Attenuation of polarization echoes in NMR: A study of the emergence of dynamical irreversibility in many-body quantum systems

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The reversal of the time evolution of the local polarization in an interacting spin system involves a sign change of the effective dipolar Hamiltonian which refocuses the “spin diffusion” process generating a polarization echo. Here, the attenuation of these echo amplitudes as a function of evolution time is presented for cymantrene and ferrocene polycrystalline samples, involving one and two five spin rings per molecule respectively. We calculate the fraction of polarization which is not refocused because only the secular part of the dipolar Hamiltonian is inverted. The results indicate that, as long as the spin dynamics is restricted to a single ring, the non-inverted part of the Hamiltonian is not able by itself to explain the whole decay of the polarization echoes. A cross over from exponential (cymantrene) to Gaussian (ferrocene) attenuation is experimentally observed. This is attributed to an increase of the relative importance of the spin dynamics, as compared with irreversible interactions, which favors dynamical irreversibility.

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1. INTRODUCTION

In a network of dipolar coupled identical spins in the solid state, the flip-flop mechanism leads to a polarization dynamics often described as “spin diffusion”. However, an ingenious NMR pulse sequence made evident that this many body evolution can be reversed by changing the sign of the effective Hamiltonian ($\mathcal{H} \rightarrow -[2] \mathcal{H}$). This practical realization of the Loschmidt daemon is possible because the sign and magnitude of the dipolar interaction depends on the orientation of dipoles relative to the internuclear axis. In recent years, it was shown that local polarization in a network of $^1\!H$ spins can be monitored using the rare $^{13}\!C$ as local probes. The local excitation is allowed to “diffuse” during a time $t_R$ with $\mathcal{H}$ and then it continues the evolution with $-[2] \mathcal{H}$. The polarization maxima appearing at around $t_R + [3] t_R$ are called polarization echoes. In practice, however, recovery of polarization is not total. In fact, the echo amplitudes attenuate with increasing $t_R$. Even when the origin for the decay of these echoes can not be easily determined, when compared for example with Hahn echoes, it was suggested that the characteristic attenuation of the echo amplitudes might be useful for the study of molecular dynamics in solids. It has also been used in its laboratory frame version to observe quantum beats and interference phenomena in molecules with few degrees of freedom.

In this last case, refocusing by external means was not the main issue, but a tool to compensate undesired evolution in the proton system while the $^{13}\!C$ is acting as a local probe. Thus, the sequence succeeded in showing a spin dynamics which is a fingerprint of the dipolar coupled system itself.

On the other hand, the pulse sequence to reverse the dipolar evolution of spin polarization might be a powerful experimental tool to test how dynamical irreversibility emerges in many-body quantum systems. This could deepen our understanding of the mechanisms leading to the observed time asymmetric behavior of macroscopic systems. From numerical simulations, it is well known that classical systems with chaotic behavior evolve showing “diffusive” properties. If at a time $t_R$ the motion is reversed, the trajectory can not be retraced but for a short period of time. This strong limitation to practical reversibility appears as a consequence of the instability which amplifies the numerical round-off errors. Such amplification of instabilities, which can be expected to grow with system size, explain why for many-body classical systems, the reversed evolution miss the initial macrostate by an amount which increases with $t_R$, the time when velocities are inverted. This contrasts with the apparent greater numerical reversibility of some simple quantum models, where the motion appears to recur to the initial state with an accuracy comparable with those errors. Even more, the application, at the reversal time $t_R$, of quite large random distortions of the relative phases of the states that expands the evolved state, is not able to destroy this “anti-diffusive” evolution. General solutions for many-body quantum systems become much more difficult to obtain. Hence, there is an obvious interest in experimental approaches to test possible hypothesis which might help to handle those cases. It is from this point of view that several questions arise: What is the functional dependence on $t_R$ of the polarization echoes? Is the attenuation rate for the polarization echoes related to any other independently measurable parameter? What kind of information can be obtained from the functional form and degree of the attenuation? Does the reversal of the spin dynamics show any instability with respect to natural fluctuations characterizing the inter-
action with the environment? Can we learn anything else about processes leading to irreversibility or “true relaxation” in magnetic resonance by using this sequence? This paper must be considered a first effort addressing these fundamental questions.

