Atmospheric Ions and Aerosol Formation

Frank Arnold

Received: 22 January 2008 / Accepted: 30 May 2008 / Published online: 15 July 2008
© Springer Science+Business Media B.V. 2008

Abstract This paper discusses atmospheric ions and their role in aerosol formation. Emphasis is placed upon the upper troposphere where very low temperatures tend to facilitate new particle formation by nucleation. New measurements addressed include: Laboratory measurements of cluster ions, aircraft measurements of ambient atmospheric ions, atmospheric measurements of the powerful nucleating gas H_2SO_4 and its gaseous precursor SO_2 . The paper also discusses model simulations of aerosol formation and growth. It is concluded that in the upper troposphere new aerosol formation via ions is a frequent process with relatively large rates. However new particle formation by homogeneous nucleation which does not involve ions also seems to be efficient. The bottleneck in the formation of upper troposphere aerosol particles with sizes sufficiently large to be climate relevant is mostly not nucleation but sufficient growth of new and still very small particles. Our recent upper troposphere SO_2 measurements suggest that particle growth by gaseous sulphuric acid condensation can be efficient in certain circumstances. If so, cosmic ray mediated formation of CCN sized particles should at least occasionally be operative in the upper troposphere.

Keywords Atmosphere · Ions · Aerosol

1 Introduction

Atmospheric ions are involved in aerosol formation. Ions may grow sufficiently to become stable aerosol particles. Ion growth requires the presence of atmospheric trace gas molecules which have the ability to attach to ions. The ion growth speed which increases with the concentration of such trace gas molecules must be sufficiently large to allow ion growth within the relatively short ion lifetime. However such conditions are met only in certain atmospheric conditions. Whether ion induced aerosol formation makes a significant contribution to the atmospheric aerosol budget therefore remains an open question.

F. Arnold (✉)
Atmospheric Physics Division, Max Planck Institute for Nuclear Physics (MPIK), P.O. Box 103980,
69029 Heidelberg, Germany
e-mail: frank.arnold@mpi-hd.mpg.de

Fig. 1 Simplified scheme of atmospheric ion-induced formation of aerosol particles followed by particle growth to CCN size. Numbers denote approximate diameters (in nm) of ions and particles. *X* denotes nucleating gas molecules and *Y* denotes condensing gas molecules

It has even been speculated that aerosol particles formed via ions may grow to the size of cloud condensation nuclei and thereby may influence clouds and climate (Ney 1959). This ion-climate connection hypothesis has recently attained considerable interest stimulated by several recent reports claiming observational evidence for a cosmic ray climate connection hypothesis (cf. Marsh and Svensmark 2000; Neff et al. 2001; Shaviv 2002; Shaviv and Veizer 2004; Harrison and Stephenson 2006). In particular observations were reported suggesting that low clouds are correlated with cosmic rays (Marsh and Svensmark 2000). However the current discussion of the cosmic ray climate connection hypothesis is highly controversial. A major point of criticism is the apparent lack of an obvious physical mechanism linking climate with cosmic radiation (CR). Several potential mechanisms have been proposed, some of which being only poorly understood. Among the proposed mechanisms, probably the one most often considered (and perhaps least speculative) involves ion induced formation of aerosol particles. Some of these new particles can grow sufficiently to act as cloud condensation nuclei (cf. Arnold 1980a, 1980b, Arnold 1981a, 1981b; Yu and Turco 2001; Eichkorn et al. 2002; Carslaw et al. 2002; Harrison and Carslaw 2003; Lee et al. 2003; Lovejoy et al. 2004; Kazil and Lovejoy 2004; Yu et al. 2002). However, ion induced CCN formation is itself not fully understood and it is uncertain whether it can significantly contribute to the atmospheric CCN population and thereby influence climate.

Aerosols influence climate in numerous direct (WMO 2001) and indirect ways (WMO 2001; Lohmann and Feichter 2005; Chen and Penner 2005). If sufficiently large, they scatter sunlight and eventually act as cloud condensation nuclei (CCN) and cloud ice (freezing) nuclei (IN), if CR mediated aerosol formation was indeed contributing significantly to the atmospheric budget of grown aerosol particles. CR would have a potential to influence climate. CR are modulated by solar activity variations, and so might also be their potential effect on aerosols and CCN. An analysis of Marsh and Svensmark (2000) identified a signature of the 11-years sunspot cycle in low clouds (cloud-coverage).

The present paper is focussed on upper tropospheric processes that lead from CR generated ions to CCN. These processes (Fig. 1) involve clustering of atmospheric trace gas molecules *X* (particularly H_2SO_4) to ions, mutual recombination (neutralization) of large cluster ions leading to stable but still very small aerosol particles, and growth of fresh aerosol particles preferably by condensation of atmospheric trace gases *Y*. The first two steps leading from ions to stable aerosol particles are termed ion induced nucleation (hereafter INU). The third step involves trace gases *X* and in addition also trace gases *Y* which have a potential to condense on stable aerosol particles and thereby induce particle growth. Several different species *Y* may be present having different equilibrium saturation pressures and therefore starting at a given temperature to attach to stable particles at different threshold particle sizes. In addition there may be present trace gases which react with particles leading to molecules which remain bound to the particle and therefore contribute to particle growth.

At first glance, ion induced CCN formation seems to be similar to what is taking place in the famous “Wilson cloud chamber” which had an important role in the development of high-energy particle physics. Tracks of ionizing high energy particles traversing the chamber are visualized by converting ions to light scattering water droplets. This is achieved by building up a very high water vapour super-saturation (about 400%) which allows efficient INU and efficient small particle growth. Here $X = Y = \text{H}_2\text{O}$.

In the atmosphere water vapour super-saturation builds up occasionally leading to cloud droplet formation. However, these super-saturations remain very small and only very rarely exceed 1% but almost never reach 2%. In contrast with the situation in a Wilson cloud chamber the minimum water droplet diameter of a stable water droplet in the atmosphere is much larger (300 nm). Hence ions cannot grow sufficiently to become stable water droplets. Ion-induced aerosol particle formation can take place only in the presence of highly super-saturated atmospheric trace gases X . Since such trace gases rapidly (within less than about one hour) condense on pre-existing aerosols, they cannot be efficiently transported in the atmosphere and must therefore be produced locally by photochemical processes.

