Electromagnetic spectrum has enormous range of energies.

Wide variety of techniques based on absorption of energy
e.g. ESR and NMR: radiowaves (MHz)
   IR – vibrations 200 – 5000 cm\(^{-1}\)
   UV-Vis – electronic transitions 10 000 – 50 000 cm\(^{-1}\)
Timescales.
A molecule/atom in its ground state interacts with a photon of energy $h\nu$. This is fast $\sim 10^{-18}$s. The relaxation back to ground state occurs at different rates depending on the energy.

If the relaxation rate is faster than any process by which the molecule could change (vibrating, changing shape), then the spectroscopic method sees molecules in a number of different states.
A ⇌ B
Isomers A and B rapidly interconvert at 10³ s⁻¹
- timescale of 10⁻³ s
In IR spectrum, we will detect both isomers despite rapid interconversion
  IR timescale 10⁻¹³ (soltn) << 10⁻³.
So see a snap shot.

In NMR time scale is 1-10 s
- Many interconversions occur at a greater rate than this. So see an average signal
- Can cool down NMR spectrum to slow down the exchange rate → peaks could separate

- This can be quantified and activation parameters (ΔG, ΔE and ΔH) can be obtained from this data

NMR has long time scale
  ESR shorter
  IR and UV-Vis very short
NMR for Inorganic Chem.
- NMR: all nuclei have a spin \( I \), calculated from # of neutrons and protons and their spin

- **Even-even** → \( I = 0 \)
- **Even-odd** → \( \frac{1}{2} \) integral
- **Odd-odd** → integral

Natural abundance - % of total element isotope found in nature

<table>
<thead>
<tr>
<th>Nat. abund.</th>
<th># p</th>
<th># n</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>99%</td>
<td>1</td>
<td>0</td>
<td>( \frac{1}{2} )</td>
</tr>
<tr>
<td>1%</td>
<td>6</td>
<td>7</td>
<td>( \frac{1}{2} )</td>
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<tr>
<td>0.3%</td>
<td>7</td>
<td>8</td>
<td>( \frac{1}{2} )</td>
</tr>
<tr>
<td>0.04%</td>
<td>8</td>
<td>9</td>
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<tr>
<td>100%</td>
<td>9</td>
<td>10</td>
<td>( \frac{1}{2} )</td>
</tr>
<tr>
<td>100%</td>
<td>15</td>
<td>16</td>
<td>( \frac{1}{2} )</td>
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<tr>
<td>99%</td>
<td>7</td>
<td>7</td>
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<tr>
<td>99%</td>
<td>6</td>
<td>6</td>
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</tr>
<tr>
<td>99%</td>
<td>8</td>
<td>8</td>
<td>0</td>
</tr>
</tbody>
</table>

Common nuclei for inorg. NMR: \(^{31}\text{P}, ^{19}\text{F}, ^{29}\text{Si}, ^{195}\text{Pt}\) \( I = 1/2 \)
NMR Basics

We need to know $I$ and $\gamma$ (magnetogyric ratio constant that is unique to each isotope)

Receptivity – how easy it is to observe the nucleus relative to H.

Nuclei with $I>1/2$ often give broad signals $\rightarrow$ quadrupole nuclei (magnetic) moment

A nucleus with $I=1/2$ has values $m_I = +1/2, -1/2$. Their energies in an external magnetic field $H_o$ are $E=-g_N\beta_N m_I H_o$

So increase $H_o$ increase $\nu$  

Selection rule $\Delta m_I = \pm 1$
Zeeman splitting – removes degeneracy by applying an external $H_o$.
In the absence of a magnetic field, the energies of an isolated nucleus is degenerate.

In general, for spin $I$, there are $2I + 1$ spin states $m_I$.

E.g. $^{11}\text{B}$: $I=3/2$, $m_I = 3/2, 1/2, -1/2, -3/2$

At a field of $H_o$ of 2.35 T, $\Delta E$ resonance gap for $H$ is $\nu=100$ MHz.
The $H_o$ does not change.

Chemical shift – magnetic field $H_o$ is applied to sample, but each nucleus in a given chemical environment experiences different effective magnetic fields due to e- shielding.

$$H_{\text{eff}} = H_o (1-\sigma)$$
We don’t measure $\sigma$ directly, measure only difference relative to a standard (in units “ppm” of the frequency of the standard)

Consider the normal $^1$H range

Note: TMS addition as standard is history. $\delta$ is calculated by computer in reference to internal deuterium lock signal or an external standard.
Different elements have different “typical ranges”.

