A Suppression Effect in ESEEM Spectra of Multinuclear Spin Systems

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Three-pulse ESEEM and HYSCORE experiments are commonly used to elucidate structural details around paramagnetic metal centres in biomolecules. Although the resulting spectra contain a lot of information, their interpretation is often challenging due to several deficiencies of the experiments. As is well known, they suffer from dead-time artefacts as well as from blind spots[1], and disordered systems can give rise to destructive interference effects[2].

We have observed another disturbing suppression effect that has up to now passed unnoticed. For multinuclear systems it is known that the ESEEM signal contains internuclear combination peaks[3]. However, the peaks at the basic ESEEM frequencies are also seriously affected. These peaks are reduced in intensity, up to the point of complete cancellation. For both three-pulse ESEEM and HYSCORE on an S=1/2 system with more than one nucleus, the amplitude of a peak of a given nucleus depends not only on its own modulation depth k_i and the blind-spot term $b_i = 1–\cos(\omega_i\tau)$, but on k_j and b_j of other nuclei as well. Peaks of nuclei with shallow modulations are strongly suppressed by nuclei with deep modulations.

This suppression effect has substantial practical consequences. It can lead to misinterpretations of ESEEM spectra. It also explains the observation that HYSCORE ^{1}H peaks are often very weak or even undetectable in the presence of strong ^{14}N peaks, which are very common in biological systems.

We present a theoretical analysis of this effect based on the product rules[4,5], numerical computations using the simulation software package EasySpin[6,7] and preliminary experimental verifications on a simple model system. In addition, we propose ways to minimize the impact of this suppression effect in experiments.

References:

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