2008 Winter School on Biomolecular Solid-State NMR
Problem Set on SSNMR of Metals
Tatyana Polenova

1. Using the point charge model, write the general expressions for the components of the EFG tensor for the central atom X in a XY_n molecule for the following molecular geometries:

a) in-plane bent (H_2O geometry), assume arbitrary bond angle;
b) trigonal bipyramidal;
c) octahedral

2. The quadrupolar coupling constants C_Q of the three nonequivalent vanadium sites in $Cs_2V_4O_{11}$ were determined experimentally, and are 1.9, 2.6, and 2.4 .MHz. From the X-ray crystal structure it is known that two sites are distorted tetrahedral pyramids, and the third one is with octahedral coordination. Can you attribute the experimental C_Q to specific coordination environments? Explain.

3. It was found that the length of the ^{51}V $\pi/2$ excitation pulse in neat $VOCl_3$ liquid is 6 μs. What are the lengths of the ^{51}V pulses required to excite i) the central transition and ii) all the satellite transitions in a solid K_3VO_4? Assume the other experimental parameters are the same.

4. Write the Hamiltonian and sketch an energy level diagram for a spin- 7/2 nucleus. Describe the effects of the first- and second- order quadrupolar interaction on the energy levels.

5. Sketch a static NMR spectrum of central and satellite transitions of a spin- 7/2 solid in the presence of the quadrupolar and chemical-shielding anisotropy interactions. Assume the solid comes as a powder and there is one nuclear site. Label the individual transitions and the salient spectral features.

6. Write the matrix representations for the basis set angular momentum operators $\hat{I}_z, \hat{I}_x, \hat{I}_y, \hat{I}_+, \hat{I}_-$

7. Write the matrix representation of the rotation operator $\hat{R}_z(\varphi)$ for a spin-3/2 nucleus.

8. Suppose you have an ensemble of nuclear spins-3/2 prepared so that your initial density operator $\rho(0) = \hat{I}_x$. Write the matrix form of the density operator after you applied a radiofrequency pulse with a phase z and a flip angle of $\pi/2$. What does this matrix correspond to?