr>
<th>element</th>
<th>proton</th>
<th>neutron</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1H$</td>
<td>1</td>
<td>0</td>
<td>1/2</td>
</tr>
<tr>
<td>$^2H$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$^{13}C$</td>
<td>6</td>
<td>7</td>
<td>3/2</td>
</tr>
<tr>
<td>$^{11}B$</td>
<td>5</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>
nuclear angular momentum spin quantum number \( I \), the "spin" of the nucleus.

- \( I = 0 \) no spin, the nucleus has no magnetic moment and no NMR properties

\[
\begin{align*}
\text{even } N_{\text{even}} & \quad I = 0 & 12C_6 & 16O_8 & 32S_{16} \\
\end{align*}
\]

\( \mu \): nuclear magnetos, magnetic dipole (spinning charge).

\( I = 0, \mu = 0 \)
Nuclei with $I = 1/2$ have especially advantageous NMR properties, and the vast majority of all NMR experiments are done with such isotopes.

$I = 1/2$ \{\text{\textsuperscript{1}H}, \text{\textsuperscript{13}C}, \text{\textsuperscript{15}N}, \text{\textsuperscript{19}F}, \text{\textsuperscript{31}P}\}

\text{eQ: electric quadrupole moment}
\text{e: electrostatic charge}
\text{Q: deviation of the nuclear charge distribution from spherical symmetry}

$l = \frac{1}{2}$, $\mu \neq 0$, $eQ = 0$
I > 0 the nucleus has spin (I = 1/2, 1, 3/2, 2, etc) and a magnetic dipole $\mu$, and thus may be suitable for NMR observation.

\[ I = \frac{3}{2}, \frac{5}{2}, \text{etc} \quad ^7\text{Li}_3 (\frac{3}{2}), ^{11}\text{B}_5 (\frac{3}{2}) \]
\[ I \geq 1. \]
<table>
<thead>
<tr>
<th>Atom</th>
<th>Isotope</th>
<th>Spin</th>
<th>Larmor frequency (MHz at 9.306 T)</th>
<th>Abundance (%)</th>
<th>Absolute sensitivity</th>
<th>Quadrupole (barn)</th>
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</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1H</td>
<td>1/2</td>
<td>-400.00</td>
<td>99.98</td>
<td>1.00E+000</td>
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<tr>
<td>Deuterium</td>
<td>2D</td>
<td>0</td>
<td>-61.40</td>
<td>0.02</td>
<td>1.45E-006</td>
<td>0.00273</td>
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<tr>
<td>Lithium</td>
<td>6Li</td>
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<td>-58.86</td>
<td>7.42</td>
<td>6.31E-004</td>
<td>-0.0008</td>
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<tr>
<td>Lithium</td>
<td>7Li</td>
<td>3/2</td>
<td>-155.45</td>
<td>92.58</td>
<td>2.70E-001</td>
<td>-0.045</td>
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<tr>
<td>Boron</td>
<td>10B</td>
<td>3</td>
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<td>3.90E-003</td>
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<td>Boron</td>
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<td>3/2</td>
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<tr>
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<td>-100.58</td>
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<td>Carbon</td>
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<td>-28.90</td>
<td>99.63</td>
<td>1.01E-003</td>
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<td>Nitrogen</td>
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<td>0.37</td>
<td>3.85E-006</td>
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<td>Oxygen</td>
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<td>54.23</td>
<td>0.04</td>
<td>1.08E-005</td>
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<td>Fluorine</td>
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<td>-376.31</td>
<td>100.00</td>
<td>8.30E-001</td>
<td>0</td>
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<tr>
<td>Sodium</td>
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<tr>
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<td>24.48</td>
<td>10.13</td>
<td>2.71E-004</td>
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<td>Aluminum</td>
<td>27Al</td>
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<td>100.00</td>
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<tr>
<td>Silicon</td>
<td>29Si</td>
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<td>79.46</td>
<td>4.70</td>
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<tr>
<td>Phosphorus</td>
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<td>-161.92</td>
<td>100.00</td>
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<td>0</td>
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<tr>
<td>Sulfur</td>
<td>33S</td>
<td>3/2</td>
<td>-30.68</td>
<td>0.76</td>
<td>1.72E-005</td>
<td>-0.055</td>
</tr>
<tr>
<td>Chlorine</td>
<td>35Cl</td>
<td>3/2</td>
<td>-39.19</td>
<td>75.53</td>
<td>3.55E-003</td>
<td>-0.08</td>
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<tr>
<td>Chlorine</td>
<td>37Cl</td>
<td>3/2</td>
<td>-32.62</td>
<td>24.47</td>
<td>6.63E-004</td>
<td>-0.0632</td>
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<tr>
<td>Potassium</td>
<td>39K</td>
<td>3/2</td>
<td>-18.67</td>
<td>93.10</td>
<td>4.73E-004</td>
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<td>Potassium</td>
<td>41K</td>
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<td>-10.24</td>
<td>6.88</td>
<td>5.78E-006</td>
<td>0.067</td>
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<tr>
<td>Calcium</td>
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<td>7/2</td>
<td>26.91</td>
<td>0.15</td>
<td>9.28E-006</td>
<td>-0.05</td>
</tr>
</tbody>
</table>
\[ I = |I_1 + I_2 + \ldots + I_n|, |I_1 + I_2 + \ldots + I_n| - 1, \ldots |I_1 - I_2 - \ldots - I_n| \]

