

## A new source of tropospheric aerosols: Ion-ion recombination

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**Abstract:** We propose a new source of aerosol particles in the lower atmosphere that is based on the formation, growth, and recombination of ubiquitous cosmogenically-generated ions. This mechanism provides a uniform, continuous fine-particle generator in the presence of precursor vapors, such as sulfuric acid, or certain organic compounds. Thus, for example, aqueous sulfate aerosols can form at sulfuric acid vapor partial pressures well below the supersaturations required for homogeneous nucleation. Detailed microphysical modeling shows that the highly nonlinear chemical/physical system comprising ions, vapors, and aerosols produces ultrafine and accumulation mode particles having characteristics similar to those detected in the lower troposphere. Accordingly, this mechanism may explain the presence of a stable boundary layer aerosol population of several hundred particles/ $cm^3$ . The theory of nucleation by ion-ion recombination (NIIR) is roughly calibrated here using observed ultrafine particle measurements, and is applied to interpret tropospheric aerosol observations.

### Introduction

Charlson et al. (1987) proposed that dimethylsulfide (DMS) emissions could lead to the formation of cloud condensation nuclei (CCN), and thus affect the microphysical and radiative properties of widespread marine boundary layer stratus clouds (Albrecht, 1989). However, the processes that control the abundances of CCN throughout the lower atmosphere remain uncertain. Nucleation of sulfuric acid vapor generated by photochemical reactions has been proposed as a source of new boundary layer aerosols that can evolve into accumulation mode particles, the largest fraction of which act as CCN. This process occurs in other parts of the atmosphere, such as in the upper troposphere (Hamill et al., 1982; Brock et al., 1995). However, whereas classical nucleation mechanisms tend to be highly localized in their effect (Hegg et al., 1990; Covert et al., 1996), measurements at remote boundary layer sites suggest a more ubiquitous and stable background population of accumulation mode particles with concentrations in the range of 100-1000/ $cm^3$  (e.g., Andreae et al., 1994; Mäkelä et al., 1997). Moreover, the binary homogeneous nucleation of sulfuric acid and water vapors is not generally favored in the boundary layer—except at isolated locations—because of pre-existing particles, which scavenge and prevent the build-up of free acid vapor (e.g., Raes, 1995).

Boundary layer aerosols can also be entrained from the free troposphere (e.g., Clarke, 1993; Raes, 1995). These particles have a characteristic “aged” size distribution with few ultrafine particles (i.e., those with diameters below about 20 nm). On the other hand, measurements of the boundary layer aerosol size distribution often show high concentrations of ultrafine particles, suggesting an *in situ* nucleation source (Weber et al.,

1996; 1997; Mäkelä et al., 1997; Raes et al., 1997), which cannot be explained in general by classical homogeneous nucleation. Considering a series of measurements in the free troposphere and boundary layer, Raes et al. (1997) detected no bursts of new particles characteristic of homogeneous nucleation, and further concluded that, while entrainment may have been responsible for some of the observed boundary layer aerosol, a slow, continuous “nonclassical” *in situ* particle source could not be ruled out.

Turco et al. (1997) have proposed that large stable ion clusters—which are known to exist in the boundary layer (Eisele, 1989)—may indeed provide a stable low-level source of new aerosols through ion-ion recombination with stabilization of the recombination clusters. A fairly uniform distribution of ionization is present throughout the lower atmosphere as a result of galactic cosmic ray bombardment. Here, this proposed particle source is incorporated into a detailed microphysical code to assess the behavior of the resulting aerosol in relation to observations.

### Nucleation by Ion-ion Recombination (NIIR)

Typical sulfuric acid vapor concentrations found in the lower atmosphere lie in the range of perhaps  $1 \times 10^6 - 1 \times 10^7 / cm^3$  (Weber et al., 1996; Eisele and Tanner, 1993), whereas the concentrations required for significant homogeneous nucleation of  $H_2SO_4/H_2O$  droplets are in the range of  $\geq 1 \times 10^8 / cm^3$ . Direct ion nucleation, where electrostatic forces stabilize the nucleation embryo, in general require  $H_2SO_4$  abundances greater than those observed (Castleman et al., 1978; Hamill et al., 1982). Nevertheless, measured  $H_2SO_4$  concentrations, corresponding to ambient supersaturations of ~10-100, can lead to the generation of large ion-molecule clusters, which upon recombination may be thermodynamically stable and grow into sensible aerosols.

