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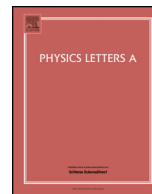


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## Response of cloud condensation nuclei (> 50 nm) to changes in ion-nucleation



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### ABSTRACT

In experiments where ultraviolet light produces aerosols from trace amounts of ozone, sulfur dioxide, and water vapor, the relative increase in aerosols produced by ionization by gamma sources is constant from nucleation to diameters larger than 50 nm, appropriate for cloud condensation nuclei. This result contradicts both ion-free control experiments and also theoretical models that predict a decline in the response at larger particle sizes. This unpredicted experimental finding points to a process not included in current theoretical models, possibly an ion-induced formation of sulfuric acid in small clusters.

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### 1. Introduction

The role of ionization in atmospheric processes by cosmic rays has been a controversial matter since it was suggested fifty years ago [1,2], and found in the correlation between global cloud cover and the influx of galactic cosmic rays (GCR) [3]. Subsequent studies have shown correlations between GCR variations and changes in aerosol counts and cloud properties in the atmosphere [4–6], but these are still disputed [7–9].

Fortunately, the issue can also be addressed in the laboratory. Experimental evidence for a microphysical mechanism was first reported in 2007 [10] and further experiments have recently added to its credibility [11,12]. These experiments initially showed that an increase in ionization leads to an increase in the formation of ultra-fine aerosols ( $\approx 3$  nm), but in the real atmosphere such small particles have to grow by coagulation and intake of condensable gases to become cloud condensation nuclei (CCN) (> 50 nm) in order to have an effect on clouds [13, Chapter 17].

Theoretical doubts about the likelihood of such particle growth into CCN have arisen from consideration of (1) the competition between the additional ultra-fine aerosols for the limited supply of condensable gases leading to a slower growth and (2) the larger losses of the additional particles during the longer growth-time to larger particles by coagulation and by other loss mechanisms. In addition there are many competing mechanisms for nucleation and growth in the atmosphere [14] which further complicate the picture. Indeed numerical studies using the current knowledge of aerosol dynamics predict that variations in the count of ultra-fine aerosols will lead only to an insignificant change in the count of CCN [15,16]. It is even suggested that an increased production of

ultra-fine particles as a result of GCR ionization leads to a reduction in the CCN count.

### 2. Experimental setup

In order to study the growth of aerosols to CCN sizes, measurements were performed in an 8 m<sup>3</sup> reaction chamber (SKY2) made from electro-polished stainless steel shown schematically in Fig. 1. One side was fitted with a Teflon foil to allow ultraviolet light (253.7 nm) to illuminate the chamber, which was continuously flushed with dry purified air. Variable concentrations of water vapor (H<sub>2</sub>O), ozone (O<sub>3</sub>), and sulfur dioxide (SO<sub>2</sub>) could be added to the chamber, where the pressure was held a few Pa above atmospheric pressure, and the temperature at around 296 K. The UV-lamps initiated a photochemical reaction producing sulfuric acid (H<sub>2</sub>SO<sub>4</sub>).

Ions were produced in the chamber by the naturally occurring GCR and by background radiation from radon, and the ionization could be enhanced with two Cs-137 gamma sources (30 MBq), mounted on each side of the chamber. The total number of aerosols generated in the chamber were measured with a TSI Model 3775 Condensation Particle Counter (CPC) with a cutoff at 4 nm. A particle size measurement was done with an electrostatic classifier (TSI model 3080) fitted with a nano-DMA (TSI model 3085) covering the range 3–65 nm and a CPC (TSI 3025A). Ultra-fine H<sub>2</sub>SO<sub>4</sub>-water aerosols ( $\approx 10$  nm) could be generated with an Electro Spray Aerosol Generator (TSI model 3480).

Concentrations of ozone were measured with a Teledyne T400 analyzer and sulfur dioxide with a Thermo 43 CTL analyzer. The chamber was also equipped with instruments to measure temperature, differential and absolute pressure, humidity, and UV intensity.

Estimates of the sulfuric acid concentrations were made by measuring the growth-rate of particle diameters above 3 nm [17].

