Solid-State NMR of Metal Sites in Biological Systems

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OUTLINE

INTRODUCTION
Metals in biology and chemistry: abundance, nuclear properties

QUADRUPOLAR INTERACTION
Quadrupolar Hamiltonian
First and second order quadrupolar interaction: lineshapes
Magnitude of quadrupolar interaction for different geometries
High resolution spectroscopy of quadrupolar nuclei: contrast with spin-1/2 systems

DETECTING SSNMR SPECTRA OF HALF-INTEGER QUADRUPOLAR NUCLEI
Small and moderate quadrupole couplings
Large quadrupole couplings
Sensitivity enhancement techniques
Resolution enhancement techniques
Additional practical considerations

RELATING THE NMR PARAMETERS TO MOLECULAR STRUCTURE
Classical electrostatic theory
Quantum mechanical calculations of NMR parameters (EFG and CSA tensors)

EXAMPLES: SSNMR OF METALS IN BIOLOGICAL SYSTEMS

ADDITIONAL LECTURE: TUTORIAL ON QUANTUM MECHANICAL CALCULATIONS OF NMR PARAMETERS
INTRODUCTION
**PERIODIC TABLE OF METALS IN BIOLOGY**

About 1/3 of all proteins contain metals.
## Biological Functions of Metals

Adapted from S. Lippard and J. Berg “Principles of Bioinorganic Chemistry”

<table>
<thead>
<tr>
<th>Element</th>
<th>Function(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>Sodium charge carrier; osmotic balance</td>
</tr>
<tr>
<td>K</td>
<td>Potassium charge carrier, osmotic balance</td>
</tr>
<tr>
<td>Mg</td>
<td>Magnesium structure; hydrolase; isomerase</td>
</tr>
<tr>
<td>Ca</td>
<td>Calcium structure; trigger; charge carrier</td>
</tr>
<tr>
<td>V</td>
<td>Vanadium nitrogen fixation; oxidase</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium essential trace element; possible involvement in glucose tolerance</td>
</tr>
<tr>
<td>Mo</td>
<td>Molybdenum nitrogen fixation; oxidase; oxo transfer</td>
</tr>
<tr>
<td>W</td>
<td>Tungsten dehydrogenase</td>
</tr>
<tr>
<td>Mn</td>
<td>Manganese photosynthesis; oxidase; structure</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron oxidase; dioxygen transport and storage; electron transfer; nitrogen fixation</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt oxidase; alkyl group transfer</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel hydrogenase; hydrolase</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper oxidase; dioxygen transport; electron transfer</td>
</tr>
<tr>
<td>Zn</td>
<td>Zinc structure; hydrolase</td>
</tr>
</tbody>
</table>
MAGNETIC PROPERTIES OF METALS

Nuclear Spins of Metals

<table>
<thead>
<tr>
<th>Spin = 1/2</th>
<th>Spin &gt; 1/2 (quadrupolar)</th>
</tr>
</thead>
</table>

- H (Hydrogen)
- Be (Beryllium)
- Mg (Magnesium)
- Na (Sodium)
- K (Potassium)
- Ca (Calcium)
- Sc (Scandium)
- Ti (Titanium)
- V (Vanadium)
- Cr (Chromium)
- Mn (Manganese)
- Fe (Iron)
- Co (Cobalt)
- Ni (Nickel)
- Cu (Copper)
- Zn (Zinc)
- Ga (Gallium)
- Ge (Germanium)
- As (Arsenic)
- Se (Selenium)
- Br (Bromine)
- Kr (Krypton)
- Rb (Rubidium)
- Sr (Strontium)
- Y (Yttrium)
- Zr (Zirconium)
- Nb (Niobium)
- Mo (Molybdenum)
- Tc (Technetium)
- Ru (Ruthenium)
- Rh (Rhodium)
- Pd (Palladium)
- Ag (Silver)
- Cd (Cadmium)
- In (Indium)
- Sn (Tin)
- Sb (Antimony)
- Te (Tellurium)
- I (Iodine)
- Xe (Xenon)
- Cs (Cesium)
- Ba (Barium)
- La (Lanthanum)
- Ce (Cerium)
- Pr (Praseodymium)
- Nd (Neodymium)
- Pm (Promethium)
- Sm (Samarium)
- Eu (Europium)
- Gd (Gadolinium)
- Tb (Terbium)
- Dy (Dysprosium)
- Ho (Holmium)
- Er (Erbium)
- Tm (Thulium)
- Yb (Ytterbium)
- Lu (Lutetium)
SPIN-1/2 METALS IN BIOLOGY

NATURALLY OCCURRING SPIN-1/2 METALS


SPIN-1/2 METALS USED AS NMR PROBES OR DRUGS

$^{111}\text{Cd}$ - replacement of native $\text{Zn(II)}$, $\text{Ca(II)}$, $\text{Mg(II)}$, $\text{Mn(II)}$, $\text{Fe(II)}$, $\text{Cu(II)}$ sites in proteins (e.g., calmodulin, transferrin, alkaline phosphatase, azurin, plastocyanin, glucocorticoid receptor, etc.)

$^{119}\text{Sn}$ - structural probe of protoporphyrin-hemoprotein interactions, in organotin antibiotics and antitumor drugs

$^{195}\text{Pt}$ - structural probe in Pt complexes used as antitumor agents to probe interactions with DNA

$^{199}\text{Hg}$ - replacement of native $\text{Zn(II)}$, $\text{Cu(II)}$, $\text{Fe(II)}$ sites in proteins (e.g., carbonic anhydrase, azurin, plastocyanin, rusticyanin, rubredoxin, Gal4, MerR, and MerP)

$^{205}\text{Ti}^+$ - structural probe for monovalent cation binding sites ($\text{K}^+$, $\text{Na}^+$) in ATPases, protein C, S-adenosylmethioneine synthetase, and pyruvate kinase;

$^{205}\text{Ti}^{3+}$ - probe of $\text{Fe}^{3+}$ sites in transferrins

Examples of metalloproteins

- **Na**: Na\(^+\) ion channels, Na\(^+\)-K\(^+\)-ATPase,
- **K**: K\(^+\) ion channels, Na\(^+\)-K\(^+\)-ATPase,
- **Mg**: restriction endonucleases, Mg\(^{2+}\)/Ca\(^{2+}\)-ATPase, phosphatase, phosphoglucomutase, DNA polymerase
- **Ca**: thermolysin, phospholipase A\(_2\), Mg\(^{2+}\)/Ca\(^{2+}\)-ATPase, neutral protease
- **V**: nitrogenase, haloperoxidases
- **Cr**: essential trace element but specific proteins are unknown
- **Mo**: nitrogenase, xanthine oxidase, nitrate reductase, formate dehydrogenase, dimethylsulfoxide reductase, sulfite oxidase
- **Mn**: SOD, photosystem II, arginase, catalase, xylose isomerase, ribonuclease H, phosphotriesterase, enolase
- **Co**: Coenzyme-B12 dependent enzymes: glutamate mutase, diol dehydrase, ribonucleotide reductase, ethanolamine ammonia lyase, methionine aminopeptidase, glucose isomerase, Co transporters
- **Ni**: Ni-Fe hydrogenases; hydrolases
- **Cu**: azurin, galactose oxidase, nitrogenase, plastocyanin, hemocyanin, Cu-Zn SOD
- **Zn**: liver alcohol dehydrogenase, carbonic anhydrase, carboxypeptidase A, Cu-Zn SOD