The general concept that stable neutral clusters can be the byproduct of the recombination of large cluster ions was proposed by Arnold (1980), and has been discussed more recently in the context of tropospheric aerosol formation by Turco et al. (1997). In the lower atmosphere, positive core ions typically consist of hydronium ( $H_3O^+$ ), ammonium ( $NH_4^+$ ), and a variety of organic ions, such as protonated pyridine ( $C_5H_6N^+$ ). In the case of negative core ions, the dominant parent molecules include nitric acid, sulfuric acid, methane sulfonic acid (MSA), and malonic acid (Eisele, 1989; Eisele and Tanner, 1991). The preferred core species, in decreasing order of thermodynamic stability, are  $HSO_4^-$ ,  $CH_3SO_3^-$ ,  $C_3H_3O_4^-$ , and  $NO_3^-$ . Hence, bisulfate core ions will be dominant when sufficient  $H_2SO_4$  is present—mainly during the day—as indicated by *in situ* data, which also show ions having masses  $>> 600$  amu (Eisele, 1989; Eisele and Tanner, 1993). Ion mobility spectra also point to families of very large positive and negative ions in the lower atmosphere (Hoppel, 1970).

The kinetics of ion growth are very efficient (for example, this is discussed by Yu and Turco, 1997, with respect to aircraft plume microphysics), and ions quickly achieve equilibrium with ambient vapors. Turco et al. (1997) argue that the composition and mass spectra of the background ions are then largely

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determined by the thermodynamics of clustering reactions. To simplify the problem, they assumed dominant positive ions consisting of water-clustered hydronium,  $H_3O^+ \cdot (H_2O)_n$ , and negative ions consisting of sulfuric acid clusters,  $HSO_4^- \cdot (H_2SO_4)_n \cdot (H_2O)_m$ . Depending on local environmental conditions, these clusters can pick up a variety of other stabilizing ligands such as those noted earlier (Viggiano and Arnold, 1995). However, for the present arguments the exact composition of the ions is not crucial.

Turco et al. (1997) point out that the relative concentrations of clusters with  $n$   $H_2SO_4$  molecules will be roughly proportional to the product of the equilibrium constants— $K$ 's—for the individual clustering steps, multiplied by the  $H_2SO_4$  concentration raised to the  $n$ -th power:

$$\begin{aligned} [HSO_4^- \cdot (H_2SO_4)_n] &\propto [H_2SO_4]^n \prod_{j=1,n} K_{j-1,j} \\ &\propto [H_2SO_4]^n \exp(-\Delta G_{0,n}/RT) \end{aligned} \quad (1)$$

where  $\Delta G_0$  is the Gibbs free energy associated with building the molecular cluster. Thermodynamic parameters are known only in a few specific cases, limiting the ability to quantify the ion spectrum (Viggiano and Arnold, 1995).

The recombination of a hydronium positive ion and sulfuric acid negative ion yields a neutral recombination cluster consisting of say,  $n$  acid molecules and  $m$  water molecules. If this cluster is large enough, it will lie above the critical size of a stable neutral mixed embryo, and will continue to grow by vapor condensation. For example, under stratospheric conditions, stable recombination embryos can result for  $\{n, m\}$  varying from  $\{3, 7\}$  to  $\{7, 2\}$  (Arnold et al., 1982).

The fraction of ion-ion recombination events that create stable nuclei is obviously a strong function of the sulfuric acid vapor concentration, which determines the sizes of the ion clusters prior to recombination, as well as the composition of the critical (stable) embryo. Some large sulfuric acid cluster ions are always present and will be stabilized upon recombination, although this number may be exceedingly small (Eq. 1). The fraction of self-stabilizing ion-ion recombination events is estimated here using the relation (derived by Turco et al., 1997, from thermodynamic arguments summarized by Eq. 1),

$$f_i = f_{io} \left( [H_2SO_4] / [H_2SO_4]_0 \right)^{n^*} = f_{io} (n_s / n_{so})^{n^*}; \quad f_i \leq 1 \quad (2)$$

where  $n^*$  is the threshold number of sulfuric acid molecules needed to form a growing recombination embryo, and  $f_{io}$  is the fraction of stabilizing recombination events at a reference vapor concentration,  $n_{so} = [H_2SO_4]_0$ . Note that, in general,  $n^*$  is also a function of the  $H_2SO_4$  supersaturation, which determines the number of acid molecules in the critical embryo.

