On the enzymatic activity of catalase: an iron L-edge X-ray absorption study of the active centre

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Catalase and methaemoglobin have very similar haem groups, which are both ferric, yet catalase decomposes hydrogen peroxide to water and oxygen very efficiently, while methaemoglobin does not. Structural studies have attributed this behaviour to their different distal environments. Here we present Fe $L_{2,3}$-edge X-ray absorption spectra of these proteins in physiological solutions, which reveal clear differences in their electronic structures, in that πback-donation of the Fe atom occurs in catalase, which confers on it a partial ferryl (Fe^{4+}) character, while this is not the case in methaemoglobin (1). The origin of the Fe^{4+} character stems from the proximal tyrosine residue. We also find that both systems are in a high spin state. Temperature effects influence the spectra of catalase only weakly, in agreement with previous studies of its chemical activity. We conclude that the high activity of catalase is not only determined by its distal environment but also by its partial ferryl character.

Reference:

(1) Emad F. Aziz *et. al.* **Physical Review Letters** 102, 68103 (2009).