On the relevance of synthetic manganese model compound to OEC of PS II: vibrational fingerprints of Mn4Ca clusters

Tychengulova A. [a], Capone M. [b], Guidoni L. [b]

[a]Sapienza University of Rome, Rome, 00185, Italy
[b] University of L'Aquila, L'Aquila, 67100 Italy

e-mail: a.tychengulova@gmail.com

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Bio-inspired catalysis for artificial photosynthesis is a widely studied field since decades, in particular with the purpose of using bio-disposable and non-toxic metals as building blocks. An artificial Mn_4CaO_4 cubane cluster with dangling Mn_4 have been synthesized in 2015 [1], showing many structural similitude with the natural oxygen-evolving complex. Even if the synthetic MnCa cluster does not show catalytic activity an accurate structural and spectroscopic comparison between the natural and the artificial systems is highly relevant to understand the catalytic mechanism. The availability of the Infrared data of the artificial cluster offers a unique opportunity to assign absolute absorption spectra on a well-defined and easier-to-interpret analogous moiety. The present work aims to interpret and to assign experimental vibrational peaks of the biomimetic complex and to compare them with the calculated spectra of the natural compound in the S_1 state. In this framework we performed normal mode calculation (NMA) [2] of the computational model obtained from the crystallographic data. Additionally, to better analyse the modes due to the Mn cluster region, we carried on the Effective Normal Mode analysis (ENMA) [3] with dynamic simulation of the system, including in this way the finite temperature correction. Our results suggest that a straightforward assignment of the experimental peaks based only on the oxidation states of the metal ions is highly misleading.

[1] Zhang et al. Science 348 (6235) (2015) 690-693
[2] Q. Cui, I. Bahar, Normal mode analysis: theory and applications to biological and chemical systems, CRC press, 2005.
[3] M.-P. Gaigeot, Infrared spectroscopy of small protonated water clusters at room temperature: An effective modes analysis, The Journal of chemical physics 138 (1) (2011) 257–264.

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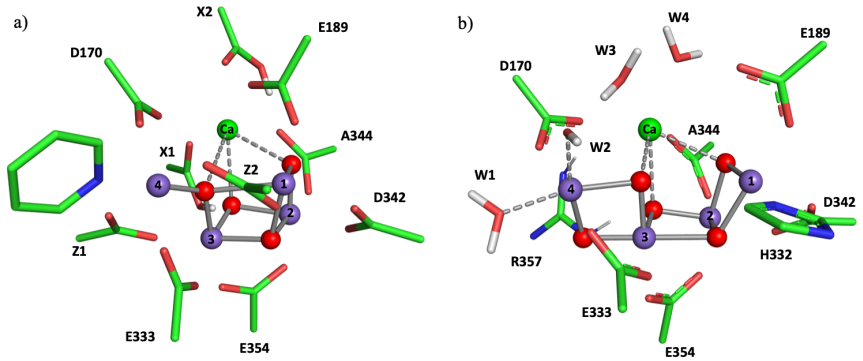

Figure 1: a) QM model of the artificial catalyst, showing the ligands named as the analogues in the natural catalyst.The ligands without analogues in the natural structure are named arbitrarily: Z1, Z2 for the carboxylate ligands; X1, X2 for the protonated carboxylic residues. b) QM model of natural complex with the first shell ligands and four water molecules.