

# Experimental Determination of Four-Time Stimulated Echoes in Liquids, Colloidal Suspensions, and Crystals

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Received March 18, 1997

**Four-time stimulated echo experiments have been used to monitor the temporal evolution of the reorientation rates of deuterated molecules or colloidal suspensions. We present extended phase cycles for this seven-pulse experiment. In order to test its performance three vastly different materials are chosen. These include a crystal in which the molecules carry out well-defined 180° flips and a supercooled liquid characterized by a distribution of jump angles centered around 10°. As an example for rotational diffusion, data on a concentrated suspension of polystyrene spheres in a viscous medium are presented.** © 1998 Academic Press

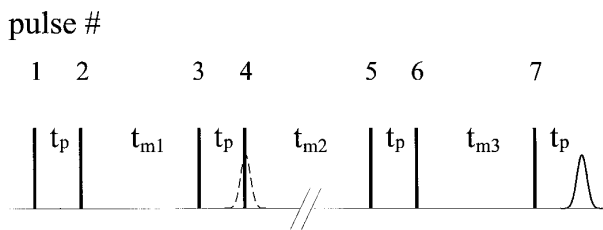
## INTRODUCTION

In order to investigate the nature of nonexponential relaxation in glass-forming materials Schmidt-Rohr and Spiess were the first to demonstrate the use of 4D NMR (1). To be able to perform this experiment in a reasonable amount of time they applied it in a reduced form to the  $^{13}\text{C}$  nuclei in amorphous poly(vinylacetate). In principle they first used a 2D experiment to select those polymer segments that have not jumped during the mixing time  $t_{m1}$ . The 2D signal intensity was then stored for a relatively long time period  $t_{m2}$  and subsequently subjected to another 2D experiment also involving a mixing time  $t_{m3}$ ; cf. Fig. 1. The finally detected magnetization originates from those segments which have been slow before and after  $t_{m2}$ , i.e., one that is sensitive to any rotational rate exchange during  $t_{m2}$ . The acquisition of multidimensional spectra in the original Schmidt-Rohr and Spiess experiment was due to the necessity of selecting a specific chemical site. Therefore in a subsequent investigation on the same polymer, but with only the carbonyl site isotopically enriched, all evolution times were kept constant and the four-time stimulated echo (4t-SE) amplitude was recorded as a function of only one of the mixing times, viz.  $t_{m2}$  (2).

In the meantime a number of studies on different polymers (3, 4) and several supercooled liquids (5–7) have been performed also with the deuteron as probe nucleus. In all these studies the evolution time  $t_p$  of course had to be fixed to a specific value which usually is subject to conflicting requirements. On the one hand,  $1/t_p$  should be much smaller than

the relevant strength of the chemical shift anisotropy or quadrupolar interaction, respectively. This constraint is usually necessary in order to be sensitive to sufficiently small jump angles. Furthermore if  $t_p$  is not short compared to  $t_{m1}$  then matters can become very complicated. This is due to the fact that then the rotational dynamics taking place during  $t_p$  cannot be neglected. On the other hand,  $t_p$  should be short since in the temperature ranges of interest the transverse spin states which exist during the evolution and detection periods typically dephase relatively quickly. The theoretical description of multidimensional NMR investigations has received considerable attention in the literature (8–12). In particular it has been shown that if the evolution time  $t_p$  is chosen long enough so that each rotational jump leads to a total loss of correlation, then specific 4t-SE's, to be discussed in detail below, are completely independent of the rotational dynamics. These functions can then be used to measure the exchange of rotational rates in real time. Note that this is different from what can be obtained in a 2t-SE experiment, where the exchange between orientational states, chemical sites, etc., is usually accessible.

