

Energy-specific TD-DFT study on the K-edge spectra of vanadium complex catalysts

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X-ray absorption near edge structure (XANES) is a powerful tool to investigate geometrical and electronic structures of a target atom. Particularly, solution phase XANES spectra of transition metal complexes enables us to get insight into the oxidation state, coordination number, and ligand-field symmetry of the metal center, which is of great use to directly observe structures of transition metal complex catalyst and sometimes even reaction intermediate. In this work, the XANES spectra of vanadium and titanium complexes were theoretically investigated based on the energy-specific time-dependent density functional theory (TDDFT). Especially, characteristic K-edge features observed experimentally in the presence of chloride ligands (Nomura et al. *J. Phys. Soc. Jpn.*, **87**, 061014, (2018)) were theoretically assigned. Although the TDDFT approach includes a large systematic error mainly from the 1s core energy level of transition metals, our results clearly showed that the shape of the pre-edge spectra can be well reproduced by simple energy shift into the calculated excitation energies (Figure 1). The doublet peak in the pre-edge region was assigned to be dipole-allowed transitions from 1s to 3d+4p hybridized orbitals. Characteristic shoulder peak observed in the chloride complex was assigned to be a couple of excitations to the chloride 4p orbitals. Interestingly, a similar but weak absorption band was also computed in the methyl complex as a couple of excitations to the C-H σ^* orbitals. However, because the excitations to the C-H σ^* orbital highly depends on the direction of the C-H bond, the shoulder peak would not be observed in the experimental condition due to the free rotation of methyl moiety. In consequence, intensity of the shoulder peak is almost proportional to the number of chloride ligands and therefore, it is of great use to detect the presence or absence of chloride ligands in unknown chemical species such like reaction intermediates.

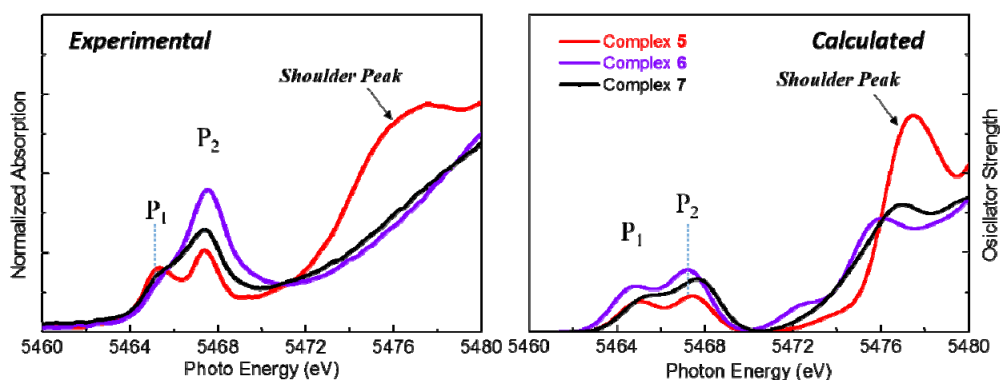


Figure 1. Experimental and calculated XANES spectra of vanadium complexes. Calculated energies were shifted by the constant values (77 eV) to fit the experimental pre-edge peaks.