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Hole burning in polycrystalline C_{60}: An answer to the long pseudocoherent tails

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NMR experiments in C_{60} reveal the origin of the "pseudocoherence" that leads to long tails in some Carr-Purcell-Meiboom-Gill (CPMG) sequences in contrast with the decay of a standard Hahn echo. We showed in a previous work [M. B. Franzoni and P. R. Levstein, Phys. Rev. B **72**, 235410 (2005)] that under certain conditions these CPMG sequences become spoiled by stimulated echoes. The presence of these echoes evidences that the long tails arise on the storage of magnetization in the direction of the external magnetic field (z polarization) involving spin-lattice relaxation times of several seconds. Hole burning experiments confirm the presence of a highly inhomogeneous line and show that the flip-flop processes are able to homogenize the line in times agreeing with those obtained through a Hahn echo sequence. As expected, the decay of the stimulated echoes is not sensitive to the quenching of the dipolar interaction through an MREV16 sequence, while the Hahn echo decay increases by a factor of 20. CPMG sequences with hard pulses and different temporal windows clearly show the relevance of the dipolar interaction in between the pulses for the generation of the long tails. In particular, the more time the flip flop is effective (longer interpulse separation), the amplitudes of the long tails decrease and their characteristic times become shorter.

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I. INTRODUCTION

Electron and nuclear spins in the solid state are good qubit candidates in order to implement gates for quantum information processing. As a consequence, many groups are nowadays working on decoherence on several kinds of spin systems. Some of the investigations point directly to the coherence time of the nuclear spins,[1–5] while others involve decoherence of electron spins because of the presence of a fluctuating nuclear-spin lattice.[6,7] Observation of very long tails in measurements of spin coherence times T_2 using some variations of the Carr-Purcell-Meiboom-Gill (CPMG) sequence[8–10] in samples as ^{29}Si,[1] C_{60},[4] and Y_2O_3 (Ref. 5) created great expectation. This is because the viability of quantum devices and quantum processors relies on long coherence times to perform the engineered operations.[11–13]

Several pulse sequences, besides the standard Hahn echo[14] $(\frac{\pi}{2})_X-\tau-(\pi)_Y-\tau-$echo have been used to measure spin-spin relaxation times T_2 denoted as

$$\text{CP1: } \left(\frac{\pi}{2}\right)_X - [\tau-(\pi)_X-\tau-\text{echo}]_n,$$

$$\text{CP2: } \left(\frac{\pi}{2}\right)_X - [\tau-(\pi)_X-\tau-\text{echo}-\tau-(\pi)_{-X}-\tau-\text{echo}]_n,$$

$$\text{CPMG1: } \left(\frac{\pi}{2}\right)_X - [\tau-(\pi)_Y-\tau-\text{echo}]_n,$$

$$\text{CPMG2: } \left(\frac{\pi}{2}\right)_X - [\tau-(\pi)_Y-\tau-\text{echo} - \tau-(\pi)_{-Y}-\tau-\text{echo}]_n. \quad (1)$$

Indeed, we emphasize that none of these measurements of T_2 yields the "true decoherence time" because the dipolar evolution itself is reversible. However, as it has been reported, even when the dipolar interaction is reversed the observed decay time still depends on it.[15–18] Then, we are still very interested in the "decoherence" times given by these spin-spin relaxation measurements.

The spin-spin relaxation time, i.e., the dipolar limited coherence time measured for C_{60} using the Hahn echo sequence was $T_{2HE}=15$ ms and similar results were obtained for CP1 and CPMG2. On the other hand, for the CPMG1 and CP2 the decay times were in the order of seconds. Under these striking results, an effort to distinguish between coherence and *pseudocoherence* times must be done.

In a previous work,[4] we proved that these long times are a consequence of the formation of stimulated echoes, after two π pulses, that are not analytically expected. In the proof, two conditions were necessary for the formation of these echoes: (1) a rf field inhomogeneity or a highly inhomogeneous line able to produce different tilting angles in different sites of the sample and (2) the absence of spin diffusion (noneffective flip-flop interactions). In this work, we show new experiments that confirm that both conditions are satisfied in C_{60}, verifying our previous hypothesis.