\[ \mathbf{J} - \hbar \hat{\mathbf{J}} \quad \text{or} \quad \hat{I} = \hat{J}/\hbar \]

\[ \mathbf{Ferdowsi University of Mashhad} \]

\[ \text{Magnetic field} \]
• Nuclei with $I > 0$ have angular momentum $P$ (spinning mass) whose direction is the spin axis. The angular momentum is quantized, and can only have one value:

\[
L = \hbar \sqrt{I(I + 1)}
\]

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Symbol</th>
<th>Quantum Numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclear Spin Angular Momentum</td>
<td>$I$</td>
<td>$0 &lt; I &lt; 9/2$ by $1/2$</td>
</tr>
<tr>
<td>Spin Angular Momentum Magnitude</td>
<td>$L$</td>
<td></td>
</tr>
<tr>
<td>Spin Angular Momentum Direction</td>
<td>$m$</td>
<td>$-I, -I + 1, -I + 2, \ldots +I$</td>
</tr>
</tbody>
</table>
Energy Levels for a Nucleus with Spin Quantum Number 1/2

Energy

No Field

m = -1/2

m = +1/2

Magnetic field
Classical description of NMR experiment - the Blosh equations

\[ \vec{\rho}(\phi) = \vec{r} \times m\vec{v} \]

Position vector of particle e
Linear momentum vector
Angular change
Planar angular momentum vector
Magnetic field produced by circulating proton
Ferdowsi University of Mashhad
In quantum physics, angular momentum is defined by:

\[ P = \frac{\hbar}{2\pi} m \]

where \( m \) is the magnetic quantum number.

The nucleus is a more complicated three-dimensional problem.

- \( P \): angular momentum
- \( J \): total angular momentum
- \( I \): dimensionless angular momentum

\[ \hat{J} = \hbar \hat{I} \quad \hat{I} = \hat{J}/\hbar \]

- \( P \): angular momentum \( \leftrightarrow \mu \): nuclear magnetos
- \( J \): total angular momentum \( \leftrightarrow \mu_N \): total nuclear magnetos

\[ \mu_N = \gamma \hat{J} = \gamma \hbar \hat{I} \]
• Nuclei with $I > 0$ also have a magnetic dipole $\mu$ (spinning charge). For the NMR experiment it is the ratio of $\mu$ to $P$ that matters (much in the way that $m/e$ is what matters in mass spectrometry). We define $\gamma$, the gyromagnetic ratio:

$$\gamma = \frac{\mu}{P}$$

In quantum physics, angular momentum is defined

$$P = \frac{\hbar}{2\pi} m$$

where $m$ is the magnetic quantum number and

$$m = (2I + 1)$$

$$\mu = \gamma P$$

$$\mu = \gamma \frac{\hbar}{2\pi m}$$
Behavior of bar magnet in the magnetic field

\[ B_0 + \rho \]

\[ \theta \]

NMR

Applied magnetic field

Precessional orbit

Spinning nucleus

Nuclear moment

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Behavior of bar magnet in the magnetic field

\[ \omega_0 (\text{rad/s}) = \gamma H_0 \]

or

\[ \nu_0 (\text{MHz}) = \left( \frac{\gamma}{2\pi} \right) H_0 \]
\[ \omega_0 \text{ (rad/s)} = \gamma H_0 \]

or in MHz

\[ \nu_0 \text{ (MHz)} = \left( \frac{\gamma}{2\pi} \right) H_0 \]

\[ E = -\vec{\mu} \cdot \vec{H}_0 = -|\mu||H_0| \cos \theta \]
The NMR transition
\[ B_0 \]

\[ E = -\frac{\gamma h B}{2} \]

\[ m = \pm \frac{1}{2}, \pm \frac{3}{2}, \pm \frac{5}{2}, \ldots \]