**UNDERSTANDING GEOMETRIC AND ELECTRONIC STRUCTURE OF THE METAL CENTERS- IMPORTANT FOR UNDERSTANDING THE FUNCTION OF THE METALLOPROTEINS; SSNMR- DIRECT PROBE**
METALS NMR IN BIOLOGICAL SOLIDS:
INFORMATION CONTENT

Presence of a particular metal site (sometimes indiscernible in X-ray structures)

Geometry of metal sites

Electronic structure of metal sites (i.e., interactions with surrounding ligands and/or solvent molecules)

Protonation states of metal cofactors/ligands

Identification of polymorphs

Dynamics of metals and/or coordinated ligands

This information sheds light on chemical reactivity of metal sites in metallobiomolecules, often unavailable from other techniques
SSNMR SPECTROSCOPY OF QUADRUPOLAR NUCLEI IN BIOLOGICAL SYSTEMS

UNTIL RECENTLY HAS BEEN CONSIDERED IMPractical:

LOW SENSITIVITY
BROAD LINES
COMPLEX SYMMETRY OF QUADRUPOLAR INTERACTION
NUCLEI WITH SPIN I > 1/2

HAVE A NON-SPHERICAL CHARGE DISTRIBUTION, POSSESS A NUCLEAR QUADRUPOLE MOMENT, $eQ$

THE NUCLEAR QUADRUPOLE MOMENT, $eQ$, INTERACTS WITH THE ELECTRIC FIELD GRADIENT, $V$, AT THE NUCLEUS

NUCLEAR CHARGE DISTRIBUTION

Spin $I = 1/2$
$Q = 0$

Spin $I > 1/2$
prolate
$Q > 0$

Spin $I > 1/2$
oblate
$Q < 0$
ELECTROSTATIC INTERACTION OF THE NUCLEUS WITH ITS ENVIRONMENT

\[ H = \int \rho(x)V(x)d^3x \]

\[ \rho(x) \text{ Nuclear charge density} \]

\[ V(x) \text{ Electrostatic potential (all charges other than nucleus under consideration)} \]

EXPAND THE POTENTIAL ABOUT THE NUCLEAR CENTER OF MASS:

\[ H = \int d^3x \rho(x) \left\{ V_0 + \sum_j \left( \frac{\partial V}{\partial x_j} \right)_0 x_j + \frac{1}{2} \sum_{j,k} \left( \frac{\partial^2 V}{\partial x_j \partial x_k} \right)_0 x_j x_k + \ldots \right\} \]

\[ \int d^3x \rho(x) = Ze \quad \text{- nuclear charge} \]

\[ \int d^3x \rho(x)x_j \equiv P_j \quad \text{- electric dipole moment} \]

\[ \int d^3x \rho(x)x_j x_k \equiv Q_{jk} \quad \text{- electric quadrupole moment tensor} \]

ELECTROSTATIC INTERACTION OF THE NUCLEUS WITH ITS ENVIRONMENT

EXPAND THE POTENTIAL ABOUT THE NUCLEAR CENTER OF MASS:

\[ H = Z e V_0 + \sum_j P_j \left( \frac{\partial V}{\partial x_j} \right)_0 x_j + \frac{1}{2} \sum_{j,k} Q_{jk} \left( \frac{\partial^2 V}{\partial x_j \partial x_k} \right)_0 x_j x_k + \ldots \]

- electrostatic energy of a point nucleus
- electric dipole term (vanishes)
- quadrupolar interaction

\[ V_{jk} \equiv \frac{\partial^2 V}{\partial x_j \partial x_k} = -\frac{\partial E_k}{\partial x_j} \quad -electric \ field \ gradient \ tensor \ elements \]

where \[ E_k = -\frac{\partial V}{\partial x_k} \quad -electric \ field \]

NUCLEAR ELECTRIC QUADRUPOLE MOMENT

MEASURES THE DEPARTURE OF THE NUCLEAR CHARGE DISTRIBUTION FROM SPHERICAL SYMMETRY

\[ eQ \equiv \int \rho_{II}(x)(3z^2 - r^2)d^3x \]

\[ \rho_{II}(x) \] - expectation value of the nuclear charge density (state with \( I = m \))

For spherically symmetric \( \rho(x) \), \( Q = 0 \)

PROPERTIES OF \( Q \):

Has dimensions of an area, of the order of magnitude \( r_n^2 \);
\( r_n \) - nuclear radius, \( 10^{-13} - 10^{-12} \) cm;
\( Q \sim r_n^2 \sim 10^{-24} \) cm²

NUCLEAR ELECTRIC QUADRUPOLE MOMENT: UNITS AND SIGN CONVENTIONS

THE QUADRUPOLE COUPLING CONSTANT FOR NUCLEUS X IS GIVEN AS

\[
C_Q^X = \frac{e^2 q Q^X}{a_0^3 h} = \frac{e V_{ZZ}^{PAS} Q^X}{a_0^3 h}
\]

where \( Q^X \) is the quadrupole moment for nucleus X.

The constants are given as

- Electron’s charge: \( e = 4.803242 \times 10^{-10} \) esu = \( 4.803242 \times 10^{-10} \) g\(^{1/2}\) cm\(^{3/2}\)s\(^{-1}\)
- Planck constant: \( h = 6.626176 \times 10^{-27} \) ergs = \( 6.626176 \times 10^{-27} \) gcm\(^2\)s\(^{-1}\)
- First Bohr orbit radius in H: \( a_0 = 0.52917706 \times 10^{-8} \) cm

using these values ...

\[
\left[ \frac{e^2}{(a_0^3 h)} \right] \times 10^{-24} \text{ cm}^2 = 2.349649 \times 10^8 \text{ Hz}
\]
**NUCLEAR ELECTRIC QUADRUPOLE MOMENT: UNITS AND SIGN CONVENTIONS**