Besides a hole burning experiment, a careful study to distinguish between coherence and pseudocoherence times obtained for the CPMG1 and CP2 sequences was made by isolating the stimulated echoes and measuring their characteristic decay times under several conditions. Also, the efficiency of the dipolar interaction in order to avoid the stimulated-echo formation was studied by allowing enough time for the operation of the flip-flop dynamics, emphasizing the importance of condition (2).

Our results do not agree with the interpretation of the long decay times reported recently by Li *et al.*[5] They assign the long tails to the dipolar evolution that occurs during the pulses. Indeed, one could substitute condition (1) by using very long pulses. In this case, the one flip terms produced by the dipolar interaction during the pulse are similar to those produced by the off resonance or the H_1 inhomogeneity. However, condition (2) is still necessary and if the dipolar interaction is important during the pulse, it will be during the interpulse times unless these intervals are too short compared with the duration of the pulses. This last situation is not usual in CPMG measurements in the solid state.

In summary, in Ref. 5 the origin of the long tails is assigned to the dipolar effect during the finite *duration of the pulses*, regardless of the evolution *in between* pulses. For us, the slow spin diffusion in between pulses is responsible for the tails, something being also necessary (H_1 inhomogeneity, differences in chemical shifts, different dipolar evolutions during the pulses) that generates nonperfect π pulses in different regions of the sample.

In order to decide which is the correct approximation or if they are both partially right, one should perform a couple of relevant experiments: (a) A measurement of the tails as a function of pulse length t_p and (b) a measurement of the tails as a function of the interpulse time τ. The experiment (a) was performed by Li *et al.*[19] and indicates that for typical solid-state NMR conditions $\gamma H_1/2\pi >$ FWHM (full width at half maximum), the tails are independent of H_1. For the interpulse analysis, we study here the amplitude and characteristic times of the tails as a function of τ. Besides, we applied the MREV16 decoupling sequence to observe its effects on the long tails.

II. EXPERIMENTAL METHODS AND RESULTS

The experiments were performed in a Bruker Avance II spectrometer and in a Bruker 300-MSL operating at 75, 45 MHz for ^{13}C and in a Bruker Avance under a 11.75 T magnet (125, 75 MHz for ^{13}C). The probes were Bruker high power cross polarization magic angle spinning (CPMAS) used under static conditions. The rotor sizes were 18 mm long and 4 or 3.2 mm outer diameter. All the experiments were conducted on resonance at room temperature. Typically, for almost every experiment the $\frac{\pi}{2}$ pulse was set as 5 μs.

A commercial sample of polycrystalline C_{60} at 99.5% purity was used without further processing. The T_1 observed for the sample was $T_1=37$ s at the 7 T magnet and $T_1=24$ s at the 11.75 T one. In Secs. II A, II C, and II D, a detailed description of the experiments we performed is provided.

A. Hole burning in C_{60}

The inhomogeneity of the C_{60} line is well shown through a hole burning experiment.[10] The experiment consists of two $\frac{\pi}{2}$ pulses, the first a selective one of duration t_p. After excitation of a portion of the line with the first pulse, free evolution is allowed during a time τ until a nonselective pulse is followed by acquisition (Fig. 1). If the line is inhomogeneously broadened, the portion of the line excited with the first pulse will form a hole. In contrast, a homogeneously broadened line will collapse as a whole, i.e., its magnitude will diminish but no hole will be observed.

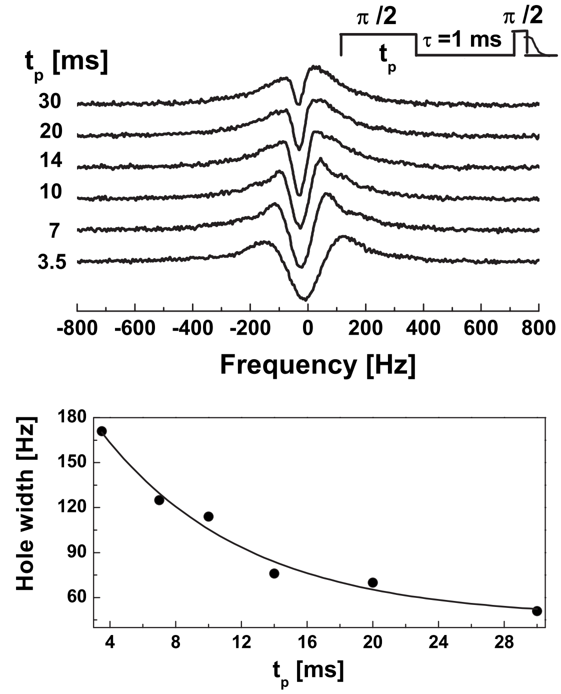

FIG. 1. Top: Hole burning sequence and spectra with holes for different selective pulse durations t_p. Bottom: The Lorentzian widths as function of pulse durations fit an exponential decay with characteristic time $t_c=9$ ms.

