Solid-State NMR of Metal Sites in Biological Systems

Tatyana Polenova
University of Delaware
Newark, DE

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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
<table>
<thead>
<tr>
<th>Periodic Table of Metals in Biology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naturally occurring metals</td>
</tr>
<tr>
<td>Metals used as probes or drugs</td>
</tr>
</tbody>
</table>
BIOLOGICAL FUNCTIONS OF METALS

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

<table>
<thead>
<tr>
<th>Element</th>
<th>Charge Carrier</th>
<th>Osmotic Balance</th>
<th>structure; hydrolase; isomerase</th>
<th>structure; trigger; charge carrier</th>
<th>nitrogen fixation; oxidase</th>
<th>essential trace element; possible involvement in glucose tolerance</th>
<th>nitrogen fixation; oxidase; oxo transfer</th>
<th>dehydrogenase</th>
<th>photosynthesis; oxidase; structure</th>
<th>oxidoxygen transport and storage; electron transfer; nitrogen fixation</th>
<th>oxidase; alkyl group transfer</th>
<th>hydrogenase; hydrolase</th>
<th>oxidase; dioxygen transport; electron transfer</th>
<th>structure; hydrolase</th>
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<tbody>
<tr>
<td>Na</td>
<td>Sodium</td>
<td>charge carrier; osmotic balance</td>
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<td>K</td>
<td>Potassium</td>
<td>charge carrier, osmotic balance</td>
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<td>Mg</td>
<td>Magnesium</td>
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<td>Ca</td>
<td>Calcium</td>
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<td>V</td>
<td>Vanadium</td>
<td>nitrogen fixation; oxidase</td>
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<td>Cr</td>
<td>Chromium</td>
<td>essential trace element; possible involvement in glucose tolerance</td>
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<td>Mo</td>
<td>Molybdenum</td>
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<td>W</td>
<td>Tungsten</td>
<td>dehydrogenase</td>
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<td>Manganese</td>
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<td>Fe</td>
<td>Iron</td>
<td>oxidoxygen transport and storage; electron transfer; nitrogen fixation</td>
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<td>Co</td>
<td>Cobalt</td>
<td>oxidase; alkyl group transfer</td>
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<tr>
<td>Ni</td>
<td>Nickel</td>
<td>hydrogenase; hydrolase</td>
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<td>Cu</td>
<td>Copper</td>
<td>oxidase; dioxygen transport; electron transfer</td>
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<td>Zn</td>
<td>Zinc</td>
<td>structure; hydrolase</td>
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### Nuclear Spins of Metals

<table>
<thead>
<tr>
<th>Spin = 1/2</th>
<th>Spin &gt; 1/2 (quadrupolar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H He Li Be Na Mg Al Si P S Cl Ar K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Sn Sb Te I Xe Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe Cs Ba Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn Fr Ra La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr</td>
<td></td>
</tr>
</tbody>
</table>
SPIN-1/2 METALS IN BIOLOGY

NATURALLY OCCURING SPIN-1/2 METALS

$^{57}$Fe-

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

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

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

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

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

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

$^{205}$Tl$^{3+}$-
- probe of 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

**QUADRUPOLAR METALS IN BIOLOGY**

**UNDERSTANDING GEOMETRIC AND ELECTRONIC STRUCTURE OF THE METAL CENTERS - IMPORTANT FOR UNDERSTANDING THE FUNCTION OF THE METALLOPROTEINS; SSNMR - DIRECT PROBE**
SSNMR SPECTROSCOPY OF QUADRUPOLAR NUCLEI IN BIOLOGICAL SYSTEMS

UNTIL RECENTLY HAS BEEN CONSIDERED IMPrACTICAL:

LOW SENSITIVITY
BROAD LINES
COMPLEX SYMMETRY OF QUADRUPOLAR INTERACTION
QUADRUPOLAR NUCLEI

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

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

- Nuclear charge density \( \rho(x) \)
- Electrostatic potential (all charges other than nucleus under consideration) \( V(x) \)

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:

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

- 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;
\( Q \sim r_n^2 \sim 10^{-24} \) cm\(^2\)

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

\[
\begin{align*}
    e &= 4.803242 \times 10^{-10} \text{ esu} = 4.803242 \times 10^{-10} \text{ g}^{1/2} \text{ cm}^{3/2} \text{s}^{-1} \\
    h &= 6.626176 \times 10^{-27} \text{ ergs} = 6.626176 \times 10^{-27} \text{ g} \text{cm}^2 \text{s}^{-1} \\
    a_o &= 0.52917706 \times 10^{-8} \text{ cm}
\end{align*}
\]

using these values ...