**SOME TYPICAL VALUES OF Q^X X 10^{24} ARE:**

<table>
<thead>
<tr>
<th>Element</th>
<th>Q^X</th>
<th>Value</th>
<th>Parentheses Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>Q^Mo</td>
<td>0.16 cm²</td>
<td>(0.022 cm²)</td>
</tr>
<tr>
<td>Zn</td>
<td>Q^Zn</td>
<td>0.15 cm²</td>
<td>(0.150 cm²)</td>
</tr>
<tr>
<td>Cu</td>
<td>Q^Cu</td>
<td>0.16 cm²</td>
<td>(0.220 cm²)</td>
</tr>
<tr>
<td>Ca</td>
<td>Q^Ca</td>
<td>0.2 ± 0.1 cm²</td>
<td>(-0.0408 cm² limited accuracy)</td>
</tr>
<tr>
<td>Cl</td>
<td>Q^Cl</td>
<td>(-0.0646 cm²)</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>Q^Cl</td>
<td>(-0.082 cm²)</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>Q^S</td>
<td>-0.064 cm²</td>
<td>(-0.0678 cm²)</td>
</tr>
<tr>
<td>Al</td>
<td>Q^Al</td>
<td>0.149 cm²</td>
<td>(0.1403 cm²)</td>
</tr>
<tr>
<td>Mg</td>
<td>Q^Mg</td>
<td>0.22 cm²</td>
<td>(0.1994 cm²)</td>
</tr>
<tr>
<td>Na</td>
<td>Q^Na</td>
<td>0.12 cm²</td>
<td>(0.1074 cm²)</td>
</tr>
<tr>
<td>O</td>
<td>Q^O</td>
<td>-0.026 cm²</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>Q^N</td>
<td>0.016 cm²</td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td>Q^Be</td>
<td>0.052 cm²</td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>Q^Li</td>
<td>-0.045 cm²</td>
<td>(-0.0401 cm²)</td>
</tr>
<tr>
<td>H</td>
<td>Q^H</td>
<td>0.00273 cm²</td>
<td>(0.002860 cm²)</td>
</tr>
</tbody>
</table>

The values in parenthesis are those deduced by P. Pyykkö [Z. Naturforsch. 47a, 189-196 (1992)].
THEREFORE, WE CAN WRITE (USING PYYKKÖ’S VALUES):

\[
\begin{align*}
C_q^{\text{Mo}} &= q_{zz}5.16923 \text{ MHz} \\
C_q^{\text{Zn}} &= q_{zz}35.24474 \text{ MHz} \\
C_q^{\text{Cu}} &= q_{zz}51.69227 \text{ MHz} \\
C_q^{\text{Ca}} &= q_{zz}(46.9930 \pm 23.4965) \text{ MHz or } -q_{zz}9.58657 \text{ MHz} \\
C_q^{\text{Cl}} &= q_{zz}(19.26712 \text{ MHz}[^{35}\text{Cl}] \text{ and } 15.17873 \text{ MHz }[^{37}\text{Cl}]) \\
C_q^{\text{S}} &= -q_{zz}15.0378 \text{ MHz or } -q_{zz}15.930620 \text{ MHz} \\
C_q^{\text{Al}} &= q_{zz}35.00977 \text{ MHz or } q_{zz}32.96558 \text{ MHz} \\
C_q^{\text{Mg}} &= q_{zz}51.6923 \text{ MHz or } q_{zz}46.852 \text{ MHz} \\
C_q^{\text{Na}} &= q_{zz}28.19578 \text{ MHz or } q_{zz}25.23523 \text{ MHz} \\
C_q^{\text{O}} &= -q_{zz}6.10909 \text{ MHz} \\
C_q^{\text{N}} &= q_{zz}3.75944 \text{ MHz} \\
C_q^{\text{Be}} &= q_{zz}12.21817 \text{ MHz} \\
C_q^{\text{Li}} &= -q_{zz}10.57342 \text{ MHz or } -q_{zz}9.422092 \text{ MHz} \\
C_q^{\text{H}} &= q_{zz}641.4542 \text{ KHz or } q_{zz}672.000 \text{ KHz}
\end{align*}
\]

Some useful ratios:

\[
\begin{align*}
Q(^{37}\text{Cl})/Q(^{35}\text{Cl}) &= 0.7880983 \\
Q(^{40}\text{K})/Q(^{39}\text{K}) &= 1.244 \\
Q(^{65}\text{Cu})/Q(^{63}\text{Cu}) &= 0.9268
\end{align*}
\]
QUADRUPOLAR HAMILTONIAN

CARTESIAN COORDINATES:

\[
H_Q = \frac{eQ}{6I(2I-1)\hbar} \hat{I} \cdot \tilde{V} \cdot \hat{I}
\]

\[
H_Q = \frac{eQ}{6I(2I-1)\hbar} \sum_{i,j=x,y,z} V_{ij} \left[ \frac{3}{2} (\hat{I}_i \hat{I}_j + \hat{I}_j \hat{I}_i) - \delta_{ij} \hat{I}^2 \right]
\]

\[
\frac{e^2Q}{4I(2I-1)\hbar} \left[ 3\hat{I}_Z^{2\text{PAS}} - \hat{I}^2 + \eta_Q \left( \hat{I}_x^{2\text{PAS}} - \hat{I}_y^{2\text{PAS}} \right) \right]
\]

\[
eq V_{ZZ}^{\text{PAS}} \quad \eta_Q = \frac{V_{XX}^{\text{PAS}} - V_{YY}^{\text{PAS}}}{V_{ZZ}^{\text{PAS}}};
\]

\[
C_Q = \frac{e^2Q}{\hbar} \quad \text{Quadrupole coupling constant}
\]
QUADRUPOLAR HAMILTONIAN

CARTESIAN COORDINATES, LABORATORY FRAME:

\[ \hat{H}_0 = -\omega_0 \hat{I}_Z; \]
\[ \begin{pmatrix} \hat{I}_X \\ \hat{I}_Y \\ \hat{I}_Z \end{pmatrix} = R(\theta, \phi) \begin{pmatrix} \hat{I}_X^{\text{PAS}} \\ \hat{I}_Y^{\text{PAS}} \\ \hat{I}_Z^{\text{PAS}} \end{pmatrix} \]

\[ \hat{H}_Q = \frac{e^2 q Q}{4 I (2I - 1) \hbar} \left\{ \frac{1}{2} (3 \cos^2 \theta - 1)(3 \hat{I}_Z^2 - \hat{I}^2) \\
+ \frac{3}{2} \sin \theta \cos \theta [\hat{I}_Z (\hat{I}_+ + \hat{I}_-) + (\hat{I}_+ + \hat{I}_-) \hat{I}_Z] + \frac{3}{4} \sin^2 \theta (\hat{I}_+^2 + \hat{I}_-^2) \right\} \\
+ \eta Q \frac{e^2 q Q}{4 I (2I - 1) \hbar} \left\{ \frac{1}{2} \cos 2\phi (1 - \cos^2 \theta)(3 \hat{I}_Z^2 - \hat{I}^2) \\
+ (\cos^2 \theta + 1) (\hat{I}_+^2 + \hat{I}_-^2) \\
+ \frac{1}{2} \sin \theta [(\cos \theta \cos 2\phi - i \sin 2\phi)(\hat{I}_+ \hat{I}_Z + \hat{I}_Z \hat{I}_+) \\
+ (\cos \theta \cos 2\phi + i \sin 2\phi)(\hat{I}_- \hat{I}_Z + \hat{I}_Z \hat{I}_-)] \\
+ (i/4) \sin 2\phi \cos \theta (\hat{I}_+^2 - \hat{I}_-^2) \right\} \]
QUADRUPOLAR HAMILTONIAN: HIGH FIELD LIMIT

