

^{7}Li intermolecular multiple-quantum coherences in liquids

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Abstract

We report here evidence for the generation of ^{7}Li multiple-quantum coherences in aqueous solutions outside of regimes where conventional multiple-quantum coherences due to alignment or quadrupolar relaxation could be observed. These coherences are shown to observe nonlinear behavior as a function of concentration, and hence these effects can be identified as arising from intermolecular multiple-quantum coherences. Due to the importance of lithium ion solutions for the study of electrochemical systems, awareness of such coherences is particularly important in the interpretation of experimental results, and new applications using lithium as a probe may become possible on this basis.

Keywords:
multiple-quantum coherences; intermolecular multiple-quantum coherences; lithium; dipolar demagnetizing fields; pulsed field gradients;

1. Introduction

^{7}Li is a fairly sensitive nucleus for NMR observation. The gyromagnetic ratio is relatively high, and the natural abundance is approximately 92%. ^{7}Li NMR spectroscopy and imaging have recently gained momentum, especially in the context of the study of lithium-ion rechargeable batteries and in the study of related electrochemical processes. Having a spin 3/2, ^{7}Li also experiences a quadrupolar interaction, though to a much lesser extent than many other nuclei, due to its relatively small nuclear quadrupole moment, and the

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low polarizability of the electron cloud. For these reasons, ^{7}Li is often regarded as an 'honorary' spin 1/2 nucleus. In liquid NMR spectroscopy, ^{7}Li also displays relatively long relaxation times for this reason, especially when compared to ^{23}Na.

On the other hand, the quadrupolar interaction does manifest itself occasionally, and has been shown to represent the major relaxation mechanism over almost the entire concentration range in aqeuous solution [1]. Furthermore, ^{7}Li was the nucleus for which the first multiple-quantum coherences arising from quadrupolar relaxation in the slow motion regime were detected [2]. Such coherences can be diagnostic of the motional regime or the asymmetry in the electron environment, and can be used to extract information about both the electric field gradient and the correlation time.

We have performed a search of such multiple-quantum coherences (MQCs) in aqueous media. Using standard MQC pulse sequences used for quadrupolar liquid-state NMR, we have found MQCs to appear even at relatively low concentrations and under conditions which would not support conventional MQC creation mechanisms. Such coherences were also at odds with the typical buildup shape expected in the slow-motion regime.

We show experiments and analyses, which support the hypothesis that intermolecular MQCs (iMQCs) in lithium ion solutions are the cause of the observed effects. Awareness of such signals and the proper characterization of these phenomena are important when searching for conventional (intramolecular) MQCs, especially when one wishes to examine motional regimes or asymmetries in the local environment.

It is also possible that such iMQCs could be used for structural investigations (including, for example, the measurement of Patterson functions [3], diffusion measurements [4], high-resolution measurements in inhomogeneous fields [5, 6, 7, 8, 9], absolute temperature imaging [10], and imaging contrast enhancement [11, 12, 13], in analogy to the work conducted mainly for ^{1}H spins. iMQCs could also lead to unusual echoes or unexpected artifacts (e.g. in signal selection or suppression) [14, 15]. It is noted that the relatively high gyromagnetic ratio and natural abundance, and the long relaxation times could make ^{7}Li a useful probe in this regard for experiments that exploit both homonuclear and heteronuclear iMQC experiments). Furthermore, it seems suitable to explore potential applications of such experiments within the context of battery electrolyte studies due to the importance of lithium in such systems, and due to the relatively high lithium ion concentrations present in these systems. There is precedent for the observation of iMQCs in ionic liquid solutions [16], and the ^{7}Li nucleus could become an important probe in this regard as well.