Energy (eV)

Magnetic Field (T)

**No applied magnetic field**

**Applied magnetic field**
\[ \vec{B}_o = 0 \]
Randomly oriented

\[ \vec{B}_o > 0 \]
Highly oriented

Each nucleus behaves like a bar magnet.
Resonance phenomena and resonance condition

\[ E_{\text{parallel}} = \frac{\gamma h H_0}{2\pi} \left(-\frac{1}{2}\right), \quad E_{\text{antiparallel}} = \frac{\gamma h H_0}{2\pi} \left(\frac{1}{2}\right) \]

\[ \Delta E = E_{\text{antiparallel}} - E_{\text{parallel}} = \frac{\gamma h H_0}{2\pi} \left(\frac{1}{2}\right) - \frac{\gamma h H_0}{2\pi} \left(-\frac{1}{2}\right) = \frac{\gamma h H_0}{2\pi} \]

\[ E = h\nu \]

\[ v = \frac{\gamma h H_0}{2\pi} \]
- continuous wave (CW) NMR
  A) constant frequency

- pulsed Fourier transform (FT)
  B) constant magnetic field
At room temperature, the number of spins in the lower energy level, $N_\beta$, slightly outnumbers the number in the upper level, $N_\alpha$. Boltzmann statistics tells us that

\[
\frac{N_\alpha}{N_\beta} = e^{-\Delta E/kT}
\]

where $N_\alpha$ is the number of nuclei at the excited state, $N_\beta$ is the number of nuclei at the ground state, $\Delta E$ is the energy difference between the two levels, $k$ is the Boltzmann constant, and $T$ is the temperature. This equation shows that as temperature decreases, the population ratio $N_\alpha/N_\beta$ decreases as well.
There is a slight excess (1,000,048 vs 1,000,000 for protons in a 300 MHz instrument) in the lower energy state.

\[
\frac{N_\alpha}{N_\beta} = e^{-\frac{\gamma h H_0}{2\pi k T}} \approx 1 - \frac{\gamma h H_0}{2\pi k T}
\]

At \( T = 300 \text{ K} \) and \( B_0 = 5.875 \text{ T (250 MHz)} \),

\[
\begin{align*}
N_\alpha &= 1 - \frac{26.7519 \times 10^{-7} \times 1.0546 \times 10^{-27} \times 5.875}{1.3805 \times 10^{-16} \times 300} \\
N_\alpha &\approx (1 - 0.00004)N_\beta = 0.99996N_\beta
\end{align*}
\]

For \( B_0 = 18.8 \text{ T (800MHz)} \),

\[
N_\alpha \approx 0.99987N_\beta
\]
NMR Transition

Ferdowsi University of Mashhad
A spin packet is a group of spins experiencing the same magnetic field strength.
The size of each vector is proportional to \((N_\beta - N_\alpha)\).
Net magnetization

\[ \vec{M} = \sum_i \vec{\mu}_i \]
The absorption of energy results in the excitation of the nucleus from the lower to higher energy level.

This process is called resonance.

After resonance, of course, the population of the different energy levels will change. The number of nuclei at the lower energy level is then reduced. In order to maintain the slight excess of nuclei at the lower energy level, which is the condition for resonance, the nuclei at the higher energy level must somehow be able to lose their energy and return to the lower energy level. The various processes that tend to restore the original equilibrium condition among the energy levels are referred to as relaxation phenomena.
\[ \dot{\mathbf{M}} = -\gamma \mathbf{H}_{\text{eff}} \times \mathbf{M} - \frac{1}{T_2} (M_u \mathbf{e}_u + M_v \mathbf{e}_v) - \frac{1}{T_1} (M_z - M_0) \mathbf{e}_z \]

- **torque from the magnetic field**
- **relaxation effects**
This process of relaxation is important because the time spent in the excited nuclei determines the width of the absorption peaks, pattern of the peaks, and ease with which the nucleus is observed.

- $T_1$ spin-lattice relaxation (longitudinal relaxation)
- $T_2$ spin-spin relaxation (transverse relaxation)

The probability of spontaneous emission of the excess energy in the form of electromagnetic radiation is negligible.
• The most important feature of spin-spin relaxation is that it determines the natural width of the lines in the spectra.