$H_Q$ TREATED BY PERTURBATION THEORY, ONLY FIRST AND SECOND ORDER TERMS ARE SIZEABLE IN MOST OF THE CASES

USE SPHERICAL COORDINATES:

$$\hat{H}_Q^{(1)} = \frac{e^2 qQ}{4I(2I-1)} \sqrt{6} V_{20} \hat{T}_{20}$$

$$\hat{H}_Q^{(2)} = \frac{C_Q^2}{\omega_L} \sum_{m \neq 0} \frac{V_{2m} V_{2-m} [T_{2m}, T_{2-m}]}{2m}$$

$$\hat{H}_Q^{(2)} = -\left(\frac{e^2 qQ}{4I(2I-1)\hbar}\right)^2 \frac{1}{\omega_L} \frac{2}{5} \times \left\{ \left[ -3 \sqrt{10} \hat{T}_{30} + \hat{T}_{10} (3 - 4I(I+1)) \right] V_{00} + \left[ -12 \sqrt{10} \hat{T}_{30} - \hat{T}_{10} (3 - 4I(I+1)) \right] V_{20} + \left[ -34 \sqrt{10} \hat{T}_{30} + 3 \hat{T}_{10} (3 - 4I(I+1)) \right] V_{40} \right\}$$
ELECTRIC FIELD GRADIENT (EFG) TENSOR: CARTESIAN COORDINATES

SYMMETRIC, TRACELESS SECOND-RANK TENSOR, $V$

$$V_{XX} + V_{YY} + V_{ZZ} = 0$$

PRINCIPAL COMPONENTS OF THE EFG TENSOR:

$$\left| V_{ZZ} \right| \geq \left| V_{YY} \right| \geq \left| V_{XX} \right|$$

NUCLEAR QUADRUPOLE COUPLING CONSTANT:

$$C_Q = \frac{V_{ZZ}(eQ)}{h}, \quad Q - electric\ \text{quadrupole\ moment}$$

ASYMMETRY PARAMETER:

$$\eta_Q = \frac{V_{XX} - V_{YY}}{V_{ZZ}}; \quad 0 \leq \eta_Q \leq 1$$
ELECTRIC FIELD GRADIENT (EFG) TENSOR: SPHERICAL COORDINATES

SYMMETRIC, TRACELESS SECOND-RANK TENSOR:

5 components, \( R_{2,m} \), where \( m = -2, -1, 0, 1, 2 \)

PRINCIPAL AXIS SYSTEM WHERE TENSOR IS DIAGONAL:

\[
\left\langle V_{2,\pm 1}^{PAS} \right\rangle = 0; \quad \left| \left\langle V_{2,0}^{PAS} \right\rangle \right| > \left| \left\langle V_{2,\pm 2}^{PAS} \right\rangle \right|
\]

NUCLEAR QUADRUPOLE COUPLING CONSTANT:

\[
C_Q = 2 \frac{eQ}{\hbar} \left\langle V_{2,0}^{PAS} \right\rangle
\]

ASYMMETRY PARAMETER:

\[
\eta_Q C_Q = 2\sqrt{6} \frac{eQ}{\hbar} \left\langle V_{2,\pm 2}^{PAS} \right\rangle
\]
ELECTRIC FIELD GRADIENT (EFG) TENSOR: POINT CHARGE MODEL

EFG TENSOR IS DETERMINED BY THE COMBINED ELECTRONIC AND NUCLEAR WAVEFUNCTION, NO ANALYTICAL EXPRESSION IN THE GENERAL CASE

THE SIMPLEST APPROXIMATION: CLASSICAL POINT CHARGE MODEL

\[ \langle V_{2,k} \rangle = \sum_{i=1}^{n} \frac{Z_i e}{d_i^3} \sqrt{\frac{4\pi}{5}} Y_{2,k}(\theta_i, \phi_i) \]

ATOMS CONTRIBUTING TO THE EFG TENSOR ARE TREATED AS POINT CHARGES, THE RESULTING EFG TENSOR IS THE SUM WITH RESPECT TO ALL ATOMS

VERY CRUDE MODEL, WORKS QUANTITATIVELY ONLY IN SIMPLEST IONIC SYSTEMS, BUT YIELDS QUALITATIVE TRENDS AND GENERAL UNDERSTANDING OF THE SYMMETRY AND MAGNITUDE OF THE EXPECTED TENSOR
ELECTRIC FIELD GRADIENT (EFG) TENSOR: POINT CHARGE MODEL

\[
\langle V_{2,k} \rangle = \sum_{i=1}^{n} \frac{Z_i e}{d_i^3} \sqrt{\frac{4\pi}{5}} Y_{2,k}(\theta_i, \phi_i)
\]

**Linear, one-coordinate:**
\[0 = 0, \phi = 0\]
\[
\langle V_{2,0} \rangle = \frac{Ze}{d^3}; \quad \langle V_{2,\pm1} \rangle = 0; \quad \langle V_{2,\pm2} \rangle = 0
\]

**Linear, two-coordinate:**
\[0_1 = 0, \phi_1 = 0; \theta_2 = \pi, \phi_2 = 0\]
\[
\langle V_{2,0} \rangle = \frac{2Ze}{d^3}; \quad \langle V_{2,\pm1} \rangle = 0; \quad \langle V_{2,\pm2} \rangle = 0
\]

**Trigonal planar:**
\[0_1 = \pi/2, \phi_1 = 0; \theta_2 = \pi/2, \phi_2 = 2\pi/3; \theta_3 = \pi/2, \phi_3 = -2\pi/3\]
\[
\langle V_{2,0} \rangle = -\frac{3Ze}{2d^3}; \quad \langle V_{2,\pm1} \rangle = 0; \quad \langle V_{2,\pm2} \rangle = 0
\]

**Tetrahedral:**
\[0_1 = 0, \phi_1 = 0; \theta_2 = 2\pi/3, \phi_2 = 0; \theta_3 = 2\pi/3, \phi_3 = 2\pi/3; \theta_4 = 2\pi/3, \phi_4 = -2\pi/3\]
\[
\langle V_{2,0} \rangle = 0; \quad \langle V_{2,\pm1} \rangle = 0; \quad \langle V_{2,\pm2} \rangle = 0
\]
NMR OF QUADRUPOLES: ENERGY LEVELS

FIRST-ORDER CORRECTION:

\[ E^1_m = \langle m | H_Q | m \rangle \]

SECOND-ORDER CORRECTION:

\[ E^2_m = \frac{\langle m | H_Q | n \rangle \langle n | H_Q | m \rangle}{E_m - E_n} \]
NMR OF QUADRUPOLES: ENERGY LEVELS

FIRST-ORDER CORRECTION:

\[ E_m^1 = \frac{e^2 qQ}{4I(2I-1)} (I(I+1) - 3m^2) \left[ \frac{1}{2}(3\cos^2 \theta - 1) \right. \]

\[ - \eta_Q \cos 2\phi (\cos^2 \theta - 1) \]

