OOP-ESEEM powder average Zech

Gianluca Marcozzi

August 2024

Chapter 1

Introduction

We focus on the dependence of OOP-ESEEM signal intensity as a function of the turning angle of the first microwave pulse of the sequence, β. This type of experiment was carried out by Zech on the PSI system [1] (p. 46) and is reproduced in Fig. **??**. The best-fit is not perfectly matching the experimental data because the model used is correct for a crystalline sample, while the experiment was carried out on a powder sample. The goal of this work is to implement a powder average algorithm to simulate the expected signal and provide a better match with the experimental data.

Figure 1.1: OOP-ESEEM intensity as a function of turning angle β. Best-fit model as in equation 1.1. Parameters: $T = 150$ K, pulse length of 24 ns. Digitized using WebPlotDigitizer from [1].

1.1 Theoretical background

For spin-correlated radical pairs, the out-of-phase ESEEM signal intensity for initial singlet state is given by [2]:

$$E_x(\rho_S) = -\frac{1}{2}\sin[2(d-J)\tau]\left[\frac{1}{2}\sin(\beta)\sin^2(2\xi) + \sin(2\beta)\cos^4(\xi)\right], \tag{1.1}$$

where d and J are the dipolar and exchange coupling respectively, β is the turning angle of the first microwave pulse of the sequence and ξ is the mixing angle. In particular, we define $\xi = \arctan[(d+2J)/(\Omega_A - \Omega_B)]$, where $\Omega_j = g_j\frac{\mu_B B_0}{\hbar} - \omega_{MW}$. This definition implies that in the limit of weakly interacting spins $\xi \to 0$ and $E_x \to \sin(2\beta)$, while in the limit of strongly coupled spins $|\xi| \to \pi/2$ and $E_x \to \sin(\beta)\xi^2$, therefore approaches $\sin(\beta)$ but vanishes at the limit.
The quantities in Eq. 1.1 that are dependent on the polar and azimuthal angles θ and ϕ are $d = \tilde{d}[\cos(\theta_D)^2 - 1/3]$, where θ_D is the angle between the external magnetic field and the direction along which the charge transfer takes place z_D,

and the mixing angle ξ, which depends on both d and the effective g-values. Notice that also the prefactor $\sin[2(d-J)\tau]$ is orientation-dependent.

I am not considering the fact that the prefactor sin(2(d - J)tau) is different for each angle because d depends on theta. Do I need to take it into consideration?

The parameters used for the PSI system are: $g_{P700+} = [2.0030, 2.0026, 2.0023]$, $g_{A1-} = [2.0062, 2.0051, 2.0022]$, Euler angles $(-10^o, -128^o, -83^o)$ for the transformation from the reference system of A1 to the one of P700, Euler angles $(0, 90^o, 0)$ for the direction of z_D in the reference system of A1 (which means that z_D is along $-x$ in this reference frame), $\tilde{d} = 0.177$ mT $= 4.9$ MHz, $J = -0.001$ mT. Notice that for this system, given the direction of z_D and given an external magnetic field pointing along θ and ϕ angles in the reference frame of A1, the simple relation $\cos(\theta_D) = -\sin(\theta)\cos(\phi)$ is verified.

For PSI, the average value of the absolute value of the mixing angle assuming inhomogenous broadening is 8^o [**empty citation**] (Timmel et al. report 41^o, but the definition of their angle is different from ours, namely $\xi = 180^o - 2 \cdot \xi_{\text{Timmel}}$)

Bibliography

[1] "Pulsed and transient electron paramagnetic resonance spectroscopy on light induced radical pairs in photosynthetic reaction centers". Aachen: Shaker, 1998.

[2] Gunnar Jeschke and Robert Bittl. "Electron Spin Echo Envelope Modulation by Electronic Spin–Spin Interactions in Radical Pairs Undergoing Electron Transfer". In: *Chemical Physics Letters* 294.4-5 (Sept. 1998), pp. 323–331. ISSN: 00092614. DOI: `10.1016/S0009-2614(98)00883-5`. URL: `https://linkinghub.elsevier.com/retrieve/pii/S0009261498008835` (visited on 01/16/2024).