

Fe₂S₂ cluster in aqueous solution: geometry, magnetic properties, and hydration from first principles

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Aqueous iron-sulfur clusters (FeS(aq)), where water molecules are molecularly coordinated to the ferrous high-spin irons, are of extreme interest in Origin of Life theories. Together with iron-sulfur minerals, it has been postulated that FeS(aq) would be capable of synthesising simple organic molecules on the early Earth, while the underlying mechanism, based on the reduction of CO₂, suggests that they may have a modern role as catalysts for CO₂ conversion [1, 2].

The study of transition metal compounds, due to strong correlation effects, represents a challenge for density functional theory (DFT). One possibility of improving their description is offered by the DFT+U approach, in which the strongly correlated electrons are treated with the addition of a Hubbard correction.

Here, we present a DFT+U investigation of the all-ferrous Fe₂S₂ cluster in aqueous solution (Fe₂S₂(aq)), which is thought to be the building unit of the first condensed mackinawite mineral. Compared to standard DFT, the geometry of Fe₂S₂(aq) resulting from DFT+U agrees better with the X-ray diffraction structure, while the magnetic coupling between the two irons is in line with that estimated from Mössbauer data [3]. Molecular dynamics trajectories predict Fe₂S₂(aq) to be stable in water, regardless of the introduction of the U correction. In spite of this, significant differences arise in the geometry, hydration, and magnetic coupling of the solvated clusters.

- [1] Wachtershauser, (1988) *Microbiol. Rev.*, **52**, 452. [2] Russell & Martin, (2004) *Trends Biochem. Sci.*, **29**, 358. [3] Albers *et Al.*, (2013) *J. Am. Chem. Soc.*, **135**, 1704.