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Methodical Aspects of 2D NMR Correlation Spectroscopy under Conditions of Ultra High Pulsed Field Gradients

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1. Introduction

Multidimensional NMR methods have become an important tool in the 1970s. In the past years a new set of experiments has developed whose postprocessing is based on a multidimensional inverse Laplace transformation rather than a Fourier transformation which provides the capabilities to find correlations between various parameters such as diffusion coefficients D and NMR relaxation times T_1 and T_2 [1,2].

The aim of the present work is to implement these techniques to our spectrometers in order to combine the concept of ultra high pulsed field gradients of up to 35 T/m [3] with modern 2D NMR correlation experiments.

2. Experimental

The main idea of 2D NMR experiments is to execute two suitable pulse sequences in succession, thus, the signal of the second subsequence depends on the NMR signal of the first one. This signal dependency enables one to design NMR experiments, which reveal the correlation between measured parameters such as T_1 and T_2 or D and T_2, respectively.

The D-T_2 correlation experiment (DRCOSY), as introduced by Hürlimann [4] for the stray field of a superconducting magnet, combines an echo experiment (D Domain) and a CPMG echo train (T_2 Domain). As opposite to this experiment, we use pulsed magnetic field gradients within the diffusion part of the pulse sequence (see, e.g. [5]) which may require a matching procedure for the gradient pulses. This holds in particular when using ultra high pulsed field gradients as outlined in [3]: If due to the finite experimental accuracy the aforementioned pair of gradients does not match exactly, the echo displaces and may even have a smaller magnitude which may lead to a wrong value of the diffusion coefficient determined. Therefore, a gradient adjustment is essential during data acquisition in order to correct for the mismatch. Here, we follow the concept suggested in [3], record the first echo completely and use it for the matching procedure. While this enables one to match the pulsed field gradients, it would exceed the size of the acquisition memory if one acquires each subsequent echo in the CPMG part with the same number of data points per echo. Therefore, the remaining echo train is acquired with only a few points per echo.

Another challenge is to find the highest gradient value necessary for a given PFG NMR experiment as it is crucial for the inverse Laplace transformation, as a model-free approach, to find a complete attenuated signal decay, regardless of whether the source of this (multi-exponential) decay is a relaxation or diffusion process. On the other hand, the determination of the echo shift, used to match the magnetic field gradients, fails without any distinct signal. To solve this conflict, a termination condition based on the signal-to-noise ratio and/or a pre-determined absolute echo shift is introduced.

For the simple case of bulk water, as a proof of working, the results of the DRCOSY are in good agreement with the expected diffusion and relaxation behaviour of water (Fig. 2).

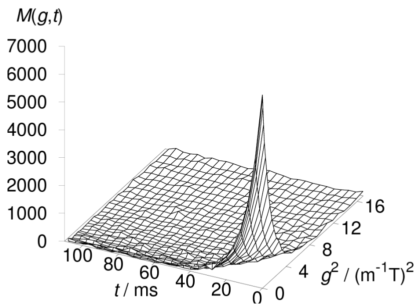

Fig. 1: Acquired map of NMR signals, CPMG on *t*-axis and echo attenuation on g^2-axis

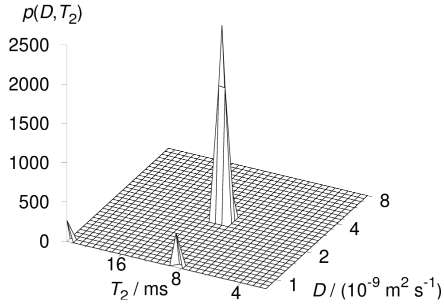

Fig. 2: inverse Laplace transformation of Fig. 1 with single peak at T_2 = 8ms and $D = 2.3\text{x}10^{-9}\text{m}^2\text{s}^{-1}$

Similar, but less complicated is the implementation of the T_1-T_2 correlation experiment [1] as no gradient matching procedure is required. The results obtained for water agree with the expected relaxation time values.

3. Conclusion

While the implementation of RRCOSY experiments into our spectrometers was straightforward, a couple of issues had to be addressed for the set up of DRCOSY experiments. Due to the use of ultra high pulsed field gradients and its ramifications we had to introduce an adjustment loop, as well as an automatic termination of the measurement based on the signal-to-noise ratio. We obtained expected behaviour of water for both T_1-T_2 correlation as well as D-T_2 correlation.

References

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