Electron Spin Resonance

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Plan

- Principles
- Goals and applications
- Example articles: $\text{Sr}_2\text{V}_3\text{O}_9$, MRFM, ESR microscopy
- Summary
About ESR

Different names:

Electron Spin Resonance
Electron Paramagnetic Resonance
Electron Magnetic Resonance

For materials with:

• Paramagnetic properties
• Unpaired electron spins

Properties:

• Very specific
• A lot of materials are ESR-silent
Compared to NMR

- Electron spins are excited, not nuclei
- Most stable molecules have all their electrons paired
- Not a lot of materials can be studied
- Less used than NMR
- Electrons are much lighter than the nuclei
- Higher magnetic moment, need greater electromagnetic frequency
- Microwave radiations

NMR: Nuclei
ESR: Electrons
Principle

• Apply magnetic field for which arranges the spins ↑ or ↓ (parallel or antiparallel)
• Electrons precess at Larmor frequency
• Zeeman effect: specific energy to each state
• Lower energy for parallel, higher for antiparallel
• Apply electromagnetic radiations to cause absorption

Equations

Electromagnetic radiations of energy
\[ \varepsilon = h \nu \]
Resonance condition
\[ \varepsilon = \Delta E \]
Separation between 2 energy levels
\[ \Delta E = g_e \mu_B B_0 \]

which comes from Larmor precession
\[ g_e = g\text{-factor}, \text{ around } 2 \]

2 choices, second is much better
• Apply constant magnetic field, vary frequency
• Use constant frequency, change magnetic field

Fundamental relation of ESR
\[ h \nu = g_e \mu_B B_0 \]

Resonance: external magnetic field and frequency are related

Microwave Radiation

Why use microwave

• Because it's electrons, need strong field or not enough resolution
• 9-10GHz meaning 0.32T-0.35T is average, gives lots of information
• Greater frequency means stronger fields
• Stronger fields are expensive and much more complicated to do

• There are experiments with higher frequencies which can be useful for ESR-silent cases, but need high field
• High field (>1T) require good superconducting magnets which can be expensive
## Microwave Bands

<table>
<thead>
<tr>
<th>Identifier</th>
<th>Frequency (GHz)</th>
<th>Wavelength (mm)</th>
<th>B (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>1-2</td>
<td>150-300</td>
<td>0.035-0.07</td>
</tr>
<tr>
<td>S</td>
<td>2-4</td>
<td>75-150</td>
<td>0.07-0.14</td>
</tr>
<tr>
<td>C</td>
<td>4-8</td>
<td>37.5-75</td>
<td>0.14-0.28</td>
</tr>
<tr>
<td>X</td>
<td>8-12</td>
<td>25-37.5</td>
<td>0.28-0.43</td>
</tr>
<tr>
<td>Ku</td>
<td>12-18</td>
<td>16.7-25</td>
<td>0.43-0.64</td>
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<tr>
<td>K</td>
<td>18-26.5</td>
<td>11.3-16.7</td>
<td>0.64-0.95</td>
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<tr>
<td>Ka</td>
<td>26.5-40</td>
<td>7.5-11.3</td>
<td>0.95-1.43</td>
</tr>
<tr>
<td>Q</td>
<td>33-50</td>
<td>6-9.1</td>
<td>1.18-1.79</td>
</tr>
<tr>
<td>U</td>
<td>40-60</td>
<td>5-7.5</td>
<td>1.43-2.14</td>
</tr>
</tbody>
</table>
Maxwell-Boltzmann Distribution

Generally, there are many paramagnetic centers

For centres in thermodynamic equilibrium

\[
\frac{n_{\text{upper}}}{n_{\text{lower}}} = \exp(-\Delta E/kT) = \exp(-h\nu/kT)
\]

- At room temperature around 9.8 GHz, little smaller than 1
- Transitions from lower energy to higher is more probable
- Net absorption of energy
Simple Example Scan

- First derivative is used instead of normal peak
- Multiple peaks are usually found because of interaction with nuclei

Interactions with Nuclei

- Atoms with non-zero spins affect magnetic moment of electron
- Electrons can have even more different states for its energy which causes multi-lined spectra
- Known as hyperfine splitting

\[ N = (2M_1L_1 + 1)(2M_2L_2 + 1) \ldots \]

E.g. For 2 equivalent spin-1/2 nuclei in 2 groups,

\[ N = (2 \times 2 \times 1/2 + 1)(2 \times 2 \times 1/2 + 1) = (2+1)(2+1) = 9 \]

http://ierc.scs.uiuc.edu/epr.html
ESR spectrometers can be portable (60kg)

Different specifications (Max. Field, Sensitivity)

Sensitivity measured in spins/G (for a S/N ratio of 1)

- Magnet
- Microwave source
- Cavity

http://www.ptb.de/en/publikationen/jahresberichte/jb2002/nachrdjahres/bilder/06.jpg
Goal

• To gain information about the medium the centres are in
• Distance between splittings give this information
• Usually much more complicated with noise

Linewidth

• Measured in terms of B
• Halfwidth: Half Width Half Maximum (HWHM)

http://www.scielo.cl/fbpe/img/jcchems/v48n4/fig1pag79.jpg
Applications

• Finding paramagnetic centers
• Radicals (unstable atoms/molecules unpaired electrons)
• ESR dating (does not destroy material)
• Medical and Biological (spin-labeling)

High-field

• Study of ESR-Silent materials
• Increased resolution of (complex) g-factor tensor
• E.g. Antiferromagnetic Resonance in Canted Antiferromagnets

Ultrawide Band Multifrequency High-Field EMR Technique: A Methodology for Increasing Spectroscopic Information
Example of ESR Focus (Article)

• Shows example of ESR results and what they can be used for

• Comparison to theoretical model

• Study over different temperature ranges
ESR of Sr$_2$V$_3$O$_9$

Linewidth as a function of temperature or angle

Images taken from article

Electron spin resonance of the low-dimensional spin-system Sr$_2$V$_3$O$_9$
Journal of Magnetism and Magnetic Materials
Volumes 272-276, Part 2, May 2004, Pages 960-961
Electron Spin Resonance Microscopy

• Trying to get micron resolution

• Difficult challenges (fast signal acquisition, higher frequency)

• Continuous wave (CW) vs Pulse

  Motivation include:

  • Molecular imaging (not affected by water like NMR)

  • Measurement of oxygen concentration \textit{in vivo}

High resolution electron spin resonance microscopy
Aharon Blank, Curt R. Dunnam, Peter P. Borbat and Jack H. Freed
Journal of Magnetic Resonance, Volume 165,
Issue 1, November 2003, Pages 116-127
Single spin detection by magnetic resonance force microscopy (MRFM)

D. Rugar, R. Budakian, H. Mamin, B. Chui,
Detection of individual electron spins

Force in attonewtons (ultrasensitive ferromagnetic tip)

Uses ESR

Considerable averaging (a lot of noise)

Allows probing below the surface (100 nm)

Similar to AFM (interferometer to detect motion of cantilever)
Summary

• ESR is valid for paramagnetic centres

• Study of radicals

• Less applicable than NMR

• Requires high frequency and magnetic fields

• Requires low temperatures

• Non intrusive