A systematic study of a family of molecular magnets using muon-spin relaxation

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$[M(HF_2)(pyz)_2]X$

- M^{2+} ions bound into a 2D square lattice by pyrazine rings. (M = Cu, Co, Ni.)
- Layers tethered by HF_2 groups.
- Structure stabilised by X^- anions (X = BF_4, ClO_4, PF_6, AsF_6, SbF_6) in pseudocubic voids.

Structure (right) is $[Cu(HF_2)(pyz)_2]PF_6$; only one anion is shown, and hydrogens on the pyz rings have been omitted for clarity.

- The Cu–pyz lattices behave as quasi-2D Heisenberg antiferromagnets, implying no long-range magnetic order for $T > 0$.

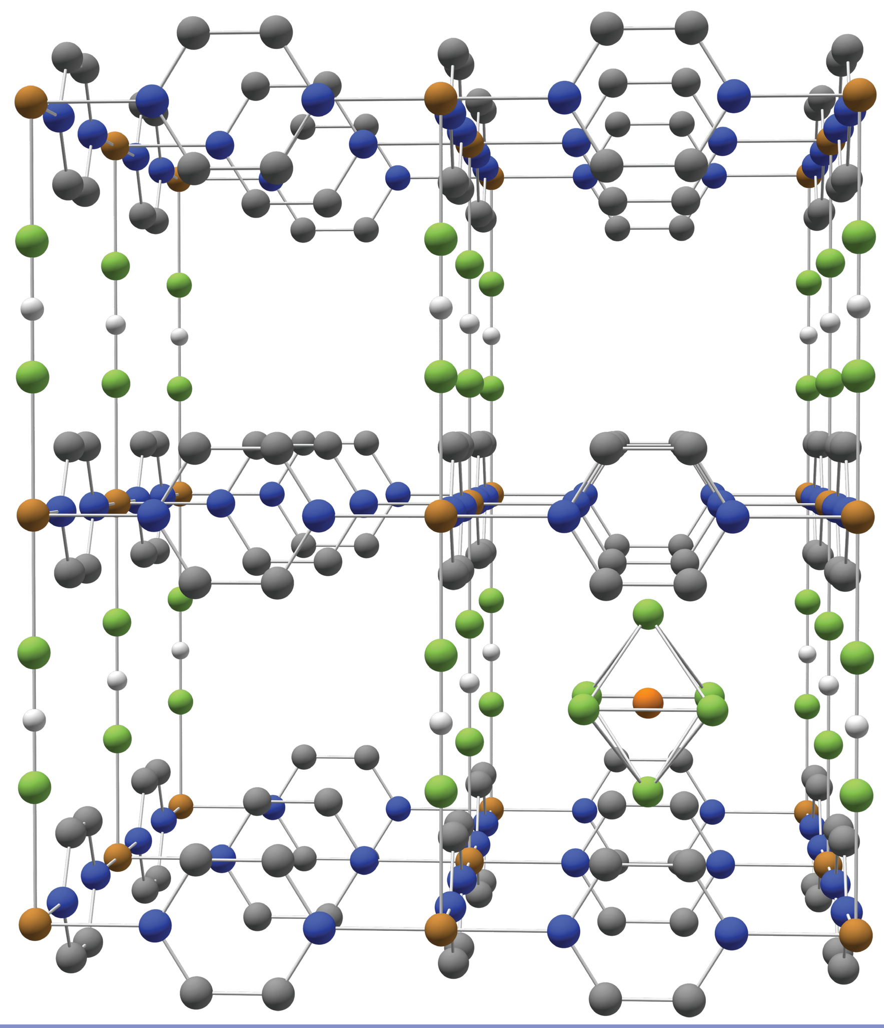
Key: Cu N C H P F

- Small inter-layer exchange $J_\perp$ gives rise to magnetic order. J and $J_\perp$ can be derived by combining T_N from μ^+SR measurements (see below), high-field magnetisation and quantum Monte Carlo simulations.

