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Enhancement of the accuracy of determination of transverse relaxation time in solution state NMR spectroscopy by using Uhrig's dynamic decoupling sequences

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Recently, a sequence with a set of non-equidistant π pulses, often referred to as the Uhrig's Dynamic Decoupling (UDD) sequence has been proposed which is shown to be more efficient in suppressing the time dependent systematic sources of dephasing originating from a bosonic bath. This work aims to investigate the potential of such non-equidistant sequences for more accurate measurement of the transverse relaxation time (T_2 in liquid state NMR. We have shown experimentally that the dynamic decoupling schemes can estimate T_2 more accurately than equidistant pulse sequence by suppressing the dephasing effects of field noise in solution state.

I. INTRODUCTION

The estimation of the transverse relaxation rates remains an important aspect of NMR spectroscopy owing to its applications in diverse fields ranging from the study of the internal motions of large molecules, the use of contrast imaging by magnetic resonance imaging (MRI), to the decoherence of qubits in the context of quantum computations and others [1–4]. The important sources of decoherence in liquid state NMR are molecular reorientations, static magnetic field inhomogeneities, molecular translational diffusion, field noise, presence of paramagnetic centres etc. In order to accurately determine the decoherence rate originating from molecular re-orientations i.e. molecular rotational diffusion, it is imperative to remove other sources of decoherences. It has been demonstrated that periodic inversion of the coherences using π pulses (echo sequences) lead to the suppression of the inhomogeneous broadening from the static magnetc field inhomogeneity contributions [5]. A generalization of spin echo sequence was proposed by Carr, Purcell and later modified by Meiboom and Gill. The scheme, commonly referred to as CPMG arrests decoherences due to the static magnetic field inhomogeneity and also due to translational diffusion, is widely employed for the determination of T_2 [6, 7]. Uhrig's Dynamic Decoupling (UDD) scheme was originally developed in the context of nuclear spins coupled to a bosonic bath, a situation often encountered in solid state NMR [8–10]. It has been shown that DD sequences can successfully enhance the transverse relaxation time of a solid state qubit system [11]. Jonas Bylander and others have demonstrated that the dynamic decoupling sequences improved the coherence time of a superconducting spin system up to $T_2 = 2T_1$ limit [12]. It has been shown that the performance of various DD sequences depends on the nature of the noise present in the system [13–15]. UDD has been theoretically shown to be optimal in suppressing decoherence due to a classical stationary Gaussian noise with hard cut-off [13, 17]. On the other hand, for soft cut-offs and for stationary telegraph noises, CPMG is the optimal sequence [14, 15].

This work aims to investigate whether DD sequences could be chosen as a superior method for routine measurement of transverse relaxation times of liquids in the presence of field noise. The field noise is assumed to be manifested in the form of a time varying magnetic field, which may originate from the leakage currents in the the shim coils or from the magnetic field drift and inefficient locking mechanism. Considering the fact that the locked magnetic field does not drift away from the target value in the long run, we speculate that the field noise (from the finite drift of the magnetic field) could be considered as a stationary classical noise.

Since DD sequences has been shown to suppress the slowly varying magnetic field effects [16, 17], it is expected that it would suppress the field noise of any kind as long as the variation of field noise with time is slow compared to the refocusing time scale. The actual extent of this noise is expected to vary from spectrometer to spectrometer[18]. However, we show later that main conclusions drawn from this study is not affected by the actual extent of field noise.

II. UDD

In the following two sections the main results of Uhrig's work and it's derivative sequences are summarized which would be repeatedly used in our work. Uhrig's work concerns with a single spin coupled to a bosonic bath which is modelled as an ensemble of harmonic oscillators with a high frequency cut-off. The bath mimics low frequency phonons present in a solid. It has been shown that a set of non-equidistant π pulses applied on the spin, more efficiently suppresses the decoherence from the spin-boson

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coupling when compared to equidistant pulse schemes. [8–10]. As shown by Uhrig, the positions of the pulses must obey a relation given by,

$$t_j = T \sin^2\left(\frac{\pi j}{2n+2}\right) \quad (1)$$

where, T is the total duration of a pulse sequence having n number of pulses, t_j denotes the time at which the j^{th} pulse is applied [8]. The sequence has earlier been reported by Deepak Dhar et al. who found similar pulse instances by minimizing the leakage probability to the orthogonal subspaces using non-uniform sequences of up to 5 π pulses [19].

