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Theoretical Description of Pulsed RYDMR: Refocusing Zero-Quantum and Single Quantum Coherences

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Abstract: A theoretical description of pulsed reaction yield detected magnetic resonance (RYDMR) is proposed. In RYDMR, magnetic resonance spectra of radical pairs (RPs) are indirectly detected by monitoring their recombination yield. Such a detection method is significantly more sensitive than conventional electron paramagnetic resonance (EPR), but design of appropriate pulse sequences for RYDMR requires additional effort because of a different observable. In this work various schemes for generating spin-echo like signals and detecting them by RYDMR are treated. Specifically, we consider refocusing of zero-quantum coherences (ZQCs) and single-quantum coherences (SQCs) by selective as well as by non-selective pulses and formulate a general analytical approach to pulsed RYDMR, which makes an efficient use of the product operator formalism. We anticipate that these results are of importance for RYDMR studies of elusive paramagnetic particles, notably, in organic semiconductors.

Keywords: organic semiconductors, RYDMR, spin chemistry, spin echo.

Dedicated to: Kev Salikhov on the occasion of his 80th birthday.

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1 Introduction

Reaction yield detected magnetic resonance (RYDMR) [1, 2] is a powerful method for investigating short-lived paramagnetic particles, which are often beyond the reach of conventional electron paramagnetic resonance (EPR) spectroscopy. In RYDMR, magnetic resonance spectra of short-lived radical pairs (RPs) are detected indirectly, by monitoring the optical absorption or fluorescence of RP recombination products. Such a method is by far more sensitive than direct EPR observation and it enables the detection of elusive radicals and RPs with nanosecond time resolution. In RYDMR, the reaction yield is altered by applying RF- or MW-fields in order to induce transitions between the RP spin states. Consequently, RYDMR signals are obtained as a dependence of the RP recombination yield on the parameters of the applied oscillating fields. Alternatively, the yield of RPs avoiding recombination can be measured, as it is done in photo-current detected RYDMR [3–6], for instance, in photo-voltaic cells [7, 8]. One more option is to detect the variation of non-equilibrium nuclear spin polarization of the RP recombination product under the action of resonant RF- or MW-fields: such a method is termed stimulated nuclear polarization [9, 10].

Developing a theoretical treatment of RYDMR is a challenging problem, which generally requires the quantitative description of both the spin dynamics and reaction dynamics of an RP. Interestingly, although RYDMR is closely related to EPR, it differs in many aspects because of the different observable. While in EPR the RP spin magnetization is detected, in RYDMR the observable is the RP recombination yield (or, sometimes, the RP separation yield). Typically, the RYDMR signal is given by the singlet-state population of an RP, i.e. it becomes maximal when the RP is brought to the singlet state under the action of MW-fields. However, in this situation the spin magnetization is zero, thus, the EPR signal becomes minimal. For this reason, EPR methods cannot be exploited in RYDMR without a pertinent modification.

In this work we focus on the theory of pulsed RYDMR, which is based on detecting spin-echo like signals by monitoring the RP recombination yield. Previously, Salikhov and Molin [11] have demonstrated that by applying a non-selective MW pulse to a singlet-born RP at the instant of time $t = \tau$ it is possible to refocus the singlet-state population at $t = 2\tau$, i.e. to obtain a spin-echo like behavior of the singlet-state population. An extension of this treatment was later performed by Shkrob [12], who considered refocusing by two MW-pulses with different phases. In our previous work [13] this possibility of creating “spin echoes” observed via the singlet-state population of an RP has been considered in detail. The key idea was to refocus the zero-quantum coherence (ZQC) in an RP. When an RP is formed in a high external high magnetic field, its eigen-states are no

longer the singlet-triplet states, but the Zeeman states with well-defined projections of the spins on the direction of the external field. The ZQC is the coherence between the $\alpha\beta$ - and $\beta\alpha$ -states of an RP (hereafter, α and β denote the spin-up and spin down states of a spin-1/2 particle). When an RP is formed in the singlet state the ZQC is formed together with the populations of the $\alpha\beta$ - and $\beta\alpha$ -states. Due to the coherent spin evolution, namely, due to the transitions between the singlet state, S , and the central triplet state, T_0 (driven by the difference in the electronic Zeeman interactions of the RP partners with the external magnetic field) [14] the ZQC starts oscillating; when there is a distribution of the oscillation frequencies the ZQC dephases and disappears. However, the dephased ZQC can be refocused by using non-selective pulses. For instance, a π -pulse allows one to refocus the ZQC completely; consequently, all RPs go back to the singlet state. When one monitors the singlet-state population, ρ_{ss} , as a function of time one would see an echo-like signal (a peak) at the instant of time when the ZQC is completely (or partly) refocused. In the previous work [13] we have also considered more complex pulse sequences using non-selective pulses, e.g. pulse sequences, which enable modulation of the spin echo due to different interactions, stimulated echo and electron-nuclear double resonance.

In this work, we further develop the theory of pulsed RYDMR and present a detailed theoretical description of RYDMR using refocusing of the ZQC. Specifically, we consider refocusing by selective pulses, which is of importance because non-selective excitation in EPR is often technically demanding. Additionally, we describe theoretical results for pulsed RYDMR using refocusing of the single-quantum coherences (SQC), i.e. transverse spin magnetization. Such methods are frequently used in electrically detected magnetic resonance (EDMR) in semiconductors, with an aim to investigate processes such as spin-dependent transport and recombination of charge carriers in photovoltaic cells. The idea behind RYDMR detection of SQCs is to generate a standard spin-echo signal and then to convert the refocused transverse magnetization into an observable, suitable for RYDMR: this is done by applying an additional $\frac{\pi}{2}$ -pulse. Here we consider refocusing of SQCs by selective as well as by non-selective pulses. Interestingly, when non-selective pulses are used, it becomes possible to obtain a modulated spin-echo signal; the modulation frequency is given by the spin-spin interaction and can thus provide information about the distribution of distances between the RP partners.

Here we obtain analytical results for the spin echo signals, which are corroborated by the product operator formalism description and by numerical calculations. In our comprehensive description we discuss the peculiarities of pulsed RYDMR and its difference to pulsed EPR. The principles of spin-echo formation

in RYDMR are described, providing a simple way for treating complex pulse sequences and allowing one to design RYDMR pulse techniques.