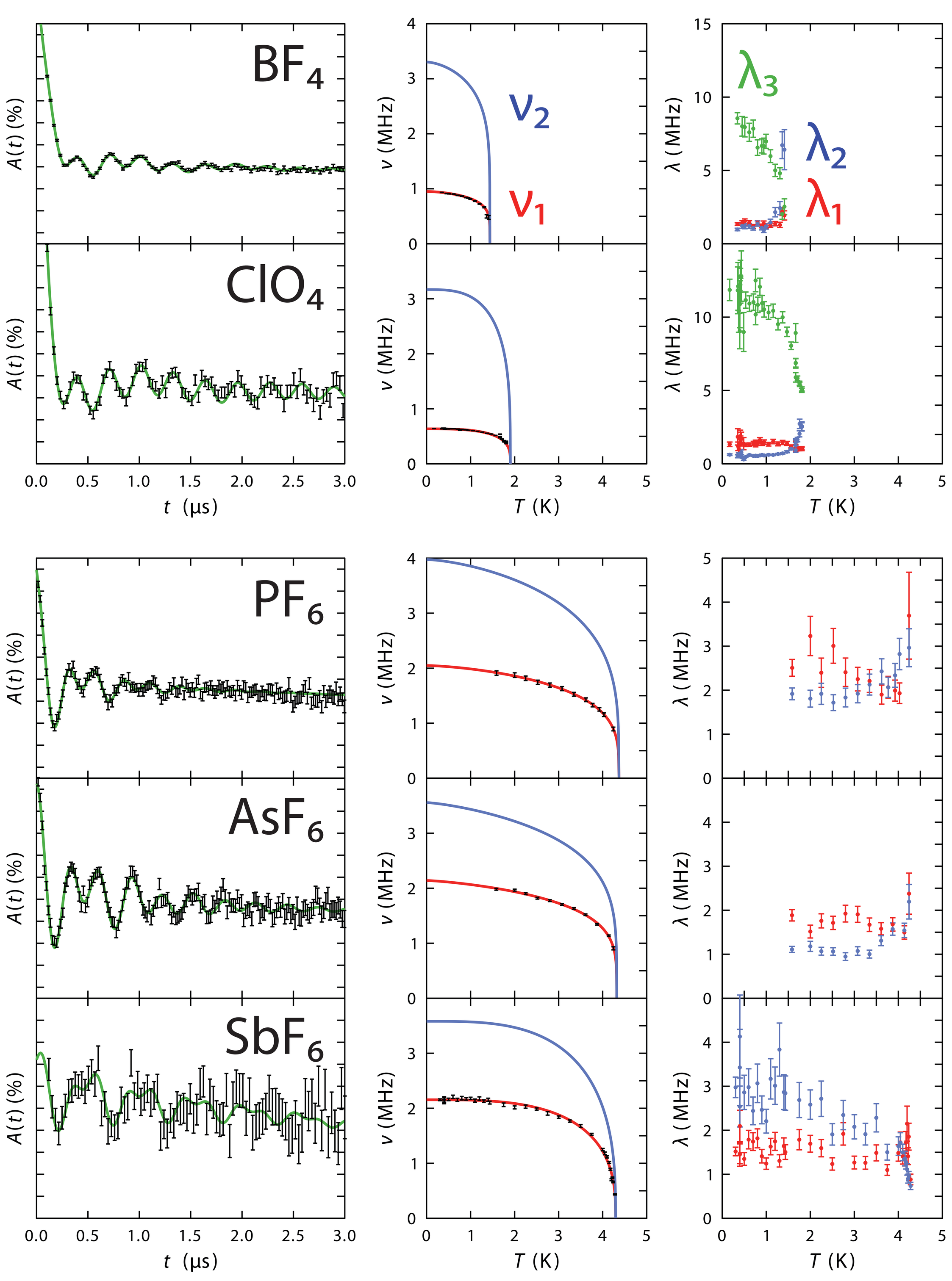
$$J_\perp / J \approx 10^{-4} \text{ for Cu...BF}_4$$

$$J_\perp / J \approx 10^{-2} \text{ for Cu...PF}_6$$

[see P. A. Goddard *et al*, NJP **10** 083025 (2008)]



Muon-spin relaxation



Typical below-T_N μ^+SR spectra, shown with frequencies and relaxation rates as a function of temperature for $[Cu(HF_2)(pyz)_2]X$.