• short time relaxation = broadening of the peaks.
• long time relaxation = more intense peaks.

\[ \Delta E \Delta t = \frac{h}{2\pi} \]

[Peek width]

\[ h\Delta v \Delta t = \frac{h}{2\pi} \]

\[ \Delta v = \frac{1}{\Delta t 2\pi} \]

NMR
• paramagnetic impurities = decrease the relaxation time

• increase viscosity = decrease relaxation times

• increase $\Delta E$ (between ground and exited state) = decrease relaxation times

• Relaxation times can provide us with some information about hydrogen bondings, relative motions of the molecule, steric effects and distances between the groups.
equilibrium magnetization
- $T_1$: return of the $z$-component to its equilibrium value $M_0$ is referred to as longitudinal relaxation.

- $T_2$: return of $M_y$ to zero is called transverse relaxation.
\[ T_1 \text{ Processes} \]

- The transfer of energy from the excited nuclei to the environment (surrounding lattice), the so-called lattice.
  
  Lattices: Solvent molecules and dissolved gases

- The energy will be transferred into kinetic and thermal energy.

- The spin-lattice process is an enthalpy process.

- The spin-lattice relaxation time is always greater than the spin-spin relaxation time.
• If the longitudinal relaxation has been completed, there cannot be any spin in the xy-plane.

\[ T_1 > T_2 \]

• The magnitude of \( T_1 \) varies to a considerable extent depending on the nucleus and Liquids usually have a \( T_1 \) of \( 10^{-2} - 10^2 \), while in solids this value is much larger.

\[ T_{1\text{ solid}} > T_{1\text{ liquid}} \]
Spin-lattice relaxation mechanisms

- dipolar relaxation
- spin-rotation relaxation
- paramagnetic relaxation
- quadrupolar relaxation
If enough energy (frequency equal to the energy difference between the spin states) is put into the system, it is possible to saturate the spin system and make \( M_Z = 0 \).
The time duration for this process called spin lattice relaxation time ($T_1$).

$$M_z = M_0 \left( 1 - e^{-t/T_1} \right)$$
\[ M_z = M_o \left( 1 - 2e^{-t/T_1} \right) \]
**T₁ Mechanism**

- $T_1$ relaxation is sometimes called spin-lattice relaxation.

- In this type of relaxation the energy lost as the nucleus returns to the lower energy state is transferred to the molecule in the form of heat. This means that the total number of nuclei in the excited state decreases.
Motions in solution which result in time varying magnetic fields cause spin relaxation.
Time varying fields at the Larmor frequency cause transitions between the spin states and hence a change in $M_z$. This screen depicts the field at the green hydrogen on the water molecule as it rotates about the external field $B_0$ and a magnetic field from the blue hydrogen. Note that the field experienced at the green hydrogen is sinusoidal.
Thermal motion (translation, rotation, etc.) of these molecules will generate magnetic fields rotating with various frequencies, since all of these motions involve the movements of charged particles and electrons. Some of these frequencies will match the Larmor frequency of the nuclei, in order that energy transfer can occur. The magnetic energy received by the lattice is then transformed into thermal energy.
There is a distribution of rotation frequencies in a sample of molecules. Only frequencies at the Larmor frequency affect $T_1$. Since the Larmor frequency is proportional to $B_o$, $T_1$ will therefore vary as a function of magnetic field strength. In general, $T_1$ is inversely proportional to the density of molecular motions at the Larmor frequency.
The rotation frequency distribution depends on the temperature and viscosity of the solution. Therefore $T_1$ will vary as a function of temperature.
At the Larmor frequency indicated by $\nu_o$, $T_1 (280 \text{ K}) < T_1 (340 \text{ K})$. The temperature of the human body does not vary by enough to cause a significant influence on $T_1$. The viscosity does however vary significantly from tissue to tissue and influences $T_1$ as is seen in the following molecular motion plot.
Precession

- If the net magnetization is placed in the XY plane, it will rotate about the Z axis at a frequency equal to the frequency of the photon which would cause a transition between the two energy levels of the spin. This frequency is called the Larmor frequency.
T₂ Processes

- In addition to the rotation, the net magnetization starts to dephase because each of the spin packets making it up is experiencing a slightly different magnetic field and rotates at its own Larmor frequency.
- The longer the elapsed time, the greater the phase difference.
- Here the net magnetization vector is initially along +Y. For this and all dephasing examples think of this vector as the overlap of several thinner vectors from the individual spin packets.

\[ T₂: \text{the transfer of energy among the processing nucleus.} \]
Two factors or combination of these two factors contribute to the decay of transverse magnetization:

A - variations in $B_o$ (an inhomogeneous $T_2$ effect)
B - molecular interactions (a pure $T_2$ molecular effect or Dipolar-Dipolar)

\[
\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_{2\text{inhomo}}}
\]
**T₂ Processes**

