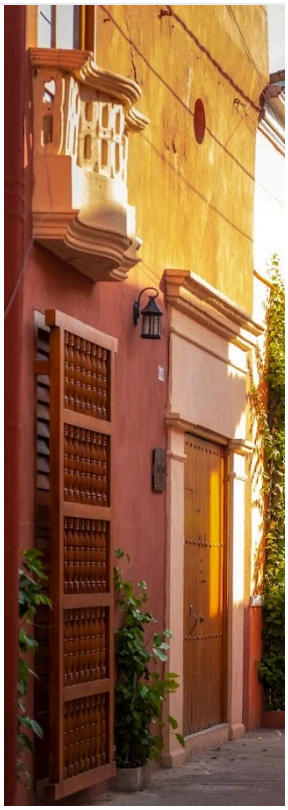

Quitel 2025

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Theoretical Study of Structures and Electronic Spectra of Lindqvist-type Polyoxometalates ($Nb_6O_{19}^{8-}$, $Mo_6O_{19}^{2-}$, and $W_6O_{19}^{2-}$)

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Polyoxometalates (POMs) are key materials in electro- and photocatalysis, including CO_2 reduction and pollutant degradation.[1,2] Thus, the study of the electronic spectra of POMs is fundamental to many of their applications. Time-dependent density functional theory (TD-DFT) is a powerful tool for investigating these quantities but has limitations in describing charge transfer and Rydberg excited states.[3,4] In these cases, range-separated hybrid functionals offer a promising alternative.[5] This study examines equilibrium structures and ultraviolet/visible (UV-Vis) spectra of Lindqvist-type POMs ($Nb_6O_{19}^{8-}$, $Mo_6O_{19}^{2-}$, and $W_6O_{19}^{2-}$) to propose an efficient computational protocol for posterior investigations in more complicated POMs. All calculations were done within Orca 5.0.4.[6] Geometry optimizations were performed by using B3LYP, PBE0, and PBE functionals along with the def2-TZVPD basis set and two implicit solvation models (CPCM/SMD), with water ($Nb_6O_{19}^{8-}$) or acetonitrile ($Mo_6O_{19}^{2-}$ and $W_6O_{19}^{2-}$) as solvent. The two solvation models produced nearly identical geometrical results, but CPCM was computationally more efficient. Considering the structural results, PBE0 provided closer agreement with the experimental data[7-9] than the other functionals considered. Thus, equilibrium structures achieved with the PBE0/CPCM combination are chosen for posterior TD-DFT calculations. The two solvation models (CPCM and SMD) also resulted in similar values for band maxima positions (band shifts < 5 nm). The two basis sets considered at this stage (def2-TZVPD and def2-QZVPD) provided similar UV/Vis results. Several exchange-correlation functionals are considered for predicting band maxima positions: PBE0, CAM-B3LYP, CAM-QTP-00, CAM-QTP-01, CAM-QTP-02, and LC-QTP. In general, PBE0 always provides the largest wavelength results for the lowest energy transitions studied, followed by CAM-B3LYP, while CAM-QTP-00 gives the smallest values among the functionals investigated. The difference between the results from PBE0 and CAM-QTP-00 is 57 nm on average. These findings provide relevant insights for future investigations to be carried on modified POMs.

Keywords:

Polyoxometalates, TD-DFT, UV-Vis spectra, Lindqvist-type

Suggested Reading / References:

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