

Supplementary data

Charge Transfers Influence on the Spin Ground State of Manganese and Iron Superoxide Dismutases: A DFT Study on a Model of the Reduced Active Site Interacting with O₂⁻

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Construction of the Models

MnSODs and FeSODs present the same set of coordinating ligands, and have active sites organized as approximate trigonal bipyramids with three histidines, one aspartate, and one hydroxyl (or water) ligand.² Their structures are highly homologous. Therefore, in order to build a model of both the reduced and oxidized active sites of the iron and manganese proteins, we have taken as a reference the crystal structure of *E. coli* Fe^{III}SOD (Brookhaven National Laboratory Protein Data Bank code: 1ISB) at 1.85 Å resolution.^{2b} We have only considered the first coordination shell surrounding the active site metal. Thus, the aspartic acid Asp156 has been replaced by an acetate group and the histidines His26, His73 and His160 have been substituted by neutral imidazol groups (FeSOD aminoacid numbering). The C β atom in histidines and C α in aspartate have been replaced by H atoms. A water molecule (Wat194) occupies the fifth coordination position. One proton of the water molecule forms a hydrogen bond to the

acetate. This hydrogen atom, after the geometrical optimisations, is retained by the carboxylate leading to the hydroxide forms of the $M^{III}SOD$. The X-ray structure shows that the apoprotein adopts a conformation that allows the approach of the O_2^- anion to the metal center between His73 and His160.^{2b} This is the position occupied by the azide ligand in the crystal structure of the *E. coli* $Fe^{III}SOD$ -azide complex ((Brookhaven National Laboratory Protein Data Bank code: 1ISC) solved at 1.80 Å resolution.^{2b} In this way, the model complexes corresponding to the active sites of the reduced proteins interacting with the superoxide anion have all been built from the crystallographic data of the *E. coli* $Fe^{III}SOD$ -azide complex. The azide ligand has been replaced by a O_2^- anion. Among the possible coordination ways of the metal center to the substrate, we have studied the conformation shown in Figure 1, that leads to an active species.⁶

All these built models have been considered as the starting point for a geometrical optimisation by DFT calculations. These optimisations have been carried out for all species in all studied spin states. The results of the geometry optimisations for the reduced and oxidized $FeSOD$ and $MnSOD$ active site models are in agreement with those found by Noodleman and Whittaker.^{2a,c} These authors, in different works, have carefully analysed the optimised geometries of active site models regarding to the experimental crystal structures of several iron and manganese SOD proteins.

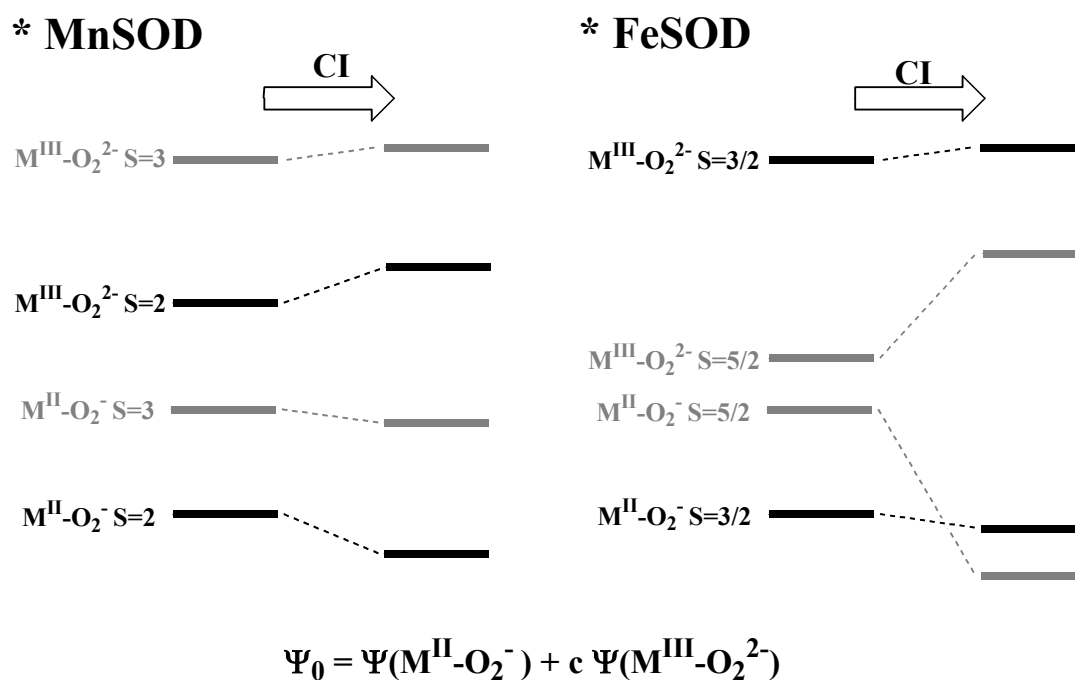


Figure S1. Simple visualisation of the configuration interactions between the ground and excited spin states for the model complexes of the active sites of $Mn^{II}SOD$ and $Fe^{II}SOD$ with the O_2^- anion.