

# Tutorials – Enjoy !

## Exercise 1: Chlorine solid state NMR experiments.

Al-O-P clusters, involving Cl<sup>-</sup> 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 ?

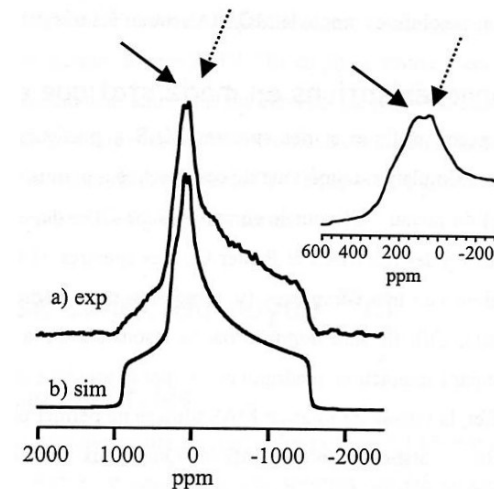


Figure 1

## Exercise 2: CSA and local symmetry.

The Figure 2 shows the <sup>199</sup>Hg MAS spectra of two mercurated compounds. In *both cases*, the MAS frequency  $\nu_{rot}$  is the same.

- ◆ Assign the spectra ! But justify the answer...
- ◆ In which case is it possible to evaluate the CSA parameters,  $\Delta_{CSA}$  and  $\eta_{CSA}$  ?

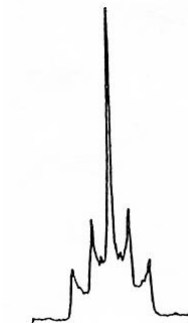


Figure 3

## Exercise 3: How to draw a 1<sup>st</sup> 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 <sup>27</sup>Al:  $I = 5/2$ . Draw the lineshape corresponding to a first-order quadrupolar interaction.
- ◆ Interpret the static <sup>27</sup>Al spectrum of KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O (Figure 3) (see Man et al., Solid State NMR, 1995).

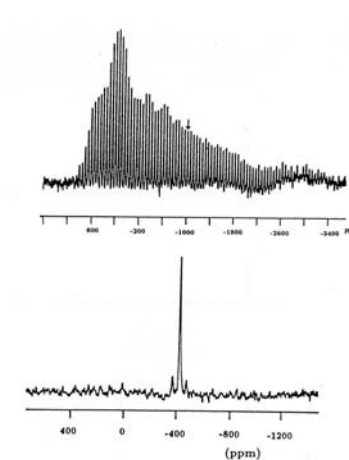
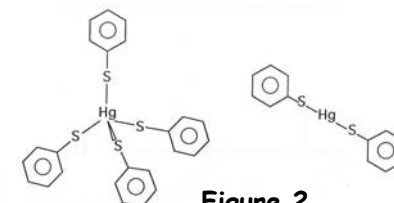