In this context, sulphuric acid (H_2SO_4) could emerge as one of the most important candidates for X as an nucleating and condensing trace gas. Being very hygroscopic, it tends to co-cluster with water vapour molecules, eventually leading to new stable aerosol particles (bi-molecular nucleation). Due to their strongly hygroscopic nature, sulphuric acid aerosol particles may act as atmospheric CCN already when their diameter exceeds only about 30 nm (at 1% super-saturation; see below).

Low temperatures favour nucleation. Therefore the cold upper troposphere represents a region of primary interest, at the condition that gases of type X are present and that their concentrations are large enough. In fact, so far only a single X -gas has been detected in the upper troposphere, namely, H_2SO_4 (cf. Heitmann and Arnold 1983; Viggiano and Arnold 1995). It is also the only Y -gas known to be present in the upper troposphere. Another feature of the upper troposphere which tends to facilitate new particle formation and growth is the relatively small surface of pre-existing aerosol particles.

After their formation in the upper troposphere, new particles may undergo downward transport into the middle and lower troposphere where they may act as CCN. Alternatively new particles formed in the upper troposphere may also experience upward transport to the lower stratosphere. If this cross-tropopause transport takes place in the tropics, it is likely that it is followed by further transport from the lower to the middle stratosphere. Hence particles formed in the upper troposphere may also experience transport into the stratosphere and thereby feed the stratospheric aerosol layer.

The present paper critically discusses tropospheric ions and ion induced formation of atmospheric secondary sulphuric acid aerosol particles and CCN in the light of new laboratory experiments and new atmospheric measurements recently made by our MPIK Heidelberg group. Emphasis is placed upon the upper troposphere where low temperatures and low abundances of pre-existing aerosol particles tend to facilitate new particle formation and growth. The present paper also places CR mediated INU into a broader perspective by comparing INU with new particle formation via homogeneous sulphuric acid nucleation (HONU), a mechanism that does not require ions.

2 Atmospheric Ions

Ions are formed in the Earth’s troposphere by numerous processes. The most important ionization sources involving air ionization are galactic cosmic rays, radio activity, and electric discharges particularly including corona and lightning.

Fig. 2 Vertical profile of the total concentration of atmospheric positive ions for daytime conditions. Also indicated are the most abundant positive and negative ion species measured by MPIK Heidelberg

Primary charged species formed by air ionization include free electrons and the simple molecular and atomic ions N_2^+ , O_2^+ , N^+ , and O^+ . Free electrons attach rapidly to O_2 leading to O_2^- . Thereafter primary positive ions and O_2^- undergo ion–molecule-reactions leading to secondary positive and negative ions, mostly complex cluster ions. Ultimately ions are lost by ion–ion recombination, and in aerosol rich air masses, also by attachment to aerosol particles. For upper tropospheric air, in the absence of aerosol particles, a steady state treatment of ion formation and ion loss by ion–ion recombination yields a total ion concentration:

$$n_i = (Q/\alpha)^{1/2} \quad (1)$$

(Q in $\text{cm}^{-3} \text{s}^{-1}$; α in $\text{cm}^3 \text{s}^{-1}$; n_i in cm^{-3}).

In the troposphere below about 12 km the ion–ion recombination coefficient α is about $1.7 \cdot 10^{-6} \text{ cm}^3 \text{s}^{-1}$ (Bates 1985), and hence $n_i = 0.0013 Q^{1/2}$.

The rate Q of CR induced ionization is largest at about 14 km altitude. At middle latitudes where the local tropopause is located at about 12 km, the maximum Q is found just above the tropopause in the lowermost stratosphere. Since CR experience partial shielding by the magnetic fields of the Sun and the Earth, Q varies with geomagnetic latitude and solar activity. It is larger at the Earth's poles compared to the equator. However, the variation of Q over a solar sunspot cycle is relatively small. At middle latitudes and around 14 km altitude Q decreases with increasing solar activity (from sunspot minimum to sunspot maximum) only from about 40 to $30 \text{ cm}^{-3} \text{s}^{-1}$. According to expression (1), at middle latitudes the corresponding variation of n_i is only 4200–4850 cm^{-3} over a solar cycle.

Therefore, a very sensitive process must be involved if the faint increase in n_i induced by the 11-year solar activity cycle is to lead to a significant increase of CCN formation via INU.

The vertical n_i profile (Fig. 2) has two pronounced maxima, one in the ionosphere (around 100–200 km), and one in the stratosphere (around 10–30 km). The ion lifetime with respect to ion–ion recombination is $t_r = 1/(\alpha \cdot n_i)$. Below 12 km altitude t_r increases

with increasing height from about 120 s (12 km) to 400 s (3 km) (Viggiano and Arnold 1995).

Therefore the time span (t_r) available for the ion chemical evolution is relatively short which implies that atmospheric trace gases involved in the conversion of primary to secondary ions and in the growth of secondary ions must be sufficiently abundant. For example for an altitude of 10 km where $t_r = 200$ s the trace gas concentration must be at least about $3 \cdot 10^6 \text{ cm}^{-3}$ (corresponding to an atmospheric mole fraction of about $3 \cdot 10^{-13}$). Here a typical ion molecule collision rate coefficient of $2 \cdot 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ was considered.

The most abundant ion species observed in the free troposphere and the stratosphere (Fig. 2) have originally been detected by the MPIK Heidelberg group (Heitmann and Arnold 1983; Möhler and Arnold 1992; Viggiano and Arnold 1995) using ion mass spectrometers on flying platforms including aircraft, balloons, and rockets. These observed major ions are complex cluster ions containing H_2SO_4 , H_2O , HNO_3 , $(\text{CH}_3)_2\text{CO}$ and CH_3CN molecules attached to core ions. These cluster ions are formed from precursor ions via ion–molecule-reactions involving the atmospheric trace gases H_2SO_4 , H_2O , HNO_3 , $(\text{CH}_3)_2\text{CO}$, and CH_3CN . Of these gases H_2SO_4 is particularly interesting as it represents a powerful nucleating agent (see above). An interesting question is whether large H_2SO_4 cluster ions involved in INU can in fact build up in the atmosphere. Another interesting question is why the observed major positive ions do not contain H_2SO_4 . Both questions will be answered below.

