

Adsorption forms of H₂O on calcium-manganese oxide clusters revealed by infrared photodissociation spectroscopy

(Graduate School of Arts and Sciences, The University of Tokyo, Japan) ○Tianyue Zhou, Manami Abe, Yufei Zhang, Satoshi Kudoh, Fumitaka Mafuné

Keywords: *Manganese oxide cluster; Infrared photodissociation spectroscopy; Quantum chemical calculation*

Calcium manganese oxides in the active site of photosystem II are considered as highly active catalysts for the oxidation of water to molecular oxygen. In photosystem II, which consists of protein ligands and an inorganic core, CaMn₄O₅, four electrons and four protons are generated from water.^{1,2} It is essential to figure out the structure of this inorganic complex. To understand interaction between inorganic core and water, adsorption forms of a water molecule onto isolated CaMn₄O_k⁺ clusters were investigated by vibrational spectroscopy and density functional theory (DFT) calculations.

CaMn₄O₅(H₂O)Ar⁺ was produced by laser evaporation of Ca and Mn metal rods in He carrier gas at 8 atm mixed with O₂ and Ar, followed by introduction of water molecules as reaction gas. To attach Ar, the gas containing CaMn₄O₅(H₂O)⁺ pass through the cooling tube cooled by a flowing liquid nitrogen to 253 K. These clusters were irradiated with an infrared laser light at 3800–3600 cm^{−1} and mass spectra were measure to obtain infrared dissociation (IRPD) spectra. The adsorption configuration was determined by comparing the IRPD spectra with quantum chemical calculations. Based on the experimental and computational findings, it is tempting to presume that CaMn₄O₅(H₂O)⁺ is dissociatively adsorbed, where one H atom bonds to one of the μ-oxo bridged oxygen atom, and the remaining OH adsorbs between metal atoms, which is consistent with the formation energy.

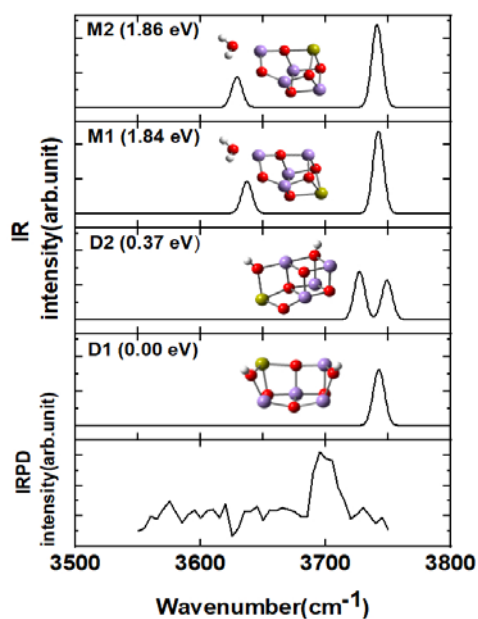


Figure 1 IRPD spectrum and vibrational spectra of the stable isomers of CaMn₄O₅(H₂O)⁺ obtained by DFT calculations. Balls in yellow, purple, red, and white represent Ca, Mn, O, and H atoms, respectively.

1) Umena, Y. et al.; *Nature* **2011**, 473 (7345), 55–60. 2) Yamanaka, S. et al.; *Chemical Physics Letters* **2011**, 511 (1), 138–145.