



香港浸會大學

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FACULTY OF SCIENCE

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JOINT COLLOQUIUM

Structure and Reactivity in Biocatalytic Centers: DFT Studies on Vanadium Oxo-peroxo Species

By

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3:30pm – 4:30pm (Tea will be served)

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Abstract

The identification of structural details in biocatalysts is of paramount importance for a reliable description of structure-reactivity relationships. Here we consider oxo-peroxo vanadium compounds such as ionic $[\text{VO}(\text{O}_2)\text{Hheida}]^-$ and $[\text{VO}(\text{O}_2)\text{ada}]^-$ or neutral $[\text{VO}(\text{O}_2)\text{bpg}]$ [1, 2]. These complexes represent efficient functional models for the vanadium haloperoxidase enzyme which acts as a halide oxidant but also as a catalyst for sulfoxidation and alcohol oxidation in living organisms. The complexes include oxygen species in very different local coordination next to vanadium: terminal vanadyl ($\text{V}=\text{O}$), dioxo ($\text{V}-\text{O}_2$), hydroxyl ($\text{V}-\text{OH}$), bridging $\text{V}-\text{O}-\text{C}$, and embedded $\text{C}-\text{O}$ species. Thus, they offer ideal test cases for examining different oxygen species in the same system in order to find out about structure sensitivity, electronic properties, and reactivity. On the other hand, the oxo-peroxo vanadium compounds can serve as test examples to study structure sensitivity of different spectroscopies applied to identify details on an atomic scale.

First, DFT cluster calculations using the StoBe code are performed [3] to determine equilibrium structures of the $[\text{VO}(\text{O}_2)\text{X}]$ compounds where the results agree nicely with data from X-ray diffraction experiments for corresponding single crystals. The analysis of vibrational modes, computed in harmonic approximation, allows an identification of differently coordinated oxygen species, such as vanadyl and di-oxo, although corresponding modes are not well localized. The theoretical spectra agree quite reasonably with experimental data from infrared and Raman measurements and evidence the different amount of vibrational coupling in the $[\text{VO}(\text{O}_2)\text{X}]$ compounds. Further, theoretical O 1s NEXAFS spectra are evaluated where corresponding partial NEXAFS spectra, providing a highly localized oxygen probe, show substantial differences amongst the different oxygen species which allows easy discrimination. These results can confirm experimental O K-shell NEXAFS data obtained for the $[\text{VO}(\text{O}_2)\text{X}]$ compounds.

Preliminary DFT calculations are also performed on reduced $[\text{VO}(\text{O}_2)\text{X}]$ complexes where oxidation reactions are assumed to remove oxygen from the di-oxo site. The theoretical infrared and O1s NEXAFS spectra show substantial differences if compared with the complexes before reduction. This can be used to interpret experimental reactivity data on an atomic scale.

- [1] G.J. Colpas, B.J. Hamstra, J.W. Kampf, and V.L. Pecoraro, *J. Am. Chem. Soc.* **118** (1996) 3469.
- [2] J.E. Molinari and I.E. Wachs, *J. Am. Chem. Soc.* **132** (2010) 12559.
- [3] L. Sun, K. E. Hermann, J. Noack, M. Hävecker, A. Trunschke, and R. Schlögl, *J. Chem. Phys.*, (2014) to be submitted.

All Interested Are Welcome!