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Coherence transfer in two-pulse double quantum (DQ) and five-pulse double- quantum modulation (DQM) sequences in EPR: Orientation selectivity and distance measurement

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Double-quantum (DQ) coherence transfers in two-pulse DQ and five-pulse DQM (double quantum modulation) EPR pulse sequences, utilized for orientation selectivity and distance measurements in biological systems using nitroxide biradicals, are investigated. Analytical expressions, along with numerical algorithms, for EPR signals are given in full details. It is shown, in general, that a finite pulse, as opposed to an infinite pulse, in conjunction with dipolar interaction between the two nitroxide radicals, is needed to produce non-zero coherence transfers in $0\boxtimes2$ and $2\boxtimes-1$ transitions. Furthermore, the simulations show that the coherence transfer, $T0\boxtimes2$, as effected by a finite pulse, is found to increases as the amplitude of the irradiation field (B1) decreases, being maximum for those coupled nitroxides, whose dipolar axis, i.e., the line joining their dipoles, relative to the external magnetic field, are oriented symmetrically about the angle $\theta_0 \tilde{} {54.47}^\circle$, at which $\left(3\cos^2\theta-1\right)=0$, for $0^\circle\le\theta\le{90}^\circle$, at $\pm{10}^\circle$ from θ_0 , being symmetric about $\theta={90}^\circle$ in the range $0^\circle\le\theta\le{180}^\circle$. It is noted that there is no such value possible for $d\le 10$ MHz. This is a new result, as far as orientational sensitivity of the forbidden DQ signal is concerned, found here with the help of long quantitative simulations for the first time. In addition, it is shown that only measurements involving one time variable are needed to obtain the Pake doublets in polycrystalline (powder) samples to determine the dipolar constant, proportional to the inverse cube of the distance between the nitroxide radicals. The analytical expressions, derived here for the various signals for fixed orientations of the two nitroxide dipoles with respect to the dipolar axis, oriented at angle θ with respect to the external magnetic field, show that, in general, the Fourier transforms of the two-pulse DQ sequence exhibit peaks at $\pm\frac{3}{2}d\times\left(3\cos^2\theta-1\right)$, whereas the five-pulse DQM sequence exhibits peaks at $\pm d\times\left(3\cos^2\theta-1\right)$; where $d=\frac{2}{3}D$, with D being the dipolar-coupling constant. Furthermore, it is found that the signals from two-pulse DQ and five-pulse DQM sequences are sensitive to the orientations of the two nitroxide dipoles, described by the Euler angles $(\alpha_1,\beta_1,\gamma_1);(\alpha_2,\beta_2,\gamma_2)$. This provides structural sensitivity to the two-pulse DQ and five-pulse DQM signals, useful for understanding details of the configuration of biomolecules. As for the numerically calculated polycrystalline (powder) averages, accumulated over 20 sets of Monte-Carlo orientations of the two nitroxide dipole moments, it is found that the Pake doublets occur at $\pm\frac{3}{2}d$ for the two-pulse DQ sequence and at $\pm d$ for the five-pulse DQM sequence. The magnitudes of coherence transfers in the transitions $0\boxtimes2$ and $2\boxtimes-1$ are found to be about the same; they depend on the amplitude of the irradiation field, as well as on the duration of the pulse. They increase significantly with increasing strength of the dipolar interaction, d, as calculated here for d=10\ and\ 30 MHz, corresponding to the value of r\ =\ 17 and 11 Å. The effect of relaxation in polycrystalline samples is considered by the use of a stretched exponential. The numerical algorithm for the five-pulse DQM sequence presented here is exploited to calculate the intensity of the five-pulse DQM signal to fit the published experimental data; a good agreement is found within the experimental error.

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