Nuclear Magnetic Resonance: Effect of Paramagnetic Ions on Relaxation Times

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Outline

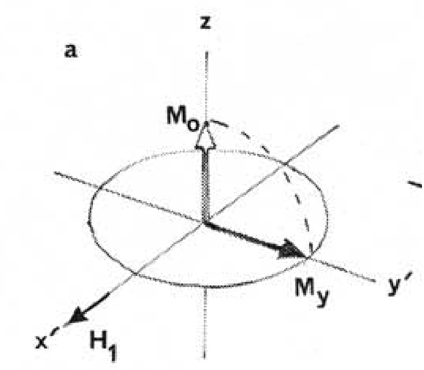
- Nuclear Magnetic Resonance
- Relaxation and Paramagnetic Ions
- A Useful Tool

History of NMR

- Rabi (1937) predicts and first observes NMR
- Purcell and Bloch (1945) measure relaxation times and their dependence on chemical properties
- Chemical shifts discovered (1950-1)
- Lauterbur (1973) applies NMR to medical imaging

Pulsed NMR

- Nuclear spins precess around static magnetic field
- Oscillatory perpendicular field $\rightarrow$ nutation
- Perpendicular spin component induces measurable current



Spin-Lattice Relaxation (T1)

- Return of spins to thermal equilibrium
- Energy transferred into molecular motions
- Lattice frequencies must be close to Larmor frequency

Spin-Spin Relaxation (T2)

- Loss of phase coherence
- Interactions between nearby spins

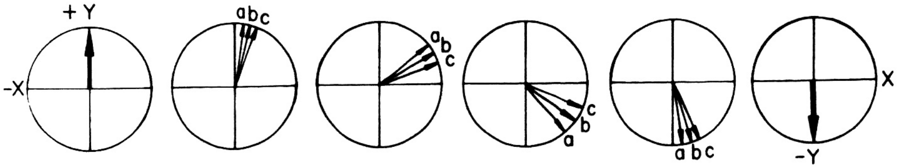
Paramagnetic Ions

- Enormous magnetic moments ($\approx$1000 times proton)
- Much larger interaction energies $\rightarrow$ smaller relaxation times
- Slow local field variations $\rightarrow$ additional T2 mechanism

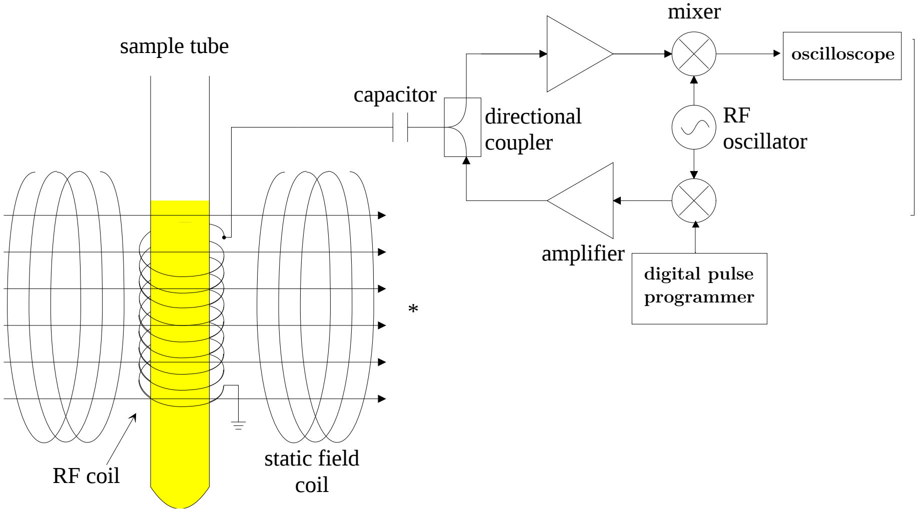
- $\frac{1}{T1} \propto$ ion concentration
- $\frac{1}{T2}$ more strongly affected

Spin Echoes

- Measuring relaxation directly has problems
  - Proximity to driving pulse
  - Inhomogeneity in static field alters observed T2
- Use 180° pulses to produce spin echoes (Hahn 1950)
  - Reverses phase decoherence from inhomogeneity



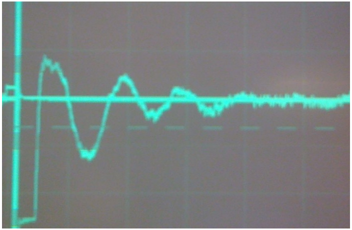
Apparatus

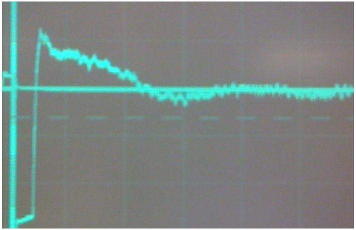


mixer
oscilloscope
sample tube
capacitor
directional coupler
RF oscillator
amplifier
digital pulse programmer
*
RF coil
static field coil

