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Citation: AIP Conference Proceedings **1527**, 302 (2013); doi: 10.1063/1.4803263
View online: http://dx.doi.org/10.1063/1.4803263
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1527?ver=pdfcov
Published by the AIP Publishing

Molecular Steps of Neutral Sulfuric Acid and Dimethylamine Nucleation in CLOUD

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Abstract. We have run a set of experiments in the CLOUD chamber at CERN, Switzerland, studying the effect of dimethylamine (DMA) on sulfuric acid (SA)-water nucleation using a nitrate based Chemical Ionization Atmospheric Pressure ionization Time-Of-Flight Mass Spectrometer (CI-APi-TOF). Experiment was designed to produce neutral high *m/z* SA-DMA clusters in close to atmospherically relevant conditions to be detected and characterized by the CI-APi-TOF. We aimed in filling up the gap in measurement techniques from molecular level up to climatically relevant aerosol particles and thus improve our understanding of the role of sulfuric acid and DMA in atmospheric nucleation.

Keywords: Sulfuric Acid, Mass Spectrometry, Chemical Ionization, Nucleation
PACS: 64.60.Q-, 82.80.Rt, 36.40.-c, 82.33.Tb, 92.60.Mt

INTRODUCTION

New particle formation in the troposphere is driven by sulfuric acid (SA) [1]. Sulfuric acid alone or with water do not nucleate efficiently enough to account for high nucleation rates observed in the atmospheric boundary layer, but other vapors are needed also to create the very first molecular clusters [2]. Quantum chemical calculations strongly suggest that dimethyl amine (DMA) assists atmospheric sulfuric acid nucleation much more effectively than other suggested compounds such as ammonia or volatile organic compounds [3]. Also recent experimental findings both from laboratory [2,4] and field [5,6] indicate that amines might have a remarkable role in atmospheric nucleation. Technical limitations have, however, restrained the fully successful measurement and identification of the neutral nucleating clusters from ambient air or ambient relevant laboratory system even though great strides have been made in recent years [5, 7]. Here, we aim to fill the gap between freshly nucleated (>3nm) aerosol particles, detectable with standard aerosol instrumentation, and molecules responsible for formation of the new particles by direct measurement of nucleating cluster population by a nitrate-ion based Chemical Ionization Atmospheric Pressure ionization Time-Of-Flight mass spectrometer (CI-APi-TOF) [7]. To do that we studied the impact of DMA addition to cluster formation in very clean environment of the CLOUD chamber containing exclusively sulfuric acid and water vapor (RH = 38%). In this work we focused on formation of neutral clusters, but it should be mentioned that besides stabilizing bases, also ions can affect the nucleation process [2].

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AIP Conf. Proc. 1527, 302-305 (2013); doi: 10.1063/1.4803263

METHODS AND INSTRUMENTATION

The CI-APi-TOF [7] utilizes a specially designed inlet for chemical ionization at ambient pressure, a design similar with the CIMS instrument [8]. The inlet part is used together with a newly designed atmospheric pressure interface time-of-flight mass spectrometer (APi-TOF) [7,9]. The ionization mechanism is very selective to strong acids and acidic clusters containing sulphuric acid.

The formed SA-DMA clusters were detected by their *m/z*-ratios and identified using exact cluster masses, isotope patterns and mass defects using a Matlab® build toolbox, tofTools [9]. The CI-APi-TOF has a tremendously low limit of detection for pure sulfuric acid and due to its selectivity it can detect exclusively acidic SA - base clusters up to 4000 Th, corresponding roughly to 3 nm in particle diameter. The CI-APi-TOF's selectivity is based on a proton transfer reaction between the reagent ion in the charger region and the acidic sample air molecules. To a first approximation, only compounds in the sample with higher proton affinity that the nitrate ion gets charged in the sample flow. Coaxial flows and electric field utilized inside the ion source prohibits any wall contact of the sample making the method superior for analysis of low vapour pressure compounds and clusters. Use of atmospheric pressure ionization and reasonably long reaction time (~0.2 s) enables effective ion-molecule interactions and, therefore, high ionization efficiency and extremely low detection threshold. New feature in the CI-system used here is that it applies a soft x-ray tube for ion production, worthwhile feature since the complications related to use of radioactive materials can be avoided.

