

Atmospheric particle formation from H₂SO₄/H₂O: An experimental study

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Motivation

Mass balances of the atmospheric aerosol have been used for more than 30 years to identify potential human influence on climate. Crucial processes, on the other hand, are controlled by the number of aerosol particles such as cloud formation, possible even certain health effects. The source processes controlling the number of secondary particles are much more complex and difficult to understand than those of the primary particles.

Sulfuric acid is a gas phase particle precursor that has been implicated for many years as a major atmospheric nucleating species. Laboratory data on binary sulfuric acid nucleation rates with water, however, are insufficient in explaining atmospheric nucleation. Ternary nucleation, involving ammonia, has been suggested as an explanation for observed particle nucleation in the atmosphere. To date, no direct experimental evidence for or against this ternary nucleation has been presented.

Here, results from laboratory experiments are reported which were conducted in the Institute for Tropospheric Research-Laminar Flow Tube (IfT-LFT).

Experimental

The experiments have been performed in an atmospheric pressure flow-tube (i.d. 8 cm; length 505 cm) at 293 ± 0.5 K (Fig. 1). The first tube section includes an inlet system for gas entrance. The middle section is equipped with 8 UV lamps for homogeneous irradiation of the tube. A non irradiated end section is attached with the sampling outlets. The analysis of the gas-phase species and the particles produced has been performed using on-line GC-FID with cryo-enrichment, a dew point sensor, an ozone analyzer, a ultra-fine particle counter for integral particle measurements, and a differential mobility particle sizer for monitoring of size distributions. The carrier gas consisted of 99 vol% N₂ (99.999999 %) and 1 vol% O₂ (99.9996 %) used for O₃ generation outside the flow tube. SO₂ was taken from a 1 ppmv calibration mixture. The total gas flow was 3.6 liter min⁻¹ resulting in a bulk residence time of 420 sec. NH₃ concentrations in the experiments were lower than atmospheric NH₃ mixing ratios over continents of 100 - 10000 pptv (1).



Fig. 1: The laminar flow tube, IfT-LFT

Results

H₂SO₄ from liquid reservoir

H₂SO₄ was taken from a liquid reservoir, passing a part of the carrier through a saturator and mixing the gas stream with humidified carrier gas at the entrance of the flow tube. Particle formation took place for H₂SO₄ concentrations above 10^{10} cm⁻³, see Fig 2. This is in line with the observations of other researchers using H₂SO₄ directly from a liquid reservoir (2-4). Especially, the r.h. dependent measurements were in reasonable agreement with the data given in (2). This experimental approach, however, showed insufficient reproducibility of the results as well as distinct memory effects probably caused by wall interactions of H₂SO₄ vapor in the transfer lines and in the mixing device.

