Water deprotonation on free manganese-oxide clusters revealed by IR multi photon dissociation spectroscopy

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The catalytically activated water splitting in plants, algea and cyanobacteria takes place at an inorganic tetra-manganese mono-calcium penta-oxygen (Mn_4CaO_5) cluster which together with its protein ligands forms the oxygen evolution complex (OEC) of photosystem II. Hence, manganese oxide is one of the materials of choice in the quest for versatile, earth-abundant water splitting catalysts. In the first step of a new hierarchical approach to probe fundamental concepts of the water splitting reactions and to aid the design of new artificial water oxidation catalysts, we present the gas phase preparation of isolated manganese oxide cluster ions, $Mn_xO_y^+$, as a simplified models of the OEC.[1] Reactivity studies with $D_2{}^{16}O$ and $H_2{}^{18}O$ in a gas phase ion trap experiment reveal the facile water deprotonation and the exchange of the oxygen atoms of the cluster with water oxygen atoms.[2]

Details of the interaction of water with manganese oxide clusters are obtained from vibrational spectroscopy employing the free electron infrared laser FELIX at Radboud University (The Netherlands). In conjunction with first-principles calculations by Uzi Landman (Georgia Institute of Technology, USA), these investigations provide fundamental insight into the interaction of water with $Mn_xO_y^+$, one water molecule at a time, and emphasize the importance of a water adsorption induced dimensionality change from 2D to 3D manganese oxide cluster structures.[3]

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