3 Ion Induced Sulphuric Acid Nucleation

This section of the paper addresses steps 1 and 2 of the scheme shown in Fig. 1 focussing on the case $X = \text{H}_2\text{SO}_4$. Recently, laboratory investigations of H_2SO_4 cluster ions have been made by two laboratories (Aeronomy Laboratory in Boulder, Colorado, and MPIK Heidelberg). The Aeronomy Lab investigations focussed on negative cluster ions containing up to 6 H_2SO_4 molecules and were made at different temperatures (Froyd and Lovejoy 2003; Lovejoy and Curtius 2001; Curtius et al. 2001; Lovejoy et al. 2004). The MPIK investigations were made at only one temperature (295 K), but include also larger negative and positive cluster ions containing up to 24 H_2SO_4 molecules (Wiedner 2000; Eichkorn 2001; Wilhelm et al. 2004; Sorokin et al. 2006). Here some of these MPIK results will be addressed.

Figure 3 shows mass distributions (envelopes) of negative cluster ions obtained in a flow reactor-mass spectrometer experiment of MPIK (Wilhelm et al. 2004; Sorokin et al. 2006). The ion mass spectrometer used was a large ion-mass spectrometer (LIOMAS) with a mass range of up to 10000 amu (atomic mass units). This instrument was developed by MPIK for measurements of atmospheric large cluster ions on aircraft platforms (see below). Synthetic air was passed through the flow reactor and traces of H_2SO_4 vapour and H_2O vapour (relative humidity: 4.1–6.2%) were added. Reagent ions introduced into the flow reactor were of the type $\text{NO}_3^-(\text{HNO}_3)_n(\text{H}_2\text{O})_w$ which are the same ions acting in the atmosphere as precursors of $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_a(\text{H}_2\text{O})_w$ ions (see above). The four mass spectra (Fig. 3) correspond to different gaseous H_2SO_4 concentrations. For the lowest H_2SO_4 concentration the spectrum is narrow, peaking around 200 amu and the major ions are $\text{NO}_3^-(\text{HNO}_3)_n(\text{H}_2\text{O})_w$ reagent ions with $n = 1$ and 2 and mostly $w = 0$. These ions were introduced into the flow reactor and unambiguously identified using a second ion mass spectrometer with higher mass resolution.

As the H_2SO_4 concentration is increased to $[\text{H}_2\text{SO}_4] = 5 \cdot 10^9 \text{ cm}^{-3}$, the spectrum becomes bi-modal and the second mode extends to 2400 amu. Now the major ions are

Wilhelm, Eichkorn, Wiedner, Pirjola, and Arnold (2004)

Fig. 3 Mass distributions of negative cluster ions measured in a laboratory flow reactor experiment of MPIK Heidelberg (Wilhelm et al. 2004; Sorokin et al. 2006). Plotted are envelopes of mass peak heights (ion count rates in arbitrary units) versus mass number (in atomic mass units). The four mass distributions correspond to different gaseous H_2SO_4 concentrations. For the lowest $[\text{H}_2\text{SO}_4]$ the ions are $\text{NO}_3^-(\text{HNO}_3)_a(\text{H}_2\text{O})_w$ cluster ions and for the 3 cases with elevated H_2SO_4 the ions are $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_a(\text{H}_2\text{O})_w$ cluster ions. For details see text

Fig. 4 Sulphuric acid mole fraction MOFA of $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_a(\text{H}_2\text{O})_w$ and $\text{H}^+(\text{H}_2\text{SO}_4)_a(\text{H}_2\text{O})_w$ cluster ions measured in the laboratory flow reactor experiment of MPIK (Sorokin et al. 2006). Also given are model calculations for cluster ions, electrically neutral $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ droplets, and droplets carrying a single elementary electrical charge. For details see text

$\text{HSO}_4^-(\text{H}_2\text{SO}_4)_a(\text{H}_2\text{O})_w$ cluster ions (hereafter termed $\text{HSO}_4^-A_aW_w$) containing numerous H_2O molecules. As $[\text{H}_2\text{SO}_4]$ is further increased the second mode shifts to larger mass numbers extending up to 4700 amu. In an analogous experiment with positive ions, cluster ions of the form $\text{H}^+A_aW_w$ were detected when gaseous H_2SO_4 was present. Again a second mode developed but remained smaller (3000 amu) compared to negative ions.

Figure 4 shows the measured H_2SO_4 mole fraction (MOFA) of $\text{HSO}_4^-A_aW_w$ and $\text{H}^+A_aW_w$ cluster ions (a is the number of sulphuric acid molecules and w is the number of water molecules contained in the cluster ion) versus a . Also shown are model simulations for cluster ions. For small a , MOFA is small for positive ions but large for nega-

tive ions. As the parameter a increases, the MOFA of positive and negative ions approach each other. Note that neutral $A_a W_w$ clusters which are also important in theories of homogeneous bi-molecular nucleation have so far not been measured (Laaksonen et al. 1995; Kulmala et al. 2004). Therefore the cluster ion measurements also help to constrain theories on homogeneous nucleation.

The above laboratory investigations of cluster ions confirm the efficiency of co-clustering of gaseous H_2SO_4 and H_2O . This co-clustering relies on strong hydrogen bonds forming between the clustering molecules. The H_2SO_4 molecule has a large gas-phase acidity and therefore tends to form strong hydrogen bonds with H_2O molecules which are not only abundant in the atmosphere but importantly possess an appreciable proton affinity. Small $HSO_4^- A_a W_w$ cluster ions have a large MOFA as the core ion HSO_4^- prefers H_2SO_4 ligands whose gas-phase acidity is much larger than the gas-phase acidity of H_2O ligands. In other words H_2SO_4 ligands bond much more strongly to HSO_4^- . Small $H^+ A_a W_w$ cluster ions have a small MOFA since H_2SO_4 and H_2O have approximately the same proton affinity but in the flow reactor gaseous H_2O was much more abundant than gaseous H_2SO_4 . For larger cluster ions ligand–ligand bonding becomes increasingly important and therefore the MOFA of positive and negative cluster ions approach each other.