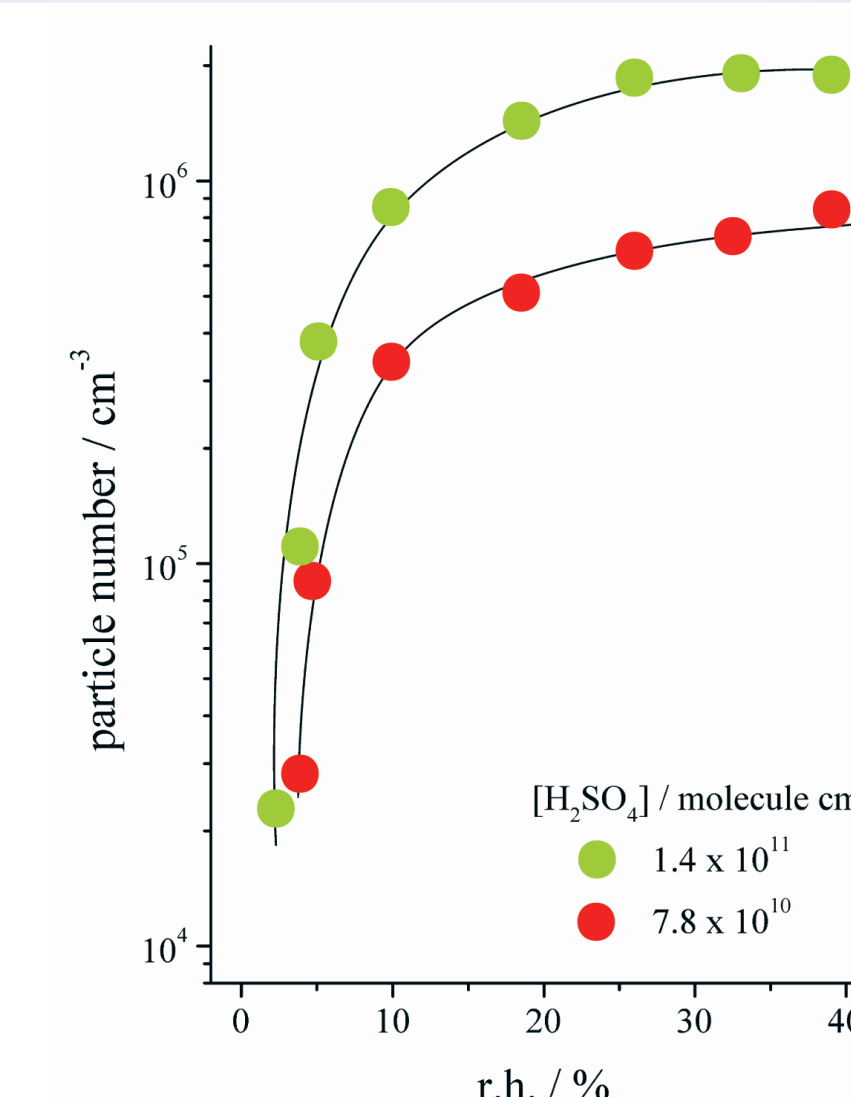


Fig. 2: Measured particle number for two different H₂SO₄ concentrations, residence time: 140 s. (H₂SO₄ from liquid reservoir)

In situ formation of H₂SO₄

As in the atmosphere, H₂SO₄ was produced in situ via the reaction of OH radicals with SO₂ in the presence of water vapor. OH radicals were formed from alkene ozonolysis or photolytically.

Ozonolysis

Experiments have been performed in the system O₃/alkene/SO₂ using α -pinene, trans-butene, and tetramethylethylene as model alkenes. Reactant concentration were kept close to atmospheric conditions. In contrast to the experiments using H₂SO₄ from a liquid reservoir formation of particles already started at H₂SO₄ concentrations of $2 \cdot 10^7$ cm⁻³ at r.h. = 28 % nearly independent of the alkene used for the ozonolysis (results not shown).

Photolysis

The pathways leading to H₂SO₄ are equal to those operating in the real atmosphere. O₃ is photolyzed forming O(¹D) atoms and the subsequent reaction with water vapor produces OH radicals. The OH radicals attack SO₂ and after reaction with O₂ the adduct HOSO₂ yields SO₃ and HO₂. The reaction of SO₃ with water vapor finally yields H₂SO₄. A hydrocarbon was added for OH radical titration. For the determination of the H₂SO₄ concentration in the flow tube, a simple kinetic model was used as follows:

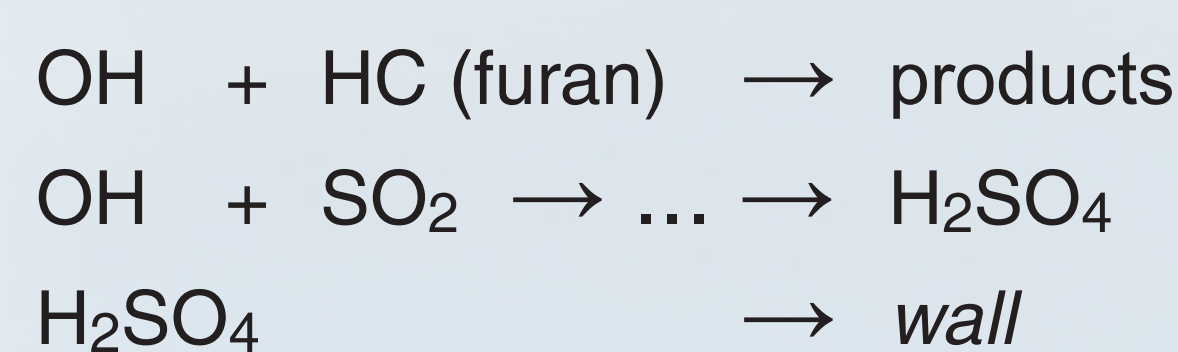


Fig. 3 shows the particles recorded for different conditions. Only in the presence of all reactants needed for H₂SO₄ formation, including UV radiation for OH radical production, formation of new particles is visible.

In Fig. 4 experimentally observed particle numbers for calculated H₂SO₄ concentration are plotted using different hydrocarbons for OH radical titration. The agreement of the results with those from ozonolysis is good.

