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Intermolecular Interactions in Ionic Complexes

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Abstract. Intermolecular interactions and microsolvation effects in isolated charged complexes are investigated by high-resolution infrared spectroscopy and quantum-chemical calculations.

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Introduction and Techniques

Ion/neutral interactions play a crucial role in many areas of physical chemistry (solvation, nucleation, electrolytic solutions, ion/molecule reactions, plasma physics, atmospheric and interstellar chemistry, combustion, catalysis) and biology (structure of biomolecules, enzymatic reactions, transmembrane ion transport). Interactions in isolated charged aggregates, also called ionic complexes or clusters, bridge the gap between weak *van der Waals* forces in neutral complexes (such as He_2) and strong chemical bonds of stable molecules (such as H_2). Until recently, our understanding of ion/neutral interactions from the microscopic point of view has been rather limited, mainly owing to the difficulties involved in the production of sufficient concentrations of these species in the gas phase. The main goal of our current research activities is to improve the fundamental knowledge of ion/neutral interactions.

The most powerful tools for the characterization of intermolecular forces in complexes are high-resolution gas-phase spectroscopy on the experimental side, and quantum-chemical calculations on the theoretical side. We combine mass-spectrometric and spectroscopic techniques to obtain infrared spectra of mass-selected ionic complexes. The spectra of *dimers* are rotationally resolved and provide detailed information about the interaction potential (structure, binding energy, vibrational frequencies, force constants, rigidity). Systematic frequency shifts in the vibrational spectra of *larger clusters* allow us to monitor the microsolvation process, *i.e.*, the formation of solvation shells and the relative stability of various structural isomers. In this way, macroscopic properties of the condensed phase can

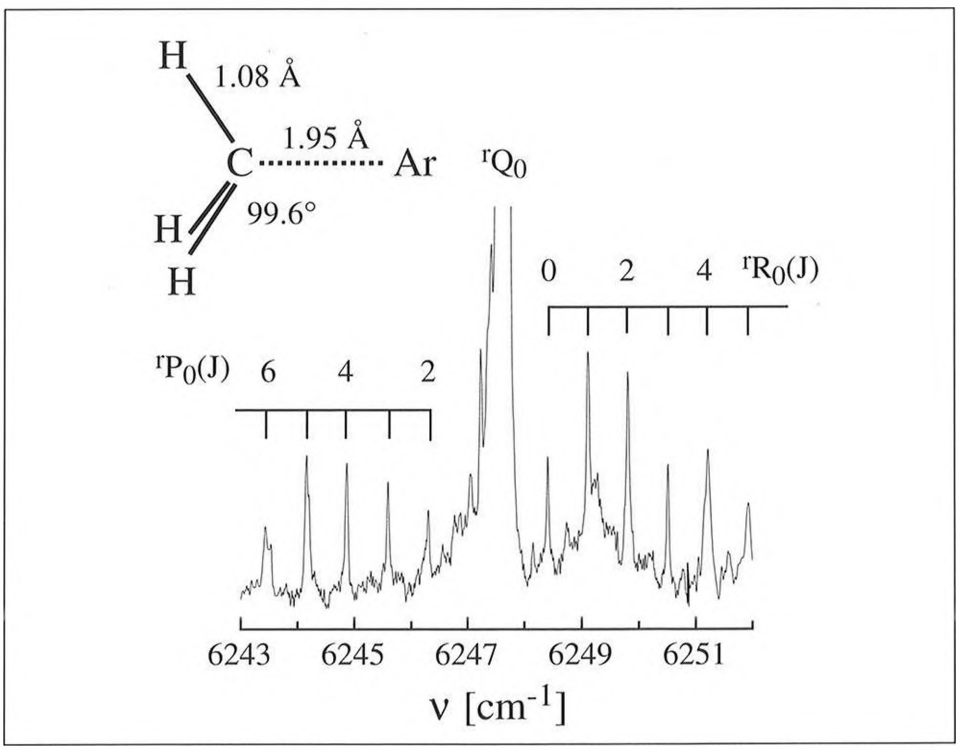

Figure. *Structure and infrared photodissociation spectrum of the $2\nu_3$ vibration of the CH_3^+–Ar dimer*

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directly be related to microscopic molecular attributes. The experimental approach is complemented by *ab initio* calculations of the intermolecular potential-energy surface, which provide information of the interaction potential not probed by the spectroscopic approach (*e.g.*, transition states and isomerization barriers).

Selected Projects

i) Dimers: In proton-bound dimers $A–H^+–B$ two bases are held together by a linear proton bond. Their properties are interesting as they are intermediates in proton-transfer reactions:

$$AH^+ + B \rightarrow A–H^+–B \rightarrow A + HB^+$$

The relative stabilities of the individual bonds in $A–H^+–B$ are determined by the proton affinities of the bases A and B, which can be varied in a systematic fashion (*e.g.*, A = H_2, N_2, O_2, CO, SiO, O, OH, H_2O, NH, NH_2, NH_3; B = He, Ne, Ar, H_2, N_2, O_2). In π-bound dimers, such as CH_3^+–X or $C_2H_2^+$–X, the base X donates electron density into a vacant orbital of the substrate (*Fig.*).

ii) Larger clusters: For larger clusters $A–H^+–B_n$, we investigate the details of the cluster growth and the influence of successive solvation on the properties of the monomer units. Often, chemical reactions within cluster ions (such as proton transfer from A to the solvent shell B_n) require the presence of a minimum number of solvent molecules.

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[1] R.V. Olkhov, S.A. Nizkorodov, O. Dopfer, *J. Chem. Phys.* **1998**, *108*, 10046.
[2] R.V. Olkhov, S.A. Nizkorodov, O. Dopfer, *J. Chem. Phys.* **1997**, *107*, 8229.
[3] R.V. Olkhov, S.A. Nizkorodov, O. Dopfer, *Chem. Phys.* **1998**, *239*, 393.

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