Indeed, a measure of the inhomogeneity of a line may arise from the minimum time between pulses needed to cross from the hole formation to the collapsed line situation. We performed the experiment in polycrystalline C_{60} and observed the formation of holes, manifesting that the line is inhomogeneously broadened. The width was calculated by fitting each spectrum to a Lorentzian line and the hole width as a function of the selective pulse duration was studied. As can be seen in Fig. 1 the hole width is not inversely proportional to t_p as ideally expected. Indeed, an exponential relationship was obtained whose characteristic time, similar to T_{2HE}, indicates that the dipolar interaction is starting to be operative during the selective pulse.

For two different durations of the selective pulse t_p, we studied the recovery of the hole by varying the evolution time between pulses, τ (see Fig. 2). The quantification of the depth of the holes is fairly straightforward because the holes do not change shape as they recover. Following Kuhns and Conradi[20] to measure the hole depth, the line shape is multiplied by a rectangular function which is +1 in the middle of the holes (in a frequency interval as wide as the holes full width half maximum), −1 on the shoulders of the hole, and zero elsewhere. The total area of this function approaches zero; the rectangular function is slightly adjusted so that an unburned line shape multiplied by the rectangular function has zero area. The total area of the product (experimental line shape times rectangular function) is taken as a quantitative measure of the hole depth.

As shown in Fig. 2 the results obtained for $t_p=20$ ms and $t_p=30$ ms are almost coincident for every evolution time τ.

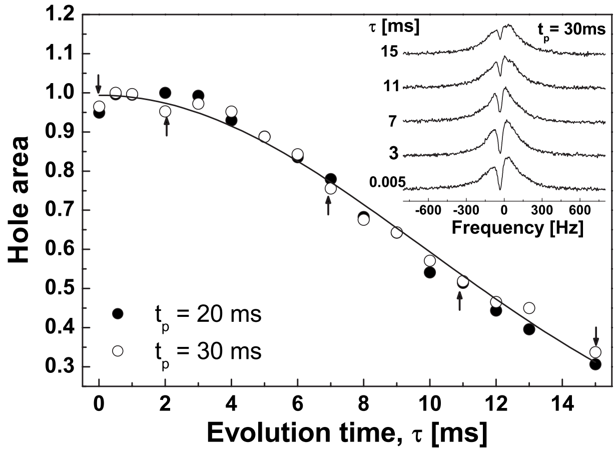

FIG. 2. Line recovery, measured through the hole area, as a function of evolution time between the pulses for two selective pulse durations. The curve fits a Gaussian with a characteristic time of 13.9 ms. In the inset, the spectra of the intermediate times indicated by arrows in the curve are shown.

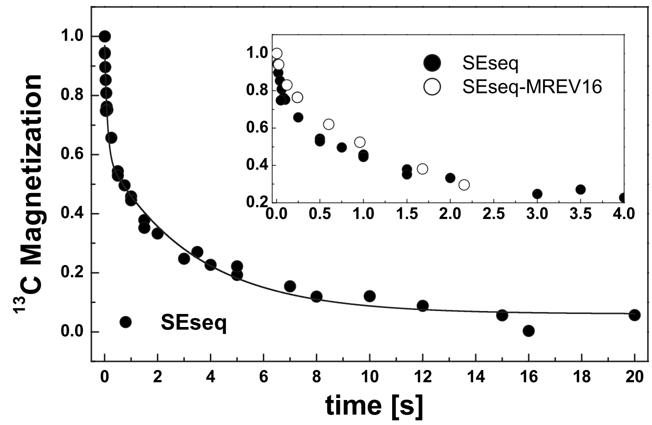

FIG. 3. Stimulated echo as a function of t_v, applying the three-pulse sequence with $\beta=\pi/2$ and $t_f=8$ ms. The curve is fitted with a double exponential decay; the characteristic times obtained were $t_{s_{SE}}=130$ ms and $t_{l_{SE}}=4.9$ s. Inset: comparison of the stimulated-echo sequence with and without MREV16 decoupling. No difference is observed.

