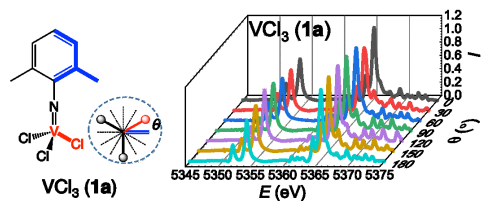


## PREDICTION AND INTERPRETATION OF TRANSITION METAL X-RAY SPECTRA USING REAL-TIME TIME-DEPENDENT DENSITY FUNCTIONAL THEORY

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Many transition metal complexes are popular catalysts for homogeneous organic synthesis. Their instantaneous geometric and electronic configurations and roles in the reaction mechanisms can be directly probed by *in-situ* K-edge X-ray absorption near-edge structure (XANES) spectroscopy. First-principles modeling is indispensable to translate the frequencies and lineshapes of K-edge absorptions into orbital and structural configurations. In the present study, we performed real-time time-dependent density functional theory (RT-TDDFT) calculations for (2,6-dimethylphenyl)imino)vanadium(V) trichloride and its methyl-substituted

derivatives, and obtained time-dependent electronic densities and transition dipole moments by solving the time-dependent Kohn–Sham equations under an applied electromagnetic field. 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. Based on our RT-TDDFT calculations, we managed to reproduce the pre-edge peaks for these species and assigned them to the dipole-allowed transitions of electrons from  $1s$  orbital to the  $3d4p$  hybridized orbitals of vanadium. Both characters align with the results from LR-TDDFT. In addition, RT-TDDFT leads to important features from the shoulder peaks, which correspond to the dipole-allowed, density-rearranging transitions of electrons from  $1s$  orbital of vanadium to its  $4p$  orbitals or the  $3p$  orbitals of chlorine. These shoulder peak features have never been provided by LR-TDDFT. From the present study, we provided a proof-of-concept that the next-generation RT-TDDFT approach is a versatile and powerful computational tool for the prediction and interpretation of X-ray spectroscopy of transition metal complexes.