EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

CERN-SPSC-2010-013
SPSC-SR-061
April 7, 2010

2009 PROGRESS REPORT ON PS215/CLOUD

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CLOUD Collaboration

1 INTRODUCTION

Aerosols exert an important influence on the climate, both directly by scattering and absorbing radiation, and indirectly by their effect on clouds. Although the sources of aerosols over large parts of the atmosphere are poorly known, nucleation of trace vapours is thought to be the major source in remote, unpolluted regions. Experimental and theoretical studies suggest that atmospheric ions, produced by galactic cosmic rays, may under certain circumstances influence aerosol-cloud processes. The CLOUD experiment [CLOUD Collaboration (2000, 2004, 2006)] aims to study under controlled conditions the effects of cosmic rays on all cloud processes: on the creation of aerosols by trace condensable vapours, on aerosol growth up to CCN sizes, on the activation of CCN into cloud droplets, on cloud microphysical interactions, and finally on the creation and dynamics of ice particles in clouds.

The first CLOUD measurements were carried out in a pilot experiment in October–November 2006, shortly after approval of the experiment by the Research Board. The pilot experiment gave a first glimpse of ion-induced nucleation and, more importantly, provided invaluable technical input for the CLOUD design [Duplissy *et al.* (2010)].

After a three-year period for design and construction, CLOUD was installed in the T11 zone of the East Hall during the second half of 2009 (Figs. 1 and 2). The installation was completed by 14 November and the experiment began operation. A special two-week extension of PS operations for CLOUD was granted by the Research Board and SPSC chair up to 7 December, 2009. This enabled CLOUD to complete a very successful first run studying the nucleation of trace sulphuric acid, which is thought to be the primary vapour responsible for new aerosol production in the atmosphere.

Fig. 1: View of CLOUD in the East Hall T11 zone during the November–December 2009 run (refer also to the schematic diagram of the experimental setup, shown in Fig. 2). The chamber is surrounded by a thermal housing through which air is circulated via the duct seen to the left. The temperature of the air is adjusted and precisely controlled by a 20 kW thermo-regulator unit seen at the far left. The pion beam, with large transverse dimensions of around 1.5×1.5 m^2, enters the chamber from the right, after passing through a counter hodoscope. The chamber is surrounded by analysing instruments which continuously extract small samples via probes that penetrate 50 cm into the chamber volume (26.1 m^3) in the mid plane. The fibre optic light guides of the UV system can be seen passing up the outside of the thermal housing, slightly to the left of centre. The white box located on the shielding wall is monitoring the galactic cosmic ray intensity in the East Hall. Additional CLOUD equipment such as the cryogenic ultrapure air supply, gas system and air circulation system, is located underneath the platform or else outside the building and is therefore not in view.

2 CLOUD DETECTOR

2.1 CLOUD facility

The CLOUD facility is shown in Figs. 1 and 2. Briefly, it comprises:

CLOUD chamber: The chamber is a 3m-diameter (26.1 m^3) electro-polished 316L stainless-steel cylinder operating at 1–1.3 bar pressure.

Ultra-violet light system: This is provided by a quartz fibre-optic system illuminated by a Hg/Xe UV light source with electrically-controlled aperture. The UV light (250-400 nm) is introduced into the chamber via 240 vacuum-tight optical fibre feedthroughs installed on top of the chamber (Fig. 3). The system provides a fairly uniform column of light inside the chamber of up to 25 mW/m^2 and is used for inducing photolytic reactions in the trace gases.

Field cage: An internal electric field is provided by two transparent electrodes at voltages of up to

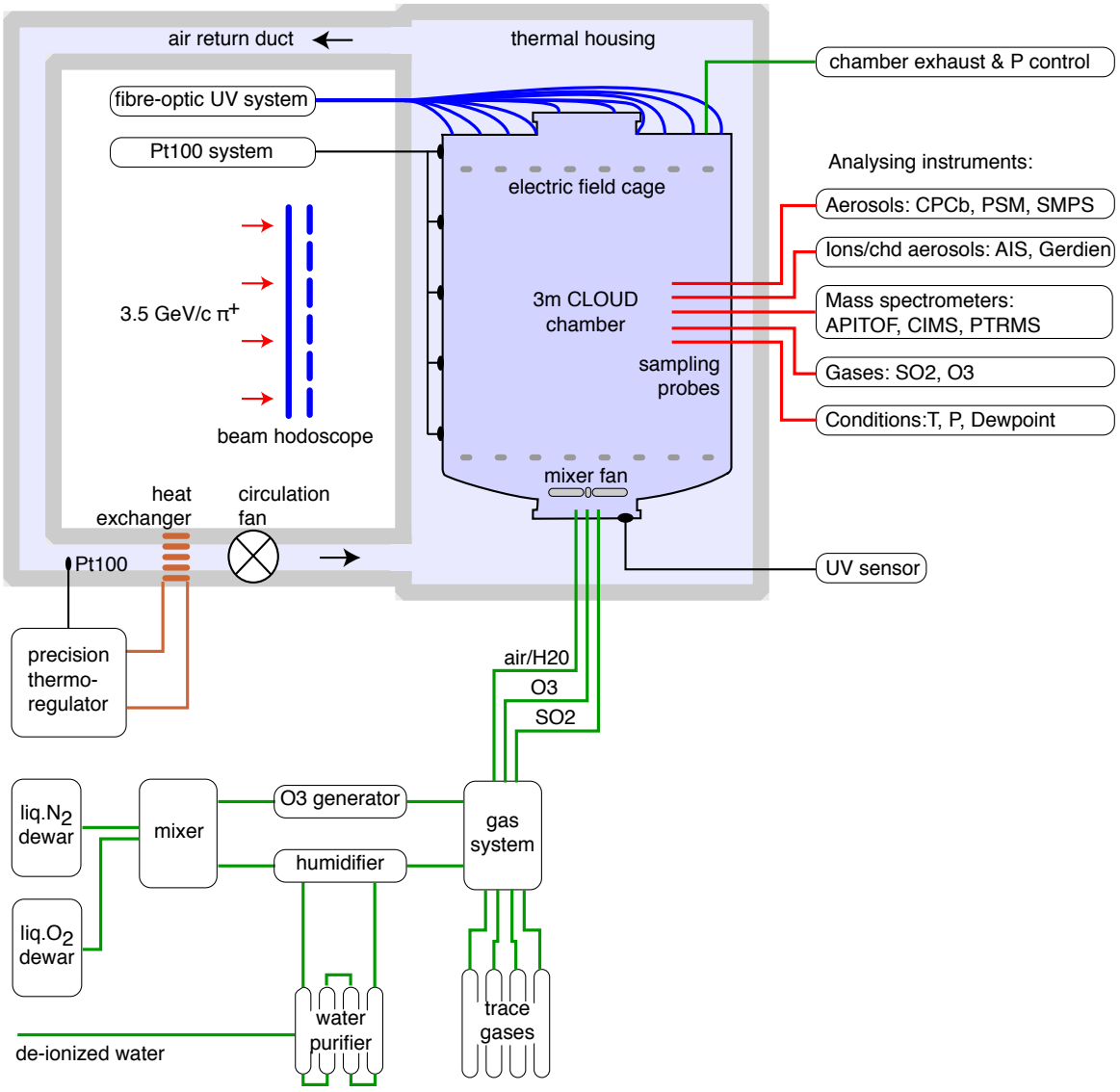

Fig. 2: Schematic diagram of the CLOUD experiment in 2009.

+50 kV and -50 kV, respectively. The electric field is used to sweep small ions and charged aerosols from the chamber when the beam is off (Figs. 3 and 5).

Internal mixing fan: A magnetically-coupled fan of diameter 60 cm ensures that the fresh make-up gas is rapidly mixed on entering the chamber (Figs. 4 and 5).

Thermal system: The chamber is surrounded by an insulated thermal housing. The temperature is controlled by precisely regulating the temperature of the air circulating in the space between the chamber and the thermal housing. Experimental runs can be performed at stable temperatures (near 0.01°C stability) between 40°C and -30°C (to be extended to -90°C in 2011). This will eventually allow the chamber to be operated at any temperature from the warmest regions of the troposphere to the coldest regions of the polar stratosphere. In addition, the chamber can be raised to 100°C for cleaning.

Gas system: Ultra-pure air is obtained from the evaporation of cryogenic liquid N_2 and liquid O_2, mixed

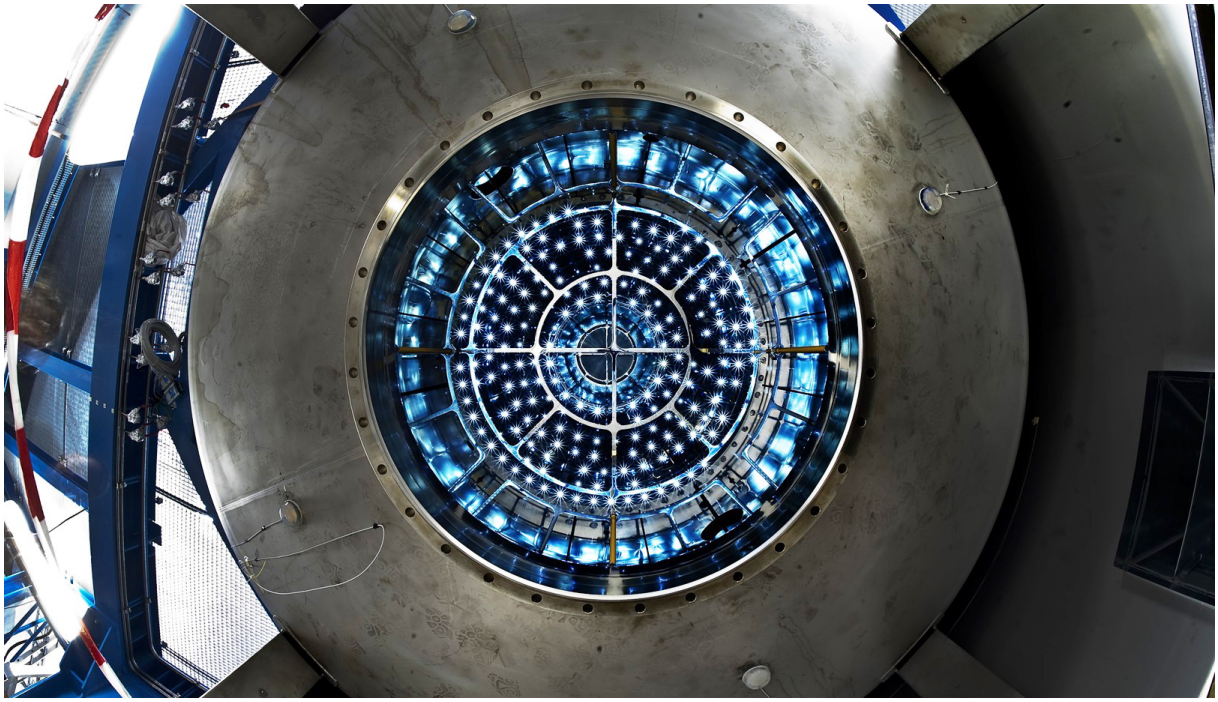

Fig. 3: Fisheye image looking up into the CLOUD chamber in November 2009, before installing the lower manhole cover and final sections of the thermal housing. The image shows the fibre optic UV illumination from 240 individual optical feedthroughs, with reflections off the electropolished interior of the chamber, the field cage electrodes and standoffs, and four of the 50 external Pt100 thermometers. The chamber is maintained at a temperature stability of around 0.01°C by a surrounding thermal housing through which precisely thermally-controlled air is circulated (Fig. 1); the duct on the right hand side of the image marks the entry point of the air at the bottom of the chamber. The chamber was operated between room temperature and 100°C in 2009, but the eventual operation range will be -90°C $\rightarrow$ +100°C, from Spring 2011 onwards.