2. Experimental

Samples were prepared from a 20 M LiCl stock solution in 90 % D_2O / 10% H_2O and diluting to the desired concentration. Experiments were performed on a Bruker 500 MHz spectrometer with a BBO probehead with a three-axis gradient system (max. gradient strength 0.5 T/m). The CRAZED pulse sequence [17] used in this work is shown in Fig. 1. The ^{7}Li $\pi/2$ pulse durations were optimized for each concentration: 1 M: 12 μs; 5 M: 11.5 μs; 10 M: 10.75 μs; 15 M: 12.75 μs). The dwell time was 800 μs, the gradient ramp duration 125 μs. The recycle delay was 15s, and the acquisition time per FID was 13s, hence allowing for adequate return to equilibrium between scans.

MQCs are selected using two gradients with strengths G and $n \cdot G$. The acquisition is shifted by n $\cdot t_E$ as well in order to have the gradient echo coincide with the point of refocusing of inherent inhomogeneities.

For experiments shown in Fig. 2 and Fig. 4, the echo time was $t_E =$ 500 ms, and G_1 was set to 10% of the maximum value and the gradient duration was 2 ms. For the results shown in Fig. 3, the echo time was $t_E =$ 5 ms, and G was set to 20% of the maximum value and the gradient duration was 1 ms. These gradients were applied along the z direction. The spoiler gradient G_{sp} was applied along the x direction, had a duration of 2 ms, and was applied with a strength of 30 %.

A simple four-step cycle (CYCLOPS) was used for both pulses and receiver phase (0,90, 180, 270°). Signals were averaged over four scans for the experiments of Fig. 2 and Fig 4, and over 256 scans for the experimental results shown in Fig. 3. 32k data points were acquired over a spectral window of 1250 Hz.

3. Results and Discussion

We provide here a short review of the established theory of intermolecular multiple-quantum coherences (iMQC) and dipolar demagnetizing field (DDF) effects as relevant for the interpretation of the results.

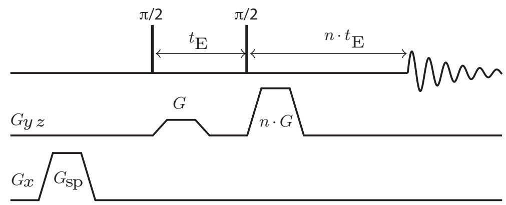

Figure 1: CRAZED pulse sequence. The encoding gradient for iMQCs was applied either along the z direction, or to check the angular dependence along a direction between the z and y axes.

The ansatz of the iMQC theory [17] is typically to write the equilibrium density matrix as

$$\rho = \prod_j (1 - aI_{jz}) \,, \tag{1}$$

where I_{jz} is the I_z operator for spin j, a is the Boltzmann population factor, which under the high temperature approximation is $a = \hbar\gamma B_0/kT$. The product is a direct product and runs over all the spins in the sample. Written in this form, it becomes clear that a single 90° pulse can generate any number of (intermolecular) multiple-quantum coherences (iMQCs). iMQCs of order n will appear with a weighting of a^n, hence a small weighting if working with thermal populations under usual conditions. The iMQC theory furthermore stipulates that following the second pulse, certain antiphase density matrix terms will evolve back into detectable single-quantum coherence [18].

Alternatively, and originally, the observed effects have been discussed in the context of multiple spin echoes and dipolar demagnetizing fields (DDF) [19, 20, 3, 21]. Often the same acronym is used under the name 'distant dipolar field' [22]. Multiple-echo signals are also sometimes referred to under the name 'nonlinear spin echoes' [23], to indicate the fact that spin evolution proceeds under a field that is influenced by prior spin evolution.

Both these theoretical approaches have their advantages and disadvantages. For example, the iMQC formalism provides great intuition and allows for using the regular density matrix framework, and considerations of phase cycling as well as the actions of pulsed field gradients for coherence selection. The disadvantage with this approach is that quantitative results are harder to obtain due to the large number of terms that one would have to consider.

The classical DDF formalism has the advantage of quantifiability, but the disadvantage that it requires nonlinear equations of motion. As a result, it is difficult to clearly predict experimental results from experiments with more pulses, unless strong simplifying assumptions are made.

