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## Disproportionation in gas-phase di-manganese oxide cluster revealed by X-ray absorption spectroscopy

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Photosystem II, with its active center a  $\text{CaMn}_4\text{O}_5$  cluster (OEC), is essential for photosynthesis and therefore  $\text{O}_2$  production in nature [1]. The understanding of the electronic structure and properties of this complex plays an important role in designing artificial water-oxidizing complexes. During oxygen formation the OEC undergoes five distinct states called  $\text{S}_0$ - $\text{S}_4$  forming the Kok cycle. Despite detailed knowledge of  $\text{S}_0$  through  $\text{S}_3$  there is still a lack of information on  $\text{S}_4$  due to challenges preparing OEC in this state [2]. However, two major competing models for  $\text{S}_4$  have been proposed in the literature which involve distinctively different oxidation states namely Mn(IV) (and an oxygen radical) and Mn(V), respectively.

We performed X-ray absorption spectroscopy (XAS) in ion yield mode at the manganese L-edge and oxygen K-edge on a series of cryogenically cooled, mass-selected manganese oxide ions at 20 K.

Here, we report on  $\text{Mn}_2\text{O}_3^+$  – a high-valent species with two  $\mu$ -oxo bridges and a terminal oxo ligand, which forms a subunit of the OEC. Using XAS we find an unusual charge disproportionation in  $\text{Mn}_2\text{O}_3^+$ , where one manganese atom is in a high oxidation state, and stability of this complex in a  $\text{H}_2\text{O}$  ligand presence. The oxidation states were identified by comparison to reference X Ray absorption spectra of other manganese compounds.

[1] N. Cox and et al. Electronic structure of the oxygen-evolving complex in Photosystem II prior to O–O bond formation. *Science*, 2014, 345, 804.

[2] J. Barber. A mechanism for water splitting and oxygen production in photosynthesis. *Nature Plants*, 2017, 3(4), 17041.

### Category

Other

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