AMBIENT AND LABORATORY STUDIES OF AEROSOL SIZE DISTRIBUTIONS AND HYGROSCOPICITY

Thesis by

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Abstract

The optical properties, health effects, atmospheric lifetime, and climate impact of ambient aerosols are influenced directly by their size distribution, chemical composition, and phase. The aerosol hygroscopicity, which is also a function of composition, governs the size and phase changes of these particles when subjected to varying ambient relative humidities (RH). This thesis presents results from a wide variety of studies involving laboratory and ambient measurements of aerosol size distributions and water uptake properties in the subsaturated regime. Time evolutions of particle size and hygroscopic growth were investigated for various secondary organic aerosol (SOA) systems generated in a smog chamber from ozonolysis of cycloalkenes and photooxidation of biogenic terpenes. SOA yields were measured at various initial parent hydrocarbon concentrations and correlated with the structure of the parent compound. The amount of water uptake of the aerosol at a reference RH was found to inversely correlate with the SOA yield. The hygroscopicity of many atmospherically relevant pure organic species was also studied using an unconventional particle generation scheme employing a nonaqueous solution. Experimental results were compared with predictions from an equilibrium thermodynamic model. In these works, organic aerosols are shown to exhibit complex hygroscopic growth, dependent on the particle chemistry, phase, and surrounding RH. Implications of the experimental techniques used on the observation of particle growth, deliquescence, and efflorescence are discussed. A number of other studies incorporating aircraft-based measurements of aerosol size distributions and hygroscopicity with other ambient measurements into various cloud microphysics models are also presented.

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Introduction

Introduction

Aerosols are ubiquitous in the atmosphere and are emitted or formed by both natural processes and anthropogenic activities. These particles affect human health, regional visibility, formation of clouds and precipitation, as well as the earth's overall energy balance, which can have far-reaching implications such as climate change. Understanding the ways in which aerosols behave, evolve, and exert these effects requires the knowledge of their formation and removal mechanism, transport processes, as well as their physical and chemical characteristics. The particle properties relevant in determining the aforementioned effects include the number concentration, size distribution, chemical composition, reactivity with other species, and response to environmental states. The hygroscopicity, i.e., the tendency for a particle to take up water, also influences the particle size distribution, phase, and degree of activity as cloud condensation nuclei, which can all in turn affect the atmospheric lifetime of the particle. Recent studies have shown that atmospheric aerosols are a complex mixture of inorganic species, such as salts and elementary carbon, and the organic fraction that can comprise hundreds of species, representing a wide variety of compound classes and origins. Unraveling the pathways responsible for forming these particles and understanding the physical and chemical changes these particles undergo in the ambient atmosphere are still very much a work in progress.

This thesis presents results from a wide range of laboratory and field experiments aimed at understanding the formation mechanism and physical and chemical characterization of submicron aerosol. Specifically, the focus has been placed on the measurements of particle size distribution and hygroscopic growth. In Chapter 2,

formation of secondary organic aerosols (SOA) in a laboratory smog chamber is described and the yields from a family of cycloalkenes are reported. Through a large number of ozonolysis experiments, the yield curves illustrating the relationship between the SOA yield and the absolute amount of organic mass formed can be generated. The relative aerosol-forming potential of different precursors is discussed on the basis of several aspects of the parent hydrocarbon structure.

In Chapter 3, hygroscopic behavior of the SOA formed in the smog chamber is presented. The parent compounds used to generate the SOA range from model compounds such as cycloalkenes of various carbon numbers and substitutions to atmospherically relevant biogenic terpenoid compounds. Using the hygroscopicity tandem differential mobility analyzer (HTDMA), measurements of the water uptake of these SOA as a function of time, particle size, and relative humidity are performed. The results are presented in the form of hygroscopic growth curves and time evolution of particle water content. In mixed organic-inorganic particles, hygroscopicity of the organic portion is calculated using a simple volume-weighting model and complementary measurement of organic fraction using the Aerodyne aerosol mass spectrometer.

Chapter 4 summarizes a set of laboratory measurements on the water uptake properties of a variety of pure organic species, including straight-chain and aromatic dicarboxylic acids, multifunctional acids, amino acids, fatty acids, and a steroid. The HTDMA-derived hygroscopic growth curves are compared with predictions from a thermodynamic model and with previous studies using different particle generation schemes and measurement techniques. Chapter 5 summarizes the findings discussed in the previous three chapters and provides suggestions for future studies.

The appendices at the end of this thesis contain results from various works in the laboratory and field campaigns. Appendices A, E, G–I , and K–M present findings from a variety of smog chamber studies on secondary aerosol formation, encompassing systems such as diiodomethane ozonolysis in the presence of UV light, cycloalkene ozonolysis, m-xylene photooxidation, terpene ozonolysis and photooxidation, and reactive uptake of carbonyl compounds onto preexisting particles. Parameters in nucleation phenomenon, aerosol yield, potential oxidation mechanism, and chemical composition of both the aerosol- and gas-phase oxidation products measured in real time and in bulk form are presented.

Appendix C describes findings on the detection of sulfur dioxide and sulfuric acid at high humidities using the chemical ionization mass spectrometer. A new ionization scheme and the effect of RH on the detection are discussed. Appendices B, D, F, J and N present a variety of observational and modeling studies that integrate measurements aboard the CIRPAS Twin Otter and other aircraft to investigate particle activation and the microphysics of cloud formation. Aerosol size distributions measured with the Caltech twin differential mobility analyzers (also known as Dual Automated Classified Aerosol Detector or DACAD) were used in these studies along with measurements of fine aerosol number concentrations, cloud condensational nuclei concentrations, submicron aerosol chemical composition, updraft velocities, and cloud droplet number and droplet size distributions.