2 Calculation method

2.1 Spin evolution

Let us study the spin evolution in an RP under the action of various MW-pulse sequences. The Hamiltonian of an RP in a high external magnetic field B_0 is as follows (in \hbar units, as written in the MW-rotating frame, ω is the MW-frequency)

$$\hat{H} = (\omega_a - \omega)\hat{S}_{az} + (\omega_b - \omega)\hat{S}_{bz} + J\hat{S}_{az}\hat{S}_{bz} = \delta\omega_a\hat{S}_{az} + \delta\omega_b\hat{S}_{bz} + J\hat{S}_{az}\hat{S}_{bz} \quad (1)$$

This Hamiltonian is valid for the times between the MW-pulses and describes the electronic spin interactions. Here \hat{S}_a and \hat{S}_b are the spin operators of the two RP partners, the a-spin and b-spin; the first two terms describe the Zeeman interactions, $\omega_a = g_a\mu_B B_0$ and $\omega_b = g_b\mu_B B_0$, of the spins with the external magnetic field ($g_{a,b}$ are the g-factors of the radicals and μ_B is the Bohr magneton); the last term stands for the spin-spin-interaction, J (including exchange and dipolar coupling); here only the secular part of this interaction is considered (high-field approximation). The expression for the spin-spin-interaction with non-secular terms neglected is valid when $|J| \ll |\omega_a - \omega_b|$. In solids the values of $\omega_{a,b}$ and J take different values depending on the orientation of the molecules; thus, there is a distribution of the $\omega_{a,b}$ and J values originating from the non-averaged anisotropic parts of the corresponding interaction tensors. Here we always assume that the EPR lines of the radicals are inhomogeneously broadened having the Gaussian shape and widths σ_a and σ_b (here given in the angular frequency units). Broadening of the EPR lines is originating from anisotropy of their g-tensors and from hyperfine couplings with magnetic nuclei in their neighborhood. When needed, it is simple to explicitly take into consideration the couplings to magnetic nuclei of the radicals by introducing the corresponding terms in the Hamiltonian.

The evolution of the density matrix, $\rho(t)$, between the pulses is given by the solution of the Liouville-von Neumann equation and it is as follows:

$$\rho(t) = \exp(-i\hat{H}t) \rho(0) \exp(i\hat{H}t) \quad (2)$$

Here $\rho(0)$ is the density matrix prior to the evolution period. In the Hamiltonian all three terms commute with each other; for this reason, to describe the evolution of the spin system one can apply them sequentially

$$\begin{aligned} \rho(t) &= \exp(-ij\hat{S}_{az}\hat{S}_{bz}t) \exp(-i\delta\omega_b\hat{S}_{bz}t) \\ &\times \exp(-i\delta\omega_a\hat{S}_{az}t)\rho(0) \exp(i\delta\omega_a\hat{S}_{az}t) \\ &\times \exp(i\delta\omega_b\hat{S}_{bz}t) \exp(ij\hat{S}_{az}\hat{S}_{bz}t) \end{aligned} \quad (3)$$

This property is helpful in analytical considerations. It is also important to note that the solution of the eigen-problem of the Hamiltonian \hat{H} is very simple; the eigen-states are the product states of the individual spins.

When a MW-pulse is applied (for instance, having the x -phase) the Hamiltonian (1) should be modified as follows:

$$\hat{H} \rightarrow \hat{H}_f = \hat{H} + \hat{H}_p; \quad \hat{H}_p = \omega_1(\hat{S}_{ax} + \hat{S}_{bx}) \quad (4)$$

Here ω_1 is the strength of the MW-field. As a consequence, the density matrix, which was equal to ρ_- before the pulse, changes as follows

$$\rho_+ = \exp(-i\hat{H}_f\tau) \rho_- \exp(i\hat{H}_f\tau) \quad (5)$$

Here τ is the pulse duration. When the pulse is ideal, the MW-field is strong and the MW-frequency is close to the resonance frequency of the spins the following simplification can be made:

$$\hat{H}_f \approx \hat{H}_p; \quad \hat{H}_f\tau \approx \varphi(\hat{S}_{ax} + \hat{S}_{bx}) \quad (6)$$

Hence, the pulse flips the magnetization of both spins by an angle $\varphi = \omega_1\tau$. In this case we can characterize MW-pulses by their flip angles and phases (i.e. the axis of rotation) by using a notation φ_x (or φ_y). When the excitation bandwidth is sufficient to flip only one of the two spins [which is the case when $\omega_1 \ll (\omega_a - \omega_b)$], e.g. the a -spin, eq. (6) should be modified as:

$$\hat{H}_f\tau \approx \varphi\hat{S}_{ax} \quad (7)$$

Here, in analytical calculations we used simpler expressions (6) and (7), whereas in numerical calculations the complete Hamiltonian (4) was used.

In principle, the RP spin evolution is also affected by (i) spin relaxation and (ii) chemical reaction. For simplicity, we neglect both factors even though the presence of the chemical reaction is a prerequisite for observing the echoes in ρ_{ss} (the reactive state is always the singlet state). We only look at the $\rho_{ss}(t)$ time trace and check whether we obtain echo-like signals. The reason why this treatment is sufficient for understanding the mechanism of the echo formation is described in the previous publication [13]. For an alternative RYDMR detection method we evaluate the difference of the populations, ΔP , of the RP states with parallel

and anti-parallel spins after applying the pulse sequence (see Section 2.3), also neglecting the effect of the chemical reaction.

2.2 Initial condition

For the initial RP spin state we consider two possibilities: the pure singlet state and “depleted” state. The state of the first kind is just the singlet state of two spins; the corresponding density matrix is expressed as follows:

$$\rho_s = |S\rangle\langle S| = \frac{1}{4}\hat{E} - \{\hat{S}_{az}\hat{S}_{bz} + \hat{S}_{ax}\hat{S}_{bx} + \hat{S}_{ay}\hat{S}_{by}\} \quad (8)$$

Here the zz -term results in the populated $\alpha\beta$ - and $\beta\alpha$ -states; while the xx - and yy -terms are responsible for the coherences between these states, which is the ZQC. When the ZQC is zero (which can be the case, for instance, when RPs are formed continuously during a sufficiently long period of time, which is longer than the time of the ZQC evolution) the density matrix is simplified as follows:

$$\rho_0 = \frac{1}{2}|\alpha\beta\rangle\langle\alpha\beta| + \frac{1}{2}|\beta\alpha\rangle\langle\beta\alpha| = \frac{1}{4}\hat{E} - \hat{S}_{az}\hat{S}_{bz} \quad (9)$$

The state of the second kind is the state with the depleted $\alpha\beta$ - and $\beta\alpha$ -states:

$$\begin{aligned} \rho_d = \frac{1}{2}|\alpha\alpha\rangle\langle\alpha\alpha| + \frac{1}{2}|\beta\beta\rangle\langle\beta\beta| = \frac{1}{2}|T_+\rangle\langle T_+| \\ + \frac{1}{2}|T_-\rangle\langle T_-| = \frac{1}{4}\hat{E} + \hat{S}_{az}\hat{S}_{bz} \end{aligned} \quad (10)$$

Such a spin state corresponds to the situation where RPs are formed in encounters in an uncorrelated spin state; however, as the time goes by, the populations of the states ($\alpha\beta$ - and $\beta\alpha$ -states) having the singlet character decay to zero. As a consequence, only the outer triplet states, T_{\pm} , remain populated. For the initial RP state given by eq. (9) and by eq. (10) we obtain essentially the same results because the spin order is very similar: it is the multiplet spin order $\hat{S}_{az}\hat{S}_{bz}$, which is either negative, see eq. (9), or positive, see eq. (10). For this reason, we obtain results only for the “depleted” state (10); the results for the initial condition given by eq. (9) can be obtained in the same way. In the context of RYDMR it is important that in all cases the RP has multiplet-spin order (spins have a preferred mutual orientation) rather than net polarization with respect to the external magnetic field.

The refocusing schemes used in the RYDMR case should be adjusted for refocusing this specific spin order.