The above laboratory experiments also explain why the major positive cluster ions observed in the atmosphere (see Fig. 2) do not contain H_2SO_4 . In the atmosphere, as in the laboratory experiment, gaseous H_2O is far more abundant than gaseous H_2SO_4 . Therefore the most abundant positive cluster ions can not contain H_2SO_4 . Even worse the atmosphere contains trace gas molecules (like $(CH_3)_2CO$ and CH_3CN) which possess substantially larger proton affinities than H_2O and therefore are the preferred inner ligands of small atmospheric positive cluster ions.

The behaviour seen in Fig. 4 indicates that under the conditions of the laboratory experiment A-attachment to $HSO_4^- A_a W_w$ ions becomes faster than thermal A-detachment for mass numbers >1300 – 1400 amu corresponding to $a > 6$. It also indicates that for $a > 6$ A-attachment occurs on every collision of a gaseous A-molecule with a cluster ion (Sorokin et al. 2006). The ultimate decrease of the second mode simply reflects a kinetic limitation resulting from the limited time span ($t_{res} = 0.8$ s) an ion resides in the flow reactor. When gaseous H_2SO_4 is added, the ion life time t_c with respect to collision with a gaseous A-molecule ranges between about 0.025 s and about 0.06 s depending on the gaseous A-molecule concentration. Hence the ratio t_{res}/t_c ranges from about 8 to 32. This implies that on average during t_{res} an ion collides with 8–32 gaseous H_2SO_4 molecules depending on the gaseous H_2SO_4 concentration. If each of these collisions would lead to A-attachment the average mass numbers of the ions would be about 1600–6000 amu (including equilibrium H_2O uptake as well). In comparison the second modes of the mass spectra of negative ions extend to largest mass numbers of 2400 to 4700 amu. Our laboratory experiments with $H^+ A_a W_w$ ions also revealed the presence of a second mode. However, compared to the second mode $HSO_4^- A_a W_w$ ions, the second mode $H^+ A_a W_w$ ions are smaller. Probably this reflects more efficient A-detachment from $H^+ A_a W_w$ ions, induced either by thermal collisions or by switching with H_2O molecules.

In the atmosphere at 10 km altitude where temperatures are very low (around 223 K at middle latitudes), thermal A-detachment from ions is expected to be very slow. Hence ion growth is expected to be limited by the number of gaseous H_2SO_4 molecule collisions an ion experiences during its life time $t_r = 200$ s. On average this number is equal to t_r/t_c where $t_c = 1/k[H_2SO_4]$ is the time needed for an ion to collide with a gaseous H_2SO_4 molecule. Here $k = 2 \cdot 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ is the ion–molecule–collision rate coefficient and $[H_2SO_4]$ is the gaseous H_2SO_4 concentration. Hence $t_c = t_r = 200$ s corresponds to

$[\text{H}_2\text{SO}_4] = 3 \cdot 10^6 \text{ cm}^{-3}$. For efficient formation of $\text{HSO}_4^- \text{A}_a \text{W}_w$ and $\text{H}^+ \text{A}_a \text{W}_w$ cluster ions at 10 km altitude $[\text{H}_2\text{SO}_4]$ need to be larger than $3 \cdot 10^6 \text{ cm}^{-3}$.

Are H_2SO_4 concentrations sufficiently high in the upper troposphere? This question will be addressed in the following section of the paper.

4 Atmospheric Sulphuric Acid

Gaseous sulphuric acid is present in the upper troposphere. It was originally detected via ambient atmospheric ion measurements by Arnold and Fabian (1980; see also review by Viggiano and Arnold 1995). Moreover, laboratory measurements (Reiner and Arnold 1993, 1994; Kolb et al. 1994; Lovejoy et al. 1996) explored the mechanism by which gaseous sulphuric acid is formed in the atmosphere.

Figure 5 shows a simplified schematic of atmospheric sulphuric acid processes. The sulphur bearing precursor gas from which gaseous H_2SO_4 is formed is SO_2 . Its sources are mostly combustion of sulphur containing fossil fuels, volcanism, and atmospheric photochemical SO_2 formation from oceanic plankton generated $(\text{CH}_3)_2\text{S}$. Of these sources fossil fuel combustion is clearly dominant. The SO_2 sinks are mostly deposition at the Earth's surface, cloud processes, and the gas-phase reaction with the hydroxyl radical OH. The OH reaction represents also the first and rate limiting step of SO_2 conversion to gaseous H_2SO_4 . Importantly, OH is recycled and therefore acts merely as a catalyst. In the upper troposphere OH is formed via O_3 photolysis and also via the photolysis of acetone $(\text{CH}_3)_2\text{CO}$ and other organic trace gases. Once formed gaseous H_2SO_4 rapidly condenses on pre-existing aerosol particles PAP (mostly within less than 1000 s). Hence a steady-state treatment yields as a first approximation $k[\text{SO}_2][\text{OH}] = [\text{H}_2\text{SO}_4]/t_s$ where $k = 1.5 \cdot 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ is the rate coefficient of the OH-reaction and t_s is the gaseous H_2SO_4 lifetime with respect to condensation. For example, for $t_s = 1000 \text{ s}$ and a typical noon-time $[\text{OH}] = 2 \cdot 10^6 \text{ cm}^{-3}$, one obtains $[\text{H}_2\text{SO}_4] = 0.003[\text{SO}_2]$ for cloud-free conditions around noon. Hence for such conditions, gaseous H_2SO_4 is to a large part controlled by SO_2 .

