

Analyzing Vanadium K-edge XANES Spectra Using Real-Time TDDFT

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Vanadium complexes play an essential role in the homogeneous catalysis of polyolefin reactions. Their reaction mechanisms can be described using the instantaneous geometric and electronic configurations of vanadium complexes and can be directly probed by the *in-situ* K-edge X-ray absorption near-edge structure (XANES) spectroscopy. Theoretical calculations are indispensable to translating the spectral features into electric and structural configurations. In the present work, we have calculated the V K-edge XANES spectra using real-time time-dependent density functional theory (RT-TDDFT) for ((2,6-dimethylphenyl)imino)vanadium(V) trichloride (**1a**) and its methyl-substituted derivatives (**1b** through **1d**). Compared to traditional linear-response TDDFT (LR-TDDFT), RT-TDDFT allows a significant rearrangement of electronic densities after photoexcitations and provides a broadband spectrum in the frequency domain after the Fourier transform of the time signals. Based on our calculations, we have reproduced the pre-edge peaks for these species and assigned them to the dipole-allowed transitions of electrons from the $1s$ orbital to the $3d4p$ hybridized orbitals of vanadium. We found that the shoulder peak corresponds to the dipole-allowed, density-rearranging transitions of electrons from the $1s$ orbital of vanadium to its $4p$ orbitals or the $3p$ orbitals of chlorine. Moreover, the calculated spectral features were significantly impacted by the evolving hyperconjugation effect as a function of the dihedral angle associated with the torsion of the V=N bond: the intensities of pre-edge and shoulder peaks depend strongly on the torsional angle for complexes with mixed chloride and methyl ligands (**1b** and **1c**).

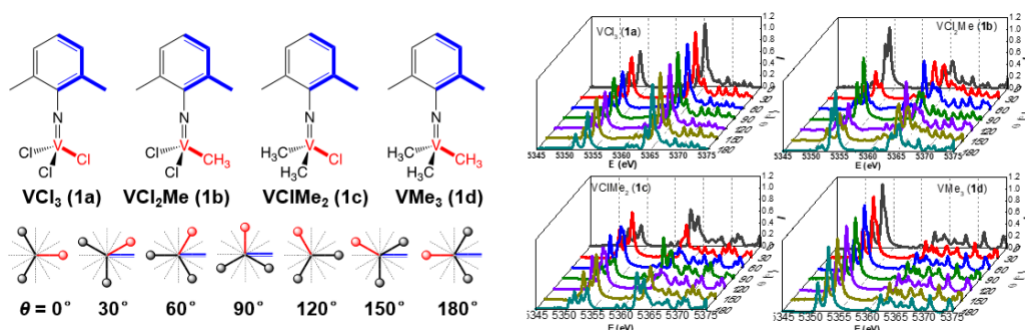


Figure 1. The calculated V K-edge XANES for complexes **1a-1d** with different dihedral angles.