2.3 RYDMR observable

In order to calculate the RYDMR signal we compute the state populations as the corresponding expectation values: $\rho_{SS} = \langle S|\rho|S\rangle$, $\rho_{T_0T_0} = \langle T_0|\rho|T_0\rangle$, $\rho_{T_+T_+} = \langle T_+|\rho|T_+\rangle$, $\rho_{T_-T_-} = \langle T_-|\rho|T_-\rangle$ and study their dependence on the timing of the pulse sequences and pulse flip angles.

RYDMR signals can be observed in two different ways. In the first observation mode, the concentration of the RP recombination product is monitored in real time [11, 15–17]. In turn, the rate of the product formation is proportional to the fraction of RPs in the singlet state, equal to $\rho_{SS}(t)$. Thus, in such an experiment it becomes possible to measure the time dependence of $\rho_{SS}(t)$. Experiments of this kind are done, for instance, for detecting radical ion pairs in non-polar solutions by monitoring the luminescence of the singlet-state recombination product [15–17]. When the luminescence time is short, the luminescence kinetics gives the $\rho_{SS}(t)$ time dependence. Consequently, when the ZQC is refocused an echo-like feature, i.e. a peak, appears in the $\rho_{SS}(t)$ kinetic trace.

The mechanism of ρ_{SS} refocusing can be rationalized using the product operator formalism [18]. In the language of the product operator treatment, the ZQC is given by the following product operators:

$$ZQC_x = \hat{S}_{ax} \hat{S}_{bx} + \hat{S}_{ay} \hat{S}_{by} \quad (11)$$

After a time period τ , this operator changes to the following one [18]:

$$\hat{A} = \cos(\delta\omega\tau) ZQC_x - \sin(\delta\omega\tau) ZQC_y, \quad ZQC_y = \hat{S}_{ay} \hat{S}_{bx} - \hat{S}_{ax} \hat{S}_{by} \quad (12)$$

Here $\delta\omega = \omega_a - \omega_b$. A non-selective π -pulse with the x-phase (for the y-phase the echo is the same and the results are obtained in the same manner) changes the sign of all y-operators, so, the operator \hat{A} changes as follows:

$$\hat{A} \rightarrow \cos(\delta\omega\tau) ZQC_x + \sin(\delta\omega\tau) ZQC_y \quad (13)$$

After another free evolution period of a duration τ both operators, ZQC_x and ZQC_y , evolve to the following result:

$$\begin{aligned} \cos(\delta\omega\tau) ZQC_x + \sin(\delta\omega\tau) ZQC_y &\xrightarrow{\tau} \cos^2(\delta\omega\tau) ZQC_x - \cos(\delta\omega\tau)\sin(\delta\omega\tau) ZQC_y \\ &+ \cos(\delta\omega\tau)\sin(\delta\omega\tau) ZQC_y + \sin^2(\delta\omega\tau) ZQC_x = ZQC_x \end{aligned} \quad (14)$$

Thus, the ZQC is completely refocused at $t=2\tau$. Besides this simplest refocusing scheme, here we consider also more complex pulse sequences.

However, the method of detection using real-time monitoring of $\rho_{ss}(t)$ is not always feasible. Consequently, for generalizing pulsed RYDMR it is necessary to switch to a different variable; likewise, the experimental protocol for observing “spin echoes” has to be modified. To do so, the following idea can be used. Generally, RPs in the S and T_0 states and in the T_{\pm} states have a different fate: when the RP can recombine only from the singlet state, RPs with anti-parallel spins, i.e. with singlet character, recombine faster, whereas those with parallel spins recombine slower. For this reason, when the RP ends up in the T_+ and T_- states after application of a MW-pulse sequence more radicals avoid recombination. RYDMR is sensitive to the fraction of such RPs: for instance, the EDMR current changes upon variation of this fraction [8]. Generally, the RP recombination yield (or separation yield) is proportional to the imbalance of populations, ΔP , of the states with parallel and anti-parallel spins after application of the pulse sequence:

$$\Delta P = P_{\uparrow\uparrow} - P_{\downarrow\downarrow} = (\rho_{T_+T_+} + \rho_{T_-T_-}) - (\rho_{SS} + \rho_{T_0T_0}) = 4\text{Tr}\{\hat{S}_{az}\hat{S}_{bz}\rho\} \quad (15)$$

The ΔP value is, in fact, given by the expectation value of the multiplet polarization of the RP. Measurements of ΔP also allow one to observe spin-echo like signals [8]. In order to observe and investigate such “spin echoes” it becomes necessary to study ΔP as a function of inter-pulse delays, or pulse flip angles (or phases). The simplest method to form and observe a “spin-echo” is as follows [8]: first, a standard EPR spin echo should be formed by refocusing the transverse spin magnetization. Consequently, a $\frac{\pi}{2}$ -pulse should be applied in order to convert the transverse magnetization into the population imbalance ΔP . When this pulse is applied exactly at the instant of time, when the spin echo is formed, the resulting ΔP value is maximal. This detection method follows closely a technique proposed in optically-detected magnetic resonance of triplet states [19]. Pulsed RYDMR techniques allow one to improve dramatically the sensitivity as compared to EPR. Furthermore, the method remedies the standard problem of EPR – the dead-time problem. This is because the measured quantity is the electric current or luminescence rather than spin magnetization.

Analytical results are obtained by using the product operator formalism, providing a simple way to analyze the effect of complex pulse sequences, of by using software for analytical calculations (e.g. Mathematica). Numerical results are obtained by calculating the time evolution of the RP density matrix and averaging the results over different values of ω_a and ω_b (coming from the finite width of the EPR lines of the radicals).

3 Results and discussion

3.1 Refocusing ZQC by non-selective pulses

In the previous work [13] we have studied the case where the initial RP state given by ρ_s . We will not repeat these results here and only briefly mention that the ZQC, which is present at $t=0$, starts evolving and becomes dephased due to the finite values of σ_1 and σ_2 . However, the ZQC evolution can be reverted by a non-selective π -pulse: when such a pulse is applied at $t=\tau$ the ZQC goes back to its initial value at $t=2\tau$. Using the same idea, more complex refocusing schemes can be designed [13].

Let us consider the case where the initial RP state is given by ρ_d (depleted S and T_0 states), see eq. (9). In this case initially the ZQC is zero, but it can be created by applying a single non-selective pulse. Indeed, from the initial density matrix we obtain after the action of a φ_x -pulse:

$$\rho_d = \frac{1}{4} \hat{E} + \hat{S}_{az} \hat{S}_{bz} \xrightarrow{\varphi \hat{S}_x} \frac{1}{4} \hat{E} + \cos^2 \varphi \hat{S}_{az} \hat{S}_{bz} + \sin^2 \varphi \hat{S}_{ay} \hat{S}_{by} + \sin \varphi \cos \varphi \{ \hat{S}_{az} \hat{S}_{by} + \hat{S}_{ay} \hat{S}_{bz} \} \quad (16)$$

The term containing the operator $\hat{S}_{ay} \hat{S}_{by}$ describes the ZQC with the amplitude

$$\text{ZQC}(0) = \rho_{\alpha\beta, \beta\alpha} = \rho_{\beta\alpha, \alpha\beta} = \frac{\rho_{ss} - \rho_{T_0 T_0}}{2} = -\frac{1}{4} \sin^2 \varphi \quad (17)$$

Strictly speaking, not only the ZQC is formed but also the Double-Quantum Coherence (DQC); however, it does not contribute to the signal in the case under study and is therefore neglected. After the ZQC is formed the spin evolution becomes exactly the same as described previously for the density matrix ρ_s . Consequently, the refocusing methods and mechanisms of the echo formation are also the same. The only difference is the initial amplitude of the ZQC: as compared to the previous case it is multiplied by the factor $-\frac{1}{2} \sin^2 \varphi$. In general, the ZQC can be formed because non-selective excitation can only drive transitions between the triplet levels but not the S-T transitions. As a consequence, the excitation pulse transfers the population from the T_{\pm} -states selectively to the T_0 state and the ZQC, which is proportional to $(\rho_{ss} - \rho_{T_0 T_0})$ [13], is formed.

