

AB INITIO INVESTIGATION OF INTRAMOLECULAR CHARGE TRANSFER IN DMABN BY CALCULATION OF TRANSIENT X-RAY ABSORPTION FEATURES

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Dual fluorescence in dimethylaminobenzonitrile (DMABN) and its derivatives in polar solvents, has been studied extensively for the past several years. Intramolecular charge transfer (ICT), in addition to the localized low-energy (LE) valence minimum, has been proposed as a mechanism for this dual fluorescence, with large geometric relaxation and molecular orbital reorganization a key feature of the ICT pathway. Herein, we have used both equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) and time-dependent density functional (TD-DFT) methods to investigate the landscape of excited state potential energy surfaces across the several geometric conformations proposed as ICT structures, including Franck-Condon (FC), twisted (TICT), partially twisted (PTICT), wagged (WICT), and rehybridized (RICT) structures. Initial geometries for each type of structure were selected for excited state PES optimizations, as well as a systematic exploration of the low-lying PESs starting from the FC geometry. We find a number of minimum-energy (near)-crossing points among the lowest three excited states leading to the eventual ICT minima. Finally, we have calculated the carbon and nitrogen K-edge transient absorption spectra for all important “signpost” structures in order to investigate the differential pump-probe features along the LE and ICT pathways.