In the present article we will provide a detailed description of *experimental* procedures. In addition the performance of the relatively complex 4t-SE experiment is tested in materials governed by different types of internal reorientational mechanisms. The molecules or molecular segments in the glass formers studied so far are characterized by reorientational jumps with typical jump angles in the range of about 10° (13, 14). New data on a glass-forming substance are presented below which extend in the so far unexplored range below about 1 ms. As a model system for a crystalline substance we have chosen dimethylsulfone (DMS), a substance in which the molecules perform 180° flips (15–17). Furthermore the relaxation in this material proceeds exponentially; i.e., there will be no slow and fast molecules present simultaneously. Consequently the four-time echo amplitude should be independent of  $t_{m2}$ , corresponding to the absence of rotational rate exchange. Going to the other extreme, i.e., to very small jump angles, one ends up with the case of rotational diffusion which is found, e.g., in colloidal dispersions. For our case we have chosen a previously investigated suspen-



**FIG. 1.** Basic pulse sequence used for the generation of four-time stimulated echoes. The experiment contains four evolution/detection intervals  $t_p$  and three mixing periods denoted as  $t_{m1}$ ,  $t_{m2}$ , and  $t_{m3}$ . For all 4t-SE's reported in this article we have set  $t_{m1} = t_{m3}$ . Some useful combinations of pulse lengths and phases are specified in Tables 1 through 4.

sion of colloidal polystyrene particles dispersed in a viscous medium (18). The main motivation for the investigation of such systems is provided by the fact that in the small-angle regime the problem of choosing a suitable evolution time  $t_p$  becomes particularly acute.

The remainder of this paper is organized as follows: In the next section we introduce the 4t correlation functions that can be measured by a seven-pulse NMR experiment and develop the basic phase cycles necessary for eliminating undesired multiple-quantum coherences. Then we demonstrate the performance of the method when applied to a crystalline material, a supercooled liquid, and a colloidal suspension, in each of which the jump angles characterizing the molecular reorientations differ greatly. In the concluding section we summarize our findings.

## FOUR-TIME STIMULATED ECHOES

The basic pulse sequence for the detection of 4t-SE's is sketched in Fig. 1. It may be viewed to consist of two standard three-pulse stimulated echo sequences with a  $90^\circ$  pulse and a mixing time  $t_{m2}$  sandwiched between them. The interleaved  $90^\circ$  pulse 4 is used to flip the (transverse) magnetization appearing in the two-time echo into the longitudinal direction. Depending on the phases and lengths of the other pulses four different 4t-SE's can be generated. In a notation similar to that used in Ref. (8) they read

$$E^{CCCC}(t_{m2}) = \langle \cos(\omega_1 t_p) \cos(\omega_2 t_p) \cos(\omega_3 t_p) \cos(\omega_4 t_p) \rangle \quad [1a]$$

$$E^{SSCC}(t_{m2}) = \langle \sin(\omega_1 t_p) \sin(\omega_2 t_p) \cos(\omega_3 t_p) \cos(\omega_4 t_p) \rangle \quad [1b]$$

$$E^{CCSS}(t_{m2}) = \langle \cos(\omega_1 t_p) \cos(\omega_2 t_p) \sin(\omega_3 t_p) \sin(\omega_4 t_p) \rangle \quad [1c]$$

$$E^{SSSS}(t_{m2}) = \langle \sin(\omega_1 t_p) \sin(\omega_2 t_p) \sin(\omega_3 t_p) \sin(\omega_4 t_p) \rangle. \quad [1d]$$

Here  $\omega_i$ 's are the orientation-dependent NMR frequencies during the evolution times  $i$  of which there are four and the brackets  $\langle \dots \rangle$  indicate a powder average. After the signals according to Eq. [1] have been recorded, they can be added, making use of the well-known trigonometric relation  $\cos \alpha \cos \beta - \sin \alpha \sin \beta = \cos(\alpha - \beta)$ . Thus functions like  $E_4^+ \equiv (E^{CCCC} + E^{SSCC})/2 = \langle \cos[(\omega_1 - \omega_2)t_p] \cos(\omega_3 t_p) \times \cos(\omega_4 t_p) \rangle$  can be obtained. By adding all four functions appearing in Eq. [1], one obtains  $E_4(t_{m2}) = \langle \cos[(\omega_1 - \omega_2)t_p] \cos[(\omega_3 - \omega_4)t_p] \rangle$  or its normalized pendant  $F_4(t_{m2}) \equiv E_4(t_{m2})/E_4(0)$ . As shown, e.g., in Ref. (8), 2t-SE's can be written analogously as  $E^{CC}(t_{m1})$  and  $E^{SS}(t_{m1})$ , where  $t_{m1}$  is a mixing time. Thus one has  $E_2(t_{m1}) \equiv [E^{CC}(t_{m1}) + E^{SS}(t_{m1})]/2$  and  $F_2(t_{m1}) \equiv E_2(t_{m1})/E_2(0)$ .

