Applications of NMR Calculations

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Experimental methods

MAS (I = 1/2)

MAS (I > 1/2)

C_Q, η_Q, δ_iso

MQMAS/STMAS

δ_iso, δ_Q
Why calculate NMR parameters?

- Spectral assignment
- Spectral interpretation
- Confirmation of experimental NMR parameters
- Additional information (anisotropy, tensor orientation, etc.,)
- Spectral prediction
- Assessment of experimental feasibility
- Flexible way to study the dependence of NMR parameters upon structure
- Testing of structural models for materials with unknown structure
- More complex properties of solids
  
  Disorder
  Dynamics
CASTEP NMR calculations

Chemical shielding \[ \delta_{\text{iso}}, \Delta_{\text{CSA}}, \eta_{\text{CS}}, (\alpha, \beta, \gamma) \]

J coupling \[ J_{\text{iso}}, (J_{\text{aniso}}) \]

Quadrupolar coupling \[ C_Q, \eta_Q, (\alpha', \beta', \gamma') \]

CASTEP parameters

Ultrasoft pseudopotentials
GGA (PBE)
k-point spacing \(~0.04 \text{ Å}^{-1}\)
Energy cut off \(~60 \text{ Ry} (~816 \text{ eV})\)

AMD Opteron cluster (2-8 cores) with Infinipath interconnects

Extended frameworks
Typically 12-250 atoms in unit cell
Considerations

How accurate are our calculations?

*How accurate do we need them to be - what do we want to know?*

*How accurate is the experimental data?*

Do we need to optimise the structure?

*Structures are of varying quality*

*\(^1\)H typically misplaced*

*Do we vary the unit cell size?*

*Do we retain the symmetry?*

What about dynamics?

*Diffraction and NMR are sensitive to different length scales and timescales*

*Measurements often performed at different temperatures*

*Significant motion on a range of timescales in the solid state*
Referencing

• Experiments are referenced to an externally to a reference sample on the same spectrometer on the same day

• How do we reference our calculations?

\[ \delta_{iso} = \sigma_{ref} - \sigma_{iso} \]

• 1. Use a simple reference structure (e.g., SiO₂, Al₂O₃, Y₂O₃) to match experiment

• 2. Reference within a calculation if many shifts are present

• 3. Reference calculated from a consideration of many different materials
1. $^{17}$O NMR of high-pressure minerals

Experiment


Experiment and Calculation

The deep Earth

Aims and objectives

Characterise anhydrous minerals
Study known hydrated minerals as models for water incorporation
Position and mechanism of hydration in nominally anhydrous minerals
Experimental challenges

- High-pressure synthesis in a multi-anvil apparatus often produces only small (few mg) amount of material, limiting sensitivity

  Samples kept as pellets rather than powders

- $^{17}\text{O}$, $^{29}\text{Si}$ and $^{25}\text{Mg}$ all have low natural abundance (0.037%, 4.7%, 10%)

  Isotopic enrichment ($^{17}\text{O} (\£500-\£2000 / g), ^{25}\text{Mg} (\£10000 / g)$)

- $^{17}\text{O}$ and $^{25}\text{Mg}$ are quadrupolar ($I = 5/2$), and spectra are additionally broadened by the quadrupolar interaction

  High-resolution approaches (e.g., MQMAS)
  More sensitive (but more technically demanding) experiments (e.g., STMAS)
  Spectral prediction and interpretation with DFT
**Orthoenstatite**

*MgSiO$_3$ (150 mg, 75% $^{17}$O)*  
9.4 T (MQMAS, 54 hours)

| $\delta_{iso}$ | $|C_0|$ | $\eta_0$ |
|----------------|---------|----------|
| 41 ppm         | 2.9 MHz | 0.19     |
| 46 ppm         | 2.8 MHz | 0.29     |
| 52 ppm         | 2.9 MHz | 0.53     |
| 56 ppm         | 2.9 MHz | 0.29     |
| 60 ppm         | 4.2 MHz | 0.78     |
| 70 ppm         | 4.8 MHz | 0.80     |
Orthoenstatite

MgSiO$_3$ (150 mg, 75% $^{17}$O)
9.4 T (MQMAS, 54 hours)