\[
\left[ \frac{e^2}{(a_o^3 h)} \right] \times 10^{-24} \text{ cm}^2 = 2.349649 \times 10^8 \text{ Hz}
\]
SOME TYPICAL VALUES OF $Q^x \times 10^{24}$ ARE:

<table>
<thead>
<tr>
<th>Element</th>
<th>$Q^x$ Value</th>
<th>P. Pyykkö Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{95}$Mo</td>
<td>$0.16 \text{ cm}^2$</td>
<td>$0.022 \text{ cm}^2$</td>
</tr>
<tr>
<td>$^{67}$Zn</td>
<td>$0.15 \text{ cm}^2$</td>
<td>$0.150 \text{ cm}^2$</td>
</tr>
<tr>
<td>$^{63}$Cu</td>
<td>$0.20 \pm 0.1 \text{ cm}^2$</td>
<td>$0.220 \text{ cm}^2$</td>
</tr>
<tr>
<td>$^{43}$Ca</td>
<td>$0.2 \pm 0.1 \text{ cm}^2$</td>
<td>$-0.0408 \text{ cm}^2$ (limited accuracy)</td>
</tr>
<tr>
<td>$^{37}$Cl</td>
<td>$-0.0646 \text{ cm}^2$</td>
<td>$-0.0678 \text{ cm}^2$</td>
</tr>
<tr>
<td>$^{35}$Cl</td>
<td>$-0.082 \text{ cm}^2$</td>
<td>$-0.082 \text{ cm}^2$</td>
</tr>
<tr>
<td>$^{33}$S</td>
<td>$-0.064 \text{ cm}^2$</td>
<td>$-0.0678 \text{ cm}^2$</td>
</tr>
<tr>
<td>$^{27}$Al</td>
<td>$0.149 \text{ cm}^2$</td>
<td>$0.1403 \text{ cm}^2$</td>
</tr>
<tr>
<td>$^{25}$Mg</td>
<td>$0.22 \text{ cm}^2$</td>
<td>$0.1994 \text{ cm}^2$</td>
</tr>
<tr>
<td>$^{23}$Na</td>
<td>$0.12 \text{ cm}^2$</td>
<td>$0.1074 \text{ cm}^2$</td>
</tr>
<tr>
<td>$^{17}$O</td>
<td>$-0.026 \text{ cm}^2$</td>
<td>$-0.026 \text{ cm}^2$</td>
</tr>
<tr>
<td>$^{14}$N</td>
<td>$0.016 \text{ cm}^2$</td>
<td>$0.016 \text{ cm}^2$</td>
</tr>
<tr>
<td>$^{9}$Be</td>
<td>$0.052 \text{ cm}^2$</td>
<td>$0.052 \text{ cm}^2$</td>
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<tr>
<td>$^{7}$Li</td>
<td>$-0.045 \text{ cm}^2$</td>
<td>$-0.0401 \text{ cm}^2$</td>
</tr>
<tr>
<td>$^{2}$H</td>
<td>$0.00273 \text{ cm}^2$</td>
<td>$0.002860 \text{ cm}^2$</td>
</tr>
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</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:

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

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

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

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

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

CARTESIAN COORDINATES, LABORATORY FRAME:

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

\[
\hat{H}_Q = \frac{e^2 qQ}{4I(2I-1)\hbar} \{ \frac{1}{2} (3\cos^2 \theta - 1)(3\hat{I}_Z^2 - \hat{I}^2) \\
+ \frac{3}{2} \sin \theta \cos \theta \{ \hat{I}_Z (\hat{I}_+ + \hat{I}_-) + (\hat{I}_+ + \hat{I}_-) \hat{I}_Z \} + \frac{3}{4} \sin^2 \theta \{ \hat{I}_+^2 + \hat{I}_-^2 \} \}
\]

\[
+ \eta_q \frac{e^2 qQ}{4I(2I-1)\hbar} \{ \frac{1}{2} \cos 2\phi (1 - \cos^2 \theta) (3\hat{I}_Z^2 - \hat{I}^2) \\
+ (\cos^2 \theta + 1)(\hat{I}_+^2 + \hat{I}_-^2) \\
+ \frac{1}{2} \sin \theta [(\cos \theta \cos 2\phi - i \sin 2\phi) (\hat{I}_+ \hat{I}_Z + \hat{I}_Z \hat{I}_+) \\
+ (\cos \theta \cos 2\phi + i \sin 2\phi) (\hat{I}_- \hat{I}_Z + \hat{I}_Z \hat{I}_-) ] \\
+ (i/4) \sin 2\phi \cos \theta (\hat{I}_+^2 - \hat{I}_-^2)
\}
\]
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:

\[
\hat{H}_Q^{(1)} = \frac{e^2 q Q}{4 I (2I - 1)} \sqrt{6} V_{20} \hat{T}_{20}
\]