As can be seen in Fig. 1 seven pulses are sufficient to generate a 4t-SE since usually there is no need to let  $t_p \rightarrow 0$  in which case it is advisable to introduce additional pulses (19). To obtain signals of proper amplitude it is convenient to use "magic" flip angles of  $54.7^\circ$  for pulses 2, 3, 6, and 7. Maximum echo amplitudes can be achieved by using  $90^\circ$  ( $45^\circ$ ) flip angles for the generation and reconversion of the longitudinal (alignment) states that exist in the first and the third mixing times. In this latter case the relative initial amplitudes (as compared to those obtained by using magic flip angles) of the 4t-SE as given in Eq. [1] are 1, 3/4, 3/4, and 9/16, respectively.

In most previous studies the mixing times were kept longer than about 1 ms in order to have sufficient time for multiple-quantum coherences to decay. Hence no special efforts were required to develop dedicated phase cycles. Since one of the major drawbacks of the 4t-SE method is that it is applicable only over a narrow temperature range, it is highly desirable to extend the time window into the range below 1 ms. Therefore we have developed a more complete phase cycle. Since below we present measurements employing only the deuteron probe, in the following we focus on this nucleus. The design of the phase cycle is carried out as follows: One sets up the first part of the experiment in such a way that after the fourth pulse only longitudinal magnetization is present. This requires a minimum of 16 added signals. The computation of the necessary phases of pulses 1–4 was performed using the standard approximations (perfect nonselective pulses, no exchange during the evolution periods, absence of relaxation effects, etc.); see, e.g., Ref. (19). Tables 1 and 2 contain the cycles for generation of the pure  $I_z \cos(\omega_1 t_p) \cos(\omega_2 t_p)$  and  $I_z \sin(\omega_1 t_p) \times \sin(\omega_2 t_p)$  signals, respectively, as well as the partial receiver phases  $\sigma_A$ . Since no transverse magnetization is generated during  $t_{m2}$ , for the remaining pulses (5–7) a simple four-cycle scheme is sufficient in order to generate the desired 4t-SE signal. The phases of these pulses are collected in Tables 3 and 4.

The basic cycle for the 4t-SE's requires the combination of the pulses from the first two with those from the latter

TABLE 1

Minimum Phase Cycle Used to Generate a Pure  $I_z \cos(\omega_1 t_p) \cos(\theta_2 t_p)$  Signal in the First Half of the 4t-SE Experiment

	$\theta_1$ 90°	$\theta_2$ 90°	$\theta_3$ 90°	$\theta_4$ 90°	$\sigma_A$
1	+X	+X	+X	+X	+1
2	-Y	-Y	-Y	-Y	+1
3	-Y	-Y	+X	+X	+1
4	+X	+X	-Y	-Y	+1
5	-X	+X	+X	+X	-1
6	+Y	-Y	-Y	-Y	-1
7	+Y	-Y	+X	+X	-1
8	-X	+X	-Y	-Y	-1
9	+X	-X	+X	+X	-1
10	-Y	+Y	-Y	-Y	-1
11	-Y	+Y	+X	+X	-1
12	+X	-X	-Y	-Y	-1
13	-X	-X	+X	+X	+1
14	+Y	+Y	-Y	-Y	+1
15	+Y	+Y	+X	+X	+1
16	-X	-X	-Y	-Y	+1

Note. The flip angles are chosen in order to achieve maximum signal. The sign of the receiver phase (which should be set to  $\pm Y$  for the shown pulse sequence) is given by  $\sigma = \sigma_A \sigma_B$ .

two tables, i.e.,  $16 \times 4$  accumulations. For the generation, e.g., of an  $E^{\text{SSCC}}$  signal one must combine one row of Table 2 with another one from Table 3. The cycles are for convenience written such that the final, useful 4t-SE signal is along  $-I_y$ . Thus the receiver phase is set to  $\sigma Y$ . Here the sign  $\sigma$  is given by the product of the partial receiver phases,  $\sigma_A \sigma_B$ . Although the tables apply to the case where maximum signal