An example of the spin evolution in such a situation is presented in Figure 1. Here we show the time dependence for two quantities, $\rho_{ss}(t)$ and $\rho_{T_0 T_0}(t)$. After the first pulse a non-zero T_0 population is formed, while ρ_{ss} is zero. Due to S- T_0 mixing driven by the difference in frequencies, $\delta\omega = (\omega_a - \omega_b)$, the population is evenly

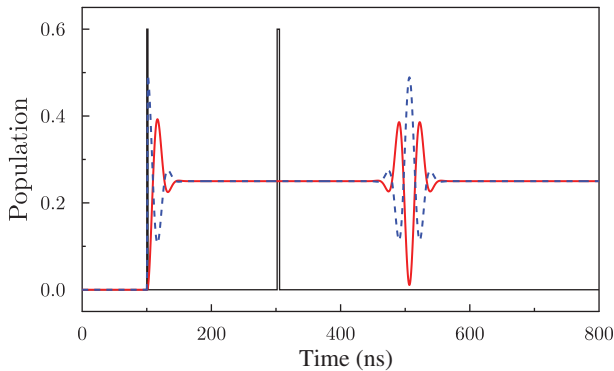


Fig. 1: Evolution of ρ_{ss} (solid line) and $\rho_{T_0T_0}$ (dashed line) under the action of pulse sequence $\left(\frac{\pi}{2}\right)_x - \tau - \pi_x - \tau$. The initial state is given by ρ_d . The envelope of the MW-pulses is shown by a thin solid line. Calculation parameters: $\delta\omega = 1$ mT, $\sigma_1 = 0.25$ mT, $\sigma_2 = 0.25$ mT, $\omega_1 = 5$ mT (during the MW-pulses), $J = 0$. The envelope of the MW-pulses is schematically shown by a thin line.

mixed between the S and T_0 states; however, application of a π -pulse enables complete refocusing of the ZQC. Thus, an echo-like signal is formed, which manifests itself as a peak in the $\rho_{T_0T_0}(t)$ dependence and as a dip in the $\rho_{ss}(t)$ time trace.

Thus, when non-selective pulses are used, it is possible to generate spin echoes when the initial state is given by ρ_s , see eq. (8), or by ρ_d , see eq. (10). In the former case the ZQC is present at $t = 0$ and it can be refocused by a single MW-pulse; in the latter case an additional MW-pulse is needed to generate the ZQC. Different pulse sequences for ZQC refocusing have been considered in our previous work [13] and can also be used when the RP is prepared in the state given by ρ_d (in this case an MW-pulse should be added to generate the ZQC).

Previously Boehme et al. [20] have considered a similar case (despite using a different terminology): generation of the ZQC by two selective $\frac{\pi}{2}$ -pulses applied to both spins (which work as a single non-selective $\frac{\pi}{2}$ -pulse) and refocusing of the ZQC by two selective π -pulses applied to both spins (which work as a single non-selective π -pulse) and obtained essentially the same result as the one shown in Figure 1. Additionally, Boehme et al. [20] have considered generation of the ZQC by a pair of selective pulses with the flip angles $\frac{\pi}{2}$ (for the a-spin) and $\frac{3\pi}{2}$ (for the b-spin) and obtained an echo-like signal of the opposite sign. This result can be easily rationalized using the product operator formalism: when the flip angles are $\frac{\pi}{2}$ and $\frac{3\pi}{2}$, the initial $\hat{S}_{az}\hat{S}_{bz}$ spin order is modified by the pulses in

the following way: $\hat{S}_{az}\hat{S}_{bz} \rightarrow -\hat{S}_{ay}\hat{S}_{by}$. That is, the ZQC sign is reverted as compared to eqs. (16) and (17). Consequently, the echo sign is reverted as well.

3.2 Refocusing ZQC by selective pulses

Refocusing of the ZQC is also possible when selective pulses are used; however, one should note that this requires additional effort. This is because the ZQC is essentially a two-spin property, as it is given by products of the individual spin operators. Therefore refocusing of the ZQC requires refocusing magnetization of both spins. For instance, when one of the spins is completely dephased (i.e. its transverse magnetization component is zero) the ZQC disappears even when the magnetization of the other spin is refocused. Consequently, one has to refocus both spins simultaneously in order to obtain an echo-like signal; thus, one has to apply pulses at the EPR frequencies of both spins. Therefore for refocusing the ZQC by non-selective pulses one should use double-resonance methods. An exceptional case where it is sufficient to refocus only one of the RP partners is given by an RP containing a radical with very long spin dephasing time.

The pulse sequences for refocusing the ZQC by selective MW-pulses are given in Figure 2. When considering the effect of these sequences we always assume that the initial state is given by ρ_s , i.e. at $t=0$ there is the ZQC present.

3.2.1 RP with a “narrow” partner

The simplest case of refocusing the ZQC by selective pulses is given by the situation where one of the radicals (for distinctness, the b-spin) has a very small inhomogeneous EPR linewidth (narrow EPR line) and thus does not require refocusing on a rather long timescale $t \sim 1/\sigma_b$. Then it is sufficient to refocus only the a-spin. Specifically, when the total duration of the pulse sequence, which is equal to $(2\tau + 2\tau_1)$, see Figure 2a, is shorter than the dephasing time of the “narrow” partner (this time is $1/\sigma_b$) it is sufficient to refocusing the ZQC by applying selective pulses only at the frequency of the a-spin.

