**Refocused Linewidths Less Than 10 Hz in 1H Solid-State NMR**

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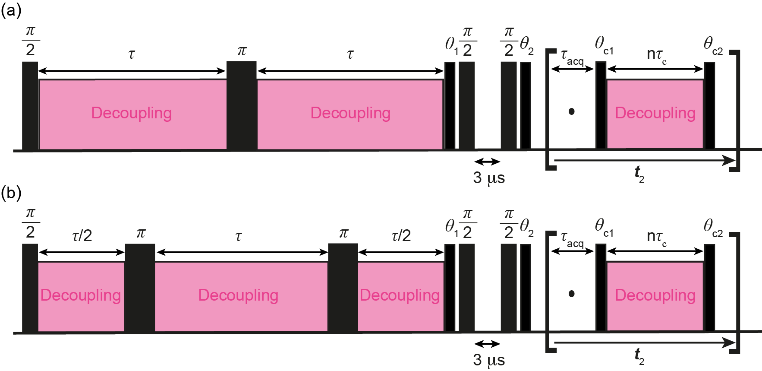
Abstract

**Coherence lifetimes in homonuclear dipolar decoupled 1H solid-state NMR experiments are usually on the order of a few ms. We discover an oscillation that limits the lifetime of the coherences by recording spin-echo dephasing curves. We find that this oscillation can be removed by the application of a double spin-echo experiment, leading to coherence lifetimes of more than 45 ms in adamantane and more that 22 ms in β-AspAla, corresponding to refocused linewidths of less than 7 and 14 Hz respectively.**

**1. Introduction**

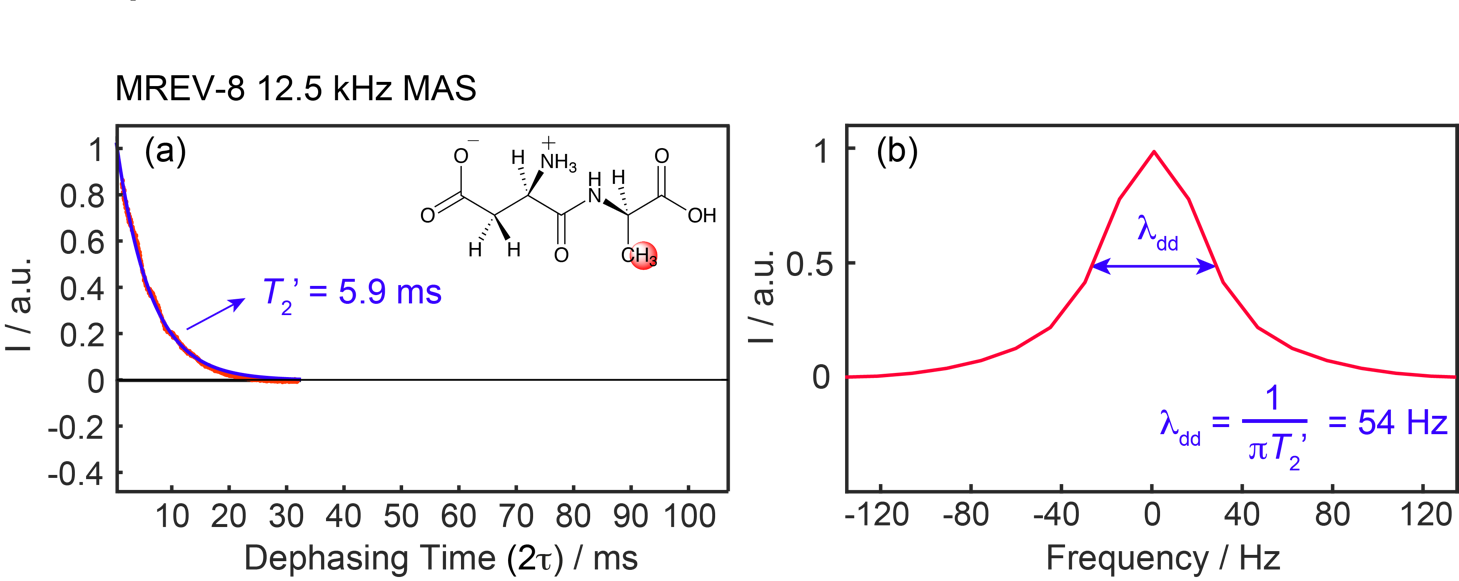
1H is by far the most commonly observed nucleus in solution state NMR spectroscopy, due to its ubiquity in chemistry, the high gyromagnetic ratio, the high natural isotopic abundance, and the rich information contained in 1H chemical shifts. In contrast, in solid-state NMR, the use of 1H NMR is limited. This is not because of a difference in the information content, but primarily for technical reasons, since the strong 1H homonuclear dipolar coupling network leads to linewidths in solids orders of magnitude larger than those in solution (where dipolar couplings are largely averaged out by molecular tumbling). This broadening masks underlying chemical shifts, significantly reducing the utility of solid-state 1H NMR spectra.

