

A computational investigation of the effects of solvent-induced electric fields on vibrational frequency shifts

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Computational vibrational spectroscopy serves as an important tool in the interpretation of the experimental infrared spectra. In this work, we benchmarked the computational vibrational spectroscopic methods including normal mode analysis (NMA) and fast Fourier transform dipole autocorrelation function (FT-DAC)[1]. We demonstrated the advantages of the FT-DAC method for flexible and anharmonic systems [1]. Then, we extended the benchmarked DFTB3/FT-DAC model to the condensed phase systems with the combined QM/MM simulations. We have investigated the effects of solvent-induced electric field on vibrational frequency shifts, known as the Vibrational Stark Effect (VSE)[2,3]. We studied acetophenone as the vibrational chromophore in a series of different polar and non-polar solvents and solvent mixtures. Linear correlations between the solvent-induced electric field and the vibrational probes frequency shift were found. An overestimation of hydrogen bonding at the DFTB3 and MM boundary was observed, whereas no such overestimation was showed at the boundary between the DFTB3 and Drude polarisable model. This emphasizes the importance of including explicit polarisations at the QM/MM simulations.

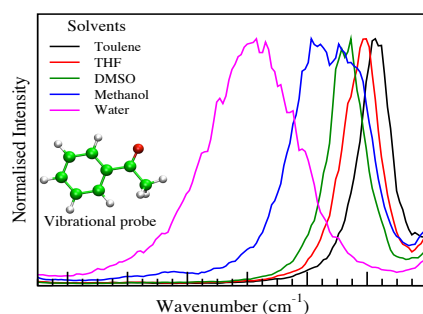


Figure 1: FT-DAC spectra in various solvents

References

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