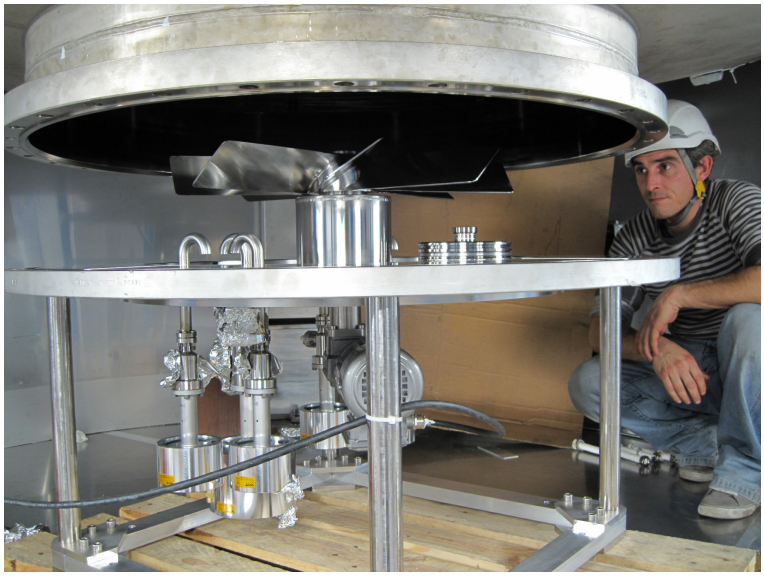

Fig. 4: CLOUD internal mixer fan and gas entry valves on the lower manhole cover.

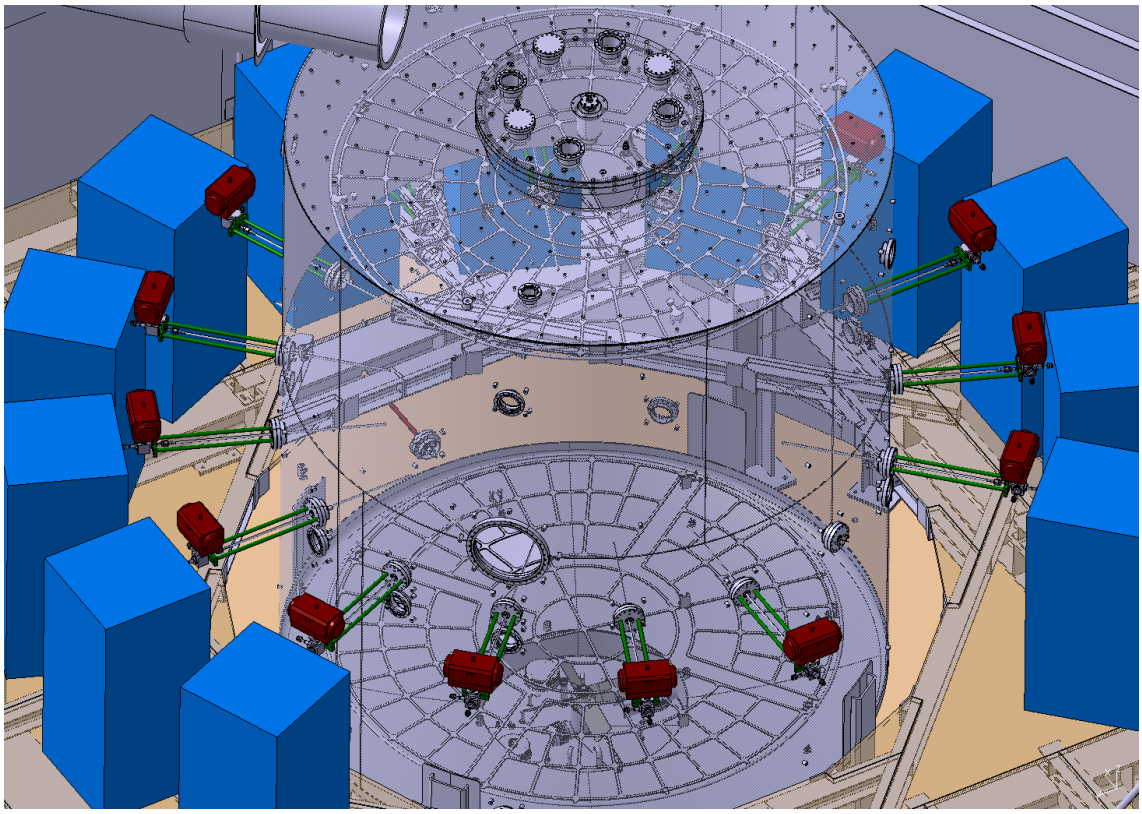

Fig. 5: CLOUD 3D model showing the chamber ports, sampling probes and valves for the analysing instruments (blue boxes). Also indicated are the UV feedthroughs on the upper surface of the chamber, as well as the transparent field cage electrodes and the mixer fan.

in the ratio 79:21, respectively. The air is humidified with a Nafion humidifier through which ultra-pure water re-circulates in a Millipore Super-Q filtration system. Ozone is added to the air by UV irradiation. Trace gases such as SO_2 are added from gas cylinders containing pressurised N_2 as the carrier. In order to compensate for gas sampling losses, there is a continuous flow of fresh gases into the chamber of 80 l/min.

Beam & GCR counters: A scintillator hodoscope (1.8×1.8 m^2) is used to measure the beam intensity and vertical/horizontal profiles. The beam is de-focused to a transverse size of about 1.5×1.5 m^2 across the chamber. A galactic cosmic ray (GCR) counter measures the local cosmic ray intensity and distribution in the East Hall.

DAQ system: Each of the instruments has its own data acquisition (DAQ) system which delivers data in real-time to the CLOUD server. A central DAQ system collects and backs up the data from the instruments, provides multi-user access for monitoring the detector performance, and controls the operating conditions of the experiment. In addition the DAQ provides real-time physics analysis using the data from multiple instruments. This information is valuable in deciding on the optimum experimental conditions for the following runs and in responding to possible surprises.

2.2 Analysing instruments

The contents of the CLOUD chamber are continuously analysed by instruments which are attached to sampling probes located in the mid plane of the chamber (Fig. 5). The following instruments were deployed in the 2009 run:

Aerosol particles

- *Condensation Particle Counter battery (CPCb):* An array of 6 CPCs to measure the aerosol particle number concentrations at various threshold diameter cutoffs (3–10 nm).
- *Particle Size Magnifier (PSM):* aerosol particle number concentrations above 1.5–2 nm threshold.
- *Scanning Mobility Particle Sizer (SMPS):* aerosol size spectrum above 8 nm diameter.

Ions/charged particles

- *Air Ion Spectrometer (AIS):* positive & negative charged & neutral aerosol size spectra above molecular (0.2 nm) threshold.
- *Gerdien counter:* positive & negative ion concentrations above molecular (0.2 nm) threshold.

Mass spectrometers

- *Chemical Ionisation Mass Spectrometer (CIMS):* H_2SO_4 concentration at 0.001 ppt sensitivity.
- *Proton Transfer Reaction Mass Spectrometer (PTRMS):* organic vapour identities and concentrations at 10–100 ppt sensitivity.
- *Atmospheric Pressure Interface Time of Flight Mass Spectrometer (APITOF):* positive and negative ion masses and concentrations in the range up to 2000 amu at up to 0.001 amu resolution in the low to medium mass range.

Gas analysers

- O_3 *gas analyser:* ozone concentration at 100 ppt sensitivity.
- SO_2 *gas analyser:* sulphur dioxide concentration at 100 ppt sensitivity.

Chamber operating conditions

- *Temperature:* a system of about fifty Pt100 thermometers measuring the temperature of the chamber walls, internal gas, thermal system and gas system, to about 0.01°C precision.
- *Pressure:* chamber relative air pressure.
- *Dew-point sensor:* relative humidity of the chamber contents to better than 0.1% precision.
- *Environmental conditions:* temperature, absolute pressure and relative humidity in the T11 experimental zone.

3 2009 RUN SUMMARY

3.1 Temperature stability

During the 2006 pilot CLOUD experiment it was found that small temperature increases of only 0.1°C would generate spurious nucleation bursts [Duplissy *et al.* (2010)]. This was attributed to the evaporation of contaminants from the walls of the chamber. This effect precluded experiments where the UV lights were switched from "off" to "on" since such transitions produced a rapid rise of the chamber temperature by several tenths of a degree.

Accordingly, a great deal of care was taken in the CLOUD design to achieve precise temperature stability. A novel fibre-optic UV system has been built which produces no parasitic heat load on the chamber. Furthermore, the CLOUD chamber is surrounded by a thermal housing with precise temperature control. The excellent performance of this system is illustrated in Fig. 6.

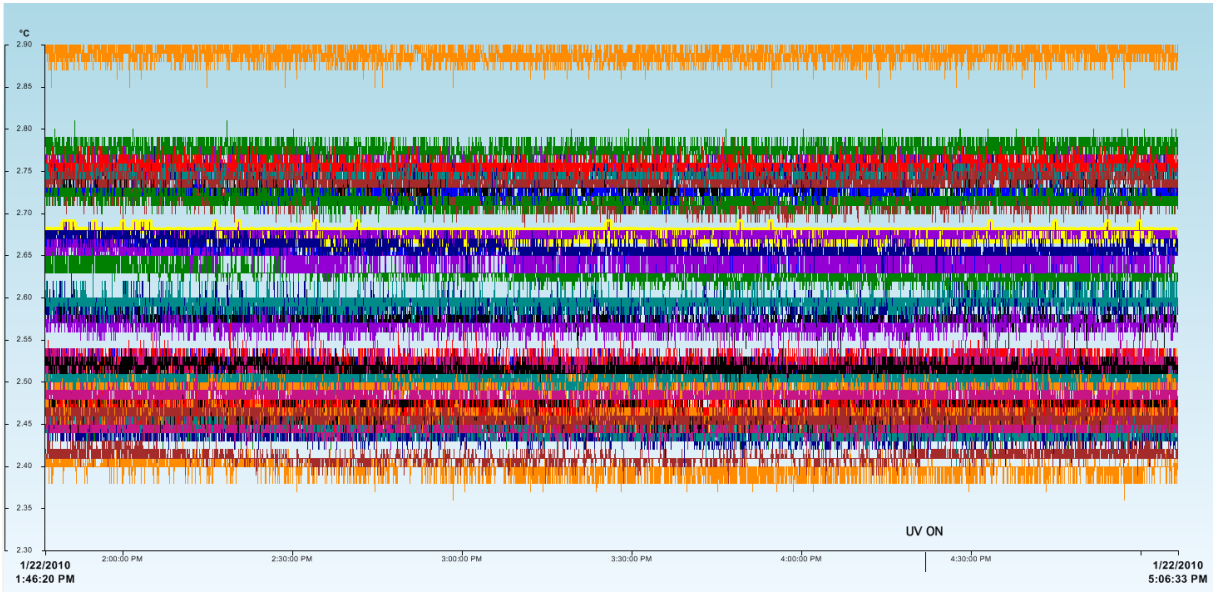

Fig. 6: An example trace of the individual Pt100 thermometers recording the temperatures of the CLOUD chamber walls over a 3h20 hour period (2.6°C mean temperature). At 4:22:00 pm the UV light was turned on at full intensity. No increase of temperature was observed on any Pt100, including an internal sensor that measures the gas temperature (purple trace, highlighted in yellow). Each tick mark on the vertical axis corresponds to 0.05°C, and the individual Pt100 resolution is 0.01°C.

3.2 Sulphuric acid production

Sulphuric acid is produced in the CLOUD chamber by the same mechanism as occurs in the troposphere. This involves first the production of hydroxl radicals from photo-dissociation of ozone:

$$\begin{aligned} O_3 + hv(< 320nm) &\rightarrow O(^1D) + O_2 \\ O(^1D) + H_2O &\rightarrow 2OH \end{aligned}$$

The hydroxyl radicals then oxidise sulphur dioxide to produce the hydroperoxyl radical and sulphur trioxide, which reacts with water to produce sulphuric acid vapour:

$$\begin{aligned} OH + SO_2 &\rightarrow HSO_3 \\ HSO_3 + O_2 &\rightarrow SO_3 + HO_2 \\ SO_3 + 2H_2O &\rightarrow H_2SO_4 + H_2O \end{aligned}$$

The concentration of H_2SO_4 in CLOUD is set by the concentrations of O_3 and SO_2, the relative humidity and the UV light intensity. During the 2009 run the range of values for each of these quantities was as follows: H_2SO_4 (5×10^4 – 5×10^8 cm^{-3}), O_3 (30–640 ppb), SO_2 (10–55 ppb), RH (30–60%), and UV intensity (0–25 mW/m^2).

The production of H_2SO_4 in the CLOUD chamber is precise and highly reproducible (see example in Fig. 7). Moreover, the UV intensity can be precisely and rapidly adjusted by the electronic aperture of the fibre-optic light source.

