

# Simultaneous measurements of gaseous sulfuric acid and SO<sub>2</sub> in the upper troposphere and lower stratosphere: Implications for the formation and growth of aerosol particles



Karl-Heinz Wohlfrom, Joachim Curtius, Berko Sierau, Johannes Schneider and Frank Arnold

Max-Planck-Institut für Nuclear Physics, Atmospheric Physics Division, PO Box 103980, D-69029 Heidelberg, Germany; email: k.wohlfrom@mpi-hd.mpg.de

## Introduction

Due to the low vapor pressures of H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O-condensates gaseous sulfuric acid plays an important role for the formation and growth of aerosol particles in the atmosphere. Measurements of the concentration of gaseous sulfuric acid are of considerable current interest to improve our understanding of the aerosol and its impact on the atmosphere and climate.

Gaseous sulfuric acid is produced photochemically in the atmosphere from its precursor gas SO<sub>2</sub> by a reaction sequence which is initiated by the reaction of SO<sub>2</sub> with OH radicals. Direct sources of SO<sub>2</sub> are mostly anthropogenic emissions, and it is also produced from oxidation of organic sulfur species in the atmosphere (see figure 1).

Measurements reported here were carried out on board the Dutch Cessna Citation 2 research aircraft within the framework of the STREAM project over Central Europe in winter 1995, and within the ACE2 campaign over Tenerife in July 1997. Simultaneous in situ IMRMS-measurements (Ion Molecule Reaction Mass Spectrometry) of gaseous sulfuric acid (H<sub>2</sub>SO<sub>4(g)</sub>) and sulfur dioxide (SO<sub>2</sub>) as well as of the trace gases HNO<sub>3</sub> and acetone which may play an indirect role in the formation and growth of aerosols at altitudes between 8 and 13 km are reported. For the measurements of SO<sub>2</sub>, HNO<sub>3</sub>, acetone, and H<sub>2</sub>SO<sub>4(g)</sub> active and passive IMRMS techniques were used as described in Möhler and Arnold, 1992, and Arnold et al., 1997.

Figure 2: A simplified schematics of the oxidation and subsequent gas-to-particle conversion of atmospheric sulfur species

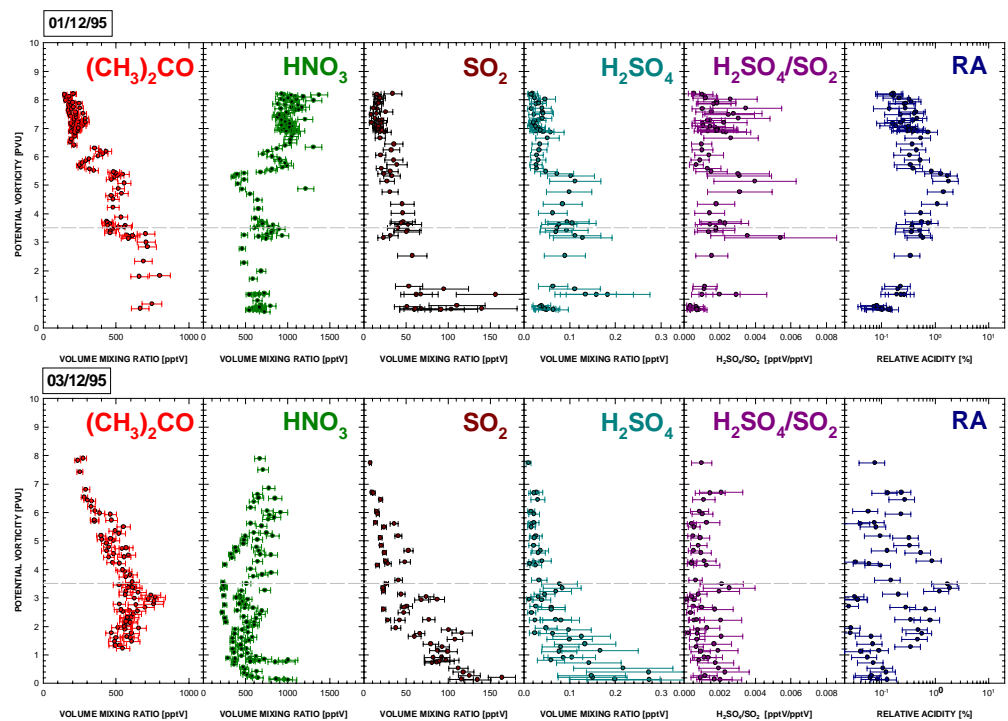
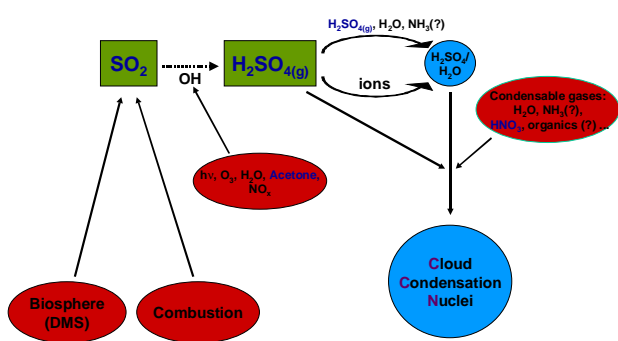


Figure 2: Aircraft borne measurements of acetone, HNO<sub>3</sub>, SO<sub>2</sub> and H<sub>2</sub>SO<sub>4(g)</sub> over middle Europe made during two flights. Potential vorticity (PV) which is a good marker for the tropopause was chosen as ordinate. Typically the tropopause is located around PV=3.5 PVU. Relative acidity is defined as vapor pressure of H<sub>2</sub>SO<sub>4(g)</sub> over a flat surface of 98% sulfuric acid.