SECOND-ORDER CORRECTION:

\[ E_m^{(2)} = - \left( \frac{e^2 qQ}{4I(2I-1)} \right)^2 \frac{m}{\omega_L} \{ - \frac{1}{5} (I(I+1) - 3m^2)(3 + \eta_Q^2) + \]

\[ \frac{1}{28} (8I(I+1) - 12m^2 - 3)((\eta_Q^2 - 3)(3\cos^2 \theta - 1) + 6\eta_Q \sin^2 \theta \cos 2\phi) \]

\[ + \frac{1}{8} (18I(I+1) - 34m^2 - 5) \left[ \frac{1}{140} (18 + \eta_Q^2)(35\cos^4 \theta - 30\cos^2 \theta + 3) \right. \]

\[ + \frac{3}{7} \eta_Q \sin^2 \theta (7\cos^2 \theta - 1) \cos 2\phi + \frac{1}{4} \eta_Q^2 \sin^4 \theta \cos 4\phi \} \]
ENERGY LEVELS IN THE PRESENCE OF QUADRUPOLAR INTERACTION

Single crystal

Central transition unaffected by first-order quadrupolar interaction

Central transition: $1/2 - -1/2$
Satellite transitions: $3/2 - 1/2$, $-3/2 - -1/2$
QUADRUPOLAR POWDER PATTERNS

SPIN-3/2 NUCLEUS; FIRST-ORDER QUADRUPOLAR INTERACTION
SATELLITE TRANSITIONS: FIRST ORDER BROADENING

\[ C_Q = \frac{e^2 q Q}{h}; \quad \nu_Q = \frac{3C_Q}{2I(2I-1)} \]

\[ \nu - \nu_L \]

\[ \nu_Q \]
SECOND-ORDER QUADRUPOLAR BROADENING: ENERGY LEVELS

\[ H_Z \quad H_{Q(1)} \quad H_{Q(2)} \]

\[ \nu_L \quad \nu_L \quad \nu_L + \nu_{Q(2)} \]
SECOND-ORDER QUADRUPOLAR BROADENING: CENTRAL TRANSITION POWDER LINESHAPES

Static

\[ \theta = 90^0 \]

\[ \theta = 0^0 \]

MAS

\[ \frac{3C_q^2}{64
\nu_L} \]

\[ \nu_L \]

\[ -\frac{C_q^2}{12
\nu_L} \]

MAS DOES NOT AVERAGE OUT THE 2ND ORDER QUADRUPOLAR BROADENING
SECOND-ORDER QUADRUPOLAR SHIFTS AND BROADENING

SECOND ORDER QUADRUPOLE SHIFTS FOR THE \((m, m-1)\) TRANSITION RELATIVE TO THE CHEMICAL SHIFT IN A POWDER SAMPLE:

\[
\Delta \nu_{m,m-1} = -\frac{3}{40} \left( \frac{C_Q^2}{\nu_L} \right) \frac{I(I+1) - 9m(m-1) - 3}{I^2(2I-1)^2} \left( 1 + \frac{\eta^2}{3} \right)
\]


SECOND ORDER QUADRUPOLE BROADENING OF SATELLITE TRANSITIONS RELATIVE TO THE CENTRAL TRANSITION WITH FAST MAS:

\[
\frac{\Delta (m,m-1)}{\Delta (\frac{1}{2}, -\frac{1}{2})} = \frac{6I(I+1) - 34m(m-1) - 13}{6I(I+1) - \frac{9}{2}}
\]

SATELLITE TRANSITIONS ARE BROADENED TO DIFFERENT EXTENTS
QUADRUPOLAR LINESHAPES IN THE PRESENCE OF CSA

$^{51}$V (spin 7/2)
$C_Q = 3.9$ MHz
$\eta_Q = 0.77$

$\delta_\sigma = -380$ ppm
$\eta_\sigma = 0.05$

MAS (17 kHz)
SECOND ORDER QUADRUPOLAR LINESHAPES IN THE PRESENCE OF CSA

\[ \kappa = 1 \]
\[ \delta_{33} \parallel V_{ZZ} \]
\[ \delta_{iso} = 54.7^\circ \]

\[ \kappa = -1 \]
\[ \delta_{11} \parallel V_{ZZ} \]
\[ \delta_{iso} = 54.7^\circ \]

(figure courtesy of Kris Ooms)
# Properties of Some Quadrupolar Metals

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Spin</th>
<th>( Q ), fm(^2 )</th>
<th>( \nu_L ), MHz (( B_0 = 14.1 , \text{T} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{23}\text{Na})</td>
<td>3/2</td>
<td>10.4</td>
<td>158.7072</td>
</tr>
<tr>
<td>(^{25}\text{Mg})</td>
<td>5/2</td>
<td>19.94</td>
<td>36.716</td>
</tr>
<tr>
<td>(^{39}\text{K})</td>
<td>3/2</td>
<td>5.85</td>
<td>28.000</td>
</tr>
<tr>
<td>(^{43}\text{Ca})</td>
<td>7/2</td>
<td>-4.08</td>
<td>40.369</td>
</tr>
<tr>
<td>(^{51}\text{V})</td>
<td>7/2</td>
<td>-5.2</td>
<td>157.728</td>
</tr>
<tr>
<td>(^{53}\text{Cr})</td>
<td>3/2</td>
<td>-15.0</td>
<td>33.912</td>
</tr>
<tr>
<td>(^{55}\text{Mn})</td>
<td>5/2</td>
<td>33.0</td>
<td>147.986</td>
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<tr>
<td>(^{59}\text{Co})</td>
<td>7/2</td>
<td>42.0</td>
<td>141.685</td>
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<td>(^{61}\text{Ni})</td>
<td>3/2</td>
<td>16.2</td>
<td>53.617</td>
</tr>
<tr>
<td>(^{63}\text{Cu})</td>
<td>3/2</td>
<td>-22.0</td>
<td>159.03</td>
</tr>
<tr>
<td>(^{67}\text{Zn})</td>
<td>5/2</td>
<td>15.0</td>
<td>37.525</td>
</tr>
<tr>
<td>(^{95}\text{Mo})</td>
<td>5/2</td>
<td>-2.2</td>
<td>39.089</td>
</tr>
</tbody>
</table>

NMR SPECTROSCOPY OF QUADRUPOLAR NUCLEI: CHALLENGES

I. Broad lines

II. MAS does not remove second-order broadenings

III. Poor sensitivity (low $\gamma$, low abundance, low concentration in biomolecules)
NMR SPECTROSCOPY OF QUADRUPOLAR NUCLEI: UNIVERSAL SOLUTIONS

1. ULTRAHIGH MAGNETIC FIELDS
2. ULTRAHIGH MAGNETIC FIELDS
3. ULTRAHIGH MAGNETIC FIELDS
NMR SPECTROSCOPY OF QUADRUPOLAR NUCLEI: FIELD STRENGTH DEPENDENCE

$^{139}$La ($I=7/2$) STATIC CENTRAL TRANSITION SSNMR SPECTRA OF LaCl$_3$

$C_Q = 15.55 \pm 0.05$ MHz

$\eta_Q = 0.0$

$\delta_{\text{iso}} = 305 \pm 5$ ppm

$\Omega = 50 \pm 10$ ppm

$\kappa = 1.0$

$\beta = 0$

NMR SPECTROSCOPY OF QUADRUPOLAR NUCLEI: AFFORDABLE SOLUTIONS
(as of January 2008)