3.3 Ion pair production

The production of ions in the chamber as a function of average T11 beam intensity (3.5 GeV/c π^+) is shown in Fig. 8). The peak beam intensity corresponds to a mean ionisation rate in the chamber of about

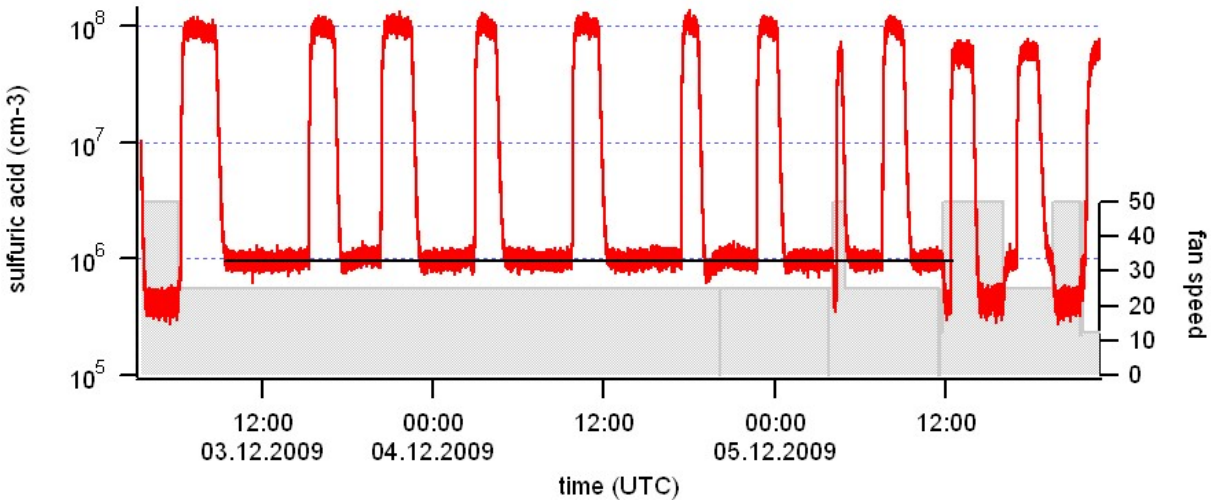

Fig. 7: Stability of H_2SO_4 production over a period of 3 days. Each of the peaks corresponds to a new nucleation burst recorded under selected conditions. The peak UV intensity was not varied for runs 1–7 and 9 but was adjusted for run 8 and the last 3 runs to reach a fixed $[H_2SO_4]$ at several fan speeds (right hand scale). The fan speed affects the H_2SO_4 wall loss rate and hence also the equilibrium concentration. The minimum H_2SO_4 concentration (at zero UV intensity) is due to evaporation from the walls of the CLOUD chamber, which gradually accumulated H_2SO_4 over the period of the campaign. The H_2SO_4 production demonstrates excellent reproducibility.

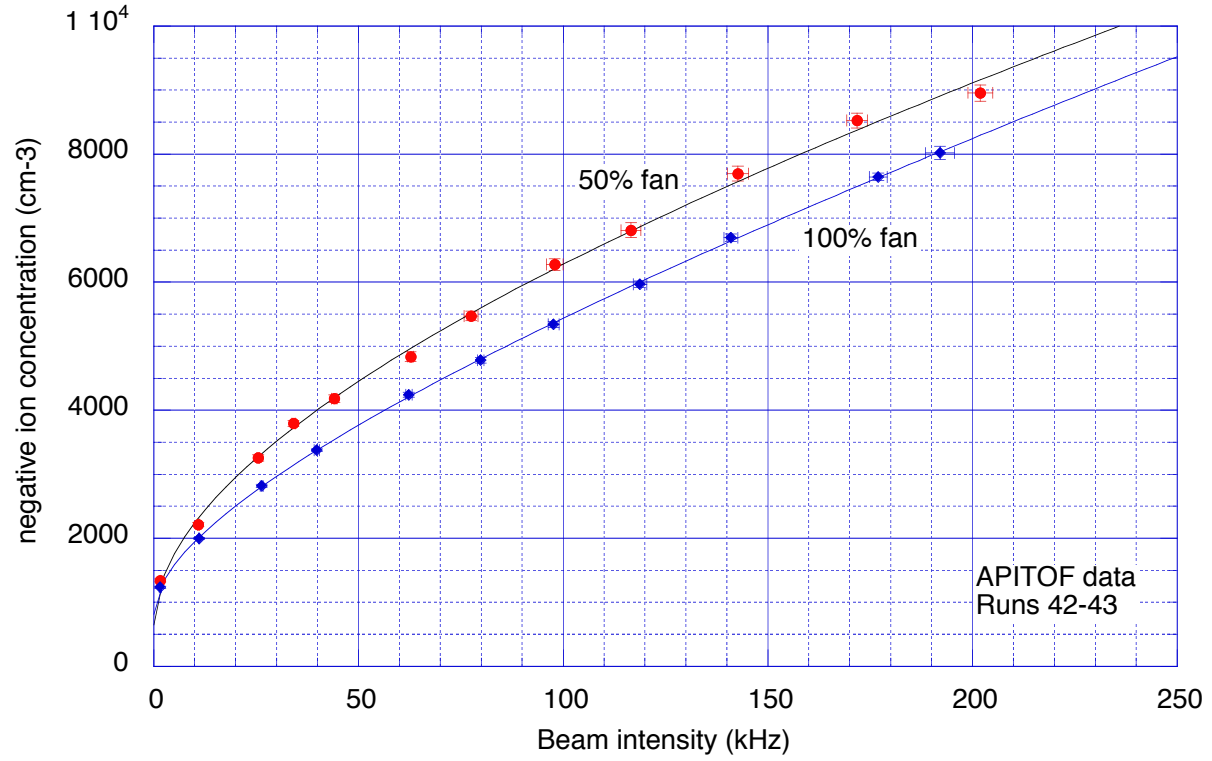

Fig. 8: Negative ion concentration in the chamber, measured with the APITOF, as a function of beam intensity and at two different fan speeds. The curves have the expected shapes based on the known ion-ion recombination coefficient and on the measured wall loss rates.

150 $\mathrm{cm^{-3}s^{-1}}$. In comparison, the ionisation rate in the atmosphere from galactic cosmic rays ranges from 2 $\mathrm{cm^{-3}s^{-1}}$ at ground level to 25 $\mathrm{cm^{-3}s^{-1}}$ in the lower stratosphere, resulting in equilibrium ion pair concentrations of around 500 $\mathrm{cm^{-3}}$ to 2500 $\mathrm{cm^{-3}}$, respectively. However, larger ion concentrations may be found at the upper and lower boundaries of clouds due to the buildup of unipolar space charge from the drift of ions in the fair-weather electric field.

3.4 Ion-induced nucleation

During the 2009 campaign a total of around 60 nucleation bursts were recorded. In contrast with the 2006 pilot experiment, no spurious (i.e. unexplained) nucleation bursts were observed. Nucleation rates were measured as a function of $\mathrm{H_2SO_4}$ concentration, relative humidity and beam intensity (ion pair concentration), at a fixed temperature of 19°C.

Unambiguous observation of ion-induced nucleation was made in the CLOUD chamber (see examples in Figs. 9 and 10). To determine the particle nucleation rates, J $\mathrm{cm^{-3}s^{-1}}$, the measured particle formation rates need to be corrected for wall losses and coagulation losses that occur in the time interval between nucleation at the critical size (near 1 nm) and detection at the CPC threshold (near 3 nm). The time interval depends on the growth rate and, in turn, on the $\mathrm{H_2SO_4}$ concentration. The particle loss rates and growth rates are parameters that must be experimentally determined; an example is shown in Fig. 11.

In addition to measuring nucleation rates, CLOUD will carry out a detailed chemical analysis of the nucleating ion clusters with the APITOF, to provide experimental input for nucleation models and theories (see example in Fig. 12).

3.5 Chamber backgrounds

Trace condensable vapour backgrounds must be kept below concentrations of around one part per trillion (2.5×10^7 $\mathrm{cm^{-3}}$ at 1 atm), which is the characteristic region of $\mathrm{H_2SO_4}$ concentrations where nucleation is observed to occur in the atmosphere. In order to try to meet this performance, extremely careful attention has been paid to the preparation of the inner surfaces, materials and welds of the CLOUD chamber and in the design of the gas and water supply systems.

A particular concern is the possibility of trace volatile organic compounds (VOCs) which, after photolysis, may create low volatility compounds that may condense onto aerosol particles and influence either the nucleation or growth processes. A careful study of VOC contaminants was made during the 2009 campaign using the PTRMS. This indicated a total VOC concentration of up to 600 ppt. Most of these VOCs are not condensable, and therefore not of concern. In fact, the PTRMS showed that the individual VOC concentrations in the CLOUD chamber are more than an order of magnitude below comparable-sized Teflon-FEP chambers [Paulsen, Dommen *et al.* (2005)], which is the predominant aerosol chamber material used elsewhere.

The APITOF provides a sensitive measurement of potentially problematic contaminants. One example is pyridine ($\mathrm{C_6H_5N}$) which can act to stabilise $\mathrm{H_2SO_4}$ in a cluster. This has been observed in the APITOF data and is estimated to have a concentration in the CLOUD chamber of about 1×10^5 $\mathrm{cm^{-3}}$ (0.004 ppt).

Although we believe CLOUD may now represent the world's cleanest large aerosol chamber, we are making strong efforts to reduce the VOC backgrounds further. We have obtained experimental evidence that these contaminants are being introduced into the CLOUD chamber by the purified water supply for the humidifier system. We are therefore undertaking a number of important changes in the water supply and filtration system which we expect will result in a substantial improvement of the water purity. These improvements include the production of ultra-pure water by burning pure hydrogen in pure oxygen at 1400°C (§5).

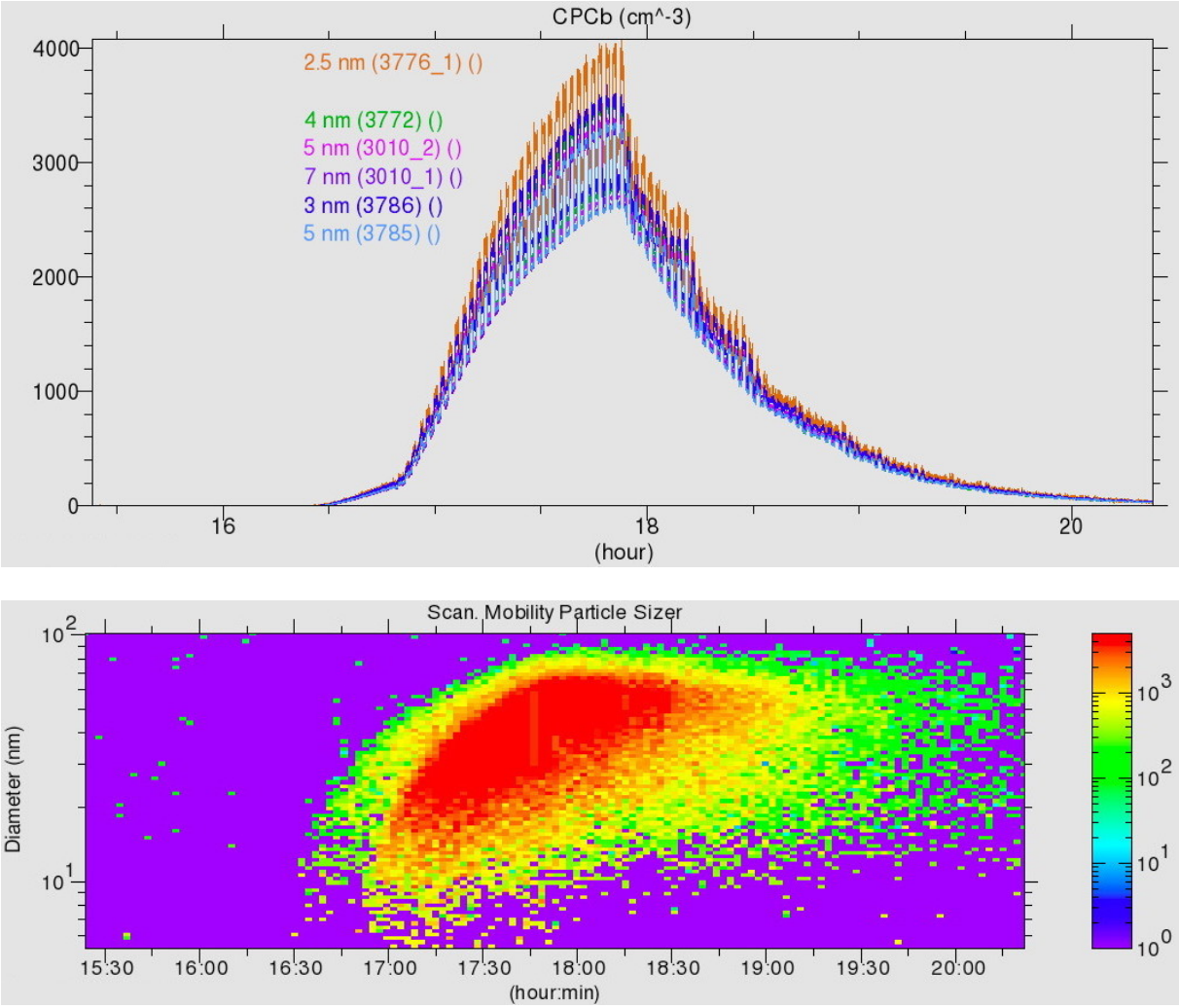

Fig. 9: An example of one of the early nucleation bursts recorded by CLOUD in November 2009. The upper panel shows the time development of the aerosol particle concentration in the CLOUD chamber measured by a battery of Condensation Particle Counters (CPCs), each set to a different detection threshold of aerosol diameter in the range 3–10 nm (the modulation is due to an alternating HV on an electrostatic precipitator in the sampling line). The lower panel shows the time-development of the aerosol size spectrum measured in a Scanning Mobility Particle Sizer (SMPS), with a detection threshold of around 8 nm. The pion beam was turned on at 16h45 and produced a sharp increase in the aerosol nucleation rate, detected shortly afterwards. This is a clear demonstration of ion-induced nucleation—although the beam intensity for this run was high and not representative of the atmosphere. The aerosol particles rapidly grew to diameters of around 50 nm, which is close to the threshold size to seed cloud droplets (lower panel). The run was ended at 17h50 and the chamber cleaned progressively in steps by alternately charging the aerosols with the beam and then sweeping them out with the electric field cage.

