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Janne Marie Soetbeer

Dynamical Decoupling in Distance Measurements by Double Electron- Electron Resonance

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"I am not aware of any other field of science outside of magnetic resonance that offers so much freedom and opportunities for a creative mind to invent and explore new experimental schemes (...)"

Richard R. Ernst, Nobel Lecture, December 9, 1992

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Abstract

The relaxation behaviour of model systems mimicking different spin-labelled electron spin environments have been studied including TEMPOL, spin-labelled T4 Lysozyme, spin-labelled WALP23 and rigid spin-labelled molecules. Carr-Purcell (CP) and Uhrig pulse sequences for a fixed total sequence time were used to record echo relaxation traces to find the optimal dynamical decoupling (DD) scheme which allows for efficient reduction of electron spin coherence losses for a given relaxation behaviour. Addition of π refocusing pulses led to stronger nuclear modulation of the recorded relaxation traces and to signal contributions from both refocused and stimulated echos at the acquisition position. The latter complication was alleviated by small time shifts introduced into the pulse sequence.

The relaxation behaviour was characterised by phase relaxation time T_m and stretch parameter ξ which were shown to both depend on the spin environment and the dominating relaxation mechanism. Deviations from literature values could be explained by the inherent nature of the relaxation measurement. DD schemes proofed most successful for $\xi > 1$ as expected from theory. Overall, Uhrig schemes allowed for stronger suppression of coherence losses for interpulse delays at which the magnetisation in CP-type set ups had already decayed.

Based on the relaxation characterisation the DD schemes were extended to corresponding DD-double electron electron resonance (DEER) experiments by addition of pump pulses for a rigid biradical model system in d_8 -OTP and T4 Lysozyme in H_2O - d_8 -Glycerol mixture. CP-type DD observer pulse sequences of order $n = 1, 2$ and 4 were used to record DEER traces. The promising relaxation study results for Uhrig-type DD schemes did not translate into a superior Uhrig-DEER experiment relative to a CP

derived set up for different reasons at X and Q band.

Signal artifacts related to m times pump spin inversion with $1 \leq m < n$ in DD-DEER experiments of order $n = 2$ or 4 were strongly reduced by increasing inversion efficiency based on pump pulse optimisation. Linear-chirp and asymmetric hyperbolic secant pulses were tested with optimal pulse parameters obtained from pulse simulation including resonator profile compensation. Measurements at Q band showed pump pulse underperformance with respect to inversion efficiencies expected from theory. This resulted in strong contributions from signal artifacts in the corresponding DD-DEER traces. Nearly full suppression of the latter were achieved at X band with sacrifices in terms of sensitivity relative to Q band.

X-band order $n = 2$ DD-DEER traces for the low concentration rigid biradical sample allowed for direct DeerAnalysis fitting without data post processing.

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Glossary

$AM(t)$	Amplitude modulation function.
$B(t)$	Intermolecular background function.
B_{eff}	Effective field created by B_1 and B_0 .
D	Dimensionality of the homogeneous spin distribution.
$F(t)$	Intramolecular form function.
$FM(t)$	Frequency modulation function.
$I(f)$	Inversion profile of pulse.
$K(t, r)$	Kernel function.
M_0	Magnetisation vector at equilibrium.
M_z	Longitudinal magnetisation.
N	Factor for extending 5-DEER experiment by $N \pi$ 5-DEER pulses.
$P(r)$	Distance distribution.
Q_{min}	Minimal adiabaticity factor at resonance.
$S(t)$	Simulated signal.
T_1	Longitudinal relaxation time.
T_2	Transverse relaxation time.
T_m	Phase memory time.
$V(0)$	Echo intensity at time zero.
$V(t)$	Primary DEER trace.
Δ	Modulation depth.
$\Delta\nu$	Total sweep width of chirp pulse.
Δt	Time increment of interpulse delays.
Ω_A	Frequency of the DEER observer pulses.
Ω_B	Frequency of the DEER pump pulses.
Ω_S	Resonance offset.
Φ_0	Ground state electronic wavefunction.
α	Regularisation parameter.
β	Flip angle of an applied microwave pulse.
β_{HS}	Truncation factor of HS pulse.
δT	Time shift to avoid observer and pump pulse overlap.
$\delta\tau$	Fixed time shift to separate refocused and stimulated echo.
$\hat{H}_0$	Spin Hamiltonian.
$\hat{H}_{\text{DD}}$	Dipole-Dipole Hamiltonian.
$\hat{H}_{\text{EX}}$	Exchange Hamiltonian.

