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Probing dispersion interactions using broadband rotational spectroscopy

“Understanding dispersion interactions in molecular chemistry” was the focus of the 121th Bunsen-Tagung, taking place in Gießen. Gießen was also the headquarter of the priority program 1807 of the Deutsche Forschungsgemeinschaft on dispersion in chemistry for the last seven years, with Peter R. Schreiner as the speaker. As such, the gecko was omnipresent at this conference (and I am sure that the colorful key chain geckos, which also function as bottle openers, are highly appreciated by many of us for future usage.) But now to some science:

The precise knowledge of the structures of molecules and molecular clusters is of fundamental interest for understanding the non-covalent intra- and intermolecular interactions that determine their shape and that keep them together. High-resolution gas-phase molecular spectroscopy employing a supersonic jet provides an outstanding tool to determine accurate molecular structures in the gas phase and thus free of solvent and crystal effects. These conditions allow for a comparison and benchmarking with quantum-chemical experiments. Inspired by the powerful network of the priority program 1807, strong collaborations between synthesis, theory, and spectroscopy were formed aiming to investigate useful model systems to evaluate the interplay between hydrogen bonding and dispersion interactions. Our main spectroscopic tool is broadband rotational spectroscopy in the gas phase, which is inherently structure sensitive and even allows for an experimental determination of bond lengths and angles. In the following, I will discuss two examples, one intra- and one intermolecular case, where dispersion interactions are decisive for the structural outcome.

One intriguing example where intramolecular dispersion interactions stabilize a molecule are the diamantane dimers ($C_{28}H_{38}$) that are covalently coupled [1]. The diamantane dimer exhibits an extremely long carbon-carbon single bond of 1.647 Å and is stable under standard conditions, contrary to the highly crowded hexaphenyl ethane, which is unstable. While, on the first glance, one would expect destabilization due to the steric effects arising from the two diamantane groups, dispersion interactions tip the balance towards stabilization for the diamantane dimer, resulting in a long C-C single bond, as obtained from X-ray diffraction studies of diamantane dimer crystals.

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Structure determination of gas-phase samples can help to evaluate, if this long C-C bond is indeed a feature of the molecule, or if it is also due to crystal packing effects. In a combined work with gas electron diffraction performed by Norbert Mitzel and coworkers and high-resolution rotational spectroscopy, we determined the structure of the oxygen-substituted molecule, namely the oxadiamantyl dimer ($C_{26}H_{34}O_2$), which was synthesized by Peter R. Schreiner and his group [2]. The inclusion of the oxygen atoms was needed to introduce a permanent electric dipole moment, which is a necessary requirement for pure rotational spectroscopy.

The analysis of the rotational spectra resulted in the experimental rotational constants of this species, which are inversely proportional to the moments of inertia and thus contain direct structural information. Together with the electron diffraction data, the length of the C-C bond connecting the two oxadiamantyl units could be determined to be 1.632(5) Å, which is well reproduced by the majority of the quantum-chemical calculations including dispersion correction and which is also in good agreement with the X-ray diffraction value of 1.643(1) Å of the crystalline species (Figure 1). This confirms the molecular origin of the long C-C single bond, stabilized by dispersion interactions despite the sterically crowded situation.

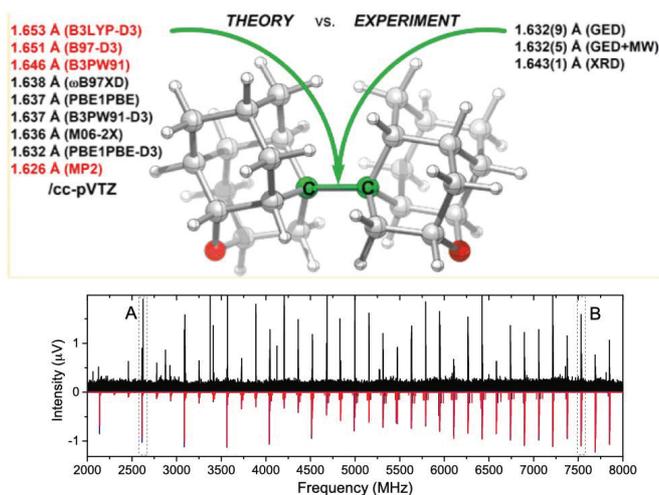


Fig. 1: Top: Experimental and theoretical bond lengths of the central C-C single bond of oxadiamantane dimer (adapted from Ref. 2) Bottom: Overview broadband rotational spectrum (adapted from Ref. 2)

Non-covalent interactions are also central to many molecular recognition events, and we are particularly interested in the interplay between different types of intermolecular interactions, and in particular between hydrogen bonding, which is rather directed

in character, and dispersion interactions. These studies are also relevant with respect to the first steps of aggregation, such as in soot and grain formation, and can thus provide important insight into the transition from the isolated molecule to the bulk.

