

Electronic structure and bonding properties of iron–sulfur clusters

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Iron–sulfur clusters are ubiquitous.[1] They are involved in many biological systems operating as active centers of proteins in processes such as photosynthesis, respiration, and nitrogen fixation.[2] Specifically, they are involved in electron transfer processes, substrate activation and binding, catalytic reactions, DNA repair, signal transductions, iron/sulfur storage, regulation of gene expression, etc.[3,4] In addition, they are significant in industrial catalysis.[5] The key for their remarkable reactivity is their low-lying electronic states. It is particularly important to be understood the intrinsic electronic structure of the Fe-S clusters as well as their modifications by their surroundings in order the functionalities of the iron-sulfur proteins to be interpreted.

Here, we present a theoretical study of the Fe_xS_y clusters, where $x=1-2$ and $y=1-4$, employing the DFT(B3LYP and TPSSH), CAS, MRCI, and CCSD(T) methodologies in conjunction with the aug-cc-pVnZ, $n=D-Q$ basis sets. The lowest energy structures of linear, planar, and three-dimensional clusters are determined. The dissociation energies for different reaction products are calculated. Corrections for the basis set superposition error are included. Finally, the electronic structure and the bonding properties of the clusters are analyzed. It is of interest that states of high spin multiplicity are low-lying in energy. The electronic energy levels of even the same spin are dense providing a natural explanation for the ubiquity of these clusters in nature and in catalysis.

References:

1. Spiro, T. G. Ed. Iron-Sulfur Proteins; Wiley-Interscience: New York, (1982).
2. D. Kessler, J. Papenbrock, *Photosynthesis Research* **86**, 391 (2005)
3. K. Brzóška, S. Meczyńska, M. Kruszewski, *Acta Biochim Pol*, **53**, 685 (2006).
4. L. C. Seefeldt, Z.-Y. Yang, D. A. Lukoyanov, D. F. Harris, D. R. Dean, S. Raagei, B. M. Hoffman, *Chem. Rev.* **120**, 5082 (2020).
5. M. S. Nurmaganbetova, M. I. Baikenov, M. G. Meiramov, A. A. Mukhtar, A. T. Ordabaeva, V. A. Khrupov, *Pet. Chem.* **41**, 26 (2001).