UNDERSTANDING STRUCTURAL PREFERENCES IN KETONE-PHENOL DISPERSION BALANCES

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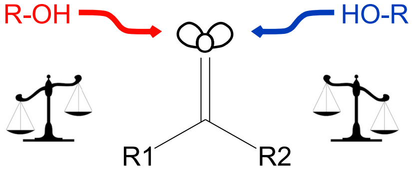

R1 ≠ R2

Ketone-solvent balances consisting of a hydrogen bond donor docking onto the carbonyl oxygen of an asymmetrically substituted ketone, such as an acetophenone derivative, generate two competing isomers. By experimentally probing the vibrational differences with FTIR spectroscopy in a supersonic jet, the abundance ratio of the two isomers at low temperatures is determined. This allows for the experimental benchmarking of theoretically predicted relative conformational energies on a kJ mol^{-1} or even finer scale.[a,b] Previous studies of acetophenone derivatives[c] with methanol and *tert*-butyl-alcohol showed good agreement between experiment and theoretical predictions and suggest a systematic cancellation of zero point vibrational energy contributions due to the two comparable docking environments, in contrast to previously presented anisole[d,e] and furan[f] complexes. These ketone-solvent balances therefore allow for a more direct benchmark of different electronic structure methods with less need for an accurate vibrational treatment beyond the double harmonic approximation. The influence of London dispersion and steric hindrances on the favored docking site in acetophenone derivative/phenol systems are explored by varying the substituentes of the ketone.

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[a] H. C. Gottschalk et al., *J. Chem. Phys.*, **2018**, *148*, 014301.

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[c] C. Zimmermann et al., *Phys. Chem. Chem. Phys.*, **2020**, *22*, 2870-2877.

[d] A. Poblotzki et al., *Phys. Chem. Chem. Phys.*, **2016**, *18*, 27265.

[e] M. Heger et al., *Phys. Chem. Chem. Phys.*, **2015**, *17*, 13045.

[f] H. C. Gottschalk et al., *Angew. Chem. Int. Ed.*, **2015**, *55*, 1921.