For a fixed H₂SO₄ concentration the number of new particles increased for increasing r.h., see Fig. 5. The increase is much more pronounced for the lowest r.h.. At r.h. = 11 %, about $4 \cdot 10^7$ cm⁻³ of H₂SO₄ are needed for producing detectable numbers of particles.

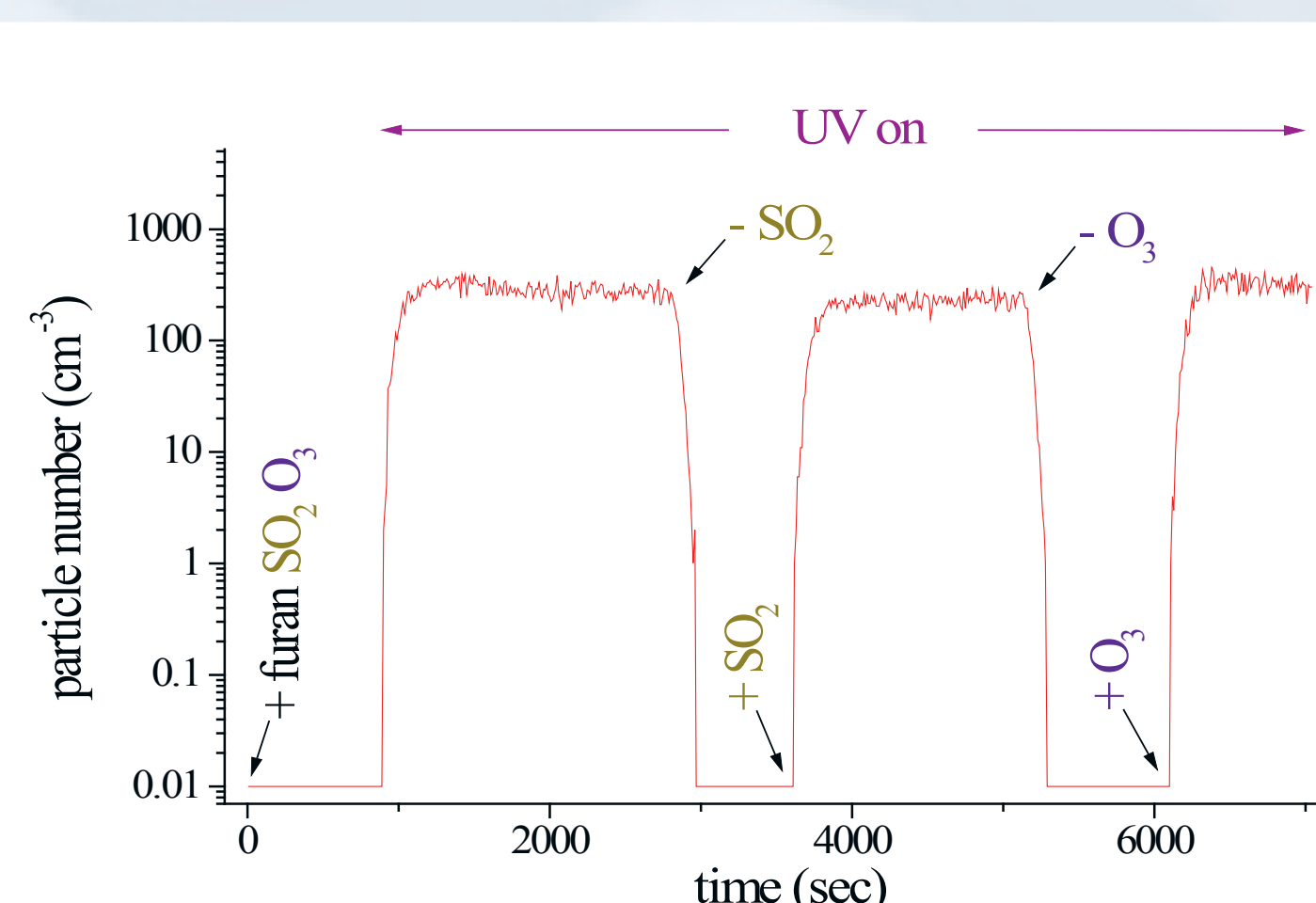


Fig. 3: Measured particles from a typical experiment for different trace gas additions; r.h. = 11 %. If needed, initial concentrations were: $[\text{O}_3] = 4.6 \cdot 10^{11}$ cm⁻³, $[\text{SO}_2] = 8.1 \cdot 10^{10}$ cm⁻³, $[\text{furan}] = 1.1 \cdot 10^{12}$ cm⁻³.