9.4 T MAS

9.4 T MQMAS

Si-O-Mg$_x$
($C_Q$ 2-3.5 MHz)

Si-O-Si
($C_Q$ 4-5.5 MHz)
Orthoenstatite

CASTEP

80 atoms in unit cell (16 units of MgSiO₃)
GGA/PBE
Ultrasoft pseudopotentials
60 Ry cut-off energy
0.04 Å⁻¹ k-point spacing
NMR calculation: 12 processors for 4 days

Referenced to forsterite (α-Mg₂SiO₄)

| O1/O21  | δ_{iso} | |C_Q| | η_Q |
|---------|---------|-----|-----|-----|
|        | 41 ppm  | 2.9 MHz | 0.19 |
|        | 41 ppm  | 3.06 MHz | 0.21 |
| O2/O22 |         |       |     |     |
|        | 46 ppm  | 2.8 MHz | 0.29 |
|        | 47 ppm  | 2.96 MHz | 0.29 |
| O3/O21 |         |       |     |     |
|        | 52 ppm  | 2.9 MHz | 0.53 |
|        | 53 ppm  | 3.03 MHz | 0.62 |
| O4/O22 |         |       |     |     |
|        | 56 ppm  | 2.9 MHz | 0.29 |
|        | 57 ppm  | 3.03 MHz | 0.35 |
| O5/O31 |         |       |     |     |
|        | 60 ppm  | 4.2 MHz | 0.78 |
|        | 62 ppm  | 4.35 MHz | 0.78 |
| O6/O32 |         |       |     |     |
|        | 70 ppm  | 4.8 MHz | 0.80 |
|        | 73 ppm  | 5.0 MHz | 0.81 |
Spectral assignment

- General linear relationship of $^{17}\text{O }\delta_{\text{iso}}$ to Si-O bond length
- Dependence upon environment type
MgSiO$_3$ (~4 mg, 75% $^{17}$O)
9.4 T (STMAS, 84 hours)

Only 1 O observed in 1D and 2D spectra?

<table>
<thead>
<tr>
<th>Pop$^n$</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta_{iso}$ (ppm)</td>
</tr>
<tr>
<td>O1</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>2</td>
</tr>
<tr>
<td>Si</td>
<td>1</td>
</tr>
</tbody>
</table>
Perovskite

CASTEP

20 atoms in unit cell (4 units of MgSiO$_3$)

GGA/PBE
Ultrasoft pseudopotentials
60 Ry cut-off energy
0.04 Å$^{-1}$ k-point spacing

NMR calculation: 12 processors for 4 hours

Referenced to forsterite ($\alpha$-Mg$_2$SiO$_4$)
Accuracy of data

- Good agreement between experimental and calculated values
- Use for spectral prediction, assignment and interpretation

\[ y = 1.09x - 2.46 \quad R^2 = 0.984 \]

\[ y = 1.016x + 0.12 \quad R^2 = 0.978 \]

\[ y = 1.027x + 3.22 \quad R^2 = 0.9992 \]
2. NMR of microporous materials

Experiment

Experiment and Calculation
Microporous materials

- Open framework solids with regular systems of channels and cavities of molecular dimensions
- High surface area
- Typical pore dimensions 4-8 Å

- Industrial uses intimately linked to structure
  - Selective sorption
  - Cation exchange materials
  - Catalysis
  - Gas storage

- Three main types
  - Zeolites: aluminosilicates and Cs, Na, etc., cations
  - AlPOs: aluminophosphates
  - MOF: Co, Zn, Sc, Mg, Mn, etc., and organic linkers
Aluminophosphates

- New family of porous solids discovered in 1982, composed of alternating AlO$_4$ and PO$_4$ tetrahedra
- Synthesised using a structure directing agent or template (typically an amine base)
- Incorporation of OH$^-$/F$^-$ into framework to charge balance and water in the pores
- Doping with Si, Ga, Mg, Mn etc., changes the catalytic properties

AIPO-14
- First synthesized in 1982 although initial confusion over the structure as the material can be prepared from a number of templates
- As-synthesized forms contain framework OH, increasing the Al coordination number
AIPO-14: NMR