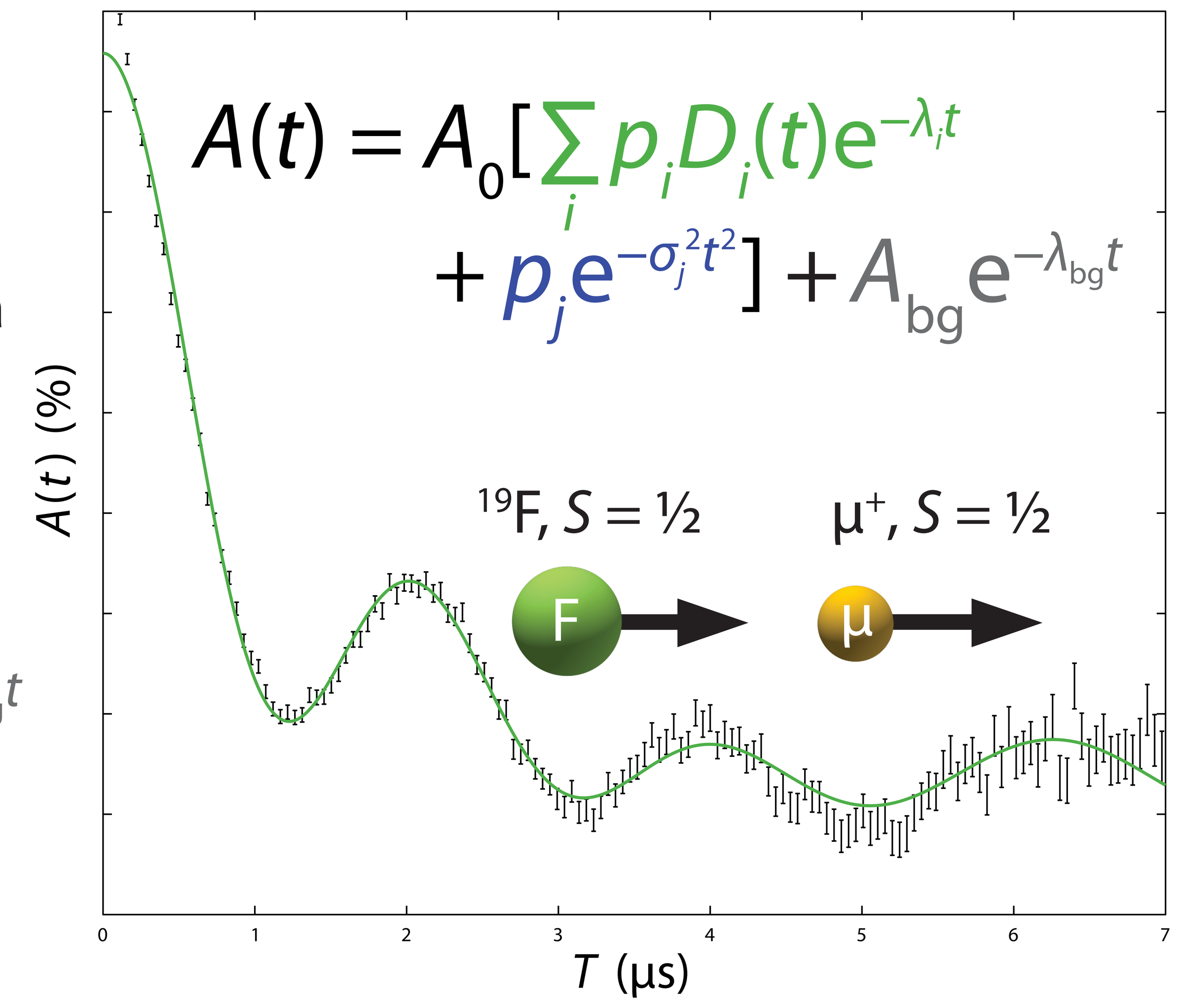
- Muon spectra show oscillations below a critical temperature T_N implying the onset of long-range magnetic order.
- Two frequencies are observed, along with a fast-relaxing component:

$$A(t) = A_0[p_1\cos(2\pi\nu_1 t+\varphi_1)e^{-\lambda_1 t} + p_2\cos(2\pi\nu_2 t+\varphi_2)e^{-\lambda_2 t} + p_3 e^{-\lambda_3 t}] + A_{bg}e^{-\lambda_{bg} t}$$

