

Influence of NH₃ on atmospheric particle formation starting from OH + SO₂

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For more than a decade the formation of new aerosol particles in the atmosphere has been the subject of intense studies in the field and in the laboratory. The formation mechanisms and the participating substances, however, have not been resolved yet (Kulmala, 2003). Large discrepancies between model-predicted nucleation rates for the favored binary system H₂SO₄ / H₂O and much higher atmospheric nucleation data were explained by various supportive additional participants such as NH₃ (Kulmala *et al.*, 2000) or organic molecules (Hoffmann *et al.*, 1998). Modeling studies predict an enhancement of binary H₂SO₄/H₂O nucleation rate by several orders of magnitude for NH₃ mixing ratios > 1ppt (2.5 · 10⁷ molecule cm⁻³) (Korhonen *et al.*, 1999). Subject of this experimental study is the role of NH₃ in the process of new particle formation starting from OH + SO₂.

The experiments have been performed in the atmospheric pressure flow-tube *Ift*-LFT (i.d. 8 cm; length 505 cm) at 293 ± 0.5 K (Berndt *et al.*, 2005). Gas-phase analysis was carried out using photoacoustic spectroscopy for NH₃ (OMNISENS: TGA 310), gas analyzers for O₃, SO₂, and NO_x (Thermo Environmental Instruments: 49C, 43C, and 42S), a butanol-based UCPC (TSI 3025) as well as a H₂O-based UCPC (TSI 3786) for integral particle measurements, and a differential mobility particle sizer (Vienna-type DMA with UCPC, TSI 3025) for monitoring of size distributions. The carrier gas consisted of synthetic air (99.9999999 %, Linde and further purification with Gate Keeper, AERONEX).

Using the NH₃ analyzer TGA 310, the carrier gas NH₃ concentration was below the stated detection limit of 0.1 ppb (2.5 · 10⁹ molecule cm⁻³). Generally, it is hard to measure and to handle NH₃ concentrations < 10¹⁰ molecule cm⁻³ caused by the high solubility of NH₃ in water and the resulting memory effects due to the presence of wetted surfaces (reactor walls, transfer lines, etc.). So it seems to be impossible to exclude (or to perform experiments with) NH₃ mixing ratios of ~1ppt (2.5 · 10⁷ molecule cm⁻³) as postulated to be sufficient for ternary nucleation H₂SO₄/NH₃/H₂O (Korhonen *et al.*, 1999). In the experiments presented here the added NH₃ concentrations were a few 10¹⁰ - 10¹² molecule cm⁻³, i.e. in the range of atmospheric levels or a bit higher. In order to evaluate the wall loss in the *Ift*-LFT NH₃ measurements have been performed at the entrance to the flow tube as well as

at the outlet port. Figure 1 shows typical experimental findings:

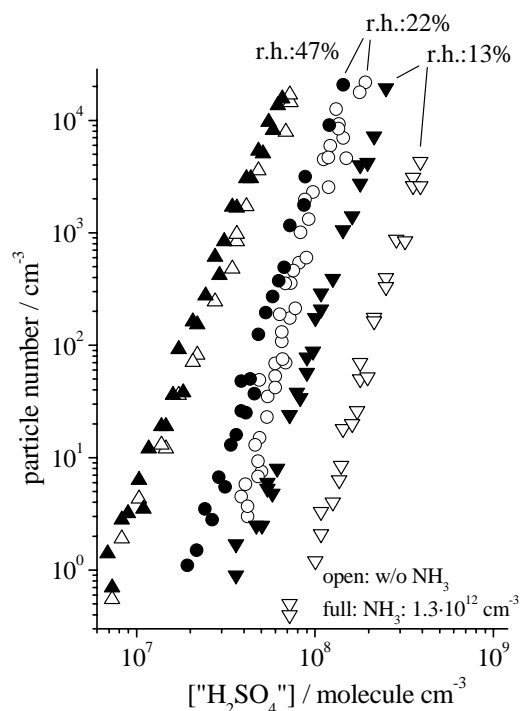


Figure 1: Detected particle number (TSI 3025) as a function of "H₂SO₄" with and without added NH₃ for different r.h.. "H₂SO₄" stands for all SO₂ oxidation products. Bulk residence time: 42 sec.

The influence of NH₃ on the formation of new particles was studied varying the residence times in the *Ift*-LFT, the humidity in the system and using different NH₃ concentrations. The results are discussed with respect to the importance of NH₃ for atmospheric nucleation.

Berndt, T., Böge, O., Stratmann, F., Heintzenberg, J., & Kulmala, M. (2005), *Science*, 307, 698-700.

Hoffmann T., Bandur, R., Marggraf, U., & Linscheid, M. (1998), *J. Geophys. Res.*, 103, 25569-25578.

Korhonen, P., Kulmala, M., Laaksonen, A., Viisanen, Y., McGraw, R., & Seinfeld, J.H. (1999), *J. Geophys. Res.*, 104, 26349-26353.

Kulmala, M., Pirjola, L., & Makela, J.M. (2000), *Nature*, 404, 66-69.

Kulmala, M. (2003), *Science*, 302, 1000-1001.