EDITORIAL

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Understanding dispersion interactions in molecular chemistry

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London dispersion interactions have been known for more than 90 years,[1] but their role in molecular chemistry has remained underrated among chemists until recently,[2] and the missing long-range electron correlation in popular density functionals[3] that is largely responsible for London dispersion accentuated the problem earlier in this century. To enhance awareness and understanding of these universally attractive forces in the context of chemistry, the Bunsentagung 2020 (General Assembly of the German Bunsen Society for Physical Chemistry, now shifted to 2022 due to the Covid-19 pandemic) and a themed *Phys. Chem. Chem. Phys.* collection of articles were initiated.

The present collection comprises 12 articles, more than half of which are co-authored by principal investigators and their teams from the priority programme SPP 1807 on "Control of London dispersion interactions in molecular chemistry", funded by the German Research Foundation between 2015 and 2021.

Diphenylether has been a frequently visited molecular object in this context.[4]

It offers two competing hydrogen bond acceptor sites with rather different properties. The ether oxygen is a classical electrostatic attractor, which is significantly attenuated by conjugation with the aromatic substituents. The latter offer dispersion-favourable π-electron-rich faces and C–H bonds for nonclassical hydrogen bonding. Their delicate interplay can be modulated by torsion angles. The Schnell and Gerhards groups study the torsional dynamics and its modulation by water as one of the least dispersively driven of all hydrogen-bonded donors by multi-spectroscopic approaches (DOI: 10.1039/D0CP04104A). While the first water remains rather undecided between electrostatics and dispersion, additional hydration is directed by hydrogen bond cooperativity and London dispersion now only determines secondary binding preferences. As the binding sites typically differ in their chemical nature, such subtle energy differences are simultaneously controlled by electronic and zero-point energy or nuclear quantum effects.

Even for bulk liquid water, dispersion interactions are shown to play an important role in a theoretical study employing classical molecular dynamics (DOI: 10.1039/C9CP06335H). While zero-point energy effects are neglected in such an approach, correction schemes are developed to overcome this and other deficiencies. As in other studies contained in

the present themed collection, the OH stretching mode is found to be a particularly sensitive probe.

When switching from water and ethers to ketones, additional isomerism arises due to the better defined barrier between the oxygen lone electron pairs.[5] This gives rise to subtle intermolecular energy balances which are largely controlled by the electronic structure, without too much interference from zero-point energy effects. That allows for a more direct probing of electronic structure inaccuracies and an infrared study of acetophenone–alcohol pairings reveals a subtle failure of dispersion-corrected density functionals to reproduce the structure of a bulky alcohol–cyclopropyl derivative (DOI: 10.1039/C9CP06128B). It appears that the DFT functionals prefer a more compact structure than experimentally observed, but microwave studies could provide a valuable test of this conjecture.

The question of hydrogen bonding *vs.* dispersive interactions was addressed multi-experimentally at room temperature for liquid racemic ibuprofen, the popular anti-inflammatory drug (DOI: 10.1039/C9CP06641A). It was found that half of the vaporization enthalpy can be attributed to carboxylic acid hydrogen bonding, and less than half of that enthalpy needs to be invested to break one of the double hydrogen bonds in the liquid. Carboxylic acid dissociation energies are higher at low temperature[6] due to the reduced weakening effect of thermal motion, and are

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perhaps even chirality-dependent.[7] The gas phase after sublimation may still exhibit molecular aggregation in such systems. In the case of ionic liquids, thermal and gas phase aggregation effects are particularly important due to the combined cohesion by ionic and dispersive forces (DOI: 10.1039/D0CP05439A). The effect of thermal motion on sublimation enthalpies can be sizeable, as revealed for a large crystallographic database which includes several achiral carboxylic acid binding motifs (DOI: 10.1039/C9CP04488D). When analysing dispersion interactions in the condensed phase, such thermal and volume effects should not be neglected, but inclusion of chiral building blocks in the database is encouraged, because it allows for subtly different effects in the solid state.[8]

A pronounced case of chirality-dependent cohesion was found in dimers of vicinal diols (DOI: 10.1039/C9CP04943F), again using a multi-experimental approach. Transiently enantiomeric conformations interact much more strongly with each other, and this heterochiral preference can be modulated by dispersion interactions among bulky substituents. The opposite strategy of using permanent chirality to disentangle the subtle interplay between dispersively dominated and classical hydrogen bonds was successfully applied to benzyl alcohol (DOI: 10.1039/D0CP04825A), where again a phenyl group serves as the dispersion energy anchor.

Inorganic dispersion energy donors based on bismuth were explored in the context of intra- *vs.* intermolecular and halide- *vs.* π-competition (DOI: 10.1039/C9CP06924K). The almost purely dispersive Bi–arene interactions are clearly on par with strong hydrogen bonds and crystal packing has a pronounced influence on molecular conformation. Porous crystals and surfaces provide suitable testing grounds for dispersion corrections in density functionals. Such benchmarking activities are described in a comprehensive study spanning zeolites and flat oxide surfaces (DOI: 10.1039/D0CP00394H), approaching chemical accuracy in some cases for these highly charged and thus challenging systems, but diverging for larger adsorbates.

Coincidentally, size-dependent London dispersion forces also play a role in the ball-mill dispersion of inorganic solids in liquids by acting as surfactants (DOI: 10.1039/C9CP05722F). Clearly, the systematic modification of materials with dispersion energy donors allows for a favourable tuning of material properties. This is further explored for the still poorly understood field of fluorous interactions in the case of phthalocyanine films (DOI: 10.1039/C9CP06709D).

Common themes in this collection include the multi-experimental character of many studies, the use of libraries of compounds to make a case, the importance of gas-phase reference studies and the application of experimental benchmarking strategies.[9] Many investigations use DLPNO-CCSD(T) wave function calculations for DFT checking and the resulting LED scheme for energy decomposition,[10] and they usually rely on harmonic estimates for the back-correction of vibrational contributions.

Once the effects of dispersion interactions in molecular chemistry are better understood by physico-chemical methods and by dispersion-corrected density functional theory,[11] they can be used even more systematically and rationally for chemical control purposes. This is a declared goal of the priority programme on "Control of London dispersion interactions in molecular chemistry" and of this themed collection.

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