

# Understanding Nature's Water Oxidation Catalyst via Theory-Driven Structure-Spectroscopy Correlations

Dimitrios A. Pantazis

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

Email: [dimitrios.pantazis@kofo.mpg.de](mailto:dimitrios.pantazis@kofo.mpg.de)

Oxygenic photosynthesis, the process that powers life on our planet, relies on light-driven oxidation of water by the oxygen-evolving complex (OEC) of photosystem II. The  $\text{Mn}_4\text{CaO}_x$  cluster of the OEC adopts different electronic and geometric forms both as it progresses physiologically through the catalytic water-oxidizing cycle, and as a result of various treatments used to probe specific aspects of its structure and function. Despite remarkable advances in crystallographic studies, the information content of such data is insufficient to produce geometric models that are uniquely defined and chemically accurate. On the other hand, magnetic resonance techniques (EPR, ENDOR, EDNMR, etc) offer the most detailed and selective insight into the electronic structure of the catalyst, but cannot receive direct structural interpretation for a system as complex as the OEC. This necessitates using spectroscopy-oriented quantum chemical modelling [1]. Here I will provide an overview of studies that focus on the identity of different EPR-detected forms of the OEC in observable states of the catalytic cycle. Such studies have provided unique insights into the catalytic mechanism of water oxidation, highlighting the inherent heterogeneity of the system, various different types of isomerism (e.g. Jahn–Teller isomerism, valence isomerism, hydration equilibria) in each state [2–4], and the crucial functional role of the protein matrix.

[1] M. Orio, D. A. Pantazis, “Successes, challenges, and opportunities for quantum chemistry in understanding metalloenzymes for solar fuels research”, *Chem. Commun.* **2021**, 57, 3952-3974.

[2] M. Drosou, G. Zahariou, D. A. Pantazis, “Orientational Jahn–Teller Isomerism in the Dark-Stable State of Nature's Water Oxidase”, *Angew. Chem., Int. Ed.* **2021**, 60, 13493-13499.

[3] D. A. Pantazis, W. Ames, N. Cox, W. Lubitz, F. Neese, “Two Interconvertible Structures that Explain the Spectroscopic Properties of the Oxygen-Evolving Complex of Photosystem II in the  $\text{S}_2$  State”, *Angew. Chem., Int. Ed.* **2012**, 51, 9935-9940.

[4] G. Zahariou, N. Ioannidis, Y. Sanakis, D. A. Pantazis, “Arrested substrate binding resolves catalytic intermediates in higher-plant water oxidation”, *Angew. Chem., Int. Ed.* **2021**, 60, 3156-3162.

## Dr. Dimitrios A. Pantazis - Short Biography

Dimitrios Pantazis studied Chemistry at the Aristotle University of Thessaloniki (Greece), where he first realized that quantum chemistry was the way to satisfy all his diverse interests in chemistry. He obtained his PhD in Computational Chemistry from the University of York (UK) with Prof. John McGrady. Following an EPSRC postdoctoral fellowship at the University of Glasgow, he joined the group of Prof. Frank Neese in Bonn and soon after he was awarded the 2010 Ernst-Haage Prize for Bioinorganic Chemistry for his developments in EPR theory and their application to the oxygen-evolving complex. In 2011 he became a group leader at the Max Planck Institute in Mülheim, becoming permanent in 2015. His research group is primarily devoted to applications of spectroscopy-oriented quantum chemistry to bioinorganic systems. He is most well-known for his contributions to the field of photosynthesis and biological water oxidation.