- Spin-spin relaxation time, $T_2$

Motion of the magnetic moments in the fixed coordinate system

Motion of the magnetic moments in the rotating coordinate system

**NMR**
In summary, the spin-spin relaxation time, $T_2$, is the time to reduce the transverse magnetization by a factor of $e$. 

$$M_{XY} = M_{XYo} e^{-t/T_2}$$
**T$_2$ Mechanism**

- The net magnetization in the XY plane goes to zero and then the longitudinal magnetization grows in until we have M$_o$ along Z.
• All of the processes occurring during the transverse relaxation will not change the total energy of the sample. Since the total energy of the spin system does not change, spin-spin relaxation is classified as an entropy process.

• $T_2$ is always less than or equal to $T_1$

\[ T_2^{\text{solid}} \leq T_2^{\text{liquid}} \]

\[ T_1^{\text{liquid}} = T_2^{\text{liquid}} \]
• In this type of relaxation the energy released when a nucleus makes the transition from high to low energy state is absorbed by another nucleus. This allows the other nucleus to move from low energy to high.

• In this case the total number of nuclei in the excited state doesn’t change. What happens is that the newly excited nuclei are no longer in synch so that the signals are out-of-phase and are subtractive instead of additive.

• Instrument parameters such as a lack of homogeneity of the magnetic field can also produce broadening of the NMR signal.
both processes ($T_2$ and $T_1$) occur simultaneously with the only restriction being that $T_2$ is less than or equal to $T_1$. 
magnetization vector rotating at the Larmor frequency

relaxation of $M_z$ magnetization to its equilibrium value looks the same as it did in the laboratory frame.
A transverse magnetization vector rotating about the Z axis at the same velocity as the rotating frame will appear stationary in the rotating frame. A magnetization vector traveling faster than the rotating frame rotates clockwise about the Z axis. A magnetization vector traveling slower than the rotating frame rotates counter-clockwise about the Z axis.
In a sample there are spin packets traveling faster and slower than the rotating frame. As a consequence, when the mean frequency of the sample is equal to the rotating frame, the dephasing of $M_{X'Y'}$ looks like this.
magnetization vector faster than the rotating frame clockwise

magnetization vector slower than the rotating frame counter-clockwise
Frequency scanning

Field scanning
- FT 2-3 s
- CW 5 min.

<table>
<thead>
<tr>
<th>$B_0$ (in Gauss)</th>
<th>MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>14100</td>
<td>60</td>
</tr>
<tr>
<td>23500</td>
<td>100</td>
</tr>
<tr>
<td>47000</td>
<td>200</td>
</tr>
<tr>
<td>70500</td>
<td>300</td>
</tr>
<tr>
<td>94000</td>
<td>400</td>
</tr>
<tr>
<td>117500</td>
<td>500</td>
</tr>
</tbody>
</table>
Chemical Shift
The absorptions occur at 

\[ \nu = \frac{\gamma}{2\pi} \frac{H_0}{\mu} \]
\[ \nu = \gamma \frac{H_0}{2\pi} \]

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Natural % Abundance</th>
<th>Spin (I)</th>
<th>Magnetic Moment ((\mu))*</th>
<th>Magnetogyric Ratio ((\gamma))*†</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1\text{H})</td>
<td>99.9844</td>
<td>1/2</td>
<td>2.7927</td>
<td>26.753</td>
</tr>
<tr>
<td>(^2\text{H})</td>
<td>0.0156</td>
<td>1</td>
<td>0.8574</td>
<td>4,107</td>
</tr>
<tr>
<td>(^{11}\text{B})</td>
<td>81.17</td>
<td>3/2</td>
<td>2.6880</td>
<td>–</td>
</tr>
<tr>
<td>(^{13}\text{C})</td>
<td>1.108</td>
<td>1/2</td>
<td>0.7022</td>
<td>6,728</td>
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<tr>
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<td>25,179</td>
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<td>(^{29}\text{Si})</td>
<td>4.700</td>
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<td>-5,319</td>
</tr>
<tr>
<td>(^{31}\text{P})</td>
<td>100.0</td>
<td>1/2</td>
<td>1.1305</td>
<td>10,840</td>
</tr>
</tbody>
</table>

* \(\mu\) in units of nuclear magnetons = \(5.05078 \times 10^{-27}\) JT\(^{-1}\)

† \(\gamma\) in units of \(10^{7}\) rad T\(^{-1}\) sec\(^{-1}\)
The NMR frequency range for various common nuclei