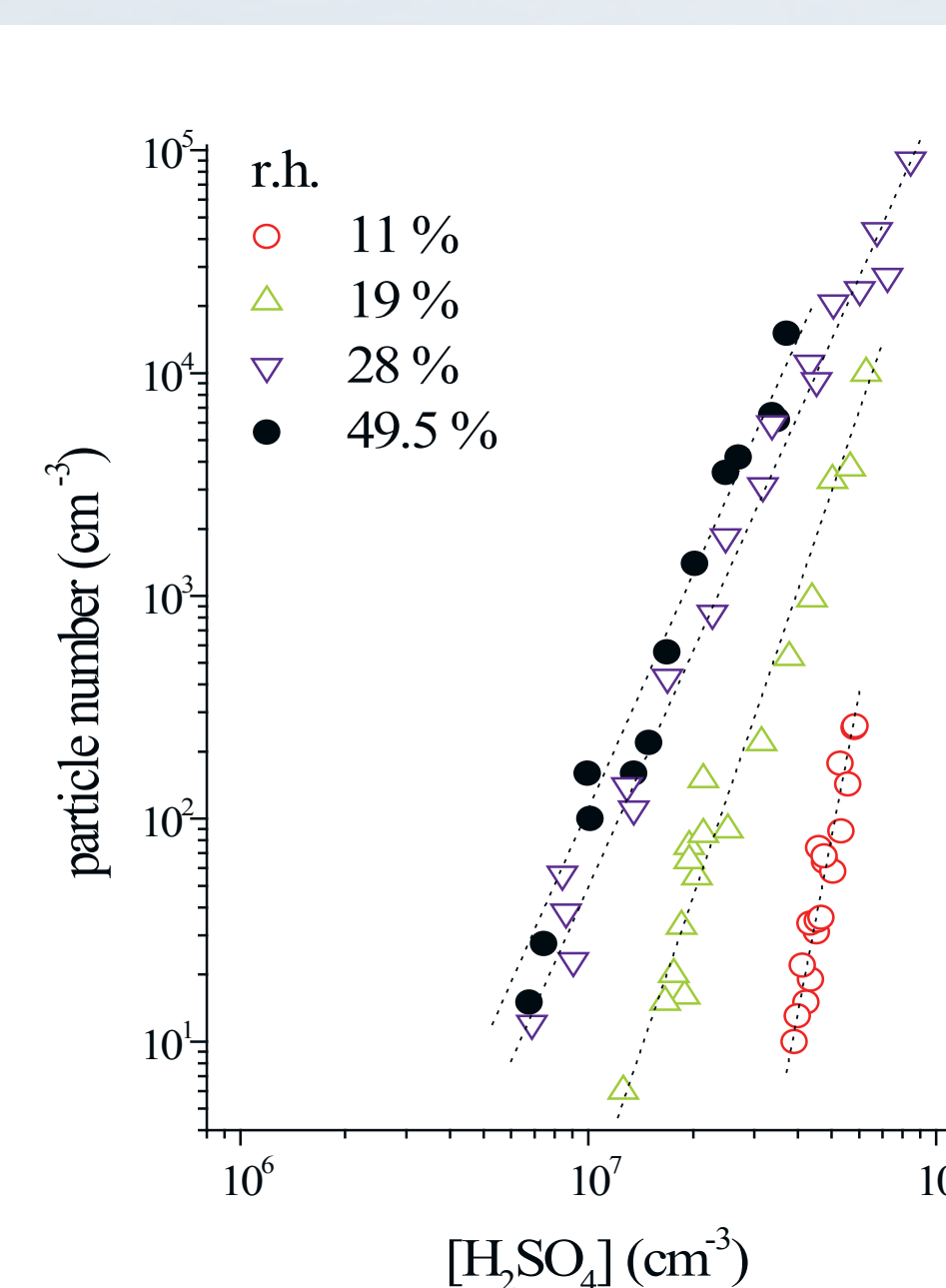


Fig. 5: Number of newly formed particles for r.h. = 11, 19, 28, and 49.5 % using furan for OH radical titration

