

Part 1: Bypassing the Multi-reference Character of Singlet Molecular Oxygen

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Abstract

Ab initio calculations on systems involving singlet molecular oxygen ($O_2(1g)$) are challenging due to significant multi-reference character arising from the degeneracy of the HOMO and LUMO orbitals in singlet oxygen. Here we investigate the strategy of bypassing singlet oxygen's multi-reference character by simply adding the experimentally determined singlet/triplet splitting (22.5 kcal/mol) to the triplet ground state of molecular oxygen. This method is tested by calculating rate constants for the reactions of singlet molecular oxygen with furan, 2-methylfuran, 2,5-dimethylfuran, pyrrole, 2-methylpyrrole, 2,5-dimethylpyrrole, and cyclopentadiene. The calculated rate constants are within a factor of 15 compared to experimentally determined rate constants. The results show that energy renement at the CCSD(T)-F12 level of theory is crucial to achieving accurate results. The reasonable agreement with experimental values validates the bypassing approach which can be used for other systems involving the 1,4-cyclo-addition of singlet oxygen. 2

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