$^{1}$H and $^{13}$C Chemical Shifts in Paramagnetic Rare Earth Metal Complexes: A First-Principles Study

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The interest in calculations of NMR chemical shifts for paramagnetic open-shell species (pNMR) has been growing fast in recent years. 1-4 Although NMR techniques are extensively used to characterize paramagnetic metal complexes in great detail, it can often be very difficult to interpret the NMR spectra without theoretical support. It is known that density functional theory (DFT) has problems in accurate description of zero-field splitting (ZFS), EPR $g$-tensors, especially for systems with orbital degeneracies, low-energy excited states, or strong spin-orbit (SO) couplings. In such difficult cases, accurate pNMR shifts can only be obtained by high-level calculations based on ab initio wave function theory (WFT).

Herein, we present a theoretical ab initio approach to investigate the paramagnetic effects on NMR chemical shifts for three paramagnetic rare earth metal (REM) complexes viz. Nd(III), Eu(III), and Yb(III). The computed values are compared with the experimental high-field NMR results. To calculate the hyperfine coupling tensor (HFC), $A$, the four-component relativistic all-electron matrix Dirac-Kohn-Sham (mDKS) approach 5 with a hybrid PBE0 functional was used. The $g$- and ZFS-tensors were computed using ab initio complete active space self-consistent field (CASSCF) methods. These results were combined to obtain the total paramagnetic chemical shifts. 6 The experimental pNMR shifts as well as the sizable difference of the $^{13}$C NMR shift for these iso-electronic species are well reproduced by the calculations.

![Figure 1](image1.png)

**Figure 1.** a) Molecular structure of Europium Complex. Experimental and calculated $^{1}$H (b) and $^{13}$C (c) chemical shifts for the Europium Complex. $H_{opt}$: DFT/BP86/Def2-TZVP, Full_opt: DFT/BP86/Def2_TZVP/COSMO (Turbomole).