

Parameterization of new particle formation starting from OH + SO₂



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Introduction

Simultaneous measurements of newly formed ultra-fine particles and H₂SO₄ in the lower troposphere reveal that new particle formation is strongly connected to the occurrence of H₂SO₄ with concentrations of about 10⁵ - 10⁷ molecule cm⁻³ and the production rate of new particles can be described by a power law equation for H₂SO₄ with an exponent in the range of 1 - 2 (Weber *et al.*, 1996, Kulmala *et al.*, 2006).

From our laboratory, using the reaction of OH radicals with SO₂ for "H₂SO₄" formation (Berndt *et al.*, 2005), experimental evidence for the formation of new particles was found for "H₂SO₄" concentrations of about 10⁷ molecule cm⁻³. Here, "H₂SO₄" stands for all products arising from the reaction of OH radicals with SO₂.

The analysis of integral number measurements by means of commercially available UCPCs revealed that measured slopes of log(N) vs. log(["H₂SO₄"]) were affected by the decreasing size-dependent counting efficiency of the UCPCs used for dp < 3nm leading to an overestimation of the slopes.

The aim of this study is to find out the optimal experimental conditions for the detection of the majority of nucleated particles with appropriate methods. Such data represent the basis for a reliable description of the overall process of nucleation in term of a power equation.

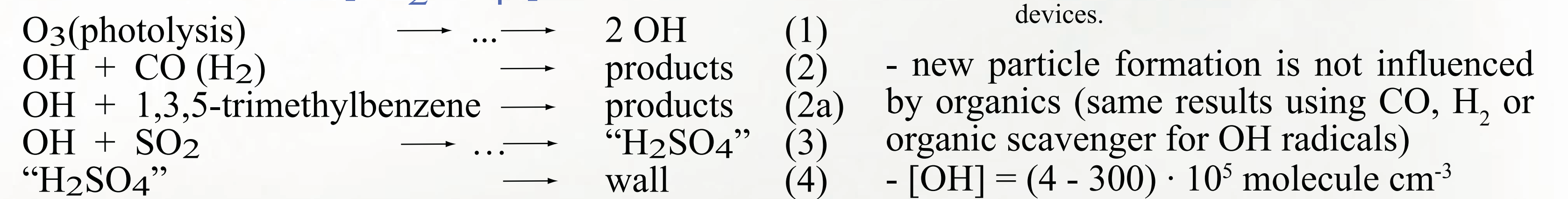
Experimental setup

Experiments have been performed in the atmospheric pressure flow-tube IfT-LFT (i.d. 8 cm; length 505 cm) at 293 +/- 0.5 K. Gas-phase analysis was carried out using analyzers for O₃ and SO₂ (Thermo Environmental Instruments: 49C and 43C) and CI-MS for H₂SO₄. Newly formed particles were detected by a butanol-based UCPC (TSI 3025), a H₂O-based UCPC (TSI 3786), a pulse-height CPC (Sipilä *et al.*, 2008) and a mixing-type CPC (Vanhanen *et al.*, 2009). NH₃ 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 · 10⁹ molecule cm⁻³.



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

Formation of ["H₂SO₄"]



CI-MS [H₂SO₄] vs. modeled ["H₂SO₄"]

