Multiple-quantum 23Na Signals Without Slow Motion

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Introduction

^{23}Na is the second-most sensitive MRI nucleus in vivo. The advent of high-field MRI scanners and the development of highly-efficient *k*-space sampling methods [1,2] have made ^{23}Na MRI a viable component of basic, as well as, clinical research. The differentiation between intra and extracellular Na is very important in the study of several neurological diseases (tumors, stroke). Multiple-quantum filters (MQF) are used to differentiate intra- vs. extracellular sodium [3].

It is known that triple-quantum (TQ) coherences may be created in the slow-motion regime, while double-quantum (DQ) coherences may be created only as a result of a residual (static) quadrupolar interaction. We demonstrate here that the mechanism of ***cross-correlated quadrupolar/paramagnetic relaxation can give rise to DQ coherences even in the absence of residual quadrupolar interactions, as well as, outside of the slow-motion regime.***

The use of paramagnetic agents hence precludes the use of DQ and TQ filtered experiments for the characterization of the intra- and extracellular sodium content [4], unless modified relaxation equations are used. Fig. 1 shows a ^{23}Na NMR spectrum of grey matter tissue bathed in a solution of TmDOTP^{5-}.

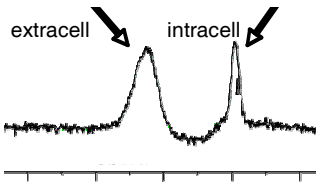

Figure 1: Grey matter with TmDOTP^{5-}

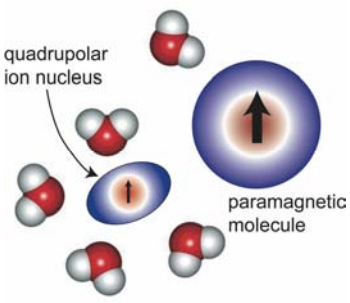

Figure 2: Quadrupolar/paramagnetic interaction

Theory

Using the Redfield Relaxation formalism, and both the quadrupolar, as well as, the paramagnetic interactions as relaxation mechanisms we obtain the following rate $R = a\left[2J_{Q,P}(0) + J_{Q,P}(\omega)\right]$ for the buildup of DQ coherence, where $J_{Q,P}(\omega)$ is the quadrupolar/paramagnetic cross-correlated spectral density function given by $J_{Q,P}(\omega) = \int C_{Q,P}(\tau)\exp(-i\omega\tau)dt$, and the molecular cross-correlation funtion $C_{Q,P}(\tau) = \left\langle F_0^Q(0)F_0^P(\tau)\right\rangle$. The theory also predicts the creation of TQ coherences from DQ coherences, and the appearance of a dynamic frequency shift, which would be reminiscent of a residual quadrupolar interaction when there is none.

Methods

Sample 1 was prepared as a 1% agarose gel solution in 10 ml of KH buffer. Sample 2 was prepared in the same way as sample 1 with the addition of TmDOTP^{5-}. Sample 3 was prepared by mixing sodium decyl sulphate, decanol, and water in the weight ratios: 37.9 : 6.7 : 55.4 to create a liquid crystalline phase. TmDOTP^{5-} was added to the liquid crystal solution and the sample was homogenized and equilibrated in a magnetic field of 11.7 T. The gray matter sample from a cow was bathed in TmDOTP^{5-} solution for 15 min before the measurement. The NMR experiments were performed on a Bruker 500 MHz Avance NMR spectrometer, operating at 11.7 T.

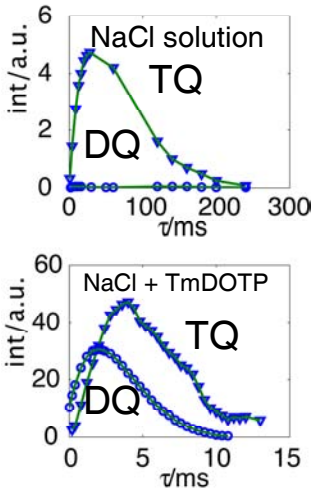

Fig. 3: DQ and TQ buildup

Results & Discussion

TQ and DQ buildup curves on sample 1 (sodium solution) show the usual behavior that no DQ coherence is created, while slow motion promotes TQ coherence (Fig. 3 top). The experimental results on sample 2 (Fig. 3 bottom), which includes the paramagnetic agent, demonstrate the creation of both DQ and TQ coherences. The buildup in this case is faster and leads to stronger signals than in the absence of the paramagnetic species.

The theory also predicts that differential linebroadening should be observed. This can be demonstrated experimentally using a sample oriented in a liquid crystal to allow for ta splitting between the three ^{23}Na transitions. The spectrum of sample 3 (containing sodium and Tm[DOTP]$^{5-}$ in a liquid-crystalline environment) is shown in Fig 4. As a result of the quadrupolar/paramagnetic cross-correlated relaxation mechanism, the left and right satellite transitions show different linewidths, thus confirming the theory.

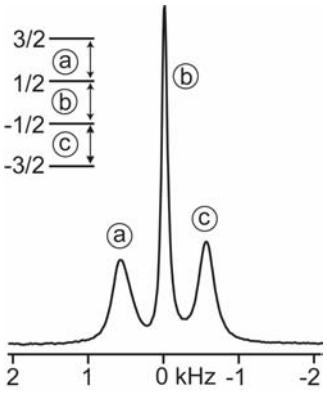

Figure 4: Differential linebroadening.

Conclusion

We demonstrated here that an interference between the quadrupolar and paramagnetic relaxation mechanisms can lead to the formation of both DQ and TQ filtered signals outside of the slow motion regime and without residual quadrupolar interactions. Differential linebroadening effects are also seen in anisotropic media. These findings are particularly useful in analyzing DQ and TQ filtered NMR and MRI experiments of tissues in the presence of paramagnetic agents. *The characterization of intra- vs. extracellular sodium signals should be possible taking into account this new theory.*

References

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