

# Manifestation of the Jahn–Teller effect in Nature’s Water Oxidase

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The active site of the oxygen-evolving complex (OEC) of photosystem II (PSII) is an oxo-bridged  $\text{Mn}_4\text{CaO}_5$  cluster that stores four oxidizing equivalents required to oxidize water into dioxygen by cycling through five oxidation states known as the  $S_0$ – $S_4$  states. Here we investigate the interplay between Jahn–Teller effects and valence isomerism, unravelling its role in efficient catalytic S-state progression. We employ quantum chemistry methods to show that the  $\text{Mn}_4\text{CaO}_5$  cluster in the resting (dark-stable)  $S_1$  state adopts orientational pseudo-Jahn–Teller isomeric forms that differ in the direction of the “dangler” Mn(III) ion pseudo-Jahn–Teller axis. The proposed structures are consistent with the available structural data and provide a simple and direct interpretation of observed  $S_1$  state EPR signals [1]. We also discuss the functional role of this structural isomerism in the emergence of valence isomerism in the  $S_2$  state [2]. Understanding nature’s unique water-oxidizing enzyme might provide invaluable guidelines for the development of artificial water-splitting catalysts.

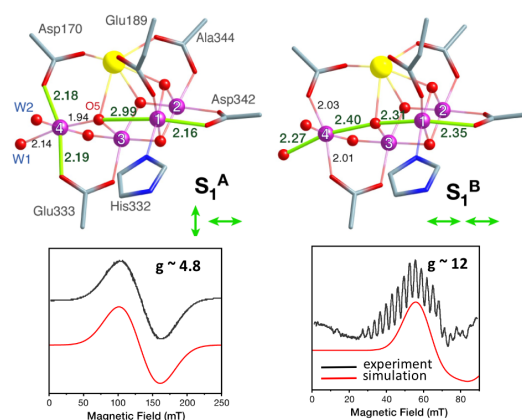


Figure caption: Proposed  $S_1$  state structures with the corresponding observed EPR signals.

[1] M. Drosou; G. Zahariou; D. A. Pantazis; *Angew. Chem. Int. Ed.* **60**, 13493 (2021).

[2] D. A. Pantazis; W. Ames; N. Cox, W. Lubitz; F. Neese; *Angew. Chem. Int. Ed.* **51**, 9935 (2012).