The sequence to reverse the dipolar evolution of a local excitation was successfully applied to a single crystal of ferrocene, Fe(C5H5)2, and cymantrene, Fe(C5H5)2. In this system the hierarchy of 1H dipolar couplings was exhaustively analyzed, leading to the conclusion that both the intra and inter-ring interactions within a molecule are important, with a further increase in the connectivity of the dipolar network given by the intermolecular interactions (see Fig. 1). A step to simplify the topology of the coupling network while keeping the ring structure as a building block, consists in the use of cymantrene, Mn(C5H5)(CO)3. Having a single ring per molecule, it excludes an important portion of the couplings (see Fig. 2). From a practical point of view, the pulse sequence is going to be useful to extract information in a wide range of different dipolar coupled systems, it should be possible to work with polycrystals. In this work, a special effort has been devoted to get as much detail as possible from polycrystalline samples.

II. EXPERIMENTAL METHODS

All the NMR measurements on polycrystalline samples of ferrocene, Fe(C5H5)2, and cymantrene, (C5H5)Mn(CO)3, with natural 13C isotopic abundance were performed at room temperature. At this temperature, the cyclopentadienyl rings of both, ferrocene and cymantrene, perform fast rotations around their five-fold symmetry axis with a very short correlation time (≈ 10−12s) giving rise to axially symmetric 13C-NMR spectra as shown in Fig. 3.

We used a Bruker MSL-300 spectrometer, equipped with a standard Bruker CP-MAS probe, operating at a 13C frequency of approximately 75.47 MHz. This frequency was finely adjusted in each system to correspond to the resonance frequency of approximately 75.47 MHz of the 13C Mn(CO)3, for the 13C bonded to a Mn(CO)3 giving rise to axially symmetric 13C-NMR spectra as shown in Fig. 3.

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A (π/2)2 pulse produces again a spatially selective polarization transfer from I to S spins. The S-spin FID is then acquired under high resolution conditions, i.e. by keeping a spin lock on the I-spin system.

III. RESULTS AND DISCUSSION

As a first step in our study we have analyzed the evolution of I polarization in a polycrystalline sample of ferrocene by using this sequence to simplify the connectivity of the dipolar network given by the intermolecular interactions (see Fig. 1). A step to simplify the topology of the coupling network while keeping the ring structure as a building block, consists in the use of cymantrene, Mn(C5H5)(CO)3. Having a single ring per molecule, it excludes an important portion of the couplings (see Fig. 2). From a practical point of view, the pulse sequence is going to be useful to extract information in a wide range of different dipolar coupled systems, it should be possible to work with polycrystals. In this work, a special effort has been devoted to get as much detail as possible from polycrystalline samples.

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\[ b = \frac{\mu_0 \gamma_I \gamma_S \hbar^2}{4\pi r_{IS}^3} \left( \frac{1}{2} (3 \cos^2 \theta - 1) \right). \] (5)

This Hamiltonian considers only the dipolar interactions of the isolated \( S \) spins with the directly bound \( I \) spins. No dipolar interactions between \( I \) spins are considered in it. They are taken into account, in a phenomenological way, through an isotropic spin-diffusion process with rate \( R \) leading to a magnetization that, for \( \Omega = 0 \) and under exact Hartmann-Hahn condition \( \gamma_I B_{1I}^y = \gamma_S B_{1S}^y \), is expressed as:

\[ M_S^y(t) = A \left\{ 1 - \frac{1}{2} \exp(-Rt) - \frac{1}{2} \exp(-3Rt/2) \cos(bt/h) \right\}, \] (6)

where \( A \) depends only on temperature and Zeeman splitting.