Later it has been shown that the applicability of UDD is not restricted to the spin-boson problem as it remains the optimum sequence for suppressing the first n terms of any accumulated phase error that can be represented as a polynomial in time [16]. For the slow fluctuations (slow compared to the time scale of the measurements, which in NMR usually ranges from milliseconds to seconds), of the effective field, a Fourier series representation could be used to analyze the accumulated phase. Such a series is convergent and as such, the removal of the first n terms suppresses the decoherence. This remains the principal reason behind the effectiveness of UDD and its derivative sequences in the context of field noise.

III. RUDD

Among the derivatives of UDD, the Realistic UDD (RUDD) sequence includes correction for the pulses of finite duration [20, 21]. RUDD sequence uses π pulses of variable duration and amplitudes, where the spacing of pulses are exactly similar to the UDD sequence. The success of RUDD sequence relies on the suppression of dephasing during the pulse as well as due to pulse imperfections. The duration of the j^{th} π pulse (τ_j) is given by,

$$\tau_j = \tau_1 \left(\frac{\sin j\theta}{\sin\theta}\right) \quad (2)$$

where, τ_1 is the duration of the 1^{st} pulse and $\theta = \pi/(n+1)$ in an 'n' pulse sequence [20].

The amplitude of the j^{th} π pulse (ν_j) can be calculated using the relation [20]

$$2\pi_j \nu_j \tau_\pi^j = \pi. \quad (3)$$

It has been shown that n pulse UDD and RUDD sequences work as high pass filter, where as CPMG does not exhibit a strict high pass behaviour [13]. Therefore, UDD or RUDD could be used as a probe to monitor the extent of slow motions of various systems, notably polymer or gel like substances.

A. Suppression of field noise

Field noises may have different sources as mentioned above, but it originates possibly most often from the lock-adjustment mechanism in the spectrometer. Typically this produces a small time dependent fluctuation of the Zeeman field [17, 18]. Let the magnetic field in the presence of the field noise be represented by $B_{tot} = B_\circ + B(t)$, where $B_\circ$ is the static magnetic field and $B(t)$ is an arbitrary function of time which can be approximated by a polynomial (since the acquisition time is finite) as

$$B(t) = \sum_i c_i t^i, \quad (4)$$

If a single quantum coherence is created and the evolution of the same is monitored in a reference frame, rotating with $\omega_\circ = -\gamma B_\circ$, the phase accumulation ($\phi_n(t)$) of the observable x-magnetization can be given by,

$$\phi_n(t) = \gamma \int B(t')dt' \quad (5)$$

The collected free induction decay shows fluctuations as expected from the random nature of $B(t)$. After signal averaging over multiple scans, the complex part of the magnetization could be written, in the spirit of time dependent purturbation theory, after a second order cumulant expansion as:

$$\langle M_x \rangle = M_x \, e^{i\langle\phi_n\rangle_t} \, e^{-\frac{1}{2}[\langle\phi_n^2\rangle_t - \langle\phi_n\rangle_t^2]} \quad (6)$$

It is important to note that the coefficients c_i vary in different scans and we denote the average phase accumulated by $\langle\phi_n\rangle_t$ and the decoherence from the field noise by $\langle\phi_n^2\rangle_t$, where the angular brackets $\langle\rangle_t$ indicate temporal averaging over multiple scans. It is assumed that the c_i s are stochastic Guassian variables since the contributions of the noise at various orders are expected to be sampled from a normal distribution. Over a large number of scans, $\langle\phi_n\rangle_t = 0$ due to the assumed stochastic nature of c_is and the magnetization decays due to the quadratic term $\langle\phi_n^2\rangle_t$. For a particular scan, ϕ_n could be written as a convergent polynomial series, since the aquisition time is finite. From equations 4 and 5, the phase acquired due to noise can be calculated as,

$$\phi_n = \gamma \sum_i \frac{c_i}{i+1} t^{i+1} \quad (7)$$

An n pulse UDD removes the first n terms which appear in the right hand side of the equation 7, where as an n pulse CPMG scheme can completely remove only the 1^{st} term of the same polynomial. Therefore, if the total time of acquisition remains finite, UDD would be a superior sequence for arresting decoherence originating from the field noise when compared to CPMG. Using similar arguments, it is expected that RUDD would be even more efficient in suppressing decoherence due to the

field noise, since this specific sequence is designed to take into account the effects of finite pulse duration.

