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Four-time ^{7}Li stimulated-echo spectroscopy for the study of dynamic heterogeneities: Application to lithium borate glass

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ABSTRACT

To study the nature of the nonexponential ionic hopping in solids a pulse sequence was developed that yields four-time stimulated-echo functions of previously inaccessible spin-3/2-nuclei such as ^{7}Li. It exploits combined Zeeman and octupolar order as longitudinal carrier state. Higher-order correlation functions were successfully generated for natural-abundance and isotopically-enriched lithium diborate glasses. Four-time ^{7}Li measurements are presented and compared with two-time correlation functions. The results are discussed with reference to approaches devised to quantify the degree of nonexponentiality in glass forming systems and evidence for the occurrence of dynamic heterogeneities and dynamic exchange were found. Additional experiments using the ^{6}Li species illustrate the challenge posed by subensemble selection when the dipolar interactions are not very much smaller than the quadrupolar ones.

1. Introduction

The correlation functions describing the ionic and molecular motion in amorphous solid electrolytes, like in most other glass forming materials, display a nonexponential temporal evolution [1]. In other words, one probes, e.g., molecular orientations or the corresponding NMR interaction tensors at two points in time separated by an interval t. The loss of correlation is then usually described by stretched exponential or other phenomenological functions. Regarding the nature of these two-time functions two limiting scenarios are discussed [2] one of which starts from the assumption that each ion couples strongly to its neighbors, e.g., via Coulomb interactions so that the correlation function describing the motion of each ion (or ionic subensemble) is intrinsically nonexponential. In the alternative scenario the dynamics of various subensembles are supposed to differ so that the macroscopically observed nonexponentiality arises as a consequence of this heterogeneity. Molecular dynamics simulation has allowed one to distinguish these two scenarios for ion conductors [3].

The question regarding the origin of nonexponentiality was first resolved experimentally using reduced four-dimensional (4D) ^{13}C NMR spectroscopy [4]. The basic idea is that by probing the molecular properties at four distinct points in time one can check whether the rate of orientational decorrelation that is measurable for the first two times differs from that for the latter two (heterogeneous scenario) or not (homogeneous scenario). It was soon recognized that the less time demanding acquisition of four-time (4t) stimulated echoes provides all relevant information as well [5,6]. Using this technique various carbon and deuteron NMR studies were performed to scrutinize the nonexponential structural relaxation of polymers [7] and supercooled liquids [8] slightly above their glass transition temperature. Under specific circumstances deuteron spin-lattice relaxation [9] and the study of NMR spectra [10,11] also helped to map out various aspects of dynamical heterogeneities in disordered materials. To tackle these questions from a different angle, experimental methods outside the realm of NMR were devised as well [12,13].

In NMR studies addressing the nature of the nonexponential correlation functions in glass forming materials spin-1/2 or spin-1 nuclei such as ^{2}H [14–16], ^{6}Li [17], ^{15}N [10], ^{13}C [4,5,6,18], or ^{109}Ag [19,20] were employed. However, several of these probes are typically characterized by long spin-lattice relaxation times, or additionally as, e.g., for ^{109}Ag by low sensitivity. Hence, in studies of materials relevant for energy applications it would be advantageous if spin-3/2 nuclei such as ^{7}Li or ^{23}Na would become accessible. However, the seven-pulse techniques previously devised to record 4t stimulated echoes, are so far not applicable for probes with $I > 1$ [21]. An exception is the $I = 5/2$ nucleus ^{17}O for which selective central-transition excitation was recently

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exploited [22]. For the current work, we developed a pulse sequence to investigate spin-3/2 nuclei for which the entire spectrum can be excited by the radio-frequency pulses (see Section 2). In Section 3 we briefly outline the limits of homogeneous and heterogeneous scenarios among which the present experiments can distinguish. Then, in Section 4 their successful application using ^{7}Li NMR is demonstrated for glassy lithium borate ion conductors that were previously characterized using ^{6}Li [23] and ^{7}Li [24,25] spectroscopy. In Section 5 the experimental results are compared with expectations for homogeneous and heterogeneous scenarios and the life time of the heterogeneity found is discussed.