1. REASONABLY HIGH MAGNETIC FIELDS
2. SPATIAL AVERAGING TECHNIQUES
3. SPIN AVERAGING TECHNIQUES
4. SENSITIVITY ENHANCEMENT TECHNIQUES
1. LET’S START WITH SIMPLE EXAMPLES
DETECTING SPECTRA OF QUADRUPOLAR NUCLEI: SMALL AND MODERATE $C_Q$

$^{51}V$ ($I=7/2$) SSNMR SPECTRA OF V-SUBSTITUTED POLYOXOTUNGSTATES:
single pulse, central and satellite transitions

$C_Q = 0.650 \text{ MHz}; \eta_Q = 0.65$
$\delta_\sigma = 200 \text{ ppm}; \eta_\sigma = 1.0$

$C_Q = 1.3 \text{ MHz}; \eta_Q = 0.8$
$\delta_\sigma = 466 \text{ ppm}; \eta_\sigma = 0.1$

$C_Q = 1.050 \text{ MHz}; \eta_Q = 0.95$
$\delta_\sigma = 418 \text{ ppm}; \eta_\sigma = 0.1$

$C_Q = 1.56 \text{ MHz}; \eta_Q = 0.35$
$\delta_\sigma = 456 \text{ ppm}; \eta_\sigma = 0.2$

DETECTING SPECTRA OF QUADRUPOLAR NUCLEI: SMALL AND MODERATE $C_Q$

$^{51}$V (I=7/2) SSNMR SPECTRA OF NH$_4$(VO)$_2$-dipicolinic acid derivative

$\delta_{iso} = -110 \pm 3$ ppm
$\Omega = 825 \pm 30$ ppm
$\kappa = 1.0 \pm 0.1$
$C_Q = 5.8 \pm 0.2$ MHz
$\eta_Q = 0.4 \pm 0.05$
$\alpha, \beta, \gamma = 0 \pm 30, 90 \pm 15, NA$

DETECTING SPECTRA OF QUADRUPOLAR NUCLEI: SMALL AND MODERATE $C_Q$

$^{55}\text{Mn (I=5/2)}$ SSNMR SPECTRA OF KMnO$_4$

$\Delta v_{\pm 5/2, \pm 3/2}$

$\Delta v_{\pm 3/2, \pm 1/2}$

$B_0 = 11.75$ T

MAS at 14 kHz

$\nu_L = 123.9 \text{ MHz}$

$C_Q = 1.56 \text{ MHz}$

$\eta_Q = 0.121$

K. J. Ooms, R. E. Wasylishen (unpublished, figure courtesy of Kris Ooms)
DETECTING SPECTRA OF QUADRUPOLAR NUCLEI: SMALL AND MODERATE $C_Q$

$^{55}\text{Mn (I=5/2) STATIC SPECTRA OF Mn}_2(\text{CO})_{10}$

$C_Q = 3.28$ MHz
$\eta_Q = 0.36$
$\delta_{\text{iso}} = -2310$ ppm
$\Omega = 105$ ppm
$\kappa = -0.95$
$\alpha,\beta,\gamma = 90, 90, 0 \degree$

K. J. Ooms, K. W. Feindel, V. V. Terskikh, R. Wasylchen, Inorg. Chem. 2006, 45, 8492-8499 (cover article; figure courtesy of Kris Ooms)
NMR SPECTROSCOPY OF QUADRUPOLAR METALS

2. LET’S MOVE ON
DETECTING SPECTRA OF QUADRUPOLAR NUCLEI: LARGE $C_Q$

$^{25}$Mg ($I=5/2$) SSNMR SPECTRA OF LABELED Mg(15-crown-5)(H$_2$O)$_2X_2$

Static
Central transition only
$B_0 = 17.6$ T

$X = I$

$X = Br$

$X = Cl$

K. J. Ooms, R. E. Wasylishen (unpublished, figure courtesy of Kris Ooms)
DETECTING SPECTRA OF QUADRUPOLAR NUCLEI: LARGE $C_Q$

$^{47}$Ti ($I=5/2$) STATIC ECHO CENTRAL TRANSITION SPECTRA OF LABELED Ti SOLIDS

$B_0 = 14.1$ T;

$C_Q = 12$ MHz (DFT/b3lyp)

TiO$_2$ (Rutile)
12 hours

Ti citrate
16 hours

Ti catecholate
24 hours

$^{47}$Ti Frequency (kHz)

K. Ooms, S. Bolte, R. Uppal, A. Valentine, T. Polenova (unpublished)
NMR SPECTROSCOPY OF QUADRUPOLAR METALS WITH LOW RECEPITIVITIY AND LARGE $C_Q$

3. NEED SENSITIVITY ENHANCEMENT
SENSITIVITY ENHANCEMENT IN QUADRUPOLES: QCPMG EXPERIMENT

QCPMG-MAS EXPERIMENT: $^{17}$O SPECTRA OF A PEROXO VANADIUM (V) COMPLEX

QCPMG-MAS (17 kHz), 122 k scans, experiment time: 17 hours

- No apodization; 
- SNR = 70

One pulse (17 kHz MAS), 315 k scans, experiment time: 26.2 hours

- 100 Hz em; 
- SNR = 17

N. Pooransingh-Margolis and T. Polenova (unpublished)
QCPMG-MAS EXPERIMENT: $^{17}$O SPECTRA OF A PEROXO VANADIUM (V) COMPLEX

$C_Q = 16$ MHz (DFT/ b3lyp)

QCPMG-MAS: 25 min
MAS at 17 kHz

1 pulse: 15 hours
MAS at 17 kHz

SIMPSON simulation
(DFT parameters)

$^{17}$O Frequency (kHz)

N. Pooransingh-Margolis and T. Polenova (unpublished)
QCPMG EXPERIMENT: $^{25}\text{Mg}$ SPECTRA

$^{25}\text{Mg} (I=5/2)$ QCPMG SPECTRA OF LABELED $\text{Mg}(15\text{-crown-5})(\text{H}_2\text{O})_2X_2$

$X = I$

$X = \text{Br}$

$X = \text{Cl}$

K. Ooms, R. Wasylishen (unpublished, figure courtesy of Kris Ooms)
SENSEITIVITY ENHANCEMENT IN QUADRUPOLARES: RAPT EXPERIMENT

SENSITIVITY ENHANCEMENT IN QUADRUPOLES: COMPARISON FOR $^{23}\text{Na}$

20:1 mixture of Na$_2$C$_2$O$_4$ and NaCl

Quadrupolar Echo
1.0

RAPT
1.4

$^{23}\text{Na}$ frequency (kHz)

N. Pooransingh-Margolis and T. Polenova
SENSITIVITY ENHANCEMENT IN QUADRUPOLES: MODIFIED QCPMG SEQUENCES

DFS-QCPMG


RAPT-QCPMG

DFS: Double Frequency Sweeps;
RAPT: Rotor Assisted Polarization Transfer
CP: Cross Polarization

