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5- and 6-pulse electron spin echo envelope modulation (ESEEM) of multi-nuclear spin systems

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Abstract

In 3-pulse ESEEM and the original 4-pulse HYSCORE, nuclei with large modulation depth ($k \approx 1$) suppress spectral peaks from nuclei with weak modulations ($k \approx 0$). This cross suppression can impede the detection of the latter nuclei, which are often the ones of interest. We show that two extended pulse sequences, 5-pulse ESEEM and 6-pulse HYSCORE, can be used as experimental alternatives that suffer less strongly from the cross suppression and allow to recover signals of $k \approx 0$ nuclei in the presence of $k \approx 1$ nuclei. In the extended sequences, modulations from $k \approx 0$ nuclei are strongly enhanced. In addition, multi-quantum transitions are absent which simplifies the spectra. General analytical expressions for the modulation signals in these sequences are derived and discussed. Numerical simulations and experimental spectra that demonstrate the higher sensitivity of the extended pulse sequences are presented.

Keywords: Pulse EPR; ESEEM; HYSCORE; Cross-suppression effect; Multi-nuclear spin system; Phase cycling

1. Introduction

Pulse electron paramagnetic resonance (EPR) techniques in general and electron spin echo envelope modulation (ESEEM) techniques in particular are widely used to determine the electronic and geometric structure of paramagnetic species [1]. The results lead to unique insights into the electronic and geometric structure of paramagnetic centers in biological systems [2,3], as they allow for the determination of small hyperfine and quadrupole couplings of nuclear spins in the molecular environment of unpaired electrons.

Recent studies found that a cross-suppression effect [4,5] distorts signal intensities in standard ESEEM experiments (3-pulse ESEEM and 4-pulse HYSCORE) if more than one nucleus contribute to the signal and can thus lead to misinterpretation of ESEEM spectra. If all nuclei have a small modulation depth parameter k, i.e. a hyperfine interaction with a small anisotropic component and a small quadrupole coupling, this effect is negligible, the nuclei do not affect each other, and the spectrum equals the superposition of the single-nucleus spectra. On the other hand, the cross-suppression effect can have a strong impact in the presence of strongly modulating nuclei, as they can cause partial or complete suppression of signals from weakly modulating nuclei coupled to the same electron spin. In some circumstances, this results in spectra where weakly coupled nuclei cannot be observed at all, although they have a sufficiently large hyperfine coupling to be resolved. As these nuclei are often of structural or functional interest, experimental ways to circumvent or alleviate the impact of the cross suppression are desirable.

In this work, we examine two extended ESEEM pulse sequences, 5-pulse ESEEM [6] and 6-pulse HYSCORE [7], that can recover signals from weakly modulating nuclei and yield spectra that are less affected by cross suppression. These sequences give ESEEM spectra with peaks at the same positions as in 3-pulse ESEEM [8] and standard 4-pulse HYSCORE [9], respectively.

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There are two reasons why spectra obtained with these extended sequences are less affected by cross suppression than the standard sequences. First, as we will show, they give substantially enhanced peak intensities for weakly modulating nuclei (those affected by cross suppression) and show decreased sensitivity towards strongly modulating nuclei (which are responsible for the cross suppression). The second reason is based on the occurence of blind spots [10,11]: In 3-pulse ESEEM and standard HYSCORE, a fixed inter-pulse delay of τ causes selective suppression of peaks at some frequencies, called blind spots. The cross-suppression effect can be counteracted by choosing τ so that peaks from strongly modulating nuclei that cause cross suppression fall on blind spots. The two extended pulse sequences have two experimentally adjustable fixed delays, τ_1 and τ_2, and they thus offer more flexibility in choosing blind spots.

This article is structured as follows: The theoretical background needed to derive and discuss the analytical expressions for the two extended sequences is summarized in Section 2. Section 3 gives details of the system and experiments used to illustrate our findings. The main part of the article is contained in Sections 5 and 6, where echo modulation signals for 2-, 3- and 5-pulse ESEEM and 4- and 6-pulse HYSCORE are compared theoretically and illustrated experimentally. Finally, Section 6 summarizes the insight obtained.

2. Theoretical background

The rotating-frame spin Hamiltonian, in angular frequency units, of an electron spin ($S=\frac{1}{2}$) coupled to N_I nuclei ($I_1=\cdots=I_{N_I}=\frac{1}{2}$) using the high-field approximation is given by [1,12]

$$H_0=\Omega_S S_z+\sum_{q=1}^{N_I}(\omega_{I,q}I_{z,q}+A_qS_zI_{z,q}+B_qS_zI_{x,q}), \tag{1}$$

where $\Omega_S=\omega_S-\omega_{\rm mw}$ is the offset between the electron resonance frequency ω_S and the frequency of the applied microwave (mw) pulse, $\omega_{\rm mw}$. $\omega_{I,q}=-g_{{\rm n},q}\mu_{\rm n}B_0/\hbar$ denotes the Larmor frequency of nucleus q.