Considering tropospheric observations (e.g., Weber et al., 1996) and stratospheric measurements (Viggiano et al., 1980; Arnold et al., 1982), baseline values of  $n_{so} = 5 \times 10^6 / cm^3$  and  $f_{io} = 1 \times 10^{-3}$  appear to be consistent (see below). A significant number of large sulfuric acid negative ion clusters are expected when  $n_s = n_{so} \geq 1 \times 10^6 / cm^3$  (e.g., Arnold et al., 1982). Moreover, under normal conditions, only a relatively small fraction of ion-ion recombination events should result in new particle formation; in other words, the number of ion clusters large enough to form stable recombination embryos is typically a rather small fraction of the total ion population. This fraction increases rapidly as the precursor vapor ( $H_2SO_4$ ) concentration increases, however. We also assume, as a baseline, that the critical number of sulfuric acid ligands needed to stabilize a neutral recombination product is,  $n^* \approx 3$ . Depending on environmental conditions (temperature, humidity, other trace species), this number may be considerably larger, or somewhat smaller (see below).

Using Eq. (2), the rate of formation of new particles,  $J_p$  ( $\# / cm^3 - sec$ ), which is proportional to the stabilized frac-

tion  $f_{io}$ , can be written as:

$$J_p = Q_i f_{io} \left( [H_2SO_4] / [H_2SO_4]_0 \right)^{n^*} \propto [H_2SO_4]^{n^*} \quad (3)$$

where  $Q_i$  is the local ionization (and recombination) rate. The maximum rate of particle formation according to this mechanism is,  $J_p \sim Q_i$  ( $\sim 1 / cm^3 - sec$ ). That is, bursts of nucleation do not occur in NIIR (although particle populations as large as  $\approx 10,000 / cm^3$  could accumulate in one hour, and  $\approx 100,000 / cm^3$  in one day).

With sulfuric acid concentrations,  $n_s$ , of  $10^6 - 10^7 / cm^3$ , measured aerosol appearance rates are in the range of  $10^{-4} - 10^{-2} / cm^3 - sec$ , respectively (Weber et al., 1996), in accord with the proposed NIIR mechanism. The precise rates will depend on a number of factors, such as the presence of species that affect ion cluster composition (Viggiano et al., 1980), and on the microphysical evolution of the newly-formed embryos. At lower sulfuric acid concentrations, kinetic factors strongly limit the sulfuric acid content of the ions and thus inhibit stable particle formation. Indeed, in this regime ( $n_s < 10^6 / cm^3$ ), the rates of aerosol production are too low ( $J_p \leq 10^{-5} / cm^3 - sec$ ) to have a discernible impact on the particulate content of the troposphere.

## Microphysical Simulations

To develop a more comprehensive picture of the ultrafine aerosol behavior predicted by the NIIR source, a comprehensive aerosol microphysics code has been applied to the problem. The basic model is discussed in previous works (e.g., Turco et al., 1979, Yu and Turco, 1997), and includes a thorough treatment of "classical" nucleation processes, coagulation, condensation/evaporation, sedimentation, and deposition for a multicomponent size-resolved aerosol system. In the present analysis, the NIIR mechanism was incorporated using Eq. (3), with  $Q_i$ ,  $f_{io}$ , and  $n^*$  as parameters. We consider sulfuric acid as the primary nucleating agent in this case, both because it is likely to be one of the most important precursors of new particles based on observations, and because its thermodynamics is better understood than other potential nucleating materials—organic compounds in particular. Nevertheless, the NIIR process should apply to a variety of aerosol precursors, including biogenic compounds. The chemistry leading to the production of sulfuric acid vapor is not explicitly treated. Rather, we include a diurnally varying production rate that is consistent with chemical calculations, and ultimately with the  $H_2SO_4$  concentrations observed in boundary layer air.