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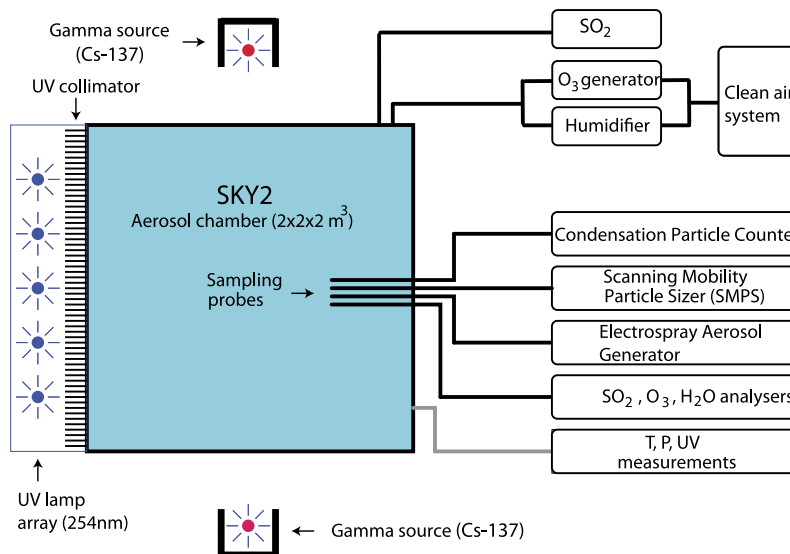


Fig. 1. Schematic diagram of the SKY2 experiment.

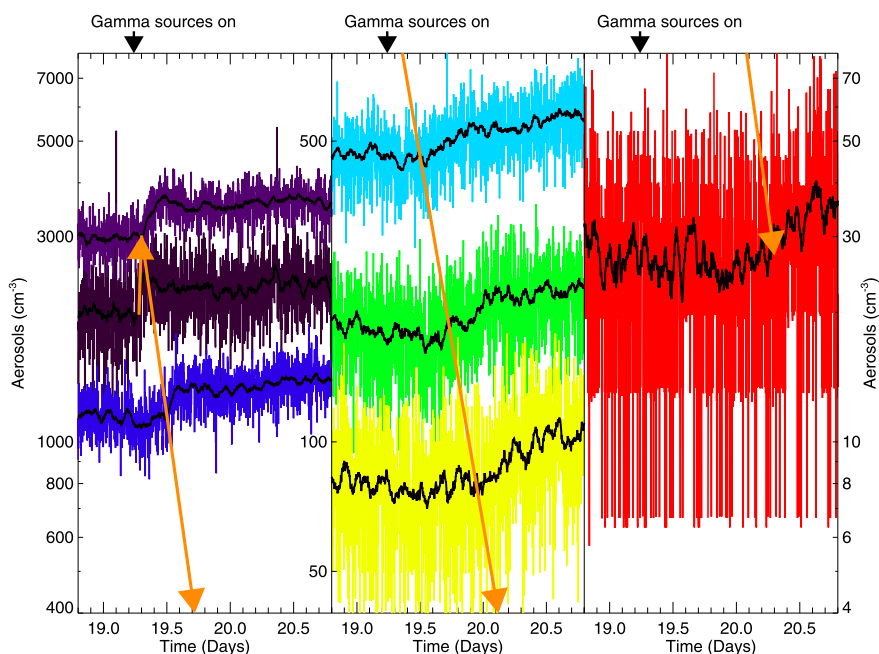


Fig. 2. During a typical experimental run, number densities of aerosol particles of increasing diameter were observed as a function of time. Left panel: 3–10 nm (black), 10–20 nm (purple), 20–30 nm (dark blue). Middle panel: 30–40 nm (light blue), 40–50 nm (green), 50–60 nm (yellow). Right panel: 60–68 nm (red). At  $\approx 19.2$  days the gamma sources were opened to increase the ionization as described in the text, and an increase in aerosol density began immediately in the 3–10 nm curve (black). Subsequently the increase in number densities slowly propagated down to the larger aerosol sizes, as shown by the slanting arrow. Note that the number of particles in the first bin (3–10 nm) is relatively low because of a lower sensitivity of the instrument to the smallest aerosols. Black curves are an average over 67.5 minutes.