The hole area as a function of τ is well fitted to a Gaussian, yielding a characteristic decay of approximately 13.9 ms similar to the coherence time T_{2HE} obtained with the Hahn echo. This is another confirmation that T_{2HE} is the coherence time associated with the dipolar interaction.

B. Stimulated echo

We developed a sequence of three pulses which provides the stimulated-echo decay time. As shown before,[4] in the stimulated-echo (SE) sequence,

$$\text{SE: } \left(\frac{\pi}{2}\right)_{\varphi_1} - t_f - (\beta)_{\varphi_2} - t_v - (\beta)_{\varphi_3} - t_f - acq, \qquad (2)$$

the stimulated and the normal echoes have the same phase if the pulse phases are taken as in the CPMG1($\varphi_1=X;\varphi_2=Y;\varphi_3=Y$) or as in the CP2($\varphi_1=X;\varphi_2=X;\varphi_3=-X$) sequences. On the other hand, for the CPMG2($\varphi_1=X;\varphi_2=Y;\varphi_3=-Y$) or the CP1($\varphi_1=X;\varphi_2=X;\varphi_3=X$) sequences the echoes appear in opposite phases because the phase of the stimulated echo is inverted. Thus, by applying the SE sequence (2) as in the CPMG1 and then as in the CPMG2 sequence, multiplied by 1 and −1, respectively (by inversion of the detection phase), we get rid of the normal echo.

By fixing $t_f=8$ ms and varying t_v, we built the stimulated-echo decay curve (see Fig. 3). The curve manifests two-time regimes that, fitted with a double exponential decay, yield a short decay time $t_{s_{SE}}=130$ ms and another of $t_{l_{SE}}=4.9$ s. The long decay time is in the same order as those observed in the CPMG1 and CP2 sequences.[4]

The long time obtained for the stimulated echo ($t_{l_{SE}}$) is well understood since it brings back magnetization preserved in the z axis to the plane. As we have proved,[4] the cause of the long tails in the CPMG1 and the CP2 sequences in C_{60} is the constructive interference between normal and stimulated echoes. Now, we are showing that, as expected, the stimulated echoes are the ones with long decay times. We performed SE sequences with $\beta=\pi$ and $\beta=\pi/2$, and both of them yielded the same decay times. In Fig. 3, we show the SE sequence with three $\pi/2$ pulses which gives the maximum signal to noise ratio.

C. Long decay times vs flip-flop dynamics

We performed the CPMG1 and the CP2 experiments for different temporal windows τ (in fact, 2τ between the π pulses). For each τ we observed that the magnetization shows a double exponential decay with a characteristic short time (t_s) and a long one (t_l). For all the experiments, the obtained t_s was very well approximated by T_{2HE} so we fixed $t_s=T_{2HE}$ and we calculated t_l. In Fig. 4 we show a CPMG1 experiment with $\tau=3.5$ ms fitted with a double exponential with $t_s=15$ ms.

After doing the same analysis for every τ, we plotted t_l vs τ for the CPMG1 and CP2 sequences (Fig. 5). It is noticeable

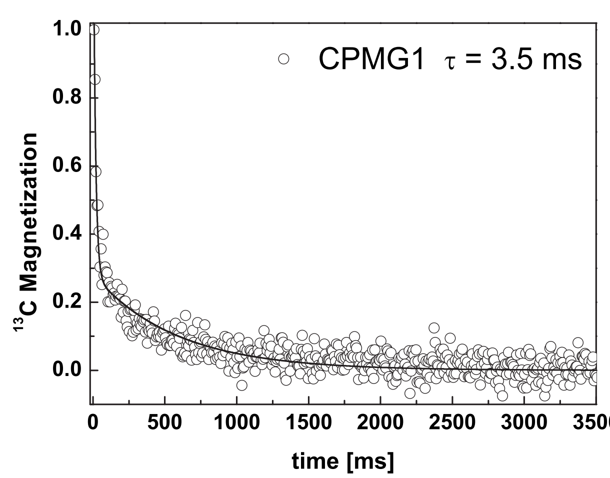

FIG. 4. CPMG1 experiment for $\tau=3.5$ ms. Double exponential decay behavior fitted with $t_s=T_{2HE}$ yields a long decay time $t_l=570$ ms.