If gaseous H_2SO_4 reaches a sufficiently large super-saturation, nucleation takes place involving INU (ion induced nucleation) and eventually also HONU (homogeneous nucleation) leading to secondary aerosol particles (SAP). These SAP grow by Y-condensation and mutual coagulation. Ultimately SAP may suffer from coagulation scavenging by PAP

Fig. 5 Simplified scheme of atmospheric gaseous H_2SO_4 processes. HONU denotes homogeneous nucleation, PAP denotes pre-existing aerosol particles, and SAP denotes secondary aerosol particles formed by HONU and ion-induced nucleation (arrow labelled ions)

Fig. 6 Compilation of the ranges of daytime atmospheric gaseous sulphuric acid concentrations measured by MPIK Heidelberg using ground-based (green bar), mountain sites (blue bar), aircraft-based (red box), balloon-based (black line), and rocket-based (black line) mass spectrometers. The dotted curve represents an equilibrium saturation curve for gaseous sulphuric acid (see text)

(pre-existing aerosol particles). Importantly, the SAP lifetime increases very markedly with increasing SAP size. Therefore SAP growth has a strong influence on SAP concentrations (see below). Whether INU and HONU become efficient critically depends on the gaseous sulphuric acid concentration $[\text{H}_2\text{SO}_4]$.

Figure 6 shows in a somewhat schematic form a compilation of the vertical distribution of daytime atmospheric gaseous sulphuric acid number concentration ranges measured by MPIK Heidelberg using mass spectrometers on the ground and on aircraft, balloons, and rockets. At ground-level and for cloud-free daytime conditions the measured $[\text{H}_2\text{SO}_4]$ range from about $1 \cdot 10^5$ – $1 \cdot 10^7 \text{ cm}^{-3}$. This substantial range of variability reflects to a large part a variability of $[\text{SO}_2]$. Data obtained in the free troposphere on a central European mountain site at 2300 m altitude range from $4 \cdot 10^5$ – $4 \cdot 10^6 \text{ cm}^{-3}$.

Data obtained in the upper troposphere by aircraft-based instruments (box in Fig. 4.2) range from about $6 \cdot 10^5$ – $6 \cdot 10^6 \text{ cm}^{-3}$. Finally data obtained in the stratosphere by balloon-based and rocket-based instruments (only an average daytime profile is shown) are around $1 \cdot 10^5$ – $3 \cdot 10^6 \text{ cm}^{-3}$ and exhibit a pronounced layer with a peak around 35 km.

Also included in Fig. 6 is an equilibrium curve representing the H_2SO_4 saturation concentration of an H_2SO_4 – H_2O mixture which is in equilibrium with atmospheric water vapour. Whenever the experimental data fall to the right of the equilibrium curve, gaseous H_2SO_4 is super-saturated. The largest H_2SO_4 super-saturations (saturation ratios > 1000) are found in the upper troposphere where temperatures are lowest. These very high super-saturations imply that thermal A-detachment from $\text{HSO}_4^- \text{A}_a \text{W}_w$ and $\text{H}^+ \text{A}_a \text{W}_w$ cluster ions can be neglected and therefore under these conditions INU should have no thermodynamic limitation.

The upper tropospheric H_2SO_4 concentrations correspond to $t_c = 100$ – 1000 s . In comparison, the ion lifetime t_r with respect to ion-ion recombination (around 200 s) falls in between the above t_c . This implies that in many situations a severe kinetic limitation ($t_r > t_c$) exists which prevents INU from becoming efficient. However occasionally t_c becomes smaller than t_r which should allow cluster ions to grow and INU to become efficient.

The major cause of these INU promoting conditions seems to be elevated SO_2 . Hence, SO_2 seems to be the major key to upper tropospheric INU and probably also HONU. However, our knowledge of upper tropospheric SO_2 is rather limited since only few data have previously been obtained by advanced instruments. Only very recently a number of advanced SO_2 measurements have been made by our group (Speidel et al. 2006) which revealed that SO_2 concentrations have a high degree of spatial variability. Around 10 km altitude SO_2 mole fractions range mostly from about 30–100 pptv but occasionally have a much larger variability from 10–3000 pptv. This implies highly variable concentrations of gaseous H_2SO_4 which in turn implies highly variable nucleation rates and particle growth rates.

5 Observations of Large Cluster Ions in the Upper Troposphere

Building on the laboratory experiments with H_2SO_4 cluster ions and the atmospheric gaseous H_2SO_4 measurements one expects large $\text{HSO}_4^- \text{A}_a \text{W}_w$ and $\text{H}^+ \text{A}_a \text{W}_w$ cluster ions to be at least occasionally present in the cold upper troposphere. If so, such ions would induce new aerosol particle formation and therefore would represent fingerprints of INU. Using our aircraft-based large ion-mass spectrometer LIOMAS we have made a search for such large cluster ions in the upper troposphere (Eichkorn et al. 2002; Arnold et al. 2008).

Figure 7 shows as an example time-series of ion composition data obtained by LIOMAS in cloud-free upper troposphere air during one aircraft flight (Arnold et al. 2008). Given are flight altitude and fractional abundances of positive and negative ions with mass numbers larger than 200, 300, and 600 amu. While the aircraft was cruising mostly around 8000 m

Fig. 7 Fractional abundances of positive and negative ions with mass numbers larger than 200 (green), 400 (yellow), and 600 (red) amu measured by MPIK Heidelberg during an aircraft mission over Central Europe. Also given is the flight altitude profile. (From Arnold et al. 2008)

altitude it occasionally intercepted air masses containing large negative and positive cluster ions with mass numbers larger than 600 amu. Negative and positive ions behave rather similar which suggests that one or several trace gases X are present which cluster to negative and positive ions. From the measured ions the concentrations of X were inferred. These range between $1\text{--}4 \cdot 10^6 \text{ cm}^{-3}$ which is very similar to the gaseous H_2SO_4 concentrations previously measured by our group in the upper troposphere around 8000 m altitude (see Fig. 6). This suggests at least that X is not more abundant than gaseous H_2SO_4 which implies that most likely X can be identified as H_2SO_4 .