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

\[
\hat{H}_Q^{(2)} = -\left( \frac{e^2 q Q}{4 I (2I - 1) \hbar} \right)^2 \frac{1}{\omega_L} \frac{2}{5} \times \left\{ \begin{array}{l}
-3 \sqrt{10} \hat{T}_{30} + \hat{T}_{10} (3 - 4I(I + 1)) \right] V_{00} \\
+ \left[ -12 \sqrt{10} \hat{T}_{30} - \hat{T}_{10} (3 - 4I(I + 1)) \right] V_{20} \\
+ \left[ -34 \sqrt{10} \hat{T}_{30} + 3 \hat{T}_{10} (3 - 4I(I + 1)) \right] V_{40}
\end{array} \right\}
\]
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:**

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

**Nuclear Quadrupole Coupling Constant:**

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

**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:

\[
\begin{align*}
\langle V^{PAS}_{2,\pm 1} \rangle &= 0; \\
\langle V^{PAS}_{2,0} \rangle &> \langle V^{PAS}_{2,\pm 2} \rangle
\end{align*}
\]

NUCLEAR QUADRUPOLE COUPLING CONSTANT:

\[
C_Q = 2 \frac{eQ}{h} \langle V^{PAS}_{2,0} \rangle
\]

ASYMMETRY PARAMETER:

\[
\eta_Q C_Q = 2 \sqrt{6} \frac{eQ}{h} \langle V^{PAS}_{2,\pm 2} \rangle
\]
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:**
\( \theta = 0, \phi = 0 \)

\[ \langle V_{2,0} \rangle = \frac{Ze}{d^3}; \quad \langle V_{2,\pm1} \rangle = 0; \quad \langle V_{2,\pm2} \rangle = 0 \]

**Linear, two-coordinate:**
\( \theta_1 = 0, \phi_1 = 0; \theta_2 = \pi, \phi_2 = 0 \)

\[ \langle V_{2,0} \rangle = \frac{2Ze}{d^3}; \quad \langle V_{2,\pm1} \rangle = 0; \quad \langle V_{2,\pm2} \rangle = 0 \]

**Trigonal planar:**
\( \theta_1 = \pi/2, \phi_1 = 0; \theta_2 = \pi/2, \phi_2 = 2\pi/3; \theta_3 = \pi/2, \phi_3 = -2\pi/3 \)

\[ \langle V_{2,0} \rangle = -\frac{3Ze}{2d^3}; \quad \langle V_{2,\pm1} \rangle = 0; \quad \langle V_{2,\pm2} \rangle = 0 \]

**Tetrahedral:**
\( \theta_1 = 0, \phi_1 = 0; \theta_2 = 2\pi/3, \phi_2 = 0; \theta_3 = 2\pi/3, \phi_3 = 2\pi/3; \theta_4 = 2\pi/3, \phi_4 = -2\pi/3 \)

\[ \langle V_{2,0} \rangle = 0; \quad \langle V_{2,\pm1} \rangle = 0; \quad \langle V_{2,\pm2} \rangle = 0 \]
NMR OF QUADRUPOLES: ENERGY LEVELS

FIRST-ORDER CORRECTION:

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

SECOND-ORDER CORRECTION:

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

FIRST-ORDER CORRECTION:

\[ E_m^1 = \frac{e^2 q Q}{4I(2I-1)}(I(I+1) - 3m^2)[\frac{1}{2}(3\cos^2 \theta - 1) \]
\[ -\eta_Q \cos 2\phi(\cos^2 \theta - 1)] \]

SECOND-ORDER CORRECTION:

\[ E_m^{(2)} = -\left(\frac{e^2 q Q}{4I(2I-1)}\right)^2 \frac{m}{\omega_L} \{ -\frac{1}{5}(I(I+1) - 3m^2)(3 + \eta_Q^2) + \]
\[ \frac{1}{28}(8I(I+1) - 12m^2 - 3)((\eta_Q^2 - 3)(3\cos^2 \theta - 1) + 6\eta_Q \sin^2 \theta \cos 2\phi) \]
\[ + \frac{1}{8}(18I(I+1) - 34m^2 - 5)[\frac{1}{140}(18 + \eta_Q^2)(35\cos^4 \theta - 30\cos^2 \theta + 3) \]
\[ + \frac{3}{7}\eta_Q \sin^2 \theta(7\cos^2 \theta - 1)\cos 2\phi + \frac{1}{4}\eta_Q^2 \sin^4 \theta \cos 4\phi] \} \]
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

