UNIVERSITY OF GOTHENBURG

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN NATURAL SCIENCE,
SPECIALISING IN CHEMISTRY

Molecular Investigations of Atmospherically Relevant Interface Processes

Ice Formation and Water Accommodation on Ice and Organic Surfaces

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Abstract

Clouds and aerosols play important roles in the climate system by affecting on atmospheric chemistry, the radiation budget of the atmosphere, and the water cycle including the formation of precipitation. Climate models with predictive power require quantitative descriptions of aerosols and clouds, but several key processes remain to be fully understood. One important example is the formation and growth of ice particles in clouds. Organic compounds also form secondary organic aerosol and coatings on existing particles including ice nuclei and ice cloud particles, which further complicate the description of cloud processes. To improve the understanding of these processes, some fundamental investigations of atmospherically relevant interface interactions are carried out, and the results and findings are summarized and discussed in this thesis.

The investigations use a newly developed environmental molecular beam (EMB) technique as the main experimental method. The principle, design and demonstration of the EMB method are described in detail. The method allows for ice surface investigations at temperatures up to 213 K, and it is employed to study gas-surface interactions under conditions relevant to the troposphere.

The main findings of this thesis are related to three research themes: (1) Ice formation via deposition mode nucleation on hydrophobic and hydrophilic surfaces is characterized. The critical supersaturation required to activate nucleation on various surfaces increases rapidly with decreasing temperature below 200 K, and adsorbed organic compounds are observed to influence the nucleation, structure and growth rate of ice. (2) Water uptake by bare ice and coated ice surfaces is investigated. The accommodation and desorption kinetics for water on bare ice is quantitatively described by a precursor model. Coatings on ice have a significant impact on water uptake, and adsorption of acids commonly found in the atmosphere tends to enhance water accommodation. (3) Water interactions with surfaces on condensed organic phases and organic coatings on graphite are characterized. Bulk accommodation is inefficient on solid organic surfaces, while water uptake is efficient on liquid phases. The surface layer on condensed *n*-butanol is shown to change gradually from solid to liquid over a 10 K temperature span around the bulk melting temperature, with major implications for water uptake.

The thesis includes the development of new experimental methods and an improved molecular-level understanding of processes at gas-solid and gas-liquid interfaces, and thereby contributes to a better description of cloud and aerosol processes in the environment.

Keywords: Environmental molecular beam (EMB), atmosphere, water, ice, organics, ice nucleation, deposition freezing, graphite, supersaturation, accommodation coefficient, deposition kinetics, collision dynamics, phase transition, alcohols, acetic acid, nitric acid, environment, green chemistry

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