

# Influence of experimental conditions on particle formation starting from OH + SO<sub>2</sub>

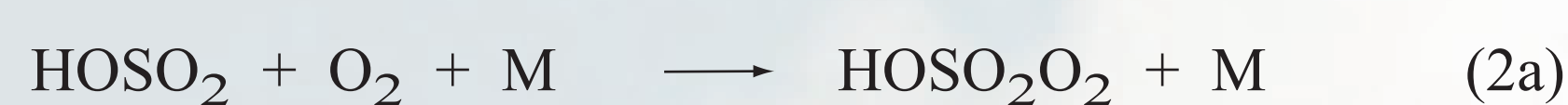
## Introduction

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 H<sub>2</sub>SO<sub>4</sub> / H<sub>2</sub>O and much higher atmospheric nucleation data were explained by various supportive additional participants such as NH<sub>3</sub> or organic molecules.

In a previous investigation of our laboratory under near-atmospheric conditions, experimental evidence for the formation of new particles in the system H<sub>2</sub>SO<sub>4</sub> / H<sub>2</sub>O was found for H<sub>2</sub>SO<sub>4</sub> concentrations of 10<sup>7</sup> molecule cm<sup>-3</sup> if "H<sub>2</sub>SO<sub>4</sub>" was produced in-situ via the reaction of OH radicals with SO<sub>2</sub> ("H<sub>2</sub>SO<sub>4</sub>" stands for all products of converted SO<sub>2</sub>), Berndt et al. (2005). In contrast, taking H<sub>2</sub>SO<sub>4</sub> from a liquid reservoir concentrations of 10<sup>9</sup> - 10<sup>10</sup> molecule cm<sup>-3</sup> are needed for new particle formation (Ball et al., 1999, Zhang et al., 2004). The accepted mechanism of atmospheric SO<sub>2</sub> oxidation is as follows:



In competition to pathway (2) HOSO<sub>2</sub>O<sub>2</sub> can be formed via:



It can be hypothesized that HOSO<sub>2</sub>O<sub>2</sub> or its hydrated species HOSO<sub>2</sub>O<sub>2</sub>(H<sub>2</sub>O)<sub>n</sub> play a role for the nucleation process explaining the different threshold concentrations for nucleation starting from liquid H<sub>2</sub>SO<sub>4</sub> or from OH + SO<sub>2</sub>.

The activities focused on experimental studies regarding the influence of NH<sub>3</sub> on new particle formation. Theoretical studies predict strong enhancement of the nucleation rate for NH<sub>3</sub> mixing ratios at pptv-level (Coffman and Hegg, 1995). Ball et al. (1999) showed experimentally an increase of the nucleation rate for NH<sub>3</sub> mixing ratios of 0.08 - 0.17 ppb and a relative humidity in the system of 5 - 15 %. In their study H<sub>2</sub>SO<sub>4</sub> from a liquid reservoir was used. Subject of this experimental study is the role of NH<sub>3</sub> in the process of new particle formation starting from OH + SO<sub>2</sub>. A comparison with atmospheric measurements includes also recent results obtained in the absence of NH<sub>3</sub> additions.