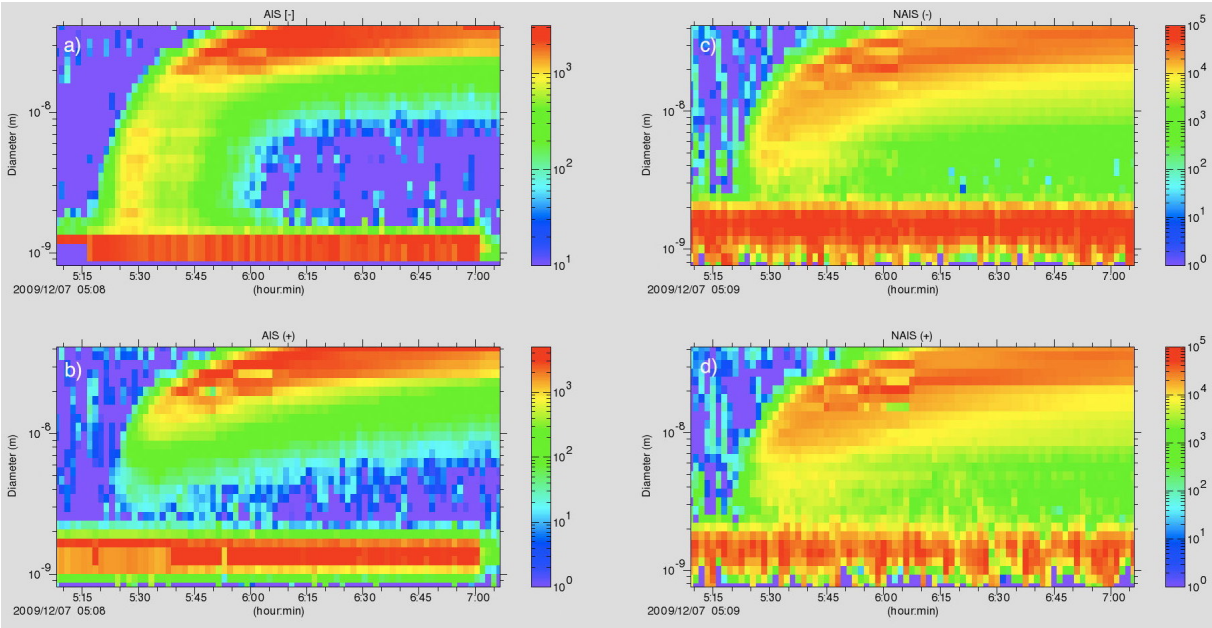

Fig. 10: A nucleation ("banana") event seen in the AIS: the time evolution of the size spectrum for a) negatively charged particles, b) positively charged particles, c) and d) neutral particles. Ion-induced nucleation by negatively-charged particles is clearly seen.

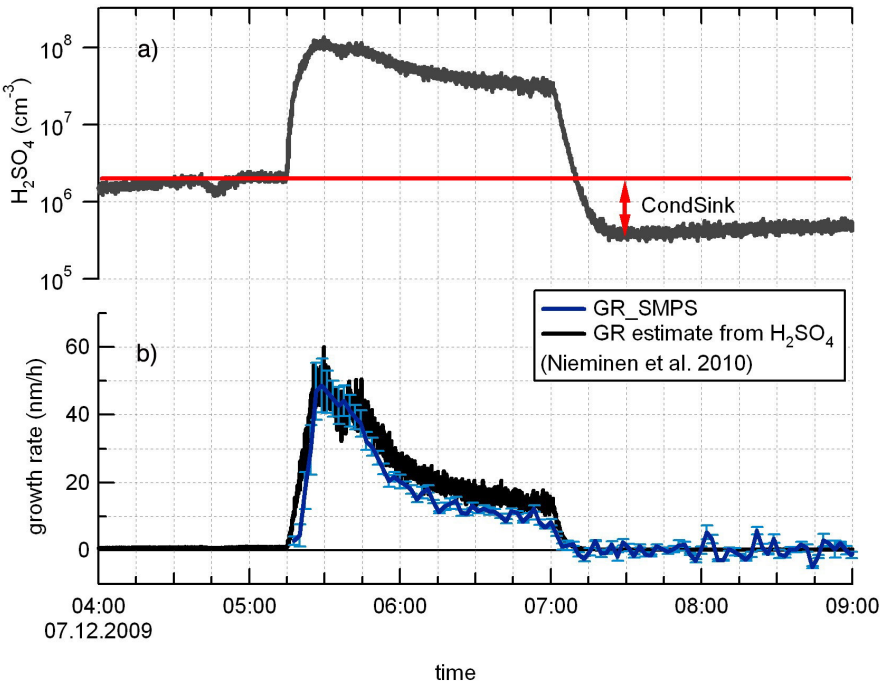

Fig. 11: Time evolution of the measured and calculated aerosol particle growth rates during the same nucleation run as seen in Fig. 10: a) sulphuric acid concentration measured by the CIMS and b) comparison of the growth rate measured by the SMPS (blue curve) with that calculated from the measured sulphuric acid concentration (black curve). The good agreement suggests that the CIMS is well calibrated. The UV light was turned on at 05h15, maintained at a constant 50% intensity and then turned off at 07h00. The depletion of the H_2SO_4 concentration due to the aerosol condensation sink is clearly seen.

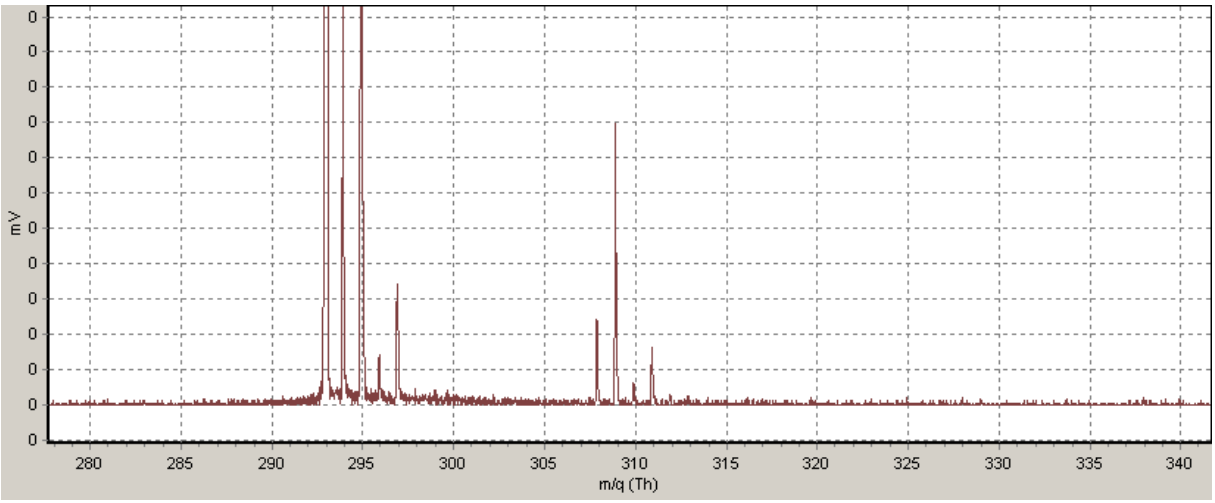

Fig. 12: An example of the high resolution chemical analysis of ions from the APITOF. The first group of peaks starting at 293 amu corresponds to the charged sulphuric acid trimer, $(H_2SO_4)_2.HSO_4^-$; five isotopes of S and O are visible, in the expected relative abundance. The second group starting at 308 amu corresponds, respectively, to $(H_2SO_4)_2.SO_5^-$, $(H_2SO_4)_2.HSO_5^-$, and two isotopes.

4 PUBLICATIONS

The results of the 2006 beam test have been published in *Atmospheric Chemistry and Physics*:

J. Duplissy *et al.*, Results from the CERN pilot CLOUD experiment, Atmos. Chem. Phys., 10, 1635–1647, 2010, <http://www.atmos-chem-phys.net/10/1635/2010/acp-10-1635-2010.pdf>.

The results of the 2009 run will be presented at the International Aerosol Conference, IAC2010, Helsinki, 29 August – 3 September 2010, <http://www.iac2010.fi>. Fifteen abstracts have been submitted, and are attached in Appendix A.

In addition, we are preparing a journal paper on the key new results from the 2009 run, for expected publication later this year.

5 CLOUD FACILITY IMPROVEMENTS IN 2009

Several improvements to the CLOUD facility are underway in preparation for the 2009 beam runs:

Thermal housing: Improvements in the thermal system vapour barrier to allow operation at low temperatures, down to -30°C, without accumulation of ice inside the thermal housing.

Chamber cleanliness: Improvements in the purity of the water used for the humidifier, by numerous detailed improvements in the re-circulating filtration system. Installation of a new water source, generated by burning pure hydrogen in pure oxygen. Installation of a quartz tube containing a high-intensity UV source for chemically breaking down and cleaning organic backgrounds in the chamber under high O_3 conditions. The tube is installed in one of the mid-plane ports of the chamber and coated with indium tin oxide to prevent surface charge buildup.

Gas system: Completion of all individual gas inlet lines, and detailed improvements to the gas supply valves. Installation of a precision (0.01°C) thermoregulator for the humidifier water to precisely control the relative humidity in the chamber. Installation of a heat exchanger on the main air inlet line to equalise its temperature with the chamber contents, before injection. Pre-mixing of the O_3 and humidified ultrapure air before entering the chamber, to avoid an "ozone plume" inside the chamber. Installation of the fast chamber exhaust system for adiabatic expansions.

Field cage: Installation of zirconia HV feedthroughs to allow operation up to 50 kV without surface charge buildup.

UV system: Increase of the UV intensity by a factor of about 5 by the addition of three more UV sources and completion of the inner two feedthrough rings on the top manhole cover.

Manhole covers: Construction of the final upper and lower manhole covers with all ports, windows, UV feedthroughs, and fans. Addition of a second internal mixer fan, on the top manhole cover. Addition of nozzles (hoods) to both fans to improve efficiency at reduced fan speeds. Operation of dual fans is expected to reduce the wall loss rates of trace gases and aerosols while maintaining good mixing of the contents of the chamber.

Sampling valves: Installation of electrical shields inside the sampling valves to protect against charge buildup on the teflon seals, which affects the transmission of small ions.

Internal Pt100 string: Installation of a radial string of five Pt100 sensors in the mid-plane of the chamber to monitor internal gas temperature inhomogeneities at 0.01°C precision.

Beam counter: Installation of an additional beam counter, covering the full aperture of the final T11 vertical bending magnet, to provide a beam telescope in coincidence with the hodoscope. This will efficiently reject cosmic rays that strike the hodoscope at glancing angles, and also allow the beam counting efficiency to be cross-checked.

DAQ: Installation of a high-performance server and real-time physics analysis using the data from multiple instruments. This information is valuable in deciding on the optimum experimental conditions for the following runs and in responding to possible physics surprises.

In addition, during the winter 2010/2011 shutdown a new thermal system will be installed to allow operation down to -90°C.