This method gave typical concentrations in the range 1–10 ppt, i.e.,  $\sim 10^7$ – $10^8$  molecules  $\text{cm}^{-3}$ .

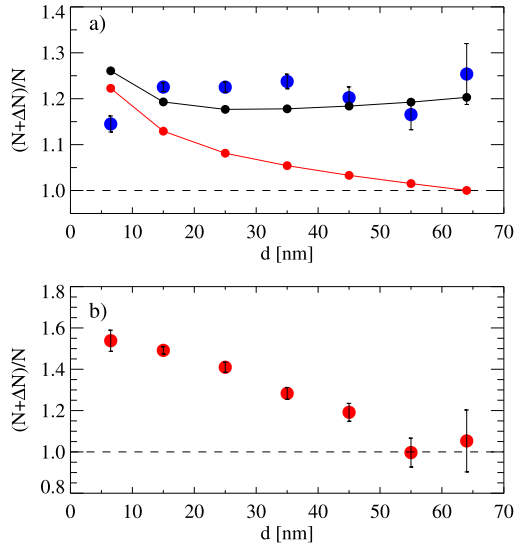
The experiments were run in a mode where steady state conditions of  $\text{H}_2\text{SO}_4$  were achieved under continuous exposure to the UV-light. Typically the gas mixture in the reaction chamber consisted of 40–50 ppb  $\text{O}_3$ , 0.8–1.0 ppb  $\text{SO}_2$  and a relative humidity of 25%.

Experiments were performed under various levels of ionization and UV intensity in the chamber. After changing one of these parameters the aerosols were allowed to grow and conditions to settle to a new steady state for a period of 24–36 hours. For example the gamma sources were opened resulting in an increase in ionization from about 3 ion-pairs  $\text{cm}^{-3} \text{s}^{-1}$  to 60 ions-pairs  $\text{cm}^{-3} \text{s}^{-1}$ . This resulted in an increase of about 20% in the formation of small

aerosols. The parameters were then kept constant for a period of about 36 hours until the new steady state was achieved.

### 3. Results

Fig. 2 shows such a run, where the number densities of seven sizes of aerosols, from 6.5 nm to 64 nm, are plotted as a function of time. When the gamma sources were opened, at  $\approx 19.2$  days, an increase in aerosol density was seen to follow directly in the 3–10 nm curve (black) and then to propagate slowly through increasing aerosol diameters up to the larger aerosol sizes. After a new steady state was reached, the gamma sources were closed, and a small decrease in aerosol density could be monitored, again



**Fig. 3.** Steady state response to a change in nucleation as a function of particle diameter, normalized to the particle number before two types of perturbation. (a) Ion-induced increase in nucleation. Blue circles are the experimental results averaged over five runs. The red curve is a typical result of a numerical simulation of the experimental situation using a standard numerical aerosol model. Notice that the expected response from the modeling decreases strongly with particle diameter in contrast with the experimental results. A much better agreement is seen with a numerical simulation in the black curve, where the concentration of sulfuric acid is held constant. (b) Control experiment where the increase in particle concentration is done by injection of  $\text{H}_2\text{SO}_4$ -water ultra-fine aerosols ( $\approx 6$ – $8$  nm) under constant UV intensity and trace gas concentrations, and no gamma source ionization. Notice that in this case the response (red circles) diminishes as aerosol size increases. Error bars are  $\pm 1$ - $\sigma$  errors.

starting quickly with the small aerosols and propagating gradually to the larger aerosols (not shown in Fig. 2).

For each experimental run the density of particles before (and after) an imposed ionization change was averaged over a period of 2.25 hours (prior to and after the change) and the mean and standard error of the mean was calculated. And finally the change in the response was averaged over five runs. The blue circles in Fig. 3a show the relative response to changes in ion-nucleation as a function of particle size, averaged over the five runs. It is seen that the response is remarkably constant over the shown size range.

