

Theoretical Studies of Effects on Hydrogen Bonds Attached to Cysteine Ligands of 4Fe-4S Clusters

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Abstract

Polymetal complexes are sometimes utilized for storage of electrons in electron transfer proteins. 4Fe-4S clusters, such as ferredoxin, HiPIP and so on, are one of the typical complexes of them. Although the series of those proteins contains similar 4Fe-4S clusters in their active sites, they show various redox potentials. For example, redox potential of ferredoxin is -400mV, while HiPIP indicates +360mV. Recent developments of X-ray structure analyses have revealed the significant difference in number of hydrogen bonding around 4Fe-4S clusters.

In this study, we examined the effects of the hydrogen bonds around HiPIP clusters by using unrestricted density functional theory (UDFT) methods. First we investigated electronic structures of naked 4Fe-4S cluster of HiPIP as illustrated in Figure 1. Next, four hydrogen bonds were attached to cysteine ligands of the cluster based on the X-ray geometry. The calculated results indicate that they do not change a form of wave functions of valence orbitals around 4Fe-4S but it strongly stabilizes orbital energies. This suggests that they give positive electrostatic fields to the clusters.



Figure 1
Calculated 4Fe-4S cluster
model (naked model)

References

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