Figure 1 illustrates the evolution of the aerosol size distribution with the NIIR source acting alone, in the presence of an initial background accumulation-mode aerosol. The largest particle variations occur within the ultrafine size range (below about 20 nm). At these sizes, a diurnal cycle in concentration is obvious, even after several days. Hence, the NIIR mechanism predicts both a day-to-night and a day-to-day variation in the ultrafine mode that correlates strongly with the presence of vapor precursors. A similar pattern of behavior has been observed by Covert et al. (1996). The ultrafine-mode particles grow relatively quickly to roughly 30–40 nm, creating a nascent accumulation mode often seen in boundary layer size spectra, with comparable numbers of particles as are measured (e.g., Clarke et al., 1996; Raes et al., 1997). In the absence of a preexisting accumulation mode, the aged ultrafine particles can grow even more rapidly into the 100-nm size range. The overall multi-modal structure predicted in Figure 1 is similar in many regards to observations (e.g., Fitzgerald, 1991).

Figure 2 shows the total particle concentrations over several days corresponding to the simulations in Figure 1. Considering the new-particle modes in Figure 1, a distinct diurnal variation is calculated, owing to the cycle of nucleation and growth during the day, and coagulation during the night. Nevertheless, the total number of particles is quite stable over time. For particles larger than  $\sim 20$  nm, the total abundance ranges from roughly 200/ $cm^3$  to 500/ $cm^3$ . These results are

