Iron-Sulfur Clusters from the Viewpoint of Condensed Matter Physics

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It is well-known that ion-sulfur clusters are responsible for the electron transfer in proteins. Recently, it has been proposed that the electron transfer by a one [4Fe-4S]$^{1+/2+}$ cluster-containing activator is accompanied by conformal changes of an helix-cluster-helix angle from 105° to 180°.[1] This gives rise to the question how electronic states of the [4Fe-4S] clusters are related to the microscopic mechanism of the conformation in the longer spatial scale. Motivated by this proposal, we are now studying the electronic states of the iron-sulfur clusters from the viewpoint of condensed matter physics.

In this talk, we discuss the present status of the understanding of the electronic states of the [4Fe-4S] cluster (Fig. 1).[2] The [4Fe-4S]$^{2+}$ system formally contains two Fe^{3+} (S=5/2) and two Fe^{2+} (S=2). Mössbauer spectroscopy indicates, however, that the four iron ions are generally equivalent, thus carrying a common charge of 2.5+. The observed equivalence can be correlated with crystallographic data that indicate D_{2d} type distortion of four iron sites, resulting in two pairs of iron sites, “Fe1- Fe2” and “Fe3-Fe4”. Total spin of the cluster is known to be S_t=0. These facts were theoretically understood by taking into account the interplay of exchange interactions between iron spins and vibronic coupling.[3] The exchange interactions consist of two parts: the superexchange terms between iron ions and the double exchange terms favoring delocalization and ferromagnetism within mixed-valence pairs. Therefore, one can describe the spin coupling of the cluster in two steps: first by the double exchange that makes the pairs, “Fe1- Fe2” and “Fe3-Fe4”, ferromagnetic and secondly by the superexchange that couples the two pairs antiferromagnetically. The interplay of the resulting spin states and vibronic coupling gives rise to the Jahn-Teller distortion from T_d to D_{2d}.

The [4Fe-4S]$^{1+}$ system usually has a S_t=1/2 ground state. However, the state with S_t=3/2 also appears at low energy and sometimes becomes the ground state.[4] This nearly degenerate feature may have an effect on the mechanism of the electron transfer.

Since the analyses of the [4Fe-4S] clusters have mainly been done based on quantum chemistry calculations,[4] alternative approaches based on condensed matter physics may be useful for fully understanding the electronic states of the iron-sulfur clusters.

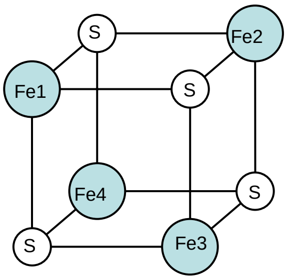

Figure 1: [4Fe-4S] cluster

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