CP-QCPMG

DECOPUPLE
SENSITIVITY ENHANCEMENT TECHNIQUES: COMPARISON FOR $^{87}\text{Rb}$ IN RbClO$_4$

R. Siegel, T. T. Nakashima, and R. E. Wasylishen, Chem. Phys. Lett., 2004, 388, 441-445; Figure courtesy of Kris Ooms
4. WHAT ABOUT RESOLUTION?
NMR SPECTROSCOPY OF QUADRUPOLAR METALS IN BIOLOGICAL SOLIDS

INTERESTING FACT:

IN METALLOPROTEINS, THERE IS TYPICALLY ONLY ONE OR VERY FEW METAL SITES PRESENT, AND RESOLUTION IS NOT SUCH AN ISSUE AS IN INORGANIC MATERIALS

THIS IS A LUXURY AND ALLOWS FOR RELATIVELY STRAIGHTFORWARD EXTRACTION OF NMR PARAMETERS FROM THE SPECTRA

OBVIOUSLY, THIS IS NOT THE CASE IN ION-BINDING PROTEINS, WHERE MULTIPLE SITES MAY BE PRESENT, SO ONE HAS TO WORRY ABOUT RESOLUTION
RESOLUTION ENHANCEMENT IN QUADRUPOLES

\[ H_{\text{diag}}^{(2)} = \frac{\omega_L}{\omega_0} \left[ a d_{0,0}^{(0)}(\beta) D_{0,0}^{(0)}(\Omega_{\text{PAS}}) \rho^\lambda_0,0 + a_2 d_{0,0}^{(2)}(\beta) \sum_{p=-2}^{2} D_{p,0}^{(2)}(\Omega_{\text{PAS}}) \rho^\lambda_{2,p} + a_4 d_{0,0}^{(4)} \sum_{p=-4}^{4} D_{p,0}^{(4)}(\Omega_{\text{PAS}}) \rho^\lambda_{4,p} \right] I_Z \]

Averaging of spherical harmonics \( Y^m_l \) of different ranks under point subgroups of the full rotation group SO(3): Rotation around a single axis is not sufficient for averaging rank 2 and 4 anisotropies.

**Symmetry**
- **Tetragonal (D\(_4\))**
  \( \ell = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \quad 8 \quad 9 \quad 10 \)
- **Tetrahedral (T)**
  \( \ell = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \quad 8 \quad 9 \quad 10 \)
- **Octahedral (O)**
  \( \ell = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \quad 8 \quad 9 \quad 10 \)
- **Icosahedral (I)**
  \( \ell = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \quad 8 \quad 9 \quad 10 \)

**Rotation (SO(3))**
\( \ell = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \quad 8 \quad 9 \quad 10 \)

**<Y\(_{lm}\)> = 0**

SPATIAL AVERAGING: DOUBLE ROTATION

β₀ = 54.74°
β₁ = 30.56°

²³Na MAS and DOR of Na₄P₂O₇

Magic Angle Spinning

Double Rotation

SPATIAL AVERAGING: QUADRUPOLAR LINESHAPES AT DIFFERENT ROTOR ANGLES

Rotor angle | Quadrupolar asymmetry parameter, $\eta_Q$
---|---
0.0 | 0.3 | 0.5 | 0.7 | 1.0
0° | ![Graph](image1.png)
30.56° | ![Graph](image2.png)
37.38° | ![Graph](image3.png)
54.74° | ![Graph](image4.png)
63.43° | ![Graph](image5.png)
70.12° | ![Graph](image6.png)
79.19° | ![Graph](image7.png)

SPATIAL AVERAGING: DYNAMIC ANGLE SPINNING

Refocusing of anisotropic frequencies with DAS echo

Pure phase absorption DAS spectra:

J. Magn. Reson. A 103, 72-83

\[ \pi/2 \rightarrow t_1 \rightarrow \pi/2 \rightarrow t_2 \rightarrow \pi/2 \rightarrow t_2 = kt_2 \]

Frequency (\( \beta_1 \))

Frequency (\( \beta_2 \))

Frequency (echo hops)

\[ ^{17}\text{O DAS Spectra of Crystobalite SiO}_2 \]

\[ 79.2^\circ \]

\[ 37.4^\circ \]

Echo in \( t_2 \) at \( kt_1 \)

Multiple pairs of rotor angles yield echoes

SPIN AVERAGING: THE MQMAS EXPERIMENT

Refocusing of anisotropic frequencies with MQMAS echo

<table>
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<tr>
<th>Spin</th>
<th>Transition (m → -m)</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/2</td>
<td>3QMAS</td>
<td>7/9</td>
</tr>
<tr>
<td>5/2</td>
<td>3QMAS</td>
<td>19/12</td>
</tr>
<tr>
<td></td>
<td>5QMAS</td>
<td>25/12</td>
</tr>
<tr>
<td>7/2</td>
<td>3QMAS</td>
<td>101/45</td>
</tr>
<tr>
<td></td>
<td>5QMAS</td>
<td>11/9</td>
</tr>
<tr>
<td></td>
<td>7QMAS</td>
<td>161/45</td>
</tr>
<tr>
<td>9/2</td>
<td>3QMAS</td>
<td>91/36</td>
</tr>
<tr>
<td></td>
<td>5QMAS</td>
<td>95/36</td>
</tr>
<tr>
<td></td>
<td>7QMAS</td>
<td>7/18</td>
</tr>
<tr>
<td></td>
<td>9QMAS</td>
<td>31/6</td>
</tr>
</tbody>
</table>

TRIPLE QUANTUM SPECTRUM IS A MIRROR IMAGE OF SQ SPECTRUM

MQMAS IN (CO)$_5$Mn-PbPh$_3$ at 21.1 T

After shearing transformation:

K. J. Ooms, K. W. Feindel, V. V. Terskikh, R. Wasylishen, Inorg. Chem. 2006, 45, 8492-8499 (cover article; figure courtesy of Kris Ooms)
Refocusing of anisotropic frequencies with STMAS echo
The satellite transition MAS spectrum is the mirror image of central transition MAS spectrum

<table>
<thead>
<tr>
<th>Spin</th>
<th>Transition</th>
<th>K</th>
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<tbody>
<tr>
<td>3/2</td>
<td>1st satellites</td>
<td>8/9</td>
</tr>
<tr>
<td>5/2</td>
<td>1st satellites</td>
<td>7/24</td>
</tr>
<tr>
<td></td>
<td>2nd satellites</td>
<td>11/6</td>
</tr>
<tr>
<td>7/2</td>
<td>1st satellites</td>
<td>28/45</td>
</tr>
<tr>
<td></td>
<td>2nd satellites</td>
<td>23/45</td>
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<tr>
<td></td>
<td>3rd satellites</td>
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<td>9/2</td>
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<tr>
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<td></td>
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<td>9/8</td>
</tr>
<tr>
<td></td>
<td>4th satellites</td>
<td>25/9</td>
</tr>
</tbody>
</table>