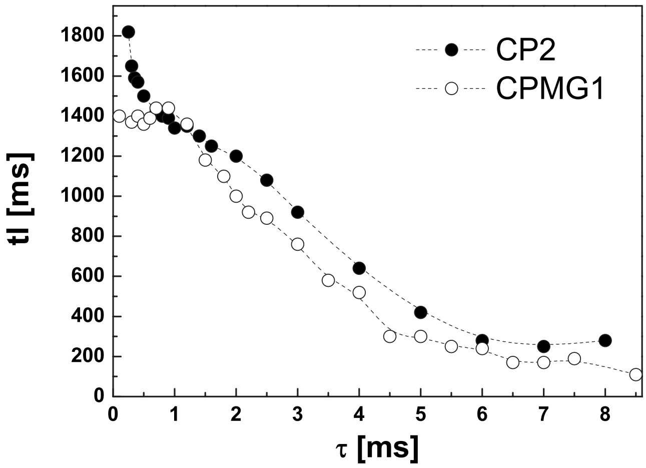

FIG. 5. The CPMG1 and CP2 experiments were repeated for many time windows τ. For each train of echoes a double exponential decay was fitted and setting one characteristic time as T_{2HE}, a longer one t_l, was obtained. t_l is plotted as a function of τ.

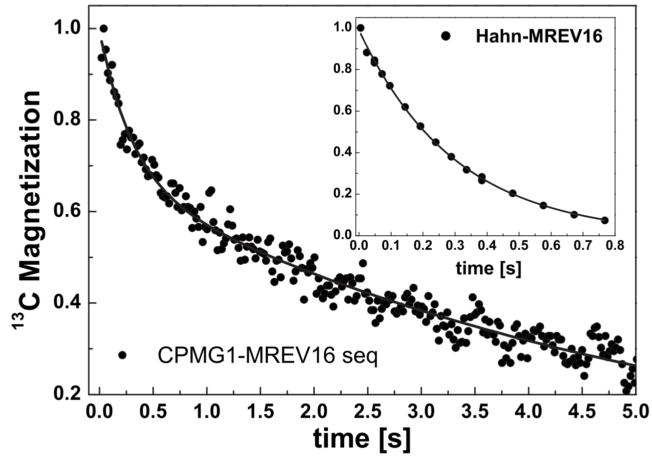

FIG. 6. Long tail obtained through the CPMG1-MREV16 sequence for $\tau_{MREV}=0.1$ ms and $c=4$. The curve is fitted with a double exponential decay; the shorter characteristic time is fixed as $t_{s_{MREV}}$ and the longer decay is $t_{l_{MREV}}=5.3$ s. In the inset the Hahn-MREV16 experiment fits an exponential decay with $T_{2MREV}=0.3$ s.

that t_l decays as a function of τ with a characteristic time which again resembles T_{2HE}! Besides, one can observe that the amplitudes of the long tails decay as a function of τ, almost disappearing for $\tau > 8$ ms.

These experiments are in very good agreement with our hypothesis and some numerical results. They show that the stimulated echoes and consequently the long tails are manifestations of the slow flip-flop dynamics: a shorter τ (no flip flop) leads to a longer decay time t_l.

D. Dipolar decoupling

The MREV16 sequence[21,22] consists of sixteen properly phased and separated $\pi/2$ pulses of duration $\tau_{\pi/2}$, with a minimum separation time τ_{MREV}. A single MREV16 cycle lasts $24\tau_{MREV}+16\tau_{\pi/2}$. As can be seen from average Hamiltonian theory,[23] the MREV16 sequence averages out the zero and first orders of the dipolar interaction.

We performed a Hahn-MREV16 echo measurement by applying c times the MREV16 sequence before and after the π pulse in the Hahn echo sequence. That is, the dipolar decoupling was operative all the time after the $\pi/2$ pulse, up to the formation of the echo where signal acquisition starts. To build the magnetization decay curve as a function of time shown in Fig. 6 we used $\tau_{MREV}=0.1$ ms and $\tau_{MREV}=0.2$ ms and varied c from 1 to 80. We obtained $T_{2HE}^{MREV}=300$ ms, instead of $T_{2HE}=15$ ms obtained with the standard Hahn echo.