Thus, the oscillations with frequency \( \omega = b/h \), experimentally observed were successfully explained. In our study, we can select molecules with their rotational axes at some specific angle \( \theta \) with respect to the external magnetic field \( B_0 \) and perform the fitting for each orientation, although strictly speaking only \( \theta = 90^\circ \) is exactly on resonance. An improvement in these fittings can be performed by considering that “spin diffusion” is not a consequence of fluctuations of isotropic fields but fields that, being essentially dipolar in origin, have the precise anisotropy given by Eq. (3). This leads to the new expression:

\[ M_S^y(t) = A \left\{ 1 - \frac{1}{2} \exp(-Rt) - \frac{1}{2} \exp(-2Rt) \cos(bt/h) \right\}. \] (7)

Figure 5 shows the experimental points and calculated curves (solid lines) for molecules with \( \theta = \frac{\pi}{2} \) (upper set of data) and with the “magic” angle \( \theta_m = \arccos 1/\sqrt{3} \) (lower set). Note that no extra free parameters are added in Eq. (6). It can be seen that the experimental curve does not decrease, especially in the first valley, as much as predicted by Eq. (3) (dotted line) or its dipolar version Eq. (6).

Further improvement of the fitting, though at high computational cost, has been reached by incorporation of an exact calculation of the intra-ring \(^1\)H-spin dynamics. The better fitting (dashed line in Fig. 5) is explained because the magnetization “hole” produced in the \( I \) polarization because of the transfer to its directly bound \( S \), is partially “filled” by magnetization from other protons in the ring during that short time. A new \( R \) parameter accounts for fluctuating fields due to inter-ring interactions.

We have performed non-linear least square fittings of the experimental points to Eq. (3) for the whole frequency spectra. That is, fittings equivalent to those shown in Fig.5 with solid lines, were performed in frequency steps of \( \approx 80 \text{Hz} \) covering the whole \(^{13}\text{C} \) spectrum of ferrocene for contact times ranging from \( 2\mu s \) to \( 3ms \). The \( A, R \) and \( b/(2\pi h) \) parameters obtained from these fits are shown in Fig.7. The first observation giving reliability to the results is that \( A \) reproduces the spectral line-shape obtained at long cross-polarization contact times. This is shown in the upper panel of Fig. (7) where the spectrum obtained with \( 2ms \) contact time is superimposed to the \( A \) values. The second fact is that \( b \) shows the expected \( (3 \cos^2 \theta - 1) \) dependence (except in the region where \( b/h \approx 0 \ll R \), where the assumptions of the model break down), which is the same as that of the resonance frequencies. This is emphasized in the graph by tracing the resulting linear dependence between \( b \) and frequency.

There is no doubt that \( R \) is a parameter giving information on the \( I-I \) dipolar coupling network. The shape of \( R \) vs. frequency does not change much by considering it as an isotropic relaxation parameter or an anisotropic (dipolar in origin) one. Its magnitude, however, does change. The dependence of \( R \) on frequency constitutes an evidence that, in contrary to the suggestions in Refs. 2 and 3, the “\(^1\)H-spin diffusion” is not restricted to one ring, not even to the complete molecule. In such a simple case, we would have a single averaged dipolar coupling proportional to \( (3 \cos^2 \theta - 1) \) as is the case for the \( I-S \) dipolar coupling \( b \) (see lower panel of Fig.7). Besides, \( R \) is a useful parameter in order to distinguish intra and inter-molecular contributions to the “spin diffusion”. For example, at the frequency corresponding to molecules with their axes at the magic angle with respect to \( B_0 \), \( R \) is entirely due to intermolecular couplings. Being more specific, only the magnetically non-equivalent molecules contribute, because even when there is communication with the equivalent ones the spin-diffusion in them is cancelled out \( (R_{intra} \approx 0) \). As can be observed in the central panel of Fig. 7, the \( R \) value at \( \theta_m \) is approximately one eighth of the maximum value. This maximum does not appear when the intramolecular coupling maximizes, but when the balance between both (intra and inter-molecular) contributions becomes maximum. Besides, it is worthwhile to note that working on a polycrystalline sample, each \( R(\theta) \) value involves an average of molecular orientations over a cone of angle \( \theta \), i.e. having the same angle with respect to \( B_0 \). In terms of characteristic times, the maximum \( R^{-1} \approx 2.7ms \) is at \( \theta_m \) while the minimum \( R^{-1} \approx 0.37ms \) occurs at \( \theta \approx 48^\circ \). At the on-resonance frequency, corresponding to \( \sigma_\perp \) in our experiments, \( R^{-1} \approx 0.73ms \). Although signal to noise ratio for cymantrene is far from the ideal situation offered by ferrocene, an acceptable fitting is still achieved at \( \sigma_\perp \) giving \( R^{-1} > 1.2ms \). The comparison of this value with that for the same orientation in ferrocene manifests the less dense network of \( I \)-spins in cymantrene.