$^{31}$P MAS

$^{27}$Al MAS

$^{27}$Al MQMAS

AIPO-14 ipa

AIPO-14 calcined
# AIPO-14 calcined: calculations

## Experimental

<table>
<thead>
<tr>
<th></th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>C$_Q$ / MHz</th>
<th>$\eta_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al1</td>
<td>4.3</td>
<td>4.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Al2</td>
<td>4.3</td>
<td>3.4</td>
<td>0.2</td>
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<tr>
<td>Al3</td>
<td>3.8</td>
<td>2.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Al4</td>
<td>4.5</td>
<td>4.9</td>
<td>0.3</td>
</tr>
<tr>
<td>P1</td>
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<td></td>
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</tr>
<tr>
<td>P2</td>
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<td></td>
</tr>
<tr>
<td>P3</td>
<td>-31.5</td>
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</tr>
<tr>
<td>P4</td>
<td>-26.7</td>
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</table>

## Calculated

<table>
<thead>
<tr>
<th></th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>C$_Q$ / MHz</th>
<th>$\eta_Q$</th>
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<tbody>
<tr>
<td>Al1</td>
<td>38.5</td>
<td>5.30</td>
<td>0.08</td>
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<tr>
<td>Al2</td>
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<td>0.26</td>
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<tr>
<td>Al3</td>
<td>40.3</td>
<td>5.55</td>
<td>0.74</td>
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<td>Al4</td>
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</tr>
<tr>
<td>P4</td>
<td>-35.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### CASTEP

- 48 atoms in unit cell (8 AlPO$_4$)
- GGA/PBE
- Ultrasoft pseudopotentials
- 60 Ry cut-off energy
- 0.04 Å$^{-1}$ k-point spacing
- NMR calculation: 12 processors for 2 days
- Referenced to berlinite (AIPO$_4$)

Forces up to 4 eV / Å
**AIPO-14 calcined: calculations**

<table>
<thead>
<tr>
<th></th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$C_Q$ / MHz</th>
<th>$\eta_Q$</th>
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</thead>
<tbody>
<tr>
<td><strong>Experimental</strong></td>
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<td>Al1</td>
<td>43</td>
<td>4.0</td>
<td>0.8</td>
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<td>Al2</td>
<td>43</td>
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<td>0.2</td>
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<td>Al3</td>
<td>38</td>
<td>2.5</td>
<td>0.6</td>
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<tr>
<td>Al4</td>
<td>45</td>
<td>4.9</td>
<td>0.3</td>
</tr>
<tr>
<td>P1</td>
<td>–21.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>–26.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>–31.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P4</td>
<td>–26.7</td>
<td></td>
<td></td>
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<tr>
<td><strong>Calculated optimized (fixed cell)</strong></td>
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<tr>
<td>Al1</td>
<td>46.5</td>
<td>3.72</td>
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<td>4.5</td>
<td>0.27</td>
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<tr>
<td><strong>Calculated optimized</strong></td>
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<tr>
<td>Al1</td>
<td>43.2</td>
<td>4.54</td>
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<td>Al2</td>
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<td>P1</td>
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<tr>
<td>P4</td>
<td>–25.3</td>
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<td></td>
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</tbody>
</table>

Forces up to 0.02 eV / Å

Forces up to 0.015 eV / Å
AIPO-14 calcined: calculations

- How much have we changed the structure?
AIPO-14 calcined: calculations

- How much have we changed the structure?

![Graphs showing Al-O and P-O bond number comparisons with different markers for initial, atoms, and atoms + cell.](image URLs)
## AlPO-14 ipa: calculations

|         | Experimental | Calculated
<table>
<thead>
<tr>
<th></th>
<th></th>
<th>¹H only optimized</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>( \delta_{\text{iso}} ) (ppm)</td>
<td>( C_Q / \text{MHz} )</td>
</tr>
<tr>
<td>Al1</td>
<td>2.7</td>
<td>5.6</td>
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<tr>
<td>Al2</td>
<td>4.4</td>
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<td>-1</td>
<td>2.6</td>
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<tr>
<td>P1</td>
<td>-20.6</td>
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<td>P2</td>
<td>-5.8</td>
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<tr>
<td>P3</td>
<td>-24.3</td>
<td></td>
</tr>
<tr>
<td>P4</td>
<td>-20.1</td>
<td></td>
</tr>
</tbody>
</table>