TABLE 2

Minimum Phase Cycle Used to Generate a Pure  $I_z \sin(\omega_1 t_p) \sin(\theta_2 t_p)$  Signal in the First Half of the Experiment

	$\theta_1$ 90°	$\theta_2$ 45°	$\theta_3$ 45°	$\theta_4$ 90°	$\sigma_A$
1	+X	+Y	+Y	+X	-1
2	+X	+Y	-Y	+X	+1
3	+X	-Y	+Y	+X	+1
4	+X	-Y	-Y	+X	-1
5	+Y	+X	+Y	+X	+1
6	+Y	+X	-Y	+X	-1
7	+Y	-X	+Y	+X	-1
8	+Y	-X	-Y	+X	+1
9	-Y	+X	+X	+Y	+1
10	-Y	+X	-X	+Y	-1
11	-Y	-X	+X	+Y	-1
12	-Y	-X	-X	+Y	+1
13	+X	+Y	+X	+Y	+1
14	+X	+Y	-X	+Y	-1
15	+X	-Y	+X	+Y	-1
16	+X	-Y	-X	+Y	+1

TABLE 3

Minimum Phase Cycle Used to Generate an  $A_z I_z \cos(\omega_3 t_p) \cos(\theta_4 t_p)$  Signal in the Second Half of the Experiment

	$\theta_5$ 90°	$\theta_6$ 90°	$\theta_7$ 90°	$\sigma_B$
1	+X	+X	+X	+1
2	+Y	+Y	+X	+1
3	-X	+X	+X	-1
4	-Y	+Y	+X	-1

Note.  $A_z$  is the longitudinal magnetization present just before pulse 5.

intensity is achieved (use of 45° and 90° pulses, only) usually more than 64 signals will have to be accumulated in order to obtain a sufficient signal-to-noise ratio. Therefore scans with all phases shifted by 90°, 180°, and 270° (CYCLOPS) are a further means to compensate for nonidealities of the spectrometer.

In order to excite the entire spectra of the amorphous samples, the lengths of the 90° pulses were set to about 3  $\mu$ s. In order to obtain a well-defined initial state a waiting time of at least  $5T_1$  should be maintained between the accumulation scans. This requirement can usually be met easily if the spin-lattice relaxation time  $T_1$  is exponential. Otherwise the repetition time should be five times longer than the longest component in the  $T_1$  distribution. If this time is not afforded then additional selection via spin-lattice relaxation which in fact may be useful in itself (20) is implicitly employed to generate the dynamic subensemble.

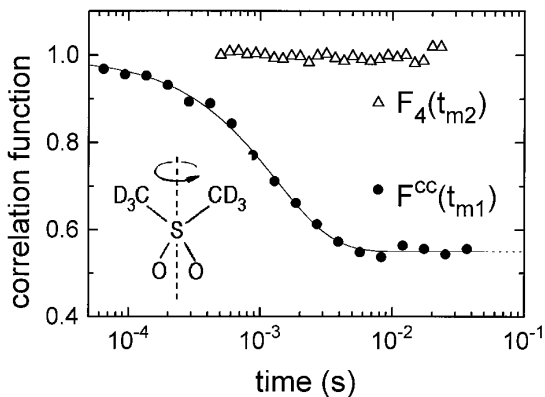
#### SINGLE EXPONENTIAL RELAXATION: ABSENCE OF RATE EXCHANGE

Dimethylsulfone molecules as sketched in Fig. 2 are well known to perform 180° flips in the solid state (15-17). Near room temperature the methyl groups carry out rapid threefold jumps leading to partially averaged deuteron field gradient tensors with principal axes oriented along the C-S bonds. Due to the molecular geometry each two-site flip reorients the principal axis of the tensors by an angle that is slightly larger than the tetrahedral one.

TABLE 4

Minimum Phase Cycle Used to Generate a Pure  $A_z I_z \sin(\omega_3 t_p) \sin(\theta_4 t_p)$  Signal in the Second Half of the Experiment

	$\theta_5$ 90°	$\theta_6$ 45°	$\theta_7$ 45°	$\sigma_B$
1	+X	+Y	+Y	-1
2	+Y	+X	-Y	-1
3	+X	+Y	-Y	+1
4	+Y	+X	+Y	+1



**FIG. 2.** Two-time and four-time correlation functions of DMS- $d_6$ . Both functions are scaled to unity for mixing times  $\rightarrow 0$ . The inset shows a sketch of the molecular structure.