The relaxation rate of a single quantum coherence of a single spin which (i) is embedded in a molecule undergoing fast rotational diffusion (leading to motional narrowing), (ii) evolves in the presence of relatively slowly varying field noise and static magnetic field inhomogeneity can be written as,

$$\frac{1}{T_2^\star} = \frac{1}{T_2} + J_{\rm FN} + R_{\rm inhom} \qquad (8)$$

where, $T_2^\star$ denotes the measured transverse relaxation time, T_2 denotes the transverse relaxation time from the fast stochastic rotational diffusion of the spin-bearing molecules, $J_{\rm FN}$ denotes the spectral density of the slowly varying field noise and is equal to the Fourier Transform of the time correlation of the field noise. $R_{\rm inhom}$ indicates the contribution from the static magentic field inhomogeneity. In the standard literature of NMR, usually the $J_{\rm FN}$ term is ignored. All symmetric sequences involving π pulses (CPMG, UDD and RUDD in this case) completely remove the $R_{\rm inhom}$ term. It is clear from equation 8 that $T_2^\star < T_2$ in the presence of $J_{\rm FN}$ and $T_2^\star$ would be longer or closer to T_2 when $J_{\rm FN}$ is suppressed.

The DD sequences from Uhrig provide a relatively sharp $1/\tau$ high pass cutoff where τ is the average time between the pulses, i.e. only the low frequency component of the noise (frequency smaller than the cutoff) are suppressed. For CPMG, no such sharp cutoff exists. The figures 2 and 3 of the reference [17], clearly demonstrates the situation. Therefore, CPMG having a soft cutoff, may remove $J_{\rm FN}$ partially, whereas, UDD and RUDD are expected to be much more effective in removing the same. Hence the measured $T_2^\star$ would be nearly equal to T_2 when it is measured with a DD sequence. In the following section we experimentally verify the claim.

IV. EXPERIMENTAL

All experiments were performed on an 11.78 T Bruker Avance III spectrometer at room temperature. To investigate the performance of various pulse schemes (CPMG, UDD and RUDD), we have chosen five different molecules with different molecular weights and consequently different rotational correlation times. The chosen spin systems are

- H_1 proton (at 7.7 ppm) of Caffeine (1,3,7-Trimethylpurine-2,6-dione, shown in figure 1, molecular weight $\approx$ 0.19 kDa) dissolved in D_2O,
- H_1, H_2 protons (magnetically equivalent, at 6.9 ppm) of Durene (1,2,4,5-Tetramethylbenzene, shown in figure 1, molecular weight $\approx$ 0.13 kDa) dissolved in deuterated DMSO.
- protons of H_2O (magnetically equivalent, at 4.7 ppm), from an H_2O and D_2O mixture of 1:1 volumetric ratio,
- H_1, H_2, H_3 and H_4 protons (magnetically equivalent, at 8.6 ppm) of a naphthalene diimide based molecule, henceforth referred to as NDI (2,7-Didodecyl-3a,5a-dihydrobenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetranone, molecular weight $\approx$ 0.6 kDa) dissolved in deuterated Chloroform.
- four of the backbone amide protons (at 8.4 ppm from Amino-buteric acid, at 8.0 ppm from L-Alanine, at 7.7 ppm from Valine and at 7.4 ppm from D-Alanine) of a polypeptide Cyclosporine-A (molecular weight $\approx$ 1.2 kDa) dissolved in deuterated Benzene.

All of the above molecules were commercially available with more than 99% purity except NDI, which was obtained from one of the spectroscopy laboratory of the institute. None of the above molecules are known to undergo conformational or spin exchange.