Finding Resonance

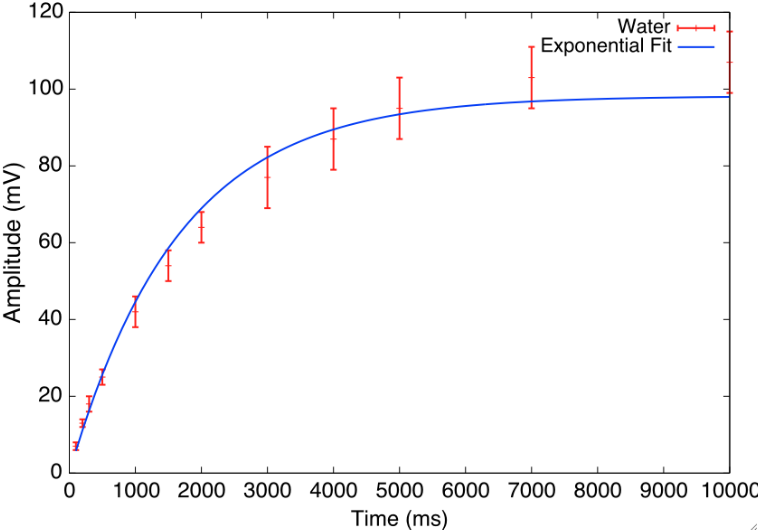
- Minimize beats
  - $\nu_{beats} = |\nu_{pulses} - \nu_{Larmor}|$





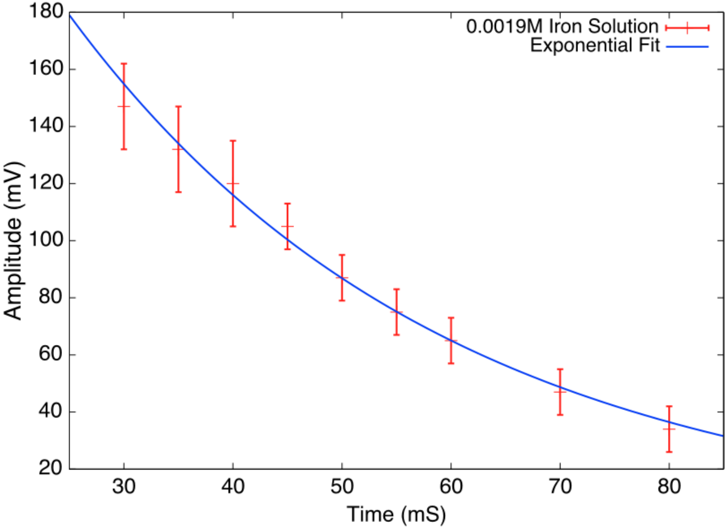
- Find most uniform B field
  - Inhomogeneity $\rightarrow$ different resonances $\rightarrow$ weaker signal
- Result: $(1.424 \pm 0.083) \cdot 10^{-26}$ J/T (3% off accepted value)

T1 Measurement



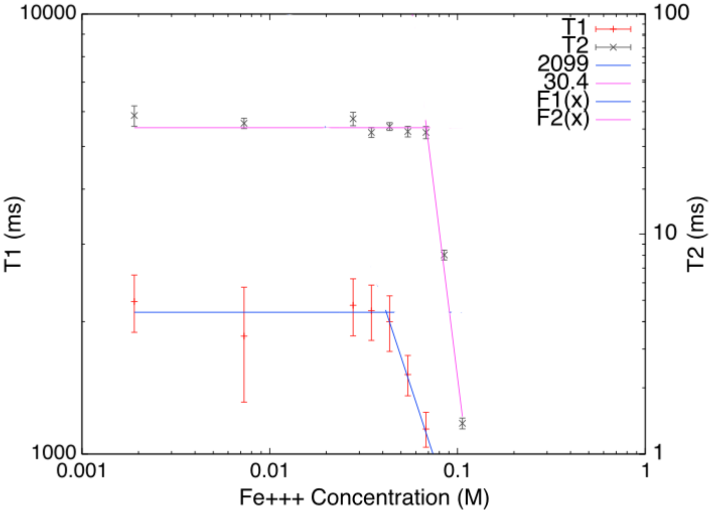
$$T1 = (2108 \pm 240)ms \qquad \chi_r^2 = 1.13$$

T2 Measurement



$$T2 = (8.86 \pm 0.16)ms \qquad \chi_r^2 = 0.13$$

Effect of Fe^{3+} Ions on T1 and T2



T_1 slope = -1.3 ± 0.4

$T_1\ \chi_r^2 = 0.07$

T_2 slope = -6.9 ± 0.2

$T_2\ \chi_r^2 = 12$

Results

- Proton magnetic moment: $(1.424 \pm 0.083) \cdot 10^{-26}$ J/T
  - Accepted value: $1.411 \cdot 10^{-26}$ J/T
- $\frac{1}{T1}$ grows linearly with Fe^{3+} concentration
- $\frac{1}{T2}$ grows faster than linearly with Fe^{3+} concentration

Improvements and Extensions

- More stable probe setup to allow more accurate determinations of field strength
- Greater sensitivity to allow use of higher concentrations
- Removing dissolved oxygen

Summary

- Observed NMR in protons at the expected frequency
- Verified expected effects of Fe^{3+} ions on relaxation times
- Suggested usefulness of NMR in chemical analysis

Questions?

- History of NMR
- Pulsed NMR
- Spin-Lattice and Spin-Spin Relaxation
- Spin Echoes
- Proton Larmor Frequency
- Effects of Fe^{3+} ions on Relaxation Times

Paramagnetism: N_2 vs. O_2