Role of organics in particle nucleation as viewed from a positive ion spectrometer

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Formation of new particles from trace gases (nucleation) has been recognized as the main source of aerosols in the atmosphere. It is estimated that nucleation can be responsible for up to 50% of the total cloud condensation nuclei (CCN) concentration (Merikanto et al., 2009). However, the formation of new particles in the atmosphere is still a poorly understood process despite its importance. In recent years sulfuric acid (H_2SO_4) has emerged as the key player in atmospheric nucleation. In many field campaigns a good correlation between the concentration of H_2SO_4 and the rate of particle nucleation was found. Laboratory experiments have shown that binary H_2SO_4-H_2O homogeneous nucleation cannot explain the observations in many regions of the atmosphere. Ion-mediated nucleation (IMN) is discussed as a potential strong source of aerosol formation and as a mechanism of influence of cosmic rays on clouds and climate. Based on model simulations Yu et al. (2008) conclude that IMN is significant on a global scale. Thus, it is very important to determine which trace species participate in the first steps of the nucleation process and which mechanisms govern the nucleation.

Experiments were performed in the CLOUD chamber which allows the study of nucleation rates under highly controlled conditions of temperature, humidity and trace gas concentrations. This 26 m^3 stainless-steel chamber is equipped with state-of-the-art instruments can be exposed to a π^+ beam coming from CERN's proton synchrotron to simulate the effect of the galactic cosmic rays on the new particle formation process. On the other hand a 20kV/m electric clearing field can be engaged to enforce an ion-free environment.

We investigated new particle formation of sulfuric acid (H_2SO_4) in the presence of compounds such as ammonia, dimethylamine ($(CH_3)_2NH$), α-pinene ($C_{10}H_{16}$) and pinanediol ($C_{10}H_{18}O_2$). The nucleation process was induced either by ozonolysis of α-pinene or OH radical reactions produced by UV-photolysis of ozone or HONO.

Here we present results obtained with the atmospheric pressure interface time-of-flight mass spectrometer (APi-TOF, Tofwerk and Aerodyne Research) operated in the positive ion mode (Junninen et al., 2010). This instrument samples directly the ions present in the CLOUD chamber through a critical orifice and measures their mass-to-charge ratio at a resolution higher than 5000 Th/Th and a mass accuracy lower than 10 ppm. Due to the high resolution of the instrument the composition of the evolving positive charged clusters could be measured for the various systems: H_2SO_4–NH_3, H_2SO_4–DMA and H_2SO_4–oxidized organics (OxOrg). In the case of the H_2SO_4–NH_3 system we observed $(H_2SO_4)_n \cdot (NH_3)_{n+1} \cdot H^+$ positive ions for low *n* and one extra molecule of ammonia for higher *n*. In the presence of DMA ammonia was substituted by DMA but the composition and stoichiometry remained essentially the same. However, the time evolution of the cluster formation was quite different for the two systems. In the case of H_2SO_4–OxOrg clusters were found in the m/z range from 200 Th up to 1500 Th. Highly oxidized organic species were observed. In all those positively charged clusters, whose chemical composition could be identified, no H_2SO_4 was observed. These results with the positive ion spectra obtained in the laboratory will be compared to measurements in the ambient atmosphere during nucleation events.

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