The $\rho_{ss}(t)$ kinetic trace for this case is presented in Figure 3; the sequence applied contains two π -pulses transferring the populations from the states S and T_0 to T_+ and T_- and also completely converting the ZQC to the DQC and back. The DQC is given by the following operators [18]:

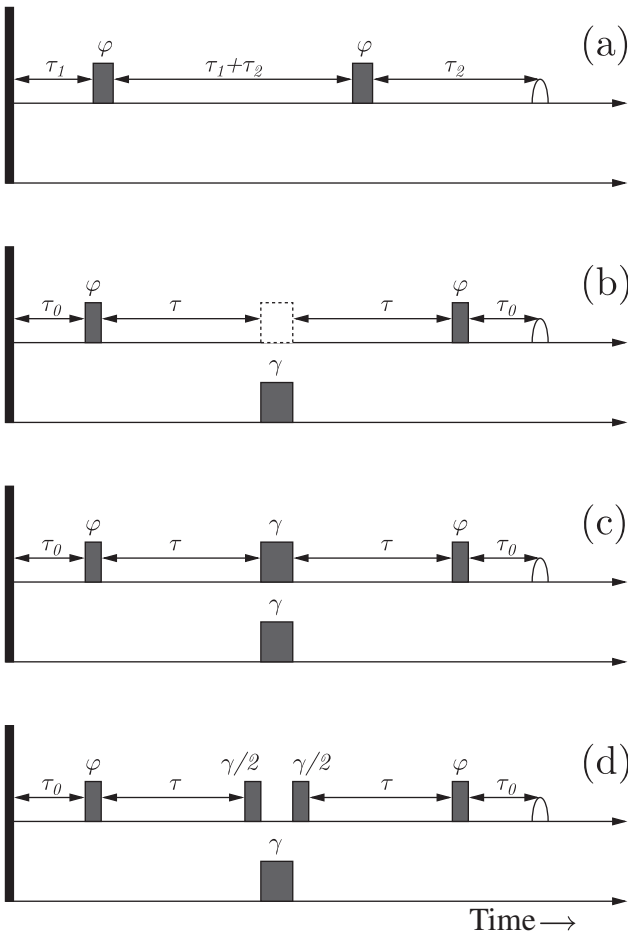


Fig. 2: Pulse sequences for refocusing the ZQC by selective pulses. Pulses are applied at two frequencies (EPR frequencies of the a-spin and b-spin) except for the case (a); pulse flip angles and delays are specified. Laser pulses are shown in black, MW-pulses are shown in gray, echo signals are shown in white. The pulse sequences for generating the primary echo are (a) and (b); the sequences (c) and (d) allow one to obtain modulation of the echo signal.

$$\begin{aligned}
 \text{DQC}_x &= \hat{S}_{ax} \hat{S}_{bx} - \hat{S}_{ay} \hat{S}_{by}; \\
 \text{DQC}_y &= \hat{S}_{ax} \hat{S}_{by} + \hat{S}_{ay} \hat{S}_{bx}
 \end{aligned}
 \tag{18}$$

Indeed, a selective pulse inverting the magnetization of only the a-spin converts the ZQC into DQC (and back), compare eqs. (11), (12) and (18). During the free evolution periods of the ZQC and DQC, the direction of the precession of the

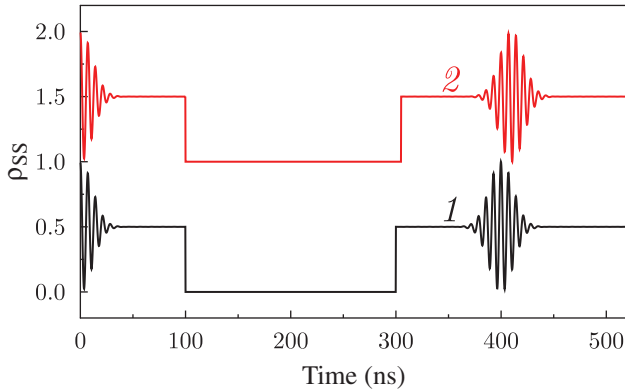


Fig. 3: $\rho_{ss}(t)$ kinetic traces for the sequence shown in Figure 2a. Here the b-spin has a narrow EPR line; the MW-pulses are applied in resonance with the a-spin. The echo formed at $t = (2\tau_1 + 2\tau_2)$ is modulated with the frequency $\delta\omega = (\omega_a - \omega_b)$. Calculation parameters: $\tau_1 = 100$ ns, $\varphi = \pi$, $\delta\omega = 5$ mT, $\sigma_1 = 0.5$ mT, $\sigma_2 = 0$, $J = 0$, τ_2 takes values 100 ns (trace 1) and 120 ns (trace 2). Curves calculated for different τ_2 are shifted along the vertical by 1.

a-spin is opposite. For this reason, when the evolution periods of the ZQC and DQC are equal, the initial ZQC is refocused, i.e. an echo is formed. This happens at $t = 2\tau_1 + 2\tau_2$; it is also necessary that the delay between the laser pulse and the first MW-pulse is smaller than the delay between the MW-pulses: otherwise, the DQC evolution period is always shorter than that of the ZQC.

Interestingly, the precession phase of the b-spin at the instant of refocusing the a-spin is different for different delays. That is, when the a-spin is refocused its phase is the same as at $t = 0$, while the b-spin freely precesses and has a different relative phase at the instant of refocusing. Consequently, the echo signal is modulated with the frequency $\delta\omega = (\omega_a - \omega_b)$.

It is important to note, that such a specific situation is, perhaps, rarely met. In more realistic cases one thus needs to refocus both spins by double-resonance methods.

3.2.2 Primary echo

When both spins need to be refocused the simplest variant of a spin-echo sequence is given by a modified sequence of the primary echo with non-selective excitation. This sequence is presented in Figure 2b; the idea behind it is that to form an echo it is necessary to refocus both spins at the same instant of time. We also keep in mind that the pulses at two different frequencies usually cannot be

applied simultaneously. For the first spin the simplest refocusing scheme is given by applying a single pulse at $t = \tau_0 + \tau$; for the second spin two pulses are applied at $t = \tau_0$ and $t = \tau_0 + 2\tau$. As a consequence, both spins are refocused at $t = 2\tau_0 + 2\tau$; thus the ZQC is partly refocused as well. The sequence does not allow one to observe modulation; the echo amplitude at $t = 2\tau_0 + 2\tau$ equals to

$$\begin{aligned} & \rho_{ss}(2\tau_0 + 2\tau) - \rho_{\tau_0\tau_0}(2\tau_0 + 2\tau) \\ &= \sin^2 \varphi \frac{1 - \cos \gamma}{4} = \frac{1}{2} \sin^2 \varphi \sin^2 \frac{\gamma}{2} \end{aligned} \tag{19}$$

It is worth mentioning that even for $\varphi = \gamma/2$ the echo amplitude does not coincide with that for the case of a single non-selective φ -pulse, which is [13]

$$\rho_{ss}(2\tau_0 + 2\tau) - \rho_{\tau_0\tau_0}(2\tau_0 + 2\tau) = \sin^4 \frac{\gamma}{2} \tag{20}$$

This difference is caused by the fact that some of the spin coherences are averaged out between the MW-pulses. If such an averaging is not complete, the echo amplitude will take an intermediate value. Results of the numerical calculations for this case are presented in Figure 4.

It is worth noting that in the case of selective pulses not only the echo amplitude but also the magnitude of the background signal $\rho_{av} = (\rho_{ss} + \rho_{\tau_0\tau_0})/2$ changes, while the echo signal is seen as a feature on top of this background. The amplitude of the echo-like feature is given by the difference $(\rho_{ss} - \rho_{\tau_0\tau_0})$ at $t = 2\tau_0 + 2\tau$.

