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Ultrafine aerosol formation via ion-mediated nucleation

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Abstract. The role of background ionization in the generation and evolution of ultrafine atmospheric particles is developed through modeling and data analysis. It is found that charged molecular clusters condensing around natural air ions can grow significantly faster than corresponding neutral clusters, and thus preferentially achieve stable, observable sizes. Detailed microphysical simulations of this process seem to explain recent measurements of ultrafine particle behavior, as well as the diurnal variation seen in tropospheric mobility spectra. The proposed ion-mediated nucleation mechanism leads to the production of new particles under conditions that are unfavorable for binary homogeneous nucleation, and provides a consistent explanation for a variety of tropospheric observations.

Introduction

Volatile aerosols in the lower atmosphere are believed to be important in the regulation of Earth's climate (e.g., Twomey, 1977; Charlson et al., 1987). However, the sources of such particles have remained elusive despite decades of intensive research. Recently, simultaneous measurements of ultrafine aerosols (having sizes as small as ~3 nm) and their precursor vapor concentrations (notably H_2SO_4) have become available to investigate this problem (e.g., Weber et al., 1996, 1997, 1998; Clarke et al., 1998). We suggest here that useful complementary information is also available from records of the air mobility spectrum, which directly samples the smallest charged nano-particles (Hõrrak et al., 1998), and that the combination of aerosol and mobility data provides a strong constraint on models of aerosol nucleation.

Based on the classical theory of binary homogeneous nucleation (BHN) involving H_2SO_4 and H_2O (e.g., Jaecker-Voirol and Mirabel, 1989), predicted nucleation rates in the lower atmosphere are usually much lower (by a factor of up to $\sim 10^{10}$) than the rates inferred from ultrafine particle measurements (e.g., Weber et al., 1996; Turco et al., 1998; Clarke at al., 1998). Ternary homogeneous nucleation (THN) that also involves ammonia (Coffman and Hegg, 1995) has been suggested as a means of accelerating this process (e.g., Weber et al., 1998). The idea is that ammonia stabilizes the critical embryo (reducing its size), and thereby substantially lowers the thermodynamic barrier to particle formation. Even so, nucleation rates based on homogeneous theory may still be kinetically limited, owing to low concentrations of the atmospheric precursors (Turco et al., 1998). Moreover, in both the BHN and THN mechanisms, the subsequent growth rate of newly-formed nano-particles, which is assumed to be driven by the condensation of H_2SO_4 together with H_2O and NH_3, appears to be a factor of ~10 too low to explain the rapid appearance of fresh ultrafine aerosols during midday (e.g., Weber et al., 1997, 1998).

We propose that some of these discrepancies between theory and observation may be explained by the intervention of background ionization in particle formation. In the past, ions have been alluded to as potential nucleation centers (e.g., Mohnen, 1971; Arnold, 1982), although definitive data were lacking to validate the concept. Notably, a recent proposal (Yu and Turco, 1997) that chemiionization from engine combustors dominates the production of volatile ultrafine particles detected in aircraft plumes provides a clear example of the strong influence electrical charge can exercise on microparticles. The chemiion theory successfully predicts the observed evolution of aircraft aerosols for a wide range of conditions (Yu et al., 1998, 1999; Kärcher et al., 1998), and has been confirmed by direct measurements of massive ion clusters in fresh plumes (e.g., Arnold et al., 1999). The primary microphysical effects associated with electrification include accelerated rates of vapor condensation and particle coagulation (Yu and Turco, 1997, 1998), as well as the production of stable pre-nucleation embryos through charge recombination (Arnold, 1980; Turco et al. 1998). The relative importance of these two processes depends on the abundance of precursor gas species and ions. The role of accelerated growth increases as the precursor gas concentration increases, and/or the ion concentration decreases.

To extend these recent studies, and interpret a wider range of related field data (e.g., Weber et al., 1997, 1998; Hõrrak et al., 1998; Clarke et al., 1998), all of the relevant interactions between charged and neutral clusters across their entire size spectrum have been integrated into a comprehensive microphysical modeling framework. The resulting integrated mechanism is referred to as "ion-mediated" nucleation (IMN).

Ion-Mediated Nucleation

Ambient ions are generated continuously, and ubiquitously, by galactic cosmic rays (GCR's) at the rate of ~2 ion-pairs/cm^{3}s at ground level, and up to ~20-30 ion-pairs/cm^{3}s in the upper troposphere (Reiter, 1992). Ions are also generated by local sources (not explicitly considered in this study) such as radioactive decay, lightning, and corona discharge. The simple primary ions quickly attract and react with trace gases such as H_2O, H_2SO_4, HNO_3, NH_3, and various organic species, rapidly forming molecular clusters, including the well-known hydronium ion series (Arnold, 1980) and sulfuric acid aggregates.

