



INSTITUT FÜR PHYSIKALISCHE CHEMIE

Studiengang MASTER OF SCIENCE Chemie

MODUL Spektroskopie und Struktur der Materie

SIMPSON – SOLID STATE NMR II

1. PULSES AND NUTATION

After having found the optimal averaging conditions for MAS, we now focus on the optimal excitation strategy. To this end, use the *pulse.in* input file provided in the Learnweb.

- a) For a given pulse power (“nutaton frequency”) vary the length of the excitation pulse between 2 μs and 10 μs to achieve maximum intensity. What is the flip angle of this pulse? [no graphic needed, append this discussion to task c)]
- b) Find the pulse length corresponding to flip angles of 180° and 360° . How can you calculate the corresponding nutation frequency? [see task a)]
- c) In practice, the experimental nutation frequency is obtained from so-called nutation curves. A script to generate these curves will be provided. Observe how the value of the nutation frequency affects the nutation curve. How do your 90° excitation pulses change? [Prepare a plot including three different nutation curves and discuss the questions in part a), b) and c).]
- d) Often it is not possible to completely average all anisotropic NMR interactions, therefore, typically broad NMR spectra are obtained. To investigate the influence of the excitation pulse length (not flip angle) on the resulting spectrum, adjust the *mas.in* input file to incorporate non-ideal excitation scheme from the *pulse.in* input file. Furthermore, reduce the MAS frequency to 1.0 kHz and increase the anisotropy to ca. 20 ppm. Test nutation frequencies between 1.0 and 50.0 kHz. How does the nutation frequency affect the final spectrum? [(Stack-)plot 3-5 suitable spectra for different nutation frequencies and discuss the observed differences]

Hint: Do not forget to calculate the correct pulse length for each nutation frequency to maintain a constant pulse flip angle of 90° .

2. DIPOLAR COUPLING

Two further SIMPSON input files are provided: *dd_static.in* and *dd_mas.in*. In analogy to exercise 1, the aim of this exercise is to understand the influence of the dipolar coupling.

- a) Using the *dd_static.in* input file, simulate the spectrum of a single crystallite for different sets of Euler Angles for the dipolar interaction (0 0 0), (0 90 0), and (90 90 0). Make sure to use the crystal file 'alpha0beta0'. Save the spectra! [(Stack-)plot the spectra and explain your observations]
- b) Now simulate a powder spectrum containing multiple crystallites by using a different crystal file ('rep10', 'rep30', 'rep100', 'rep2000', 'zcw28656'). How many crystallites are necessary for sufficient powder averaging? [Prepare a meaningful graphic including 3-5 spectra, which crystal file would you prefer ? How would a ^{19}F spectrum of Polytetrafluoroethylene (Teflon) look like?]
- c) Vary the strength of the dipolar coupling and observe the influence on the spectra. [(Stack)Plot three suitable spectra to explain the influence of the DD coupling]
- d) Simulate the effect of Magic Angle Spinning (MAS) on the dipolar coupling by using the *dd_mas.in* input file (you might need to adjust some parameters). Start with a MAS frequency of 1.0 kHz and a crystal file of 'rep168'. Vary the number of 'gamma_angles' between 1 and ca. 20 until the spectrum is not changing (i.e. convergence of the gamma_angles). [Plot spectra for different gamma angles and explain the differences]
- e) Next, vary the MAS frequency until the dipolar coupling is averaged completely. [(Stack)Plot three suitable spectra and explain why averaging the dipolar coupling is extremely important for ssNMR of organic materials.]

3. QUADRUPOLEAR INTERACTION

The quadrupolar interaction is one of the strongest anisotropic interactions in solid-state NMR. First order perturbation theory is often not sufficient to describe the quadrupolar interaction, therefore regular MAS cannot average the quadrupolar interaction completely. The goal of this exercise is to understand the effect of the quadrupolar interaction on MAS spectra of ^{11}B and ^{27}Al . To this end, two new input files *qc_static.in* and *qc_mas.in* are provided.

- a) Using the *qc_static.in* simulate the spectrum of a single crystallite for different sets of Euler Angles for the CSA interaction (0 0 0), (0 90 0), and (90 90 0). Make sure to use the crystal file 'alpha0beta0'. Afterwards simulate a powder spectrum. Save the spectra! [(Stack)Plot the spectra and explain the differences]
- b) Change the spin system from ^{11}B to ^{27}Al and perform the same steps as in a). [Prepare a similar graphic and explain the differences]
- c) Use the *qc_mas.in* to simulate a MAS spectrum of a single ^{27}Al species with a C_Q of 0.5 MHz and 5.0 MHz. [(Stack)plot both spectra and explain your observations]
- d) Change the detect operator from I1p to I1c to only detect the central transition (use a high C_Q of ca. 5 to 10 MHz). Vary the asymmetry parameter from 0 to 1 and the B_0 field from 100 MHz to up to 900 MHz. Explain your observations.[Prepare two graphics that are suitable to discuss the influence of the asymmetry parameter and the B_0 field]

Extra: The excitation of triple quantum coherence is an essential feature of the MQMAS experiment. Use the *tq_mas.in* to simulate the triple quantum excitation efficiency of a hard rectangular pulse at a given nutation frequency (25 kHz, 50 kHz, 100 kHz, and 200 kHz). What can you learn?