## Results in absence of NH<sub>3</sub>

### "Apparent" nucleation rate

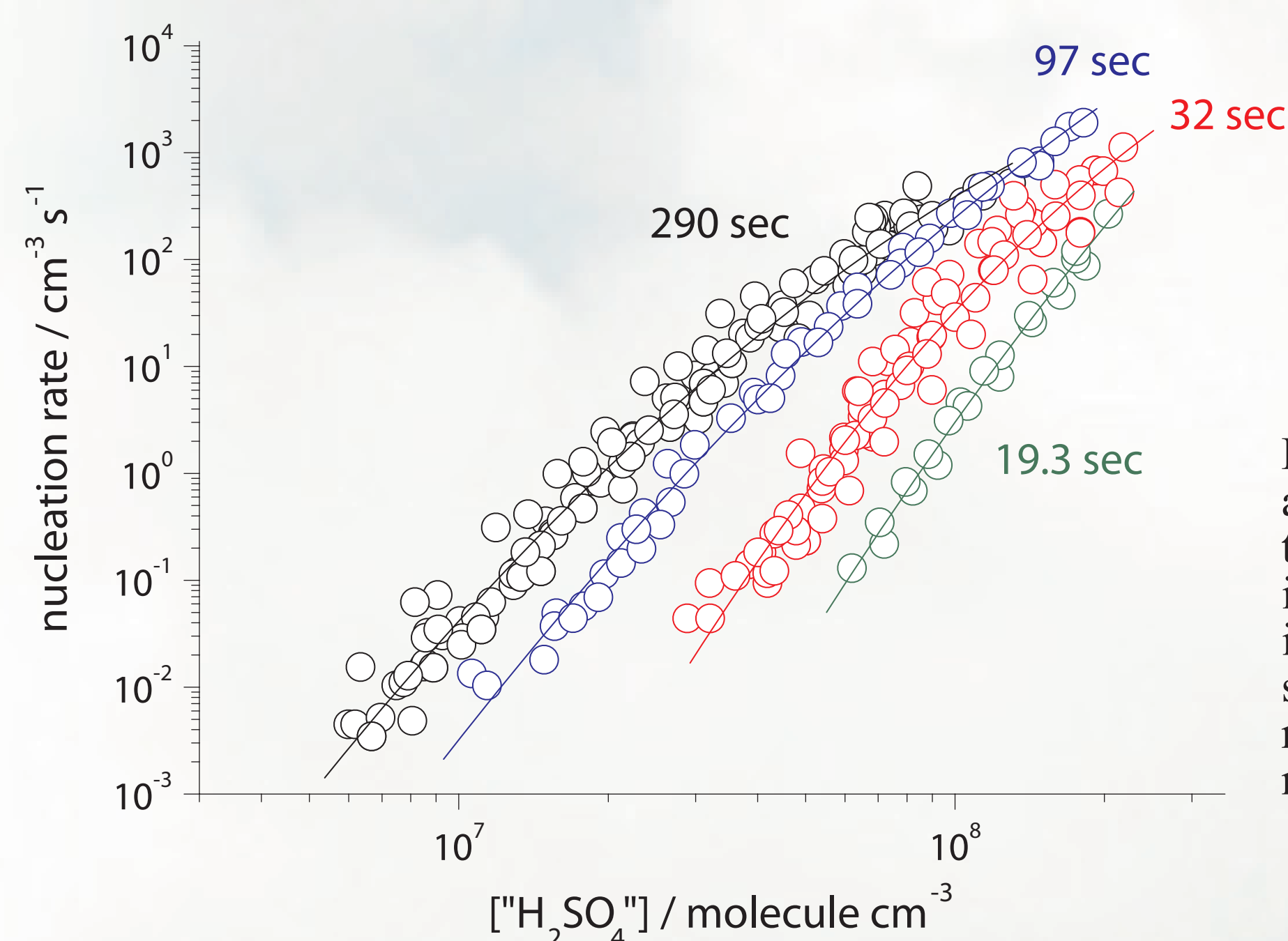


Figure 1: "Apparent" nucleation rate as a function of "H<sub>2</sub>SO<sub>4</sub>" concentration for different residence times in the flow tube. The nucleation rate is obtained by dividing the measured total particle number by the residence time in the irradiated middle section, r.h.: 22%, TSI 3025.

Nucleation rate vs. ["H<sub>2</sub>SO<sub>4</sub>"] shows a clear dependence on the residence time, the increase of residence time results in an increase of the observed nucleation rate. Obviously, for longer times a larger fraction of nucleated particles is able to grow up to the detectable size. Furthermore, insufficient CPC counting efficiency is more important for smaller particles (relatively low ["H<sub>2</sub>SO<sub>4</sub>"]) than for larger particles (higher ["H<sub>2</sub>SO<sub>4</sub>"]) leading to an overestimation of the slope log N vs. log ["H<sub>2</sub>SO<sub>4</sub>"] and, consequently, also for log J vs. log ["H<sub>2</sub>SO<sub>4</sub>"]. Both effects are the cause of the "Apparent" nucleation rates.

