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van der Waals Molecules II: Introduction

The fact that, after six years, van der Waals molecules are again the subject of a *Chemical Reviews* thematic issue provides clear evidence that the study of these systems continues to be actively pursued and points to recognition of their scientific importance. Indeed, since the appearance of the earlier issue (van der Waals Molecules, *Chem. Rev.* 1988, No. 6), investigation into the properties of these systems has grown enormously, with especially spectacular developments arising from the application of advanced spectrometric techniques to elucidate the details of the intermolecular forces responsible for their bonding and stability. This trend is reflected in the present issue—six of 14 contributions are devoted to spectroscopic studies of van der Waals systems.

Although the chemistry of individual molecules is generally dominated by covalent bonding, van der Waals forces govern the interactions within collections of molecules and are responsible for the stability of intermolecular complexes, surface bonding of solutions, and possible adsorbed species and even for the existence of the condensed liquid state. The level of detail that can be acquired in studies of carefully chosen van der Waals molecules far exceeds that usually achievable in investigations of bulk systems. Hence, the findings serve to bridge, at the molecular level, the knowledge of the varying interactions that occur as a gas-phase molecule transcends into the condensed phase. van der Waals interactions between solute and solvent, or between adsorbate and surface, are the same as or similar to those among atoms and molecules in an atomic or molecular cluster. Consequently, studies of atomic and molecular clusters, both experimental and theoretical, can be expected to elucidate the nature of the forces stabilizing these systems which will be of value not only in the fields of chemistry and physics, but also biology. Biochemical reactions are driven by solvation phenomena which can be clearly exposed through studies of van der Waals molecules and processes of energy transfer in intermolecular complexes.

The present issue concerns the role of van der Waals systems in chemistry and physics and deals mostly with molecular clusters, with primary attention paid to intermolecular forces and bonding. We hope to demonstrate that fruitful interplay between experiment and theory serves to facilitate a rather

complete description of a cluster. This issue contains experimental and theoretical contributions, and it was our aim to generate the maximum overlap possible between systems studies, experimentally and theoretically. This gives the reader the chance to confront results obtained by these two approaches individually and to witness the synergism which can arise from their combination.

Theoretical investigations on small molecular clusters (with less than a dozen atoms) are summarized by Chałasiński and Szczęśniak; larger, benzene-containing clusters are the subject of a contribution by Hobza, Selzle, and Schlag. This review is an especially relevant example of the benefits and new insights that can be obtained through a combination of theory and experiment. Spectroscopic evidence of structure and bonding of these and other clusters is found in papers by Felker, Maxton, and Schaeffer (Raman spectroscopy); Leopold, Fraser, Novick, and Klemperer (microwave and infrared spectroscopy); Neusser and Krause (mass-analyzed pulsed field threshold ionization spectroscopy); and Müller-Dethlefs, Dopfer, and Wright (zero kinetic energy (ZEKE) spectroscopy).

The ultimate goal of theory is to fully and consistently describe the cluster and to reproduce all its properties, such as structure, geometry, stabilization energy, and the intermolecular potentials involved. This is not an easy task and both variational and perturbational methods of quantum theory are applied. The straightforward use of the former technique is complicated by the unbalanced description of the supersystem and subsystems that results from the basis set superposition error. The review by van Duijneveldt, van Duijneveldt-van de Rijdt, and van Lenthe deals with this problem. Application of perturbational methods can shed light on the nature of the stabilizing forces; this topic is discussed by Jeziorski, Moszynski, and Szalewicz. Among the cluster properties mentioned, the intermolecular potential has a special position because it provides a bridge between experiment and theory. The spectra of van der Waals systems can be obtained for this potential, but conversely, this potential can also be generated from appropriate spectroscopic data. The review by van der Avoird, Wormer, and Moszynski, as well as that of Elrod and Saykally, is connected with this subject.

Four contributions are more or less related to interactions in solution or at the surface. In both situations the pair interactions should be augmented by many-body terms (as discussed in the review by Elrod and Saykally which describes experimental study of many-body effects). The very large clusters form an intermediate between gas and condensed phases. Structure and reactivity of large hydrogen-bonded clusters is reviewed by Garvey, Herron, and Vaidyanathan, while the subject of the dynamics and reactivity of Rydberg molecules in van der Waals clusters is discussed by Shang and Bernstein. Solvent can be considered as a large assembly of molecules, and the solute-solvent interaction can be evaluated by computer experiments. The other possibility is to describe a solvent as a continuum; the contribution of Tomasi and Persico is devoted to this subject. Finally, a paper by Sauer, Ugliengo, Garrone, and Saunders deals with the interactions of a molecule with a surface, although here cluster approaches also play an important role.

Continued successful growth in the study of van der Waals systems will be dependent upon progress in the development of new experimental (spectroscopic) techniques, faster and larger computers, and new theoretical procedures. New and fascinating results have appeared since the publication of the first thematic issue (van der Waals Molecules) six years ago, and many of the important developments are reviewed in the present issue (van der Waals Molecules II). We hope that within approximately six years we will be able to prepare van der Waals III, monitoring the progress over the next years. This may be, however, already in the next millennium.

A. Welford Castleman, Jr.
The Pennsylvania State University

Pavel Hobza
J. Heyrovský Institute of Physical Chemistry
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