6 PHYSICS AIMS AND BEAM REQUEST

2010, May/June: Nucleation studies at various H_2SO_4 concentrations, relative humidities and beam intensities, at temperatures down to around -30°C. The requested beam time is 4 weeks + 1 week contingency (31 May - 2 July 2010). Extensive periods of open access to the T11 experimental zone are required outside the beam operation periods to allow for instrument setup and calibrations, and for installation work on the CLOUD facility

2010, October/November: Nucleation studies at H_2SO_4 concentrations, relative humidities and beam intensities, at various temperatures down to around -30°C, and with additional trace amounts of NH_3 and volatile organic compounds at atmospheric concentrations. The requested beam time is 4 weeks + 1 week contingency (16 October - 22 November 2010).

2011: Continuation of nucleation and growth studies to CCN sizes, together with initial studies of cloud droplets and ice particles (adiabatic expansions in the CLOUD chamber).

Acknowledgements

We would like to thank CERN PH-DT, EN-MME, EN-MEF and TE-VSC for their excellent support during the installation of CLOUD in the T11 zone and, in addition, to thank the CERN machine team for their efficient operation of the PS. We also thank the CERN Research Board, the Director for Research, S. Bertolucci, the SPSC chair, C. Vallée, and the SPSC & PS Coordinator, H. Breuker, for granting a special two-week extension of PS operations for CLOUD, which allowed the present results to be obtained.

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APPENDIX A: CLOUD ABSTRACTS SUBMITTED TO THE INTERNATIONAL AEROSOL CONFERENCE, IAC2010, HELSINKI, 29 AUGUST – 3 SEPTEMBER 2010

The CLOUD experiment at CERN

Duplissy, Jonathan[1], Baltensperger, Urs[3], Haider, Stefan[1], Mathot, Serge[2], Minginette, Pierre[2], Onnela, Antti[1], Walther, Hansueli[3], Wilhelmsson, Mats[2], Kirkby, Jasper[1], and the CLOUD collaboration

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Keywords: CLOUD experiment, aerosol chamber, galactic cosmic rays, nucleation, instrumentation.

The possible influence of cosmic rays on aerosols and clouds is of considerable interest (Carslaw, 2009). The CLOUD experiment at CERN aims to study under controlled conditions the effects of cosmic rays on nucleation, cloud droplets and ice particles. Technical input for the CLOUD design was obtained in a pilot experiment in 2006 (Duplissy *et al.*, 2010). CLOUD was installed at CERN in 2009 and a successful first campaign was carried out in November-December to study ion-induced and neutral binary nucleation of H_2SO_4 and H_2O. We describe here the experimental setup.

The chamber is a 3m-diameter electro-polished 316L stainless-steel cylinder (26.1 m^3). A field cage comprising two transparent electrodes at voltages of up to +30 kV and -30 kV, respectively, is installed inside the chamber to allow the removal of ions, when required. The contents of the chamber are irradiated by UV light in the range 250-400 nm. The UV is introduced via 240 optical fibre feedthroughs installed on top of the chamber. The chamber is surrounded by an insulated thermal housing. The temperature is controlled by precisely regulating the temperature of the air circulating in the space between the chamber and the thermal housing. Experimental runs can be performed at stable temperatures (near 0.01°C) between 40°C and -30°C (to be extended to -90°C in 2011). In addition, the chamber can be raised to 100°C for cleaning.

The chamber is exposed to a 3.5 GeV/c secondary pion beam from the CERN PS, corresponding to the characteristic energies and ionization densities of cosmic ray muons in the lower troposphere. The beam intensity can be adjusted to cover the natural range from ground level to the stratosphere. The beam is de-focused to a transverse size of about 1.5x1.5 m^2 across the chamber.

Ultra-pure air is obtained from the evaporation of cryogenic liquid N_2 and liquid O_2, mixed in the ratio 79:21, respectively. The air is humidified with a Nafion humidifier through which ultra-pure water re-circulates in a Millipore Super-Q system. Ozone is added to the air by UV irradiation. Trace gases such as SO_2 are added from gas cylinders containing pressurised N_2 as the carrier. The chamber instrumentation includes PTRMS, CIMS, Nano-SMPS, CPC battery, PSM, API-ToF, NAIS, Gerdien, dew point sensor, SO_2 and O_3 analyser, as well as T, P and UV sensors. In order to compensate for sampling losses, there is a continuous flow of fresh gases into the chamber of 80 l/min. An internal fan ensures good mixing of the fresh gases.

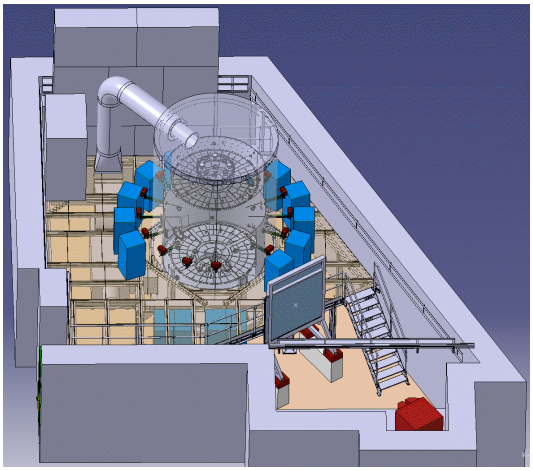

Figure 1. An illustration of CLOUD in the T11 experimental zone at the CERN PS. The de-focused particle beam exits a dipole magnet (bottom right), crosses the hodoscope counter (middle) and then traverses the 3m-diameter CLOUD chamber. The instruments (blue boxes) analyse the contents of the chamber via sampling probes fitted with valves.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement no. 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project no. 01LK0902A), from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence program (project no. 1118615).

Carslaw, K. (2009). *Cosmic rays, cloud and climate*. Nature, 460, 332-333.

Duplissy, J. *et al.* (2010). *Results from the CERN CLOUD experiment*, Atm. Chem. and Phys., 10, 1635-1647.

The global impact of a simulated change in the nucleation rate on atmospheric aerosol

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Keywords: ion-induced nucleation, Forbush decreases, galactic cosmic rays, modelling.

A link between cosmic rays and the climate is supported by several empirical datasets (Kirkby, 2007). The CLOUD consortium was formed to investigate the mechanisms by which the climate might be altered by a modulation in the intensity of cosmic rays. A likely candidate for this climate mechanism is ion-induced nucleation, the process by which atmospheric ions facilitate the formation of sulphate aerosol from sulphuric acid vapour and water vapour (Carslaw *et al*., 2002).

The Global Model of Aerosol Processes (GLOMAP) developed at the University of Leeds is an ideal tool for assessing the impact of a change in nucleation on the climate (Spracklen *et al.*, 2007). GLOMAP features online microphysics, including nucleation, condensation and coagulation, and simulates the behaviour of black and organic carbon, sea salt and sulphate aerosol.

In the longer term, we will use GLOMAP to model the interactions of ions and aerosols explicitly. For this study we have used an existing nucleation mechanism included in GLOMAP (Vehkamäki *et al.*, 2003) to place some bounds on the expected response to changes in the particle formation rate due to galactic cosmic rays (GCRs).

Increased solar magnetic activity causes a decrease in GCRs on three time scales. The best known is the same 11-year solar cycle which modulates sunspots. Other longer cycles provide an amplitude variation of the 11-year cycle. On shorter time scales, however, powerful ejections of charged particles from the sun can cause reductions in terrestrial GCR levels over a period of days to weeks. This is known as a Forbush decrease.

There has been great interest in the recent Svensmark *et al.* (2009) paper, which shows a correlation between Forbush decreases and observations of Angström exponent, cloud water content, liquid water cloud fraction (LCF) and low infra-red-detected clouds. However, other authors have since examined the proposed trends in LCF and global cloud cover, and found no statistically significant correlation in the data.

To simulate the effect of a Forbush decrease on atmospheric aerosol, GLOMAP was run for ten days with daily output. The nucleation rate was then decreased globally by a factor of {0.85, 0.5, 0.15, 0} for two days. A control run with no decrease in nucleation was also simulated. The daily model output was analysed for a further 15 days in each scenario to assess the impact of a two-day Forbush decrease with a range of magnitudes on the aerosol size distribution.

In the free troposphere, concentrations of condensation nuclei responded rapidly and substantially to the change in the nucleation rate, but soon returned to normal levels. In the boundary layer, condensation nuclei took longer to recover because the particles are partly supplied from coagulated particles transported down from the free troposphere (Merikanto *et al*., 2009). Only a minor reduction in cloud condensation nuclei was observed. A longer event at 85% nucleation will be simulated, as well as a Forbush decrease in a pre-industrial atmosphere where it may have a larger impact.

Metzger *et al.* (2010) found that a nucleation rate of the form $J = k\,[H_2SO_4]^m \times [NucOrg]^n$ produced better agreement with observations. Combining this kinetic mechanism with the findings of the CLOUD 2009 experiment, we will suggest upper bounds for the impact of the enhancement in nucleation caused by ions on condensation nuclei, cloud condensation nuclei and cloud droplet number concentration.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement no. 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project no. 01LK0902A), from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence program (project no. 1118615).

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Modelling of CLOUD chamber chemistry

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Keywords: modelling, CLOUD experiment, sulphuric acid, ion-induced nucleation

There is currently an ongoing discussion whether ion-induced nucleation (IIN) plays an important role in the earth climate system Kirkby (2007), Carslaw (2002), Marsh (2000). The CLOUD project (Cosmics Leaving OUtdoor Droplets, see e.g. Duplissy et al. 2010) is designed to study IIN and its potential influence on climate. An important key to interpret the results from chamber experiments is a detailed understanding of the chemical processes leading to the main aerosol precursor components, where in the case of the CLOUD experiment sulphuric acid can be considered as the most important one.

The results presented in this work will focus on the CLOUD-09 experiment. During this experiment the nucleation of sulphuric acid and water was studied for the neutral case and under the presence of artificially generated or natural ions produced by Galactic Cosmic Rays (GCR) inside a 27 m³ electro-polished stainless steel chamber at CERN.

One of the key parameters of the experiment is the concentration of sulphuric acid on which the production rate of new particles strongly depends. Sulphuric acid is produced in situ by the reaction of hydroxyl radicals (OH) with sulphur dioxide (SO_2). The source of OH is the hydrolysis of water vapour with singlet oxygen (O(1D)), where O(1D) is produced via ozone photolysis.

We will present results of a model that calculates the sulphuric acid concentration. Therefore we calculate the steady state concentration and also use a fully time-resolved numerical model (ASAD, Carver et al, 1997), originally designed for atmospheric applications. This model is adjusted to the conditions inside the CLOUD chamber in order to follow the evolution of the sulphuric acid concentration from the first few seconds of each experimental run. For both methods we use data published by IUPAC and JPL (2006). The possibility of non ideal mixing inside the chamber and its influence on the chemistry will be subject of future studies.

The calculated sulphuric acid concentration will be compared with values measured by a Chemical Ionization Mass Spectrometer (CIMS). Within the model experimentally determined wall loss rates are implemented. These wall losses depend on the speed of a fan that was used to mix the gas/particle-system inside the chamber. Dependence of loss rates on relative humidity are taken into account by a humidity dependent diffusion coefficient. The actinic flux, needed to estimate the O(1D) production, is derived by different methods. 1.) Fitted to the sulphuric acid concentrations measured by the CIMS, 2.) determined by the observed SO_2 depletion, 3.) calculated from the measured UV light power inside the chamber and the spectrum of the UV source.

Besides this rather simple model that is based on a steady state assumption and contains only a few components, results from

We thank Glenn Carver from the University of Cambridge for providing us the ASAD code.
We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement number 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project number 01LK0902A), from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence program (project number 1118615).

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Ion measurements during the first H_2SO_4 nucleation experiments at the CLOUD chamber

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Keywords: atmospheric ions , ion-induced nucleation, sulfuric acid, CLOUD experiment.

Nanoparticle formation in the boundary layer is a frequent phenomenon (Kulmala et al., 2004). Sulfuric acid has been identified as a plausible candidate to participate in the nucleation (Weber et al. 1996). Ion-induced nucleation is one of the possible pathways for new particle formation in the atmosphere but it is still unclear how important the contribution of ions is with respect to neutral pathways. Ion concentration and their size distribution are key quantities to understand ion-induced nucleation processes and dynamics.