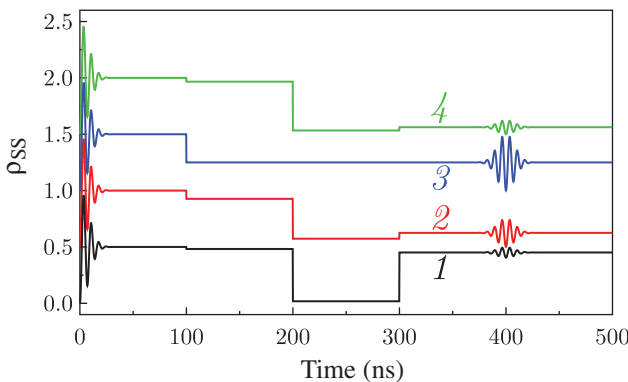


Fig. 4: $\rho_{ss}(t)$ kinetic traces for the sequence shown in Figure 2b. The calculation parameters are: $\tau_0 = \tau = 100$ ns, $\gamma = \pi$, $\delta\omega = 5$ mT, $\sigma_1 = \sigma_2 = 0.5$ mT, $J = 0$; the parameter φ takes the following values: $\pi/6$ (trace 1), $\pi/4$ (trace 2), $\pi/2$ (trace 3), $5\pi/6$ (trace 4). Curves calculated for different φ are shifted along the vertical by 0.5.

The changes of the background level are seen because some of the population goes to the T_{\pm} states and does not contribute to the signal anymore; the resulting populations of the T_{\pm} states varies depending on the delays of the pulsed sequence (Figure 2).

Now let us discuss echo modulation effects.

3.2.3 Echo modulation

Modulation of the echo is caused by “branching” of the EPR transitions, for instance, by simultaneous excitation of EPR transitions from one state to some other states. Excitation of a single EPR transition or subsequent excitation of different transitions with a large time delay allowing coherences to vanish cannot give any modulation. Thus, in the primary echo sequence (Figure 2b) there is no modulation of the echo. For obtaining the modulation it is needed to excite several EPR transitions simultaneously.

In accordance with this discussion, in order to observe the modulation due to the secular part of the electronic spin-spin interaction, the sequence presented in Figure 2c is proposed here. This sequence contains a non-selective pulse providing the “branching” and two selective pulses. The “non-selective” pulse here is composed of two simultaneously applied selective pulses with the same flip angle. In this case the echo is formed at $t = 2\tau_0 + 2\tau$; the echo amplitude is

$$\begin{aligned} & \rho_{ss}(2\tau_0 + 2\tau) - \rho_{\tau_0\tau_0}(2\tau_0 + 2\tau) \\ &= \frac{1}{4} \sin^2 \frac{\gamma}{2} [\sin^2 \varphi (1 + \cos \gamma) + (1 - \cos \gamma)(1 + \cos^2 \varphi - \sin^2 \varphi \cos J\tau)] \end{aligned} \quad (21)$$

When $\varphi = 0$ the result coincides with that in the case of one non-selective pulse. In Figure 5 the kinetic traces for this sequence are presented.

A problem arising with the sequence shown in Figure 2c is that it requires a non-selective pulse, which is composed of two simultaneously applied selective pulses. When this cannot be done for technical reasons one should split one of the selective pulses into two. The corresponding sequence is shown in Figure 2d containing five selective pulses. The idea is the same as previously: one non-selective pulse is cut into three selective pulses. The corresponding kinetic traces are presented at Figure 6. These kinetics traces are similar to those shown in Figure 5, but, strictly speaking, they are different because of the more complex evolution driven by additional pulses.

As one can see, the echo signal is modulated: the echo intensity depends on the delay τ , see eq. (21), due to the spin-spin coupling. The possibility of obtaining

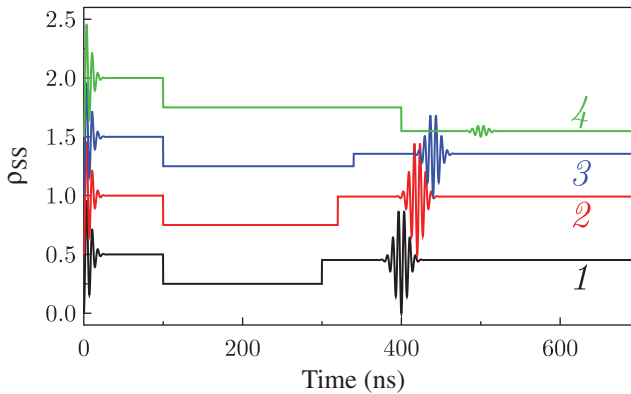


Fig. 5: $\rho_{ss}(t)$ kinetic traces for sequence presented in Figure 2c. The calculation parameters are: $\tau_0 = 100$ ns, $\gamma = \pi$, $\varphi = \pi/2$, $\delta\omega = 5$ mT, $\sigma_1 = \sigma_2 = 0.5$ mT, $J = 0.5$ mT; the parameter τ takes the following values: 100 ns (trace 1), 110 ns (trace 2), 120 ns (trace 3), 150 ns (trace 4). Curves calculated for different τ are shifted along the vertical by 0.5.

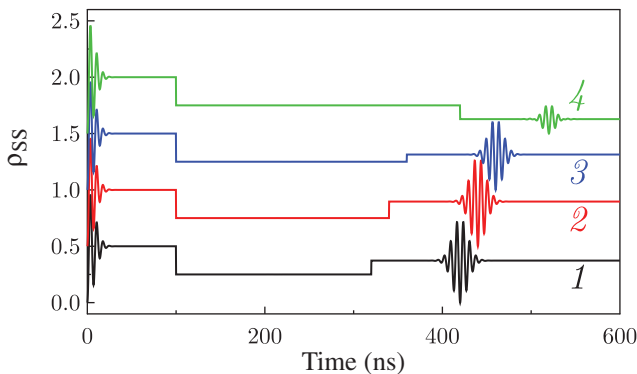


Fig. 6: $\rho_{ss}(t)$ kinetic traces for sequence presented in Figure 2d. The calculation parameters are: $\tau_0 = 100$ ns, $\gamma = \pi$, $\varphi = \pi/2$, $\delta\omega = 5$ mT, $\sigma_1 = \sigma_2 = 0.5$ mT, $j = 0.5$ mT; the parameter τ takes the following values: 100 ns (trace 1), 110 ns (trace 2), 120 ns (trace 3), 150 ns (trace 4). Curves calculated for different τ are shifted along the vertical by 0.5.

the modulation depends on whether the delay between second and fourth pulses is short enough (for the spin coherence to vanish) or not.

3.3 Refocusing SQCs

Spin magnetization cannot be monitored directly by observing singlet-state and triplet-state populations. The reason is that the corresponding product operators

($\hat{S}_{ax}, \hat{S}_{ay}, \hat{S}_{bx}$ and \hat{S}_{by}) do not have any singlet character. Thus, by choosing $\rho_{ss}(t)$ an observable we have no access to SQCs. This situation can be remedied by measuring ΔP and modifying the pulse sequence. Although the magnetization components do not contribute to ΔP , see eq. (15), the SQCs can be transformed into ΔP by using additional pulses [8]. In this way the “spin echo” can be observed by monitoring ΔP as a function of the delays between the pulses.

Let us describe how the “spin echo” can be obtained in this observation mode. Here we take ρ_d as the initial density matrix, i.e. we leave out the ZQC. We assume that the MW-pulses are selective and affect only one of the RP partners. Therefore, even when the ZQC is present at $t=0$ it does not contribute to the signal.