2. Design of four-time ^{7}Li stimulated echoes

As mentioned, seven-pulse sequences are suitable to record 4t stimulated echoes. The general scheme for such a sequence is shown in Fig. 1. It involves four evolution times t_p that are usually all equally long. During these times phase encoding with the relevant precession frequencies takes place. The idea behind this sequence is that by a suitable choice of the first mixing time t_{m1} a dynamical subensemble is selected and its properties can then be investigated by variation of the mixing times t_{m2} and/or t_{m3}.

Let us now consider the situation for ^{7}Li where the first-order quadrupolar interaction $H_Q = \omega_Q T_{20}$ usually prevails, here written in terms of the irreducible spherical tensor operator T_{20} of rank 2. The quadrupolar frequency

$$\omega_Q = \frac{1}{2}\delta_Q(3\cos^2\theta - 1 - \eta\sin^2\theta\cos 2\phi) \tag{1}$$

to depends on the anisotropy $\delta_Q = \frac{1}{2}e^2qQ/\hbar$ and on the asymmetry η of the electric field gradient (EFG) tensor in its principle axis system at the Li site. The angles θ and ϕ specify the orientation of this tensor relative to the external static magnetic field. The four evolution times t_p are separated by three mixing times t_{m1}, t_{m2}, and t_{m3}. During each of these intervals the phase information, $\omega_Q(t_{mi})t_p \equiv \omega_i t_p$ with $i = 1, 2, 3$, is stored in long-lived longitudinal carrier states. While the sequence in Fig. 1 looks similar to those for spin-1/2 or spin-1 nuclei [18,26], the present coherence pathway necessarily differs from previously applicable ones. Furthermore, so far pure Zeeman order ($\propto T_{10}$) or pure spin-alignment order ($\propto T_{20}$) were exploited as longitudinal carrier states. Here instead, we make also use of the mixed octupolar ($\propto T_{30}$) plus Zeeman state that has recently turned out useful in ^{7}Li stimulated-echo spectroscopy [27]. The 4t-echo sequence which we have devised can be considered as an extension of the two-time echo sequence invented by Jeener and Broekaert $X_{\varphi1,-} - t_p - Y_{\varphi2,-} - t_m - X_{\varphi3,-} - t_p -$ acq [28]. The presently chosen notation, e.g., $X_{\varphi,-}$, indicates the application of a nonselective X-pulse with flip angle φ. The subscript minus sign signals that the results originating from pulses with $+\varphi$ and with $-\varphi$ are subtracted, i.e., that $(X_{+\varphi} - X_{-\varphi})/2$ is considered. Appropriate phase cycling furthermore ensures elimination of double quantum coherences. This can be achieved by adding the signals generated using an $X - t_p - Y$ (in brief: XY) pulse pair and another XY pair for which the pulse phases have been rotated by 90°, i.e., Y −X. This way, using the density operator formalism delineated in [29], for $I = 3/2$ nuclei one is able to create signals of the type [21]

$$F_2^{\sin}(t_p, t_m, t_a) = \frac{9}{20}\Phi_{1,2,3}\langle\sin(\omega_1 t_p)\sin(\omega_2 t_p)\rangle. \tag{2}$$

Here, the factor $\Phi_{1,2,3} = \sin(\varphi_1)\sin(2\varphi_2)\sin(2\varphi_3)$ parameterizes the signal attenuation if the flip angles deviate from their optimal values $\varphi_1 = 90°$ and $\varphi_2 = \varphi_3 = 45°$. The angular brackets designate an ensemble average.