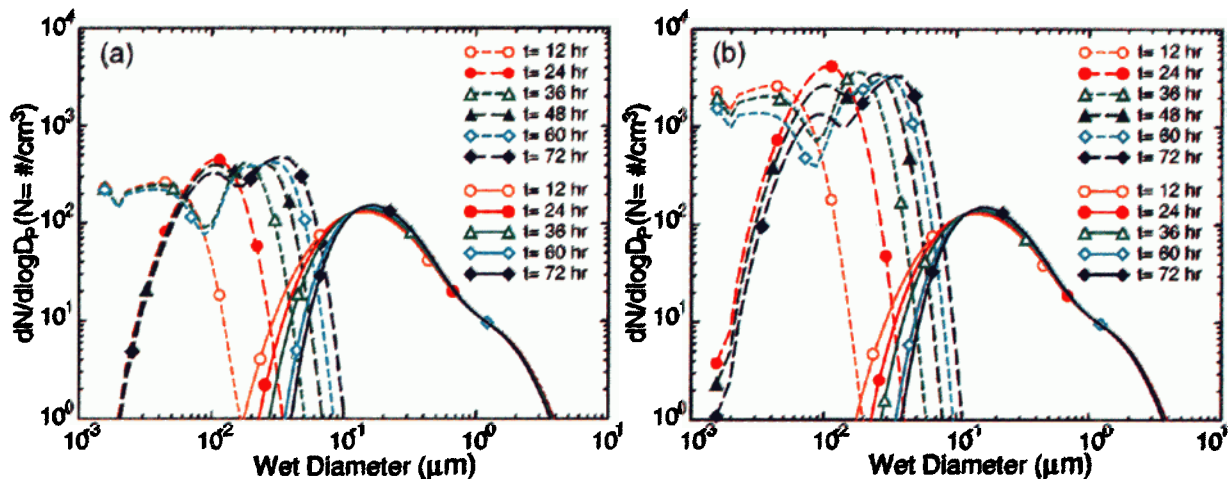


Figure 1. Particle size distributions at noon and midnight. At  $t=0$ , only a “background” aerosol is assumed to be present (solid lines). Subsequently, an ultrafine particle mode forms (broken lines in the figure). Panel a)  $f_{io}=0.001$ ; b)  $f_{io}=0.01$ . The initial diameter of the stable ion-ion recombination nuclei is taken to be  $1.0\text{ nm}$ , and the production (nucleation) rate is defined by Eq. (3), where  $Q_i = 2(\text{ion-pairs}/\text{cm}^3\text{-sec})$ ,  $n_{so} = 5 \times 10^6 (\text{cm}^{-3})$ , and  $n^* = 3$ . The sulfuric acid vapor production rate is parameterized for these calculations as,  $P_s = \pi P_{so} \sin[\pi(t-6)/12]$ , where  $P_{so} = 1 \times 10^4 (\text{cm}^{-3}\text{sec}^{-1})$ . The background aerosols at  $t=0$  consist of: i) an accumulation mode ( $H_2SO_4$ ) with a dry mass density of  $1.00\text{ }\mu\text{g}/\text{cm}^3$ ,  $r(\text{mass})=0.26\text{ }\mu\text{m}$ , and  $\sigma = 2.16$ ; ii) a coarse mode ( $NaCl$ ) particles with a dry mass of  $8.00\text{ }\mu\text{g}/\text{cm}^3$ ,  $r(\text{mass})=1.00\text{ }\mu\text{m}$ , and  $\sigma = 1.8$ .

consistent with the predictions of a simplified analytical model describing the *steady-state* particle population associated with the NIIR mechanism (Turco et al., 1997); sensitivity studies carried out with that model suggest that NIIR is capable of creating a stable concentration of several hundred particles/ $\text{cm}^3$  under a wide variety of conditions owing to nonlinear interactions between the ions, vapors, and aerosols.

Verification of the nucleation rates predicted by Eq. (3) is difficult under atmospheric conditions. Weber et al. (1996) simultaneously measured ultrafine particle and sulfuric acid vapor concentrations at a number of locales, and used these data to estimate nucleation rates, assuming that particles roughly  $3\text{ nm}$  in diameter represent freshly-generated, growing embryos. In Figure 3, we have recreated a comparable series of “measurements” of nucleation rates using information from our model. Referring to these inferred values as “apparent” nucleation rates, it is obvious that they display a much wider range of values than the actual nucleation rates used to generate the size distributions in Figure 1 (noting that the actual nucleation

rates are confined to the line labeled ‘ $J_p$ ’ in Fig. 3, for which there is a single value at each  $H_2SO_4$  concentration). While the “apparent” nucleation rates in Figure 3 vary by several orders of magnitude for each specific  $H_2SO_4$  concentration, even greater variability would be expected to arise from differences in the composition and history of individual air masses.

The behavior of the “apparent” aerosol formation rates observed by Weber et al. (1996; see their Fig. 1) is explained in

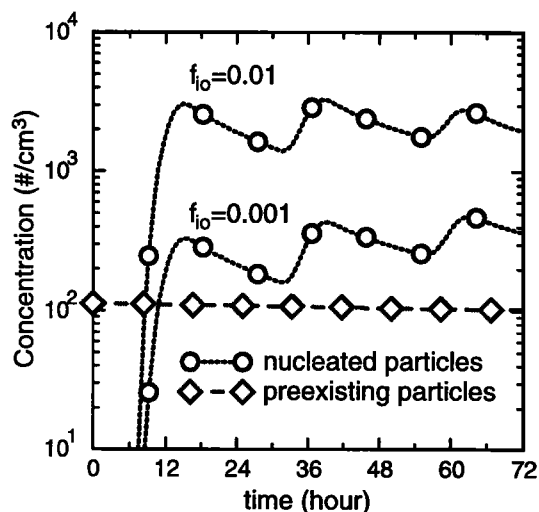


Figure 2. Time evolution of total particle concentrations corresponding to the simulations in Figure 1. The variations in the total number of preexisting background aerosols are nearly identical for both of the cases illustrated.

