Anomalous power dependence near a clock transition in molecular nanomagnets

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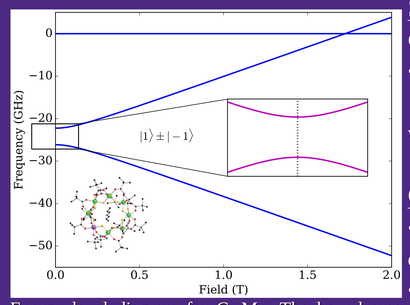
Abstract

Clock transitions in solid state systems have recently gained interest, due to their use in reducing spin decoherence which makes them an attractive feature for quantum computing. We have done electron-spin resonance (ESR) studies of the molecular nanomagnets Cr7Mn and Ni4, with spins S = 1 and 4 respectively, and report an anomalous power dependence in the vicinity of a clock transition for both molecules. Single-crystal samples are placed in the loop of a loop-gap resonator, with the sample's easy axis parallel to both the dc and rf magnetic field (parallel-mode ESR). As the applied rf power is increased, the coupling between the sample and the resonator decreases. When the frequency matches the zero-field splitting of the sample, this decoupling causes a bump to appear in the resonance peak, while at higher frequencies the greatest decoupling occurs at lower fields than the resonance peak. This suggests that the mechanism behind the decoupling is associated with the nonlinearity of the avoided crossing, and could be related to the suppression of spin decoherence. We report the results of both continuous wave and pulsed ESR experiments on dilute samples of Cr7Mn and Ni4, and identify saturation as the mechanism behind this decoupling.

Molecular Nanomagnets (MNMs)

- Molecule behaves like single spin
- Chemical tunability of Hamiltonian parameters



Energy level diagram for Cr_7Mn. The boxed area highlights the clock transition being measured, labeled by the associated superposition states. Lower Inset: A schematic of Cr_7Mn.[2] Right Inset: Zoomed-in view of clock transition, showing the suppression of field dependence at zero field.

Sample

Cr_7Mn: $S = 1$

- Spin Hamiltonian:

$$\mathscr{H} = -DS_z^2 + E(S_x^2 - S_y^2) + g\mu \mathbf{B}\cdot\mathbf{S}$$

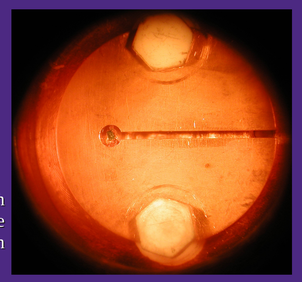
where D = 24.2 GHz, E = 1.95 GHz

Clock Transitions (CTs)

- Transverse anisotropy causes avoided crossing
- Field dependence is minimized at anti-crossing
- Dipole fluctuations (changes in local field due to surrounding spins) are significant source of decoherence
- Atomic clocks use such transitions to suppress noise
- Experiments[1] show large increase in T_2 at CT for certain MNMs

Electron Spin Resonance (ESR)

- Custom loop-gap resonators (LGRs) with tunable frequencies, high filling factors, and $Q \sim 2000$
- Parallel-mode ESR to excite forbidden transitions
- Resonator Q decreases when coupled to sample
- Sweep DC field through transitions
- Experimental temperature range: 1.8 - 2 K
- Microwave power range: -31 to 5 dBm

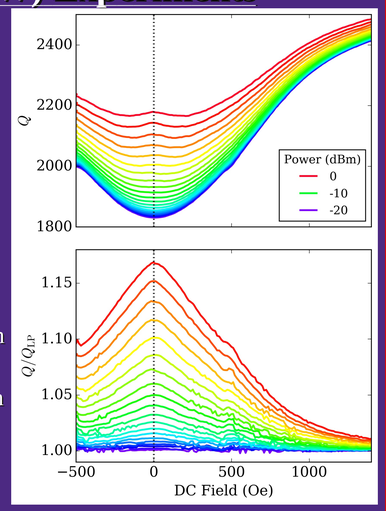


LGR mounted in copper shield, with the loop on the left and the gap on the right. A Cr_7Mn sample is mounted in the loop.

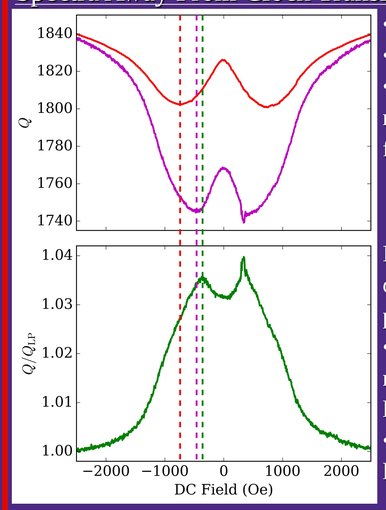
Continuous Wave (CW) Experiments

Spectra At Clock Transition

- Cr_7Mn at 4.00 GHz
- Resonance peak (minimum of Q) centered at zero field
- As power increases, zero-field peak shortens and broadens, eventually gaining a central bump
- Q increases with power, so coupling decreases
- By dividing spectrum at lowest power (Q_{LP}) from higher powers, we get fractional change (Q/Q_{LP})
- Peak in Q/Q_{LP} (decoupling peak) is sharper than resonance peak, suggesting it is related to the field dependence minimum at the clock transition