Except for Cyclosporine-A, the selected protons either do not exhibit measurable scalar coupling with other nuclei of the same molecule or are magnetically equivalent. The choice ensures that the decay of the measured echoes are free from modulations due to scalar coupling and the relaxation rates could be estimated using mono-exponential fitting of the relaxation data. For Cyclosporine-A, the assignments were taken from the work of Oschinat et. al. [22]. The backbone protons which give four clear and non-overlapping doublets were chosen from the finger-print region of the proton 1D spectrum.

The time instants of both the UDD and RUDD schemes were estimated using equation (1). For RUDD sequence, the duration of π pulses were calculated using equation 2. All experiments involving echo sequences used similar phase cycles to ensure that only refocusing is used for the generation of echoes. The strength of the applied radio-frequency field was 17.48 KHz for both UDD and CPMG experiments. For RUDD, same power was used for the first pulse of the sequence and for the subsequent pulses, equation 3 was used for the calculation of powers.

The experiments were performed using two protocols as shown in the Fig. 2. In the first protocol (henceforth referred to as n-protocol), the number of pulses (n) was kept fixed for the collection of an echo and duration of the pulse block T was varied such that the echoes could be obtained after T. In the second protocol (henceforth referred to as T-protocol), the lengths of the pulse blocks (T) were kept fixed (each having n pulses) and the pulse blocks were repeatedly used (concatenated). The echoes were collected after the application of an integer multiple of pulse blocks. For Cyclosporin-A, to avoid the echo modulations due to the scalar coupling, we have

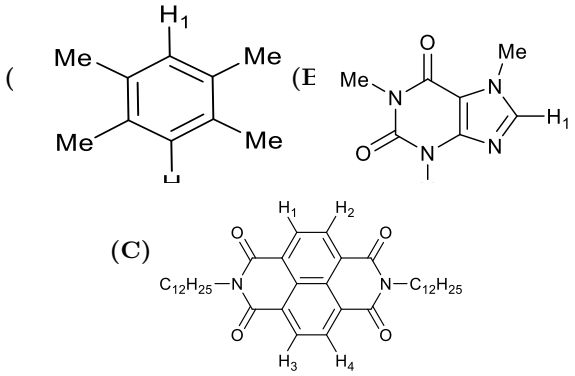

FIG. 1. The chosen spin systems: (A) H_1 and H_2 of Durene, (B) H_1 of Caffeine and (C) H_1, H_2, H_3, H_4 of NDI.

TABLE I. Table showing T_2 values of selected protons of Caffeine, Durene and water recorded using n-protocol. The numbers in the parentheses indicate the errors in the last digit of printed T_2 values.

		Durene	Caffeine	Water	NDI
Sequence	n	T_2 (s)	T_2 (s)	T_2 (s)	T_2 (s)
CPMG	8	0.30(2)	0.43(4)	0.58(4)	0.97(8)
	12	0.32(3)	0.53(4)	0.62(3)	1.02(5)
	16	0.48(4)	0.54(4)	0.64(3)	1.06(7)
	8	0.36(4)	0.47(4)	0.77(2)	1.23(7)
UDD	12	0.42(4)	0.58(7)	0.79(1)	1.22(5)
	16	0.48(6)	0.62(6)	0.82(1)	1.29(5)
	8	0.48(6)	0.59(7)	0.80(5)	1.21(5)
RUDD	12	0.8(1)	0.8(1)	0.80(5)	1.23(7)
	16	1.5(7)	1.0(2)	0.93(1)	1.30(5)

performed only T-protocol with the small pulse block time of 1 and 5 ms. Since the n-protocol involves much longer delay values, this protocol was not used for the determination of T_2 for cyclosporine to avoid the coupling induced modulation. In all tables, for notional simplicity, measured transverse relaxation time is denoted as T_2 and not $T_2^\star$.

To exemplify the presence of the field noise, the proton spectrum of $CHCl_3$, dissolved in Acetone-D_6 was repeatedly recorded to collect a series of free induction decay (FID). The spectral width was chosen to be small enough to avoid the ^{13}C satelite peaks. Each FID was recorded using a single scan to avoid the averaging of noises. The complex part of the recorded FID yields the first order contribution of the field noise as is evident from equation (6). Some of the recorded FIDs show the presence of the field noise in the form of sinusoidal transients.

TABLE II. Table showing T_2 values of H_1 of Caffeine as obtained by using T-protocol. The numbers in the parentheses indicate the errors in the last digit of printed T_2 values.