The 1H spectral resolution can be improved dramatically by using combined rotation and multi-pulse spectroscopy (CRAMPS) approaches [2], involving the simultaneous application of magic angle spinning (MAS) [3, 4] and pulse sequences that lead to homonuclear dipolar decoupling while retaining isotropic chemical shifts. Originating in the pioneering work of Lee and Goldburg [5] and Waugh and co-workers [6] many homonuclear dipolar decoupling sequences have been developed so far. These include schemes based on the LG sequence, such as FFLG, FSLG and PMLG, [7-9] and schemes based on WHH-4, such as MREV-8 and BR-24 [10-12]. .Other strategies to average out higher orders of the dipolar coupling Hamiltonian include high order truncation (HOT) [13, 14] and symmetry based multiple-pulse sequences [15]. An alternative approach was introduced by Sakellariou et *al*. with the introduction of DUMBO-1 [1, 16], a decoupling scheme found by numerical optimization. The same approach, but using direct experimental optimization gave birth to the eDUMBO family [17, 18] and to LG4 [19, 20]. These are today considered the state of the art decoupling sequences, together with PMLG [21]. With these pulse sequences it is possible to reduce the linewidths of the proton peaks by two orders of magnitude, which is enough to distinguish the isotropic chemical shifts in relatively simple organic solids. Note that the substantial improvement in resolution is, as always with such spectra, obtained at the expense of sensitivity, which decreases due to the need to open the noise filters to allow fast detection. However, despite this remarkable progress, natural abundance proton spectra are still characterized by linewidths exceeding 100 Hz, and the reasons for this apparent limit on 1H resolution are still not well understood.



**Figure 1**. Single echo (a) and double echo (b) pulse sequences for *T*2’ measurements. The detailed pulse program, experimental details for the spectra recorded, and the phase cycle are given in the experimental section and the ESI. The angles *θ*1 and *θ*2 are adjusted according to the decoupling sequence used during *t*1 and *t*2 evolution [1].

Here, we probe the limits on resolution by measuring transverse dephasing times (*T*2’) [22] under homonuclear decoupling. We find that coherence lifetimes are limited by the appearance of a coherent oscillatory behaviour that leads to a residual anisotropic splitting. We characterise this behaviour in series of organic solids, where it appears to be general, and we show that the symmetry of the interaction is such that it responds to π pulses in different ways. We find that the oscillation can be completely removed in a double spin-echo experiment. This leads to coherence lifetimes of more than 45 ms in adamantane and more that 22 ms in β-AspAla, corresponding to refocused linewidths of less than 7 and 14 Hz respectively.



**Figure 2**: (a) Dephasing curve for the CH3 resonance of powdered β-AspAla recorded using the pulse sequence of Figure 1a. The spectra were acquired with a MAS rate of 12.5 kHz. During 2*τ* the MREV-8 sequence was used for decoupling, with 156.25 kHz 1H RF power (90° pulse length of 1.6μs) and length of a decoupling cycle (*τ*c) of 31.8μs. A total of 512 2*τ* values were used, each one acquired with 32 scan. Experimental points are shown in red, and the blue line corresponds to the best fit to an exponential decay, leading to a *T*2’ of 5.9 ms. (b) Fourier transform of the experimental dephasing curve shown in (a). The full linewidth at half-height is measured to be 54 Hz.