In the DDF formalism, the appearance of higher order echoes is explained as follows:

Following the first pulse in the sequence, spins precess under the action of a pulsed field gradient to acquire a phase $\phi(z) = \gamma G z \delta$, with δ being the gradient pulse duration. Depending on the relative phase of the second pulse, part of the magnetization is converted to z-magnetization, imparted with a $\cos\phi(z)$ modulation. Any transverse magnetization remaining will hence precess under the action of the static field plus this additional modulated field, as represented by

$$\exp(-i(B_0 + M_0 \cos\phi(z)). \tag{2}$$

Leaving aside the regular precession motion under B_0, the modulated portion can be cast into terms indicating precession at multiples of the precession frequency:

$$\exp(-i(M_0 \cos\phi(z)) = \sum_n a_n J_n(x) \exp(-im\phi), \tag{3}$$

which explains the origin of the multiple echoes.

This precession can be undone in part by the application of an additional pulsed field gradient for a specific amount of time, thereby allowing the refocusing of any of the terms of this series.

Most iMQCs have been observed for ^{1}H spins, although originally the effects of DDF have been identified for ^{3}He [19], in the form of multiple echoes. With hyperpolarization, it was shown that iMQC could be seen for ^{13}C nuclei [24]. Heteronuclear iMQCs or DDFs (from ^{1}H) were further detected using ^{129}Xe [25], ^{31}P [26], and ^{13}C nuclei [27].

To test for the existence of iMQCs in lithium ion solutions, we performed experiments using the pulse sequence in Fig. 1, which is a version of the CRAZED sequence (or nonlinear echo sequence). According to conventional NMR theory, one would only produce signals if the two pulsed field gradient areas were the same. To test for higher order iMQCs occurring during the period between the two pulses, n was chosen to be 2, 3, 4, in order to select for double-quantum, triple-quantum, and quadruple-quantum coherences during the first evolution period.

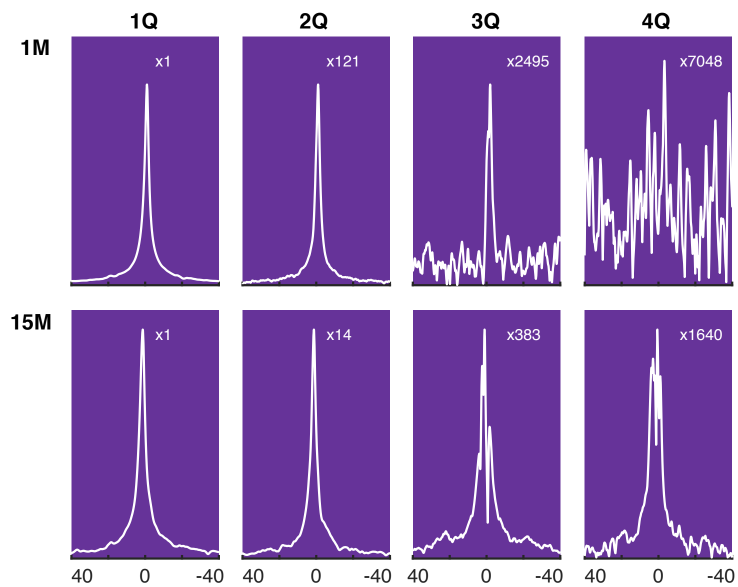

Figure 2: ^{7}Li spectra obtained from the CRAZED experiment when selecting the indicated coherence orders by adjusting $n = 1$, 2, 3, 4. The magnification factor is shown in the top right corner of the plots. The results are shown for both a 1 M and a 15 M LiCl solutions in 90%/10% H_2O/D_2O.

Results of this experiment performed on a select series of Li-ion aqueous solution samples are shown in Fig. 2. As is seen, higher iMQCs are clearly observed even for the 1 M sample, but the quadruple-quantum experiment gives signals mostly in the noise. By contrast, the 15 M sample allows detecting even the quadruple quantum coherence with ease (within four scans).