$\hat{H}_{\text{EZ}}$	Electron Zeeman Hamiltonian.
$\hat{H}_{\text{HF}}$	Hyperfine Hamiltonian.
$\hat{H}_{\text{NQ}}$	Nuclear Quadrupole Hamiltonian.
$\hat{H}_{\text{NZ}}$	Nuclear Zeeman Hamiltonian.
$\hat{H}_{\text{ZFS}}$	Zero-Field Hamiltonian.
$\hat{I}$	Nuclear Spin vector operator.
$\hat{S}$	Electron spin vector operator.
$\hbar$	Reduced Planck constant, $1.054571726(47) \cdot 10^{34}$ J.s.
κ	Normalised inversion quality of pulse.
λ	Fraction of spins excited by pump pulse.
$\langle S_{Ay} \rangle$	Expectation value of the S_{Ay} operator corresponding to observable magnetisation.
μ	Macroscopic moment.
μ_0	Vacuum permeability.
$\mu_{\text{B}} = \beta_{\text{e}}$	Bohr magneton.
$\nu_1(f)$	Resonator profile.
ν_{DD}	Dipole dipole coupling in frequency units.
ν_{final}	Final frequency for chirped pulse relative to observer frequency.
ν_{initial}	Starting frequency for chirp pulse relative to observer frequency.
ν_{mw}	Frequency of the microwave radiation.
ω_0	Larmor frequency.
ω_{eff}	Effective frequency.
ω_{mw}	Microwave frequency of applied pulse field.
ρ	Spin density.
σ_{echo}	Density operator at the echo position.
σ_{eq}	Density operator at thermal equilibrium.
τ	Interpulse delay.
θ	Polar angle between $\vec{B}_0$ and $\vec{r}$.
θ, ϕ	Polar angles in PAS of g.
$\underline{1}$	Unit tensor.
$\underline{A}$	Hyperfine tensor.
$\underline{D}$	Dipolar coupling tensor.
$\underline{I}$	Exchange coupling tensor.
$\underline{g}$	g tensor.
$\underline{\hat{1}}$	Unit vector.
$\vec{B}$	External static magnetic field (0, 0, B_0).
$\vec{B}_0$	Static magnetic field vector.
$\vec{B}_0^T$	Transposed external magnetic field vector.
$\vec{B}_1(t)$	Pulse field.
$\vec{r}$	Spin-spin vector of length r.
ξ	Stretch parameter in relaxation law.
a_{s}	Pulse amplitude.

f	Instantaneous frequency.
h	Order of the HS h pulse.
k	Spin density parameter.
l	Orbital angular momentum quantum number.
m	Number of spin inversion by π pulse.
n	Order of the dynamical decoupling scheme.
p_k	Probability that pulse k inverts a spin.
q_k	$= 1 - p_k$.
t_p	Pulse length.
t_{acq}	Acquisition time.
t_{dip}	Total dipolar evolution time.
t_{max}	Maximum dipolar evolution time.
t_r	Rise time of pulse.
$ \frac{d\theta(t)}{dt} $	Instantaneous angular velocity.
R	Distance between proton and spin density center.
I	Exchange coupling tensor.
a_{iso}	Isotropic hyperfine coupling constant.
AM	Amplitude modulation.
B_0	z component of the static magnetic field vector.
CP	Carr Purcell.
CW	Continuous wave.
d	Dipole-dipole coupling.
$d_8\text{Gly}$	Deuterated glycerol.
$d_8\text{-OTP}$	Deuterated o -terphenyl.
DD	Dynamical decoupling.
DEER	Double Electron Electron Resonance.
DTT	Butan-2,3-diol-1,4-dithiol.
EPR	Electron Paramagnetic Resonance.
FID	Free induction decay.
FM	Frequency modulation.
g_e	g -value for free electron.
g_{eff}	Effective g value.
GUI	Graphical user interface.
HGly	Glycerol.
M	Macroscopic magnetisation in vector picture treatment.
MOPS	3-morpholinopropane-1-sulfonic acid.
MTSSL	(1-Oxyl-2,2,5,5-tetramethylpyrroline-3-methyl) methanethiosulfonate.
PAS	Principle Axis System.
Q	Adiabaticity factor.
S/N	Signal-to-Noise ratio.
SDSL	Site-directed spin labelling.
TWT	Traveling wave tube.

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