The physics of electrically-charged clusters and ultrafine particles has been discussed by Yu and Turco (1998). In the present work, image capture and three-body trapping (Hoppel and Frick, 1986) are included when calculating enhancement factors for ion-neutral and ion-ion interactions. The effect of charge on the coagulation kernel is very strong for small clus-

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ters, but decreases as the cluster sizes increase. The estimated enhancement factor for the aggregation of an H_2SO_4 molecule with a charged cluster is ~14 at a cluster diameter, d_p = 0.55 nm, and ~7 at d_p = 3 nm. Note that the calculated coagulation kernels for ion-neutral and ion-ion (oppositely–charged) interactions at the molecular scale are consistent with laboratory values of ion-neutral reaction rate constants (e.g., Viggiano et al., 1980) and ion-ion recombination coefficients (Nolan, 1943), respectively. As a result of charge effects, the growth of sub-nanometer clusters to measurable sizes (~2–3 nm) may be accelerated by a factor of up to ~10.

An electrostatic enhancement in the rate of condensation of vapor onto charged clusters might be critical in the generation of new condensation nuclei. The formation of sensible aerosols, in fact, is an outcome of the competition between the growth of new particles and their scavenging by ambient aerosols. For typical atmospheric conditions, there is sufficient H_2SO_4 vapor available to allow some of the larger ion clusters to evolve into stable, rapidly growing microparticles. Neutral molecular clusters, on the other hand, are less likely to surpass critical size because of their lower stability and slower growth rates.

We have developed an advanced particle microphysics (APM) code to study the interactions between neutral and charged clusters and particles at all sizes, as well as their coupling to the vapor phase. The APM keeps track of the compositions and size distributions of different particle types, and treats the entire course of aerosol nucleation and growth as a unified collisional (kinetic) mechanism. Previous applications of the APM model offer details on this approach (Yu and Turco, 1997, 1998; Yu et al., 1998, 1999; Kärcher et al., 1998).

Linking Air Mobility with Aerosol Formation

The APM model has been applied to analyze air mobility spectra recorded at the Tahkuse Observatory (Hõrrak et al., 1998). The mobility (in units of $cm^2V^{-1}s^{-1}$) of a particular ion is equivalent to the average velocity (cm/s) attained in an electrical field of 1 V/cm. The mobility varies inversely with ion mass (or size) and air density (e.g., Tammet, 1998). For the present simulations, the ambient ionization rate was set at 2 ion-pairs/cm^3s, and the initial ion concentration, at 1000/cm^3. The background aerosol size distribution was initialized to reproduce consistently the measured properties of the largest ions (d > 20 nm) contributing to the observed mobility spectra (Figure 1). As a matter of convenience, a simple binary H_2SO_4-H_2O composition was assumed for all of the particles. Moreover, the diurnal production rate of H_2SO_4 vapor, and thus its peak concentration, was adjusted to reproduce the observed maximum abundance of intermediate ions (detected at ~14:30; see Figure 1). As a consequence, the H_2SO_4 vapor has a peak concentration of 2.8×10^7/cm^3 at 13:50.

Figure 1 compares the simulated evolution of the size distribution of positive intermediate ions with the distributions deduced from mobility spectra measured over the course of one day. The IMN theory reproduces variations in the ion size distribution reasonably well, with some differences in the details. For example, a minimum in the ion concentration is both measured and predicted to lie between two mobility families: one consisting of small primary cluster ions (<1 nm), and a second comprised of freshly-nucleated charged micro-clusters

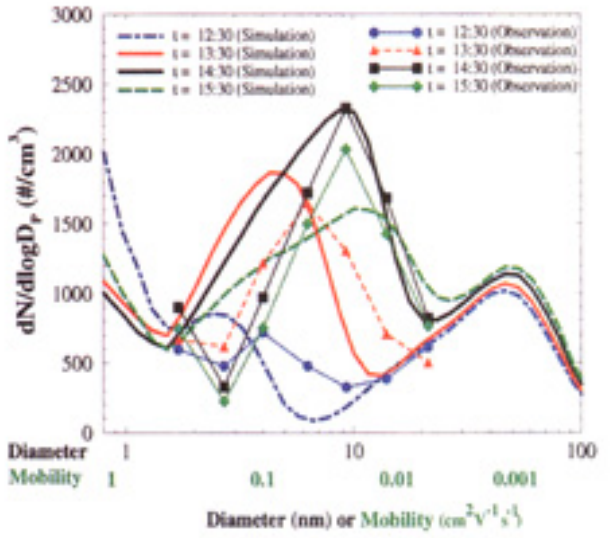

Figure 1. Simulations and observations of the evolution of the positive ion size distributions deduced from mobility spectra measured within the boundary layer. Hourly-average data (symbols) are taken from Hõrrak et al. (1998), corresponding to a series of observations on October 20, 1994. The ion size spectra are shown as a function of particle diameter and charge-carrier mobility.

(~3 nm at 12:30). However, the predicted ion size at the minimum (~1.8 nm diameter) is somewhat below the observed size (~2.8 nm). Nevertheless, the growth rate of the intermediate ion peak, and the evolution of the mobility spectrum over the course of the day, are well delineated by the model. The simulations also clearly indicate that background ions are capable of evolving into nano-particles, and accumulating in the ultrafine size range.