It is of interest to contrast the above experiment to a situation without ionization and a constant  $\text{H}_2\text{SO}_4$  production subject to an increase in ultra-fine aerosols ( $d \approx 6$ – $8$  nm). The experimental procedure is first to reach steady state conditions using a constant UV intensity and trace gas concentrations as before, followed by a constant injection of  $\text{H}_2\text{SO}_4$ -water ultra-fine aerosols produced by the Electrospray Aerosol Generator. Fig. 3b displays the response, averaged over 3.5 hours, as a function of aerosol sizes to the aerosol injection. It is seen that in this case the response is diminishing as a function of size in accordance with the theoretical expectations.

The experimental results can be compared with numerical simulations of a general dynamics equation of aerosols. The evolution of the cluster distribution is given by [13]

$$\frac{\partial N_k}{\partial t} = \frac{1}{2} \sum_{j=2}^{k-1} K_{j,k-j} N_j N_{k-j} - \sum_{j=1}^{\infty} K_{k,j} N_k N_j - \frac{\lambda}{r_i^\gamma} N_k + \beta_{k-1} N_{k-1} - \beta_k N_k + S \delta_{k,k_0} \quad (1)$$

where  $N_k$  is the number density of clusters each containing  $k$  sulfuric acid molecules, assuming that the equilibrium concentration of water molecules in each cluster is reached instantaneously [18].  $K_{k,j}$  is the coagulation coefficient determined from Laakso et

al. [19], and can be used for all Knudsen numbers and hence from diameters of  $< 1$  nm to  $> 1$  microns. The radius  $r_i$  of a cluster with  $i$   $\text{H}_2\text{SO}_4$  molecules and a number of water molecules depends on the humidity [13, Chap. 10]. Particle loss to the chamber walls is approximated with the  $\lambda/r_i^\gamma$  term where  $\gamma$  is determined experimentally to  $\gamma = 0.69 \pm 0.05$  from the decay of particles in the chamber, and  $\lambda = (6.2 \pm 2.0) \cdot 10^{-4} \text{ nm}^\gamma \text{ s}^{-1}$ .  $S$  is the production of new critical clusters with size given by  $k_0$   $\text{H}_2\text{SO}_4$  molecules. The nucleation rate  $S$  is either a constant  $S = S_0$  or function of the  $\text{H}_2\text{SO}_4$  concentration, e.g.  $S = \alpha [\text{H}_2\text{SO}_4]^2$ , where  $\alpha$  is a constant. The  $\beta_k$ -term describes the condensation of  $\text{H}_2\text{SO}_4$  molecules in the gas phase to the  $k$ 'th cluster and are found according to Laakso et al. [19], with the value 1 of the mass accommodation coefficient [20], and a mean free path from Lehtinen et al. [21].

The equation governing the sulfuric acid concentration is

$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = P_{\text{H}_2\text{SO}_4} - (L + \lambda_{\text{H}_2\text{SO}_4})[\text{H}_2\text{SO}_4] \quad (2)$$

where  $P_{\text{H}_2\text{SO}_4}$  is the production of gaseous sulfuric acid. The second term  $L$  is the loss of  $\text{H}_2\text{SO}_4$  molecules to the aerosols by condensation. The last term is the loss of  $\text{H}_2\text{SO}_4$  molecules to the chamber walls, and is determined from extrapolating the size dependent aerosol losses to the size of a  $\text{H}_2\text{SO}_4$  molecule to  $\lambda_{\text{H}_2\text{SO}_4} = (7.2 \pm 3.0) \cdot 10^{-4} \text{ s}^{-1}$ . The model is described in more detail in Bondo et al. [22].

#### 4. Discussion

The red curve in Fig. 3a shows the result of a numerical simulation of an increase in the nucleation similar to the experimental situation, where the production term of  $\text{H}_2\text{SO}_4$  is kept constant, but the concentration of  $\text{H}_2\text{SO}_4$  can vary. The response goes slowly to zero with increasing size of the clusters, due to a smaller concentration of  $\text{H}_2\text{SO}_4$ . This simulation of the aerosol dynamics is consistent with a number of recent simulations which show very small responses at CCN sizes to a change in the nucleation rate. In their MODGIL simulation Pierce and Adams found responses of 0.004% in CCN (at 0.2% supersaturation) to a 4-fold increase in new particle formation, and in another simulation (IONLIMIT) they found a 0.08% change in CCN (again at 0.2% supersaturation) to a 24% increase in nucleation [15].

