Chem8028(1314) - Spin Dynamics: Spin Interactions

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see also IK m106
Nuclear spin interactions (diamagnetic materials)

- Electric
  - Quadrupole coupling
  - Isotropic chemical shift

- Magnetic
  - Chemical shifts
    - Chemical shift anisotropy (CSA)
  - Spin-spin couplings
    - J-coupling
    - Direct dipole-dipole coupling
Chemical Shift

Chemical Shift Terms. These terms represent the indirect magnetic interaction of the external magnetic field and the nuclear spins, through the involvement of the electrons:
Direct dipole-dipole coupling

Direct Dipole-Dipole Couplings. These represent the direct magnetic interactions of nuclear spins with each other:
J-couplings. These represent the indirect magnetic interactions of nuclear spins with each other, through the involvement of the electrons.
Nuclear quadrupole coupling (1)

Quadrupolar Couplings. These represent the electric interactions of spin > 1/2 nuclei with the surrounding electric fields:

spin > 1/2 only
Spin System

spin-spin coupling

chemical shift
Spin System Ensemble
(perfectly rigid solid)

all spin interactions are coherent
(the same all the time, and the same for each member)
Spin System Ensemble (liquid)

most spin interactions are incoherent (fluctuating, and different for each member)
most spin interactions are *incoherent* (fluctuating, and different for each member)
Spin Interactions

• **coherent**
  - same for all spin systems in the ensemble
  - $\Rightarrow$ NMR peak *frequencies*

• **incoherent**
  - fluctuating in time
  - a snapshot would show differences between different spin systems in the ensemble
  - $\Rightarrow$ *linewidths* and *relaxation*


Coherent interactions

• **Solids:**
  ‣ chemical shifts (both isotropic and CSA)
  ‣ DD-couplings
  ‣ J-couplings

• **Isotropic liquids:**
  ‣ isotropic chemical shifts
  ‣ J-couplings
Coherent spin interactions (isotropic liquids)
Coherent spin interactions (solids)
Isotropic and anisotropic spin interactions

• Isotropic: independent of molecular orientation with respect to the magnetic field
• Anisotropic: dependent on molecular orientation with respect to the magnetic field
  ▶ often represented by a tensor (drawn as a 3D ellipsoid)
Tensors

Spinach representation
Tensors

Spinach representation

principal axes
J-coupling

J-couplings. These represent the indirect magnetic interactions of nuclear spins with each other, through the involvement of the electrons.
J-coupling Hamiltonian: homonuclear case

\[ H^J_{jk} = 2\pi J_{jk} \mathbf{I}_j \cdot \mathbf{I}_k \]

\[ \mathbf{I}_j \cdot \mathbf{I}_k = I_{jx} I_{kx} + I_{jy} I_{ky} + I_{jz} I_{kz} \]
J-coupling Hamiltonian: heteronuclear case

\[ H_{jk}^J = 2\pi J_{jk} I_{jz} I_{kz} \]
Direct dipole-dipole coupling

*Direct Dipole-Dipole Couplings.* These represent the direct magnetic interactions of nuclear spins with each other:
Direct dipole-dipole coupling

The magnetic field generated by one spin influences its neighbour.
Dipole-dipole coupling constant

\[ b_{jk} = -\left(\frac{\mu_0}{4\pi}\right)\frac{\hbar\gamma_j\gamma_k}{r_{jk}^3} \quad \text{(in rad s}^{-1}\text{)} \]

Note: The DD coupling in Hz is \( b_{jk} / 2\pi \)

Examples:
- Two protons at 3Å separation: DD coupling = -4.5 kHz
- Two \(^{13}\text{C}\)'s at 1.5Å separation: DD coupling = -2.2 kHz
- Two \(^{13}\text{C}\)'s at 5Å separation: DD coupling = -61 Hz
- Two \(^{13}\text{C}\)'s at 8Å separation: DD coupling = -15 Hz
DD Hamiltonian: homonuclear

\[ b_{jk} = -\left( \frac{\mu_0}{4\pi} \right) \frac{\hbar \gamma_j \gamma_k}{r_{jk}^3} \]

\[ H^{DD}_{jk} = d_{jk} \left( 3I_{jz} I_{kz} - \mathbf{I}_j \cdot \mathbf{I}_k \right) \]

\[ d_{jk} = b_{jk} \times \frac{1}{2} \left( 3\cos^2 \theta_{jk} - 1 \right) \]
DD Hamiltonian: heteronuclear

\[ b_{jk} = -\left( \frac{\mu_0}{4\pi} \right) \frac{\hbar \gamma_j \gamma_k}{r_{jk}^3} \]

\[ H_{jk}^{DD} = d_{jk} 2I_{jz} I_{kz} \]

\[ d_{jk} = b_{jk} \times \frac{1}{2} \left( 3\cos^2 \theta_{jk} - 1 \right) \]
Principal axes of DD coupling

The principal z-axis of the DD coupling between two spins is along the internuclear vector.
Chemical Shift

Chemical Shift Terms. These terms represent the indirect magnetic interaction of the external magnetic field and the nuclear spins, through the involvement of the electrons:
Mechanism of chemical shift

- Flow of electrons
- Induced field
- Nuclear spin

B^0
CSA

Powder Spectrum

Individual Peaks
Chemical shift depends on molecular orientation with respect to the field.
Oriented $^{15}$N-labelled spider silk

