Benchmarks for electronically excited states: CASPT2, CC2, CCSD, and CC3

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A benchmark set of 28 medium-sized organic molecules is assembled that covers the most important classes of chromophores including polyenes and other unsaturated aliphatic compounds, aromatic hydrocarbons, heterocycles, carbonyl compounds, and nucleobases. Vertical excitation energies and one-electron properties are computed for the valence excited states of these molecules using both multiconfigurational second-order perturbation theory, CASPT2, and a hierarchy of coupled cluster methods, CC2, CCSD, and CC3. The calculations are done at identical geometries (MP2/6-31G*) and with the same basis set (TZVP). In most cases, the CC3 results are very close to the CASPT2 results, whereas there are larger deviations. Statistical evaluations of the calculated vertical excitation energies for 223 states are presented and discussed in order to assess the relative merits of the applied methods. CC2 reproduces the CC3 reference data for the singlets better than CCSD. On the basis of the current computational results and an extensive survey of the literature, we propose best estimates for the energies of 104 singlet and 63 triplet excited states. © 2008 American Institute of Physics. [DOI: 10.1063/1.2889385]

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