

Solvent Effects on Electronic Absorption, Fluorescence and Phosphorescence of Acetone and Benzene in Water: A QM/MM Study

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Polar and non-polar solutes (acetone and benzene) dissolved in ambient water (AW) and supercritical water (SCW) are investigated theoretically using a sequential quantum mechanics (QM)/molecular mechanics (MM) method.[1, 2, 3] We find both of aqueous acetone and aqueous benzene under high temperatures present three distinctive regions: low-density gas-like region, supercritical region and high-density liquid-like region. The plateau behavior of solvatochromic shift in the supercritical region is ascribed to the solvent clustering around the solute, which is a fundamental phenomenon of supercritical fluids (SCFs). The density dependence of our calculated coordination number of the first solvation shell nicely reproduces the trend of electronic absorption spectral shift and verifies the solvent clustering phenomenon of SCFs and its relationship with SCF's physico-chemical properties.

Besides the electronic absorption spectral shift, we also revisit the solvent effects on the fluorescence and phosphorescence spectra of aqueous acetone.[4] It is found that such effects are very small or even negligible when compared with the large solvent effect for electronic absorption and are caused by the reduced dipole moments of acetone and accordingly much less hydrogen bonds for aqueous acetone in the electronic excited states S_1 and T_1 comparing to the ground state S_0 .

In our sequential QM/MM studies, we also examine the effects of size of QM region, the choice of the density functional and the choice of the basis set as well as the sampling time length on the simulated results.[3, 4] It is revealed that the inclusion of the solvent molecules within the first solvation shell into the QM region to account for the exchange-correlation between a solute and neighboring solvent molecules is important for the highly accurate spectral shift calculations, especially vital for the non-polar solutes whose interactions with the solvents are dominated by the quantum dispersions. At the same time, sufficiently large surrounding partial charge region ($r_{cutoff} \geq 15 \text{ \AA}$) as well as the functional corrections to describe the long-range corrections are also essential for the study of the electronic excited states in condensed phase.

[1] Ma, H., Ma, J. *J. Chem. Phys.*, 135:054504, 2011.

[2] Ma, H. *J. Chem. Phys.*, 136:214501, 2012.

[3] Ma, H., Ma, Y. *J. Chem. Phys.*, 137:214504, 2012

[4] Ma, H., Ma, Y. *J. Chem. Phys.*, in revision.