**2. Experimental**

The powdered samples of β-AspAla ((2S)-2-amino-3-{[(1S)-1-carboxyethyl]carbamoyl}propanoic acid, purity > 99%), alanine (2-aminopropanoic acid, purity > 99%) and adamantane (Tricyclo[3.3.1.13,7]decane, purity > 99%) were purchased from Bachem, Acros Organics and Sigma-Aldrich respectively. All samples were used without further purification.

Experiments were performed on Bruker Ascend 400 and Ascend 500 wide-bore Avance III NMR spectrometers operating at Larmor frequencies of 400.13 and 500.43 MHz, equipped with H/X/Y 3.2mm and 1.3mm probes. When the 3.2mm probe was used, the samples were restricted to the central third of a rotor with inner diameter of 2.2mm in order to maximize rf homogeneity.

*T*2’ measurements were performed using the sequences shown in Figure 1. Figure 1a shows the single echo pulse sequence introduced by Elena et *al*. [17]. It is a pseudo-2D experiment with the application of a spin echo sequence (*τ* - *π* - *τ*) and with a homonuclear decoupling sequence applied during the *τ* periods. In Figure 1b we show a double spin-echo sequence. It consists of two consecutive spin echo blocks, with homonuclear decoupling applied during *τ* periods. In both sequences, the phase of the homonuclear decoupling sequence is carefully chosen in order to align the plane of the effective field during decoupling to be perpendicular to the magnetization after the first *π*/2 pulse [1]. At the end of the 2*τ* evolution a pulse of angle *θ*1 is applied, which flips the magnetization from the tilted transverse plane to the (x,y) plane in the rotating frame, and is then followed by a z-filter, and acquisition of the high resolution 1H spectra obtained by sampling the FID during acquisition windows inserted between homonuclear dipolar decoupling periods [20]. We found that phenomenologically the addition of a pair of compensation pulses *θc*1 and *θc*2 at the beginning and at the end of each decoupling pulse, originally developed for the acquisition with LG4 decoupling [20], also provides better results for direct acquisition with eDUMBO-122. Their lengths were independently optimized, together with the length of *θ*2,in order to provide the highest resolution with the lowest intensity of artefacts. Note that the sequence used for acquisition of the signal in *t*2 has no bearing on the dephasing behaviour studied here occurring during the *τ* periods. (Full details of acquisition parameters, phase cycles and pulse sequences are given in ESI).

Experiments were performed at MAS rates of 3, 12.5 and 22 kHz. For each sample and at each spinning rate all the parameters of the homonuclear dipolar decoupling scheme were carefully optimized in a 1D CRAMPS experiment in order to obtain the highest resolution. Direct acquisition was performed using the homonuclear decoupling sequence that provided the highest resolution in a 1D CRAMPS experiment of the sample under analysis – BR-24 at 3kHz MAS and eDUMBO-122 at 12.5 and 22kHz MAS. For β-AspAla and alanine spectra the scaling factors were determined experimentally by comparing the peak positions in the decoupled spectra with the one obtained with a single pulse experiment under MAS. For adamantane spectra we used the theoretical scaling factors, since the two resonances are not resolved. All chemical shifts are referenced to pure liquid tetramethylsilane (TMS) at 0 ppm. After optimization, the *T*2’ measurement was performed by acquiring a series of 1D high resolution 1H spectra where the time *τ* of decoupling was systematically increased. The dephasing curve was obtained by integrating each peak and by plotting the area as a function of the time *τ*. The processing of the spectra, as well as the extraction of the experimental 1H linewidths, were done using the Bruker program TopSpin 3.5. The post-processing procedures (extraction of 1D spectra, evaluation of the area under each peak, fitting and extraction of *T*2’ value) were done in MATLAB using a home-written script.



