PROBING THE INTRINSIC ELECTRONIC EFFECTS OF THE $[Fe_4S_4]^{2+}$ CLUSTER ON THE REDOX POTENTIALS OF FERREDOXINS AND HIGH POTENTIAL Fe-S PROTEINS

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Iron-sulfur proteins are ubiquitous in living systems. The bacterial ferredoxins and high potential iron-sulfur proteins are the simplest examples of Fe-S proteins with a [4Fe-4S] active center. We report a combined photodetachment photoelectron spectroscopic and theoretical study of a series of bioinorganic analog complexes, $[Fe_4S_4X_4]^{2-}$ (X = SH, SCH3, Cl, Br, I), in the gas phase to elucidate the intrinsic electronic contributions to the redox potentials of both the $[Fe_4S_4]^{2+/1+}$ and $[Fe_4S_4]^{3+/2+}$ redox couples. We found that the intrinsic redox potential of $[Fe_4S_4]^{3+/2+}$ increases with the decrease of the donor capability of the terminal thiolate ligands, whereas it is relatively insensitive to the bridging sulfides. The major factors contributing to the intrinsic redox potential changes in the $[Fe_4S_4]^{2+/1+}$ redox pair is the donor property of the bridging sulfide, as well as the terminal thiolate ligands. We also studied the different contributions of bridging and terminal H-bonds to the two different redox couples.