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How Do Amines Affect the Growth of Recently Formed Aerosol Particles

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Abstract. Growth rates of recently born nanometer-scale particles were measured during the CLOUD experiments at CERN. Combining the data from several recently developed measurement techniques allowed us to follow the growth of the particles starting from molecules to molecular clusters and finally to climatically relevant particles. We studied the binary system with sulphuric acid and water, and the ternary systems with ammonia or dimethylamine added to the chamber, both in purely neutral situation, and with ionization from cosmic rays or the CERN particle beam.

Keywords: CLOUD, nucleation, particle growth, amines
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INTRODUCTION

Secondary particle formation in the atmosphere produces a significant amount of the atmospheric aerosol load and cloud condensation nuclei [1]. Particle formation begins with nucleation of the atmospheric vapors to form molecular cluster, which then need to grow for forming stable aerosol particles. The particle growth rate determines what fraction of the newly formed particles reach sizes, where they start to have a relevance to the climate, before they are scavenged by different loss processes.

Studying nucleation and the initial growth of the clusters have been limited by our inability to detect the relevant vapors in low enough concentrations or the recently formed cluster, especially in their neutral form. With the state-of-the-art instrumentation at the CLOUD chamber, we could fill the gap between measurement of gases, clusters and aerosol particles, and thus study the whole particle formation process starting from a molecular level.

Sulphuric acid have been established as the key compound for particle formation. However, it has been debated what other vapors participate in the nucleation or early growth process. Recently a lot of both theoretical and experimental studies have pointed towards ammonia or amines being strong candidates for an assisting vapor [*e.g.* 2].

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METHODS

The CLOUD experiment

The CLOUD chamber at CERN is a $26 m^3$ steel chamber filled with ultrapure gases for minimizing gaseous contaminants. With a high-voltage clearing field, all ions can be removed from the chamber for studying nucleation in purely neutral conditions. Alternatively, we can let natural cosmic radiation, or the beam from the CERN proton synchrotron create ions in the chamber [3].

The sulphuric acid in the CLOUD chamber was produced with a UV-light system. For ternary experiments we added variable amounts of ammonia or dimethylamine to the chamber. The vapor concentrations used were on an atmospherically relevant level, and they were monitored carefully.

The Particle Size Magnifier

The particle size distribution and particle growth rate between about 1 – 3 nm was measured with an Airmodus A09 Particle Size Magnifier [4], which is a diethylene glycol based mixing-type Condensation Particle Counter. By scanning the saturator flow rate we could change supersaturation reached inside the instrument, and thus the size of the particles that are activated. The relation between supersaturation and mobility diameter was established based on accurate laboratory calibration using ammonium sulphate clusters and particles produced in a tube furnace and size selected with a high-resolution DMA [5].

The (CI-) APi-TOF

The Atmospheric Pressure Interface – Time-of-Flight (APi-TOF) mass spectrometer [6] was used to measure the mass spectra of negatively or positively charged ions during the CLOUD experiments. We identified the clusters containing sulphuric acid and ammonia/dimethylamine from the spectra, and calculated also their growth rate, converting the mass of the clusters to a mobility diameter. The same was done for neutral clusters detected with the CI-APi-TOF, which equipped with a chemical ionization inlet [7].

THE GROWTH RATES IN DIFFERENT SYSTEMS

We found that the growth rate in the binary sulphuric acid – water system, with additional vapors present only as impurities, the growth rates were mainly well predicted by kinetically limited condensation of sulphuric acid [8]. However, when alkaline vapors, especially dimethylamine, were added to the chamber, the growth rates increased beyond what could be explained by the condensation of the measured amounts of the vapor molecules.

With the mass spectrometric methods we observed that sulphuric acid forms rapidly acid-base clusters with ammonia or dimethylamine. Thus the total amount of sulphuric acid available for growing of the particles could be much larger than the measured sulphuric acid monomer concentration. This implies that measurements of the distribution of neutral clusters as well as measurements of alkaline vapors are needed for fully explaining particle formation and growth in different systems.

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