Dipolar Coupling and Solids NMR

BCMB/CHEM 8190
Liquids v. Solids
One can collect similar spectra but some tricks are required

$^{13}$C solution, sat’d glucose, 8 min

$^{13}$C CP-MAS, 30 mg cellulose, 9 min
The Classical Dipole-Dipole Interaction:

\[ E = \frac{\mu_0}{4\pi} \left( \frac{\mu_1 \cdot \mu_2}{r^3} - 3(\mu_1 \cdot r)(\mu_2 \cdot r)/r^5 \right) \]

\[ r = i \, r_x + j \, r_y + k \, r_z = i \, r \sin\theta \cos\phi + j \, r \sin\theta \sin\phi + k \, r \cos\theta \]
Quantum Mechanical Dipolar Coupling

\[
\mu = (\gamma \hbar / 2\pi)(i I_x + j I_y + k I_z) = (\gamma \hbar / 2\pi)f(I_z, I_{+, -})
\]

\[
H_D = (\mu_0 \gamma_1 \gamma_2 \hbar^2)/(16\pi^3 r^3)(A + B + C + D + E + F)
\]

A, B, C .. Grouped by type of operator, 0, 1, 2 Quantum

A = - I_{z1} I_{z2}(3\cos^2 \theta - 1), \quad B = (1/4)(I_{+1} I_{-2} + I_{-1} I_{+2}) (3\cos^2 \theta - 1)

................

E = -(3/4)(I_{+1} I_{+2})\sin^2 \theta \exp(-2i\phi), \quad F = ........
To First Order Only $I_{z1}I_{z2}$ Term is Important

A doublet would result – much like scalar coupling but large: as much as -60,000 Hz for a $^{13}$C-$^1$H pair.

Splittings are angle dependent – ranging from -60,000 to +30,000. In a solid all possibilities superimpose: The result is a powder pattern.

Points at 90° on a sphere are most abundant.
Other Anisotropies in NMR

\[ H = H_{CSA} + H_D + H_Q \ldots \]

All share the following property:

**Solution:** \[ < 3 \cos^2 \theta' - 1 > = 0 \]

**Solids:** \[ (3 \cos^2 \theta' - 1) \neq 0 \]

CSA powder pattern
Techniques in Solids NMR

- Cross Polarization (CP)
- Magic Angle Spinning (MAS)
- High power decoupling
Cross Polarization Improves Sensitivity

Magnetization transfer via dipolar coupling.

Hartman-Hahn:

\[ \gamma_I B_I = \gamma_S B_S \]
Magic Angle Spinning

- All interactions can be written in terms of $Y^{2}_0(\theta) = \frac{3\cos^2(\theta) - 1}{2}$
- $Y^{2}_0(\theta)$ can be transformed to another frame using Wigner Rotation elements: $Y^{2}_0(\theta) = \sum_{m=-2}^{2} D^{2}_{m0}(\theta'',\phi'') Y^{m}_m(\theta',\phi')$
- $D^{2}_{m0}(\theta'',\phi'') = \frac{4\pi}{5} Y^{2}_m(\theta'',\phi'')$
- With rapid averaging over $\phi''$, all terms except $Y^{2}_0(\theta'')$ go to zero
- Selecting $\theta'' = 54.7^\circ$, all interactions, regardless of $\theta'$ value, are zero
- $(3\cos^2(\theta) - 1) = (3\cos^2(\theta') - 1) <3\cos^2(54.7^\circ) - 1> = 0$

Dipolar couplings
CSA $= 0$
Quadrupolar couplings
100 MHz Spectrometer with HFC Transmission-Line Probe
High power decoupling

Solution $^{13}\text{C}^{-1}\text{H}$ \( J \approx 125 \text{ Hz} \)

Solid $^{13}\text{C}^{-1}\text{H}$ \( J + D \approx 125 \text{ kHz} \)
Cellulose

What is this peak?

13C (10 minute spectra)

CP-MAS, 3 kHz, with decoupling

3 kHz, with decoupling

3 kHz, no decoupling

0 Hz, with decoupling
Spinning Sidebands are Frequently Seen

When rotation rate is not >> anisotropies
Resonance position is modulated by rotation
Sidebands at the spinning frequency are produced

There are tricks that remove these:
TOSS – Total Suppression of Spinning Sidebands
180º pulses during rotor cycle dephases sideband magnetization but preserves center band magnetization
Peptide 1,2-$^{13}$C$_2$-Gly

(9 minute spectra)

CPMAS 5kHz dec on

CPMAS 5kHz dec off

5kHz dec on

5kHz dec off
Biomolecular Applications
Spider Silk

Nephila edulis
Nature as Engineer

- Strongest fiber
- $\beta$-sheet
- Poly-Ala = crystalline
- Poly-Gly = amorphous
Spider Silk and SS-NMR

- Torsion angle pairs to resolve backbone structure
- Ala in two different environments
- Dynamics
Rhodopsin

- Absorbs light in visible region
- Binds retinal

Rhodopsin in simulated bilayer
Theoretical and Computational Biophysics Group,
Schulten Laboratory
Univ. Illinois Urbana-Champaign

http://www.blackwellscience.com/matthews/rhodopsin.html
Antibiotics & bacterial growth
New Solids NMR Assignment Strategies
Parallel Solution Methods

Aliphatic region of the $^{13}$C,$^{13}$C CP MAS PDSD of Zn-MMP-12 (16.4 T, 11.5 kHz MAS frequency, 15 ms mixing time). (Balayssac, Oschkinat, 2007)
2D solid-state NMR spectra of uniformly $^{15}$N,$^{13}$C-labeled Aβ$_{1-40}$ amyloid fibrils. (a) 2D $^{13}$C-$^{13}$C NMR spectrum, obtained in a 14.1-T magnetic field with 13.6-kHz magic-angle spinning, using a 2.94-ms finite-pulse radio-frequency-driven recoupling (fpRFDR) sequence for spin polarization transfer in the mixing period. (b) 2D $^{15}$N-$^{13}$C spectrum, obtained with frequency-selective $^{15}$N-$^{13}$C cross-polarization followed by fpRFDR in the mixing period.

SOLIDS NMR REFERENCES


