

**Corrections to Theoretical Study of Dioxygen Induced Inhibition of [FeFe]-Hydrogenase** [*Inorg. Chem.* **2009**, *48*, 7127].  
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Recently, we discovered that one reaction energy reported in our paper was affected by a technical error. The strongly exothermic coordination energy of O<sub>2</sub> of −64.5 kcal/mol (BP86/TZVP) to the terminal Fe<sub>d</sub> atom of the [2Fe]<sub>H</sub> subsite was, in part, due to slight variations in the position of the fixed hydrogen atoms of the methyl groups in the educt compared to the product, which led to a molecular energy of the oxygen-free fragment that was too high. We repeated the calculations with consistent input coordinates and obtained with BP86/SVP and BP86/TZVP significantly less exothermic energies of −8.1 and −8.7 kcal/mol, respectively (in the case of NH instead of O in the dithiolate bridge, the O<sub>2</sub> coordination energy is −7.0 kcal/mol). We obtain a more exothermic result of −16.7 kcal/mol with TPSS/TZVP. With the B3LYP functional endothermic as well as exothermic reaction, energies result depending on the size of the basis set used.

For the reduced H<sub>red</sub> state, i.e., in the [Fe(I)Fe(I)] form of the [2Fe]<sub>H</sub> subsite, with −12.5 kcal/mol (BP86/TZVP), we calculated an energy quite comparable to that of the oxidized form, which resembles the situation in the original publication. Taking these corrected coordination energies into account, we find that the formation of the terminal oxygen adduct is less exothermic than that of the alternative isomers discussed in the paper. However, the original situation that favors the terminal coordination product is restored when a larger structural model is considered that includes the C<sub>α</sub> atoms of the cysteine residues as present in the crystal structure, thereby better capturing the degrees of freedom accessible in the protein (also note that the distal iron of the [2Fe]<sub>H</sub> subsite represents the place of first contact for dioxygen entering the environment of the active site). All further results and conclusions regarding the possible reaction paths following the oxygen addition published are basically unchanged by the error affecting the coordination energy of O<sub>2</sub> to the terminal Fe<sub>d</sub> atom and remain thus valid.

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