		CPMG	UDD	RUDD
n	T (ms)	T_2 (s)	T_2 (s)	T_2 (s)
8	10	1.82(4)	1.89(3)	2.13(6)
8	5	1.95(2)	2.06(5)	2.4(1)
16	10	1.9(2)	2.09(5)	2.9(2)
16	5	2.40(3)	2.64(5)	2.9(2)

TABLE III. Table showing T_2 values of the singlet coming from four chemically equivalent protons, labelled as H_1, H_2, H_3, H_4 of NDI obtained by using T-protocol. The numbers in the parentheses indicate the errors in the last digit of printed T_2 values.

		CPMG	UDD	RUDD
n	T (ms)	T_2 (s)	T_2 (s)	T_2 (s)
8	10.0	1.35(4)	1.57(1)	1.59(1)
8	5.0	1.48(4)	1.56(1)	1.58(1)
16	10.0	1.42(4)	1.55(1)	1.56(2)
16	5.0	1.46(4)	1.56(1)	1.58(3)

TABLE IV. Table showing T_2 values of backbone amide protons, J-coupled to $\alpha-$H for four selected amino acid residue of Cyclosporin-A. The residues are indicated in the header of the table as, Abu=Amino butyric acid, A1=L-Alanine, V=Valine and A2=D-Alanine. The numbers in the parentheses indicate the errors in the last digit of printed T_2 values. The '$-$' symbol represents distortion in obtained spectra, such that the deconvolution and subsequent extraction of T_2 values could not be carried out.

			H(Abu)	H(A1)	H(V)	H(A2)
Sequence	n	T (ms)	T_2 (s)	T_2 (s)	T_2 (s)	T_2 (s)
CPMG	8	5	0.16(1)	0.17(1)	-	-
UDD	8	5	0.16(1)	0.18(2)	0.23(2)	0.18(1)
RUDD	8	5	0.18(1)	0.22(1)	0.26(1)	0.23(1)
CPMG	8	1	0.15(1)	0.17(1)	0.19(2)	0.23(1)
UDD	8	1	0.17(1)	0.20(1)	0.25(1)	0.25(1)
RUDD	8	1	0.16(1)	0.18(2)	0.23(1)	0.25(1)

V. RESULTS AND DISCUSSION

Table I lists the T_2 values measured by various pulse schemes using n-protocol. The length of echo train T has been varied from 10 ms to 1 s. In all the cases, the T_2 values obtained by UDD are longer than the T_2 obtained by using CPMG. Similarly, the T_2 values obtained by RUDD are longer than or equal to that of UDD. Since the cutoff frequency for the echo sequences are $\sim 1/\tau$, therefore for an n pulse sequence having block time T (as in the T-protocol), the cutoff frequency would be n/T. Hence for the experiments with 10 ms block time and 8 pulses the cutoff frequency is 800 Hz where as for experiments with

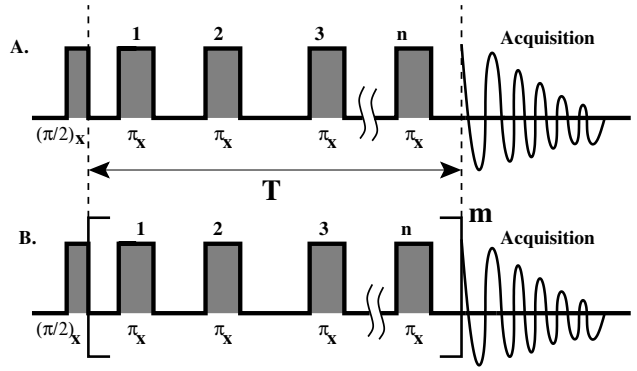

FIG. 2. A pictorial representation of pulse schemes of two experimental protocols: A. n-protocol, where n number of pulses are employed and T is varied to collect echoes at various times. and B. T-protocol, where $n \times m$ number of pulses are employed and echoes are collected after mT time. The brackets in subfigure B indicate the repetition of an n pulse block of duration T, resulting in a concatenated sequence.