During the CLOUD (Cosmics Leaving OUtdoor Droplets) experiment 2009, several experiments of sulfuric acid-water neutral and ion induced nucleation were performed in an aerosol chamber. In this experiment, Galactic Cosmic Rays (GCR) and the Proton Syncrotron (PS) accelerator at CERN were used sources to generate ions in the 26.1 m^3 CLOUD aerosol chamber filled with ultra-pure air produced by cryogenic liquids. Both GCR and PS beam were constantly monitored respectively by a GCR counter and by an hodoscope.

The ion concentration in the CLOUD chamber was measured with a Neutral cluster and Air Ion Spectrometer, (NAIS, Mirme et al., 2007). The NAIS is able to measure air ion number size distributions in the mobility equivalent diameter range of 0.8 to 40 nm and correspondingly neutral particle number size distributions from ~2 to 40 nm mobility diameter. The total concentration of ions with mobility diameter smaller than 16 nm was detected with a self-made Gerdien ion counter, built following the guidelines presented in Aplin & Harrison (2000). A comparison between the two instruments is shown in Figure 1.

Based on the measured GCR and beam intensities we were able to calculate the expected ion concentrations in the chamber as a function of beam intensity. The calculated ion concentrations were then compared with the measured values in the NAIS and Gerdien counters. The growth and formation rates were also calculated based on the NAIS size distributions to characterize the particle formation processes taking place in the chamber.

The ratio of formation rates of charged and total particles give information about the contribution of ion-induced nucleation. The charged fraction of the particles also gives such information, they were both retrieved from the NAIS ion- and total-mode size distributions. A switchable ion-trap equipped CPCB (Condensation Particle Counter Battery) can also retrieve similar information and both methods will be compared.

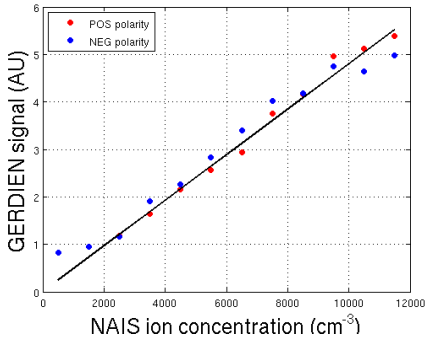

Figure 1. Comparison between ion concentration measured by NAIS and Gerdien counter.

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Modification of the PARNUC aerosol nucleation model for application to CLOUD aerosol chamber measurements

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Keywords: Ion-induced nucleation, wall losses, PARNUC nucleation model, CLOUD experiment.

A potential connection between cosmic ray intensity, low cloud cover and climate has been postulated [Marsh and Svensmark, 2000; Carslaw et al., 2002; Kirkby, 2007]. Ion-induced nucleation could be the mechanism to explain such a connection due to the increased ion-production by galactic cosmic rays. Therefore a better understanding of ion-induced nucleation mechanisms is of crucial importance.

To improve the scientific knowledge about ion-induced nucleation, the CLOUD-project (Cosmics Leaving OUtdoor Droplets) was established at CERN (European Organization for Nuclear Research). The experimental setup consists of an aerosol chamber into which a beam of particles is sent from a proton synchrotron to investigate the effects of ions on the aerosol production under controlled laboratory conditions.

The nucleation processes in the chamber can be modelled with PARNUC (PARametrized NUCleation), a programme originally developed to study nucleation in the atmosphere [Kazil and Lovejoy, 2007]. It calculates the steady state production rates of neutral and charged sulphuric acid/water particles, which represent the formation of new aerosol particles from the gas phase. The calculation is performed for predefined ambient conditions, such as temperature, precursor gas concentration of sulphuric acid and water, ion-production rate and preexisting particle concentration. The formation rate of particles exceeding a given size is calculated. The calculation is based on the semi-analytical solution of an aerosol system in steady state. The parametrised rate coefficients of sulphuric acid uptake and loss by sulphate aerosol particles are calculated from laboratory and theoretical thermodynamic data [Lovejoy et al, 2004; Kazil and Lovejoy, 2007].

Since PARNUC was intended for use in a free atmosphere model, some modifications and new parametrisations had to be implemented into the programme to allow its application to the CLOUD aerosol chamber conditions.

One characteristic of the CLOUD chamber is the steady internal gas circulation resulting from stirring by a fan. This causes an increased reduction of particles due to deposition to the chamber walls, which is dependent on the fan speed. Therefore, especially the adequate implementation of the particle wall loss is important.

The expression of the wall loss is $dN_i/dt=-\beta N_i$, where N_i is the particle number concentration, the index i indicates the number of sulphuric acid molecules present in a cluster or a particle and β is the wall loss rate coefficient.

The diffusion to the walls is approximated by the Brownian diffusion through the quasi-laminar boundary layer of the wall. The average thickness of the quasi-laminar layer at the chamber walls is a function of the fan speed. It is assumed that the wall loss rate is proportional to the diffusion coefficient. Different assumptions for this coefficient are studied. Model results for diffusional loss and residence time in the chamber are presented and compared to the data from the CLOUD measurements.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement no. 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project no. 01LK0902A), from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence program (project no. 1118615).

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Overview of first results on ion-induced nucleation from the CLOUD experiment at CERN

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Keywords: CLOUD experiment, aerosol chamber, galactic cosmic rays, ion-induced nucleation, sulphuric acid.

There is considerable palaeoclimatic evidence for an important solar influence on climate change on the centennial time scale, but the mechanism is not yet understood (Kirkby, 2007). A candidate is a possible influence of cosmic rays on aerosols and clouds (Carslaw *et al.*, 2002; Carslaw, 2009). However, given the many sources of variability in the atmosphere – and the lack of control of the cosmic ray flux – demonstrating overall cause and effect beginning with changes in ionisation rate and ending with observations of perturbed clouds is challenging. For these reasons the CLOUD experiment has recently begun operation at the CERN Proton Synchrotron with the aim to study, under controlled conditions, the effects of cosmic rays on aerosol nucleation and growth to CCN, and on cloud droplets and ice particles (CLOUD collaboration, 2000).

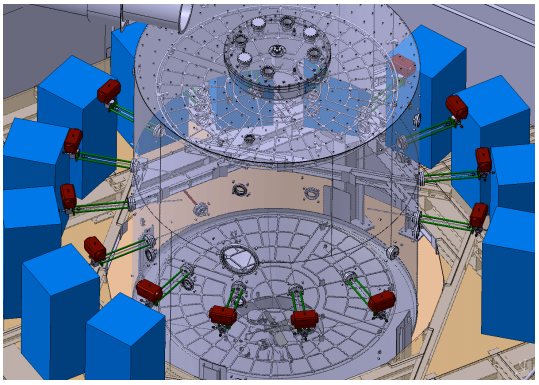

Figure 1. The CLOUD experiment at CERN.

The CLOUD experiment (Fig. 1) is optimised to study ion-aerosol-cloud interactions. Technical input for the design was obtained in a pilot experiment in 2006 (Duplissy *et al.*, 2010). The CLOUD chamber is a 3m-diameter electropolished stainless-steel cylinder of volume 26 m^3. Great care has been taken to suppress trace background contaminants in the chamber and to eliminate stray electric fields due to residual surface charges on insulators. To study ion-mediated processes, the chamber is exposed to a de-focused 3.5 GeV/c secondary pion beam from the CERN PS, matching the ionisation conditions anywhere in the troposphere or stratosphere. To study neutral processes, an internal electric field is applied to sweep rapidly from the chamber the background ionisation from galactic cosmic rays.

The contents of the CLOUD chamber are continuously analysed by instruments attached to sampling probes. An array of optical fibres on the top plate of the chamber provides UV light for photolytic reactions. The chamber is surrounded by an insulated thermal housing which precisely controls the temperature between 40°C and -30°C (to be extended to -90°C in 2011). In addition, the chamber can be raised to 100°C for cleaning the inner walls. The nominal operating pressure is one atmosphere. However, adiabatic expansions can be made of about 0.2 bar to provide supersaturated water vapour conditions for the creation and growth of droplets and ice particles. This will be used for future studies of the influence of cosmic rays on cloud microphysical processes.

CLOUD was installed at CERN in 2009 and a successful first campaign was carried out in November-December to study ion-induced and neutral binary nucleation of gas-phase H_2SO_4 and H_2O. This paper will present a synthesis of the main results from the first campaign. More in-depth information and analyses can be found in other papers presented at this conference.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement no. 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project no. 01LK0902A), from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence program (project no. 1118615).

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Sulphuric Acid Measurements at the CLOUD chamber

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Keywords: CIMS, sulphuric acid, nucleation, CLOUD experiment

Sulphuric acid is known to be one of the key components for atmospheric nucleation. During laboratory and field studies many experiments have tried to elucidate at what concentrations of sulphuric acid relevant concentrations of aerosol particles are being formed. However, the results from these studies can differ by orders of magnitude. While in some cases the concentration of sulphuric acid has been estimated from various parameters, the direct measurement of sulphuric acid with a Chemical Ionization Mass Spectrometer (CIMS) gives the most direct results.

Here, we report on sulphuric acid measurements with a CIMS that have been performed during the CLOUD-09 experiment at CERN. The CLOUD project (Cosmics Leaving OUtdoor Droplets, see Duplissy et al., 2010) tries to answer the question whether ion induced nucleation plays an important role for the Earth's climate. The CLOUD chamber that has been set-up at CERN is a unique facility allowing to study the nucleation and the growth rates of particles under very controlled conditions with and without ions (at different concentrations) being present.

In order to interpret and compare the results from CLOUD-09 quantitatively it is crucial to have reliably sulphuric acid concentration data. The CIMS that was used to measure H_2SO_4 during CLOUD was built by Greg Huey's group at Georgia Tech and makes use of the reaction between sulphuric acid and NO_3^- primary ions which leads to the formation of HSO_4^- ions that are being detected with a quadrupole mass spectrometer (Berresheim et al., 2000).

During CLOUD-09 the CIMS worked very reliably and we estimate that its detection limit was below 10^5 molecules of sulphuric acid per cm^3. Besides the good detection limit, also the reproducibility of the CIMS measured concentrations was remarkably good and indicated that there was virtually no drift in the measured values for given conditions. E.g. one could predict, based on the results from previous runs, what concentration of sulphuric acid would result for a given UV light intensity, SO_2 and O_3 concentration.

In this work we will present results of the H_2SO_4 concentrations measured during CLOUD-09. Furthermore, we will present experimentally determined loss factors within the 1.3 m long stainless steel sampling line that was used and compare this value to calculated loss factors. The measurement of this factor is possible by using our calibration system that can be used to measure known concentrations of H_2SO_4 with and without a sampling line in between the calibration system and the CIMS.

Besides presenting the calibrated CIMS values we also compare these to values that were derived from two other independent methods: (1) SO_2 was used during CLOUD as precursor gas for generating H_2SO_4 via the reaction between OH and SO_2 and further reactions with O_2 and H_2O. A trace-level SO_2 analyzer (Model 43i-TLE, Thermo Scientific) was used for measuring $[SO_2]$ inside the chamber. During the experimental runs a small decrease in $[SO_2]$ could be observed that was clearly correlated with the time when the UV light was turned on and the $[H_2SO_4]$ started to increase. Therefore, this decrease in $[SO_2]$ is a quantitative measure for the H_2SO_4 production rate. From the measured wall loss rate the steady-state $[H_2SO_4]$ is then further calculated. (2) Another independent method for estimating $[H_2SO_4]$ is based on analyzing the measured particle growth rates (Nieminen et al., 2010). These were observed with Condensation Particle Counters (CPCs) and a Scanning Mobility Particle Sizer (SMPS) system.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement no. 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project no. 01LK0902A), from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence program (project no. 1118615).

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A unique UV fibre-optic system for H_2SO_4 production inside the CLOUD chamber

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Keywords: CLOUD chamber, H_2SO_4 nucleation, UV light, OH radicals

Although aerosol formation processes have been the subject of investigation by many scientists, further research and detailed description of nucleation processes are essential to better understand atmospheric aerosols, their processes and influences on the global climate.

Sulfuric acid plays a key role in atmospheric aerosol formation (Kulmala, 2003). According to Berndt *et al.* (2008), sulphuric acid produced after reaction of OH radicals with SO_2 nucleates much more effectively than when evaporated from liquid reservoir.

To investigate the effect of ionizing particle radiation on aerosol formation from trace sulphuric acid vapour, the CLOUD experiment uses a UV system to produce OH radicals necessary for the oxidation of SO_2.

The design requirements for the UV system include: a) a flux in the UVB region comparable to the ground-level actinic flux, b) near uniform illumination within the CLOUD chamber (Fig.1), c) low thermal load on the chamber (Duplissy *et al.* 2010), d) compatible with the chamber operation in the temperature range between -90 and +100°C, and e) compatibility of materials and components with ultra high vacuum (UHV) standards. The UV fibre-optic system of CLOUD successfully fulfils these criteria.