- $^{15}_N$
- $^{77}_{Se}$
- $^{13}_C$
- $^{119}_{Sn}$
- $^{31}_P$
- $^{19}_F$

Frequency ranges:
- 250.00015 MHz
- 249.99985 MHz

$^{1H}$
\[
\Delta E = \gamma \hbar B_0 = \hbar \nu
\]
• For protons $\gamma = +2.67 \times 10^8 \text{ rad s}^{-1} \text{ T}^{-1}$, if magnetic field of 4.7 T calculate the Larmor frequency?

\[
\nu_0 = \frac{1}{2\pi} \gamma (1 + \delta) B_0
\]

\[
= \frac{1}{2\pi} \times 2.67 \times 10^8 \times 4.7 = -200 \times 10^6 \text{ Hz}.
\]

• chemical shift zero

• Calculated $\omega_0$?
200 MHz

400 MHz

inc. magnetic field strength, Gauss

NMR
secondary magnetic field \( H_{\text{sec}} = \sigma H_0 \)  

external magnetic field 

diamagnetic shielding constant
Shielded Protons

- A naked proton will absorb at 70,459 gauss.
- A shielded proton will not absorb at 70,459 gauss so the magnetic field must be increased slightly to achieve resonance.
\[ H_{\text{eff}} = H_0 - H_{\text{sec}} \]

\[ \sigma = \sigma_{\text{dia}} + \sigma_{\text{para}} + \sigma_{\text{neig}} + \sigma_{\text{sol}} \]
The diagram shows a chemical structure with peaks labeled with arrows pointing to specific chemical shifts. The structure is labeled with the formula H₃C-C-O-CH₃, indicating a compound with a carbonyl group and a methyl group. The peaks are marked at specific ppm values on the x-axis.
less shielded lower field (downfield)
more shielded higher field (upfield)

increasing magnetic field strength ($B_0$)
Electron density = \frac{\text{Number of electrons}}{\text{Number of protons}}

<table>
<thead>
<tr>
<th>Aromatic compounds</th>
<th>(\pi)-Electron density</th>
<th>(1^H) chemical shift, (\delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.676</td>
<td>10.9</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>9.17</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>7.27</td>
</tr>
<tr>
<td></td>
<td>1.11</td>
<td>6.75</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>5.37</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>5.65</td>
</tr>
</tbody>
</table>
The unit of the chemical shift

The chemical shift of a nucleus is the difference between the resonance frequency of the nucleus and a standard, relative to the standard. This quantity is reported in ppm and given the symbol delta.

\[
\text{chemical shift (ppm)} = \frac{\text{shift downfield from TMS (Hz)}}{\text{total spectrometer frequency (MHz)}}
\]

\[
\delta = \frac{(\nu - \nu_{\text{REF}}) \times 10^6}{\nu_{\text{REF}}}
\]
\[
(\delta_2 - \delta_1) = 10^6 \times \frac{\nu_2 - \nu_{\text{TMS}}}{\nu_{\text{TMS}}} - 10^6 \times \frac{\nu_1 - \nu_{\text{TMS}}}{\nu_{\text{TMS}}}
\]

\[
= 10^6 \times \frac{\nu_2 - \nu_1}{\nu_{\text{TMS}}}
\]

\[
(\nu_2 - \nu_1) = 10^{-6} \times \nu_{\text{TMS}} \times (\delta_2 - \delta_1).
\]
References in NMR

- The TMS signal, which is at the right-hand side of the spectrum, is clearly distinguished from most other resonances. Since the carbon atom is more electronegative than silicium, the methyl groups bonded directly to the silicium atom are shielded more, and therefore resonate at the high field (on the right-hand side of the spectrum). There are also some compounds whose protons resonate on the right side of the TMS signal. These signals mostly arise from the protons located in the strong shielding area of the aromatic compounds. We will discuss this kind of compound later.
- 2. TMS is a cheap and readily available compound.
- 3. TMS is chemically inert. There is no reaction between TMS and the sample.
- 4. TMS has a low boiling point (27 °C). It can be easily removed from the sample by evaporation after the spectrum is recorded.
- 5. The 12 protons of TMS produce a sharp signal. Even at lower TMS concentrations, the reference signal can be easily recognized.
$\text{BF}_3$ $\text{H}_3\text{PO}_4$ $85\%$ $\text{CFCl}_3$ $\text{LiCl}$ $\text{CF}_3\text{COOH}$ $\text{[Al(H}_2\text{O})_6]\text{Cl}_3^+$ $\text{Rh}$ $\text{H}_3\text{PO}_4$
Exercise

To determine the chemical shifts, we apply eq. 23. For example, the methyl resonance absorbs 143 Hz downfield from the TMS signal on a 60 MHz instrument. We find a chemical shift of 2.35 ppm. The methyl proton resonance on a 100 MHz instrument appears 235 Hz downfield from the TMS signal. The calculation of the chemical shift gives the same δ-value of 2.35 ppm.