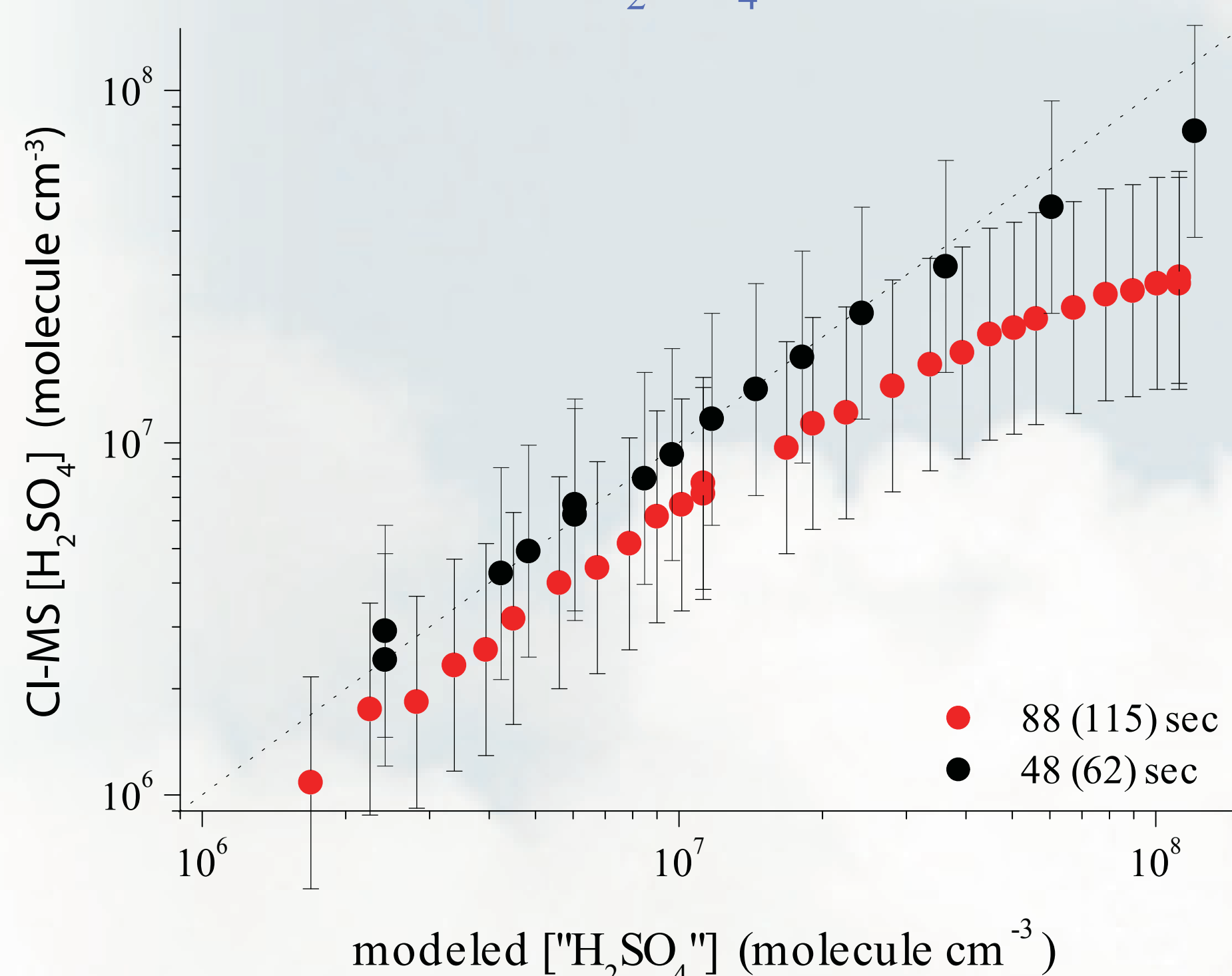


Figure 1: r.h. = 22%.

Comparison of measured H₂SO₄ with modeled "H₂SO₄" concentrations at the outlet of IfT-LFT for different residence times in the flow tube.

