UNIVERSITY OF GOTHENBURG

DEPARTMENT OF CHEMISTRY AND MOLECULAR BIOLOGY

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

MOLECULAR-LEVEL INVESTIGATIONS OF WATER-ORGANIC SYSTEMS OF ATMOSPHERIC RELEVANCE

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The doctoral thesis will be defended publicly in English, with permission from the Science Faculty, on Friday the 31st of January 2020 at 13:00 in room 10:an, Chalmers University of Technology, Kemigården 4, Gothenburg

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ISBN: 978-91-7833-768-2 (print)
ISBN: 978-91-7833-769-9 (pdf)
http://hdl.handle.net/2077/62520

ABSTRACT

It is known that aerosol particles may have warming and/or cooling effects on the climate and negative health effects that depend on their chemical and physical properties. However, current understanding of atmospheric particles' effects is poor due to the diversity of their constituents and associated variations in properties. Important components are volatile organic compounds that are emitted from both natural and anthropogenic sources into the atmosphere and may condense onto existing particles or nucleate and contribute to formation of new particles. Organics may account for 20 to 90% of the total particle mass, and some may be enriched at particles' surfaces while others are mixed in their bulk. This may substantially influence the hygroscopicity of particles, which is highly significant as the water contents strongly affect their other physical and chemical properties. The water content may influence particle viscosity, which has feedbacks on gas-particle partitioning patterns and diffusion within the particles, and hence the chemical composition of both the gas and particle phases. The hygroscopicity also influences the critical supersaturation required for droplet activation, and thus affects cloud physics. The hygroscopicity also influences the radiative forcing of particles. However, there are needs for better fundamental understanding of interface processes on aerosol particle surfaces. Hence, ways to improve knowledge of these interactions are required. The Environmental Molecular Beam (EMB) technique can provide valuable information about the dynamics and kinetics of gas-surface interactions at near-ambient pressures. Thus, it may help efforts to elucidate processes at atmospherically relevant surfaces, and the doctoral project that led to this thesis focused on its uses, limitations and possible refinements.

The thesis is based on five papers. The first presents and evaluates improvements to an EMB instrument, involving introduction of a grated interface between high-pressure and high-vacuum regions. The improved instrument has demonstrated utility for studying water interactions with volatile surfaces at higher pressures (up to 1 Pa) than previously achievable. The grated interface also enables angular-resolved measurements, which are essential for complete understanding of the gas-surface processes taking place during EMB experiments. The other papers present results from four EMB studies of interactions between water and organic surfaces consisting of condensed layers of nopinone, *n*-butanol and valeric acid (chosen as proxies for atmospherically relevant compounds). The investigations showed that these experimental surfaces may have water trapping probabilities close to unity, and accommodate water to varying extents. They also showed that desorption kinetics are significantly influenced by functional groups present on the surfaces, the degree to which these groups facilitate water binding, and the surfaces' phase state. Accommodation coefficients were found to range from 5 to 40% on solid surfaces and up to to 80% on liquid surfaces.

Keywords: EMB method, desorption kinetics, water uptake, organic surfaces