$^{117}\text{Sn}$ 3000ppm

$^{207}\text{Pb}$ 12000ppm

Relative integration of peaks can give # of nuclei represented by peak. Good for $^1\text{H}$, $^{31}\text{P}$, $^{19}\text{F}$; can be inaccurate for $^{13}\text{C}$, $^x\text{M}$

Chemically equivalent nuclei resonate together
Spin-spin coupling

The field at a given nucleus will be affected by the spins on neighbouring nuclei.

If a neighboring nucleus has $I=1/2$, it can align with or against the applied field $H_o$, so the proton being observed can see $(H_o + H_N)$ and $(H_o - H_N)$ equally.
Another way to consider this:
Generally, $n$ equiv. nuclei of spin $I$ give $(2nI+1)$ lines.

Pascal’s triangle is only valid for $I=1/2$!

$(n$ equiv. nuclei of $I_j), (m$ of spin $I_k)$ give $(2nI_j+1)(2mI_k+1)$ lines etc.
Many nuclei with $I > 1/2$ have “quadrupole moments”

<p>| | | | |</p>
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<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>$^7$Li</td>
<td>3/2</td>
<td>$^{14}$N</td>
<td>1</td>
</tr>
<tr>
<td>$^{10}$B</td>
<td>3</td>
<td>$^{73}$Ge</td>
<td>9/2</td>
</tr>
<tr>
<td>$^{11}$B</td>
<td>3/2</td>
<td>$^{51}$V</td>
<td>7/2</td>
</tr>
</tbody>
</table>

e.g. $^{11}$B-H
2 N coupled to an I=1/2 nucleus (ignore quadrupolar broadening)
Factors affecting magnitude of $J$

1. Independent of the applied magnetic field
2. Nature and # of bonds intervening the 2 nuclei.
   - angles between bonds also intervene
     a) generally, fewer bonds = stronger coupling

   b) Trans coupling > cis coupling

   c) directly depends on product of magnetogyric ratio.
      Therefore different nuclei give different $J$
Example: Find the geometry of ClF$_3$

Ir complex
Second-order spectra (when coupling constants are similar)
- Only occurs for coupling between nuclei of the same type
- When $J_{AB} \approx |\delta_A - \delta_B|$ get complex spectra → need computer simulation
- If an NMR is more complex than expected, it could be 2nd order

• Run spectra at high-field machine → makes 2nd order spectra into 1st order
  - spreads peaks out
NMR of spin-dilute systems

e.g. cis-Pt(Et₃P)₂Cl₂
e.g. $\text{W(CO)}_6$ $^{13}\text{C NMR}$
e.g. Si$_2$H$_6$

e.g. KBH$_4$ dissolved in D$_2$O

$^1$H NMR

Most spin-dilute elements have abundances of $<$15%, so don’t have to worry about multiple nuclei present.

Exceptions: 2 Pt active molecule, Xe
Paramagnetic NMR

- Unpaired e- are moving charges, so they induce a large magnetic field
  - Vast impact on NMR
- Paramagnetic compounds relax much faster than diamagnetic (1-10s, vs $10^{-3}$s)
  - Very broad peaks; coupling info is lost due to fast relaxation
  - Protons closer to the unpaired e- are more broad than those far away
  - Shifted peaks; huge shielding and deshielding effect

$^1$H NMR range: ±500 ppm

Applications:
1. Determine spin density
   - Where is e- delocalized in the molecule? The direction of peak shift gives this information (complex)
2. Metalloprotein active site analysis
3. Magnetic Resonance Imaging
4. NMR shift reagents
   - e.g. Ln(III), fast relaxation, cause shifts surrounding molecules, but are $^1$H NMR invisible
Magnetic Resonance Imaging
- NMR of H$_2$O
- Different relaxation rates of H$_2$O in different parts of your body gives the final image
- Increase relaxation rate differences to give a better contrast, detailed picture
- Contrast agent: Gd(III), Mn(II)
  - Very fast relative rates
  - Gd(III) complexes target to specific body regions, increase H$_2$O rel. rate → better contrast

Superparamagnetic Fe$_3$O$_4$ nanoparticles
Press Release

6 October 2003

The Nobel Assembly at Karolinska Institutet has today decided to award The Nobel Prize in Physiology or Medicine for 2003 jointly to

Paul C Lauterbur and Peter Mansfield

for their discoveries concerning "magnetic resonance imaging"

Summary

Imaging of human internal organs with exact and non-invasive methods is very important for medical diagnosis, treatment and follow-up. This year’s Nobel Laureates in Physiology or Medicine have made seminal discoveries concerning the use of magnetic resonance to visualize different structures. These discoveries have led to the development of modern magnetic resonance imaging, MRI, which represents a breakthrough in medical diagnostics and research.