Influence of NH₃

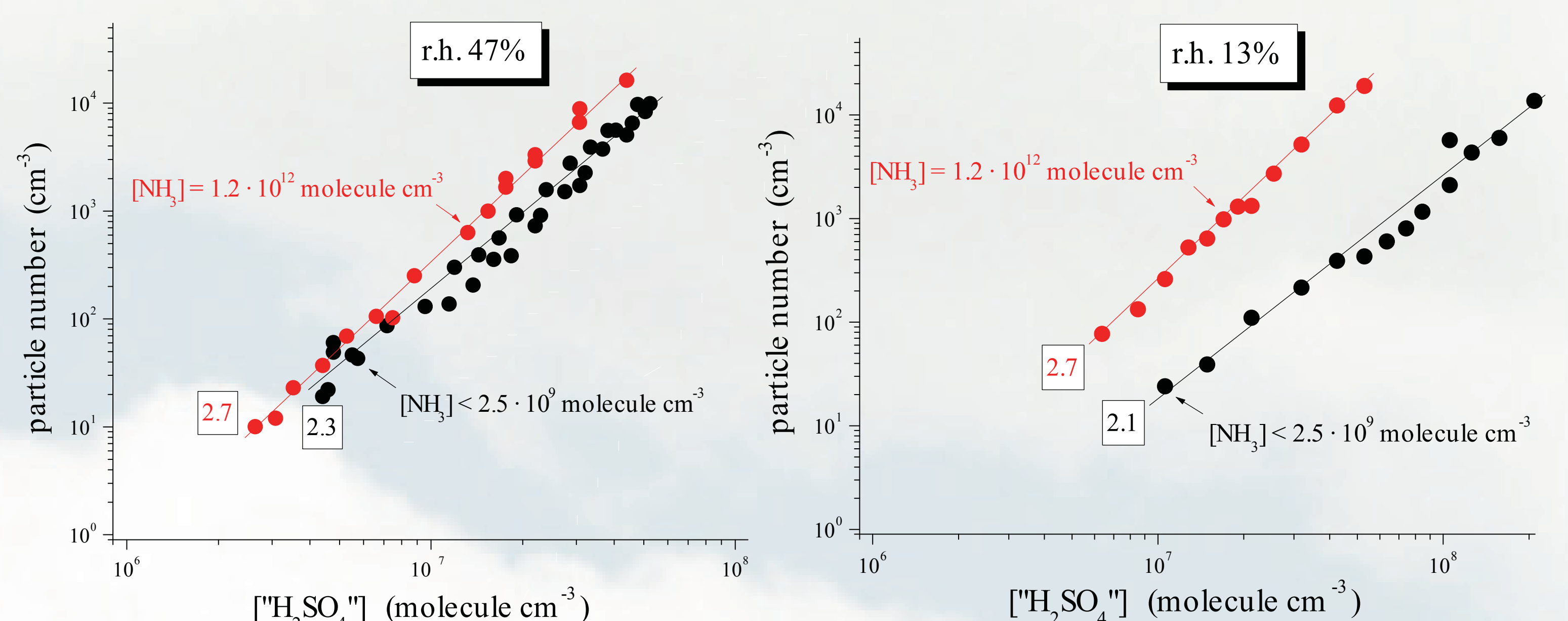


Figure 4a/b: Residence time of 32 (42) sec. Particle counting by means of PH-CPC (dp > 1.5 nm). Particle measurements have been performed after stabilisation of NH₃ concentration in the tube (measurement at inlet and outlet).

NH₃ is of less importance for nucleation using atmospheric conditions

CI-MS [H₂SO₄] vs. modeled ["H₂SO₄"] shows a clear curvature for relatively high H₂SO₄ concentrations. This behaviour is more pronounced in experiments with high residence time in the tube. Deviation from linearity can be explained roughly by an additional 2nd order process consuming H₂SO₄.

