# Vanadium Substituted Lindqvist Polyoxometalates: Theoretical Study of Structures and Electronic Spectra

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## Highlights

- Vanadium substitution in Lindqvist POMs introduces new low-energy absorption bands;
- TD-DFT with PBE0 geometries provides reliable UV-Vis spectra simulations;
- QTP functionals show better correlations with experimental excitation energies;
- QTPs outperform other functionals for absorption intensities, correctly reproducing experiments.

## Abstract

Although absorbing only ~5% of incident sunlight, polyoxometalates (POMs) are key materials in electro- and photocatalysis, such as $CO_2$ reduction and pollutant degradation [1,2]. Thus, the search for more efficient POMs motivates addenda metal substitution (notably with vanadium) [3]. Therefore, the understanding of their electronic spectra is crucial. Time-dependent Density Functional Theory (TD-DFT) is widely used, but it is unable to accurately describe charge-transfer and Rydberg states with traditional DFT functionals, although range-separated hybrids seem to provide promising alternatives [4,5]. In this work, equilibrium structures and ultraviolet/visible (UV-Vis) spectra of pure ($Nb_6O_{19}^{-8}$, $Mo_6O_{19}^{-2}$, and $W_6O_{19}^{-2}$) and substituted ($VMo_5O_{19}^{-3}$, $VW_5O_{19}^{-3}$, and $VW_5O_{19}^{-4}$) Lindqvist POMs were studied with Orca 5.0.4 [6] (def2-TZVPD basis sets and CPCM solvation with acetonitrile are considered). Mean Absolute Deviations (MADs) relative to experimental structures [7–9] were 0.017, 0.022, and 0.012 Å with B3LYP, PBE, and PBE0, respectively, recommending to the use of PBE0 for geometrical investigations. Tests carried out with 50-200 states showed that high-energy transitions require, at least, 200 states to proper comparison with experiments. Vanadium substitution introduces new lower-energy bands, which is consistent with experimental data [3]. All functionals systematically overestimate excitation energies and PBE0 and CAM-B3LYP give the lowest MADs. However, linear regressions against experimental data [3,11-14] are more appropriate to investigate substitution effects. Hence, Quantum Theory Project (QTP) functionals (CAM-QTP-00, CAM-QTP-01, CAM-QTP-02, and LC-QTP), which are based on Correlated Orbital Theory arguments, yield the strongest correlations for excitation energies ($r^2 \approx 0.76$-$0.79$) and slopes closer to unity (≈ 1.08 with LC-QTP). For absorption intensities, correlations are generally lower ($r^2 < 0.60$), but QTP functionals outperform the others ($r^2 \approx 0.45$–$0.57$) and correctly reproduce the relative order of bands. Furthermore, after excluding less reliable intensity data, $r^2$ values for QTPs improve to 0.85-0.94.

[1] Wang, Sa., et al. *Chem. Rev*., **2015**, 115, 4893-4962
[2] Gu, J., et al. *Mater. Today Energy*, **2021**, 21, 100760
[3] Tucher, J. et al. *Dalton Trans.*, **2012**, 41, 1477-9226
[4] Runge, E., et al. *Phys. Rev. Lett.*, **1984**, 52, 997
[5] Mendes, R., et al. *J. Chem. Phys.*, **2021**, 154, 074106
[6] Neese, F., *WIREs Comput. Mol. Sci.*, **2012**, 2, 73-78
[8] Friis, H., et al. *Mineral. Mag.*, **2017**, 81, 543-554
[9] Fuchs, J., et al. *Acta Crystallogr.*, **1978**, 34, 1764-1770
[10] Jiang, N., et al. Inorg. Chem., **2015**, 54, 7171-7180
[11] Cruywagen, J. J., et al. *Polyhedron*, **1985**, 4, 545-550
[12] Nomiya, K., et al. *Polyhedron*, **1987**, 6, 519-524
[13] Ravelli, D., et al. *J. Comput. Chem.*, **2011**, 32, 2983-2987
[14] Shiels, D., et al. *Inorg. Chem.*, **2024**, 49, 23304–23316

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