Reliable distance distributions in the nanometer range from 5-pulse Double Electron Electron Resonance (DEER)

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Double Electron Electron Resonance (DEER) enables determination of distance distributions in the nanometer range by Electron Paramagnetic Resonance (EPR). In DEER, a refocused echo is recorded at the observation frequency while the distance to a partner spin is probed by time-dependent excitation at a second frequency (the pump frequency). Due to the dipolar interaction between the two spins, the observed echo is modulated with a frequency which depends on the distance between the two spins. The accessible observation window and thus distance range can be significantly prolonged by the use of dynamically decoupled multi-pulse versions of this experiment [1,2]. Such experiments, however, are not free of artefacts. On coherent spectrometers, artefacts due to additional coherence transfer pathways occur and can be removed by systematic change of the pulse phases [3]. On both coherent and incoherent spectrometers, overlap of the observer and pump frequency bands causes additional signals of dipolar origin, hereafter called band overlap artefacts. Furthermore, incomplete population inversion in the pump band gives rise to a so-called partial excitation artefact.

Using the 5-pulse DEER experiment with pulses from an arbitrary waveform generator (AWG), we show how pulse parameters can be optimized in order to suppress or completely remove the artefacts due to band overlap, so that only the partial excitation artefact remains. For removal of the partial excitation artefact, we present a data processing procedure that works without previous knowledge of the artefact amplitude or shape and without sensitivity loss. Two 5-pulse DEER traces are recorded in which the artefact position is shifted with respect to the wanted signal. Using the difference of the two traces, the artefact is identified and corrected for. Artefact removal is demonstrated for both simulated and experimental data acquired at different frequencies, for shaped as well as rectangular pump pulses, for a variety of distance distributions and spin environments. The algorithm is stable down to low S/N ratios and in the regime of moderate background decay. We show that 5-pulse DEER recorded with optimized pulse parameters and, if necessary, artefact-corrected by our algorithm gives access to correct distance distributions and a prolonged distance range.

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