Importance of detection efficiency

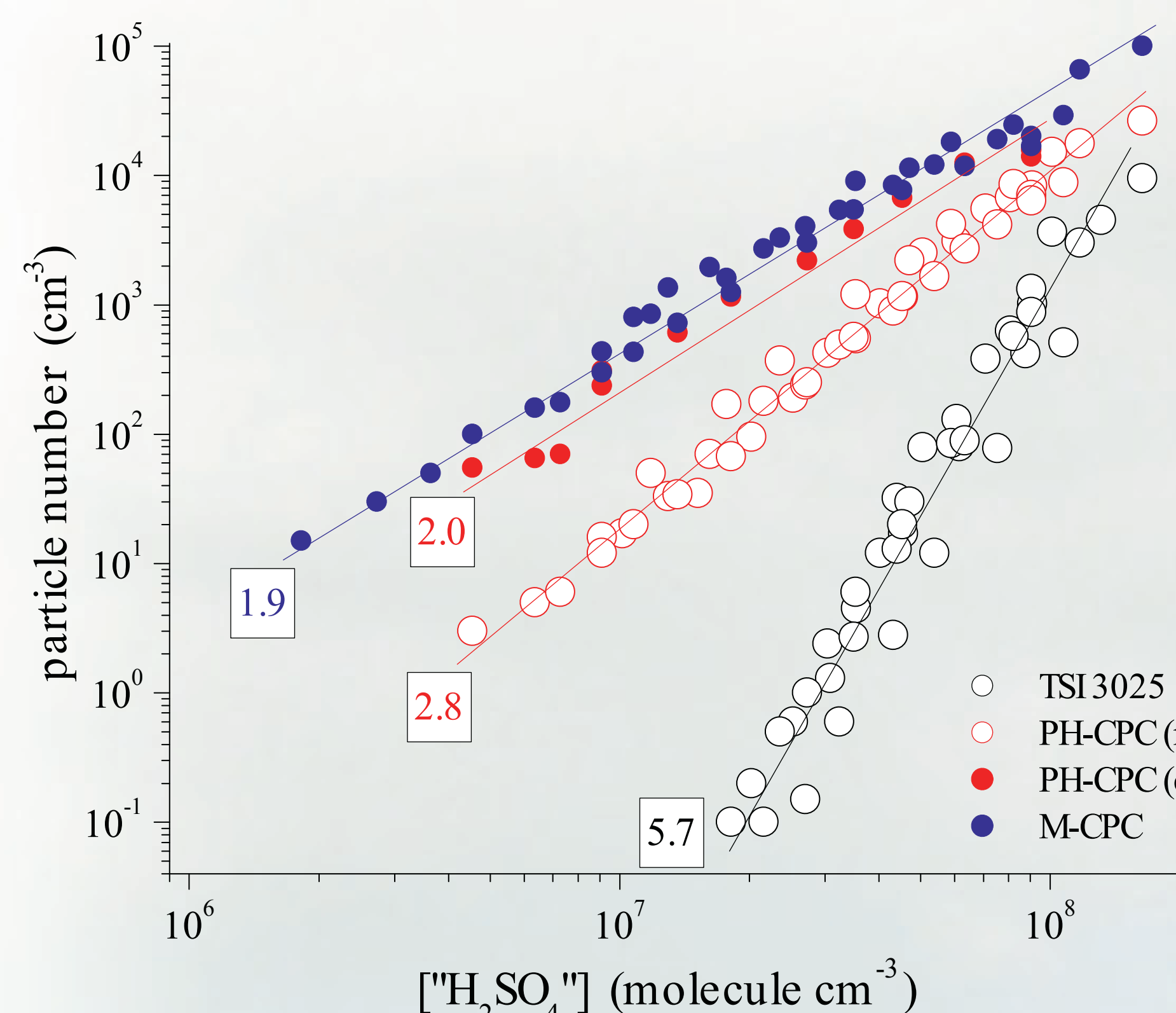


Figure 2: r.h.: 22%, residence time of 88 (115) sec.

Simultaneously measured particle numbers using TSI 3025, pulse-height CPC and mixing-type CPC. Given PH-CPC (corr.) numbers represent the slopes log(N) vs. log(["H₂SO₄"]).