The local \( I \)-polarization in ferrocene as detected in the \( S \)-spin by using the pulse sequence sketched in Fig. 4 is displayed in Fig. 8. Experimental parameters are given in the caption. It can be noticed that for each delay time \( t_1 \) a maximum in the local polarization, called polarization echo, is obtained at a time \( t_2 = \left[ \frac{1}{2} \right] t_1 + t_m \),
where \( t_m \approx \frac{3}{2} (t_p + t_d) / 2 \) is the time spent to compensate for the I-spin evolution occurring during the short cross polarization pulses \( t_d \) and \( t_p \). It is not difficult to see that at \( t_1 \approx 240 \mu s \) almost 50\% of the initial polarization has not been able to refocus, reflecting the irreversible part of the evolution which leads to the decay of the polarization echo amplitudes. Superimposed to the curves, there are some high-frequency (\( \approx 59 k Hz \)) oscillations which are particularly noticeable around the maximum amplitude of the echo. These oscillations are well above the experimental error and its quantum origin has been explained previously. A similar study was performed in cymantrene, where the curve for \( t_1 = 0 \) is displayed in Fig.9. It can be seen there, that the quantum interferences are better developed than in ferrocene: a quantum beat at 400 \( \mu s \) reflects the discrete nature of the system where the I-spin evolution occurs, while a mesoscopic beat insinuated at 600 \( \mu s \) indicates the finite size of the ring. This can be understood in terms of the better isolation of one cyclopentadienil ring protons from other ring protons, as can be inferred from the crystalline structure of cymantrene (Fig. 2) as compared with ferrocene (Fig. 1). Besides, recording of the local polarization around their maxima in cymantrene, for the same delay times \( t_1 \) studied in ferrocene, allows us a comparative analysis of the attenuation of polarization echoes. The experimental amplitudes of the polarization echoes \( M_{PE} \) obtained for each system are plotted in Fig. 10 as a function of the total forward evolution \( t_R \). According to the discussion above we have \( t_R = \frac{3}{2} (t_1 + t_2^M + 2t_m) \approx t_1 + 2t_m \) with \( t_1 = 0 \mu s, 80 \mu s, 160 \mu s \) and \( 240 \mu s \), the time at which the maximum polarization occurs. The experimental data clearly show different functional dependence of the decay of the echo amplitude on \( t_R \). Data of Ferrocene are Gaussian-like while those of Cymantrene are exponential. According to our previous work, the correct normalization of the data requires \( M_{PE}(t_R = 0) \equiv 1 \). This allows us to compare different systems. It is well known that decoherence would lead to an ergodic distribution of polarization. In Ferrocene, the inter-ring and intermolecular I-I interactions are both very important, then one expects a significant spreading of the refocused polarization. By choosing an asymptotic value of 0 a good fittings to a Gaussian is obtained with a characteristic time as the only free parameter. In contrast, the rings of cymantrene are better isolated within the experimental times \( t_R \leq 335 \mu s \). Then we choose the asymptotic value of \( 1 / 5 \) for the exponential decay obtaining a good fitting. Irreversible interactions are those we have not been able to reverse in our experiments. This is the situation of the non-secular terms in the Hamiltonian. In order to study whether they are responsible for the attenuation of the polarization echoes, we performed exact calculations of the spin dynamics using parts A to F of the sequence sketched in Fig.4 for a cyclopentadienil ring with a single \(^{13}\)C. While the \( \pi / 2 \) pulses are considered ideal, evolution during the short cross polarization times \( t_d \) and \( t_p \) is described with the complete Hamiltonian following the scheme by Levitt et. al. During time \( t_1 \) the Hamiltonian is:

\[
\mathcal{H}_1^I = \mathcal{H}_I + \mathcal{H}_{II}^I + \mathcal{H}_{IS}^I, \tag{8}
\]

where

\[
\mathcal{H}_I = -\hbar \gamma I B^I_{1I} \sum_k I^y_k \tag{9}
\]

and

\[
\mathcal{H}_{IS} = \sum_k b_k 2I^y_k S^z. \tag{10}
\]