As the expected result shown by the red curve in Fig. 3a is contradicted by the experimental results (blue circles) an obvious question is whether the ionization by gamma rays may produce sufficient  $\text{H}_2\text{SO}_4$  in the gas phase to replace the expected loss of  $\approx 3$ – $7\%$  from the additional particles (estimated from numerical simulations). Each ion pair will on average [23,24] produce two OH molecules. Therefore with an ionization of  $60 \text{ ion-pairs cm}^{-3} \text{ s}^{-1}$  the production will be  $120 \text{ molecules cm}^{-3} \text{ s}^{-1}$ . From the experimentally estimated losses and growth rates the production of  $\text{H}_2\text{SO}_4$  from the photolysis is  $3.5 \cdot 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$ . If every OH molecule becomes an  $\text{H}_2\text{SO}_4$  molecule its production will be 0.3% of the photolysis, i.e. 10 times lower than estimated loss of  $\text{H}_2\text{SO}_4$ . From the experiment it is known that only a minor fraction of the OH are consumed in the pathway that leads to  $\text{H}_2\text{SO}_4$ . It is therefore safe to conclude that the production of  $\text{H}_2\text{SO}_4$  by this path is at least an order of magnitude too small to explain the observed. Another main chemical species produced in moist air ( $\text{N}_2$ - $\text{O}_2$ - $\text{H}_2\text{O}$ ) is nitric acid ( $\text{HNO}_3$ ) that potentially could help the condensational growth of the aerosols. Experimentally it is found that each ion-pair produces 0.4  $\text{HNO}_3$  molecules [25], which in the chamber leads to a production of  $24 \text{ cm}^{-3} \text{ s}^{-1}$   $\text{HNO}_3$  molecules. This production is only 0.07% of the photolysis production of  $\text{H}_2\text{SO}_4$ , and therefore nearly 40 times too small to explain the experimental results. Additionally the presence of a charge on a cluster can enhance growth via electrostatic effects [14]. But this

effect diminishes with size and is negligible above 10 nm [26] and thus cannot explain that we observe the same relative effect all the way to sizes larger than 60 nm.

In a second simulation, illustrated in the black curve in Fig. 3a, the concentration of  $\text{H}_2\text{SO}_4$  is artificially held constant. In this case the response of larger particles to the additional nucleated particles is not going to zero and the match to the experimental results is much better. How, then, is the growth of the particles sustained? The indication from the second numerical simulation is that effectively there is no decrease in the concentration of condensable gases, even though the UV photolysis of  $\text{H}_2\text{SO}_4$  is held constant throughout the duration of the experiment. But the additional ion-nucleated particles should effectively decrease the  $\text{H}_2\text{SO}_4$  concentration with  $\approx 3\text{--}7\%$ .

A possible explanation could be that the charged clusters are producing additional  $\text{H}_2\text{SO}_4$  molecules from reactions involving negative ion chemistry of  $\text{O}_3$ ,  $\text{SO}_2$  and  $\text{H}_2\text{O}$ , where a negative ion can be reused in a catalytic production of several  $\text{H}_2\text{SO}_4$ . Such reactions were first suggested in Svensmark et al. [10], and also in a recent experiment [27] looking at isotope fractionation of sulfur from either UV or from ion-induced generation of  $\text{H}_2\text{SO}_4$ , where the sulfur isotope fractionation was used to distinguish the different pathways leading to  $\text{H}_2\text{SO}_4$ . It was found in the presence of ionization alone, that for each ion-pair  $27.8 \cdot 10^6$   $\text{H}_2\text{SO}_4$  molecules were produced, using extreme gas mixing ratios, i.e. 0.01%  $\text{SO}_2$ , 400 ppb  $\text{O}_3$ , 40% RH  $\text{H}_2\text{O}$  and 1000 ion-pairs  $\text{cm}^{-3} \text{s}^{-1}$ . Scaling to the present experiment gives a production of 38.9  $\text{H}_2\text{SO}_4$  molecules pr. ion-pair, and so a total production of  $\approx 2.3 \cdot 10^3$   $\text{H}_2\text{SO}_4$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ . This amounts to an increase of  $\approx 7\%$  in the production of  $\text{H}_2\text{SO}_4$  molecules which is sufficient to compensate for the numerically determined  $\approx 3\text{--}7\%$  decrease in  $\text{H}_2\text{SO}_4$  concentration caused by the increase in number of aerosols. Recent *ab initio* calculations have confirmed that an ion catalyzed cycle for sulfuric acid production is possible [28–30] and that this cycle may contribute with significant levels of sulfuric acid in chamber experiments such as this study.