**Figure 3**: Dephasing curves for CH3 (a) CHAla (b) OH (c) and CHAsp (d) resonances of β-AspAla recorded using the pulse sequence of Figure 1a. The spectra were acquired using a MAS rate of 12.5 kHz. During 2*τ* a 64 phase-step eDUMBO-122 sequence was used for decoupling. The proton RF power during decoupling was 130 kHz with a time of 24.5 μs for each cycle. A total of 64 *t*1 points with 32 scans were collected.

Results and discussion

Figure 2a shows the measured spin-echo dephasing curve (in red) for the methyl resonance of β-AspAla recorded under MREV-8 decoupling with 12.5 kHz sample spinning. The same resonance in the corresponding 1D spectra (Figure S1) has a full linewidth at half height (*Δ*) of 182 Hz (which yields *T*2\*= 1/π*Δ* = 1.7 ms). As shown in Figure 2a in blue, the measured spin-echo dephasing curve best fits to an exponential decay (S(2*τ*)=*a*\*exp(-2*τ*/ *T*2’)) yielding *T*2’ = 5.95 ms, which in turn corresponds to a residual linewidth due to coherent non-refocusable interactions (the “homogeneous” interactions accordingly to the definition of Maricq and Waugh)[23] of 54 Hz, as show in Figure 2b. The homogeneous interactions (not corrected here for the scaling factor of the sequence, which conceptually should only be applied to the refocusable terms) are thus estimated to be about half of the inhomogeneous contributions (the refocusable ones). This is broadly in line with previous observations [24].

When using the highest performance methods available today, we expect to see a lengthening of the coherence lifetimes, accompanying the reduction in observable spectral linewidths. However, here we discover unexpectedly that at longer coherence lifetimes, the dephasing curves deviate significantly from simple exponential decays. As a representative example, Figure 3 shows the dephasing curves for four of the eight resonances of β-AspAla acquired using eDUMBO-122 at a spinning rate of 12.5 kHz. In all cases the dephasing curves have significantly longer T2’ than for MREV-8, as expected, but they deviate from the exponential case with the appearance of a strongly oscillating component. The Fourier transforms of these curves seen in Figure 3 show that these residual coherent homogeneous interactions present during decoupling lead to a splitting of up to 80 Hz. This behaviour is observed for several decoupling sequences, such as eDUMBO-122, LG4 and BR-24, over a range of MAS rates between 3 and 22 kHz. This oscillating contribution is the primary limiting factor for the lifetime of the decay. Removing this residual splitting would lead to line narrowing in the spectra. We note that the 80 Hz splitting here is roughly 0.3% of the typical 1H-1H dipolar coupling between geminal protons. Identifying the origin of the residual splitting from a theoretical standpoint is thus a very challenging problem that will be addressed in the future. However, we have been able to characterise the transformation properties of the interaction from an experimental standpoint.



**Figure 4**: Behaviour of dephasing curves for different numbers and timings of π pulses. Results from different experiments are shown in different colours, corresponding to the labels shown and with the nomenclature explained in the text. (a), (b) and (c) are the dephasing curves of the CH3 resonance of β-AspAla recorded at 500 MHz. (a) and (b) were acquired with eDUMBO-122 at 12.5 and 22.0 kHz MAS respectively. (c) was acquired with BR-24 at 3.0 kHz MAS. During decoupling 1H RF power was set to 130 kHz in (a), 125 kHz in (b) and 156.25 kHz in (c). Decoupling cycles length was 24.5 μs in (a), 27.4 μs in (b) and 95.4 μs in (c). (d) shows the dephasing curves of the CH and CH2 resonances of adamantane acquired at 400 MHz. Here the spectra was decoupled with eDUMBO-122 using a MAS rate of 22.0 kHz. 1H RF power during decoupling was 125 kHz with a time of 27 μs for each cycle.