- Additional template, water and hydroxyl groups in structure
- Agreement not as good but assignment possible and in agreement with experiment

Forces up to 2.4 eV / Å
Forces up to 0.02 eV / Å
AlPO-14 ipa: motion

- Evidence for dynamics from temperature dependent broadening in STMAS experiment
- Not present in the calcined material
AIPO-14 ipa: calculations

- Much smaller differences in structure than for the calcined material
- NMR parameters very sensitive even to these small changes
AlPO-15

Experimental

<table>
<thead>
<tr>
<th></th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>$C_Q$ / MHz</th>
<th>$\eta_Q$</th>
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</thead>
<tbody>
<tr>
<td>Al1</td>
<td>2.5</td>
<td>3.1</td>
<td>0.8</td>
</tr>
<tr>
<td>Al2</td>
<td>-5.0</td>
<td>8.3</td>
<td>0.8</td>
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<td>P1</td>
<td>-14.3</td>
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<tr>
<td>P2</td>
<td>-20.5</td>
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</table>

Calculated ($^1$H opt)

<table>
<thead>
<tr>
<th></th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>$C_Q$ / MHz</th>
<th>$\eta_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al1</td>
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<td>-3.2</td>
<td>0.73</td>
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<tr>
<td>Al2</td>
<td>-4.2</td>
<td>8.3</td>
<td>0.87</td>
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</tr>
<tr>
<td>P2</td>
<td>-19.0</td>
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<td></td>
</tr>
</tbody>
</table>

Structure from synchrotron charge density measurements

CASTEP

100 atoms in unit cell (8 AlPO$_4$ 4 (NH$_4$)$_4^+$ 4 OH$^-$ 8 H$_2$O)

GGA/PBE

Ultrasoft pseudopotentials
60 Ry cut-off energy
0.04 Å$^{-1}$ k-point spacing

NMR calculation: 12 processors for 3 days

Referenced to berlinite (AlPO$_4$)

Forces up to 0.1 eV / Å
3. $^{89}$Y NMR of pyrochlore ceramics

Experiment

Experiment and Calculation
Nuclear waste remediation

- Pyrochlores proposed as host phases for the encapsulation of Ac/Ln nuclear waste

- Over last 50 years 1400 metric tons of Pu produced, and the amount is increasing at 70-80 tons per year

- Long lived isotopes $^{239}$Pu (24,100 y), $^{237}$Np (2.1 million y) and $^{233}$U (160,000 y)

- Good candidate for synthetic wasteforms
  
  High crystal chemical flexibility ( > 500 compositions)
  Tolerant of defects/substitutions
  Variable oxidation states
  High waste loading
  Low leach rates
  Resistant to radiation damage
  Natural analogues
Pyrochlores

- Pyrochlore: $A_2B_2O_7$
- Ordered superstructure of fluorite with 1/8 O removed in an ordered manner (Fd–3m)
- 2 cation sites $^\text{VIII}_A$ 2+, 3+ $^\text{VI}_B$ 5+, 4+
- $Y_2(Sn,Ti)O_7$ solid solution

$^{89}$Y NMR
- Spin quantum number $I = 1/2$
- 100% natural abundance
- Large chemical shift range
- Low gyromagnetic ratio (1/16th of $^1$H)
- Long $T_1$ relaxation times (~1000 s)
- $^{89}$Y background in rotor
Pyrochlores: $^{89}$Y NMR
Pyrochlores: analysis

- Assume that Y is found only on the VIII A site
  
  What would the chemical shift be if Y was on the B site?

- Assume that the chemical shift determined only/primarily by number of Sn/Ti
  
  How does the shift change as a NNN Sn/Ti is substituted?

- Assume the spatial arrangement has negligible effect on the chemical shift
  
  Is there a shift difference between the different arrangements?