Influence of water vapour

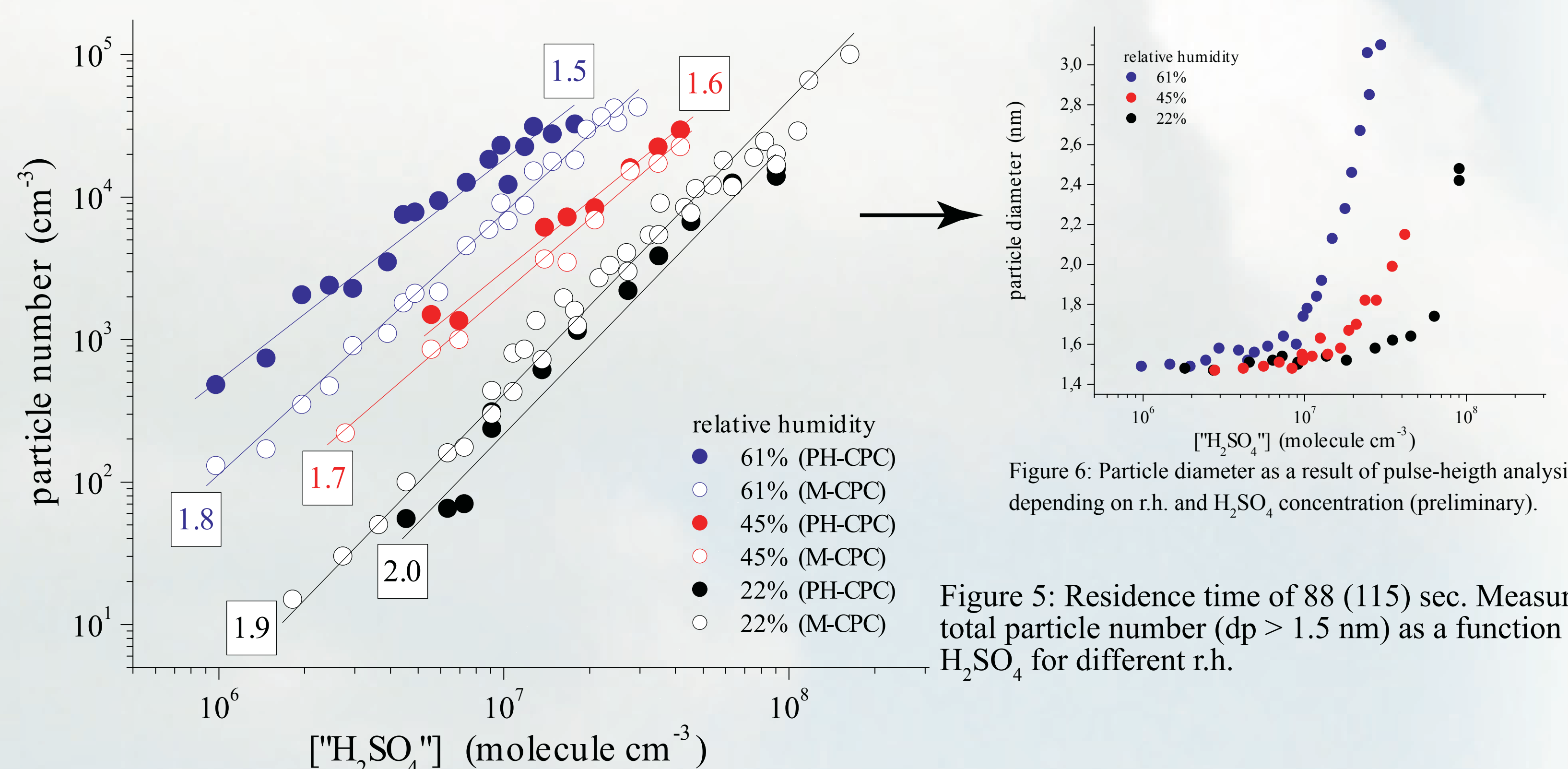


Figure 6: Particle diameter as a result of pulse-height analysis depending on r.h. and H₂SO₄ concentration (preliminary).

Figure 5: Residence time of 88 (115) sec. Measured total particle number (dp > 1.5 nm) as a function of H₂SO₄ for different r.h.

Threshold H₂SO₄ concentrations needed for nucleation as well as the slope log(N) vs. log(["H₂SO₄"]) are strongly dependent on the counting efficiency of the CPC used. "High sensitivity counters" have a cut-off size of about 1.5 nm.