In general, the hyperfine part of the Hamiltonian is related to the principal values $A_{11,q}$, $A_{22,q}$ and $A_{33,q}$ of the orthorhombic hyperfine interaction matrix $\boldsymbol{A_q}$, and two polar angles θ_q and ϕ_q describing the orientation of the external magnetic field $\boldsymbol{B}_0=(0,0,B_0)$ with respect to the frame where the hyperfine interaction matrix is diagonal [13]:

$$\begin{aligned}A_q&=A_{33,q}\cos^2\theta_q+\sin^2\theta_q(A_{11,q}\cos^2\phi_q+A_{22,q}\sin^2\phi_q),\\ B_q&=\sqrt{B_{x,q}^2+B_{y,q}^2},\\ B_{x,q}&=\frac{1}{2}\sin\theta_q\cos\theta_q[(2A_{33,q}-A_{11,q}-A_{22,q})\\ &\quad+\cos(2\phi_q)(A_{22,q}-A_{11,q})],\\ B_{y,q}&=\frac{1}{2}\sin\theta_q\sin(2\phi_q)(A_{22,q}-A_{11,q}).\end{aligned} \tag{2}$$

For an axially symmetric hyperfine interaction, A_q and B_q are related to the principal values $A_{\perp,q}$ and $A_{\parallel,q}$ of the hyperfine tensor and can be expressed as function of the isotropic and dipolar hyperfine coupling constants, $a_{{\rm iso},q}$ and T_q, by

$$\begin{aligned}A_q&=A_{\parallel,q}\cos^2\theta_q+A_{\perp,q}\sin^2\theta_q=T_q(3\cos^2\theta_q-1)+a_{{\rm iso},q},\\ B_q&=3T_q\sin\theta_q\cos\theta_q,\end{aligned} \tag{3}$$

where θ_q is the angle between the external magnetic field and the electron–nucleus axis [1].

The resonance frequencies of nucleus q associated with the $\alpha(m_S=+\frac{1}{2})$ and $\beta(m_S=-\frac{1}{2})$ electron spin manifolds are

$$\omega_{\alpha,\beta,q}=\sqrt{(\omega_{I,q}\pm A_q/2)^2+(\pm B_q/2)^2}. \tag{4}$$

The pseudo-secular part B_q of the hyperfine tensor tilts the quantization axes of the nuclear spins for each m_S manifold by an angle

$$\eta_{\alpha,\beta,q}=\arctan\frac{\pm B_q/2}{\omega_{I,q}\pm A_q/2} \tag{5}$$

with respect to $\boldsymbol{B}_0$. The half-angle between the two nuclear quantization axes is given by $\eta_q=(\eta_{\alpha,q}-\eta_{\beta,q})/2$. The modulation depth parameter k_q, a fundamental quantity of ESEEM, is

$$k_q=\sin^2(2\eta_q)=\left(\frac{B_q\omega_{I,q}}{\omega_{\alpha,q}\omega_{\beta,q}}\right)^2 \tag{6}$$

with $0\leqslant k_q\leqslant 1$. It is a measure of the degree of dissimilarity of the nuclear sublevels in the α and the β electron manifolds.

The behavior of the spin system during a pulse sequence is described by the evolution of the density operator σ [1,14–16]. The density operator at a time t is given by

$$\sigma(t)=\ldots P_2Q_{t_1}P_1\sigma_0P_1^{-1}Q_{t_1}^{-1}P_2^{-1}\ldots \tag{7}$$

where P_j represent pulse propagators and Q_{t_j} free evolutions. In the ideal pulse approximation, the static Hamiltonian H_0 is neglected during the microwave pulse, so that

$$P_j={\rm e}^{-{\rm i}\beta_jS_{x(y)}} \tag{8}$$

is the propagator for a pulse with flip angle β_j and phase $x(y)$. The propagator during free evolution is

$$Q_{t_j}=U^\dagger{\rm e}^{-{\rm i}H_0^{\rm diag}t_j}U \tag{9}$$

with [1]

$$H_0^{\rm diag}=UH_0U^\dagger\qquad U=\prod_{q=1}^{N_I}{\rm e}^{-{\rm i}(\eta_{\alpha,q}S_\alpha+\eta_{\beta,q}S_\beta)I_{y,q}}. \tag{10}$$

At the beginning of the pulse sequence, the system is at thermal equilibrium. Conventionally, this is represented by $\sigma_0=-S_z/M$, where $M=\prod_q(2I_q+1)$ is the total num-