Let us now treat the 4t sequence sketched in Fig. 1 written here as $(X_1Y_2) - t_{m1} - (X_3Y_4) - t_{m2} - (X_5Y_6) - t_{m3} - X_{\varphi7,-} - t_p -$ acq where the phase cycling described above is assumed for each pulse pair. Analogous to the $F_2^{\sin}$-experiment, starting from initial z-magnetization ($\propto T_{10}$) the first two pulses (X_1Y_2) generate a pure quadrupolarly modulated spin-alignment state

$$\rho(t_{m1}) = -\frac{3}{2\sqrt{5}}\sin(\varphi_1)\sin(2\varphi_2)\sin(\omega_1 t_p)T_{20} \tag{3}$$

under the action of H_Q. Here $\rho(t)$ designates the density matrix after the time interval t. The third pulse $X_{\varphi3,-}$ then leads to the transversal superposition state

$$\begin{aligned}\rho(t_{p2}) = {} & \frac{9}{20}\Phi_{1,2,3}\sin(\omega_1 t_p)\sin(\omega_2 t_p)T_{11}^{(a)} \\ & + i\frac{3}{4}\sqrt{\frac{3}{5}}\Phi_{1,2,3}\sin(\omega_1 t_p)\cos(\omega_2 t_p)T_{21}^{(s)} \\ & + \frac{3}{10}\sqrt{\frac{3}{2}}\Phi_{1,2,3}\sin(\omega_1 t_p)\sin(\omega_2 t_p)T_{31}^{(a)}\end{aligned} \tag{4}$$

at the end of the second evolution time. In Eq. (4) $T_{lm}^{(a,s)}$ denote symmetric or antisymmetric combinations of spherical tensor operators of rank l and order m [29]. The first term on the right hand side of Eq. (4) corresponds to the $F_2^{\sin}$ function of Eq. (2). In the present context and with a suitably chosen mixing time t_{m1}, two-time functions of this type can act as dynamical low-pass filters [13]. The next pulse, $Y_{\varphi4,-}$, transforms the $T_{11}^{(a)}$ and $T_{31}^{(a)}$ coherence terms into a linear combination

$$\begin{aligned}\rho(t_{m2}) = {} & \frac{9}{20}\Phi_{1,2,3}\sin(\varphi_4)\sin(\omega_1 t_p)\sin(\omega_2 t_p)T_{10} \\ & + \frac{9}{160}\Phi_{1,2,3}[\sin(\varphi_4) + 5\sin(3\varphi_4)] \times \sin(\omega_1 t_p) \\ & \times \sin(\omega_2 t_p)T_{30}\end{aligned} \tag{5}$$

of the longitudinal spin states T_{10} and T_{30}. The $T_{21}^{(s)}$ contribution appearing in Eq. (4) is eliminated by the described phase cycle.

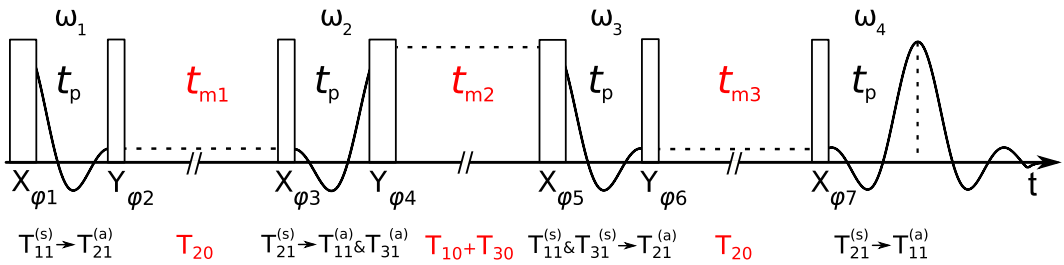

Fig. 1. Pulse sequence suitable to measure sin-sin-sin-sin stimulated echoes. The four precession frequencies ω_1 to ω_4 relevant during the various evolution times t_p are indicated as well as the three mixing times t_{m1}, t_{m2}, and t_{m3}. Such a sequence is suitable, e.g., to check whether one can filter a subensemble using the first three pulses and store it with a fourth pulse for later use. Then this subensemble can be analyzed via the sequence represented by the last three pulses. The path of the longitudinal carriers and transverse (coherence) states relevant for the formation of 4t ^{7}Li (spin $I = 3/2$) stimulated echoes is summarized below the sequence.