In a recent study employing rotational spectroscopy and quantum-chemical calculations, we analysed the complexes of thiophenol, i.e., its dimer and its trimer [3], and compared the experimentally observed dimer and trimer structures with previous results obtained for phenol [4]. Our results show that the larger, more polarizable and less electronegative sulphur atom forms weaker hydrogen bonds compared to oxygen, which in turn provide significant structural flexibility due to the longer S-H bond. This structural flexibility allows for the phenyl groups in the thiophenol dimers and trimers to arrange such as to optimize dispersion interactions, while there are more structural constraints in the case of phenol.

The experimentally observed and energetically preferred thiophenol dimer structures include both a hydrogen bond between the two SH groups and a parallel-displaced arrangement of the two phenyl rings, similar to one of the two low-energy structures of the benzene dimer. As mentioned, the thiophenol dimer structure differs from the one of the phenol dimer (Figure 2). The phenol dimer adopts a structure to accommodate both a hydrogen bond of the OH groups and CH- π interactions of the two phenyl groups instead of the parallel-displaced arrangement. Symmetry-adapted perturbation theory (SAPT2+3) calculations provide us with an estimate of the contributions of the different types of intermolecular interactions. They reveal that, indeed, the thiophenol dimer is dominated by dispersion interactions arising from the parallel-displaced phenyl rings, while the electrostatic contributions are weaker. The situation is reversed for the phenol dimer, where the electrostatic contribution from the strong hydrogen bond is the dominant type of interaction.

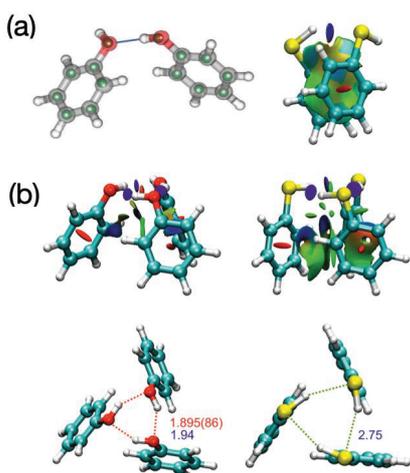


Fig. 2: Comparison of the structures of the phenol and thiophenol dimers (a) and trimers (b) along with results from SAPT calculations, where the green color indicates dispersion interactions. (The thiophenol cluster structures are adapted from Ref. 3, and the structure of the phenol dimer is adapted from Ref. 4.)

Interestingly, the influence of a sulphur substitution is less significant for the experimentally observed trimer structures, for which very similar geometries are obtained for both phenol and thiophenol (Figure 2). They are of C_3 symmetry with a cyclic hydrogen

bond network involving the OH or the SH group, respectively, and CH- π interactions between the three phenyl rings. The major difference is, again, expressed in the longer hydrogen bonds for the thiophenol case, which allows for stronger CH- π interactions between the phenyl rings. However, contrary to the dimer case, this does not result in a different structure, but just in a tighter arrangement of the phenyl groups.

These two examples should highlight that dispersion interactions are omnipresent and can be decisive contributions to stabilize molecules like the (oxa)diamantyl dimer or to tip the balance towards a specific docking preference as in the case of the thiophenol dimer. These studies are just two out of many research contributions to dispersion-related questions discussed at the Bunsen-Tagung 2022 and are tackled within the priority program 1807 “Control of London dispersion interactions in molecular chemistry”.

References

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Melanie Schnell is a professor for Physical Chemistry at the Christian-Albrechts-Universität zu Kiel since 2017, in a joint position with DESY, where she leads the research group “Spectroscopy of molecular processes”. Her main research activities concentrate on a better understanding of structure, function, and chirality on the molecular level. To reach these goals, her group develops novel spectroscopic methods, especially in the area of rotational spectroscopy. Melanie Schnell studied chemistry at the Universität Hannover and Universität Bonn and obtained her PhD from the Universität Hannover. In her PhD thesis, she investigated flexible molecules using rotational spectroscopy in the gas phase under the supervision of Jens-Uwe Grabow. She performed a PostDoc stay at the National Institute for Standards and Technology in Gaithersburg, MD, USA and then moved to the Department of Molecular Physics of the Fritz-Haber-Institut in Berlin to learn how to generate and use cold molecules. In 2010, she accepted a W2-equivalent research group leader position of the Max Planck Society and moved to Hamburg, where she set up her independent research group on molecular spectroscopy, employing the chirped-pulse Fourier transform microwave spectroscopy technique. In 2014, she was awarded an ERC Starting grant to perform astrochemical research.