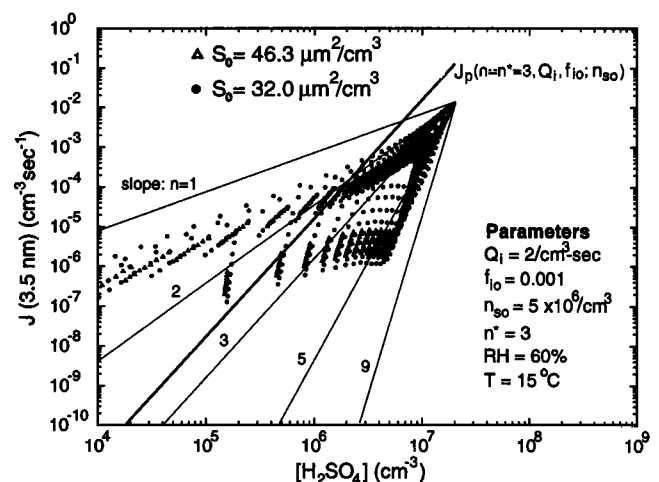


Figure 3. “Apparent” sulfuric acid nucleation rates based on the simulations in Figure 1a, with two initial background aerosol surface area densities,  $S_0$ . Here, predicted sulfuric acid vapor concentrations and ultrafine particle abundances (at a diameter of roughly  $3.5\text{ nm}$ ) are used to calculate the apparent formation rates of new particles using the analytical approach of Weber et al. (1996). Each point on the plot represents a specific apparent nucleation rate sampled over a multi-day simulation at 15 minute intervals. The nucleation rates tend to increase from their lowest values (at low  $H_2SO_4$  concentrations) in the early morning hours, toward peak values (and  $H_2SO_4$  concentrations) around midday, back to moderate values (and low  $H_2SO_4$ ) in the afternoon. For comparison, the actual nucleation rate,  $J_p$  (Eq. 3), is plotted, along with lines that define a range of possible dependencies of  $J$  on  $[H_2SO_4]^n$ .

our simulations by time delays inherent in the chemical-microphysical system under investigation. For example, in the morning hours, the abundances of 3–4 nm particles are very low—having been depleted during the previous evening by coagulation, while new particles have not yet been formed and grown into this size range—giving the appearance of instantaneous “slow” nucleation, even though sulfuric acid vapor concentrations may be significant. In late afternoon, on the other hand, the 3–4 nm particle population has been elevated, implying apparently “fast” nucleation despite declining acid vapor concentrations. The resulting nucleation rates thus exhibit a seemingly wide range of dependencies on the precursor  $H_2SO_4$  concentration (compare the lines marked with slopes of 1 to 9 in Fig. 3). Dependencies having slopes  $\approx 1$  ( $J_p \propto [H_2SO_4]^1$ ) occur early or late in the day when the 3–4 nm particle concentration is relatively invariant. Dependencies with slopes  $\approx 9$  ( $J_p \propto [H_2SO_4]^9$ ) appear after mid-morning, when freshly nucleated particles begin to grow rapidly into the 3–4 nm size range at relatively high  $H_2SO_4$  concentrations.

## Discussion

Nucleation by ion-ion recombination (NIIR) in the lower atmosphere offers a possible explanation for the maintenance of the background tropospheric aerosol. The NIIR mechanism is strongly constrained by nonlinear interactions between ion processes and aerosol microphysics, tending to establish a relatively steady number of particles uniformly distributed throughout the lower atmosphere. The thermodynamically-based NIIR mechanism can explain terrestrial as well as marine aerosol formation. It is well-known, for example, that a variety of organic compounds readily attach to ions, and organic ultrafine aerosols originating over land are found even in marine environments (Novakov and Penner, 1993).

Homogeneous binary nucleation is not precluded in circumstances where large precursor supersaturations are attained. However, the NIIR process should be favored; as particles are scavenged from an air-mass by precipitation, for example, ions that are always present will respond to generate new fine aerosols to take their place. Some of these will grow into condensation nuclei, in part through cloud processing (Hoppel et al., 1986). Indeed, we envision at least three stages of aerosol formation in the troposphere: at the lowest vapor supersaturations, ion-ion recombination can provide a steady background source of new particles; at considerably higher supersaturations, direct nucleation of ions can quickly lead to ultrafine particle concentrations of  $\sim 10^3$ – $10^4/cm^3$  (Hamill et al., 1982); finally, at unusually high supersaturations, homogeneous nucleation may generate very large fine-aerosol concentrations.

The NIIR mechanism for aerosol formation is not yet well defined at the molecular level. Additional detailed studies of the composition and stability of large tropospheric ions, as well as their neutral recombination products—particularly those containing acids and organics—should be undertaken, as should carefully designed observations of the rates of new particle generation in clean air masses. Nevertheless, comparisons with measured “apparent” aerosol nucleation rates allow the NIIR process to be roughly calibrated. From such an analysis, we conclude that particle formation via ion-ion recombination is consistent with a variety of observations of fine aerosols in the lower atmosphere.

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