Ab Initio QM/MM calculations of the solvatochromic shifts of a chromophore in ionic liquids

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We are currently investigating the polarity and the solvent effects of some room-temperature ionic liquids by evaluating the solvatochromic shifts of a chromophore immersed in the ionic liquids. One of the important tasks in the excitation energy calculation in solutions is to sample a lot of statistically uncorrelated solvent configurations. Since the diffusive motion of molecules in the ionic liquids are significantly slow, adequate sampling of uncorrelated configurations is enormously difficult by an *ab initio* QM/MM molecular dynamics calculation. To circumvent this problem, we have recently developed an efficient QM/MM-based method to calculate vertical excitation energies of a molecule in condensed phases[1]. The method approximates the QM/MM energies of the system in the ground and excited states by Taylor expansion around a reference state (determined by the mean-field QM/MM method[2,3,4]), which bypasses the need to perform a QM calculation at each configuration along a long MD trajectory. The explicit electronic polarization of the solvent molecules can also be included in this method. Thus, we can estimate the contribution from the nonequilibrium solvation effect of the ionic liquids to the solvatochromic shifts. We will show absorption spectra of a DMPNA molecule calculated at the MRMP2/CASSCF(12*e*,10*o*)/6-311G(2*d*,2*p*) level in some imidazolium-based ionic liquids and discuss the solvation structures and solvation effects.

References

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