### "Real" particle numbers

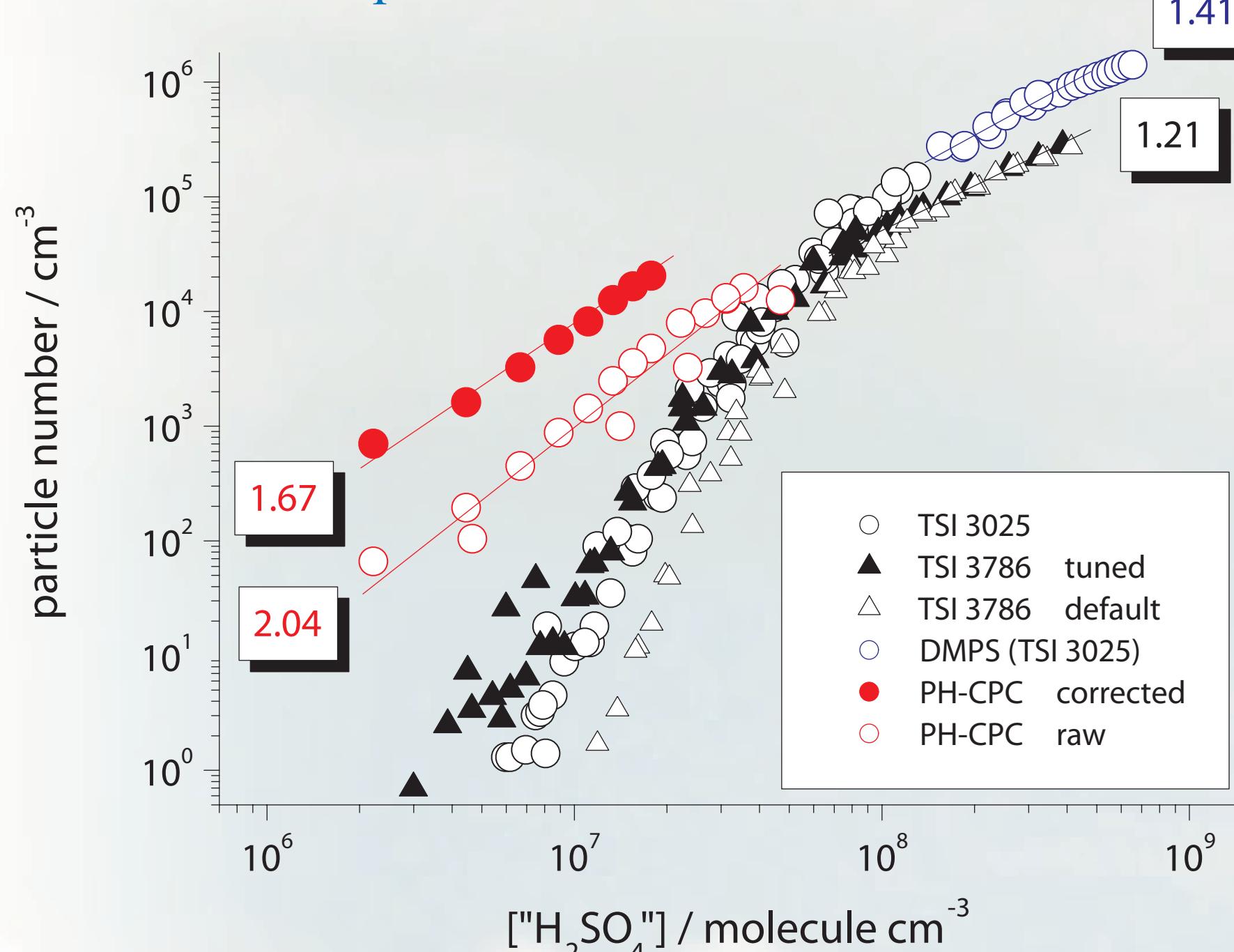


Figure 2: Measured total particle number using three different types of CPCs for integral measurements as well as from DMPS. Given numbers represent the slopes log N vs. log ["H<sub>2</sub>SO<sub>4</sub>"], (TSI 3786: N > 50.000 cm<sup>-3</sup>; DMPS: N < 750.000 cm<sup>-3</sup>), r.h.: 22%, total flow rate: 3.33 standard litre min<sup>-1</sup> (residence time in irradiated middle section: 290 sec).