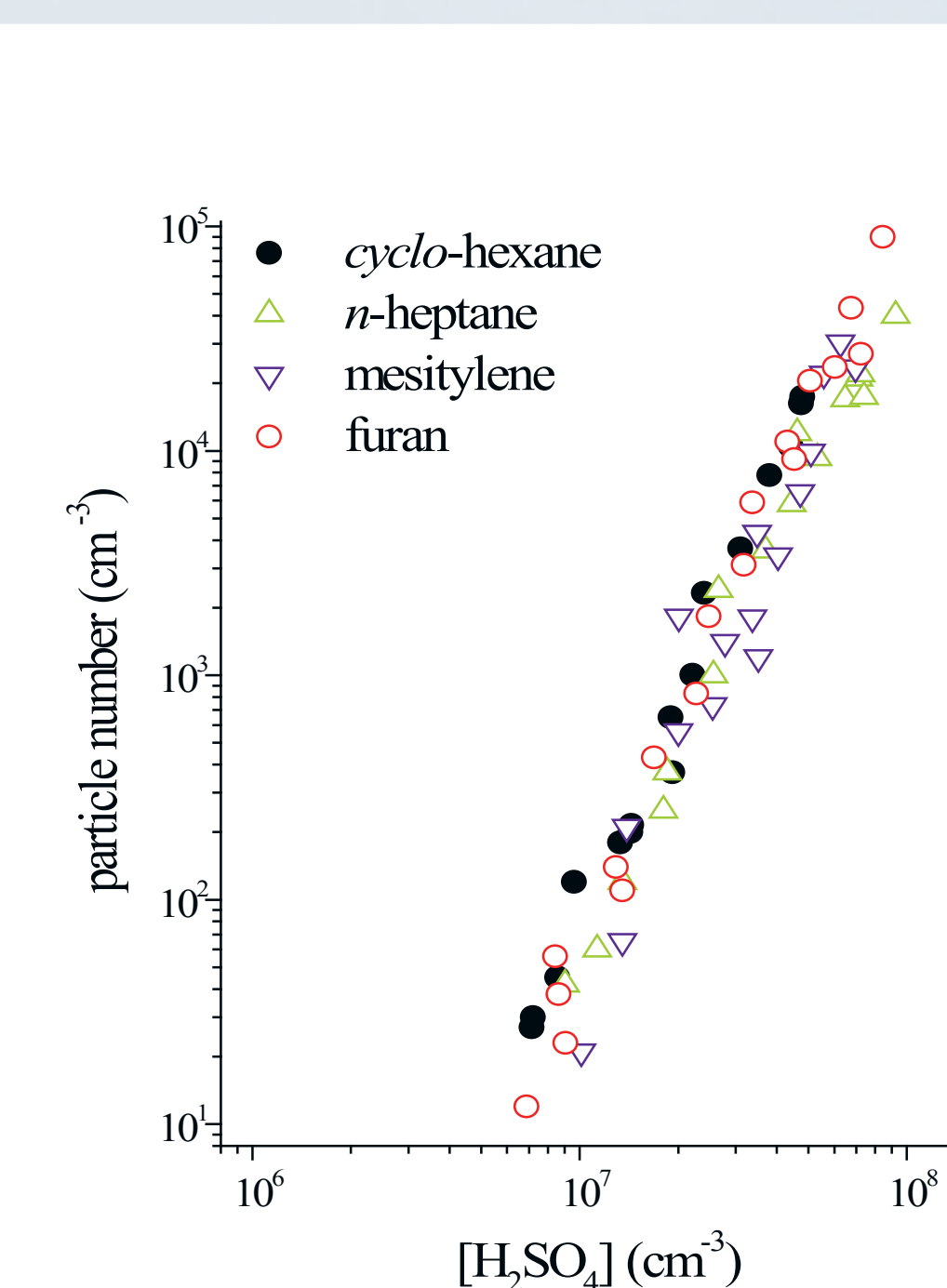


Fig. 4: Observed particle numbers for different hydrocarbons for OH radical titration; r.h. = 28%. Initial concentrations were: $[\text{O}_3] = (4.4-9.8) \cdot 10^{11}$ cm⁻³, $[\text{SO}_2] = (5.9-81) \cdot 10^9$ cm⁻³, $[\text{HC}] = (1.1-11) \cdot 10^{12}$ cm⁻³.

Summary

For the first time it is shown under laboratory conditions that in the presence of water vapor and for NH₃ concentrations lower than in the atmosphere, particle formation occurs at atmospheric H₂SO₄ concentration levels. Currently available binary nucleation theories are not able to describe this findings. A further step to understand atmospheric new particle formation has been taken which opens the possibility for a simpler and more accurate quantification of atmospheric nucleation rates.

References

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