Assuming X to be gaseous H_2SO_4 the rate J_i of ion-induced nucleation was calculated (Arnold et al. 2008). Around 8000 m altitude J_i ranges mostly from $3\text{--}25 \text{ cm}^{-3} \text{ s}^{-1}$. The latter value is equal to the maximum possible $J_i = Q$ where Q is the ionization rate. When $J_i = Q$, all ions become stable aerosol particles. Also calculated was the rate J_h of homogeneous bi-molecular nucleation (which does not require ions (Arnold et al. 2008). For the flight sections with low concentration of X , J_i tends to exceed J_h whereas for the section with high X concentrations J_h exceeds J_i . Even the highest J_h of about $100 \text{ cm}^{-3} \text{ s}^{-1}$ are much smaller than the highest possible J_h dictated by the rate at which an H_2SO_4 molecule collides with another H_2SO_4 molecule. Note that a nucleation rate of $3 \text{ cm}^{-3} \text{ s}^{-1}$ is already relatively high allowing the formation of more than 10000 aerosol particles $\text{cm}^{-3} \text{ hr}^{-1}$.

The above example of the atmospheric situation encountered during a single upper troposphere flight demonstrates that in the cold upper troposphere CR mediated INU (ion induced nucleation) can be very efficient. However this example also demonstrates that HONU (homogeneous nucleation) is also efficient and may become even more efficient than INU.

6 Aerosol Growth

Growth of newly formed, still very small aerosol particles is important for at least three reasons. Only sufficiently large particles become long lived, scatter sunlight efficiently, and eventually act as CCN and IN. Particle growth proceeds by Y condensation and coagulation. Growth by Y condensation may involve various types of different trace gases Y_i . Our gaseous H_2SO_4 measurements made in ground level air (Fiedler et al. 2005) indicate that gaseous H_2SO_4 contributes on average only about 5% to the growth of particles with diameters larger than 3 nm. Probably growth is mostly due to so far unidentified condensable organic trace gases. These condensable organics must be formed by chemical reactions involving relatively short lived organic precursor gases.

However in the upper troposphere the situation may be different. Here the short lived organic precursor gases may be less important since they are probably destroyed already during transport from the surface to the upper troposphere. In contrast, SO_2 , the precursor of gaseous H_2SO_4 , lives longer (about 10–20 days; see above) and therefore in the upper troposphere gaseous H_2SO_4 formation can continue for about 10–20 days. Hence new particles generated in the upper troposphere by INU or HONU can grow at least by gaseous H_2SO_4 condensation. Note that gaseous H_2SO_4 condensation does not require particularly low temperatures (see Fig. 6) and therefore can take place also in the middle and lower troposphere. This implies that particles formed in the upper troposphere may still continue to grow by gaseous H_2SO_4 condensation after downward transport and can act as CCN at lower altitudes.

Figure 8 shows as an example a 10 day model simulation (Arnold et al. 2008) considering an air mass which has ascended to 10 km and resided there for 10 days at clear-sky

Fig. 8 Results of a 10 day model simulation, for 10 km altitude, of number concentrations N_d of atmospheric aerosol particles with diameters larger than d nm. The air mass under consideration was assumed to ascend to 10 km altitude and reside there for a period of 10 days in cloud-free conditions. The initial SO_2 mole fraction was assumed to be 200 pptV. For details see text. (From Arnold et al. 2008)

conditions. After arrival at 10 km the initial SO_2 concentration was 200 pptV. The diurnal maximum OH concentration is $1 \cdot 10^6 \text{ cm}^{-3}$ which implies an e-folding lifetime for SO_2 of about 23 days.

On day 1, as the sun is rising, OH increases, leading to H_2SO_4 production. As a consequence H_2SO_4 rises to about $2 \cdot 10^7 \text{ cm}^{-3} \text{ s}^{-1}$ leading to HONU which in turn leads to a rise of the total aerosol particle number concentration N_{tot} to nearly $1 \cdot 10^5 \text{ cm}^{-3}$. Also the number concentrations N_4 and N_6 of particles with diameters larger than 4 and 6 nm rise steeply maximizing on day 1. In the afternoon as the solar elevation decreases OH, H_2SO_4 decrease steeply again. Also N_{tot} and to a lesser extent also N_4 and N_6 decrease due to coagulation. On the following days, the diurnal H_2SO_4 maximum decreases to about $4 \cdot 10^6 \text{ cm}^{-3}$ which is due to the decrease of OH and the increase of the aerosol surface leading to a decrease of the condensational H_2SO_4 lifetime. After day 1 the diurnal N_{tot} maxima nearly vanish, reflecting decreased HONU and increased scavenging of new particles via coagulation. The N_{12} , N_{20} , and N_{30} curves maximize on days 2, 4, and 6.

Note that the model results of particle formation and growth depend very critically on temperature, relative humidity, SO_2 , OH, and the initial aerosol surface. For example, when increasing the initial aerosol abundance, an increasing fraction of the photochemically formed H_2SO_4 will condense on pre-existing particles rather than nucleate.

In the atmosphere water vapour super-saturations are usually less than 1% and almost never exceed 2%. The corresponding minimum diameters of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ aerosol particles acting as CCN are about 30 nm and 20 nm respectively.

An inspection of Fig. 8 reveals that within about 6 days the concentration N_{30} of particles with diameters larger than 30 nm (CCN sized particles) increases very substantially from 60 cm^{-3} to nearly 1000 cm^{-3} .

Particle growth is not controlled by temperature but is controlled by the rate of gaseous sulphuric acid formation which in turn is proportional to $[\text{SO}_2] \cdot [\text{OH}]$. The concentration of SO_2 is controlled by emissions of SO_2 and SO_2 -precursors at the Earth's surface, by atmospheric transport of these species, and by SO_2 removal by clouds.

Also, OH concentrations may be higher than considered by the above model case. This is particularly true for summer and for low latitudes. Higher OH will reduce the SO_2 lifetime and increase the rate of gaseous H_2SO_4 formation. In turn this will increase new particle formation and growth.

Variations of the CR ionization rate Q induce a variation of the INU rate J_i . However, the N30 reached after 10 days substantially depends on J_i only if J_i is sufficiently larger than J_h and only if J_i is less than about $1 \text{ cm}^{-3} \text{ s}^{-1}$.