Figure 4 shows the difference between the dephasing curves acquired with the basic single π pulse Hahn echo sequence [25], and a series of different experiments in which we use two or three π pulses to form an echo with different pulse phases and timings. This is motivated by the idea that while the residual that we observe in Figure 3 is not refocused by a single π pulse, there are many examples in the literature of how permutation in general might lead to better averaging of residuals [10, 11, 13-15, 26-31], and for π pulses in particular the archetypal example is the Meiboom-Gill modification of the Carr-Purcell echo train experiment [32].

The different experiments will be denoted using a combination of the symbols *E*α and *π*α, where *E* and *π* are used to describe the building block used to construct the sequence, and α represents the phase of the π pulse inside the corresponding building block. *E*αrepresentsa Hahn echo building block composed of *τ*-*π*α-*τ*. The phase α is defined with respect to the phase of the first π/2 pulse, with x being the same phase as the initial pulse, y a phase shift of 90°, of 180° and of 270°. So, for example, the symbol *E*y can be used to represent the sequence composed by *π*/2x-*τ*-*π*y-*τ*, or *π*/2y-*τ*-*π-*x-*τ*. In the same way, it is possible to define the double spin-echo experiment (*π*/2x-*τ*-*π*y-2*τ*-*π*y-*τ*) as *E*y*E*y, (*π*/2x-*τ*-*π*y-2*τ*-*π*x-*τ*) as *E*y*E*x and so on. The symbol *π*α is a building block composed of only a single π pulse of phase α, with α defined as described above. For example, a sequence composed of two echoes with a π pulse in the middle (*π*/2x-*τ*-*π*y-*τ*-*π*y-*τ*-*π*y-*τ*) is described as *E*y*π*y*E*y.

From the data shown in Figure 4 we first notice that the oscillating component previously introduced in the dephasing curves of Figure 3 is present also for other samples, at different spinning rates, and for decoupling with different homonuclear dipolar decoupling sequences.

Figure 4 also shows how the application of a different number of spin echo blocks changes the behaviour of the dephasing curves dramatically. In all cases the double spin-echo *E*y*E*y sequence (in green) removes the oscillation that leads to negative intensities when the curve is acquired with the *E*y sequence. In contrast, if a π pulse is inserted between the two spin echoes (experiment *E*y*π*y*E*y, in light blue in Figure 4) the oscillation is re-introduced, but with a frequency which is about half of the original one.



**Figure 5**: The left column shows dephasing curves for the CH3 resonance of Ala (a), β-AspAla (b) and the CH and CH2 resonances of adamantane (c-d). Dephasing curves were acquired with the pulse sequences in Figure 1a (red) and Figure 1b (green). MAS rate was set to either 22.0 kHz in (a) and (c) or 3.0 kHz in (b) and (d). For decoupling in (a) and (c) we used eDUMBO-122, with 1H RF power of 125 kHz and decoupling cycles lengths (*τ*c) of 27.4 μs in (a) and 27 μs in (c). (b) and (d) were acquired decoupling with BR-24, using 156.25 kHz 1H RF power (90° pulse length of 1.6μs) and *τ*c of 95.4μs in (b) and 125 kHz 1H RF power (90° pulse length of 2μs) and *τ*c of 104.4μs in (d). A total of 64 τ points with 32 scans were collected for both single and double echo experiments in (a), (c) and (d). In (b) 256 τ points were collected for the single echo and 64 for the double echo, in both cases with 32 scans. The right column shows the Fourier transforms of the corresponding dephasing curves. The curves in (a), (b) and (d) were acquired at 500 MHz, the one in (c) at 400 MHz.

The data for triple and quadruple echoes, *E*y*E*y*E*y in orange and *E*y*E*y*E*y*E*y in blue, seem to indicate that they also largely remove the oscillating component. Other combinations of echoes and π pulses were tested and are shown in Figure S4.

