

Excitation Energies of Oligoacenes by the General Multi-Configuration Quasi-Degenerate Perturbation Theory

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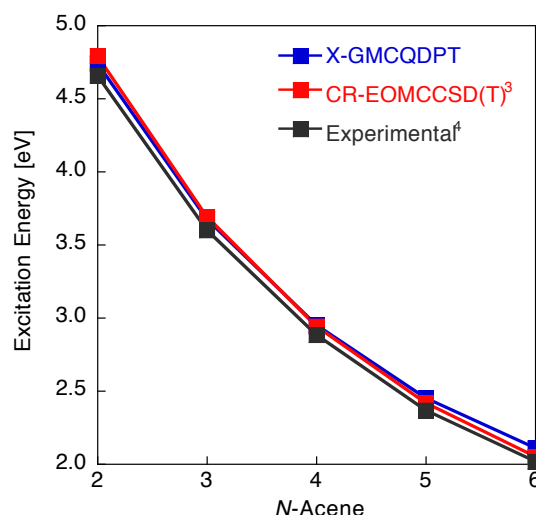
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Abstract

Optically-allowed and –forbidden excitation energies of oligoacenes, which increase the π -conjugation size and open-shell character with the increase in the size, have been evaluated using the general multi-configuration quasi-degenerate perturbation theory (GMCQDPT)¹ method. Several types of restricted and complete active space (RAS/CAS) schemes are examined in order to clarify the appropriate choosing of active space for a description of low-lying excited states of these molecules. RAS is classified into RAS1, RAS2 and RAS3, where RAS2 includes (HOMO- i)–(LUMO+ i) pair orbitals ($i = 0, 1, \dots$), while RAS1 and RAS3 include orbitals ranging from none to full π valence. Full configurations are considered in RAS2, while singly and doubly excitations from RAS1 to RAS2/3 as well as from RAS2 to RAS3. Since the zeroth-order Hamiltonian (H_0) significantly affects the computational results at the second order multi-reference perturbation level of theory, we employ both the conventional (GMCQDPT)¹ and the extended GMCQDPT (X-GMCQDPT)² methods, the former of which defines H_0 based on an expectation value of the Fock-like operator using the multi-configuration wavefunction, while the latter of which has the same diagonal elements as well as off-diagonal ones in H_0 . We elucidate the active-space size dependences of the convergence behavior of excitation energies calculated by each method [(X-)GMCQDPT, RAS/CAS], and compare with experimental and other theoretical calculation results of the completely renormalized equation-of-motion coupled-cluster with singles, doubles and noniterative triples method (see Figure 1).

Figure 1 Optically-allowed (HOMO-LUMO transition) singlet excitation energies of oligoacenes. N represents the number of fused rings.



References: [1] H. Nakano *et al.* *J. Comput. Chem.* **23**, 1166 (2002). [2] A. A. Granovsky *J. Chem. Phys.* **134**, 214113 (2011). [3] K. Lopata *et al.* *J. Chem. Theory Comput.* **7**, 3686–3693 (2011). [4] S. Grimme *et al.* *ChemPhysChem* **3**, 292 (2003).