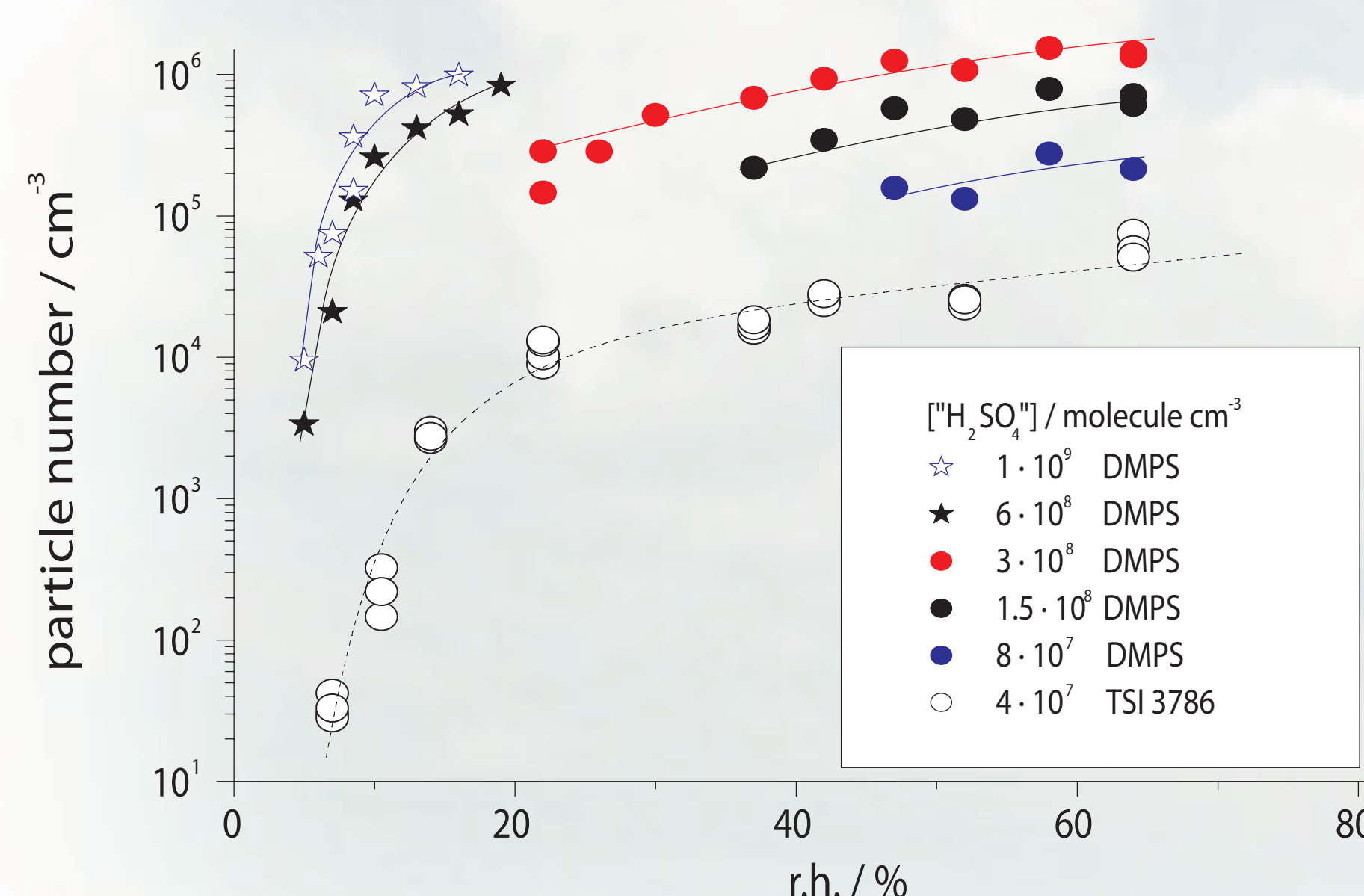


Figure 3: Total particle number as a function of r.h. for different "H<sub>2</sub>SO<sub>4</sub>" concentrations; DMPS: dp > 2.75 nm, total flow rate: 3.33 standard litre min<sup>-1</sup> (residence time in irradiated middle section: 290 sec).

## Experimental setup

Experiments have been performed in the atmospheric pressure flow-tube IfT-LFT (i.d. 8 cm; length 505 cm) at 293 +/- 0.5 K. The first tube section (56 cm) includes an inlet system for gas entrance (humidified air premixed with CO, SO<sub>2</sub>, and O<sub>3</sub>). The middle section (344 cm) is equipped with 8 UV lamps for a homogeneous irradiation. A non-irradiated end section (105 cm) holds the sampling outlet. Gas-phase analysis was carried out using analyzers for O<sub>3</sub> and SO<sub>2</sub> (Thermo Environmental Instruments: 49C and 43C), a butanol-based UCPC (TSI 3025), a H<sub>2</sub>O-based UCPC (TSI 3786) as well as pulse height CPC for integral particle measurements, and a differential mobility particle sizer (Vienna-type DMA with UCPC, TSI 3025) for monitoring of size distributions. The pulse height CPC (PH-CPC) comprises a TSI-3025A ultrafine CPC with modified optics and a multichannel analyzer, e.g. Weber et al. (1998), allowing particle detection for sizes well below 2 nm in mobility diameter (Sipilä et al., 2008). NH<sub>3</sub> concentrations in the carrier gas were measured before entering the flow tube as well as at the outlet by means of a trace gas monitor TGA 310 (OMNISENS) with a stated detection limit of 2.5 · 10<sup>9</sup> molecule cm<sup>-3</sup>.



Head of the flow tube: Non-irradiated first section with the gas inlets as well as the gas mixing devices

### Determination of ["H<sub>2</sub>SO<sub>4</sub>"]



The effective photolysis rate coefficient k<sub>4</sub> was determined in each experiment measuring the O<sub>3</sub> decay. With the knowledge of k<sub>4</sub> along with k<sub>5</sub> - k<sub>7</sub> taken from literature as well as the concentrations for O<sub>3</sub>, CO, and SO<sub>2</sub> the resulting "H<sub>2</sub>SO<sub>4</sub>" concentration in the tube was calculated solving the resulting differential equations. All experiments have been done in the absence of organics.