The contribution \( \mathcal{H}_{II}^I \) takes into account the non-secular part of the I-spin dipolar interactions which were neglected in Eq. (6). On the other hand, evolution during time \( t_2 \), taking into account both \( \pi / 2 \) pulses on the I-system, can be described by:

\[
\mathcal{H}^2 = \overline{\mathcal{X}}(\frac{\pi}{2}) \{ \mathcal{H}_{II} + \mathcal{H}_S + \mathcal{H}_{IS} \} X(\pi / 2) = [-2] \mathcal{H}_{II} + \mathcal{H}_S + \sum_k b_k 2I^y_k S^z, \tag{11}
\]

where \( \mathcal{H}_{II} \) is given in Eq. (6) and

\[
\mathcal{H}_S = -\hbar \gamma S B^y_{IS} S^y. \tag{12}
\]

Fig. 11 shows the results of the complete sequence calculation. The attenuation generated is much slower than the experimentally observed, giving a decay of less than 10\% for times where the experiment shows around 50\%. It was verified by excluding one term at a time that the only term producing a visible attenuation of the polarization echoes is \( \mathcal{H}_{IS} \) during \( t_1 \). This term transforms some I-spins polarization into I-S coherence. Increase on the size of the system to six, seven, and eight protons shows no faster decays than the ring with five protons, as long as the ring topology is kept and a single \( S \) is included in the spin dynamics. If those non-invertible terms were responsible for the attenuation of the polarization echoes in Ferrocene, the spin dynamics in the actual complex proton network should play a relevant role amplifying their effects. Due to the magnitude of the computation involved, we have not been able so far to treat other topologies of the I-network in a systematic way.

**IV. CONCLUSIONS**

We used the structural properties of cymantrene and ferrocene, which determine their different networks of dipolar coupled hydrogens, to test how this topology influences the “diffusion” of a local excitation. We also studied the polarization echoes which describe the “anti-diffusion” process or backward evolution. With respect
to the evolution forward in time, we have seen that cymantrene gives better developed quantum beats when compared with ferrocene. This is caused by the fact that the I-I couplings network is better limited to one ring. However, from the attenuation of the oscillations we conclude that there is still an appreciable amount of I-I intermolecular couplings acting at intermediate times. With regard to the attenuation of the polarization echoes, cymantrene presents an exponential decay in contrast with ferrocene where a Gaussian decay of the polarization echoes is observed.

The exponential regime is quite clear when there is an irreversible process with a characteristic time \( \tau_0 \) shorter than the typical time for the spin dynamics. Then, the probability to return to the initial state would be given by the survival probability, which is proportional to \( \exp[-t/\tau_0] \). This seems to be the case for cymantrene, where a strong local source of relaxation could be traced back to the quadrupolar nature of the Mn nucleus (nuclear spin 5/2).

