Dipolar Coupling and Solids NMR

March 30, 2005
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:

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

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

\[ \mu = (\gamma h/2\pi)(i \mathbf{I}_x + j \mathbf{I}_y + k \mathbf{I}_z) = (\gamma h/2\pi)f(\mathbf{I}_z, \mathbf{I}_{+,\text{-}}) \]

\[ \mathbf{H}_D = (\mu_0 \gamma_1 \gamma_2 h^2)/(16\pi^3 r^3)(A + B + C + D + E + F) \]

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

\[ A = - \mathbf{I}_{z1}\mathbf{I}_{z2}(3\cos^2\theta - 1), \quad B = (1/4)(\mathbf{I}_{+1}\mathbf{I}_{-2} + \mathbf{I}_{-1}\mathbf{I}_{+2}) (3\cos^2\theta - 1) \]

………..

\[ E = -(3/4)(\mathbf{I}_{+1}\mathbf{I}_{+2})\sin^2\theta\exp(-2i\phi), \quad F = \ldots \]
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.

Splitting 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

\[ \mathcal{H} = \mathcal{H}_{\text{CSA}} + \mathcal{H}_{\text{D}} + \mathcal{H}_{\text{Q}} \ldots \]

All share the following property:

Solution: \( < 3 \cos^2 \theta' - 1 > = 0 \)

Solids: \( (3 \cos^2 \theta' - 1) \neq 0 \)
Techniques in Solids NMR

• Cross Polarization (CP)

• Magic Angle Spinning (MAS)

• High power decoupling
Cross Polarization

Magnetization transfer via dipolar coupling.

Hartman-Hahn:

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

Magic Angle Rotation of Solids:

\[(3 \cos^2 \theta' - 1) < 3 \cos^2 \theta - 1> = 0\]

\[\theta = 54.7^\circ\]

Dipolar couplings
CSA
Quadrupolar couplings
High power decoupling

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

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

(10 minute spectra)
Spinning Sidebands are Frequently Seen

When rotation rate is not $\gg$ 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
180° pulses during rotor cycle dephases sideband
magnetization but preserves center band magnetization
Peptide
1,2-$^{13}$C$_2$-Gly

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
- β-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

http://www.blackwellscience.com/matthews/rhodopsin.html
Antibiotics & bacterial growth

Schaefer Laboratory, Washington University, St. Louis, MO
SOLIDS NMR REFERENCES


