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LETTER

Double exchange versus J inequality in $Fe_3S_4^0$ clusters

Ivano Bertini*, Fabrizio Briganti
Department of Chemistry, University of Florence, via Gino Capponi 7, 50121 Florence (Italy)

and Claudio Luchinat
Institute of Agricultural Chemistry, University of Bologna, viale Berti Pichat 10, 40127 Bologna (Italy)

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The interpretation of the Mössbauer isomer shift and hyperfine coupling of reduced $Fe_3S_4^0$ clusters (Fig. 1) required [1–3] the introduction of a delocalization parameter B [4–10] in the expression for the energy levels of the cluster. Such a parameter describes electron delocalization within one Fe^{2+}–Fe^{3+} pair, and is responsible for lowering more the energies of the levels with larger local S for the mixed valence pair (e.g. S_{12} in the scheme) eventually giving a ground state $S_{Fe^{3+}Fe^{2+}}=9/2$. This pair is then antiferromagnetically coupled with the third Fe^{3+} to give total $S=2$. The experimental data were reproduced [1, 2] with $J_{12}=J_{13}=J_{23}=J$ and $B_{12}/J>2$.

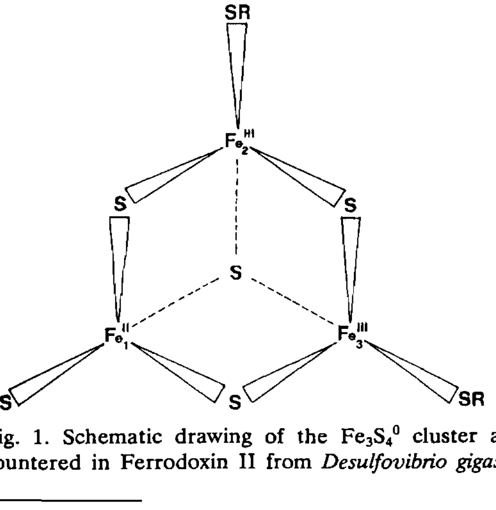

Fig. 1. Schematic drawing of the $Fe_3S_4^0$ cluster as encountered in Ferrodoxin II from *Desulfovibrio gigas*.

We are going to show now that this ratio is model dependent. In Fig. 2 the energy levels for a system with $B_{12}/J=2.5$ are reported and compared with those for a system with $J_{12}/J=0.4$ and $B_{12}=0$. The eigenvalues and eigenfunctions of the two approaches are similar. This shows that an alternative model can be used with one of the $J_{Fe^{2+}Fe^{3+}}$ smaller than $J_{Fe^{3+}Fe^{3+}}$. The former value can be formally due to a ferromagnetic contribution analogous to B. This model is as good and reasonable, since it proposes a smaller J for the mixed valence pair than for the oxidized pair, as expected [11, 12]. Of course a B value is needed anyway to make the two iron ions in the mixed valence pair equivalent, but in the latter model it can be so small to be ineffective for the eigenvalues. Its actual determination must rely on experiments designed to extract selective information on B. Such experiments typically are bound to intensity and energy position of the intervalence band when observed [13, 14]. The two approaches would be experimentally indistinguishable if J is as large as it is in oxidized Fe_2S_2 clusters ($\simeq 400$ cm^{-1} [11, 12]), because then the population of the excited states up to room temperature is very small. Indeed, recent magnetic data on a Fe_3S_4 cluster in the temperature range 1.8–200 K indicate negligible population of excited states having $S\neq 2$ [15].

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*Author to whom correspondence should be addressed.

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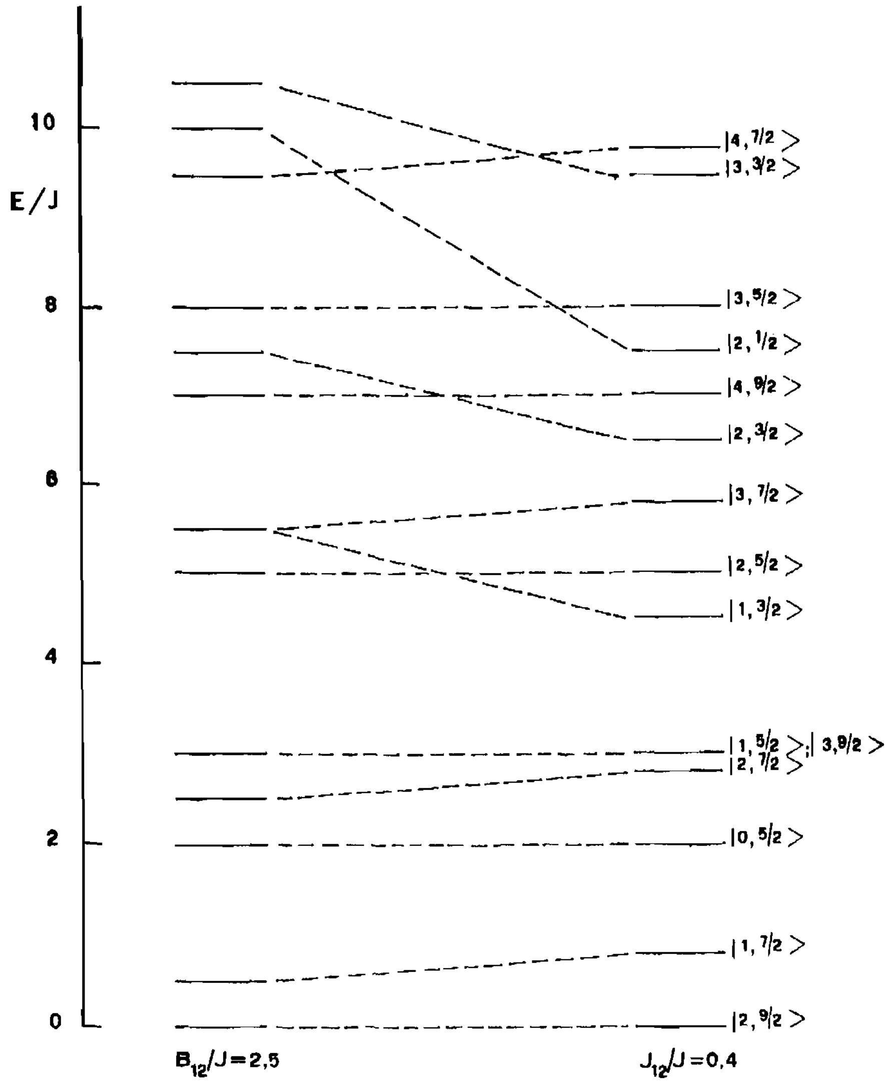

Fig. 2. Low-lying energy levels for the $Fe_3S_4^0$ cluster of Fig. 1 calculated with (A) all J values equal and $B_{12}/J = 2.5$, or (B) $J_{12}/J = 0.4$ and $B_{12} = 0$. The eigenfunctions expressed in terms of total S and S_{12} are also shown. Note the overall similarity, especially for the lowest group of levels.

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