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Experimental study on the influence of dimethylamine on the detection of gas phase sulfuric acid using Chemical Ionization Mass Spectrometry (CIMS)

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Abstract. Based on quantum chemistry calculations it has been suggested that the quantitative detection of gas phase sulfuric acid (H_2SO_4) by use of Chemical Ionization Mass Spectrometry (CIMS) could be biased in the presence of gas phase amines such as dimethylamine (DMA). An experiment was set up at the CLOUD aerosol chamber to test the quantitative detection of H_2SO_4 by CIMS by directly comparing the measured H_2SO_4 with and without DMA being present in the sample air. It was found that the H_2SO_4 cluster distribution changes but the CIMS detection efficiency is not strongly influenced.

Keywords: Chamber study, CLOUD experiment, sulfuric acid, new particle formation.
PACS: 82.60.Nh

INTRODUCTION

The nucleation of particles in the atmosphere is an important source for the atmospheric particle population and model calculations suggest that it could be responsible for about half of the global cloud condensation nuclei[1]. Sulfuric acid (H_2SO_4) is widely recognized as the most important substance driving atmospheric aerosol nucleation[2]. The method commonly used to detect gas phase H_2SO_4 is Chemical Ionization Mass Spectrometry (CIMS) which allows very sensitive detection of H_2SO_4 down to levels below 1×10^5 molecule per cubic centimeter[3,4]. For detection with a mass spectrometer, H_2SO_4 is converted into bisulfate ions (HSO_4^-) by reaction with nitrate ions ($NO3^-$) which can be clustered with nitric acid (HNO_3) or water molecules. Viggiano et al. showed that these reactions proceed with reaction rates close to the collision limit[5]. Recently, Kurtén et al. raised the question in how far this detection scheme is still valid if amines are present in the sample air[6]. Potentially the reaction with NO_3^- could be considerably less efficient if the H_2SO_4 molecules are each clustered with one or two dimethylamine (DMA) molecules. As these clustered H_2SO_4 molecules will continue to participate in the nucleation and growth – most

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likely even more efficiently than the bare molecules – it is desired to measure the gas phase concentration of H_2SO_4 molecules regardless of whether they occur as the bare H_2SO_4 molecule or clustered with amines (or other molecules such as water or ammonia). The detection of gas phase H_2SO_4 could be interpreted to yield much lower H_2SO_4 concentration if the detection scheme was less efficient in the presence of amines. Although this effect was predicted to be only on the order of ten percent by the most reliable quantum chemistry computations[6] it was decided to investigate this potential influence by a dedicated experimental study at the CLOUD aerosol chamber at CERN.

EXPERIMENTAL METHODS

The CLOUD aerosol chamber[7] allows the stable in situ production of gaseous H_2SO_4 from the SO_2 + OH reaction[8]. The H_2SO_4 concentration is monitored by a well-calibrated CIMS instrument[3] (THS Instruments) as well as CI-APiTOF mass spectrometry[4] (Tofwerk AG/Aerodyne Research, Inc.). It is an important advantage of the CLOUD aerosol chamber that contamination by amines, or other condensable organic or inorganic species are kept to extremely low levels (few pptv level or below) and a large number of these species is constantly monitored. Furthermore, loss of H_2SO_4 due to nucleation, wall losses and gas dilution in the chamber is monitored as well by various instruments and other potentially influencing factors such as relative humidity, gas temperature and pressure are also kept precisely constant[7]. This allows conducting nucleation experiments and other process studies at atmospherically-relevant levels.

We performed a series of measurements by creating a range of different H_2SO_4 concentrations (H_2SO_4 ranging from 1×10^6 to 1×10^8 cm^{-3}) in the CLOUD chamber, first without any measurable amounts of DMA present in the chamber (< 0.2 pptv), and then repeating the exact same measurements while introducing DMA at levels of 10 and 40 pptv into the chamber. DMA levels are monitored by use of ion chromatography[9].

RESULTS

While the additional DMA substantially influences the observed cluster distribution, the detailed analysis shows that the detection efficiency of the CIMS is not affected strongly by the presence of DMA. Results will be quantified and discussed at the conference.

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