

Inter- and Intramolecular Hydrogen Bond Strengths Modeled with Quantum Chemistry

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I present the computation of both inter- and intramolecular hydrogen bond strengths from first principles. Quantum chemical calculations conducted at the dispersion-corrected density functional theory level¹ including free energy and solvation contributions are conducted for (i) one-to-one hydrogen-bonded complexes of alcohols to N-methyl pyrrolidinone measured by an infrared spectroscopy method² and (ii) a set of experimental intramolecular hydrogen bond-forming phenol and pyrrole compounds,³ with intramolecular hydrogen bond strengths derived from a nuclear magnetic resonance method. The computed complexation free energies in solution show a good correlation to experiment of $R^2 = 0.69$ with a root mean square error of 4.25 kJ mol^{-1} . The intramolecular hydrogen bonding free energies in solution show an even better correlation at $R^2 = 0.79$ with a root mean square error of 5.51 kJ mol^{-1} . These results can be used as a guide on how to build reliable quantum chemical databases for computed hydrogen bonding strengths.

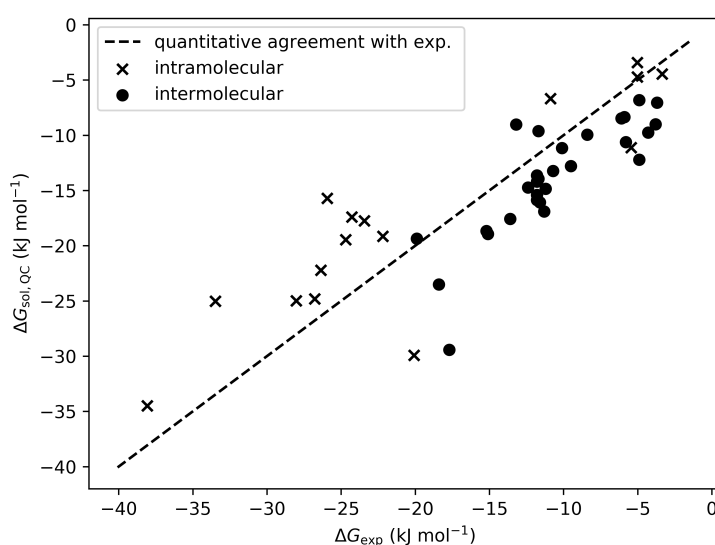


Figure 1: Comparison of experimental and computed free energies in solution for two sets of inter- and intramolecular hydrogen bonds.

References

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