7 Conclusions

The preceding discussion suggests that ion induced nucleation INU is a frequent process in the cold upper troposphere. However, homogeneous nucleation HONU also occurs. According to the model simulations reported by Arnold et al. (2008), upper troposphere INU and HONU rates are relatively high even for typical SO_2 mole fractions. Therefore the bottleneck of upper troposphere CR mediated formation of CCN sized particles seems to be new particle growth and not new particle formation by INU and HONU. In fact, the gaseous $[\text{H}_2\text{SO}_4]$ required to allow new particle growth to become efficient is mostly more than sufficient for INU.

Particle growth by gaseous H_2SO_4 condensation is to a large part controlled by SO_2 . In fact, spatial and temporal variations of upper troposphere SO_2 should have a much stronger effect on N30 (after 6 days) than the small variations of the CR ionization rate. Therefore more information on upper troposphere SO_2 and its spatial and temporal variability is needed. Furthermore efforts should be made to detect additional condensable gases Y which may eventually be present in the upper troposphere.

Acknowledgements The work presented here took place in close collaboration with DLR-IPA and the University of Helsinki. Financial support by the Max Planck Society is appreciated.

References

- F. Arnold, Multi-ion complexes in the stratosphere – Implications for trace gases and aerosol. *Nature* **284**, 610–611 (1980a). doi:[10.1038/284610a0](https://doi.org/10.1038/284610a0)
- F. Arnold, Ion-induced nucleation of atmospheric water vapour at the mesopause. *Planet. Space Sci.* **28**, 1003 (1980b). doi:[10.1016/0032-0633\(80\)90061-6](https://doi.org/10.1016/0032-0633(80)90061-6)
- F. Arnold, Solvated electrons in the upper atmosphere. *Nature* **294**, 732 (1981a). doi:[10.1038/294732a0](https://doi.org/10.1038/294732a0)
- F. Arnold, Ion nucleation – A potential source for stratospheric aerosols. *Nature* **299**, 134 (1981b). doi:[10.1038/299134a0](https://doi.org/10.1038/299134a0)
- F. Arnold, R. Fabian, First measurements of gas phase sulfuric acid in the stratosphere. *Nature* **282**, 55 (1980). doi:[10.1038/283055a0](https://doi.org/10.1038/283055a0)
- F. Arnold, S. Wilhelm, L. Pirjola, Cosmic ray induced formation of aerosol particles and cloud condensation nuclei: First detection of large negative and positive cluster ions in the upper troposphere (2008, in preparation)
- D.R. Bates, Ion–ion recombination in an ambient gas. *Adv. In Atomic and Molecular Physics*, vol. 20 (1985)
- K.S. Carslaw, R.G. Harrison, J. Kirkby, Cosmic rays, clouds and climate. *Science* **298**, 1732–1737 (2002). doi:[10.1126/science.1076964](https://doi.org/10.1126/science.1076964)
- Chen, Penner, Uncertainty analysis of the first indirect aerosol effect. *Atmos. Chem. Phys.* **5**, 2935–2948 (2005)
- J. Curtius, K.D. Froyd, E.R. Lovejoy, Cluster ion thermal decomposition (I): Experimental kinetics study and ab initio calculations for $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_x (\text{HNO}_3)_y$. *J. Phys. Chem. A* **105**, 10867–10873 (2001). doi:[10.1021/jp0124950](https://doi.org/10.1021/jp0124950)
- S. Eichkorn, Development of an aircraft-based ion mass spectrometer with a large mass range: Measurements in the laboratory, aircraft exhaust plumes and the upper troposphere. PhD thesis. University of Heidelberg (2001)
- S. Eichkorn, S. Wilhelm, H. Aufmhoff, K.H. Wohlfrom, F. Arnold, Cosmic ray-induced aerosol-formation: First observational evidence from aircraft-based ion mass spectrometer measurements in the upper troposphere. *Geophys. Res. Lett.* **29** (2002). doi:[10.1029/2002GL015044](https://doi.org/10.1029/2002GL015044)