## Results in presence of NH<sub>3</sub>

### "Real" particle numbers

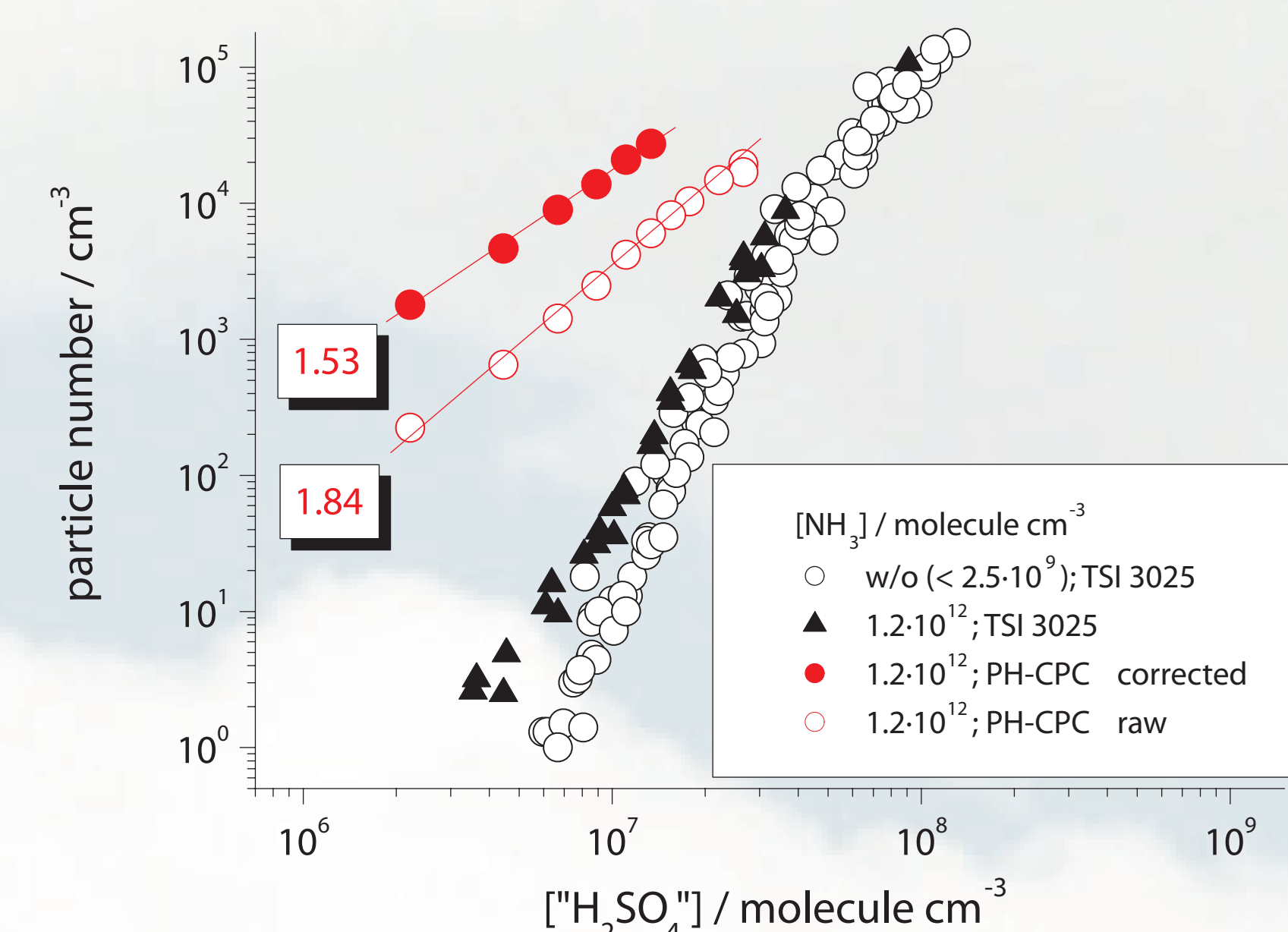


Figure 4a: Total particle numbers vs. "H<sub>2</sub>SO<sub>4</sub>" concentration in absence and presence of NH<sub>3</sub> using TSI 3025 and PH-CPC, r.h.: 22%, total flow rate: 3.33 standard litre min<sup>-1</sup> (residence time in irradiated middle section: 290 sec).