Comparison with Young *et al.*, ACP, 2008

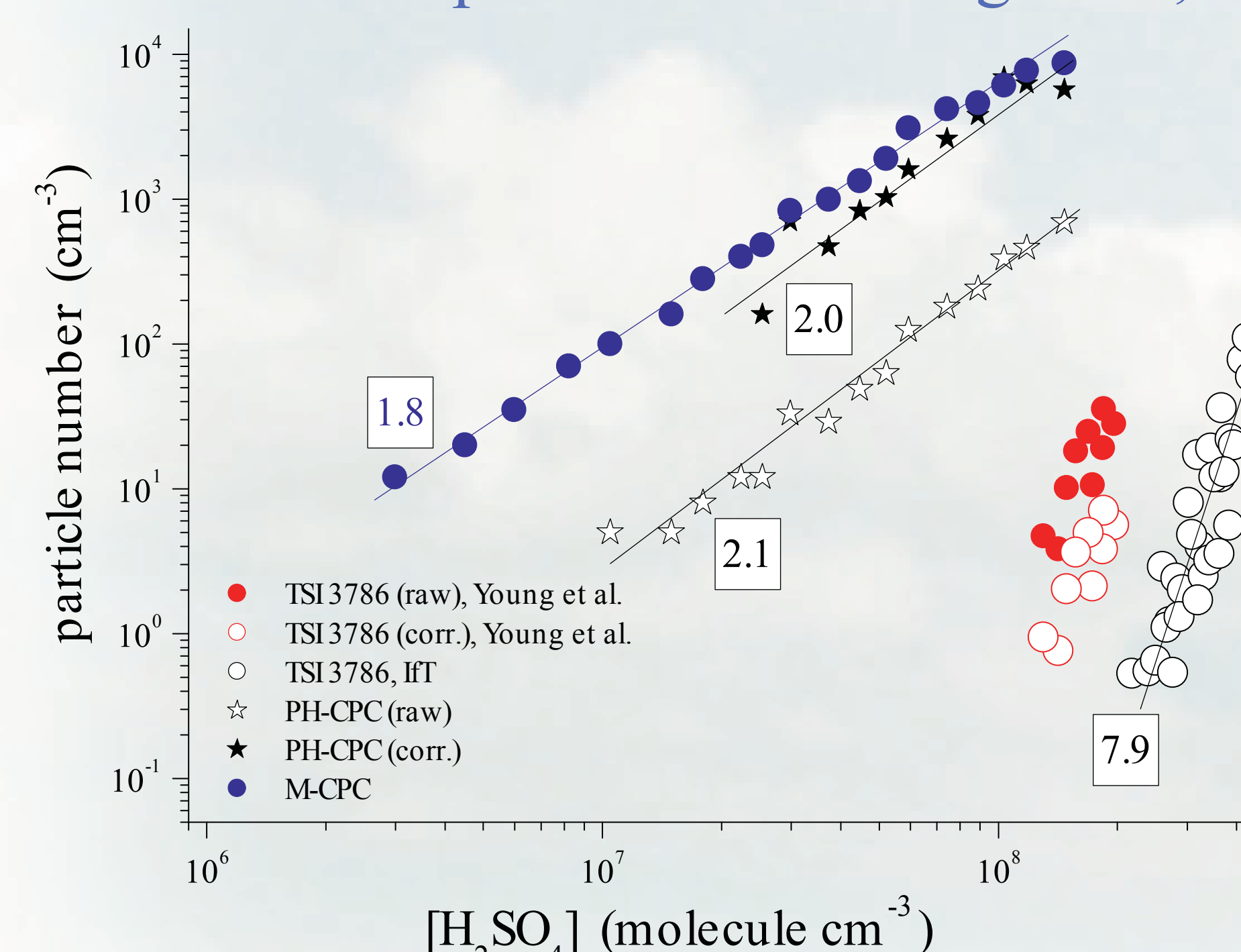


Figure 3: r.h.: 15%, residence time of 19 (25) sec.

Young *et al.* and IfT results using TSI 3786 are nearly the same. The difference is probably due to different H₂SO₄ profiles in the tube.

TSI 3786 clearly underestimates number of newly formed particles!

Parameterization and application to the atmosphere

Overall best fit (20°C, residence time: 88 sec, dp > 1.5 nm):

$$J = 1 \cdot 10^{-19} \text{ cm}^{-3} \text{ s}^{-1} ([\text{H}_2\text{SO}_4]/\text{cm}^{-3})^{1.86} ([\text{H}_2\text{O}]/10^{15} \text{ cm}^{-3})^{3.08}$$

