

SOLUTE-SOLVENT INTERACTIONS - INTRODUCTORY REMARKS TO THE FOURTH  
INTERNATIONAL SYMPOSIUM ON SOLUTE-SOLUTE-SOLVENT INTERACTIONS

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The liquid state is notoriously difficult to describe on a molecular level. This is true for pure liquids as well as for liquid mixtures and solutions. In contrast to the vapor phase and the crystal there is no easy to define idealized model system for the liquid state. In order to overcome this disadvantage combined efforts by theoretical studies and experimental investigations are even more advisable than in other fields. Therefore, one of the main ideas had been to encourage the dialogue between theorists and experimentalists when the late Prof. Carpeni initiated this series of conferences on specific solute-solvent interactions by organizing the first meeting in Marseille. Six years later these problems have not at all lost their importance. Again it was a predominant goal of the present meeting to bring scientists from different fields together and to initiate further improvement of the molecular interpretation of the various phenomena observed in solution chemistry. This is reflected already by the eight plenary lectures presented here which deal with quantum chemical studies on intermolecular forces (H. Lischka), statistical mechanics of liquids (F. Kohler), diffraction studies on ionic solutions (A. H. Narten and R. Triolo), static and dynamic dielectric properties of liquids (L. Sobczyk), infrared and n.m.r. spectroscopy of ionic solutions (M. C. R. Symons), a thermodynamical theory of transport coefficients in dilute ionic solution (J. C. Justice and M. C. Justice), empirical models for solvent effect on chemical reactions (U. Mayer) and specific solvent influences on the mechanisms of inorganic reactions (D. W. Watts).

In these introductory remarks we shall try to point out some features of necessary and fruitful interactions between theoretical studies and experimental investigations from the fields of intermolecular forces and solute-solvent interactions with the aid of a few more or less arbitrarily selected examples.

The first example deals with hydrogen bonded dimers in the gaseous state: apart from a few strongly associated complexes wherein the molecules are held together by two or more hydrogen bonds like in the dimers of carboxylic acids, reliable thermodynamic and structural information on vapor phase dimers is rare. About eight years ago the first accurate quantum chemical calculations on the three most simple systems of this class,  $(\text{H}_2\text{O})_2$  (Ref. 1),  $(\text{HF})_2$  (Ref. 2) and  $\text{H}_2\text{O} \cdot \text{HF}$  (Ref. 3) were published. These studies yielded molecular geometries and electric moments of the three complexes. Many subsequent calculations confirmed the first results or improved them slightly. A few years later molecular beam studies reached high technical perfection and could be applied to these vapor phase dimers as well: the Stark effect in the microwave range gave information on the electric dipole moments together with the three moments of inertia of the dimers  $(\text{HF})_2$  (Ref. 4) and  $(\text{H}_2\text{O})_2$  (Ref. 5). Some time later the heterodimer has been investigated as well (Ref. 6). In all three cases the experimental results alone do not allow complete analysis of complex geometry and electronic rearrangement. The combination of theoretical and experimental data, however, brought our present, highly certain structural information on the dimers together with the described confirmation of the results from quantum chemical calculations.

The influence of three-body forces on the properties of dense vapors, liquids and crystals of the noble gases has been frequently discussed in the past (Ref. 7). Careful analysis revealed that third virial coefficients do not provide evidence for significant deviations from pairwise additivity unambiguously (Ref. 8). So far, the comparison of experimental data on rare gas liquids with the results of computer simulations by molecular dynamics was found to be not conclusive either as far as the contributions of three-body forces are concerned. Thus, the solid state remains as the most reliable source of information at present. The first theoretical studies by Jansen (Ref. 9) seemed to resolve the paradoxon of rare gas solids: the closely packed, face centered cubic (fcc) crystals formed by all noble gases except helium which crystallizes in the expected hexagonal closely packed (hcp) lattice were shown to be stabilized by the contribution of three-body potentials. Later on, the basic assumptions made in Jansen's calculations turned out to be weakly justified. More recently, the stability of the fcc-lattices of the heavier rare gas solids has been attributed to crystal field polarization effects (Ref. 10). At present, accurate quantum chemical calculations of "near Hartree-Fock" quality are available for the two lighter trimers  $\text{He}_3$  (Ref. 11) and  $\text{Ne}_3$  (Ref. 12). Calculations including electron correlation effects can be expected for the near future. Most probably the role of three-body forces with respect to the stability of rare gas clusters will be clarified soon by common efforts of theory and experiment.

Proton transfer is one of the most simple and most important elementary steps in uncatalysed and enzyme controlled reactions. In polar solvents proton transfer is escorted by large changes in the structure of the solvent surrounding the centers of the reaction. Hence, the dynamics of these processes is very complicated (Ref.13). Despite an enormous quantity of experimental results from spectroscopy and chemical relaxation kinetics our knowledge on the molecular details of proton migration is still very fragmentary. Only two years ago the first molecular dynamics studies on the solvation of ions appeared in the literature (Ref.14). This year the first attempt to investigate the solvation of polar molecules in polar solvents by molecular dynamics has been reported (Ref.15). Although, the intermolecular potentials applied so far were very crude and the present techniques used in molecular dynamics studies of polar particles are not free from systematic errors yet one may expect substantial progress in the future. Cooperation between theorists and experimentalists in the field of proton transfer reactions hopefully will clarify the essential dynamical details of such an important class of elementary processes.

The analytical molecular approach to solution chemistry inevitably will be limited to investigations of some typical phenomena by way of largely idealized and fairly simple examples. The enormous variety and complexity encountered with reactions in solution most likely will never be accessible to complete analysis of the molecular details. There is an ample field for the phenomenological or empirical approach to solute-solvent interactions. As our last example we choose the extended donor-acceptor approach to molecular interactions introduced by Gutmann (Ref.16). Starting out from the basic principles of donor-acceptor interactions the regularities of structural changes in condensed matter are put into a few rules which appear to be almost universally applicable to questions concerning structures and properties of solutions and solids and even to problems in surface chemistry.

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