High-Field EPR Identification of a Spin Clock Transition in the $[Cp'_3Pr^{II}]^-$ Qubit with a 4f²5d¹ Configuration

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Recent work on molecular spin qubits has demonstrated significant enhancements in coherence through the engineering of so-called clock transitions, or optimal operating points at which the quantum spin dynamics become desensitized to magnetic noise. Notably, previous EPR studies conducted at the MagLab for a lutetium(II) molecule with a filled f-shell and a lone unpaired electron occupying a mixed 5d/6s orbital revealed a colossal electron-nuclear hyperfine interaction, giving rise to a massive 9 gigahertz clock transition with associated long spin coherence times [Nat. Chem. **14**, 392 (2022)].

The present investigation sought to explore whether large hyperfine clock transitions are possible in other lanthanide (Ln) ions with partially filled f-shells. The strategy relies on the fact that reduction of certain Ln^{III} ($4f^n$ configuration) ions to Ln^{II} results in the extra electron occupying a mixed 5d/6s orbital, giving rise to a $4f^n(5d/6s)^1$ configuration. The trick then is to identify Ln^{III} ions with non-magnetic singlet ground states, requiring an even f-electron count, e.g., Pr^{III} with a $4f^2$ configuration. Achieving a singlet ground state then boils down to molecular design. Finally, reducing to Pr^{II} results in a $4f^2(5d/6s)^1$ configuration with an effective two-level spin-½ ground state.

Residual exchange coupling between the lone 5d/6s electron and the anisotropic $4f^2$ spin-orbital moment, along with a colossal electron-nuclear hyperfine interaction, gives rise to an EPR spectrum that is impossible to interpret at low fields. However, in the high-field limit, the different components (x, y and z) of the spectrum are well resolved and easily interpretable, yielding a unique set of Zeeman (g_i) and hyperfine ($A_i, i = x, y, z$) parameters (see **Fig. 1**). In turn, this enabled identification of a low field clock transition and demonstration of appreciably enhanced spin coherence for this prototype molecular lanthanide spin qubit.

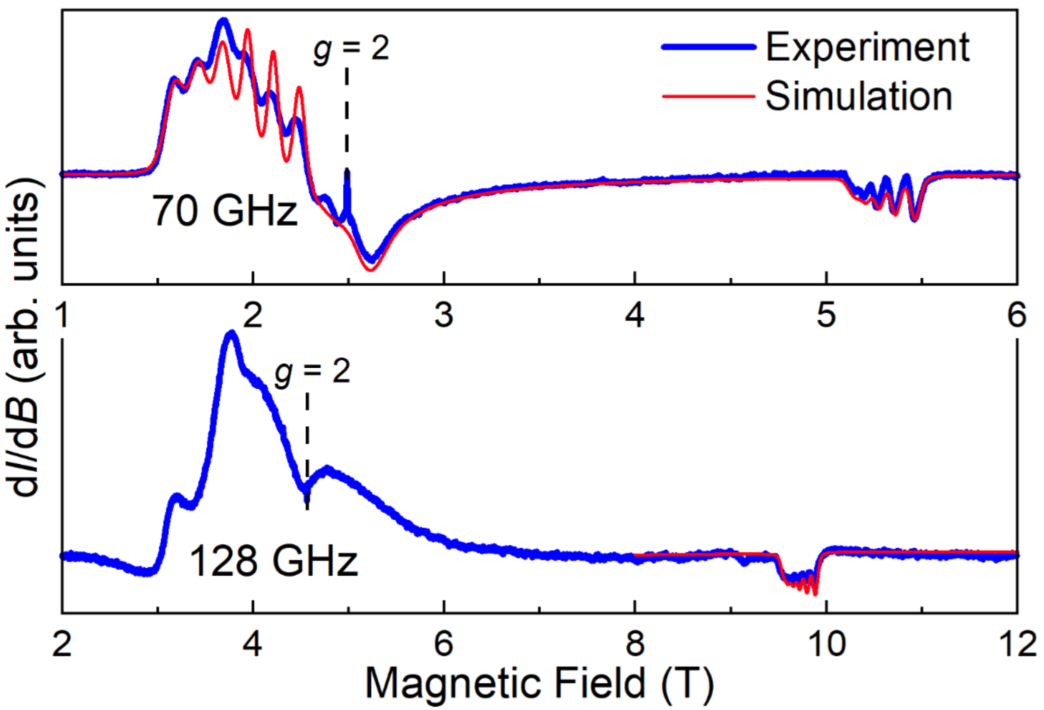

Fig. 1. Multi-frequency, high-field EPR spectra of the $[K(crypt)]^+[Cp'_3Pr^{II}]^-$ complex, which has an effective spin-½ ground state. Different components of the Landé *g*-tensor are well-resolved at the highest frequency. Spectral simulations then allow determination of the *g*- and *A*-tensor components.

Facilities and instrumentation used: EMR program, 15/17 Tesla Transmission Spectrometer

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