Zhao and Asakura (2001)

vary angle between the silk fibre and the magnetic field
Chemical shift tensor

\[ B_{ij}^{\text{induced}} = \vec{\delta}^j \cdot B_{\text{applied}} \]

The induced field is not (usually) parallel to the applied field.
Principal axes

There are three special directions in which the induced field is parallel to the applied field. These are called the principal axes of the chemical shift tensor (denoted $(X,Y,Z)$). The principal axes are in general different for different chemical sites.
Principal values

When the applied field is along a principal axis, the induced field is proportional to the applied field, multiplied by a number, called the principal value of the chemical shift tensor.

\[
\begin{align*}
B_{ij}^{\text{induced}} \text{ (along } X) &= \delta_{XX}^j B^{\text{applied}} \text{ (along } X) \\
B_{ij}^{\text{induced}} \text{ (along } Y) &= \delta_{YY}^j B^{\text{applied}} \text{ (along } Y) \\
B_{ij}^{\text{induced}} \text{ (along } Z) &= \delta_{ZZ}^j B^{\text{applied}} \text{ (along } Z)
\end{align*}
\]
The mean of the three principal chemical shift values is called the *isotropic chemical shift*. This is the “chemical shift” reported in solution NMR.

\[ \delta_{iso}^j = \frac{1}{3} \left( \delta_{XX}^j + \delta_{YY}^j + \delta_{ZZ}^j \right) \]
Assignment of the principal axes

By convention, the principal axes are assigned so that:

- The Z-axis is the one for which the principal value is *furthest* from the isotropic shift;
- The Y-axis is the one for which the principal value is the *closest* to the isotropic shift;
- The X-axis is the *other one*
Chemical shift anisotropy

The difference between the isotropic shift and the principal value which is furthest from it is called the chemical shift anisotropy (CSA)

$$\delta^j_{aniso} = \delta^j_{ZZ} - \delta^j_{iso}$$
Biaxiality

The difference between the x and y principal values is usually quantified by the biaxiality* $\eta$:

$$\eta^j = \frac{\delta^j_{YY} - \delta^j_{XX}}{\delta^j_{aniso}}$$

If $\eta$ is zero, the x and y principal values are the same, and the CSA tensor is said to be uniaxial

*Sometimes called (misleadingly) the asymmetry
Static spectrum (powder pattern)
Powder patterns

\[ \delta_{\text{aniso}}^j < 0 \]

\[ \eta^j = 0 \]

\[ 0 < \eta^j < 1 \]

\[ \eta^j = 1 \]

uniaxial CSA tensor

biaxial CSA tensor
Shielding convention

• Bad news: In many papers and books, CSA is specified using a shielding parameter $\sigma$, with \textit{opposite sign} to the (deshielding) chemical shift $\delta$

$$\sigma_{aniso}^j = -\delta_{aniso}^j$$

• Even worse news: some authors write $\sigma$ when they mean $\delta$!
Nuclear quadrupole coupling (1)

Quadrupolar Couplings. These represent the electric interactions of spin > 1/2 nuclei with the surrounding electric fields:

spin > 1/2 only
Quadrupolar spin Hamiltonian

Full form of spin interaction:

\[ \hat{\mathcal{H}}_{Q,\text{full}}^j = \frac{3eQ_j}{4I_j(2I_j - 1)} \left\{ V_0^j (3\hat{j}^2_{\parallel} - \hat{j}_j \cdot \hat{j}_j) + V_{+1}^j (\hat{j}_j \hat{j}_{\perp} + \hat{j}_{\perp} \hat{j}_j) + 
V_{-1}^j (\hat{j}_j^+ \hat{j}_{\perp} + \hat{j}_{\perp} \hat{j}_j^+) + V_{+2}^j (\hat{j}_j^-)^2 + V_{-2}^j (\hat{j}_j^+)^2 \right\} \]

1st order term (usually sufficient for \(^2\text{H}\)):

\[ \hat{\mathcal{H}}_{Q}^j = \frac{3eQ_j}{4I_j(2I_j - 1)} V_0^j (3\hat{j}^2_{\parallel} - \hat{j}_j \cdot \hat{j}_j) . \]

For other nuclei, the 2nd order term is usually needed as well.
Nuclear quadrupole coupling (2)

- 1st-order: shifts spin energy levels according to $M^2$
- 2nd-order: shifts energy levels in a more complicated way

$I=3/2$:

$|+3/2>$

$|-3/2>$

$|-1/2>$

$|+1/2>$

$|+3/2>$

1st-order $Q$  2nd-order $Q$
Relative Magnitudes of Interactions (before motional averaging)

CHEMICAL SHIFT  DIPOLE-DIPOLE  J-COUPLING  QUADRUPOLE COUPLING

spins > 1/2 only
Interactions after motional averaging

spins > 1/2 only
Motionally-averaged spin interactions: isotropic liquids
Motionally-averaged spin interactions: spins-1/2 in solids
Motionally-averaged spin interactions: spins > 1/2 in solids
Summary

• Only spins >1/2 experience electric spin interactions (electric quadrupole interaction)
• The chemical shift is a three-body interaction between the applied field, the electrons, and the nuclei
• The CSA is described by three principal values and three principal axes
• The DD coupling is directly proportional to the inverse cube of the distance between the nuclei
• The DD principal axis system is aligned along the internuclear vector
• In high magnetic field, all interactions may be replaced by their secular (1st-order) parts, except the large quadrupole coupling, where the 2nd or higher terms must be included as well.