Figure 2

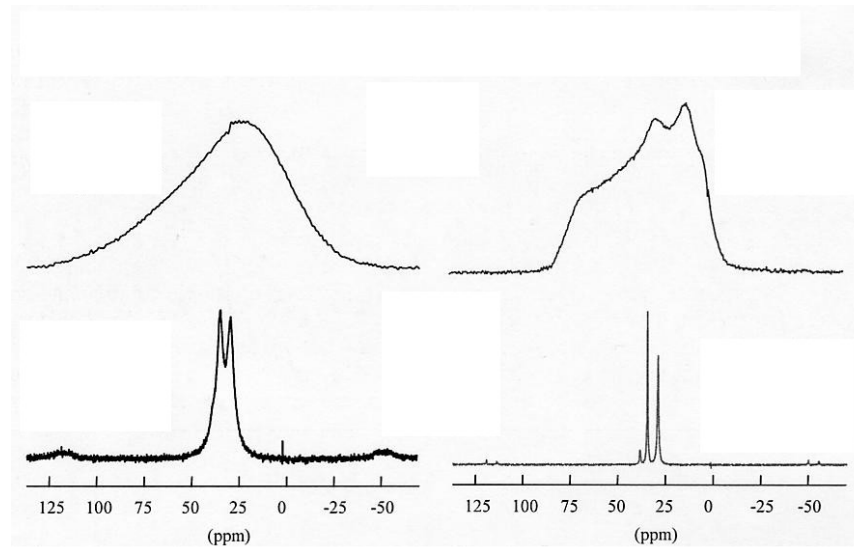


	NA (%)	$\gamma$ ( $10^7$ rad T <sup>-1</sup> s <sup>-1</sup> )	$10^{28}Q/m^2$	$D^p$	$\nu$ /MHz
<sup>35</sup> Cl	75.53	2.62	-0.1	0.00356	9.81
<sup>37</sup> Cl	24.47	2.18	-0.079	0.00066	8.17
<sup>1</sup> H	99.98	26.75		1	100

### Exercise 4: MAS and high power decoupling.

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

◆ *Who is who?*

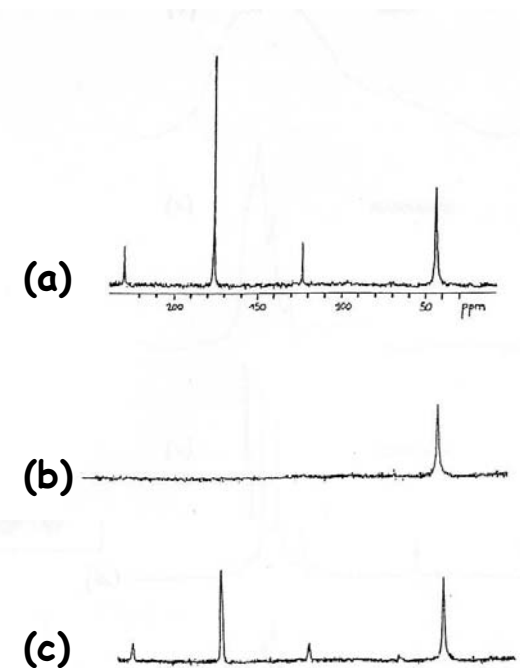


**Figure 4**

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

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

- ◆ Spectrum **(a)** ( $t_{\text{CP}} = 1$  ms): assign the peaks. Evaluate  $\nu_{\text{rot}}$ .
- ◆ Spectrum **(b)**:  $t_{\text{CP}}$  has been modified. Do we have  $t_{\text{CP}} \gg$  or  $\ll 1$  ms?
- ◆ Spectrum **(c)**: the same as **(a)**... but a parameter has been modified. Which one?



**Figure 5**

### Exercise 6: High field $^{27}\text{Al}$ MAS NMR spectra.

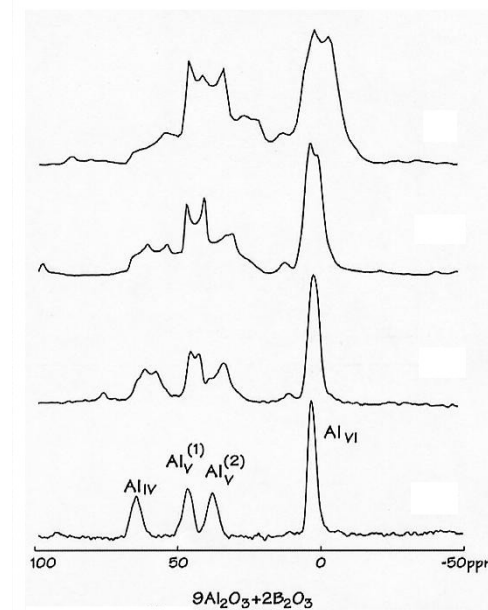
The **Figure 6** shows four  $^{27}\text{Al}$  MAS spectra of  $9(\text{Al}_2\text{O}_3)-2(\text{B}_2\text{O}_3)$  (see Massiot, Gan, J. Am. Chem. Soc., 2003).