\[ \frac{1}{2} \leftrightarrow -\frac{1}{2} \]

\[ \frac{-3}{2} \leftrightarrow -\frac{1}{2} \]

\[ \frac{3}{2} \leftrightarrow \frac{1}{2} \]

\[ +\frac{C_Q}{2}, +\frac{C_Q}{4}, -\frac{C_Q}{4}, -\frac{C_Q}{2} \]

\[ \nu, \text{Hz} \]
SATELLITE TRANSITIONS: FIRST ORDER BROADENING

\[ C_Q = \frac{e^2 q Q}{h}; \quad \nu_Q = \frac{3C_Q}{2I(2I-1)} \]
SECOND-ORDER QUADRUPOLAR BROADENING: ENERGY LEVELS
SECOND-ORDER QUADRUPOLAR BROADENING: CENTRAL TRANSITION POWDER LINESHAPES

\[ \frac{3C^2_Q}{64v_L} \quad \frac{C^2_Q}{12v_L} \]

\( \theta = 90^\circ \)
\( \theta = 0^\circ \)
\( \theta = 41.8^\circ \)

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:

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


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

\[
\Delta \left( m, m-1 \right) = 6I(I+1) - 34m(m-1) - 13
\]

\[
\Delta \left( \frac{1}{2}, -\frac{1}{2} \right) = 6I(I+1) - \frac{9}{2}
\]

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

$^{51}\text{V}$ (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

\[ \kappa = 1 \]
\[ \delta_{33} \parallel \text{to} \ V_{ZZ} \]
\[ \delta_{iso} = 54.7^\circ \]
\[ 90^\circ \]
\[ 0^\circ \]

\[ \kappa = -1 \]
\[ \delta_{11} \parallel \text{to} \ V_{ZZ} \]
\[ \delta_{iso} = 54.7^\circ \]
\[ 90^\circ \]
\[ 0^\circ \]

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

$\eta_Q = 0.0$

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

- $C_Q = 0.650$ MHz; $\eta_Q = 0.65$
  $\delta_\sigma = 200$ ppm; $\eta_\sigma = 1.0$

- $C_Q = 1.3$ MHz; $\eta_Q = 0.8$
  $\delta_\sigma = 466$ ppm; $\eta_\sigma = 0.1$

- $C_Q = 1.050$ MHz; $\eta_Q = 0.95$
  $\delta_\sigma = 418$ ppm; $\eta_\sigma = 0.1$

- $C_Q = 1.56$ MHz; $\eta_Q = 0.35$
  $\delta_\sigma = 456$ ppm; $\eta_\sigma = 0.2$

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

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

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

DETECTING SPECTRA OF QUADRUPOLAR NUCLEI: SMALL AND MODERATE C_Q

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

$\nu_L = 123.9$ MHz
$C_Q = 1.56$ MHz
$\eta_Q = 0.121$

$B_0 = 11.75$ T
MAS at 14 kHz

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$_2$(CO)$_{10}$

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

K. J. Ooms, K. W. Feindel, V. V. Terskikh, R. Wasylischen, Inorg. Chem. 2006, 45, 8492-8499 (cover article; figure courtesy of Kris Ooms)
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

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; TiO$_2$ (Rutile) 12 hours

$C_Q = 12$ MHz (DFT/ b3lyp) 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 RECEPTIVITY 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 Mg(15-crown-5)(H$_2$O)$_2X_2$

$X = I$

$X = \text{Br}$

$X = \text{Cl}$

K. Ooms, R. Wasylileshen (unpublished, figure courtesy of Kris Ooms)
SENSITIVITY ENHANCEMENT IN QUADRUPOLES: RAPT EXPERIMENT

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

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

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

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

DFS-QCPMG


RAPT-QCPMG


CP-QCPMG

DFS: Double Frequency Sweeps;
RAPT: Rotor Assisted Polarization Transfer
CP: Cross Polarization
SENSITIVITY ENHANCEMENT TECHNIQUES: COMPARISON FOR $^{87}$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

\[ H_{\text{diag}}^{(2)} = \frac{\omega_L}{\omega_0} [a d_{0,0}^{(0)}(\beta) D_{0,0}^{(0)}(\Omega_{\text{PAS}}) \rho_0^\lambda + a_2 d_{2,0}^{(2)}(\beta) \sum_{p=-2}^{2} D_{p,0}^{(2)}(\Omega_{\text{PAS}}) \rho_{2,p}^\lambda + a_4 d_{0,0}^{(4)} \sum_{p=-4}^{4} D_{p,0}^{(4)}(\Omega_{\text{PAS}}) \rho_{4,p}^\lambda ] I_Z \]