- V. Fiedler, M. Dal Maso, M. Boy, H. Aufmhoff, J. Hoffmann, T. Schuck et al., The contribution of sulphuric acid to atmospheric particle formation and growth: a comparison between boundary layers in Northern and Central Europe. *Atmos. Chem. Phys. Discuss.* **5**, 1–33 (2005)
- K.D. Froyd, E.R. Lovejoy, Experimental thermodynamics of cluster ions composed of H_2SO_4 and H_2O . 2. Negative ion measurements and ab initio structures. *J. Phys. Chem. A* **107**, 9812–9824 (2003). doi:[10.1021/jp0278059](https://doi.org/10.1021/jp0278059)
- R.G. Harrison, K.S. Carslaw, Ion-aerosol-cloud processes in the lower atmosphere. *Rev. Geophys.* **41**, 1012 (2003). doi:[10.1029/2002RG000114](https://doi.org/10.1029/2002RG000114)
- R.G. Harrison, D.B. Stephenson, Empirical evidence for a nonlinear effect of cosmic rays on clouds, *Proc. R. Soc. A* (2006)
- H. Heitmann, F. Arnold, Composition measurements of tropospheric ions. *Nature* **306**, 747 (1983). doi:[10.1038/306747a0](https://doi.org/10.1038/306747a0)
- J. Kazil, E.R. Lovejoy, Tropospheric ionization and aerosol production: A model study. *J. Geophys. Res.* **109** (2004). doi:[10.1029/2004JD004852](https://doi.org/10.1029/2004JD004852)
- C.E. Kolb, J.T. Jayne, D.R. Wornshop, M.J. Molina, R.F. Meads, A.A. Viggiano, Gas phase reaction of sulfur trioxide with water vapour. *J. Am. Chem. Soc.* **116**, 10,314–10,315 (1994). doi:[10.1021/ja00101a067](https://doi.org/10.1021/ja00101a067)
- M. Kulmala, H. Vehkamäki, T. Petäjä, M. Dal Maso, A. Lauri, V.-M. Kerminen et al., Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J. Aerosol Sci.* **35**, 143–176 (2004). doi:[10.1016/j.jaerosci.2003.10.003](https://doi.org/10.1016/j.jaerosci.2003.10.003)
- A. Laaksonen, V. Talanquer, D.W. Oxtoby, Nucleation: measurements, theory, and atmospheric applications. *Annu. Rev. Phys. Chem.* **46**, 489–524 (1995). doi:[10.1146/annurev.pc.46.100195.002421](https://doi.org/10.1146/annurev.pc.46.100195.002421)
- Lee et al., Particle formation by ion nucleation in the upper troposphere and lower stratosphere. *Science* **301**, 1886–1889 (2003). doi:[10.1126/science.1087236](https://doi.org/10.1126/science.1087236) Medline
- U. Lohmann, J. Feichter, Global indirect aerosol effects: a review. *Atmos. Chem. Phys. Discuss.* **5**, 715–737 (2005)
- E.R. Lovejoy, J. Curtius, Cluster ion thermal decomposition (II): Master equation modeling in the low pressure limit and fall-off regions. Bond energies for $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_x (\text{HNO}_3)_y$. *J. Phys. Chem. A* **105**, 10,874–10,883 (2001). doi:[10.1021/jp012496s](https://doi.org/10.1021/jp012496s)
- E.R. Lovejoy, D.R. Hanson, G.G. Huey, Kinetics and products of gas-phase reactions of SO_3 with water. *J. Phys. Chem.* **100**, 19,911–19,916 (1996)
- E.R. Lovejoy, J. Curtius, K.D. Froyd, Atmospheric ion-induced nucleation of sulphuric acid and water. *J. Geophys. Res.* **109** (2004). doi:[10.1029/2003JD004460](https://doi.org/10.1029/2003JD004460)
- N.D. Marsh, H. Svensmark, Low cloud properties influenced by cosmic rays. *Phys. Rev. Lett.* **85**, 5004–5007 (2000). doi:[10.1103/PhysRevLett.85.5004](https://doi.org/10.1103/PhysRevLett.85.5004) Medline
- O. Möhler, F. Arnold, Gaseous sulphuric acid and sulfur dioxide measurements in the arctic troposphere and lower stratosphere: Implications for hydroxyl radical abundances. *Geophys. Res. Lett.* **19**, 1763–1766 (1992). doi:[10.1029/92GL01807](https://doi.org/10.1029/92GL01807)
- U. Neff et al., Strong coincidence between solar variability and the monsoon in Oman between 9 and 6 kyr ago. *Nature* **411**, 290–293 (2001). doi:[10.1038/35077048](https://doi.org/10.1038/35077048) Medline
- E.P. Ney, Cosmic radiation and the weather. *Nature* **183**, 451–452 (1959). doi:[10.1038/183451a0](https://doi.org/10.1038/183451a0)
- T. Reiner, F. Arnold, Laboratory flow reactor measurements of the reaction $\text{SO}_2 + \text{H}_2\text{O} + \text{M} \rightarrow \text{H}_2\text{SO}_4 + \text{M}$: Implications for gaseous H_2SO_4 and aerosol formation in the plume of jet aircraft. *Geophys. Res. Lett.* **20**, 2659–2662 (1993). doi:[10.1029/93GL02996](https://doi.org/10.1029/93GL02996)
- T. Reiner, F. Arnold, Laboratory investigations of gaseous sulfuric acid formation via $\text{SO}_2 + \text{H}_2\text{O} + \text{M} \rightarrow \text{H}_2\text{SO}_4 + \text{M}$: Measurements of the rate constant and products identification. *J. Chem. Phys.* **101**, 7399–7407 (1994). doi:[10.1063/1.468298](https://doi.org/10.1063/1.468298)
- N.J. Shaviv, Cosmic ray diffusion from the galactic spiral arms, iron meteorites, and a possible climatic connection. *Phys. Rev. Lett.* **89**, 051102 (2002). doi:[10.1103/PhysRevLett.89.051102](https://doi.org/10.1103/PhysRevLett.89.051102) Medline
- N.R. Shaviv, J. Veizer, Celestial driver of phanerozoic climate? *GSA. Today* **13**(7) (2004)
- A. Sorokin, F. Arnold, D. Wiedner, Flow reactor experiments and model calculations of sulfuric acid-water cluster ion formation and ion-induced nucleation. *Atmos. Environ.* **40**, 2030–2045 (2006).
- Speidel et al., Sulfur dioxide measurements in the lower, middle and upper troposphere: Deployment of a novel aircraft-based chemical ionization mass spectrometer with permanent in-flight calibration. *Atmos. Environ.* (2007)
- A.A. Viggiano, F. Arnold, Ion chemistry and composition of the atmosphere, in *Handbook of Atmospheric Electrodynamics*, vol. 1 (CRC Press, Boca Raton, 1995)
- D. Wiedner, Flow reactor investigations of aerosol particle formation by ion induced nucleation: The $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ system. Diploma thesis. University of Heidelberg, 2000
- S. Wilhelm, S. Eichkorn, D. Wiedner, L. Pirjola, F. Arnold, Ion-induced aerosol formation: new insights from laboratory measurements of mixed cluster ions $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_a (\text{H}_2\text{O})_w$ and $\text{H}^+ (\text{H}_2\text{SO}_4)_a (\text{H}_2\text{O})_w$. *Atmos. Environ.* **38**, 1735–1744 (2004). doi:[10.1016/j.atmosenv.2003.12.025](https://doi.org/10.1016/j.atmosenv.2003.12.025)

- WMO, in *Climate Change 2001: The Scientific Basis*, ed. by J.T. Houghton et al. (Cambridge University Press, Cambridge, 2001)
- F. Yu et al., Altitude variations of cosmic ray induced production of aerosols: Implications for global cloudiness and climate. *J. Geophys. Res.* **107** (2002). doi:[10.1029/2001JA000248](https://doi.org/10.1029/2001JA000248)
- F. Yu, R.P. Turco, From molecular clusters to nanoparticles: Role of ambient ionisation in tropospheric aerosol formation. *J. Geophys. Res.* **106**, 4797–4814 (2001). doi:[10.1029/2000JD900539](https://doi.org/10.1029/2000JD900539)