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

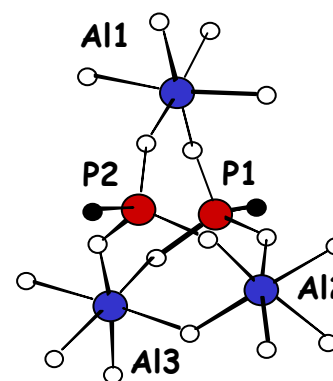
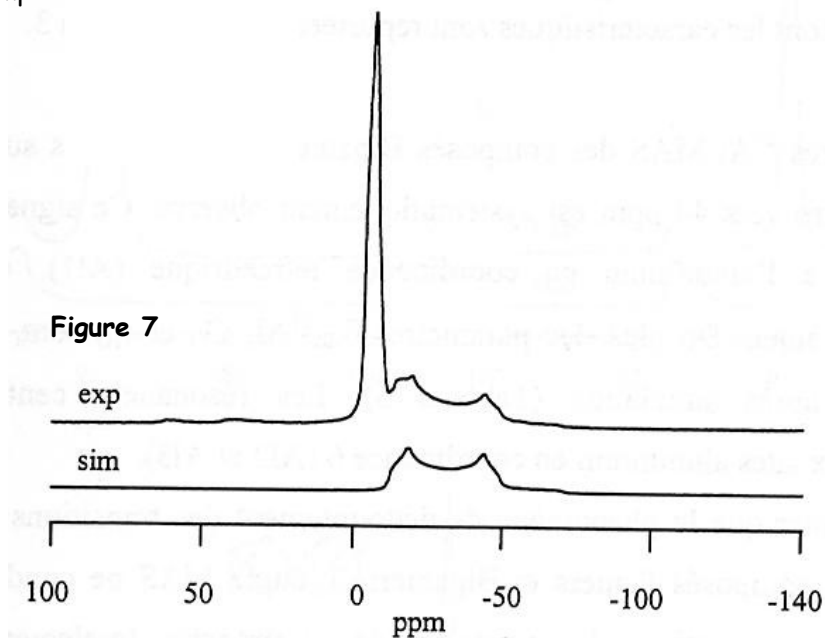
### Exercise 7: $^{27}\text{Al}$ studies of Al-O-P clusters.

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

- ◆ Try to assign the lines.
- ◆ Is the quadrupolar interaction a good indicator for the characterization of  $^{27}\text{Al}$  sites in these compounds?



**Figure 6**



### Exercise 8: Highly resolved spectra for quadrupolar nuclei.

The **Figure 8** presents  $^{27}\text{Al}$  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?

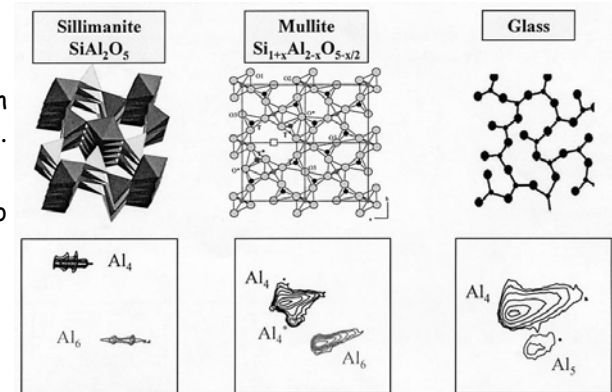


Figure 8

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

The **Figure 9** shows two  $^{29}\text{Si}$  spectra of a glass:  $2\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ . 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»  $v_{\text{rot}}$ ?

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.

