^{23}Na DQF Signal Induced by Paramagnetic Shift Reagents: Dependence on the Pseudo-Contact Shift

P. Rong[1], G. Navon[2], and A. Jerschow[1]

[1]New York University, New York, NY, United States, [2]Tel Aviv University, Tel Aviv, Israel

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 commonly done by the use of paramagnetic shift reagents. However the signal of the intracellular Na is often masked by that of the extracellular Na whose concentration is much higher. Triple-quantum coherences may be created as a result of a residual quadrupolar interaction and for species experiencing slow-motion. Thus triple-quantum filtered (TQF) NMR was suggested to quench the extracellular Na signal [3]. We have demonstrated earlier 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 [4]. From these, TQF signals can be created as well, although these appear in second order.

In this work we show that the DQF intensity and buildup rates correlate with the pseudo-contact shift of the paramagnetic species, which points to the effect being caused by the anisotropy of the paramagnetic center. The effect is demonstrated by examining a series of LnDOTP compounds. Notably, it is shown that, for example, ***GdDOTP does not lead to DQ effects, while TmDOTP leads to strong effects.***

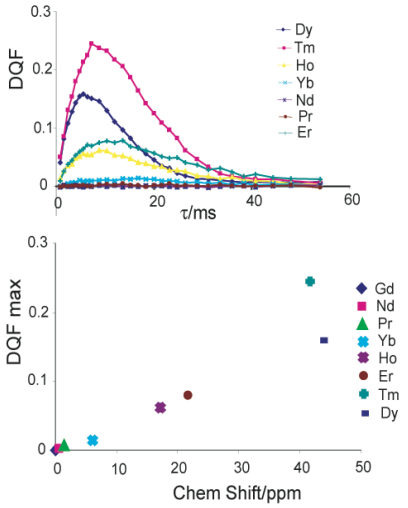

Figure 1: DQF intensity buildup vs. τ (top) and DQF max intensity vs. the absolute values of the pseudocontact shifts for the LnDOTP series (bottom).

Theory

Cross correlation between two relaxation mechanisms occurs if they are governed by correlated motions. Since both the quadrupolar interaction and electron spin *g* anisotropy, which is responsible for pseudocontact shifts, are modulated by the molecular rotational motion, cross correlation between them is expected. Using the Redfield Relaxation formalism, and both the quadrupolar, as well as, the paramagnetic interactions as relaxation mechanisms one can 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, which is linearly dependent on the pseudo-contact shift. The theory also predicts the creation of TQ coherences from DQ coherences, albeit to a lower extent, as they appear in second order. A differential linebroadening effect is predicted as well, which changes with the sign of the pseudocontact shift.

Materials and methods

Sample preparation: LnDOTP were synthesized by heating solutions of the corresponding chlorides with DOTP ligand (Macrocyclics), and adjusting the pH. The liquid crystalline samples were 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 or DyDOTP were then added to the liquid crystal solution and the samples were homogenized and equilibrated in a magnetic field of 11.7 T. The NMR experiments were performed on a Bruker 500 MHz Avance NMR spectrometer, operating at 11.7 T.

Results and Discussion

In examining the DQF buildup rates for ^{23}Na in isotropic solutions, we find a clear correlation between the pseudo-contact shifts of the different LnDOTP compounds and the DQF buildup (Fig. 1). This is an indication for the susceptibility mechanism contributing to relaxation. Cross-correlated relaxation theory allows one to describe the buildup rate in terms of the pseudo-contact shift. A differential linebroadening effect accompanies this phenomenon, which is demonstrated in a liquid crystalline environment. It is further found that upon the reversal of the pseudo-contact shift in going from TmDOTP (41.7 ppm) to DyDOTP (-43.8 ppm) [5], one may observe a reversal of the differential line broadening effect for Na in a liquid crystal (Fig. 2).

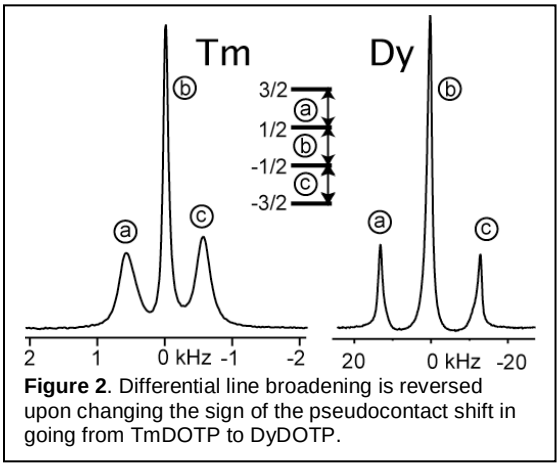

Figure 2. Differential line broadening is reversed upon changing the sign of the pseudocontact shift in going from TmDOTP to DyDOTP.

Conclusions

We demonstrate here that an interference between the quadrupolar and paramagnetic relaxation mechanisms can lead to the formation of both DQF signals outside of the slow motion regime and without residual quadrupolar interactions. Differential line broadening effects are also seen in anisotropic media. Furthermore, the mechanism of this relaxation effect is identified as originating from the pseudo-contact interaction between the paramagnetic center and the ^{23}Na nucleus. These findings are particularly useful in analyzing DQ and TQ filtered NMR and MRI experiments of tissues in the presence of paramagnetic agents.

References

[1] FE Boada, JS Gillen, GX Shen, SY Chang, KR Thulborn: Fast three dimensional sodium imaging. Magn. Reson. Med. 37 (1997) 706-15.

[2] A Borthakur, I Hancu, FE Boada, GX Shen, EM Shapiro, R Reddy: In vivo triple quantum filtered twisted projection sodium MRI of human articular cartilage. J. Magn. Reson. 141 (1999) 286-90.

[3] I Hancu, FE Boada, GX Shen: Three-Dimensional Triple-Quantum–Filtered 23Na Imaging of In Vivo Human Brain. Magn. Reson. Med. 42 (1999) 1146-54.

[4] W Ling , A Jerschow: Relaxation-allowed nuclear magnetic resonance transitions by interference between the quadrupolar coupling and the paramagnetic interaction. J. Chem. Phys 126 (2007) 064502

[5] AD Sherry, CFGC Geraldes, WP Cacheris, Inorg. Chim. Acta, 1987, 139:137-139