

# Bond strengths in the gas phase, in solution, and in silico: dispersion effects and big molecules

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Van der Waals attractive forces have often been neglected because each individual interaction is small. Nevertheless, for organic and organometallic molecules of distinctly moderate size, e.g. 100-200 atoms, the large number of small, attractive interactions lost upon cleavage of a covalent bond can add up to a significant contribution to the bond dissociation energy, in the range of tens of kcal/mol. Whereas structural evidence for an “extra” stabilization has been reported, experimental measurement of bond dissociation energies for large molecules in the gas phase are surprisingly rare. We report a comprehensive study of 36 proton-bound dimers for which a central  $^+N-H\cdots N$  bond is constant, but the number and extent of non-bonding interactions can be varied systematically. We report experimental BDE measurements in the gas phase, and in solution, accompanied by computational studies using DFT and DLPNO-CCSD(T) methods taken to the CBS limit. Moreover, we include solvation with dispersion-corrected PCM models. We find that dispersion does indeed make a net attractive contribution to bond dissociation energies in the gas phase, amounting to tens of kcal/mol, but that this contribution is largely canceled out in solution, thus bringing the gas-phase observations of van der Waals attraction and the solution observations of steric repulsion into agreement. We present ideas on how this more detailed knowledge of an universal, non-covalent interaction may be manipulated rationally to modulate bond strengths, in general.