- Assume that any longer range effects are small/negligible
  
  For the same NNN arrangement how different can the chemical shift be?
Pyrochlores: calculations

CASTEP

GGA/PBE
Ultrasoft pseudopotentials
50 Ry cut-off energy
0.04 Å⁻¹ k-point spacing

\( \text{Y}_2\text{O}_3, \text{Y}_2\text{Ti}_2\text{O}_7, \text{Y}_2\text{Sn}_2\text{O}_7, \text{YAlO}_3, \text{Y}_2\text{O}_2\text{S}, \text{YF}_3, \alpha-\text{Y}_2\text{Si}_2\text{O}_7 \) and \( \beta-\text{Y}_2\text{Si}_2\text{O}_7 \)

Referenced to \( \text{Y}_2\text{O}_3 \)

For pyrochlores 88 atoms in unit cell

NMR calculation: 16 processors for 10 hours

\[ \begin{align*}
\text{Experiment } \delta_{\text{iso}} & \quad \text{Calculated } \delta_{\text{iso}} \\
-100 & \quad 0 \\
0 & \quad 100 \\
100 & \quad 200 \\
200 & \quad 300
\end{align*} \]

134 – 184 ppm

326 ppm

2-55 ppm

221 ppm

\( \text{\textsuperscript{VIII}}\text{Y A site} \)

\( \text{\textsuperscript{VI}}\text{Y B site} \)
Pyrochlores: approach

Y$_2$Sn$_2$O$_7$/Y$_2$Ti$_2$O$_7$

“embed” cluster into unit cell

gallery optimisation / NMR
Pyrochlores: results

\[ \text{Y}_2\text{Ti}_2\text{O}_7 \]

\[ \text{Y}_2\text{Sn}_2\text{O}_7 \]

\[ \delta_{\text{iso}} \text{(ppm)} \]

\[ n_{\text{Sn NNN}} \]

\[ n_{\text{Sn NNN}} \]
Pyrochlores: results

- Deviation of 6-10° away from linear for O-Y-O bond angle
- Lengthening of a number of the Y-O bonds
Pyrochlores: results

• Why do these distortions occur?
  - *Lattice fixed to be* $Y_2Sn_2O_7$ *or* $Y_2Ti_2O_7$
  - *Local substitution of different size cations*
  - *Substitutions reproduced periodically - need to try supercells*

• Do the anomalous shifts have any impact upon the experimental analysis?
  - *Over 500 $^{89}Y$ shifts calculated using both* $Y_2Sn_2O_7$ *and* $Y_2Ti_2O_7$
  - *Anomalous shifts present in <3% of cases*

\[ P(n \text{ Sn NNN}) = \Omega p^6 (1 - p)^{6-n} \]

Random distribution of Sn and Ti on the pyrochlore B sites
4. Disorder and dynamics in humites

Experiment


Experiment and Calculation

Humite minerals

- Proposed as possible models for defect H incorporation into mantle silicates (e.g., Mg$_2$SiO$_4$), but synthesized at relatively low pressure

- Humite minerals have the general formula
  \[ n\text{Mg}_2\text{SiO}_4\cdot\text{Mg(OH)}_2 \]

- where \( n = 1 \) (norbergite), 2 (chondrodite), 3 (humite) and 4 (clinohumite)
Humite minerals: $^{17}$O NMR

- Forsterite
- Chondrodite
- Clinohumite

9.4 T MAS

9.4 T MQMAS

9.4 T STMAS
Humite minerals: approach

- Two $^1$H sites H1 and H2 which are 50% occupied by diffraction
- Two nearby H1 cannot be occupied simultaneously

CASTEP

38/66 atoms in unit cell

GGA/PBE
Ultrasoft pseudopotentials
50 Ry cut-off energy
0.05 Å$^{-1}$ k-point spacing

NMR calculation: 16 processors for up to 1 day

Referenced to forsterite
Humite minerals: calculations

9.4 T MQMAS

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Calculated Sum</th>
<th>Calculated Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chondrodite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clinohumite</td>
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</tbody>
</table>

δ₁ (ppm)
Humite minerals: calculations

- $^1$H dynamics cause a change in the magnitude/orientation of nearby $^{17}$O quadrupolar tensors.
- This will cause a change in the quadrupolar splitting for any one crystallite, $\Delta \nu^J$.