To demonstrate the creation of iMQCs further, experiments were performed for a series of samples, and for relatively short echo times (t_E=5 ms). The intensities in these samples are shown in Fig. 3 as compared to the single-quantum intensity. Overall, this series of experiments demonstrates that one can generate i2QC and i3QC with relative ease even at such short echo times. iMQCs of order four or higher remained within uncertainty levels under these conditions, but as seen in Fig. 2, these are easily observed when using longer echo times.

The noise relevant for determining perceptible signal amplitudes is not only the thermal noise, but is also determined by the limit of coherence selection quality imposed by pulsed field gradients. Comparing the iMQC intensities, as seen in Fig. 3, demonstrates that the rise of iMQC is stronger than linear as a function of concentration, a clear indication of iMQCs. Therefore, one can exclude coherence selection quality as a source of influence on the results.

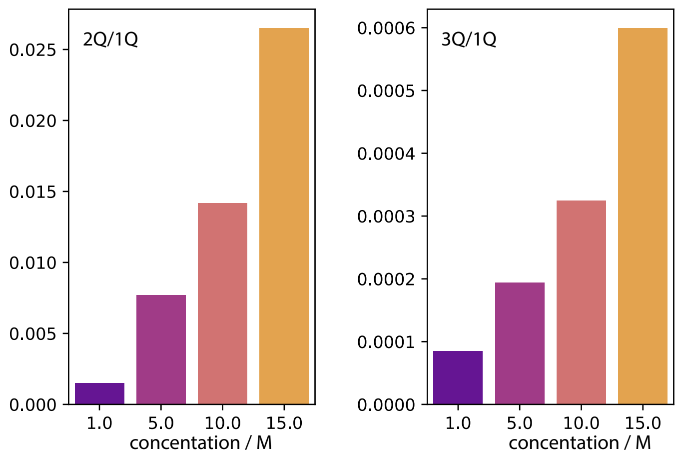

Figure 3: CRAZED intensities (2Q, 3Q) normalized to the single quantum intensity (1Q).

The possibility of the creation of conventional MQCs from either the slow motion regime or from residual quadrupolar couplings was considered. These were ruled out, however, because (1) slow-motion MQCs require a minimum of two pulses to be generated (and a minimum of a total of three pulses including reconversion and detection), (2) these MQCs are unlikely to arise at such short echo times as used for the experiments of Fig. 3, (3) residual quadrupolar couplings are not expected to exist in aqueous solutions of small molecules at moderate magnetic fields, (4) the correlation times of salt solutions are not expected to vary over a large enough range to warrant the appearance of MQCs from slow motion [1], and (5) the occurrence of MQCs would not have a strongly nonlinear character as a function of concentration based on the known changes of correlation times over the concentrations [1].

Two further potential sources for such observations were ruled out: (1) Effects of incomplete T1 relaxation can be ruled out for the 15M sample because the determined T_1 value (3.3-3.4s) is much shorter than the sum of the recycle delay (15s) and the acquisition time (13s). Furthermore, if there were such an effect, it would become weaker with higher concentration (where T_1 shortens), which is opposite to what is observed. (2) Radiation damping was ruled out by comparing T_1 measurements with saturation recovery (3.3s) and with inversion-recovery (3.4s) for the 15M sample. These values are in line with previously measured constants [1]. The saturation recovery experiment included saturation by three 90° pulses, followed by a spoiler gradient, each along a different direction. If there were significant radiation damping, then the measurement with inversion-recovery would produce a much shorter value. Furthermore, the nutation curve amplitudes followed ordinary (sine-line) behavior, another sign for the absence of radiation damping.

As a final piece of evidence, we provide results from CRAZED experiments performed with the gradient direction inclined at different angles θ relative to the z axis. True iMQC or DDF effects would produce results scaled by $\frac{1}{2}(3\cos^2\theta - 1)$ due to the rotational properties of the dipolar field [21]. The experimental results observe this trend very clearly as shown in Fig. 4, which is perhaps the strongest evidence for the presence of iMQCs, since there are no other known effects that would depend on the gradient direction in such a way.