Averaging of spherical harmonics \( Y_{lm}^n \) 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** (D4)
  \( \ell = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6 \ 7 \ 8 \ 9 \ 10 \)

- **Tetrahedral** (T)
  \( \ell = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6 \ 7 \ 8 \ 9 \ 10 \)

- **Octahedral** (O)
  \( \ell = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6 \ 7 \ 8 \ 9 \ 10 \)

- **Icosahedral** (I)
  \( \ell = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6 \ 7 \ 8 \ 9 \ 10 \)  
  simultaneous averaging of rank-2 and 4 anisotropies

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

SPATIAL AVERAGING: DOUBLE ROTATION

$\beta_0 = 54.74^0$
$\beta_1 = 30.56^0$

$^{23}\text{Na} \text{ MAS and DOR of Na}_4\text{P}_2\text{O}_7$

Magic Angle Spinning

Double Rotation

SPATIAL AVERAGING: QUADRUPOLAR LINESHAPES AT DIFFERENT ROTOR ANGLES

<table>
<thead>
<tr>
<th>Rotor angle</th>
<th>Quadrupolar asymmetry parameter, $\eta_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>0°</td>
<td></td>
</tr>
<tr>
<td>30.56°</td>
<td></td>
</tr>
<tr>
<td>37.38°</td>
<td></td>
</tr>
<tr>
<td>54.74°</td>
<td></td>
</tr>
<tr>
<td>63.43°</td>
<td></td>
</tr>
<tr>
<td>70.12°</td>
<td></td>
</tr>
<tr>
<td>79.19°</td>
<td></td>
</tr>
</tbody>
</table>

SPATIAL AVERAGING: DYNAMIC ANGLE SPINNING

Refocusing of anisotropic frequencies with DAS echo

Pure phase absorption DAS spectra:

$^{17}$O DAS Spectra of Crystobalite SiO$_2$

Multiple pairs of rotor angles yield echoes

SPIN AVERAGING: THE MQMAS EXPERIMENT

Refocusing of anisotropic frequencies with MQMAS echo

<table>
<thead>
<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>

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

After shearing transformation:

K. J. Ooms, K. W. Feindel, V. V. Terskikh, R. Wasylshen, Inorg. Chem. 2006, 45, 8492-8499 (cover article; figure courtesy of Kris Ooms)
SPATIAL AVERAGING: STMAS EXPERIMENT

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>
</tr>
</thead>
<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>
</tr>
<tr>
<td></td>
<td>3rd satellites</td>
<td>12/5</td>
</tr>
<tr>
<td>9/2</td>
<td>1st satellites</td>
<td>55/72</td>
</tr>
<tr>
<td></td>
<td>2nd satellites</td>
<td>1/18</td>
</tr>
<tr>
<td></td>
<td>3rd satellites</td>
<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
$\text{Na}_2\text{SO}_4/\text{Na}_2\text{C}_2\text{O}_4$ mixture

Practical guide to SSNMR of half-integer quadrupoles: A. P. M. Kentgens (1997) Geoderma 80, 271-306
**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 \( \omega_{RF} \):

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

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

Pulse response for the central transition:

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

**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

Curves simulated in SIMPSON;
RELATING NMR OBSERVABLES TO MOLECULAR STRUCTURE

NMR Spectrum $\leftrightarrow$ NMR Parameters $\leftrightarrow$ Local geometry

$\uparrow$

Chemical structure (reactivity)

I. Calculation of experimental NMR parameters

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

II. Theoretical prediction of fine structure constants from 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 $C_Q$

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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
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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University of Delaware:
Current Colleagues:
Stephanie Bolte
Yun Han
Kristin Nuzzio
Kris Ooms
Sivakumar Paramasivam
Shangjin Sun
Lex Vega
Jun Yang
Past Group Members:
Wenlin Huang
Dabeiba (Daby) Marulanda
William Perea
Neela Pooransingh-Margolis
Mark Schopfer
Tarjani Thaker
Chris Willis

Collaborators on metals NMR
University of Amsterdam:
Ron Wever
Rokus Renirie
Zulfiqar Hasan
Colorado State University:
Debbie C. Crans
Bharat Baruah
Jason Smee
University of Hamburg:
Dieter Rehder
Hunter College:
Lynn Francesconi
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