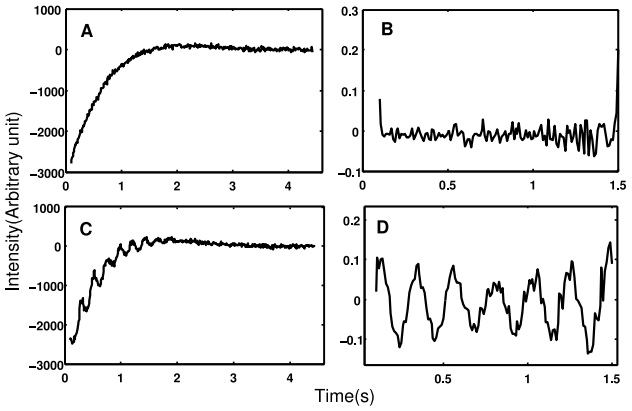

FIG. 3. An illustration of FID and corresponding field noise as extracted from two single scan experiments on $CHCl_3$ in Acetone-D_6. (A) shows an FID where no signature of the field noise was found. (B) shows the corresponding $\gamma B(t)$ extracted from the initial part of the FID in the unit of rad s^{-1}. (C) and (D) shows the similar sequences as before, but recorded in the presence of the field noise.

5 ms block time and 16 pulses the cutoff frequency is 3.2 KHz. Therefore, by appropriately comparing the T_2 values one may estimate the extent of the spectral densities originating from noises of various frequency components.

Table II and III lists the measured transverse relaxation times for the selected proton of Caffeine and NDI as obtained by T-protocol. The number of pulses used in each scheme were varied between 8 and 16, on the other hand, the durations of the pulse block (T) were also varied between 5 ms to 10 ms. The tables list the measured values of T_2 as the parameters of the measuring sequences are varied. The values of T_2 measured by RUDD and UDD are equal or longer when compared to CPMG for the same set of parameters (T and n). As the number of pulses applied in a given sequence is increased, the enhancement of measured T_2 values are observed. It is evident from the tabulated values of T_2 (shown in table I), for all the chosen systems – when compared to CPMG – the DD schemes consistently yield longer T_2 The T_2 from RUDD are generally longer than that of the UDD which in turn yields longer T_2 than the CPMG. For NDI molecule, UDD and RUDD show almost identical enhancements when compared to CPMG (Table III). Since the cutoff frequency is 800 Hz (for 8 pulses in 10 ms block time), the field noise frequencies are expected to be smaller than this cutoff. As a result, the lowering of the block time or increasing the number of pulses does not result in any further enhancement. Similarly, for the large polypeptide Cyclosporine-A, (R)UDD sequences yield improved values compared to CPMG, however within the experimental errors the performances of UDD and RUDD are almost same. This again hints at the frequency range of the field noise being smaller than the lowest cutoff used for the experiments (1.6 KHz corresponding to 8 pulses in 5 ms block time).

It is clearly shown from the table I, that there is a non-uniform enhancements of T_2 values for different molecules. The relaxation rates (inverse of T_2) are sum of the spectral densities of noises of various origin. The success of (R)UDD sequences relies on efficient suppression of the spectral densities of the low frequency noises. Hence, the difference of the inverse of lowest measured T_2 (from CPMG with smallest no of pulses for n protocol) and the highest measured T_2 (from RUDD with highest no of pulses for the same protocol) provides an approximate way of evaluating the enhancement. We find that the calculated enhancements are 2.7 Hz for Durene, 1.3 Hz for Caffeine, 0.65 Hz for water, 0.26 Hz for NDI and $\sim$ 1.4 Hz for various amide protons of the finger print region of Cyclosporine-A. Since there is no clear dependence of enhancements on the molecular weights of the samples (and therefore on the rotational correlation time), we attribute the enhancement to the varying degree of the field noise present during the experiments. The field noise is presumed to originate from the inefficient locking mechanism to correct for the magnetic field drift. Since such drifts are intermittent therefore the extent of the field noise may vary from time to time.

