ACS Local Section
North Jersey

On the effects of differential scalar relaxation and chemical exchange in perfect echo NMR spectroscopy of AX spin systems

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Abstract:
Spin echoes (SE) refocus chemical shift evolution in weakly coupled homonuclear AX spin systems but leave scalar coupling evolution intact, leading to contamination of the in-phase (IP) echo with anti-phase (AP) coherence. In contrast, the so-called perfect echo (PE), which consists of two SEs flanking a central 90° pulse, can minimize the contribution of AP coherence at the echo, with complete refocusing of homonuclear scalar coupling evolution expected in AX systems based on product operator analysis. However, this precludes the consideration of the effects of differential scalar relaxation (DSR) from the interconversion of IP and AP coherences during a PE or a train of PE echoes (PE-CPMG). In this work, the effects of DSR on an AX spin system subject to a PE or PE-CPMG are considered, and the resulting theoretical spin dynamics are discussed. Exact analytical expressions characterizing the IP and AP coherences of each spin as a function of PE time τ_{PE} are derived for a single PE and show relaxation-induced oscillations (RIOs) superimposed onto the decay envelopes of IP coherences along with the concomitant generation of AP coherence, even when pulses are assumed to be ideal, instantaneous, and on-resonance for both spins. Numerical simulations reveal that oscillations in the decay envelop may persist under a PE-CPMG, and that the relaxation of the IP coherences is sensitive to pulse sequence timing in terms of both the repetition rate $1/T_{PE}$ and total relaxation period. In general, rapid pulsing quenches the AP components and slows down relaxation, though RIOs persist. Notably, specific values of $1/T_{PE}$ termed dispersion resonances – result in effectively decoupled and non-oscillatory IP decay profiles. We extend our analysis to an AX system undergoing a global two-state exchange process. In direct analogy to DSR, differences between $R_{ex,I}$ and $R_{ex,S}$ – each spin's exchange-induced relaxation enhancements – may induce oscillations in the IP decay profiles and concomitantly generate AP coherence. Moreover, each spin's effective relaxation enhancement is shown to depend on both $R_{ex,I}$ and $R_{ex,S}$. The analysis of the spin dynamics reported here may be of interest in the further understanding, development, and optimization of PE and PE-CPMG-based pulse sequences, particularly those intended to be used for the accurate measurement and quantification of the underlying dynamics of a homonuclear AX systems undergoing chemical exchange.

Connection Information

This will be a virtual meeting hosted via Microsoft Teams. A Link will be posted closer to the date. Further information can be found on the NMR Topical Group website.

Please reach out to Rongfeng Zheng (rongfeng.zheng@bms.com) or QingZhe Ni (qingzhe.ni@merck.com) with any questions.

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