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Double nuclear coherence transfer (DONUT)-HYSCORE: A new tool for the assignment of nuclear frequencies in pulsed EPr experiments

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Abstract

A two-dimensional experiment, termed DONUT-HYSCORE (double nuclear coherence transfer hyperfine sublevel correlation) designed to obtain correlations between nuclear frequencies belonging to the same electron spin manifold is presented. The sequence employed is π/2-τ--π/2-t1-π-τ2- π-t2-π/2τ1-echo, and the echo is measured as a function of t1 and t2 whereas τ1 and τ2 are held constant. It is complementary to the standard HYSCORE experiment which generates correlations between nuclear frequencies belonging to different M(s) manifolds and is particularly useful for 14N nuclei. The experiment is first demonstrated on a single crystal of copper- doped l-histidine hydrochloride monohydrate where the modulations are induced by a single 14N nucleus, the remote nitrogen in the imidazole group. HYSCORE and DONUTHY-SCORE experiments were carried out on two crystal orientations. In the first, one Cu2+ site contributes to the echo and all six nuclear frequencies together with the expected correlation were observed. In the second, 12 frequencies corresponding to two Cu2+ ions at different crystallographic sites appeared and all expected correlations were detected as well. This rather trivial example demonstrates that the DONUT-HYSCORE pulse sequence indeed generates correlations within the M(s) manifolds. The value of the DONUT-HYSCORE experiment is demonstrated on a frozen solution of a vanadyl complex with a bis-hydroxamate ion binder (VO-RL515). The modulations in this complex arise from the two InN nuclei in the hydroxamate groups, and orientation-selective three-pulse ESEEM (electron spin-echo envelope modulation) spectra showed a number of well-resolved peaks. An unambiguous assignment of all peaks and their orientation dependences could not be achieved through HYSCORE alone because at certain orientations frequencies of one of the M(s) manifolds were absent or overlapped with those of the other manifold. The application of the DONUT-HYSCORE experiment provided new correlations that led to the complete assignment of the ESEEM frequencies, thus paving the way for future systematic spectral simulations for the determination of the best-fit Hamiltonian parameters. This example shows that, in the case that the HYSCORE experiment cannot distinguish between two sets of frequencies belonging to the same M(s) manifold in different centers (or orientations) because signals from the other manifold are missing or overlapping, the DONUT-HYSCORE becomes most valuable.

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