$$
\nu_1 = \frac{\nu_0^{\text{PAS}}}{2} \left(3 \cos^2 \beta_1 - 1 + \eta_q \sin^2 \beta_1 \cos 2\gamma_1\right)
$$

$$
\nu_2 = \frac{\nu_0^{\text{PAS}}}{2} \left(3 \cos^2 \beta_2 - 1 + \eta_q' \sin^2 \beta_2 \cos 2\gamma_2\right)
$$

- If the rate constant is comparable to $\Delta \nu^J$ this will cause motional broadening in any experiment affected by the first-order quadrupolar interaction.
- Broadening of STMAS not MQMAS spectra.
Humite minerals: calculations

- Good agreement when $\log_{10}(k / s^{-1}) \sim 5.5$
- Estimate rate constant for H1 - H2 interchange $k \sim 3.2 \times 10^5 \text{ s}^{-1}$
Humite minerals: $^2$H NMR

$^2$H NMR of clinohumite (9.4 T)

$^2$H quadrupolar echo
$\tau = 20 \mu s$
9.4 T

<table>
<thead>
<tr>
<th></th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$\Delta_{CSA}$ (ppm)</th>
<th>$\eta_{CS}$</th>
<th>$C_Q$ / kHz</th>
<th>$\eta_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H 1</td>
<td>2.1</td>
<td>11.85</td>
<td>0.110</td>
<td>276.3</td>
<td>0.027</td>
</tr>
<tr>
<td>H 2</td>
<td>1.4</td>
<td>9.66</td>
<td>0.162</td>
<td>272.3</td>
<td>0.048</td>
</tr>
</tbody>
</table>

- Plot of $\ln(\Delta \nu_{1/2})$ against $1/T$ gives activation energy of $\sim 26$ kJ mol$^{-1}$
Humite minerals: substitutions

- In nature, humite minerals can have substantial amounts of F or Ti incorporated.
- By diffraction, only a single $^1\text{H}$ species is observed in substituted humites.
- Hydrogen bonding restricts $^1\text{H}$ to the H1 site.

$^2\text{H}$ MAS
Humite minerals: $^{19}\text{F} \text{NMR}$

$^{19}\text{F} \text{MAS (30 kHz) NMR of clinohumite (14.1 T)}$

CASTEP

Up to 128 atoms in unit cell

GGA/PBE

Ultrasoft pseudopotentials
50 Ry cut-off energy
0.04 Å$^{-1}$ k-point spacing

NMR calculation: 16 processors for up to 3 days

Referenced to set of simple inorganic fluorides
Humite minerals: $^{19}$F NMR

$^{19}$F refocussed INADEQUATE MAS (30 kHz) spectrum of clinohumite (14.1 T)

Use two-dimensional correlation experiments to attempt to support assignment
Indicates a through-bond interaction

- Is the “INADEQUATE” transfer via the J coupling?
Humite minerals: $^{19}$F NMR

- Is the “INADEQUATE” transfer via the J coupling?

“Through space” J couplings known in the literature

$\sim$170 Hz interaction observed in solution between two $^{19}$F in phenanthrene derivatives which are 5 bonds apart
(Mallory et al. J. Am. Chem. Soc. 122, 4108 (2000))

17 Hz interaction observed between two $^{19}$F in reductase complex which are 398 bonds apart

Involves direct overlap of the F lone pairs - ab initio calculations
(Bryce and Wasylishen, J. Molec. Struc. 602-603, 463 (2002))
Humite minerals: $^{19}$F NMR

$^{19}$F J-resolved experiment (14.1 T, 30 kHz)

Preliminary CASTEP calculations using a $3 \times 1 \times 1$ supercell produced values of 12.5 and 3.6 Hz.

Note large J anisotropy predicted (~225 and 41 Hz).
Why calculate NMR parameters?

- Spectral assignment
- Spectral interpretation
- Confirmation of experimental NMR parameters
- Additional information (anisotropy, tensor orientation, etc.)
- Spectral prediction
- Assessment of experimental feasibility
- Flexible way to study the dependence of NMR parameters upon structure
- Testing of structural models for materials with unknown structure
- More complex properties of solids
  - Disorder
  - Dynamics