We have studied a polycrystalline sample of fully deuterated DMS at a temperature of 314 K. First we have measured the spin-alignment signal for several evolution times  $t_p$ . As expected the  $\langle \sin(\omega_1 t_p) \sin(\omega_2 t_p) \rangle$  function decayed in an exponential fashion with a time constant  $\tau$  that is independent of  $t_p$ . We obtain  $\tau = 1.3$  ms in accord with previous studies. The decay time of the quadrupolar order is found to be much longer,  $T_{1Q} = 35$  ms. For subsequent measurements we have, for convenience, chosen  $t_p = 15 \mu\text{s}$ . The two-time correlation function  $\langle \cos(\omega_1 t_p) \cos(\omega_2 t_p) \rangle$  normalized using the independently measured spin-lattice relaxation time,  $T_1 = 21$  ms, is shown in Fig. 2. It decays in an exponential fashion to a value near 0.5 indicative for a two-site jump process (21). Since no rate exchange is possible in this crystalline substance, the four-time correlation function  $\langle \cos[(\omega_1 - \omega_2)t_p] \cos[(\omega_3 - \omega_4)t_p] \rangle$  should be constant. As can be seen in Fig. 2 this expectation is nicely confirmed by the experimental data.

### RATE EXCHANGE IN A SUPERCOOLED LIQUID

In order to test the performance of the phase cycle we have used fully deuterated, supercooled *ortho*-terphenyl which has been studied before using 4t-SE's (5). For the measurements presented in Fig. 3 we have chosen a temperature of  $T = 257.7$  K. Here the spin-lattice relaxation time,  $T_1 = 0.70$  s, was used to normalize the  $t_{m2}$  dependence of the 4t-SE's. The filter times  $t_{m1} = t_{m3}$  were set to 0.7 ms (22) and the evolution interval was  $t_p = 25 \mu\text{s}$ . In Fig. 3 it is seen that  $E^{\text{CCCC}}$  and  $E^{\text{SSSS}}$  functions strongly depend on  $t_{m2}$  while there is only little variation with this mixing time for  $E^{\text{CCSS}}$  and  $E^{\text{SSCC}}$ . All curves show a smeared step and for long  $t_{m2}$  the 4t-SE's exhibit well-defined plateau values. From the data alone it cannot be ruled out that for mixing times  $t_{m2} \gg T_1$  the 4t-SE's will be not constant. However, since neither the spin-lattice relaxation decay

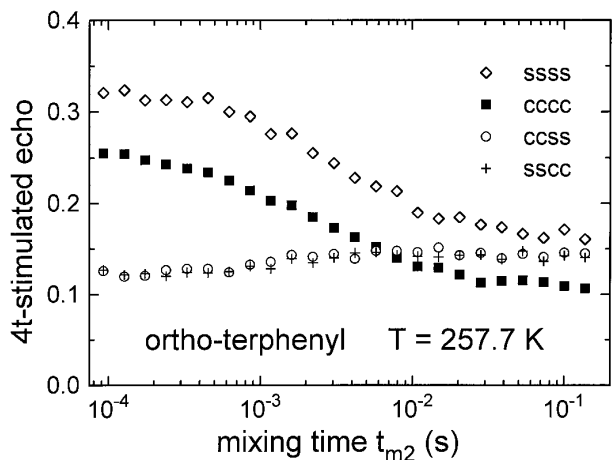
curves nor the 2t-SE's show indications for a two-step decay it appears very unlikely that the 4t-SE's will depend on  $t_{m2}$  for longer times.

As far as the short time limit of the rate exchange period  $t_{m2}$  is concerned we note that for the data shown in Fig. 3 we have  $t_{m2} \geq 3t_p$ . As can be inferred from Fig. 3 the 4t-SE's are constant to within experimental error for shorter  $t_{m2}$ . This means that essentially no rate exchange takes place during the evolution periods. A detailed analysis and interpretation of this type of data can be found elsewhere (6).