Let us consider selective pulses applied at the frequency of the a-spin, i.e. the MW-pulses do not affect the b-spin. In this situation, for obtaining RYDMR echo-type signals it is needed that the first spin is manipulated in the proper way [8]. Let us now consider how this can be done for different pulse sequences.

A vector model of the spin evolution for sequence

$$\left(\frac{\pi}{2}\right)_x - \tau - \pi_x - \tau_1 - \left(\frac{\pi}{2}\right)_x \tag{22}$$

for $\tau_1 = \tau$ is presented in Figure 7. When the initial RP state is $|T_+\rangle$ the first $\frac{\pi}{2}$ -pulse orients the a-spin along the y-axis (or anti-parallel to the y-axis).

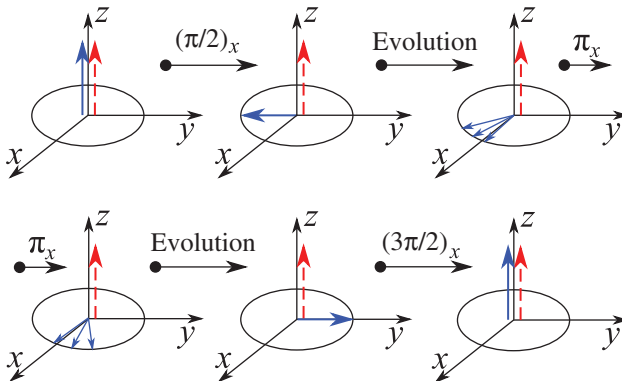


Fig. 7: Vector model of the spin evolution during SQC refocusing. Selective pulses affect only the a-spin and do not change the state of the b-spin. Initially the $|T_+\rangle$ state is populated; the spin magnetization vectors are solid arrow (a-spin) and dashed arrow (b-spin). The pulse sequence is given by eq. (22), when $\tau_1 = \tau$ the final spin state is exactly the same as the initial state. Here refocusing of the T_+ state is shown; refocusing of the T_- state can be done in the same way.

After that, the a-spin starts to precess about the z-axis and gets dephased due to the distribution of the ω_a frequency during a time period of a duration τ . After a π -pulse and the second free evolution period of a duration $\tau_1 = \tau$ the magnetization of the a-spin is refocused, and it is directed parallel to the y-axis. Then the last $\frac{\pi}{2}$ -pulse returns the system back into the initial $|T_+\rangle$ state. When we start from the $|T_-\rangle$ state the result is the same: the pulse sequence also restores the initial spin order. However, once $\tau_1 \neq \tau$ there is no exact refocusing of the a-spin in the transverse plane and the $|T_+\rangle$ state population is not recovered by the last MW-pulse. Thus, by varying τ_1 and measuring ΔP one can obtain an echo-like signal, i.e. a peak in the $\Delta P(\tau_1)$ curve appearing at $\tau_1 = \tau$. When the last $\left(\frac{\pi}{2}\right)_x$ -pulse is changed to a $\left(\frac{3\pi}{2}\right)_x$ -pulse and $\tau_1 = \tau$ the resulting spin magnetization of the a-spin is opposite to its initial magnetization, i.e. the resulting state is a state with anti-parallel electron spins. For this reason, in the sequence $\left(\frac{\pi}{2}\right)_x - \tau - \pi_x - \tau_1 - \left(\frac{3\pi}{2}\right)_x$ we expect a dip in the $\Delta P(\tau_1)$ curve at $\tau_1 = \tau$.

The spin evolution can also be interpreted in the language of product operators. Here we start with the $\hat{S}_{az}\hat{S}_{bz}$ spin order, which is converted into $-\hat{S}_{ay}\hat{S}_{bz}$ by applying a MW-pulse selectively to the a-spin. This term represents an SQC, which is not pure spin magnetization: such an SQC is termed anti-phase magnetization. This SQC evolves due to the Zeeman interaction of the a-spin with the external field in the following way: $\hat{S}_{ay}\hat{S}_{bz} \rightarrow \hat{S}_{ay}\hat{S}_{bz} \cos(\omega_a - \omega)t - \hat{S}_{ax}\hat{S}_{bz} \sin(\omega_a - \omega)t$ and also gets dephased due to the distribution of the ω_a frequency. By applying a π_x -pulse this spin evolution is reverted and at $\tau = 2\tau$ the initial SQC is converted into $\hat{S}_{ay}\hat{S}_{bz}$. An additional pulse converts this anti-phase magnetization back into the $\hat{S}_{az}\hat{S}_{bz}$ spin order, thus, $\Delta P(2\tau) \neq 0$. So, although we apply pulses to only one of the two electron spins of the RP, we refocus essentially the initial two-spin order, as confirmed by the product operator treatment. When there is an interaction between the two spins, the SQC is also completely refocused (when selective pulses are used). The spin evolution is different when the MW-pulses are non-selective and flip both spins: in this situation the echo signal is modulated by the spin-spin interaction, see below.

An echo-type signal can also be generated by modifying the pulse sequence, for instance, by varying the phase of the π -pulse and by varying the flip angle of the last pulse. For instance, with the sequence $\left(\frac{\pi}{2}\right)_x - \tau - \pi_y - \tau_1 - \left(\frac{3\pi}{2}\right)_x$ we obtain the same result as with the sequences given by eq. (22). Indeed when the π -pulse has the y-phase it refocuses the magnetization parallel to the x-axis at $t = 2\tau$; by a $\left(\frac{3\pi}{2}\right)_x$ -pulse this magnetization is rotated and the spin system goes

back to its initial state. Thus, in the $\Delta P(\tau_1)$ there is a peak at $\tau_1 = 2\tau$. When the last pulse is a $\left(\frac{\pi}{2}\right)_x$ -pulse it brings the system to a state with anti-parallel spins, i.e. the echo is negative as it results in a decreased $\Delta P(\tau_1 = \tau)$ value. In all these cases the echo amplitude is the same; only its sign (with respect to the background) is different. Modulation caused by electronic spin-spin interaction is not observed in all these cases.

Typical $\Delta P(\tau_1)$ dependences are shown in Figure 8. As expected, the “echo” is a peak or a dip at $\tau_1 = \tau$ on top of a constant background. In Figure 8 we also compare the sequence given by eq. (22) and the sequences with the flip angle of the last pulse changed to $\frac{3\pi}{2}$. In the first case, see Figure 8a, the echo is positive (in accordance with the discussion presented above); in the second case, see Figure 8b, the echo is negative.