- A phenomenological fit of the precession frequencies extracts critical parameters:

$$\nu(T) = \nu(0)\,[1-(T/T_N)^\alpha]^\beta$$

Compound	T_N [K]	$\nu_1(0)$ [MHz]	$\nu_2(0)$ [MHz]	β	α
Cu...BF_4	1.44	0.95	3.30	0.18	1.6
Cu...ClO_4	1.91	0.64	3.2	0.25	2.6
Cu...PF_6	4.37	2.05	3.98	0.26	1.5
Cu...AsF_6	4.32	1.66	3.56	0.22	1.3
Cu...SbF_6	4.29	2.12	3.36	0.34	3.0
Ni...PF_6	5.9	9.3	12.1	0.2	-
Ni...SbF_6	12.25	9.00	12.30	0.34	3.1

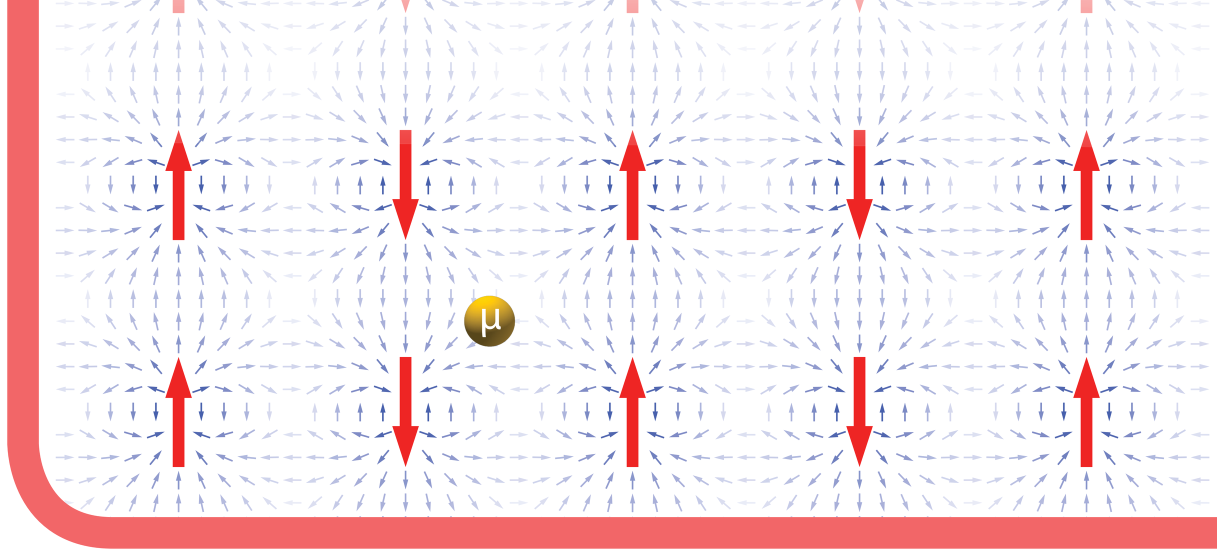


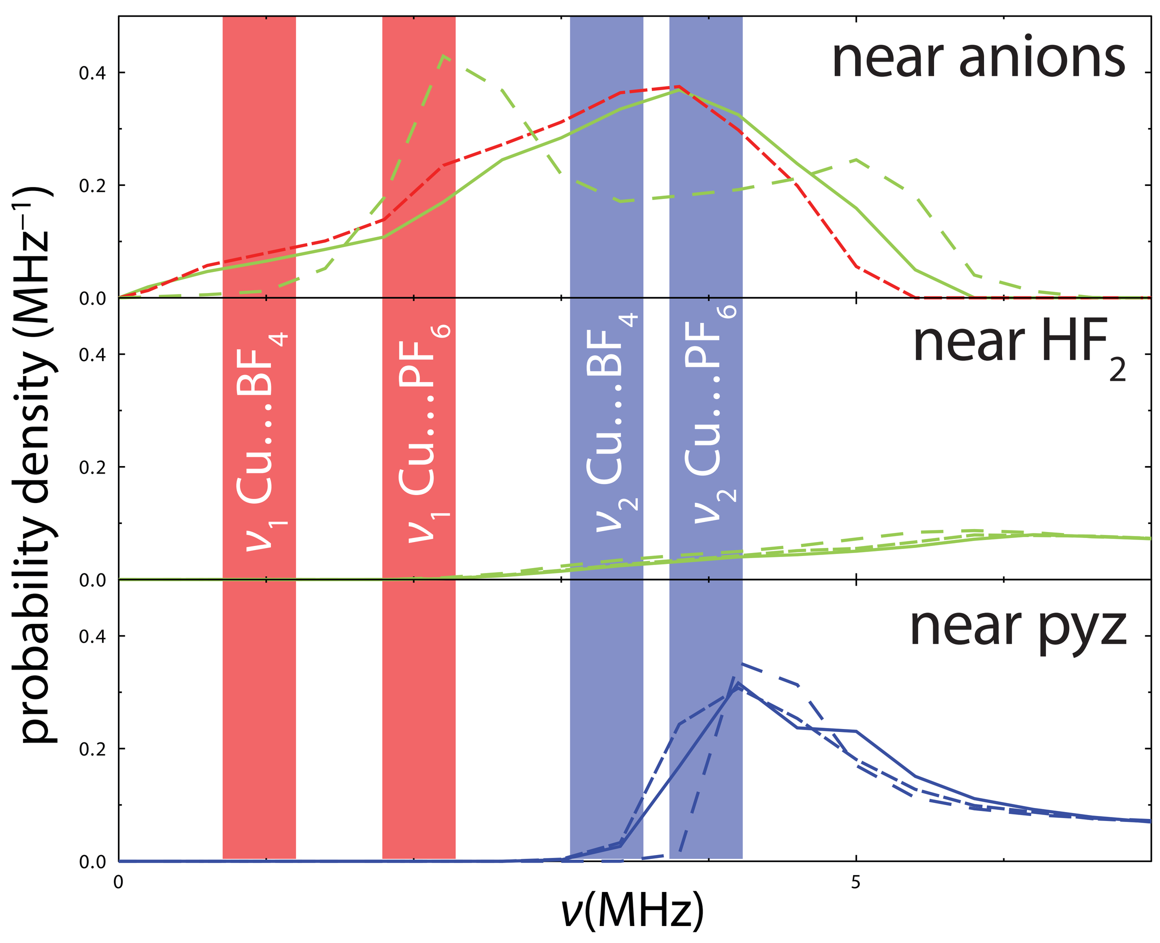
- For $T_N < T < 100$ K, small-amplitude, low-frequency oscillations are observed. These are caused by entanglement of a muon and a fluorine nuclear spin. [see T. Lancaster *et al*, PRL **99** 267601 (2007)]
- Fit $D_i(t)$ to examine details of this interaction, such as F–μ separation, number of entangled nuclei, etc.
- Most compounds fit well with one Fμ component and one FμF component; only Fμ observed in Cu...ClO_4.

Muon site determination

- Dipole field simulations treat all moments in the crystal as classical point dipoles. Summing over these allows the field at the muon site to be established.

$$\nu = 135.5\ \text{MHz T}^{-1} \times |\mathbf{B}|$$





Key: Cu...BF_4 ——— Cu...ClO_4 - - - - Cu...PF_6 — — —

- Probability densities of frequencies at plausible muon sites are evaluated.
- Lower frequencies only present near anions.
- Fμ oscillations in the Cu...ClO_4 compound mean there must be a muon site near the HF_2. This accounts for the higher frequency observed.
- The large range of high frequencies found near the pyrazine rings may explain the fast-relaxing component.

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