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Ternary H_2SO_4-H_2O-NH_3 Neutral and Charged Nucleation Rates for a Wide Range of Atmospheric Conditions

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Abstract. The formation of new particles for the ternary system involving sulfuric acid, water vapor and ammonia has been studied in detail. The nucleation rates were obtained from experiments at the CERN CLOUD chamber which allows the measurement of new particle formation under very well defined conditions. Some of its key features are the suppression of contaminants at the technological limit and a very precise control of a wide range of temperatures, trace gas concentrations and nucleation rates. The effect of ionizing radiation on the ternary nucleation rates was investigated by using the CERN proton synchrotron beam (beam conditions), natural galactic cosmic rays (gcr conditions) as well as the high voltage clearing field inside the chamber to suppress the effect of charges (neutral conditions). The dependence of the nucleation rate on ion concentration, sulfuric acid and ammonia concentration as well as temperature was studied extensively. This way, an unprecedented set of data was collected giving insight into the role of neutral and charged ternary NH_3 nucleation and the relative importance of the different parameters.

Keywords: Chamber study, CLOUD experiment, New particle formation, Ammonia.
PACS: 92.60.Mt , 64.60.Q-

TERNARY H_2SO_4-H_2O-NH_3 NUCLEATION

New particle formation is an important atmospheric process affecting cloud formation, visibility and climate as well as air chemistry and human health. Generally, atmospheric boundary layer nucleation events cannot be explained by the binary nucleation of sulfuric acid and water vapor. Therefore, it had been suggested that ammonia could be an important compound which lowers the nucleation barrier when added as a ternary substance[1-4]. Indeed, a recent CLOUD (Cosmics Leaving OUtdoor Droplets) experiment has shown that ternary nucleation involving NH_3 is significantly enhancing the formation of new particles by a factor of 10 to 1000 over the nucleation

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rates for the binary system[5]. However, the addition of ammonia can still not account for the high nucleation rates observed in the boundary layer at temperatures of 5°C or warmer. In these regions ternary organic vapors are most likely required to explain the high nucleation rates[6,7].

Nevertheless, at high latitudes or in the upper troposphere where temperatures are colder and other ternary vapors occur at too low concentrations, ammonia can still play an important role. Therefore, on a global scale the effect of ammonia for new particle formation can be significant and needs to be studied. Ammonia is also a compound of interest because its emissions are, similar to SO_2, strongly linked with anthropogenic activity. Ammonia emissions from livestock waste, volatilization of NH_3-based-fertilizers, biomass burning and crops comprise a big part of the total emissions. It is thought that these have led to a doubling of the total ammonia emissions since pre-industrial times and that a significant further increase will occur in the future[8,9].

With respect to the climate discussion it is of great interest to elucidate the impact of ionizing radiation on new particle and CCN formation. Recent results from CLOUD have shown that galactic cosmic rays can lead to a significant enhancement of the nucleation rates for the binary and the ternary NH_3 system under some conditions (FIGURE 1)[5]. It is, however, necessary to extend the available data set for a wider range of tropospheric conditions – especially with respect to colder temperatures. In a second step this data can then be used in models to investigate the sensitivity of the nucleation rates and the formation of CCN due to the different parameters on a global scale.