Refocusing of SQCs with subsequent conversion of SQCs into ΔP can also be performed by using non-selective pulses. Interestingly, in this case it also becomes possible to obtain the modulation of the signal due to the electronic

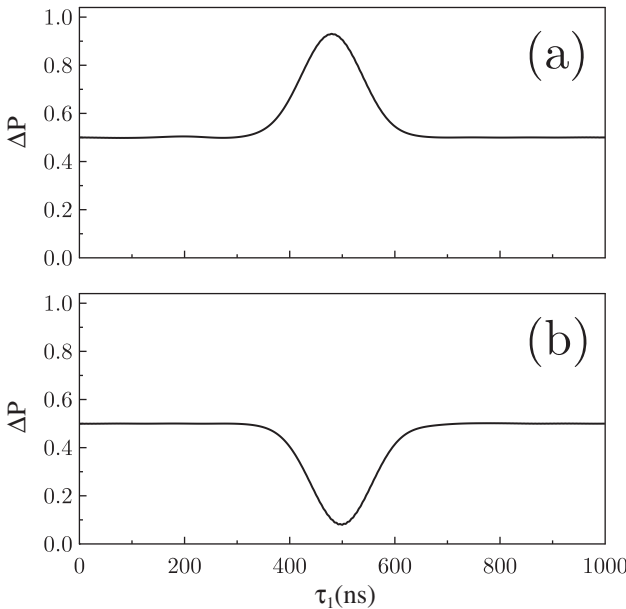


Fig. 8: Dependence of ΔP on τ_1 for RYDMR using refocusing of SQCs. In (a) the pulse sequence is $\left(\frac{\pi}{2}\right)_x - \tau - \pi_x - \tau_1 - \left(\frac{\pi}{2}\right)_x$, in (b) the pulse sequence is $\left(\frac{\pi}{2}\right)_x - \tau - \pi_x - \tau_1 - \left(\frac{3\pi}{2}\right)_x$. Calculation parameters: $\delta\omega = 5$ mT, $\tau = 500$ ns, $\sigma_1 = \sigma_2 = 0.1$ mT, $J = 0$; the MW-pulses are selective, $\omega_1 = 1$ mT.

spin-spin interaction. Indeed, from EPR experiments it is known that for a pair of spins having multiplet polarization, $\hat{S}_{az}\hat{S}_{bz}$, the action of the sequence $(\pi/4) - \tau - \pi$ results in an echo signal formed at $t = 2\tau$. Interestingly, this echo is the “out-of-phase” echo [21–24], meaning that the spin magnetization is refocused along the x-axis of the rotating frame rather than along the y-axis (assuming that the MW-pulses have the x-phase). Such an echo is also modulated due to the coupling between the two spins.

A similar idea can be utilized in RYDMR for observing modulation; however, the pulse sequence needs to be modified because of the different observable. Indeed, in RYDMR, only two-spin order can be observed, therefore the schemes used to refocus spin magnetization do not fit for the purposes of RYDMR. As we have shown above for refocusing of SQCs, only refocusing of the anti-phase magnetization gives rise to RYDMR-echoes. The components of the anti-phase magnetization are indeed represented by products, i.e. by the two-spin order of the kind $\hat{S}_{ay}\hat{S}_{bz}$, thus being suitable for observing echo-type signals in RYDMR. So, pulse sequences for RYDMR should take into account the fact that anti-phase magnetization should be refocused rather than the normal “in-phase” magnetization.

The simplest pulse sequence for generating and refocusing SQCs by non-selective pulses is as follows:

$$\left(\frac{\pi}{4}\right)_x - (\tau) - \pi_x - (\tau_1) - \left(\frac{\pi}{4}\right)_x \quad (23)$$

assuming that the initial spin order is given by the density matrix ρ_d . The pulse sequence works in the following way. The first pulse creates the spin order $-\frac{1}{2}\{\hat{S}_{ay}\hat{S}_{bz} + \hat{S}_{az}\hat{S}_{by}\}$, which is the anti-phase magnetization. This spin order evolves due to (i) the Zeeman interactions of the spins with the external field and (ii) spin-spin coupling. The π -pulse reverts the evolution due to ω_a and ω_b but not the evolution due to the spin-spin interaction. For this reason, refocusing of the anti-phase magnetization at $t = 2\tau$ is incomplete and the refocused anti-phase magnetization is modulated. Interestingly, prior to the last pulse the pure spin magnetization, $(\hat{S}_{ax} + \hat{S}_{bx})$, is refocused out-of-phase, i.e. along the x-axis of the rotating frame and is sine-modulated. This refocused magnetization is suitable for EPR detection but not for RYDMR detection. At the same time, the anti-phase magnetization is refocused in-phase, i.e. we refocus the spin order $(\hat{S}_{ay}\hat{S}_{bz} + \hat{S}_{az}\hat{S}_{by})$, and it is cosine-modulated. This two-spin order is suitable for RYDMR detection as it can be converted back into the $\hat{S}_{az}\hat{S}_{bz}$ -order by the last pulse (although not completely). In this situation the calculated $\Delta P(2\tau)$ value is as follows:

$$\Delta P(2\tau) = \frac{1}{2} - \frac{\cos(J\tau)}{2} \quad (24)$$

Thus, when ΔP is plotted as a function of $\tau_1 = \tau$ it contains modulation coming from the spin-spin interaction. Like in dipolar EPR spectroscopy [25, 26], such modulations can provide information about the distance between the radicals in an RP (when the dipolar interaction dominates over the exchange interaction) or exchange interaction (in the opposite case). In general, in the sequence given by eq. (23) the $\frac{\pi}{4}$ -pulse can be replaced by a φ_x -pulse; however, the conditions for the spin-echo are optimal when $\varphi = \frac{\pi}{4}$. The reason is that $\varphi = \frac{\pi}{4}$ provides the best conversion between the multiplet spin order and the desirable SQC, i.e. the anti-phase magnetization. Modifications of the pulse sequence (23) can also be treated in a similar way and rationalized using the product operator formalism. For instance, it can be shown that upon variation of the phase of the π -pulse from π_x to π_y the resulting $\Delta P(2\tau)$ changes as follows:

$$\Delta P(2\tau) = \frac{1}{2} + \frac{\cos(J\tau)}{2} \quad (25)$$

4 Conclusions

A general theoretical approach to pulsed RYDMR is developed. We demonstrate that it is possible to generate “spin echoes” by refocusing ZQCs and SQCs; such echo-type signals can be detected by either observing the RP singlet-state population, $\rho_{ss}(t)$, as a function of time or by applying an additional MW-pulse and measuring the RP recombination yield. For ZQC refocusing we have proposed new schemes, which make use of selective pulses (in contrast to the case of non-selective excitation, which was studied before [13]). We also demonstrate that SQC-derived spin echoes can be formed by selective as well as by non-selective pulses. In the latter case, the echo signal is modulated due to the interaction between the electron spins in an RP. Our numerical results are supported by an analytical treatment and product-operator consideration, proving a clear interpretation of the RP spin dynamics.

Our results are of interest for extending the scope of RYDMR; specifically, for sensitive detection and detailed characterization of short-lived RPs and charge carriers in organic semiconductors. In particular, the pulse sequences presented here hold promise for studying spin-correlated charge-carrier pairs in polymer:fullerene solar cells. These “charge transfer states” mediate the

conversion between photo-generated excitons and separated charge carriers and thus critically influence the solar cell efficiency. It was recently shown that pulse EPR techniques can provide information on the distance between both charge carriers forming a charge transfer state [27]. In addition, EDMR experiments have revealed a clear signature of these intermediate states as well and could demonstrate their influence on the electrical photocurrent generated in organic solar cells [28]. Building on these experimental results, the RYDMR pulse sequences described in this article open the intriguing perspective of determining the spin-spin coupling within those charge transfer states that directly contribute to the photocurrent. A second application of the methodology outlined here may be the identification of excitation transfer pathways that are involved in loss mechanisms in organic solar cells [29, 30]. In general, our treatment also paves the way to designing new pulse sequences for RYDMR.

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