<table>
<thead>
<tr>
<th>60 MHz instrument</th>
<th>100 MHz instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_{CH_3} = \frac{143 \text{ Hz}}{60,000,000 \text{ Hz}} \times 10^6 = 2.35 \text{ ppm}$</td>
<td>$\delta_{CH_3} = \frac{235 \text{ Hz}}{100,000,000 \text{ Hz}} \times 10^6 = 2.35 \text{ ppm}$</td>
</tr>
<tr>
<td>$\delta_{CH_2} = \frac{222 \text{ Hz}}{60,000,000 \text{ Hz}} \times 10^6 = 3.70 \text{ ppm}$</td>
<td>$\delta_{CH_2} = \frac{370 \text{ Hz}}{100,000,000 \text{ Hz}} \times 10^6 = 3.70 \text{ ppm}$</td>
</tr>
<tr>
<td>$\delta_{arom} = \frac{431 \text{ Hz}}{60,000,000 \text{ Hz}} \times 10^6 = 7.18 \text{ ppm}$</td>
<td>$\delta_{arom} = \frac{718 \text{ Hz}}{100,000,000 \text{ Hz}} \times 10^6 = 7.18 \text{ ppm}$</td>
</tr>
</tbody>
</table>
Increase electron density
Decrease electron density
Diamagnetic Shift
Paramagnetic Shift
Deshield
Upfield
Shield
Downfield
NMR
## Exercise

<table>
<thead>
<tr>
<th>Alkyl halide</th>
<th>Substituent X</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
</tr>
<tr>
<td>CH₃X</td>
<td>4.3</td>
</tr>
<tr>
<td>CH₂X₂</td>
<td>5.4</td>
</tr>
<tr>
<td>CHX₃</td>
<td>6.2</td>
</tr>
</tbody>
</table>
Ring current effect (diamagnetic ring current)

- MAGNETIC ANISOTROPY
1,6-methano[10]annulene

$\delta_{H_a} = 7.27 \text{ ppm}$

$\delta_{H_b} = 6.95 \text{ ppm}$

$\delta_{H_c} = -0.5 \text{ ppm}$
Paramagnetic ring current


$\delta_{Ha} = 16.0 \text{ ppm}$

[12]-Annulene [12]

$\delta_{\text{ring}} = 2.07 - 3.65 \text{ ppm}$

[16]-Annulene [13]

$\delta_{\text{ring}} = -3.95 \text{ ppm}$

$\delta_{\text{CH}_3} = 21.0 \text{ ppm}$
Carbon-carbon and carbon-oxygen double bonds
Magnetic anisotropy of carbon-carbon and carbon-hydrogen bonds and their effect on chemical shifts
• **van der Waals effects?**

• A strong steric interaction between a proton and a neighboring group (it can also be a proton) will exist when these groups are in close proximity because of the molecular geometry. This steric interaction will arise from the touching and overlapping of van der Waals radii. The steric perturbation of the C-H bond involved causes the charge to drift towards the carbon atom. The reduced spherical symmetry of the electron distribution causes a paramagnetic contribution to the shielding constant.
The effect of concentration, solvent and temperature on the chemical shift

- Concentration
- Temperature

Cycloheptatriene

Norcaradiene
NMR
Spin-Spin Splitting

\[ H_1 = H_{\text{total}} + H_b \quad (H_b \text{ parallel}) \]

\[ H_2 = H_{\text{total}} - H_b \quad (H_b \text{ antiparallel}) \]

\[ \nu = \gamma \frac{H_0}{2\pi} \]
\[ k = 2nl + 1 \]
Two neighbors give a triplet
\((n + 1 = 3)\) \((\text{area} = 1)\)

One neighbor gives a doublet
\((n + 1 = 2)\) \((\text{area} = 2)\)