RESULTS AND CONCLUSIONS

When DMA was added to the chamber the CI-APi-TOF was used for exclusive detection and identification of formed molecular clusters. The time series showing the behavior of selected cluster signals in presence of H_2SO_4 and DMA in the chamber is presented in Figure 1. The limit of detection for sulfuric acid monomer and sulfuric acid cluster lies in the ppq-range ($3 \cdot 10^4$ molec cm^{-3} for SA monomer). The identity and chemical nature of these clusters will be discussed.

From the detected cluster signals measured with both Particle Size Magnifier (PSM, Airmodus®) and CI-APi-TOF we also calculated nucleation rates for runs with different [H_2SO_4] and for DMA addition of from 0.5 to 40 ppt. The comparison of two instruments showed remarkable agreement with multiple different SA monomer concentrations. Results are compared also to atmospheric observations and conclusions about the role of DMA+H_2SO_4 nucleation in the atmosphere are drawn.

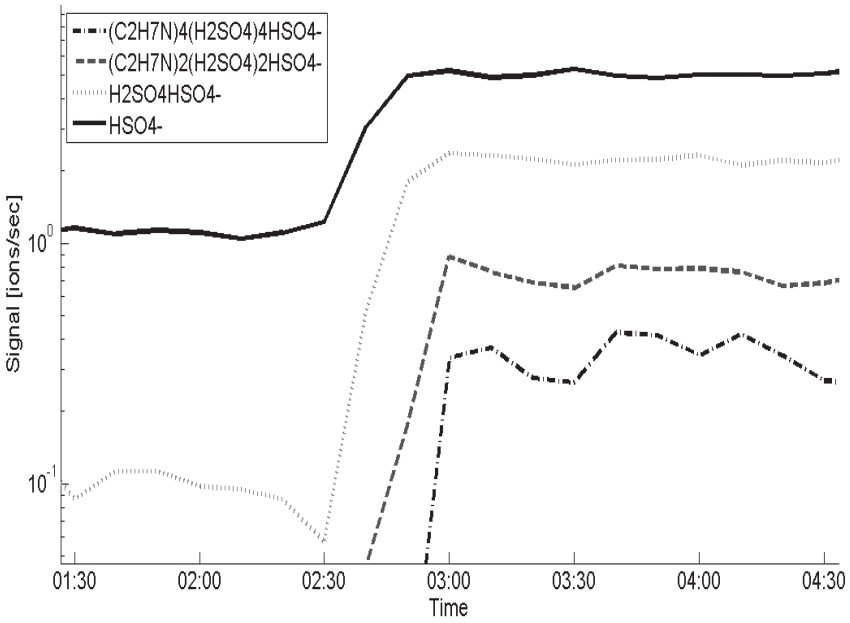

FIGURE 1. Time series of sulfuric acid and selected SA-DMA clusters after DMA addition to the chamber. Identification of these clusters will be discussed later.

ACKNOWLEDGEMENT

We would like to thank CERN for supporting CLOUD with important technical and financial resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC Seventh Framework Programme (Marie Curie Initial Training Network "CLOUD-ITN" no. 215072, MC-ITN "CLOUD-TRAIN" no. 316662, and ERC-Advanced "ATMNUCLE" grant no. 227463), the German Federal Ministry of Education and Research (project nos. 01LK0902A and 01LK1222A), the Swiss National Science Foundation (project nos. 200020_135307 and 206620_130527), the Academy of Finland (Center of Excellence project no. 1118615), the Academy of Finland (135054, 133872, 251427, 139656, 139995, 137749, 141217, 141451), the Finnish Funding Agency for Technology and Innovation, the Nessling Foundation, the Austrian Science Fund (FWF; project no. P19546 and L593), the Portuguese Foundation for Science and Technology (project no. CERN/FP/116387/2010), the Swedish Research Council, Vetenskapsrådet (grant 2011-5120), the Presidium of the Russian Academy of Sciences and Russian Foundation for Basic Research (grants 08-02-91006-CERN and 12-02-91522-CERN), the U.S. National Science Foundation (grants AGS1136479 and CHE1012293) and Pegasos (400798).

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