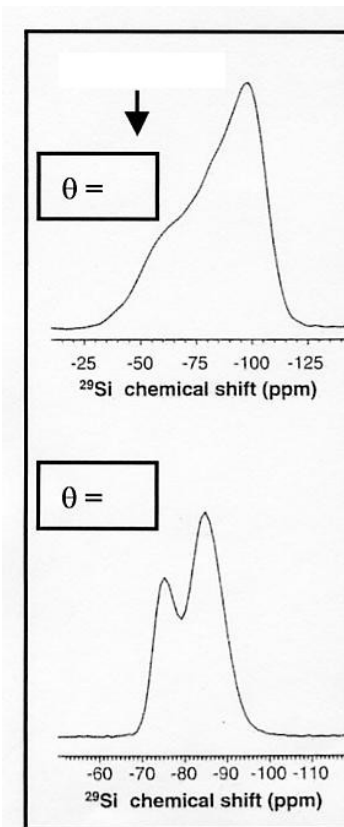


Figure 9

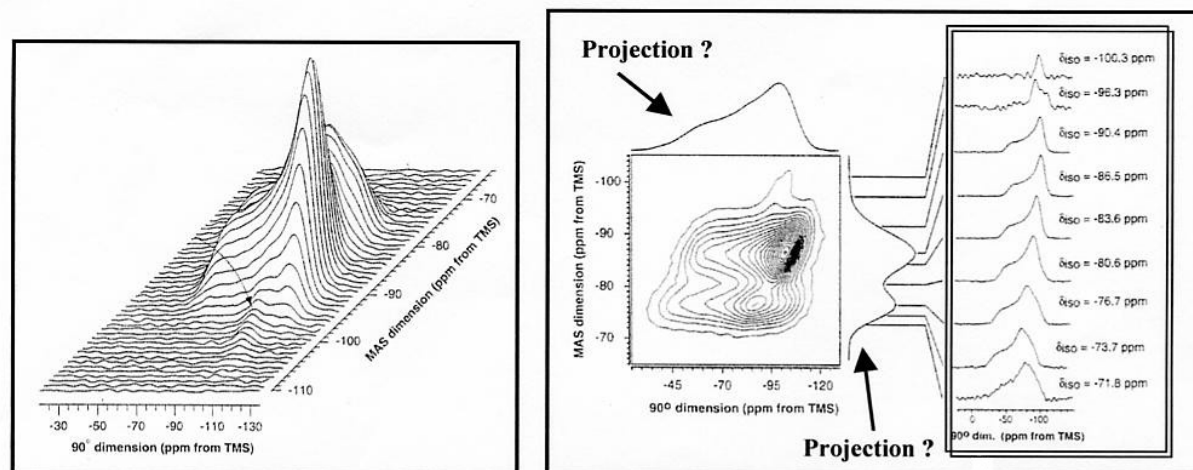


Figure 10

# Experimental session - 300 & 400 AVANCE spectrometers



## keywords:

tuning and matching a probe

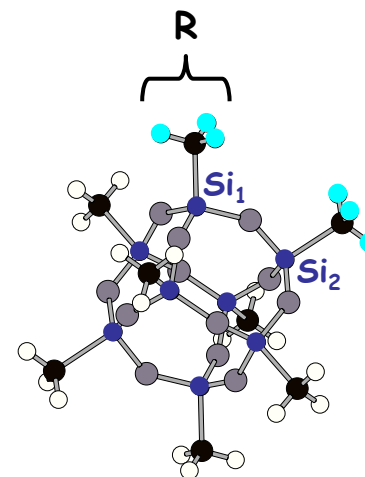
static and MAS spectra

the CP MAS experiment

the Hartmann-Hahn condition

$^1\text{H}$  MAS NMR

$^{27}\text{Al}$  MAS NMR

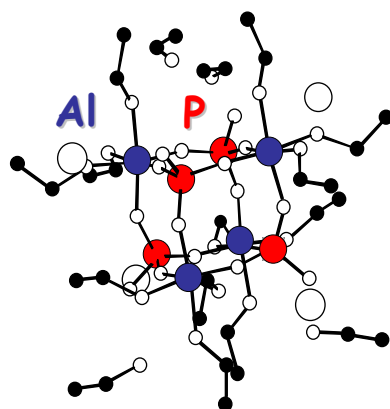


silsesquioxanes  $(\text{R-SiO}_{1.5})_8$

R = methyl, vinyl...

space group:  $\bar{R}3$

two sites:  $\text{Si}_1$  and  $\text{Si}_2$



Al-O-P cubane clusters

space group:  $\bar{I}4$

one site:  $\text{Al}_1, \text{P}_1, \text{Cl}_1$