Atomic nuclei in a strong magnetic field rotate with a frequency that is dependent on the strength of the magnetic field. Their energy can be increased if they absorb radio waves with the same frequency (resonance). When the atomic nuclei return to their previous energy level, radio waves are emitted. These discoveries were awarded the Nobel Prize in Physics in 1952. During the following decades, magnetic resonance was used mainly for studies of the chemical structure of substances. In the beginning of the 1970s, this year’s Nobel Laureates made pioneering contributions, which later led to the applications of magnetic resonance in medical imaging.
Electron Spin Resonance

• Principle is similar to NMR. Unpaired e- has s=1/2, \( m_s = \pm 1/2 \)
• In an external magnetic field, get Zeeman splitting

• At the resonant frequency \( \nu \), see an absorption:
  In NMR \( \nu \rightarrow \text{MHz (radiowaves)} \)
  For e-, \( \nu \rightarrow \text{GHz (microwave)} \)

  NMR: sweep frequency, keep \( H_o \) constant, so scale is in Hz, ppm
  ESR: sweep field, keep \( \nu \) constant, so scale is in Gauss

ESR signal engineering – shows 1\textsuperscript{st} derivative of the signal
Where do we use it?

Unpaired e- found in organic radicals, transition metals, lanthanides

Note that e- e- coupling (e.g. in a d^2 system) is very complex

Nuclear Hyperfine Splitting
- Unpaired e- can couple to magnetically active nuclei. (e.g. proton radical)

Nuclear splitting is much smaller than e- splitting energies
- Termed “hyperfine coupling”
- Symbol a_x  x = nucleus coupled to e-
Example: VO(acac)$_2$  V(IV),  d$^1$,  I=7/2 for V

As in NMR, coupling to $n$ equiv. nuclei gives $(2nI_i + 1)$ lines
  
  e.g.  • CH$_3$  
  e.g.  • C$_6$H$_6$

ESR and NMR are often complementary with regard to paramagnetic compound

•  A compound with a strong ESR spectrum may be NMR silent
•  A compound with a strong NMR spectrum may be ESR silent
•  A diamagnetic compound has no unpaired e-, so will have no ESR spectrum
Information we can get:
1. **M**\(^+\) ion (parent ion)
   - if observable, gives MW of compound (if Z=1)
   - high resolution MS accurate to 1ppm
     
     e.g. CO vs N\(_2\), MW=28
     
     CO = 27.9994 vs N\(_2\) = 28.01348

     HRMS is used in great deal in organics esp. in natural products

2. Isotope pattern
   - characteristic of elements present (from rel. abundances)
     
     e.g. - halides (Cl and Br)
     
     - many TM have complex isotopic signatures (e.g Mo, W, Pt, Os, Hg)

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![Diagram](image)

**Fig. 4.7** Schematic diagram of an electron ionization (or electron impact, EI) mass spectrometer. During operation, the interior of the instrument is evacuated.
Multiple halides give specific pattern (probabilities predict intensities) e.g. PFBr₂

“isotopomers” defined as 2 compounds differ only by isotopic mass of 1 or more atoms

3. Fragmentation patterns
   - often fragments of the M⁺ ion fall off
   - observe these frag. at lower masses
   - often see the loss of ligands one at a time

   e.g. Fe(CO)₅  M⁺ = 196 amu
Crystallography

X-ray diffraction
• Need a single crystal (~0.02 mm³)

Problems:
- scattering of x-rays is by the electron and is proportional to $Z^2$ (atomic #)
- x-ray scattering cross-sections increase with increasing Z
- Hard to find H atoms, especially M–H
- Hard to differentiate atoms of $\Delta Z = 1$
Neutron diffraction
• neutrons are diffracted by nuclei – similar cross-section for all elements
• Can locate H atoms by “neutron diffraction”
• Can differentiate different isotopes or elements of similar atomic numbers (e.g. O and F)
• Useful for magnetic compounds

A comparison of scattering cross-sections

![Graph showing comparison of X-ray and Neutron scattering cross-sections.](image)

**Fig. 1.** The core of the [Fe(η²-H₂)(H)(dppe)]⁺ cation, as determined by neutron diffraction [4]. Note the characteristically large ‘size’ of the hydrogen atoms often found in dihydrogen complexes, caused by high thermal and librational motion. The H–H axis in this compound is eclipsed with one of the P–P axes, and the H–H distance is 0.82(2) Å.
Challenges:

- Need a neutron source
  - produced in atomic fission processes from a Uranium target
  - neutrons generated in nuclear reactor are slowed down using heavy water to give $\lambda \sim 100\text{pm}$
  - then monochromated
- Brookhaven, Oak Ridge National laboratories (U.S.), Grenoble (France)
- need large crystals (several mm$^3$)

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For all crystallography, solid state information may not equal solution structure!

- One crystal might not be the same as the bulk material
- Crystal must be single crystal