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Studiengang MASTER OF SCIENCE Chemie

MODUL Spektroskopie und Struktur der Materie

# SIMPSON – SOLID STATE NMR III

## 1. SPIN-ECHO:

Due to hardware constraints, a real NMR spectrometer cannot record the FID directly after the excitation pulse. A short delay – the so-called “dead-time” delay – is necessary to ensure no interference of the pulse with the acquisition, since this has consequences for data acquisition in solid-state NMR. The aim of this exercise is to investigate the effect of this delay and to study techniques to compensate for it.

- a) Starting point for the simulations is the *mas.in* input file from the exercise of the day before. Simulate the effect of the receiver dead time by adding a delay after the excitation pulse before the acquisition. Add a delay of 15  $\mu$ s. What do you observe for different delays? How can this effect be compensated? [Prepare a graphic including 3-5 spectra of different dead-time delays and explain your observation]
- b) Adjust the CSA parameters to investigate the effect of the receiver dead-time on a very broad NMR spectrum. [Plot two spectra simulated with strongly different CSA values and explain your observations]
- c) In the lectures, you heard about the so-called “Hahn-Echo” experiment. Write the SIMPSON code for an echo pulse sequence. Perform simulations for (i) equal echo delays and (ii) non-equal echo delays. [Plot the spectrum of (i) with two spectra from (ii) using different conditions for the two delays and explain the differences.]

## 2. REDOR: MEASURING DIPOLAR INTERACTIONS

One of the most widely used experiments is the so called “Rotational Echo Double Resonance” – REDOR – experiment. It is used to measure the heteronuclear dipolar coupling constant, which in turn can be used to calculate distances between different nuclei. The input file *REDOR.in* contains already everything necessary to simulate simple REDOR curves for a two-spin system ( $^{13}\text{C}$ - $^{15}\text{N}$ ).

- a) Vary the dipolar coupling constant from 100 Hz up to 12 kHz. How does the shape of the dephasing curve change? [Prepare a graphic including 3-5 REDOR curves and explain the differences]
- b) Perform simulations for a dipolar coupling constant of about 1.5 kHz. Vary the spin rate from 2 kHz up to 25 kHz.  
n.b.: When going to higher spinning speeds you might have to adjust the rf power! [(Stack)Plot REDOR curves for 3-5 different spinning frequencies, How and why does the dephasing curve change? ]
- c) For a coupling constant of 1.5 kHz and a spin rate of 15 kHz vary the rf power from 15 kHz to 50 kHz and describe the observed effect. [Prepare a suitable graphic including 3-5 REDOR curves for different rf powers and explain the differences]
- d) How can you calculate the distance from the observed heteronuclear dipolar coupling constant? [Include the respective formula in the protocol and calculate the internuclear distance of the  $^{13}\text{C}$ - $^{15}\text{N}$  two spin system with a dipolar coupling constant of 1.5 kHz.]

### **3. FITTING EXPERIMENTAL SPECTRA**

In the presence of several superimposed resonance lines and/or different internal interactions, experimental solid-state NMR data are often extremely complicated and difficult to interpret. However, numerical simulations e.g. SIMPSON enable the identification of different species and determine their characteristic NMR parameters. For this purpose, it is often useful to fit iteratively the simulated lineshape to the experimental spectrum. The parameters used to generate the simulation with the lowest deviation from the experimental spectrum (here low rms value) are assumed to be reasonable close to the true values. Following the introduction of the fitting routine, three different experimental spectra are provided ( $^{13}\text{C}$  intro and two tasks).

- a)  $^{31}\text{P}$  MAS NMR spectrum. Determine the number of  $^{31}\text{P}$  species and the relevant NMR parameters. Here, homonuclear dipolar couplings can be neglected. [Explain the choice of your spin system/fitting parameters. (Stack)plot the experimental and the final simulated spectrum and list the extracted parameters]
- b)  $^{11}\text{B}$  MAS NMR spectrum of an organoborane. Which interaction is responsible for the observed lineshape. [Determine important NMR parameters and prepare a graphic analogously to a)]