High-Spin Versus Broken Symmetry – Effect of DFT Spin Density Representation on the Geometries of Two Diiron (II) Model Compounds.

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Abstract

Unrestricted density functional theory calculations have been conducted on two diiron(II) synthetic model compounds containing antiferromagnetically coupled high-spin irons for which crystallographic structures and Raman spectral data are available. Three density functionals have been employed: BPW91, PWC and BOP. The study compares the effects on optimized geometries and harmonic vibrational frequencies of high-spin and broken symmetry antiferromagnetically coupled singlet representations of the spin density distribution. The geometries around the diiron centers in the high-spin and broken symmetry representations are found to be similar, both markedly different from those arising from the spin-paired representation. Small differences between the high-spin and broken symmetry results are seen in bond lengths, angles, Raman frequencies and spin densities associated with oxo and peroxo bridges between the irons.