Another revealing experiment performed in the C_{60} sample was the CPMG1-MREV16. The CPMG1-MREV16 sequence is a CPMG1 with a variable number (c) of MREV16 cycles applied between the π pulses. In this case, $\tau=c(24\tau_{MREV}+16\tau_{\pi/2})$, where 2τ represents, as before, the temporal window between the π pulses of the CPMG1 sequence. As shown in Fig. 6, by applying the CPMG1-MREV16 for $\tau_{MREV}=100$ μs, $c=4$ and so $\tau=9.92$ ms ($2\tau \approx 20$ ms is longer than T_{2HE}) we observed long tails in the magnetization, even longer than those obtained for the CPMG1 sequence without MREV16. The magnetization manifested two different decay times: a short one that could be fixed as $t_{s_{MREV}}=T_{2HE}^{MREV}\approx 0.3$ s and a longer one of $t_{l_{MREV}}=5.3$ s. This is almost three orders of magnitude longer than $T_{2HE}\approx 15$ ms, as was also reported for silicon when this sequence was applied.[3]

Evidently, these long tails in C_{60} do not yield decoherence times, but in analogy with the situation without decoupling, they are a consequence of the stimulated echoes. Indeed, as in the pure CPMG1 sequence, we were able to identify a short decay time which agrees with T_{2HE}^{MREV} and a long one in the same scale of times than the stimulated-echo decay. Moreover, we repeated the stimulated-echo decay time experiment by applying the MREV16 sequence between the intermediate $\pi/2$ pulses and varying τ_{MREV} between 0.1 and 1 ms and c between 1 and 90. As expected, no difference was observed when compared with the plain SE sequence (see inset in Fig. 3).

III. CONCLUSIONS

The experiments shown in this work confirm the two hypotheses made in our previous work.[4] We have proved that the C_{60} line is inhomogeneously broadened. This condition is the key ingredient for the formation of the stimulated echoes. In this inhomogeneous sample, the differences in resonance frequencies are larger than the dipolar couplings, making ineffective the flip-flop mechanism. Consequently, the different deviations from π pulses (regardless of origin) cannot be averaged out through dipolar interactions, as would occur with homogeneous samples.

It was also verified that the decay time obtained through a Hahn echo experiment T_{2HE} is the time which characterizes the flip-flop process while the long tails are pseudocoherences, a consequence of the stimulated echoes. Another remarkable fact is the importance of the absence of the flip flop in the formation of the long tails, observed for the CPMG1 and CP2 sequences: the more time we allow for the flip-flop process to become effective, the shorter are the characteristic times of the long tails, as can be seen in Fig. 5. These experiments are a very strong demonstration that *the long tails are a manifestation of the slowness of spin diffusion*.[4]

Our explanation contrasts with the argument espoused by Li *et al.*[5] They claim that the delta pulse approximation is not valid and the long tails are a consequence of dipolar interactions during the pulses. Indeed, the theoretical model proposed by Li *et al.* to reproduce qualitatively the experimental results can be explained with the stimulated-echo picture. By considering the finite duration of the pulses evolving under an artificially increased dipolar interaction one spin flip, two spin flips, and three spin-flip terms appear that can account for the phenomenological "difference in the tilting angle" with respect to a perfect π pulse. Thus, they build a distribution of different pulses in different sites of the sample, and consequently, the formation of stimulated echoes with magnetization stored in the H_0 axis. But still, the long tail formation requires the absence of spin diffusion. Clearly, a strong flip-flop mechanism during the interpulse delay will be efficient to average out the differences of the tilting angles quenching the stimulated echoes.

With regard to the effect of the finite duration of the pulses, as can be seen in Fig. 13 of Ref. 19 the CPMG1 tail height is insensitive to large changes in pulse strength. In the mentioned experiment the authors obtained the same tail height for pulses strong enough to excite from 4 to 450 times the FWHM so, as all the pulses set in C_{60} or in ^{29}Si excite more than 200 or 300 times the FWHM, the delta pulse approximation is correct and the long tails cannot be a consequence of finite pulse durations. Moreover, from average Hamiltonian calculations,[5] one can see that as soon as the interpulse time τ is longer than the pulse duration t_p, the latter will have a negligible effect. This is effectively observed in their experiments in ^{29}Si as a function of t_p for $\tau = 1.096$ ms, where as soon as $t_p < 300$ μs there is no dependence on t_p. Everything points to the fact that the important ingredient for the long tails is a chemical shift distribution or equivalent.

