

Abstract Submitted
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(1) Modeling emissive charge-transfer states in solution phase functionalized silsesquioxanes. (2) On symmetry hidden charge transfer states: Lessons for the design of functionals¹ BARRY D. DUNIETZ, SHAOHUI ZHENG, HEIDI PHILLIPS, EITAN GEVA, University of Michigan —

Range separate hybrid functionals are used to study the charge transfer processes in chromophores attached to silsesquioxanes molecular species. We investigate the experimentally observed red shifting of the emission spectra in comparison to the spectral shift for the individual ligand. Solvent effects are accounted for via a combination of constrained density functional theory and the polarizable continuum (PCM) model. We quantitatively reproduce the experimental red shift and identify the emissive state as a ligand-to-ligand, rather than a ligand-to-silsesquioxane, charge-transfer state. We also find that the enhanced red-shift cannot be explained without accounting for solvation effects and demonstrate the importance of using a range-separated hybrid functional, as opposed to more traditional functionals such as B3LYP, to obtain reliable predictions regarding the emissive state. If time allows we will also discuss the limitations and successes of RSH functionals in treating the case of charge transfer processes that are hidden by system symmetry. We use related models to draw insight for designing improved functionals.

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