Anisole–Water and Anisole–Ammonia Complexes in Ground and Excited (S_1) States: A Multiconfigurational Symmetry-Adapted Perturbation Theory (SAPT) Study

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Streszczenie

Binary complexes of anisole have long been considered paradigm systems for studying microsolvation in both the ground and electronically excited states. We report a symmetry-adapted perturbation theory (SAPT) analysis of intermolecular interactions in anisole-water and anisole-ammonia complexes within the framework of the multireference SAPT(CAS) method. Upon the $S_1 \leftarrow S_0$ electronic transition, the hydrogen bond in the anisole-water dimer is weakened, which SAPT(CAS) shows to be determined by changes in the electrostatic energy. As a result, the water complex becomes less stable in the relaxed S_1 state despite decreased Pauli repulsion. Stronger binding of the anisole-ammonia complex following electronic excitation is more nuanced and results from counteracting shifts in the repulsive (exchange) and attractive (electrostatic, induction and dispersion) forces. In particular, we show that the formation of additional binding N-H···π contacts in the relaxed S_1 geometry is possible due to reduced Pauli repulsion in the excited state. The SAPT(CAS) interaction energies have been validated against the coupled cluster (CC) results and experimentally determined shifts of the $S_1 \leftarrow S_0$ anisole band. While for the hydrogen-bonded anisole-water dimer SAPT(CAS) and CC shifts are in excellent agreement, for ammonia SAPT(CAS) is only qualitatively correct.

Słowa kluczowe

Colloids, Excited States, Interaction Energies, Mathematical Methods, Oligomers

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