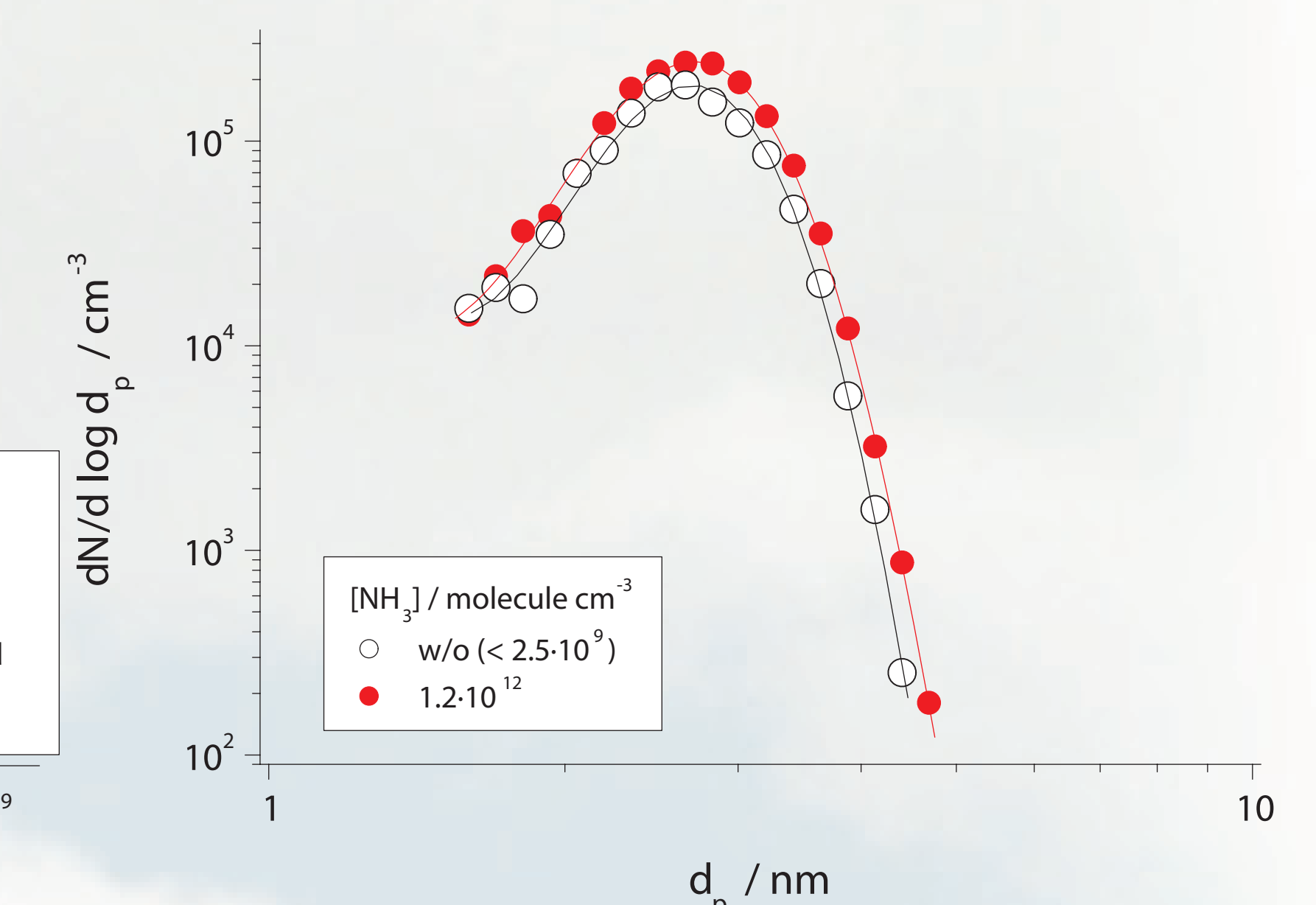


Figure 4b: Size distributions measured in absence and presence of NH<sub>3</sub> for a "H<sub>2</sub>SO<sub>4</sub>" concentration of 9·10<sup>7</sup> molecule cm<sup>-3</sup>, cf. conditions as given in figure 4a.