Figure 1. Fisheye image from under the CLOUD chamber: fibre optic illumination and reflections on electropolished interior. (Picture by Maximilien Brice, CERN, Switzerland)

Various measurements aiming to characterise the UV system were performed both in the laboratory and in the CLOUD chamber. Parameters analysed included angle of the outcoming lightcone, transmission efficiencies and uniformity of distribution both within each bundle and inside the chamber. The maximum UV intensity expected inside the CLOUD at 100% aperture was calculated taking into account total power from the UV source, transmission efficiencies through fibres, feedthrough, and through the chamber, fraction of fibres installed, and useful power below 317nm. Additionally, the actual UV power intensity was measured inside the CLOUD chamber.

The fact that the UV fibre-optic system providing high UV power to the CLOUD exercises no thermal effect on the chamber itself can be considered as a unique feature of this system. Knowing that small increases in temperature may invariably trigger nucleation bursts, the temperature neutrality of the UV system represents a substantial improvement within the CLOUD experiment set-up (Duplissy *et al.*, 2010).

A novel UV fibre-optic system design and its performance at the CLOUD chamber will be presented.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under the grant agreement no. 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project no. 01LK0902A), and from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence Program (project no. 1118615).

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Background characterization of the CLOUD chamber facility

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Keywords: CLOUD, aerosol chamber, nucleation, PTR-TOF, volatile organic compound

New particle formation events have been observed frequently and worldwide (Kulmala, Vehkamaki et al. 2004). However their contribution to the regional and global budget of atmospheric particles is still an open question. This points to the fact that atmospheric new particle formation at a microscopic level is poorly understood, not least due to the fact that laboratory data have so far not been successful in explaining atmospheric nucleation.

One problem limiting the quality of laboratory studies are trace impurities of condensable vapours (e.g. ammonia or organic compounds) which could participate in the aerosol nucleation and growth processes. Recent studies indeed suggest that organic compounds may strongly influence aerosol nucleation from sulphuric acid and water vapour (Zhang et al. 2009; Metzger et al. 2010). Those compounds are extremely difficult to detect especially at the low concentration levels of a “clean experiment”. Nevertheless their presence in very low concentration might still be sufficient to influence laboratory experiments. Moreover they might differ in concentration (absolute and relative to the concentration of the nucleating vapours) and chemical composition from the real atmosphere. Thus a detailed knowledge of possible impurities in laboratory systems is needed for a quantitative interpretation of the data.

CLOUD (Cosmics Leaving OUtdoor Droplets) is a collaborative effort to investigate the influence of galactic cosmic rays (GCRs) on ions, aerosols, cloud condensation nuclei (CCN) and clouds (Duplissy et al. 2009). Experiments are conducted in a unique aerosol chamber facility at CERN. The chamber was carefully designed and prepared following stringent standards of cleanliness to keep trace impurities of condensable vapours at ultra-low levels.

Here we report a thorough characterization of the chamber background contaminants facilitating data from Proton-transfer reaction mass spectrometry (PTR-MS) and a recently developed Proton Transfer Reaction Time-of-Flight instrument. PTR-MS is an emerging technique that has already found a wide range of applications in analytical science. It allows real-time measurements of volatile organic compounds (VOCs) in air with a high sensitivity (limit of detection several tens of ppt). In addition the PTR-TOF instruments mass resolving power of 4000 - 5000 and the mass accuracy of 5 ppm allows for the unambiguous sum-formula identification of e.g. hydrocarbons or oxygenated VOCs (Graus et al.). The co-addition of a series of stored PTR-TOF mass spectra (e.g. over a period of 10 to 30 minutes) allows to reach a limit of detection in the ppqv range by post experimental data processing.

We will discuss sources of trace impurities and will present efforts to reduce those during the first phase of the CLOUD operation. The results are discussed with respect to other chamber or flow tube facilities.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement number 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project number 3511030001), and from the Swiss National Science Foundation.

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Particle formation rates during the first CLOUD experiment

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Keywords: ion induced nucleation, sulfuric acid, CLOUD experiment.

Formation of atmospheric aerosol has been observed in a wide range of atmospheric conditions in many different locations and altitudes all over the globe (Kulmala *et al.*, 2004). Nucleation and subsequent condensational growth increase the total number of particles and modify the aerosol size distribution in the atmosphere, affecting the global radiation balance through both direct and indirect effects. Among the various nucleation mechanisms that occur in the atmosphere the ion induced nucleation mechanism is still poorly understood. One of the goals of the CLOUD experiments at CERN is to investigate to what extent the presence of ions in the atmosphere affects the formation of new particles (Kirkby *et al.*, 2007).

Numerous experiments have been performed in the new 26 m^3 stainless steel CLOUD aerosol chamber placed at the T11 beam line of the CERN Proton Synchrotron (PS) during the fall 2009 experiment. The PS provided an adjustable and precisely measurable beam of artificial cosmic rays, spanning the atmospheric ionization range from the upper troposphere to ground level (Duplissy *et al.*, 2009). Several particle formation events were observed following both neutral and charged pathways with a wide range of nucleation rates and growth rates at sulfuric acid concentrations comprised between 10^6 and 10^9 cm^{-3} and a relative humidity between 30% and 60%.

The investigation of the nucleation mechanism requires a detailed analysis of the initial steps of particle growth. In order to retrieve a detailed size distribution at the beginning of the nucleation event we employed a condensation particle counter (CPC) battery beside the standard size distribution measurement with a scanning mobility particle sizer (SMPS). The CPC battery consisted of 4 butanol-based and 2 water-based CPCs with different cut-off curves (D_{50} between ~ 2.5 and 7 nm). This allowed a more accurate determination of the initial growth rates where the SMPS measurement suffers from high diffusion losses, low charging probability and low time resolution. Furthermore an electrostatic precipitator placed in front of the CPC battery permitted the direct determination of the charged fraction of particles (Figure 1).

According to the nucleation theorem the number of molecules involved in the nucleation is directly related to the power law of the nucleation rate (Curtius, 2006). However, the detection limit of state of the art instrumentation is above the sizes at which the nucleation occurs. The CPC battery measurement reduces these uncertainties in the extrapolation of the "real" nucleation rate. The nucleation rates extrapolated from the CPC battery is then compared to the nucleation rates obtained from a mixing type CPC with a cut-off smaller than 2 nm.

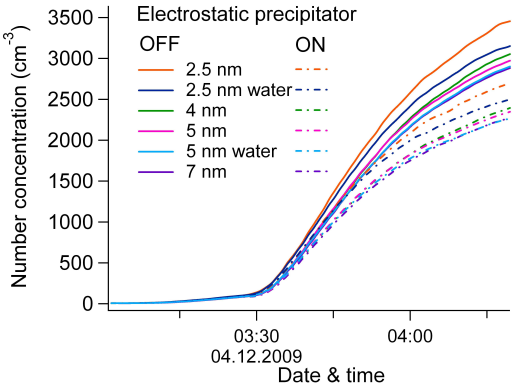

Figure 1. CPC battery output during run 36. The electrostatic precipitator removes the charged fraction.

A comparison of the neutral and charged nucleation rates and growth rates will be presented and the initial steps of the new particles formation will be discussed.

Acknowledgments: We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement number 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project number 01LK0902A), from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence program (project no. 1118615).

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Development and Characterization of different Calibration Methods for a Sulphuric Acid, CIMS

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Keywords: CIMS, sulphuric acid, calibration method, CLOUD experiment

A major portion of atmospheric particles is formed by nucleation, i.e. by gas-to-particle conversion, where sulphuric acid is assumed to be the most important precursor gas. Binary homogeneous nucleation (BHN) of sulphuric acid and water (H_2SO_4/H_2O) is very likely one of the most important atmospheric nucleation processes (Curtius, 2006). However, laboratory experiments that try to determine at what sulphuric acid concentrations the onset of atmospherically relevant nucleation rates occur, sometimes differ by order of magnitudes. In addition, it is not yet clear whether Ion Induced Nucleation (IIN) has a substantial impact on atmospheric aerosol formation. This question is being investigated within the CLOUD project.

During the CLOUD-09 experiment a Chemical Ionization Mass Spectrometer (CIMS) was used to measure the concentration of gaseous sulphuric acid. In order to reliably interpret the measured concentrations it is essential to calibrate this instrument. Here we present several different methods allowing quantitative measurements.

The chemical ionization mass spectrometer used during CLOUD-09 has been developed for continuous long term measurements of ultra-low H_2SO_4 concentrations by Greg Huey's group at the Georgia Institute of Technology.

The principle of this measurement is based on the reaction between H_2SO_4 and NO_3^- primary ions and the detection of HSO_4^- ions by a mass spectrometer. Mainly due to errors in the rate coefficient and a potential difference between the dwell time and the reaction time, it is necessary to calibrate the CIMS.

Therefore, this work focuses on the performance of a newly set-up calibration system. This system is based on the production of H_2SO_4 through the reaction of known concentrations of SO_2 molecules and OH radicals. OH is formed by the photodissociation of water vapor inside a quartz tube, which is illumintaed by a bandpass-filtered 185 nm light from a mercury lamp (Young et al., 2008). In order to produce known amounts of water vapor, a nitrogen flow is pushed through deionized water in a temperature-controlled bubbler.The components of the calibration unit are indicated in Fig 1. All major components (lamp, quartz tube, optical system, photodiode) are installed in a metal box, which is purged with a constant N_2 flow rate in order to provide a stable photon flux. The concentration of H_2SO_4 is derived from the gas concentrations the flow rates, the geometry and the UV light intensity.

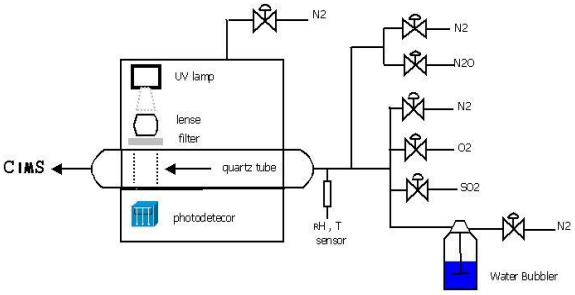

Fig. 1: A schematic of the calibration unit.

One key issue of this method is the fact that the spatial distribution of the absolute UV light intensity needs to be known precisely in order to calculate the produced H_2SO_4 correctly (Reimann, 2000). In order to avoid this potential source of error, we have tried to calibrate our photodiode by producing NO from illuminating N_2O and N_2 with the same UV light intensity used during the H_2SO_4 production. The NO concentration can be measured easily and from the reaction time the UV intensity can be calculated. This method is compared to the independent method of determining the $[H_2SO_4]$ by liquid ion chromatography. Therefore, the gas that leaves the quartz tube containing the H_2SO_4 is bubbled through a water bath and its concentration is derived from the SO_4^- signal. Another advantage of our set-up is the fact that it is a stand-alone system, i.e. it can be used to intercompare different H_2SO_4 - CIMS with the same calbration method.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement number 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project number 01LK0902A), from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence program (project number 1118615).

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Young, L. H. et al., Atmos. Chem. Phys., 8, 4997 ï 5016 (2008)

High-resolution mass spectrometry revealing ion cluster chemistry during the first H_2SO_4 nucleation experiments at the CLOUD chamber

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Keywords: CLOUD, sulfuric acid, cluster, nucleation, mass spectrometry.

Mechanisms have been proposed that link solar variability with changes in the climate through effects of cosmic rays on weather, aerosols and clouds (Carslaw *et al.*, 2002). However, the physical details, as well as the significance, of those mechanisms remain unclear.

The CLOUD (Cosmics Leaving OUtdoor Droplets) experiment at the CERN Proton Synchrotron (PS) aims at understanding the possible influence of cosmic rays on aerosol particles and clouds. It provides exceptionally clean and well-defined experimental conditions in an aerosol chamber of 26.1 m^3, together with the possibility of simulating cosmic rays "on demand".

It has been well established that nucleation from gaseous precursors form an important source of particles in the atmosphere, and that sulfuric acid plays a crucial role in atmospheric nucleation (e.g. Kulmala *et al.*, 2004, and Riipinen *et al.*, 2007). Hence, in the first measurement period of CLOUD (November and December 2009) one focus was on the investigation of sulfuric acid nucleation under different conditions (e.g. varying beam intensity).