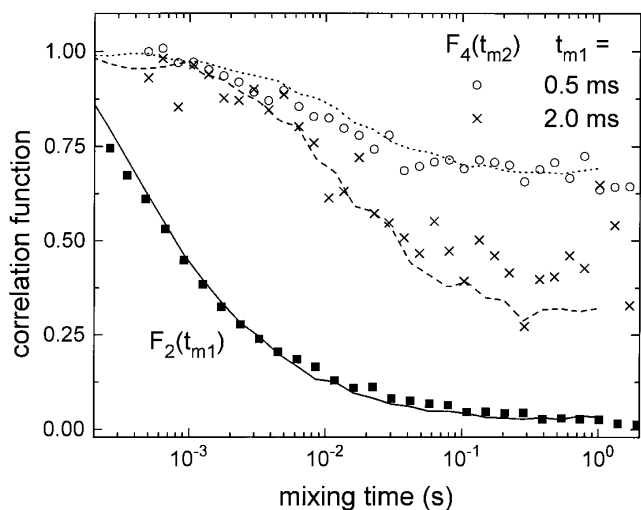
### FILTERING IN THE PRESENCE OF ROTATIONAL DIFFUSION?

We have used the colloidal polystyrene- $d_8$  spheres suspended in a protonated 1:4 glycerol:water mixture that has been studied previously (18). For our investigation we have chosen a sample for which the volume fraction of the solid material is 35.2%. The measurements that are shown below were taken at  $T = 286$  K. At this temperature the rotational correlation function could be characterized using a stretched exponential function  $\Phi(t) \propto \exp[-(t/\tau)^\beta]$  with  $\langle \tau \rangle = 35$  ms and  $\beta \approx 0.7$  (18). From the solvent viscosity  $\eta$  and  $\langle \tau \rangle = 4\pi\eta r^3 / (3k_B T)$  the mean particle radius was estimated to be  $r = 250$  nm in good agreement with results from light scattering. The small size dispersity of the polystyrene spheres was found to be insufficient to explain the stretching of  $\Phi(t)$  (18).

In order to characterize the colloidal system in a way which is similar to that of the other materials we have measured the correlation functions with an evolution time of  $t_p = 30 \mu\text{s}$  (23). The results are shown in Fig. 4. It is seen that  $F_2(t)$  decays on a time scale of about  $\tau_2 = 1$  ms, i.e., much faster than  $\Phi(t)$ , as generally expected for rotational



**FIG. 3.** Various 4t stimulated echoes as a function of the rate exchange interval  $t_{m2}$ . The measurements have been carried on a previously characterized *ortho*-terphenyl sample (5, 13).



**FIG. 4.** Normalized two- and four-time correlation functions of a colloidal suspension of deuterated polystyrene in a viscous medium. All measurements were taken at  $T = 286$  K using an evolution time  $t_p = 30$   $\mu$ s. The lines are the results of simulating rotational jump motion with a jump angle of  $\varphi = 1^\circ$  but not including dynamic rate exchange as described in the text. Good agreement is obtained within the experimental uncertainty (and taking into account the “noise” in the simulated curves). Hence when  $t_p$  is not chosen such that  $F_2$  represents the angular jump function, then a considerable rotational contribution can show up in  $F_4$ .

diffusion (24). But it must be stressed that, unlike in the previous examples, in the present case  $F_2$  cannot be considered the angular jump correlation function. It is seen that  $F_2$  decays in a nonexponential fashion. This behavior can be described by a stretched exponential with an exponent of  $\beta \approx 0.42$  or, alternatively, by a log-Gaussian distribution of correlation times; cf. the solid line in Fig. 4. Neither one of these descriptions is however fully satisfactory.

The 4t-SE’s  $F_4$  corrected for spin–lattice relaxation ( $T_1 = 2.34$  s,  $\beta = 0.71$ ) are shown in Fig. 4 for  $t_{m1} = t_{m3} = 0.5$  and 2 ms. The final plateau values decrease with increasing  $t_{m1}$  while the characteristic time scales of the  $F_4(t_{m2})$  functions increase. Furthermore the stretching of these functions is less pronounced than that of  $F_2$ . All these observations, at first glance, are similar to those made in supercooled liquids (5). However, in the following we will see from straightforward simulations (25) that in the present case no dynamic exchange need be involved in order to explain the shape and time dependences of the 4t-SE’s.