### Influence of relative humidity

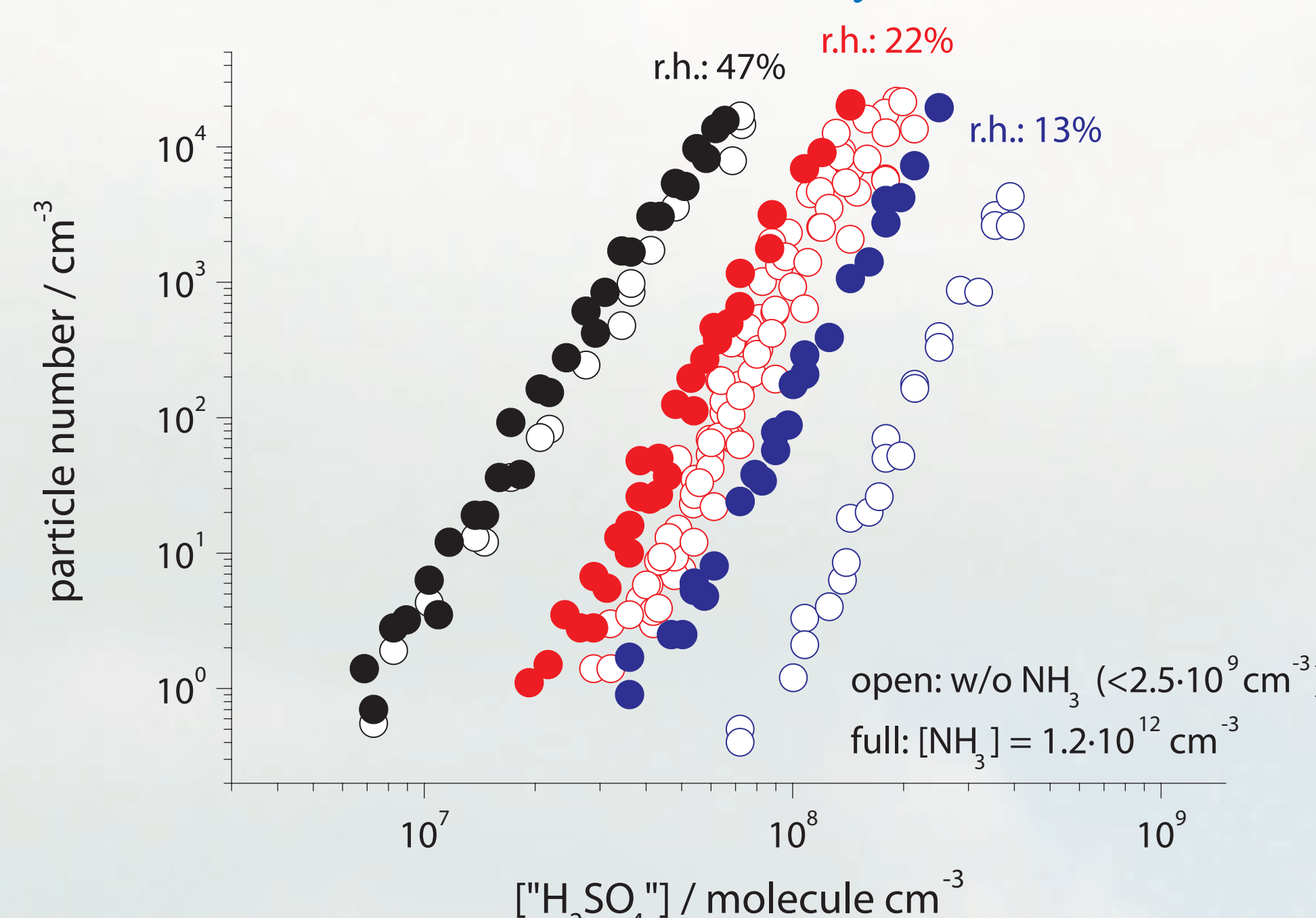
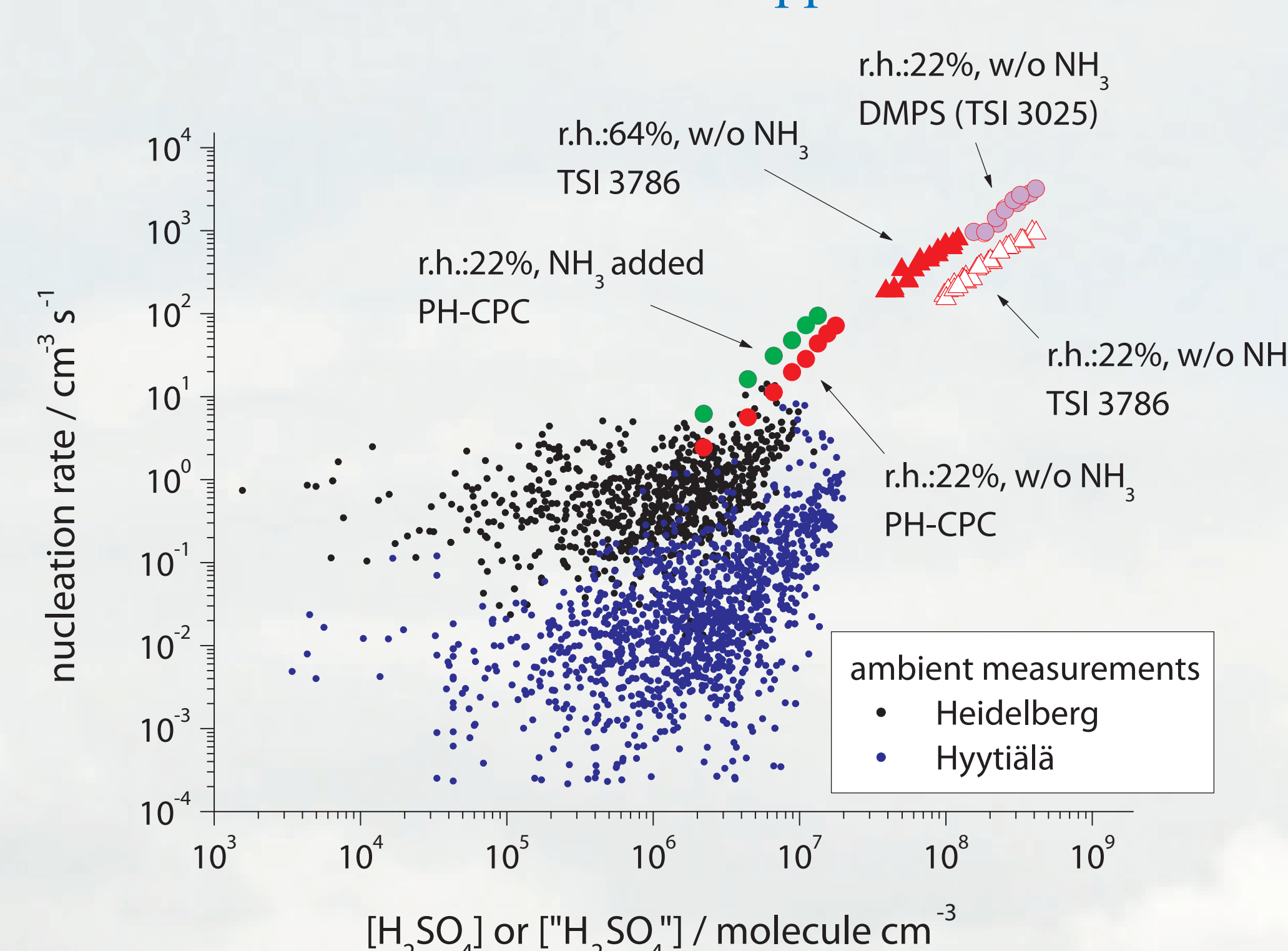


