Tutorials – Enjoy!

Exercise 1: Chlorine solid state NMR experiments.

Al–O–P clusters, involving Cl\(^-\) anions as counter-ions have been studied by solid state Cl NMR (Figure 1) (see Azaïs et al., Solid State NMR, 2003).

♦ Which isotope was chosen? Why? (see the data below).

♦ What is the strongest interaction expected at each Cl site? Interpret the lineshape shown in Figure 1.

♦ The spectra were recorded on a «600 MHz» spectrometer (the highest field available at that time...). Why? What is the Cl frequency for the chosen isotope?

Exercise 2: CSA and local symmetry.

The Figure 2 shows the \(^{199}\text{Hg}\) MAS spectra of two mercurated compounds. In both cases, the MAS frequency \(\nu_{\text{rot}}\) is the same.

♦ Assign the spectra! But justify the answer...

♦ In which case is it possible to evaluate the CSA parameters, \(\Delta_{\text{CSA}}\) and \(\eta_{\text{CSA}}\)?

Exercise 3: How to draw a 1\(^{st}\) order Q lineshape?

Consider an I nuclear spin (I=n/2 with n > 1).

♦ How many single quantum transitions do you expect?

♦ Let us take the case of \(^{27}\text{Al}\): I = 5/2. Draw the lineshape corresponding to a first-order quadrupolar interaction.

♦ Interpret the static \(^{27}\text{Al}\) spectrum of KAl(SO\(_4\))\(_2\).12H\(_2\)O (Figure 3) (see Man et al., Solid State NMR, 1995).

<table>
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<th></th>
<th>NA (%)</th>
<th>(\gamma) ((10^7 \text{ rad T}^{-1} \text{ s}^{-1}))</th>
<th>(10^2\text{BQ/m}^2)</th>
<th>(D^0)</th>
<th>(\nu) /MHz</th>
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</table>

Figure 1

Figure 2

Figure 3
Exercise 4: MAS and high power decoupling.

The Figure 4 shows four $^{31}$P spectra related to Zn phosphonate containing protons (see Massiot et al., Chem. Mater., 1997). Two of them where obtained under static conditions; two of them under MAS conditions. Two of them where obtained with high power $^1$H decoupling and two of them without.

$*$Who is who?

![Figure 4](image)

Exercise 5: $^{13}$C CP MAS spectra of glycine H$_2$N-CH$_2$-COOH.

Various $^{13}$C CP MAS spectra of glycine are presented in Figure 5 (at 75 MHz) (see Laupretre, Ecole de RMN des Houches, 1997).

$*$ Spectrum (a) ($t_{CP} = 1$ ms): assign the peaks. Evaluate $\nu_{rot}$.

$*$ Spectrum (b): $t_{CP}$ has been modified. Do we have $t_{CP} \gg$ or $\ll 1$ ms?

$*$ Spectrum (c): the same as (a)... but a parameter has been modified. Which one?

![Figure 5](image)
Exercise 6: High field $^{27}$Al MAS NMR spectra.

The Figure 6 shows four $^{27}$Al MAS spectra of $9(\text{Al}_2\text{O}_3)$-$2(\text{B}_2\text{O}_3)$ (see Massiot, Gan, J. Am. Chem. Soc., 2003).

♦ The rotation frequency $\nu_{\text{rot}}$ is fixed. A single experimental parameter has been modified. Which one?
♦ Explain precisely the differences between the spectra.

Exercise 7: $^{27}$Al studies of Al-O-P clusters.

The Figure 7 shows the $^{27}$Al MAS spectrum of a molecular Al-O-P cluster (see Azaïs et al, Eur. J. Inorg. Chem., 2002).

♦ Try to assign the lines.
♦ Is the quadrupolar interaction a good indicator for the characterization of $^{27}$Al sites in these compounds?
Exercise 8: Highly resolved spectra for quadrupolar nuclei.

The Figure 8 presents $^{27}$Al spectra related to Sillimanite, Mullite and to a glass (see Massiot in «High Magnetic Fields: Applications in Condensed Matter Physics and Spectroscopy», 2002). One unique angle of reorientation was involved in the experiments.

♦ What is the experiment used? Why? Can you think at other sequences leading potentially to the same results?
♦ Why are the correlation signals broader in the case of mullite and of the glass?

Exercise 9: 2D $^{29}$Si correlation experiment in glasses.

The Figure 9 shows two $^{29}$Si spectra of a glass: 2 Na$_2$O.3 SiO$_2$. One spectrum is obtained at $\theta = 90^\circ$ and the other one under MAS conditions (see Florian, Grandinetti, J. Non Cryst. Solids).

♦ Who is who? Why are the lines rather broad even at «infinite» $\nu_{\text{rot}}$?

The Figure 10 presents a 2D correlation involving an evolution at $\theta = 90^\circ$ and the acquisition of the signal at $\theta = 54.7^\circ$.

♦ Draw the sequence. Why is it an «anisotropic/isotropic» correlation?
♦ Interpret precisely the 2D data.
Experimental session – 300 & 400 AVANCE spectrometers

keywords:

- tuning and matching a probe
- static and MAS spectra
- the CP MAS experiment
- the Hartmann-Hahn condition

$^1$H MAS NMR

$^{27}$Al MAS NMR

silsesquioxanes $(R-SiO_{1.5})_8$

$R =$ methyl, vinyl...

space group: $R3$

two sites: $Si_1$ and $Si_2$

space group: $I4$

one site: $Al_1$, $P_1$, $Cl_1$