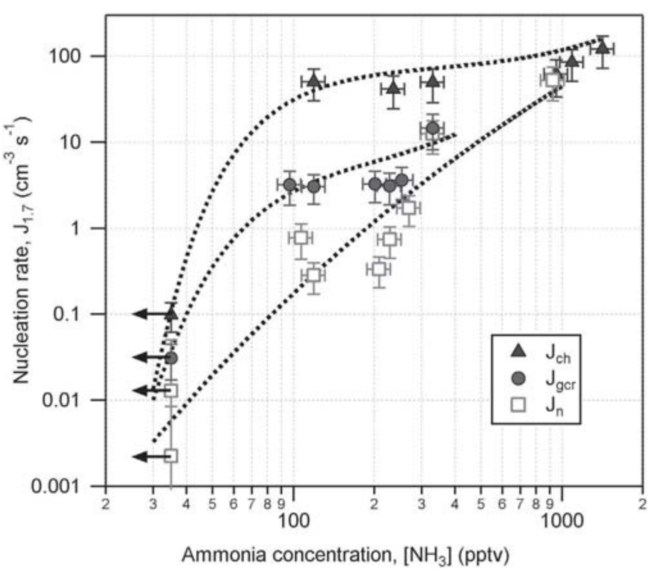

FIGURE 1. Nucleation rate as function of the ammonia mixing ratio (data from ref. 5). Temperature was 278 K and $[H_2SO_4]$ was 6.3×10^7 cm^{-3}. Nucleation rates were measured at neutral (J_n), galactic cosmic ray (J_{gcr}) and CERN pion beam conditions (J_{ch}).

EXPERIMENTAL METHODS

Nucleation rate measurements presented have been performed during the CLOUD3, CLOUD5 and CLOUD7 experiments at CERN between October 2009 and December 2012. The CLOUD chamber is designed to study the effect of ionizing radiation on particle formation, growth and activation to ice or cloud droplets under extremely well controlled conditions. It consists of a 3 m diameter electro-polished stainless steel cylinder with a volume of 26.1 m^3. The chamber is surrounded by a thermal housing, and air circulating in the space between the chamber and the insulation was used to control the internal temperature between 208 and 300 K during the ternary NH_3 nucleation experiments.

Sulfuric acid has been measured by Chemical Ionization Mass Spectrometry (CIMS) at concentrations between ~$1x10^6$ and ~$1x10^9$ cm^{-3} during nucleation events. To achieve a homogenous mixing the sulfuric acid production was initiated in-situ through illumination of the chamber with a UV fibre-optic system. The ammonia originated from a gas bottle and was further diluted with nitrogen to achieve the desired concentration. The diluted NH_3 flow was then introduced into the CLOUD chamber where it was rapidly mixed into the chamber air by means of two magnetically driven stainless steel fans. The instrumentation used to measure the ammonia concentrations (between several pptv and ~1000 pptv) comprised of a LOng Path Absorption Photometer (LOPAP)[10], an Ion Chromatograph (IC)[11] and a Proton-TRansfer Mass Spectrometer (PTR-MS)[12]. The determination of the [NH_3] at concentrations lower than several pptv and at temperatures lower than the freezing point of water is challenging due to instrumental limitations. Under these conditions the ammonia concentrations were mainly derived from estimating the ammonia background (when no ammonia was intentionally flown into the chamber) as well as from calibration measurements which relate the amount of ammonia flown into the chamber and its measured concentration at 5°C.

TABLE 1 summarizes the parameter space which was covered at CLOUD for the ternary NH_3 system. Several hundred individual nucleation rate measurements were obtained from these experiments.

TABLE 1. Parameter space covered by the CLOUD experimental runs. [a]The lowest ammonia concentrations under background conditions were not directly measured (see text for details). [b]Different relative humidities (RH) were tested but it was found that the nucleation rates were not very sensitive to changes in the humidity for the range studied.

Parameter	range
Temperature	208 to 300 K
[H_2SO_4]	~$1x10^6$ to $1x10^9$ cm^{-3}
[NH_3]	[a]<10^{-2} to ~10^3 pptv
[b]RH	10 to 100%
Ion concentration	0 (neutral) to ~$5x10^3$ cm^{-3}

THEORETICAL CALCULATIONS

Recently, a lot of progress has been made in describing the formation of new particles from first principles through quantum chemical calculations[13,14]. Such calculations have been made also for the ternary system involving ammonia. The results from the ACDC model[13] are compared to the experimentally determined nucleation rates. In addition, calculations have been made which yield the nucleation rate at the kinetic limit for a given concentration of sulfuric acid. These results yield the upper limit of the nucleation rate and are used as a cross-check for the experimental values. Furthermore, they are used to identify the conditions where nucleation is limited by the kinetics of the colliding clusters.

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