$^{23}\text{Na STMAS spectra of Na}_2\text{SO}_4/\text{Na}_2\text{C}_2\text{O}_4$ mixture

ADDITIONAL PRACTICAL CONSIDERATIONS: MAGIC ANGLE SETUP

Practical guide to SSNMR of half-integer quadrupoles: A. P. M. Kentgens (1997) Geoderma 80, 271-306

$^{23}$Na MAS of NaNO$_3$
$C_Q = 337$ kHz
ADDITIONAL PRACTICAL CONSIDERATIONS: SELECTIVE VS. NON-SELECTIVE PULSES

NON-SELECTIVE EXCITATION: \( \omega_{RF} \gg \omega_Q \)

Pulse response for the central transition: sinusoidal modulation of signal intensity as a function of the pulse length \( \tau \), with frequency \( \omega_{RF} \):

\[
S(\tau) = \left[ \frac{3(1+1/2)}{4l(l+1)} \right] \sin(\omega_{RF} \tau)
\]

SELECTIVE EXCITATION: \( \omega_{RF} \ll \omega_Q \)

Pulse response for the central transition:

\[
S(\tau) = \left[ \frac{3}{4l(l+1)} \right] \sin((1+1/2) \omega_{RF} \tau)
\]

INTERMEDIATE REGIME: \( \omega_{RF} \sim \omega_Q \)

Complex pulse response for the central transition; basis for nutation spectroscopy and numerical calculations to determine \( C_Q \)

Practical guide to SSNMR of half-integer quadrupoles: A. P. M. Kentgens (1997) Geoderma 80, 271-306
ADDITIONAL PRACTICAL CONSIDERATIONS:
NUTATION SPECTROSCOPY

Spin-7/2  
$\omega_{RF} = 44$ kHz  
no CSA

$\tau(\pi/2) = 5.68$ µs

Curves simulated in SIMPSON;
I. Determination of experimental NMR parameters from numerical simulations

Find unique solution to $C_Q$, $\eta_Q$, $\delta_\sigma$, $\eta_\sigma$, $\alpha$, $\beta$, $\gamma$

II. Theoretical prediction of NMR parameters from model molecular geometry

Classical electrostatic model (EFG)- only in simple ionic compounds
Quantum mechanical calculations (Density Functional Theory) (EFG, CSA)
DFT CALCULATIONS CAN EXPLAIN THE MAGNITUDE OF $C_Q$

$^{51}$V SPECTROSCOPY OF DIPICOLINIC ACID DERIVATIVES

Nominal coordination geometry: heptacoordinate, large $C_Q$ expected

Experimental $C_Q$: 3.43 MHz (small)

Electrostatic potential surface (ESP):

Reveals capped square planar charge distribution, consistent with small $C_Q$

DFT ANALYSIS OF MOLECULAR ORBITALS

51V SPECTROSCOPY OF DIPICOLINIC ACID DERIVATIVES

EXAMINE THE SYMMETRY OF MO’S TO

UNDERSTAND THE CONTRIBUTIONS TO

THE 51V MAGNETIC SHIELDING TENSOR

METALS NMR IN BIOLOGICAL SOLIDS: SELECTED EXAMPLES

INFORMATION CONTENT OF HALF-INTEGER QUADRUPOLES SSNMR

Presence of a particular metal site (sometimes indiscernible in X-ray structures)

Geometry of metal sites

Electronic structure of metal sites (i.e., interactions with surrounding ligands and/or solvent molecules)

Protonation states of ligands

Identification of polymorphs

Dynamics of metals and/or coordinated ligands

This information sheds light on chemical reactivity of metal sites in metallobiomolecules, often unavailable from other techniques
EXAMPLE 1: 

$^{67}$Zn SSNMR OF CARBONIC ANHYDRASE

Spectra are pH-independent contrary to the proposed catalytic mechanism; DFT calculations indicate hydroxide coordinated to Zn ($C_Q = 8-10$ MHz) and rule out water ligand ($C_Q = 25-35$ MHz, inconsistent with the SSNMR results)

EXAMPLE 1: 

\(^{67}\text{Zn}\) SSNMR OF CARBONIC ANHYDRASE

Revised mechanism proposed from \(^{67}\text{Zn}\) SSNMR results; accounts for the pH-independent spectra and coordinated hydroxide.

EXAMPLE 2:

$^{67}\text{Zn}$ SSNMR OF HUMAN NUCLEOTIDE EXCISION REPAIR PROTEIN XPA

$C_Q = 4.9$ MHz

$\eta_Q = 0.84$

$\delta_{iso} = 327.6$ ppm

(a) Experimental $^{67}\text{Zn}$ NMR spectrum of XPA-MBD at 9.4 T and 25 K, with 25 Hz conventional line broadening (LB),
(b) Data from part apodized with 5 Hz conventional and 1 kHz matched LB and zero filled to double the echo spacing,
and (c) simulation utilizing parameters described in the text with 25 Hz conventional and 1.5 kHz matched LB.
All spectra are conventionally zero filled to 512 kpoints.

EXAMPLE 4:

$^{23}$Na SSNMR OF Na$^+$ IN A DNA QUADRUPLEX

$^{23}$Na SSNMR spectra reveal three types of sodium and the presence of motions in the quadruplex; intriguing hypothesis that motions are axial rotations of the stacked G-quartet assembly.
EXAMPLE 5:
$^{59}$Co SSNMR OF VITAMIN B$_{12}$ POLYMORPHS

$^{59}$Co SSNMR spectra reveal presence of two polymorphs of vitamin B$_{12}$


“Wet”: $C_Q = 27.8 \pm 0.3$ MHz
“Dry”: $C_Q = 26.1 \pm 0.4$ MHz

EXAMPLE 6:

$^{59}$Co SSNMR OF PORPHYRIN COMPLEXES

$^{59}$Co SSNMR spectra exhibit large shielding and quadrupolar anisotropies; experimental anisotropies deviate for those expected for octahedral complexes; interaction is proposed between the metal orbitals and the aromatic ligand orbitals.

EXAMPLE 8: 

\[ ^{51}V \text{ SSNMR OF VANADIUM HALOPEROXIDASES} \]

\[ ^{51}V \text{ SSNMR spectra of vanadium chloroperoxidase- reveal unexpected protonation states of the vanadate cofactor} \]

Experiment \hspace{3cm} DFT calculations

Experiment

Simulation

\[ c_\Omega = 10.5 \pm 1.5 \text{ MHz} \]
\[ \eta_\Omega = 0.55 \pm 0.15 \]
\[ \delta_\nu = -520 \pm 13 \text{ ppm} \]
\[ \eta_\nu = 0.4 \pm 0.05 \]
\[ c_{\text{iso}} = -507.5 \text{ ppm} \]

SOME BOOKS AND GENERAL REVIEWS ON QUADRUPOLES


A. Abragam “Principles of Nuclear Magnetism” (1963) Oxford University Press, Oxford


M. E. Smith ME and E. R. H. van Eck “Recent advances in experimental solid state NMR methodology for half-integer spin quadrupolar nuclei” (1999) Prog. NMR Spectr. 34 (2): 159-20


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