An obvious question is how the above results are related to the real atmosphere where spatial and temporal scales are much larger than what can be obtained in the experiment. Due to the smaller spatial scales in the experiment ( $2 \times 2 \times 2 \text{ m}^3$ ) the loss of trace gasses and particles to the walls makes it necessary to grow particles faster ( $\approx 1.5$  day) to CCN sizes than in the real atmosphere ( $\approx 3\text{--}6$  days). The experimental concentration of the trace gas  $\text{SO}_2$  is therefore higher (0.8–1.0 ppb  $\text{SO}_2$ ) than in the real atmosphere ( $\approx 0.1$  ppb). For an aerosol growth by mainly condensation the growth velocity ( $\text{SO}_2$  concentration) divided with the loss is a fundamental parameter in the general dynamics equation of aerosols, Eq. (1), and therefore simple scaling of the  $\text{SO}_2$  concentration to the loss parameter suggest that the effect should persist even in situations with lower  $\text{SO}_2$  concentration and smaller losses.

A second observation is that the change in ionization used in the experiment ( $60$  ion-pairs  $\text{cm}^{-3} \text{s}^{-1}$ ) is much larger than changes observed from solar maximum to solar minimum ( $\approx 10\text{--}30\%$  of  $10$  ion-pairs  $\text{cm}^{-3} \text{s}^{-1}$ ) [5, Supplementary material]. It is however relevant to note that the main source of ionization in the atmosphere is caused by cosmic rays and the experimental situation is not too far from turning the cosmic ray ionization on or off all together. The experiment is therefore suggesting that the ion-mechanism is responsible for a sizable fraction of the CCN produced in the atmosphere simply by allowing particles to grow faster with smaller resulting losses.

It is less clear if the variations in ionization caused by solar activity can be seen in changes in the CCN production in the real atmosphere. In other words if a 10% change in the ionization could result in an  $\approx 1\text{--}2\%$  change in CCN concentration, which is of the order expected to have a observable impact on clouds [15]. Since

nucleation and growth in the atmosphere vary with temperature, pressure, and concentration of gases, the impact of the observed effect will depend on the specific location in the atmosphere. For instance trace amounts of base molecules such as ammonia can greatly affect nucleation. The nucleation rates in our experiment as a function of sulfuric acid concentration ( $16 \text{ cm}^{-3} \text{s}^{-1}$  for  $(2\text{--}4) \cdot 10^7 \text{ cm}^{-3}$  of sulfuric acid, in one experiment) seem to fit with atmospheric observations reported by e.g. Chen et al. [31] indicating that other species than sulfuric acid and water were present in our chamber. The discussion on how the suggested catalytic cycle may be affected by other species has been begun in Bork et al. (2012) [30], but is still require more work yet to complete. It is suggested that numerical simulations and further experiments may be part of resolving this issue.

## 5. Conclusion

So in conclusion it has been shown that an increase in ion-induced nucleation survives as the clusters grow into CCN sizes in direct contrast to the present neutral experiment and current theoretical expectations. It is proposed that an ion-mechanism exists which provides a second significant pathway for making additional  $\text{H}_2\text{SO}_4$ , as a possible explanation of the present experimental findings. Irrespective of the detailed mechanism leading to the results presented here they provide a possibly important missing piece of the puzzle as to why responses in aerosol to variations in ionization have been seen in cloud properties.

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