We have simultaneously simulated the two- and four-time echo functions using a continuous time random walk method as follows (26): In the first step we have generated  $\theta(t)$  trajectories, where  $\theta$  is the angle enclosed by the direction of the external magnetic field and the principle axis of the electric field gradient tensor at the deuteron site. The lifetime  $t_{it}$  of an angular state  $\theta_i$  was drawn at random from an exponential waiting-time distribution  $p(t_{it}) \propto \exp(-t_{it}/\tau_m)$  as is appropriate for a Poisson process (27). Then a random

rotational jump involving a jump angle  $\varphi$  was performed; i.e.,  $\theta_{i+1} = \arccos[\sin \theta_i \sin \varphi \cos \psi + \cos \theta_i \cos \varphi]$  was determined, with  $\psi$  chosen at random between 0 and  $2\pi$ . From the trajectories the correlation functions have been calculated according to Eq. [1] in a straightforward manner. In order to obtain a powder average the procedure was repeated about  $10^5$  times and care was taken that the starting angles were isotropically distributed. The mean values  $\tau_m$  of the waiting time distributions were drawn from a Gaussian characterized by a width that was adjusted such that a reasonable match with the  $F_2$  function was achieved. For a given trajectory the magnitude of  $\tau_m$  was kept constant; i.e., no dynamical exchange was allowed for. The rotational diffusion process was mimicked by using jump angles  $\varphi = 1^\circ$ .

The results of our calculations as presented in Fig. 4 are seen to describe the 4t-SE’s very well. This means that even without taking rate exchange into account the 4t-SE’s can show a pronounced dependence on  $t_{m2}$  if the evolution time  $t_p$  is too small to allow for an effective filtering. In such a case the four-time correlation functions are obviously seen to contain contributions from the rotational correlation decay.

## SUMMARY

The 4t-SE technique was previously applied to supercooled liquids and polymers only. These substances are characterized by rotational jump angles of the order of (some)  $10^\circ$  and furthermore the mixing times were restricted to the range above about 1 ms. We have introduced a phase cycle which removes unwanted multiple-quantum coherences thereby allowing one to extend the dynamical range of the method by about one decade as demonstrated for supercooled *ortho*-terphenyl. Using a material for which no rate exchange is possible, we then investigated whether the  $F_4$  function shows the expected independence on  $t_{m2}$ . Our results on DMS in which the molecules perform  $180^\circ$  flips show that this is indeed the case. Most instructive is our study of a colloidal suspension. Here the particles undergo a rotational diffusion process so that no efficient geometric filtering is possible using a finite evolution time  $t_p$ . We have found that in such circumstances the 4t-SE can be dominated by contributions not from dynamic rate exchange but from the rotational motion.

## ACKNOWLEDGMENTS

We thank B. Geil for making available the DMS sample, J. Kanetakis for supplying the polystyrene suspension, and S. C. Kuebler for discussions. Financial support by the Sonderforschungsbereich 262 (D9) is gratefully acknowledged.

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21. Note that the plateau value oscillates around 0.5 and is reached asymptotically for  $t_p \rightarrow \infty$ .
22. The two-time echo  $E^{CC}$  decays with an average relaxation time of 4.2 ms; see Ref. (6).
23. Due to rapid transverse dephasing much longer evolution times are impracticable, anyway.
24. J. E. Anderson, *Faraday Symp. Chem. Soc.* **6**, 82 (1972). We note that for larger values of  $t_p$  even faster decays are to be expected for  $F_2(t)$  since  $\tau_2 \propto \langle \varphi^2 \rangle$  for small rotation angles  $\varphi$ .
25. Analytical calculations are possible; however, these hardly converge in the limit of small jump angles; see S. Wefing, S. Kaufmann, and H. W. Spiess, *J. Chem. Phys.* **89**, 1234 (1988).
26. For a more complete description, see Ref. (7).
27. N. G. van Kampen, "Stochastic Processes in Physics and Chemistry," North-Holland, Amsterdam (1992).