The interpretation of the Gaussian decay of the polarization echoes observed in ferrocene is more subtle. The absence of obvious irreversible interactions requires the consideration of small non-inverted terms, the most significative of these are the I-S non-secular terms. However, as long as we consider a spin dynamics restricted to a single ring, those terms are not enough to explain the decay which occurs in a time scale typical of the dipolar dynamics. The ingredient that was left out from the calculation is the complex topology of the actual network where the spin dynamics occurs. This is expected to be very relevant at a time \( t_{mb} \), at which the quantum beats attenuate. In general, weak non-invertible terms produce fluctuations at a rate \( 1/\tau_{mb} \) leading to local spin flips whose effect can be considered a damage or disease that propagates through the network, due to the natural spin dynamics, like an epidemic. Thus, the damage spreads with the “spin diffusion” rate. When the dipolar evolution is reverted (by external means) the modified spin configurations can not warrant a return to the initial state. That is, some reversible part of the dynamics (e.g. the inter-ring dipolar interaction) paves the way to the extraordinary efficiency of small irreversible fluctuations. This is consistent with the results obtained by Lacelle\(^\text{[2]}\) for the reversibility of classical spins with a dynamics described by a cellular automaton model. The interplay between reversible dynamics and irreversible interactions, resembles\(^\text{[3]}\) the process that causes electrical resistivity in an impure metal at low temperatures. In this case, reversible collisions with impurities (with rate \( 1/\tau_{imp} \)) favor the effectiveness of the irreversible electron-phonon interaction (with rate \( 1/\tau_0 \ll 1/\tau_{imp} \)) and set the diffusion coefficient \( D \propto \tau_{imp} \). Another analogous situation is the unstable quantum oscillator\(^\text{[4]}\) where the reversible potential favors dissipation. Since the study of dynamical irreversibility in many body quantum systems is still in its infancy, there is much room for numerical and analytical studies to verify the main suggestion of our experiment: that these systems can present a local instability amplifying the natural fluctuations of the environment.

It is interesting to emphasize that the systems experimentally studied show a crossover between the different physical regimes while the attenuation of the polarization echo occurs on the same time scale. This is possible because the slower spin dynamics of cymantrene is compensated by its much stronger fluctuating environment.

In summary we have shown the suitability of this new NMR pulse sequence\(^\text{[5]}\) as a tool in the study of fundamental questions about dynamical irreversibility. Our work has settled a conceptual framework allowing for the identification of the relevant parameters governing such phenomenon, that should stimulate the design of new experiments.

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The polarization is locally injected by cross-polarization from a short cross-polarization time during which the $I$ sense during a period of molecules with their rotational axis at the magic angle at short contact time there is almost no signal from spectra have essentially the same amplitude at the exact irradiation frequency. Note that both in its (room temperature) monoclinic form with space group $P2_1/a$ as described in ref. 11. Two unit cells are included for comparison with Fig. 2. The compound crystallizes in the monoclinic space group $P2_1/a$ with four molecules per unit cell. A) Proton polarization is locally injected by cross-polarization from $S$ to $I$ during $t_d$. B) Dipolar evolution of the spin locked $I$-spin polarization is allowed for a time $t_1$. C) With a $(\pi/2)_x$ pulse, the proton magnetization is turned into the $z$-axis where D) dipolar evolution occurs in the reverse sense during a period $t_2$. E) A $(\pi/2)_{-x}$ pulse, followed by F) a short cross-polarization time $t_p$, to the $x$-axis of the $S$-spins, allows for detection minimizing quantum interference between dashed and dotted pathways of probability amplitudes of polarization. G) Acquisition is done under high resolution conditions.

**Figure 5:** $^{13}$C magnetization as function of contact time in a simple cross polarization experiment in ferrocene powder. The amplitudes have been frequency selected from the axially symmetric spectra. Data in the upper part of the plot correspond to molecules with the five-fold axis perpendicular to the external magnetic field ($\theta = \pi/2$), and the lower part to molecules at the magic angle $\theta = \theta_m$. The experiment was performed with $\omega_1/2\pi=44.6\text{kHz}$. The dotted curve corresponds to a non-linear least square fitting to Eq. (3). Solid lines are fittings to Eq. (3). Dashed line includes exact dynamics in a ring besides the dipolar relaxation parameter.

**Figure 6:** $^{13}$C magnetization as function of contact time in a simple cross polarization experiment for cymantrene molecules with their five-fold axes approximately perpendicular to the external magnetic field.

**Figure 7:** Parameters obtained by fitting all the experimental curves of the type displayed in Fig. 5 to Eq. (3). Fittings for orientations differing in approximately $80^\circ$ from $\theta_m$ are shown in the upper part of the plot. The experimental points are shown as squares, and the upper and lower curves correspond to molecules with their five-fold axes perpendicular and approximately parallel to the external magnetic field, respectively. The experimental data have been properly normalized experimental polarization echo amplitudes (maxima of the curves in Figs. 8 and 9) for the approximate frequency of the $\pi/2$ pulse. The solid curves are obtained from simulations of the dynamical evolution of the magnetization with the sequence in Fig. 4. The solid curve for $t_1+t_2=95\mu s$ is shown in Fig. 8.

