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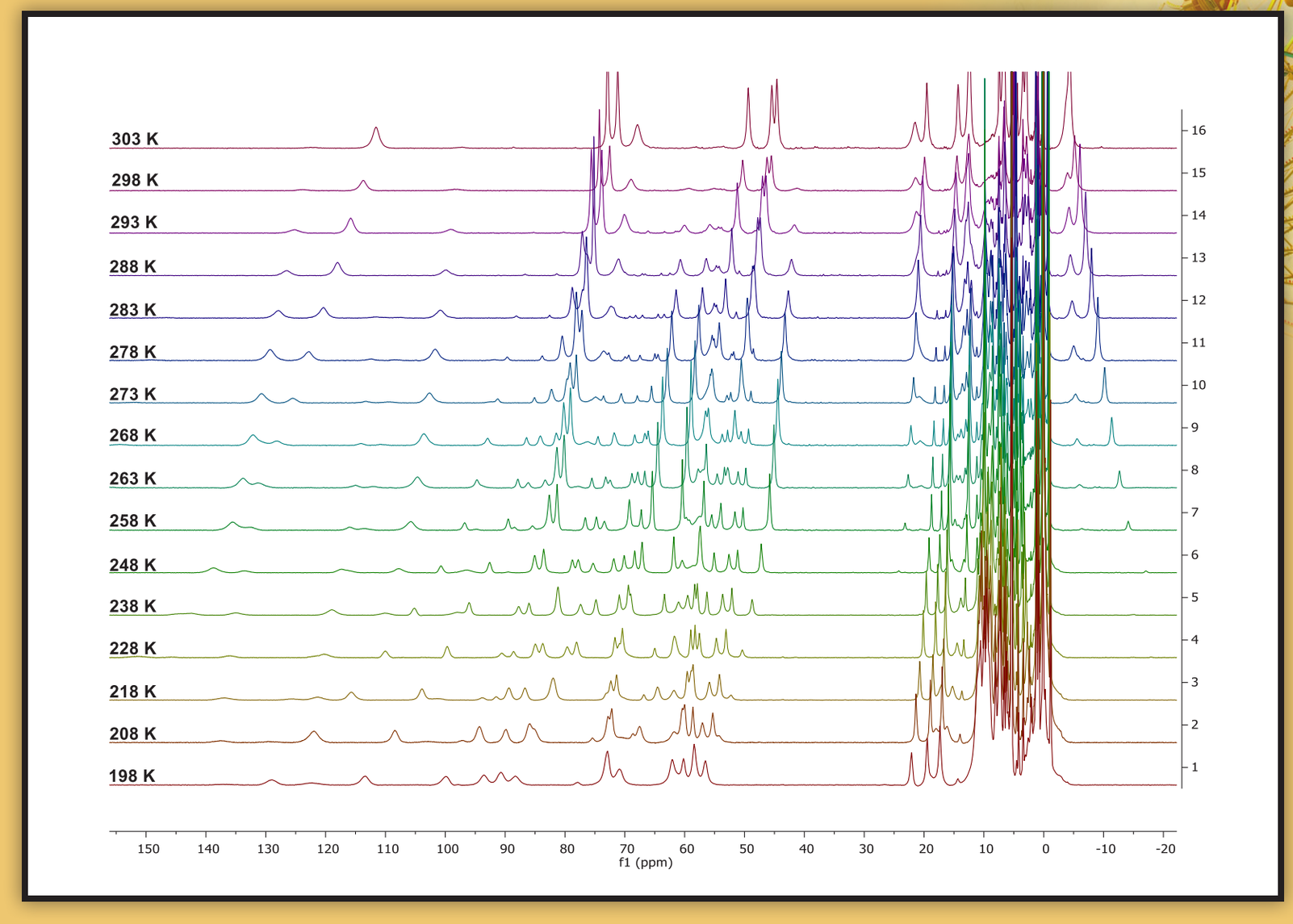
SCIENCE



Site-differentitated, high spin 2Fe(II)2Fe(III) cluster + 1 atm. CO in CD_2Cl_2

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Field strength: 500 MHz

Why is this your favorite spectrum?

High spin iron clusters often have beautiful NMR spectra featuring paramagnetically shifted resonances. We had prepared a redox series of site-differentiated tetranuclear iron clusters (4Fe(II) through Fe(II)3Fe(III)), all of which were found to reversibly bind up to two molecules of CO. The small influence of redox chemistry on the affinity of these clusters for CO was unusual and we were interested in measuring the sequential CO binding constants. As it turned out, 1H-NMR spectroscopy was the only technique capable measuring the concentrations of the CO-free and CO-bound clusters (relative to a paramagnetic internal standard) as a function of temperature. These measurements allowed us not only to confirm the small effect of 1e- redox chemistry on the CO binding affinities, but also to deconvolute the relative effects of redox chemistry localized at specific sites within the cluster.

Comments: Between sample preparation and equilibration at each temperature, series of temperature measurements took roughly 18hrs. Sample preparation would begin at 6 AM. Spectra would be collect at various temperatures in the absence of CO until about 1 or 2 PM. CO would then be added and NMR spectra collected until about midnight. This had to be done multiple times for each redox state and, as it turned out, in multiple solvents. I was relieved when we got the reviews back on our paper-the reviewers did not ask for any additional VT-NMR experiments!