The use of multiple echo sequences leads to longer apparent decays, which correspond to narrower homogeneous broadening. In Figure 5 we show results that demonstrate the better performance of the double spin-echo *E*y*E*y sequence if compared to the *E*y version. From the Fourier transforms of the dephasing curves it is possible to see the remarkable narrowing in the linewidth obtained with the application of the *E*y*E*y experiment. In the case of eDUMBO-122 at 22.0 kHz MAS, the linewidth of the CH3 resonance of alanine obtained in a 1D experiment, *Δ*\*, is 112 Hz (Figure S3). Of this residual broadening, the contribution of coherent non-refocusable interactions is 70 Hz as revealed from the *E*y *T*2’ experiment. With the *E*y*E*y experiment these contributions can be reduced to about half of their original values, leading to a residual broadening of 40 Hz (Figure 5a). Figure 5b shows the dephasing curves of the methyl resonance of the β-AspAla, acquired decoupling with BR-24 at 3.0 kHz MAS. In a 1D experiment this resonance has *Δ*\* = 166 Hz, of which 38 Hz are due to coherent interactions. The application of a double spin-echo leads to a *T*2’ of about 22.7 ms, which corresponds approximately to a broadening of 14 Hz. The last two curves of Figure 5 were obtained for the CH2 and CH resonances of adamantane using eDUMBO-122 at 22.0 kHz MAS using BR-24 at 3.0 kHz MAS. Due to their small difference in isotropic chemical shift, the two resonances cannot be resolved and therefore the dephasing curves are the sum of both. In the 1D CRAMPS spectra we obtained linewidths (*Δ*\*) of 68 and 86 Hz by decoupling with eDUMBO-122 and BR-24 respectively. The *E*y *T*2’ experiments reveal that the contribution of coherent homogeneous interactions to the total linewidths corresponds to 36 Hz out of 68 Hz when decoupling with eDUMBO-122 and 40 Hz out of 86 Hz when using BR-24. In both cases the application of the *E*y*E*y experiment is able to substantially reduce the amount of non-refocusable interactions. In the first case, the line broadening is reduced to 21 Hz, about half of the starting value. This gain in lifetime is even greater for the second curve, for BR-24, with a residual non-refocusable broadening of only 7 Hz (*T*2’=45.2 ms) recorded with the *E*y*E*y experiment, which corresponds to an increase of more than a factor four as compared to the natural resolution. We note that the difference in magnetic fields used should have little effect on the refocused linewidths. The difference in performance here should then be related to the intrinsic performance of the two sequences under these conditions.

Conclusions

The aim of this work was to explore the current limits of 1H resolution in NMR of organic solids at natural abundance. To better understand the contributions to the residual line broadening, a set of *T*2’ measurements were performed with multiple echo configurations. The measurements were performed on different samples of powdered organic solids (β-AspAla, alanine and adamantane), decoupling with different schemes over a range of MAS rates between 3 and 22 kHz, and at two different 1H frequencies (400 and 500 MHz). We discovered that the coherence lifetime, and consequently the spectral resolution, is limited by the presence of an oscillation when the experiments were done using homonuclear dipolar decoupling sequences. We observed this oscillation for the sequences which provide the best resolution in 1D 1H spectra, such as eDUMBO-122 and BR-24. We found that the oscillation produces a residual anisotropic splitting of up to 80 Hz, a significant contribution to the total observed linewidths which are on average about 100-150 Hz for organic solids. The study of the behaviour of this oscillation under the influence of an higher number of π pulses revealed that it can be removed by the application of a double spin-echo (*E*y*E*y) experiment. As a consequence, the coherence lifetime is extended, and line broadening due to non-refocusable interactions is significantly reduced. In summary, we were able to characterize a limiting factor for 1H resolution in solid-state NMR, and we were able to remove it by using a double spin-echo sequence, reducing the contribution of non-refocusable interactions to as little as 7 Hz.

**Acknowledgments**

We are grateful for financial support from Swiss National Science Foundation Grant No. 200021\_160112. The authors acknowledge Andrew Pell (Stockholm) and Moreno Lelli (Florence) for interesting discussions.

Conflicts of interest

There are no conflicts to declare

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