The Atmospheric Pressure Interface Time-of-Flight Mass Spectrometer (APi-TOF) is a high-resolution mass spectrometer, built by Tofwerk AG, Thun, Switzerland, and described in detail in Junninen *et al.* (2010). Sampling occurs from atmospheric pressure through a critical orifice. While passing through differentially pumped chambers, the sampled ions are focused and guided to the mass spectrometer. During the operations at the CLOUD chamber, the specified mass accuracy was < 20 ppm, with a resolving power of 3000 Th/Th. Note that no ionization of the sampled aerosol was performed, and only "natural" ions are detected by this setup.

In the course of the experiments, sulfuric acid nucleation events were produced in the chamber. Ions participating in those nucleation events were predominantly negatively charged due to the low proton affinity of sulfuric acid and related molecular clusters. Due to the cleanliness of the chamber, the negative ion species registered by the APi-TOF were almost exclusively sulfur-containing compounds or clusters, the composition of which could be determined mainly based on their exact masses. The identified cluster ions were found to contain up to 11 sulfuric acid molecules, up to 3 ammonia molecules, as well as organic compounds. A part of a typical spectrum during one experiment is shown in figure 1. The appearance of the larger clusters coincides with the onset of particle formation as detected by other instruments. The analysis of the collected data is ongoing, and we expect to gain detailed insights on the ions and cluster kinetics involved in sulfuric acid nucleation.

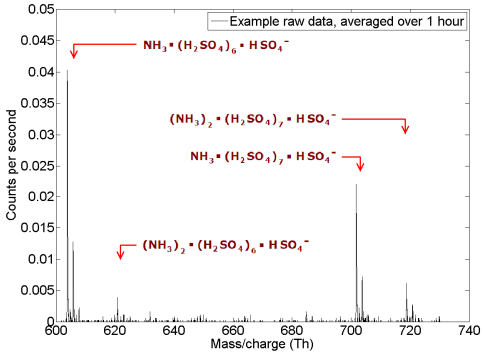

Figure 1. Part of a typical negative ion spectrum, and interpretations for the largest signals in this section.

We thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the PS. This research was funded by the EC's 7th Framework Programme (grant agreement number 215072: Marie Curie Initial Training Network "CLOUD-ITN"), the German Federal Ministry of Education and Research (project number 01LK0902A), the Swiss National Science Foundation, and the Academy of Finland Center of Excellence program (project number 1118615).

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Real-time analysis of particle nucleation and growth rates in the CLOUD experiment

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Keywords: CLOUD experiment, aerosol chamber, cosmic rays, data acquisition, nucleation, growth rate.

The possible influence of cosmic rays on aerosols and clouds is of considerable interest (Carslaw, 2009). The CLOUD experiment at CERN aims to study under controlled conditions the effects of cosmic rays on nucleation, cloud droplets and ice particles.

The CLOUD experiment involves a 3m stainless steel aerosol chamber exposed to a pion beam from the CERN Proton Synchrotron. A suite of instruments continuously analyse the contents of the chamber via sampling probes. Each instrument has it's own data acquisition system which delivers data in real-time to the CLOUD server.

A central data acquisition (DAQ) system collects and backs up the data from the instruments, provides multi-user access for monitoring the detector performance, and controls the operating conditions of the experiment. In addition the DAQ provides real-time physics analysis using the data from multiple instruments. This information is valuable in deciding on the optimum experimental conditions for the following runs and in responding to possible surprises.

Real-time analysis of nucleation events is based on the empirical formula:

$$\frac{dN_3}{dt} = K.[H_2SO_4]^p_{(t-dt)}.[RH]^q.(1+f[IP]^r_{(t-dt)}) - B.N_{3(t)}$$

This equation describes the time evolution of the aerosol concentration measured in a 3nm CPC as a function of sulphuric acid concentration, relative humidity (RH), ion pair concentration (IP) and a global aerosol loss rate (B). A detailed study has been carried out to determine each of the parameters in the above equation: the time shift, *dt*, to account for the delay between nucleation and detection of new particles; the various loss terms (diffusion to the walls, gas dilution, and particle coagulation); the power dependencies of the variables; and the scale factors.

The model predictions use the real-time measurements from several instruments: CPC battery and PSM for particle concentrations, SMPS/AIS for particle diameters, CIMS for $[H_2SO_4]$, dew-point/Pt100 sensors for RH, and AIS for ion pairs. The equation is fitted using a nonlinear numerical *Levenberg-Marquardt* algorithm. An example fit is shown in the figure below. In this paper we derive the parameters of the empirical model from the CLOUD data and then compare the measured and modeled particle nucleation and growth rates.

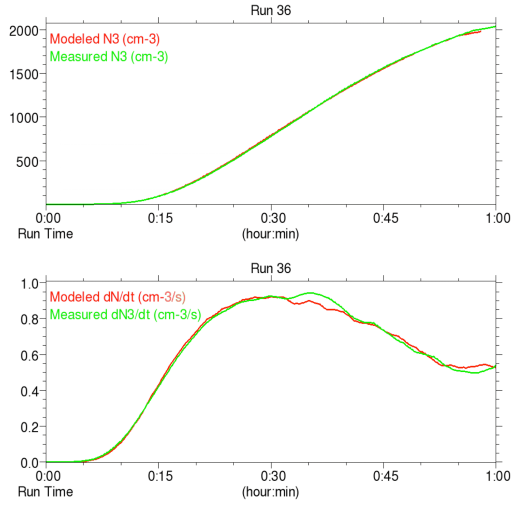

Figure 1. Example of a real-time fit to a nucleation event. The upper panel show the (smoothed) particle concentration, N_3, measured by a 3nm CPC (green curve) during the first hour of a nucleation event. The measured production rate, dN_3/dt, is shown in the lower panel (green curve). The red curves show the modelled values from simultaneous measurements of $[H_2SO_4]$, RH, and ion pairs.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement no. 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project no. 01LK0902A), from the Swiss National Science Foundation, and from the Academy of Finland Center of Excellence program (project no. 1118615).

Carslaw, K. (2009). *Cosmic rays, clouds and climate*. Nature, 460, 332-333.

CLOUD humidification system: the effect of the mixing fan

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Keywords: CLOUD experiment, humidification system, relative humidity.

In the Cloud 2009 experiment, the CLOUD chamber, a cylindrical electropolished stainless steel research vessel (26m^3) located at CERN, was used to simulate the influences of ions in atmospheric new particle formation under controlled laboratory conditions. For the atmospheric new particle formation, besides sulphuric acid, the relative humidity plays a major role. Therefore, the water vapour concentration in the chamber was carefully controlled and the gases fed into the chamber were distributed within via a mixing fan, operating at different fan speeds. A considerable number of runs were dedicated to study the influence of relative humidity on nucleation events. In this paper we study the possible effect of different fan speeds on chamber temperature, dew point, and relative humidity.

For the CLOUD 2009 experiment a humidification system suitable to provide a stable dew point was used. The system is based on a humidifier, which allows water molecules to be absorbed into the walls of a Nafion® tube and then be transferred into a dry gas stream. Besides the dew point, the key for the stability of relative humidity inside the chamber was an efficient chamber thermal jacket. For the relative humidity studies, the CLOUD internal chamber temperature and the dew point temperature at its outlet were recorded. The relative humidity was maintained in a range between 30 and 60 per cent and the fan speed was set to values within its full range depending on the experimental needs.

Figure 1 illustrates the performance of the humidification and thermal systems for three different runs. Each run was performed at a different fan speed (25, 50 and 100 %). The mean values of internal chamber temperature, $T_{chamber}$, relative humidity, RH inside the chamber and dew point, DP temperature at the chamber outlet with the corresponding standard deviations are given as a function of fan speed. No significant effect of the fan on either the mean values of $T_{chamber}$, RH, and DP or the respective standard deviations could be observed.

We conclude that the performance of the humidification system and the mixing fan was sufficient to provide stable and well mixed conditions for the nucleation experiments carried out.

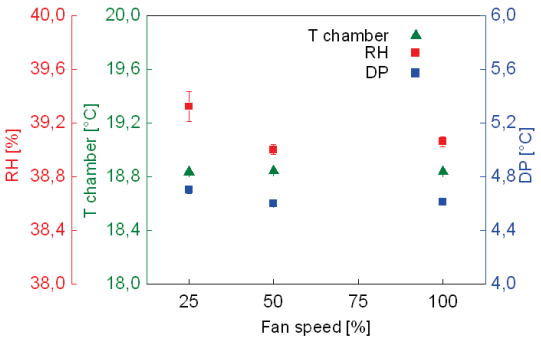

Figure 1. Chamber temperature (green triangles), relative humidity (red squares) and dew point (blue squares) with the corresponding standard deviations as a function of fan speed.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement number 215072 (Marie Curie Initial Training Network "CLOUD-ITN"), from the German Federal Ministry of Education and Research (project number 01LK0902A), from the Swiss National Science Foundation and from the Academy of Finland Center of Excellence program (project number 1118615).

Performance of an Expansion Type Condensation Particle Counter with Rapid Cut – Off Size Adjustment

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Keywords: nucleation, nano particles, CPC, CLOUD experiment

The physical as well as the chemical properties of nano particles are of special interest in various scientific fields, e. g. when atmospheric nucleation events are studied or within the wide field of nano - technology and its applications. However, especially the measurement of particles smaller than 3 nm in diameter is still an experimental challenge.

An instrument that is capable of measuring such small particle sizes is the expansion condensation particle counter (ECPC, see Saghafifar et al. 2009). The principle of this measurement technique is based on generating a strong adiabatic expansion of nearly saturated air to reach a high supersaturation that leads to an activation of small particles and lets them grow further to optically detectable sizes.

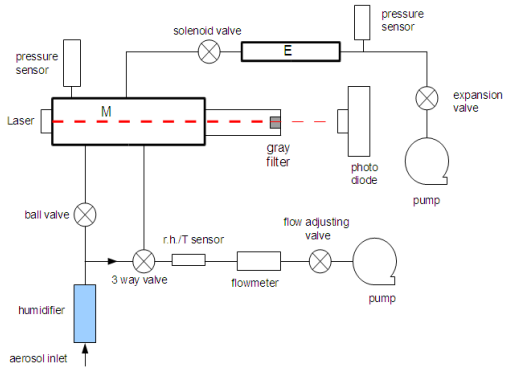

Fig. 1: Schematic of the instrument

The principle of one measurement cycle can be explained by the following steps and the schematic diagram in Fig. 1.: (1) Humidified aerosol is led into the main measurement chamber M. (2) The ball valve closes and the 3-way valve switches to isolate the aerosol. (3) The solenoid valve switches rapidly in order to connect chamber M with the partly evacuated chamber E, thereby initiating the expansion of air as well as the homogeneous growing of particles due to the condensation of water vapor. (4) The scattered light of the ensemble of growing particles is measured. For this purpose a certain volume is illuminated by a laser. The data is further evaluated using Mie theory which delivers the number density of particles. (5) The produced data is analyzed automatically by a LabVIEW program.

Every 5 to 10 s a new measurement cycle starts. This gives the opportunity to perform fast measurements of aerosol number concentrations.

The relative humidity and temperature sensor is one important component that has been added to the redesign of the original instrument. Those two parameters are measured at the beginning of each measurement cycle as they are essential for calculating the saturation ratio and the cut off diameter. This gives good control over the thermodynamic parameters within the CPC (i. e. the temperature after the expansion) whereas within most of the commercially available CPCs there is no possibility of rapidly changing the needed thermodynamic parameters.

In this particular design the two pressure sensors are installed to monitor the pressure ratio between chambers E and M. This pressure ratio can be adjusted to a defined value prior to each expansion. With the good control over the thermodynamic parameters and the variable pressure ratio, which is the main factor for calculating the saturation ratio, the cut off size can be changed easily in between two measurement cycles. This feature allows us in principle to perform coarse number size distribution measurements of particles in the size range below 20 nm. Not only the results from these experiments but also the basic theory this method relies on in this work will be presented.

The laser is directly coupled to the measurement cell to avoid any disturbances from ambient light. As the initial laser intensity I_0 needs to be known to perform the number density calculations a gray filter has been installed to attenuate the direct laser light by a factor of 100. This allows to perform a simultaneous measurement of the attenuated I_0 and the scattered light signal and therefore gives the opportunity to perform a fully automated measurement where no additional manual changes are needed to operate the instrument.

We would like to thank CERN for supporting CLOUD with important technical resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC's Seventh Framework Programme under grant agreement number 215072 (Marie Curie Initial Training Network "CLOUD - ITN"), from the German Federal Ministry of Education and Research (project number 01LK0902A), from the Swiss National Science Foundation and from the Academy of Finland Center of Excellence program (project number 1118615).

Saghafifar H. et. al. (2009) Aerosol Science and Technology, 43:8, 767 – 780