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 Mn₄CaO₅ cluster that stores four oxidizing equivalents required to oxidize water into dioxygen by cycling through five oxidation states known as the S₀–S₄ 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 Mn₄CaO₅ cluster in the resting (dark-stable) S₁ 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 S₁ state EPR signals [1]. We also discuss the functional role of this structural isomerism in the emergence of valence isomerism in the S₂ state [2]. Understanding nature’s unique water-oxidizing enzyme might provide invaluable guidelines for the development of artificial water-splitting catalysts.