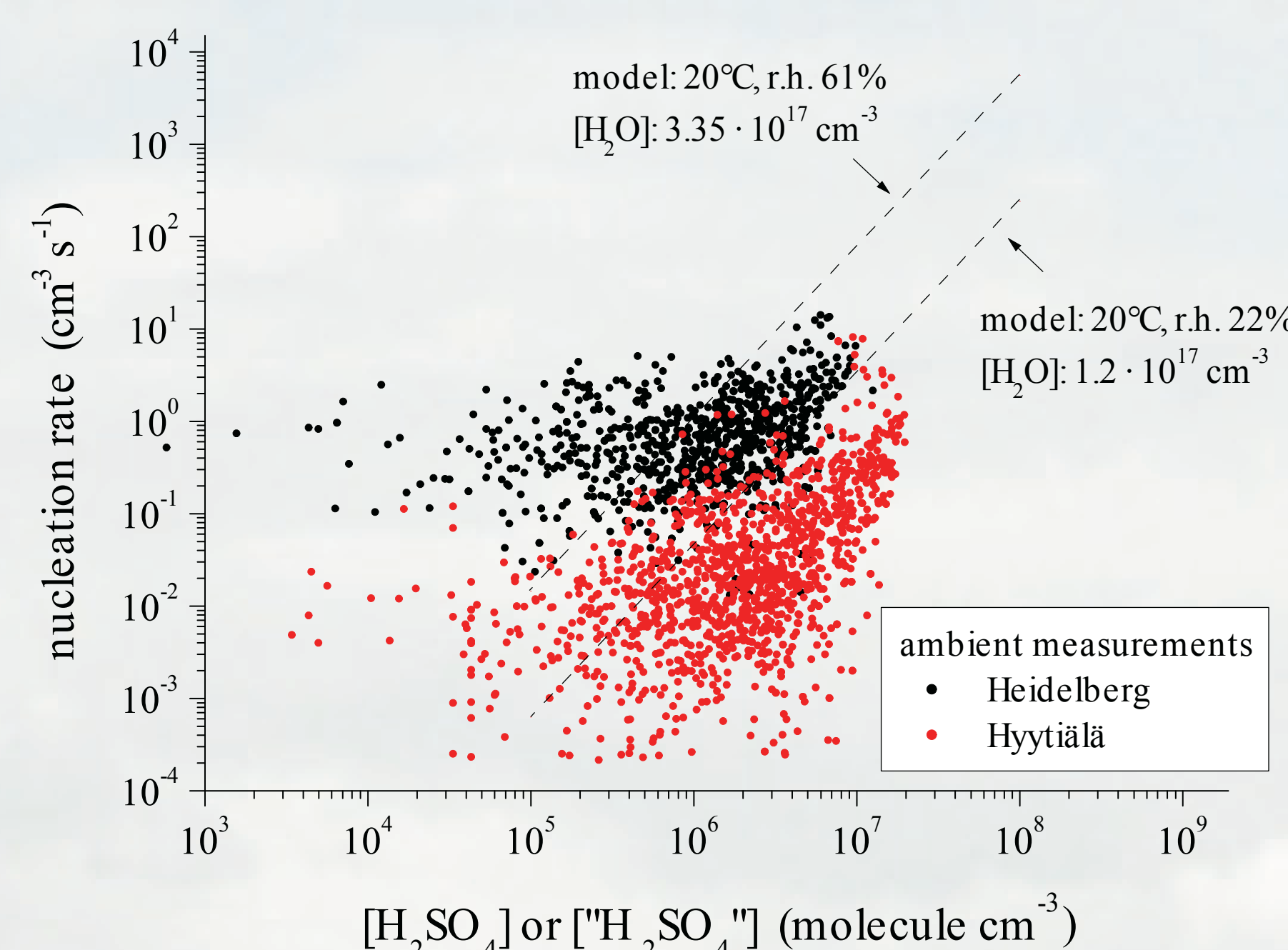


Figure 7: Comparison of J vs. [H₂SO₄] or ["H₂SO₄"] data measured either in lower atmosphere or in laboratory. Ambient measurements from Heidelberg (28.2. - 3.4.2004) and from Hyttialä (5.4. - 16.5.2005) were adopted from Riipinen *et al.* (2007). Ambient data can be described with a power-law dependence on H₂SO₄ with typical exponents of 1 - 2, cf. Riipinen *et al.* (2007).

References:

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