From the stimulated-echo decay sequence developed here, it was evident that its decay time is in the order of seconds as the long tails are. Moreover, it was proved that the characteristic SE decay is independent of the dipolar interaction: i.e., it is the same regardless of the application of the MREV16 sequence that averages out the dipolar interaction. As a consequence, after the constructive interference between the normal and the stimulated echoes, long tails in the decay of the magnetization are found not only for the CPMG1 and CP2 sequences but also for the CPMG1-MREV16.

In summary, the lines of the three samples (Si, C_{60}, and Y_2O_3) that have manifested the presence of long tails have in common FWHMs at least 1 order of magnitude larger than their respective dipolar couplings $k = \frac{\mu_0}{4\pi}\frac{\gamma^2\hbar}{2\pi d^3}$. Besides, the stimulated (anomalous) echoes have also been observed in silicon.[1] This leads us to think that the conclusions obtained from our experiments in C_{60} might be generalized to these other systems, which should be revised under the light of these new findings. Moreover, caution should be taken in any system satisfying the conditions of the hypothesis before talking about "coherence."

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[1] A. E. Dementyev, D. Li, K. MacLean, and S. E. Barrett, Phys. Rev. B **68**, 153302 (2003).
[2] S. Watanabe and S. Sasaki, Jpn. J. Appl. Phys., Part 2 **42**, L1350 (2003).
[3] T. D. Ladd, D. Maryenko, Y. Yamamoto, E. Abe, and K. M. Itoh, Phys. Rev. B **71**, 014401 (2005).
[4] M. B. Franzoni and P. R. Levstein, Phys. Rev. B **72**, 235410 (2005).
[5] D. Li, A. E. Dementyev, Y. Dong, R. G. Ramos, and S. E. Barrett, Phys. Rev. Lett. **98**, 190401 (2007).
[6] E. Abe, K. M. Itoh, J. Isoya, and S. Yamasaki, Phys. Rev. B **70**, 033204 (2004).
[7] R. de Sousa, N. Shenvi, and K. B. Whaley, Phys. Rev. B **72**, 045330 (2005).
[8] H. Y. Carr and E. M. Purcell, Phys. Rev. **94**, 630 (1954).
[9] C. Slichter, *Principles of Magnetic Resonance*, 3rd ed. (Springer-Verlag, Berlin, 1990).
[10] E. Fukushima and S. Roeder, *Experimental Pulse NMR: A Nuts and Bolts Approach* (Addison-Wesley, Reading, MA, 1981).
[11] D. P. DiVincenzo, Science **270**, 255 (1995).
[12] B. Kane, Nature (London) **393**, 133 (1998).
[13] D. G. Cory, A. F. Fahmy, and T. F. Havel, Proc. Natl. Acad. Sci. U.S.A. **94**, 1634 (1997).
[14] E. L. Hahn, Phys. Rev. **80**, 580 (1950).
[15] S. Zhang, B. H. Meier, and R. R. Ernst, Phys. Rev. Lett. **69**, 2149 (1992).
[16] P. R. Levstein, G. Usaj, and H. M. Pastawski, J. Chem. Phys. **108**, 2718 (1998).
[17] G. Usaj, H. M. Pastawski, and P. R. Levstein, Mol. Phys. **95**, 1229 (1998).
[18] H. M. Pastawski, P. R. Levstein, G. Usaj, J. Raya, and J. Hirschinger, Physica A **283**, 166 (2000).
[19] D. Li, Y. Dong, R. G. Ramos, J. D. Murray, K. MacLean, A. E. Dementyev, and S. E. Barrett, Phys. Rev. B **77**, 214306 (2008).
[20] P. L. Kuhns and M. S. Conradi, J. Chem. Phys. **77**, 1771 (1982).
[21] W. K. Rhim, D. D. Elleman, and R. Vaughan, J. Chem. Phys. **59**, 3740 (1973).
[22] P. Mansfield, M. J. Orchard, D. C. Stalker, and K. H. B. Richards, Phys. Rev. B **7**, 90 (1973).
[23] U. Haeberlen, *High Resolution NMR in Solids: Selective Averaging–Supplement 1 for Advances in Magnetic Resonance* (Academic, New York, 1976).