Spectra Away From Clock Transition



- Cr_7Mn at 5.62 GHz
- Peaks centered at non-zero fields
- Decoupling peaks centered at lower fields than resonance peaks, closer to region of minimized field dependence

Pulses

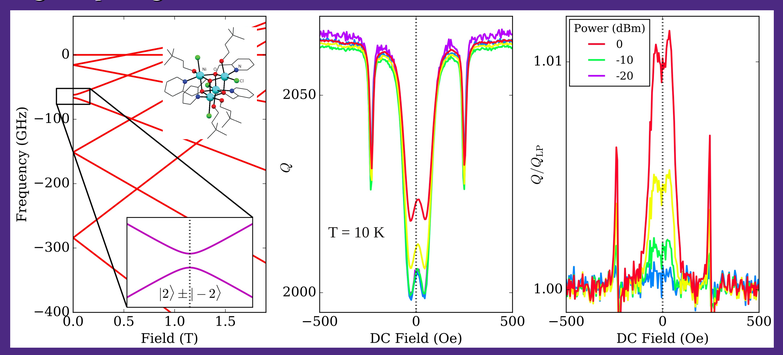
In order to probe the possibility that the decoupling is due to saturation, we perform two-pulse measurements.

- If high power is saturating, the sample should remain saturated for a time, decaying at longitudinal relaxation rate T_1
- By varying the delay τ between pulses and looking for a decay in Q we can find T_1

Addendum: Ni_4

We see a similar effect in the $S = 4$ molecular nanomagnet **Ni_4**, diluted to 5% with diamagnetic Zn_4: $(Ni_4)_{0.05}(Zn_4)_{0.95}$

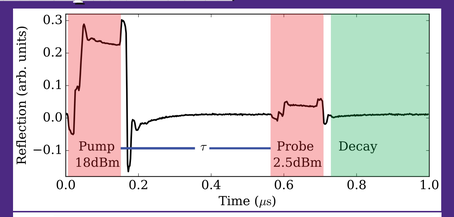
- Two conformational states at low temperature, with slightly different anisotropies giving CT splittings of 3.8 and 4.6 GHz



Pump Probe Experiments

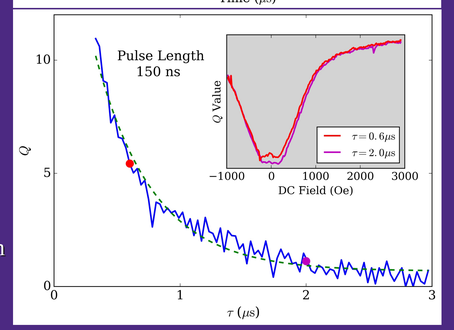
τ Sweeps

- Sit at zero field and vary τ from 300 to 3000 ns
- Decay in Q seen with a time constant of **$T_1 \sim 450 \pm 80$ ns**
- Decay not seen without pump
- Increasing field decreases the decay amplitude, but *not* T_1
- These results are consistent with saturation

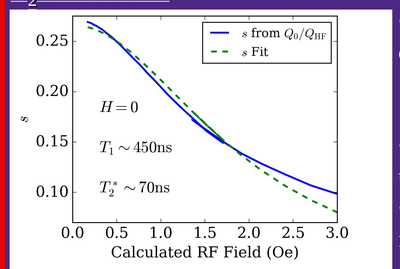


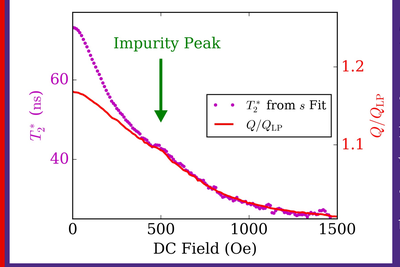
Field Sweeps

- DC field swept for delay times of 600 and 2000 ns
- Small but measurable decrease in Q with increasing τ seen at zero field
- Consistent with CW measurements



T_2^* Extraction





- We can use the saturation parameter s to determine T_2^* from T_1

$$s = (1 + \gamma^2 H^2 T_1 T_2^*)^{-1}$$

- s is extracted by comparing Q/Q_{LP} to uncoupled value at high field
- We calculate our expected RF field using the formulation from Ref. [3]

$T_2^* \sim 70$ ns

- By applying this calculation to a range of fields, we see that T_2^* is peaked at zero field, with a similar shape to Q/Q_{LP} at higher fields
- Different shape around zero field possibly due to CW heating effect

Conclusions

- Cr_7Mn exhibits decoupling with increased power
- Pulsed experiments show that this effect is consistent with saturation enhanced by the increased coherence time at the clock transition
- T_2^* appears to be enhanced at clock transition in non-dilute sample
- We measure $T_1 \sim 450$ ns and $T_2 \sim 10$-100 ns in Cr_7Mn

Acknowledgements

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