Equivalent protons behave as a group.
\[ H_1 = H_{\text{total}} - 2H_b \quad (H_b \text{ antiparallel}) \]
\[ H_2 = H_{\text{total}} - H_b + H_b = H_{\text{total}} \quad (H_b \text{ parallel and antiparallel}) \]
\[ H_3 = H_{\text{total}} + 2H_b \quad (H_b \text{ parallel}) \]
\[ H_1 \quad H_2 \quad H_3 \quad H_4 \quad (H_b \text{ all antiparallel}) \]
\[ H_2 = H_{\text{total}} - H_b \quad (H_b \text{ two antiparallel, one parallel}) \]
\[ H_3 = H_{\text{total}} + H_b \quad (H_b \text{ two parallel, one antiparallel}) \]
\[ H_4 = H_{\text{total}} + 3H_b \quad (H_b \text{ all parallel}) \]
- Pascal's triangle (I=1/2)

### Relative Peak Intensities of Symmetric Multiplets

<table>
<thead>
<tr>
<th>Number of Equivalent Protons Causing Splitting</th>
<th>Number of Peaks (multiplicity)</th>
<th>Area Ratios (Pascal’s triangle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1 (singlet)</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>2 (doublet)</td>
<td>1  1</td>
</tr>
<tr>
<td>2</td>
<td>3 (triplet)</td>
<td>1  2  1</td>
</tr>
<tr>
<td>3</td>
<td>4 (quartet)</td>
<td>1  3  3  1</td>
</tr>
<tr>
<td>4</td>
<td>5 (quintet)</td>
<td>1  4  6  4  1</td>
</tr>
<tr>
<td>5</td>
<td>6 (sextet)</td>
<td>1  5  10  10  5  1</td>
</tr>
<tr>
<td>6</td>
<td>7 (septet)</td>
<td>1  6  15  20  15  6  1</td>
</tr>
</tbody>
</table>
first-order spectra

Second-order spectra

*first-order spectrum*: the proton is only coupled to other protons that are far away in chemical shift. The splitting pattern depends on the magnetic field. The first-order splitting pattern is allowed to multiplicity rule \((N+1)\) and Pascal’s triangle to determine splitting pattern and intensity distribution.

The second-order splitting at the lower field can be resolved into first-order splitting pattern at the high field.
\[ \frac{\delta_H^a - \delta_H^b}{J_{ab}} = \frac{30}{10} = 3 \quad \text{for a 60 MHz instrument} \]

\[ \frac{\delta_H^a - \delta_H^b}{J_{ab}} = \frac{200}{10} = 20 \quad \text{for a 400 MHz instrument} \]
High-order splitting pattern

High-order splitting pattern takes place when chemical shift difference in hertz is much less or the same that order of magnitude as the $j$ coupling.

\[ \frac{\Delta \nu}{J} \leq 8 \]

The second order pattern is observed as leaning of a classical pattern.: the inner peaks are taller and the outer peaks are shorter in case of AB system. This is called the “roof effect.”

Here is other system as an example: $A_2B_2$ (Fig 5). The two triplet incline toward each other. Outer lines of the triplet are less than 1 in relative area and the inner lines are more than 1. The center lines have relative area 2.

a) first-order pattern and b) second-order pattern of $A_2B_2$ system
H-D
• $n = 1$

In $^1H$-NMR spectroscopy, only one molecule exists for this special case, which is the hydrogen molecule. The coupling between the hydrogen atoms is $^1J = 280$ Hz and is of only theoretical interest.

• $n = 2$

When the number of bonds between the coupled protons is two, these protons are bonded to the same carbon atom and the coupling is called geminal coupling $^2J$. Geminal coupling can be observed between the protons of a $-CH_2-$ group, provided that they are not chemically equivalent.
The number of bonds between the coupled protons is three. The commonest and most useful coupling encountered in $^1\text{H-NMR}$ spectroscopy is vicinal coupling, which is denoted by $^3J$. This coupling is observed between adjacent protons. The bond between the carbon atoms can be a single as well as a double bond. A double bond is counted as a single bond. A few selected examples of vicinal coupling are illustrated below.
The number of bonds between the coupled protons is four. When the number of bonds between the coupled protons is greater than three, these couplings are called long-range couplings. Long-range couplings are observed in cyclic saturated compounds, in particular when the ring system is strained and has a bicyclic structure. Allylic coupling and meta coupling are also typical examples of long-range couplings through four bonds. Some examples of long-range couplings over four bonds are presented below.
Couplings that arise from the interaction of protons separated by five bonds are also called long-range couplings. These couplings are observed in aromatic systems and homoallylic systems.
Spin-Spin Splitting to Different Protons

- Doublet of doublets

Diagram showing trans coupling and geminal coupling.

NMR
Coupling with the proton $H_2$.

Coupling with the methylenic protons.
Coupling with the proton $H_2$

Coupling with the methyl protons