

Photoexcitation Calculations of Benzoic Acid Derivatives as Model Natural Organic Ligands

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Objective

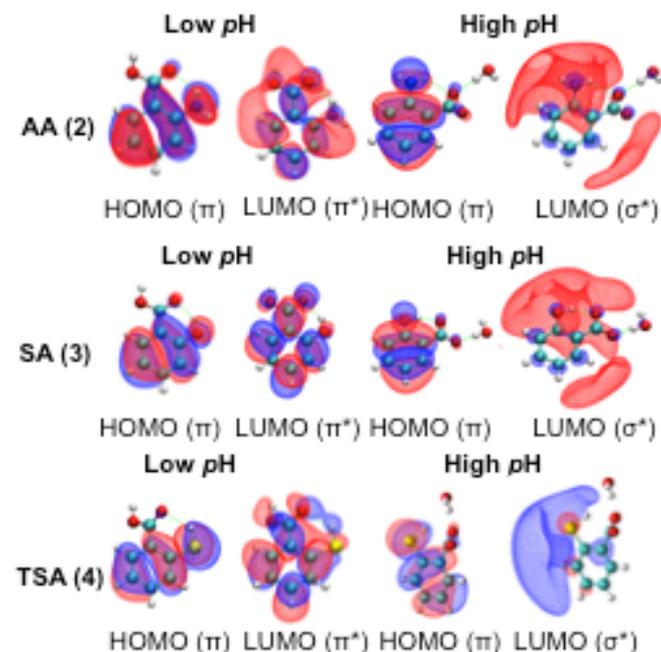
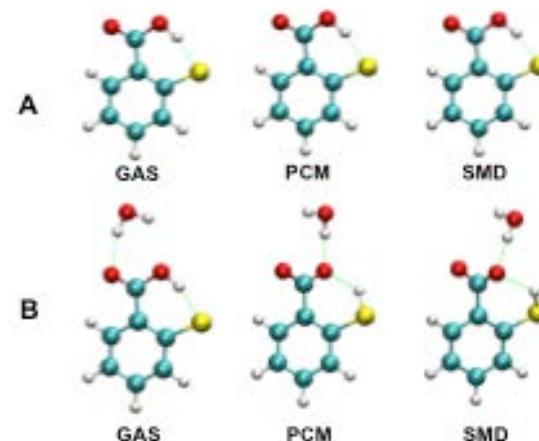
- A systematic evaluation of the TDDFT method for the study of the photoreduction of Hg^{2+} in aqueous solution in the presence of benzoic acid derivatives (BAs).

New Science

- A continuum-cluster approach was found to correctly describe both the structure and photo excitation of BAs. In this approach, an explicit water molecule interacts with the negatively charged carboxylate group and the solvent is simulated with a dielectric continuum model.
- At environmentally relevant pH (5-8), the photo excitations of $-\text{NH}_2$, $-\text{OH}$ and $-\text{SH}$ substituted BAs (e.g., anthranilic acid, salicylic acid and thiosalicylic acid) lead to $\pi\sigma^*$ excitations.

Significance

- The $\pi\sigma^*$ excitation may attribute the radical formation and subsequent Hg^{2+} reduction proposed in previous report (He et al. 2012. Sci. Total Environ.).



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Benzoic acid derivatives (BAs) of environmental relevance exhibit various photophysical and photochemical characteristics. Here, time-dependent density functional theory (TDDFT) was used to calculate photoexcitations of eight selected BAs and the results were compared with UV spectra determined experimentally. High-level gas phase EOM-CCSD calculations and experimental aqueous phase spectra were used as the references for the gas-phase and aqueous-phase TDDFT results, respectively. A cluster-continuum model was used in the aqueous-phase calculations. Among the 15 exchange-correlation functionals assessed, five functionals, including the meta-GGA hybrid M06-2X, doubly hybrid B2PLYPD, and range-separated functionals CAM-B3LYP, ω B97XD and LC- ω PBE, were found to be in excellent agreement with the EOM-CCSD gas phase calculations. These functionals furnished excitation energies consistent with the pH dependence of the experimental spectra with a standard deviation of ~ 0.20 eV. A molecular orbital analysis revealed a $\pi\sigma^*$ feature of the low-lying transitions of the BAs. The CAM-B3LYP functional showed the best overall performance for TDDFT calculations of processes involving photoexcitations of benzoic acid derivatives. The best functional assessed in this work is now being applied in an ongoing study of Hg²⁺ photoreduction with BAs in the aqueous solution.

Guo, H.-B., F. He, B. Gu, L. Liang and J.C. Smith. 2012. Time-dependent density functional theory assessment of UV absorption of benzoic acid derivatives. *J. Phys. Chem. A* 116:11870-11879. (doi: 10.1021/jp3084293).