Figure 5: Total particle numbers vs. "H<sub>2</sub>SO<sub>4</sub>" concentration in absence of NH<sub>3</sub> (< 2.5·10<sup>9</sup> molecule cm<sup>-3</sup>) and presence of NH<sub>3</sub> (entrance: 1.2·10<sup>12</sup> molecule cm<sup>-3</sup>; outlet: 1.1·10<sup>12</sup> molecule cm<sup>-3</sup>) for three different relative humidities, total flow rate: 30 standard litre min<sup>-1</sup> (residence time in irradiated middle section: 32 sec) TSI 3025.

In agreement with former results, a distinct increase of total particle number with increasing r.h. was observed for the measurements performed in the absence of NH<sub>3</sub>. NH<sub>3</sub> addition increased the total particle number by about one order of magnitude at r.h. = 13%, by a factor of 3 - 5 at r.h. = 22% and by a factor of less than two at r.h. = 47%. From mechanistic point of view it is highly speculative to explain this r.h. dependence. A possible reason could be the competing steps i) reaction of SO<sub>3</sub> with 2 water molecules (or with the dimer) producing H<sub>2</sub>SO<sub>4</sub> and ii) reaction of SO<sub>3</sub> with NH<sub>3</sub> producing sulfamic acid. Sulfamic acid can significantly contribute to particle formation and growth.

## Application to the atmosphere



Laboratory: slope log N vs. log ["H<sub>2</sub>SO<sub>4</sub>"] = 1 - 2 (nearly independent on NH<sub>3</sub> addition)

Figure 6: Comparison of J vs. [H<sub>2</sub>SO<sub>4</sub>] or ["H<sub>2</sub>SO<sub>4</sub>"] data measured either in lower atmosphere or in laboratory. Ambient measurements from Heidelberg (28.2. - 3.4.2004) and from Hyytiälä (5.4. - 16.5.2005) were adopted from Riipinen et al. (2007). Ambient data can be described with a power-law dependence on H<sub>2</sub>SO<sub>4</sub> with typical powers of 1 - 2, cf. Riipinen et al. (2007).

### References:

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