**Figure 8:** Ferrocene experimental data as function of $t_1+t_2$ using the sequence in Fig. 4 with $\omega_1/2\pi=44.6\text{kHz}$, $t_c=2\mu s$, $t_s=1\mu s$, $t_d=t_p=85\mu s$, for $t_1=0\mu s$, $80\mu s$, $160\mu s$ and $240\mu s$.

**Figure 9:** Cymantrene experimental data as function of $t_1+t_2$ using the sequence in Fig. 4 with $\omega_1/2\pi=44.6\text{kHz}$, $t_c=2\mu s$, $t_s=1\mu s$, $t_d=t_p=95\mu s$, for $t_1=0\mu s$.

**Figure 10:** Efficiency of the Loschmidt daemon. The properly normalized experimental polarization echo amplitudes (maxima of the curves in Figs. 8 and 9) $M_{PE}$ for ferrocene and cymantrene as function of the time $t_R$. Solid lines represent fittings of the experimental points to Gaussian and exponential laws respectively.

**Figure 11:** Theoretical calculation (to be compared with Fig. 8) for the $^{13}$C polarization in a five proton ring of ferrocene after the pulse sequence A-F sketched in Fig. 4. The high frequency oscillations are explained by the non-ideality of the $^{13}$C probe and they have an approximate frequency of $\omega_{1f}$. They are quantum interferences caused by the failure of full transfer of polarization between $I$ and $S$ spins.

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VI. FIGURE CAPTIONS

**Figure 1:** Crystalline structure of ferrocene, Fe(C$_5$H$_5$)$_2$ in its (room temperature) monoclinic form with space group $P2_1/a$ as described in ref. 11. Two unit cells are included for comparison with Fig. 2.

**Figure 2:** Crystalline structure of cymantrene (C$_5$H$_5$)Mn(CO)$_3$ according to crystallographic data on ref. 12. The compound crystallizes in the monoclinic space group $P2_1/a$ with four molecules per unit cell.

**Figure 3:** $^{13}$C-NMR spectra of polycrystalline ferrocene after a simple cross-polarization experiment with 85 $\mu$s and 3ms contact times respectively. The arrow indicates the exact irradiation frequency. Note that both spectra have essentially the same amplitude at $\sigma_\perp$ but at short contact time there is almost no signal from molecules with their rotational axis at the magic angle with the external magnetic field $B_0$.

**Figure 4:** Pulse sequence for refocusing the evolution of $^1H$ spin ($I$-spin) polarization. $S$-spin ($^{13}$C spin) polarization in the $y$-axis is prepared by $I$-$S$ cross polarization. The $S$ magnetization is kept spin locked for a time $t_s$ during which the $I$-spin coherence decays to zero. A) Proton polarization is locally injected by cross-polarization from $S$ to $I$ during $t_d$. B) Dipolar evolution of the spin locked $I$-spin polarization is allowed for a time $t_1$. C) With a $(\pi/2)_x$ pulse, the proton magnetization is turned into the $z$-axis where D) dipolar evolution occurs in the reverse sense during a period $t_2$. E) A $(\pi/2)_{-x}$ pulse, followed by F) a short cross-polarization time $t_p$ to the $x$-axis of the $S$-spins, allows for detection minimizing quantum interferences between dashed and dotted pathways of probability amplitudes of polarization. G) Acquisition is done under high resolution conditions.
\[ t_c = 85 \mu s \]

\[ t_c = 3000 \mu s \]
$^{13}$C Magnetization

$t_c$ [μs]
Local Polarization

$(\text{C}_5\text{H}_5)\text{Mn(CO)}_3$

t$_p = t_d = 95 \mu s$
\[
\tau > \tau_{mb}
\]

\[
\tau < \tau_{mb}
\]
Local Polarization vs $t_1 + t_2$ [µs]