## Measurements in the upper troposphere and lower stratosphere over middle Europe

Two flights were performed in December 1995 within the framework of the STREAM project. These flights took place over the North Sea on December 1 and 3, 1995, in the early afternoon. Vertical profiles of the measured volume mixing ratios of acetone, HNO<sub>3</sub>, SO<sub>2</sub> and H<sub>2</sub>SO<sub>4(g)</sub> can be seen in figure 2. As vertical coordinate Potential Vorticity (PV) calculated from ECMWF analyses by KNMI, Netherlands, was chosen instead of pressure altitude. PV is a good marker for the tropopause which is considered to be around 3.5 PVU. Since the altitude as well as the structure of the tropopause was very different on both days the choice of PV facilitates a comparison.

Observed ratios H<sub>2</sub>SO<sub>4(g)</sub>/SO<sub>2</sub> scatter around 1.5 · 10<sup>-3</sup> which suggests that H<sub>2</sub>SO<sub>4(g)</sub> is in fact formed from

SO<sub>2</sub> and that H<sub>2</sub>SO<sub>4(g)</sub>-loss (mostly via condensation on aerosol particles) leads to a H<sub>2</sub>SO<sub>4(g)</sub> - lifetime of τ(H<sub>2</sub>SO<sub>4(g)</sub>)=10<sup>12</sup> cm<sup>3</sup>s/(OH) · H<sub>2</sub>SO<sub>4(g)</sub>/SO<sub>2</sub> = 25 minutes for (OH)=10<sup>6</sup> cm<sup>3</sup>s<sup>-1</sup>. The measured partial pressure of gaseous sulfuric acid is high enough to reach saturation with respect to a flat surface of 98 % liquid sulfuric acid (this is expressed in the right panels of figure 2 in terms of relative acidity which is defined analogous to relative humidity). Because of the much lower saturation vapor pressure of a more diluted sulfuric acid-water solution this indicates that the formation of sulfuric acid-water aerosol particles via homogeneous bi-molecular H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O nucleation is may take place in the upper troposphere.

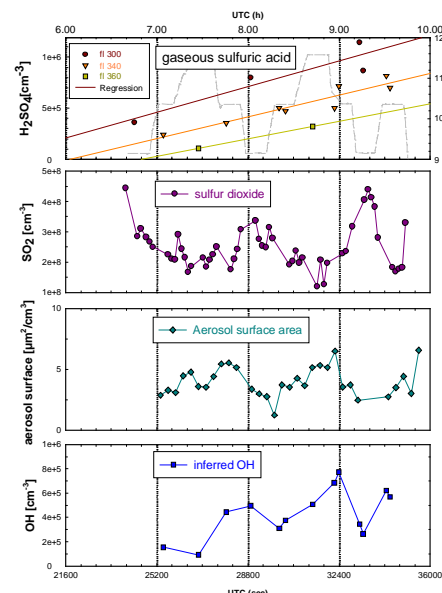
## Sulfur dioxide and gaseous sulfuric acid at sunrise

The SO<sub>2</sub> data obtained during six measurement flights of the ACE 2 campaign in July 1997 in the vicinity of Tenerife reveal rather low values between 10 and 200 pptv at altitudes between 1 and 12 km. On July 13 a measurement flight was performed starting in the early morning to monitor the evolution of particles and aerosol precursor gases with changing solar elevation.

Figure 3 shows the temporal evolution of gaseous sulfuric acid for the three different flight levels encountered sequentially (top panel). On the three altitude levels H<sub>2</sub>SO<sub>4(g)</sub> increases as the sun rises towards the zenith. This is most probably due to the production of H<sub>2</sub>SO<sub>4(g)</sub> from SO<sub>2</sub> via OH whose concentration increases with increasing solar elevation.

Since the loss of gaseous sulfuric acid molecules is determined by condensation onto particles knowledge of the preexisting particle surface areas can be used to calculate the number densities of OH radicals necessary to obtain a given number density of gaseous sulfuric acid when a stationary state is reached. The result of such a

Figure 3: H<sub>2</sub>SO<sub>4(g)</sub>, SO<sub>2</sub>, and aerosol particle surface area density measured over Tenerife shortly after sunrise which took place around 5.0 UTC. At each flight level gaseous sulfuric acid number densities increase with solar elevation which is expected since OH increases.



calculation is shown in figure 6 where aerosol surface densities measured by the University of Stockholm have been used along with our H<sub>2</sub>SO<sub>4(g)</sub> and SO<sub>2</sub> measurements to infer OH concentrations.

## Summary and conclusions

Simultaneous measurements of SO<sub>2</sub> and H<sub>2</sub>SO<sub>4(g)</sub> were made in the upper troposphere and lower stratosphere. Volume mixing ratios range between 10 and 250 pptv (SO<sub>2</sub>), and between 0.02 and 0.3 pptv (H<sub>2</sub>SO<sub>4(g)</sub>). A positive correlation of H<sub>2</sub>SO<sub>4(g)</sub> and SO<sub>2</sub> was observed which is consistent with the view that gaseous sulfuric acid is produced in the gas phase via reaction of SO<sub>2</sub> with OH and removed mostly by condensation onto aerosol surfaces. Whether particles can be produced by homogeneous bimolecular nucleation of H<sub>2</sub>SO<sub>4(g)</sub> and H<sub>2</sub>O is also dependent on other parameters. It requires small preexisting particle surfaces and large (SO<sub>2</sub>)·(OH). Our measured (H<sub>2</sub>SO<sub>4(g)</sub>) suggests that homogeneous nucleation may take place occasionally.

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## References

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