Often CPMG sequences are repeatedly applied with variable delay between pulses to probe motional time scales. We observe (from the reference [17]) that the frquencies at which noises are completely passed by CPMG and (R)UDD are nearly same, but UDD clearly suppresses the low frequency components, whereas CPMG partially removes such components. As a result, it is possible that if the sample is also subjected to slow motion or spin exchange with characteristic time of the order of milliseconds, then DD sequences would also remove the spectral densities originating from such sources since the nature of the phase accumulation by the spin systems would be nearly same for all slow stationary processes. If an efficient locking mechanism is employed to completely remove the field noise, then the extent of the

slow motion could be probed by varying the block time T and by using DD sequences with hard cutoff.

For the n-pulse DD and CPMG blocks of duration T, a smaller T results in a larger bandwidth of the pulse block. As a result, pulse block with smaller T results in longer T_2 values as one can verify from table II. So, the T-protocol DD sequence is a more suitable method for measuring T_2 Also, for a fixed T, increasing the number of pulses (n) results in better suppression of the field noise. Tables I, II, III and IV corroborate the observation.

Molecules under translational diffusion do contribute to the decoherences under linear magnetic field gradient, as shown in the pioneering works of Carr and Purcell [6]. However, in the absence of an external gradient the minimum spectral line-width achieved in the spectrometer is under 0.5 Hz which indicates the inhomogeneity is of the order of 10^{-4} gauss. Considering a sample length of 1 cm, the typical gradient experienced by the molecules are small enough so that the dephasing due to the translational diffusion $\gamma^2 G^2 D$ is negligible in the high resolution NMR spectrometer. As a result, the decoherence mainly originates from the field noise and the molecular reorientations. Since the time scale of the molecular reorientations is of the order of nanoseconds − picoseconds, the effects of such reorientations are not suppressed by the pulse sequences used in these experiments.

In order to avoid the additional artefacts due to evolution of homonuclear coupled spin systems (scalar coupling), usually the delays in CPMG are chosen to be small (compared to 1/4J). CPMG suppresses the heteronuclear couplings by inverting the spins of only one type (either ^{13}C or ^{1}H). Also the shorter delays are preferred in CPMG to avoid unwanted relaxation pathways from CSA-DD cross correlations. For the DD sequences, the refocussing effects (for homo- or heteronuclear scalar coupling) would be exactly similar as that of CPMG since the sequences are symmetric in time and use only π pulses like CPMG. The effects of CSA-DD cross-correlations should also have identical influence on the T_2 measurement as that of CPMG.

The signature of the field noise is evident from Fig. 3. The noise can be exemplified in the form of time dependent drift of the magnetic field which is corrected by the locking mechanism time to time, resulting in oscillatory nature . The magnetic field drift in the spectrometer is intermittent. The experimental proof of the effectiveness of dynamical decoupling sequences indirectly indicates the presence of field noise. It is expected that in the absence of field noise DD schemes and CPMG will result in same value of transverse relaxation time. Therefore, the DD schemes in general **are** claimed for to be the better method of measuring T_2.

A major disadvantage of the RUDD sequence is the low bandwidth of the pulses employed near the middle of the sequence. As a result of this low bandwidth, RUDD can effectively be used only for the systems which are nearly on resonance. As an example, for an 8 pulse RUDD block, the 4th and the 5th pulses were of almost 3 times the duration (1/3 of the bandwidth) of the 1st and the last pulses. While this does not pose a constraint for a sample with low spectral width, but for other nuclei which experience wide spectral widths (^{13}C, ^{19}F and others), this may result in loss of performance of RUDD sequences in comparison to UDD particularly near the tails of the spectrum.

On the other hand, UDD sequence which employs hard pulses of similar durations, suffer from no such disadvantages. For the determination of T_2 for a large number of shifts (as one needs for analysing the protons of proteins or similar large molecules), UDD would be the preferred method at the expense of the accuracy of the result.

VI. CONCLUSIONS

We have exemplified that a subclass of dynamic decoupling pulse sequences outperform the routinely used sequences such as CPMG for the measurement of the transverse relaxation time in liquid state NMR. The performance enhancement results from the better suppression of field noise which may have its origin in external vibrations, inefficient locking mechanism etc. Consequently, such sequences would result in better estimation of the molecular correlation time of liquid molecules. These new sequences are expected to play an important role in uncovering the dynamics of the large bio-molecules in solution state, which has a wide range of the transverse relaxation rates and also in the study of solvent relaxation in the context of polymer chemistry.

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