4. Conclusion

We have shown evidence for the existence of intermolecular multiple-quantum coherences in aqueous solutions of lithium chloride. Other potential sources of such MQCs are ruled out in the systems studied. The existence of these effects could be especially important when one wishes to observe conventional (intramolecular) MQCs, for example for the analysis of systems in slow motion or in partially aligned media. Furthermore, it is possible that these iMQCs could find applications for probing periodic structuring, measuring diffusion, absolute temperature mapping, or high resolution spectroscopy in inhomogeneous media (e.g. in a device). The observed signals depend on overall polarization, and hence one would expect such signals to become much stronger with hyperpolarization. It should also be possible to find such effects for hyperpolarized ^{6}Li solutions, especially because ^{6}Li has very long relaxation times.

5. Acknowledgements

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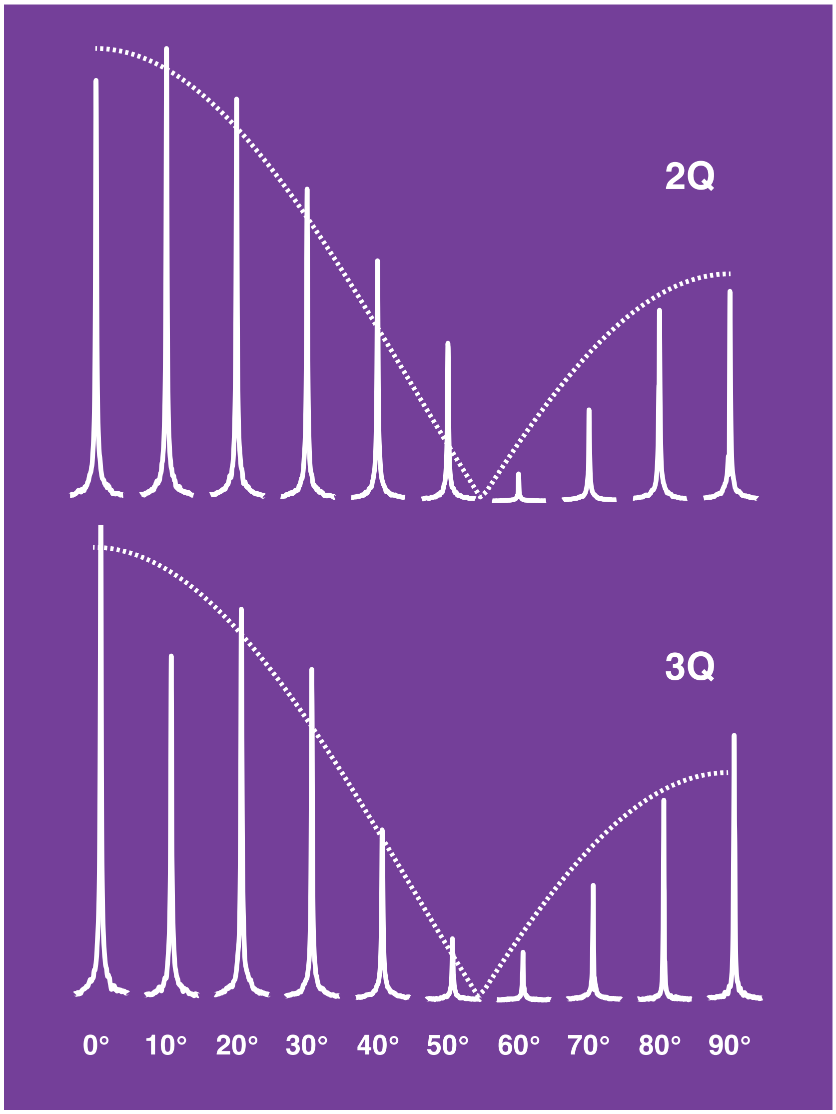

Figure 4: ^{7}Li magnitude spectra obtained from the CRAZED experiment as a function of the gradient direction specified by the angle θ between the z and the y axis. The experiments were performed for the 15M sample. Both 2Q and 3Q experiments show clear signs of the expected behavior (the dotted line represents $\frac{1}{2}|3\cos^2\theta - 1|$ as a guide).