

## van der Waals Molecules III: Introduction

This thematic issue on van der Waals (vdW) molecules follows earlier issues on this subject (*Chemical Reviews* **1988**, Vol. 88, No. 6 and *Chemical Reviews* **1994**, Vol. 94, No. 7) after another period of six years. It documents important new directions of development in the field, achieved both in experiment and in theory, and should give an idea of its future potential. The issue includes 15 contributions and altogether more than 4000 references.

Why are vdW interactions so topical? It is well known that these weak interactions play an important role in chemistry, physics, and in particular in the biodisciplines. Since all life on earth may be viewed as a matter of supramolecular chemistry, with vdW forces playing a central role, the understanding of these interactions is important for any progress in the targeted synthesis of new drugs. Even in the age of combinatorial chemistry it remains true that progress in designing highly specific drugs is strongly accelerated by intimate knowledge of the intermolecular forces that control the specificity of interaction and the binding constant of complexes such as those between drugs and DNA, RNA, or a protein.

The research reviewed in this issue spans subjects ranging from clusters of biomolecules to the femtochemistry of clusters of solvent molecules. Another noteworthy feature is the tightened link between theory and experiment, achieved in the last couple of years also for vdW interactions in larger clusters. This extremely successful cooperation has provided much useful information on the structure, energy, properties, and dynamics of vdW complexes, as demonstrated in several of the present contributions.

In this issue new laser spectroscopic methods will be presented, which allow, for example, a precise structural characterization of clusters of hydrogen-bonded species with more than 10 molecules or the interrogation of ultrafast reactions in clusters, studied in real time. Astonishing progress in theoretical chemistry has been driven by highly efficient computational algorithms and computer hardware. Thus, molecular clusters that were considered computationally intractable until recently are now studied with nearly spectroscopic accuracy. Very important and new theoretical developments concern the description of solvation effects allowing theory to bridge the gap from gas-phase to liquid-phase complexes.

Large portions of chemistry and all of biology occur in the liquid phase, and our understanding of cluster behavior in that phase can help us understand these very basic processes.

Buck and Huisken lead us into the world of hydrogen-bonded small water and methanol clusters produced in supersonic beams or adsorbed on or embedded in rare-gas host clusters. The structure-sensitive method applied is vibrational predissociation spectroscopy. Brutschy deals with the structures of these fundamental solvent clusters in interaction with substituted benzene molecules. The effects of electron-withdrawing and -donating substituents map the influence of charge density and binding sites on the topology of the weak  $\pi$  and  $\sigma$  hydrogen bonds between an aromatic solute and a polar solvent. Neusser and Siglow apply high-resolution optical spectroscopy to determine the exact structure of hydrogen-bonded heterodimers in different electronic states and present a new spectroscopic approach to the accurate study of the ionic states of a cluster. Results on weakly bonded clusters of biological interest are reviewed by Desfrancois, Carles, and Schermann. By applying a novel technique to produce multipole bound anion states, the structure of neutral highly polar complexes, typical for clusters of biomolecular relevance, can be unravelled in a surprisingly direct way. This article also presents fundamental landmarks for the future extension of cluster studies into the realm of biochemistry. The review of Bieske and Dopfer portrays the transition from vdW to ionic or even covalent bonding in solvated ions. They illustrate the wealth of information derived from rotationally resolved spectra of proton or  $p/\pi$ -bound small ionic clusters, which are ideal models for obtaining deeper insight into the roots of proton transfer and of intermediates in electrophilic and nucleophilic substitution reactions. The structure of ionic clusters can often be characterized by ZEKE or MATI spectroscopy combined with REMPI spectroscopy, a subject reviewed by Dessent and Müller-Dethlefs. With these high-resolution photoelectron/photoion spectroscopic techniques, theoretical concepts concerning solvated ions can be tested in great detail.

A second group of experimental reports addresses chemistry in solvent clusters. The issue of charge separation of a salt molecule, such as NaI, dissolved

in small clusters of water or acetonitrile is primarily a subject of femtosecond spectroscopy, as discussed by Dedonder-Lardeux, Grégoire, Juvet, Martrenchard, and Solgadi. The report of Zhong and Castleman on Coulomb explosion experiments with clusters subjected to intense laser fields aims in the same direction. The perspective of arresting ephemeral intermediates of chemical reactions under microsolvation is particularly relevant for getting microscopic insight into reaction mechanisms and cage effects. Thus, real-time chemistry in vdW clusters is a very important and prolific field at the present stage of cluster research work. Reactions of hydrated ions are another important subject, relevant for the understanding of ion chemistry in solution or in the stratosphere. They are reviewed in the article of Niedner-Schatteburg and Bondybey, which treats unusual ion stabilities and size-dependent kinetic behavior.

Several of the vdW subjects studied by laser techniques are also the subject of focus for modern empirical and quantum chemical methods, as described in the theoretical contributions to this issue. Those cover isolated gas-phase clusters and microsolvated clusters as well as clusters in the liquid phase. Attention is paid to the development and parametrization of intermolecular potentials and the use of supermolecular (variational) and perturbational *ab initio* techniques. All theoretical papers emphasize close cooperation with experiments.

Engkvist, Åstrand, and Karlström discuss intermolecular potentials that are obtained from wave functions containing polarization terms (many-body) and are still suitable for computer simulations. Practically all empirical potentials used for simulations are based on experimental data and/or combination of experimental and theoretical data and do not include polarization terms (are pairwise additive). In the near future we expect new developments in the realm of design and parametrization of new potentials. Wormer and van der Avoird describe the relation between intermolecular potentials and rotationally resolved spectra of vdW molecules. The spectra and potentials are closely connected; experimental data can be used to probe intermolecular

potentials, but also, accurate intermolecular potentials can discriminate between various experimental results. Kim, Tarakeshwar, and Lee investigate microsolvated  $\pi$  systems and compare theoretically predicted structures and vibrational spectra with experimental data. Supramolecular and perturbational (SAPT) theoretical data are briefly discussed. Orozco and Luque describe theoretical methods suitable for the description of solvation in biological systems. Chałasiński and Szcześniak discuss the current state of the *ab initio* theory of vdW interactions considering both variational and perturbational (SAPT) approaches for both closed-shell and open-shell vdW systems. Hobza and Havlas describe anomalous X–H...Y H-bonding which is manifested by the contraction of the X–H bond and a blue shift of the X–H stretch frequency.

In summary, although the roots of modern cluster studies date back some 20 years, vdW clusters are still a very prolific model system for the study of the details and of the origin of intermolecular forces and of their effects on most fundamental chemical, physical, and biochemical processes from a molecular point of view. For theoreticians, these clusters represent a great challenge due to the weakness of the interactions and the complexity of the encountered structures, and these challenges are encountered even in systems of moderate size. A maximum overlap of experiment and theory is mandatory for further progress in this field. The perspective for a fourth special issue on this subject in about another six years seems to be very good, due to the considerable progress still underway and the central role that vdW interactions play in nature.

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