The model results are somewhat sensitive to the calculated critical embryo size (~1.8 nm as noted above, which is based on the classical droplet model). Under prevailing conditions, however, the actual critical size may have been larger. Similarly, a small shift in the calibration of the mobility curves at small ion sizes would resolve the discrepancy. Another potential source of divergence arises because the observational time series was, by necessity, collected at a fixed site in a continually varying air mass, whereas the simulation represents the time evolution of a single "average" air mass. In addition, several key parameters, including the ambient aerosol surface area, local ionization rate, and precursor gas concentrations, are not well constrained.

While the intermediate ions are continuously produced by condensation on small, electrified clusters, they are also constantly neutralized by oppositely-charged ions, and are scavenged by ambient aerosols. These competing processes control the growth and decay in the number of intermediate ions in Figure 1. Before 14:30, the ion sizes and total number steadily increase. However, after 14:30, while the ion size still tends to increase slightly, the number decreases sharply due to neutralization by small ions. Corresponding to this evolution of the intermediate ion size distribution (and corresponding mobility spectrum), the total concentration of newly formed ultrafine particles (charged + neutral, with diameters, d_p >2.5 nm) increases rapidly from ~900/cm^3 at 11:00 to 6000/cm^3 by 15:30.

Particle Formation in Clean Continental Air

Simultaneous measurements of H_2SO_4 vapor and ultrafine particles (in the size range, 2.7 nm $\leq d_p \leq$4 nm) have been reported for clean continental sampling sites (e.g., Weber et al., 1996, 1997, 1998). Here, we focus on data recorded at Idaho Hill, Colorado on September 21, 1993 (Weber et al., 1997). Since the variations in H_2SO_4 were accurately measured in this case, its production rate was constrained in the APM model to match the observed mean behavior (the measured and predicted values are compared in Figure 2a.). Other data were also available to initialize and constrain the simulation, including the ambient aerosol size distribution and surface area (55 $\mu m^2/cm^3$ at d_p >15 nm), air temperature (283 K), and relative humidity (32%). The air ionization rate was fixed at 2 ion-pairs/cm^3s, and the initial ion concentration, at 1000/cm^3.

Figure 2b compares the computed and measured total ultrafine aerosol concentrations. The ultrafine particles are defined within two size ranges—2.7 nm < d_p< 4 nm, and 2.7 nm < d_p < 4.5 nm—which illustrates the potential sensitivity of particle counts to instrumental sampling efficiency near the cut-off size. It is remarkable that, even though H_2SO_4 concentrations remained quite low most of the day, and never exceeded 1x10^7/cm^3, ultrafine particle counts rose dramatically in the late morning (after ~10:00). The IMN mechanism reproduces this behavior, whereas classical BHN theory would have forecast no particle formation under such conditions. The calculated ultrafine particle abundances appear to respond to changes in H_2SO_4 at roughly the same rate indicated by the data. The greater variability in the measurements is most likely associated with the changing air masses sampled during the experiment. Of course, the model prediction is subject to a number of uncertainties, especially with regard to the initial stages of ion growth.

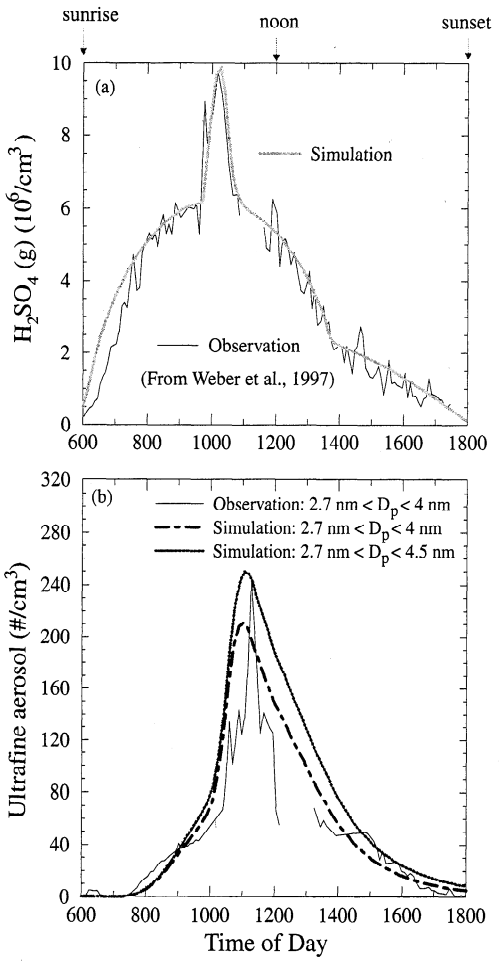

Figure 2. Simulated and measured (a) H_2SO_4 vapor concentrations, and (b) ultrafine aerosol abundances, at a remote land site.

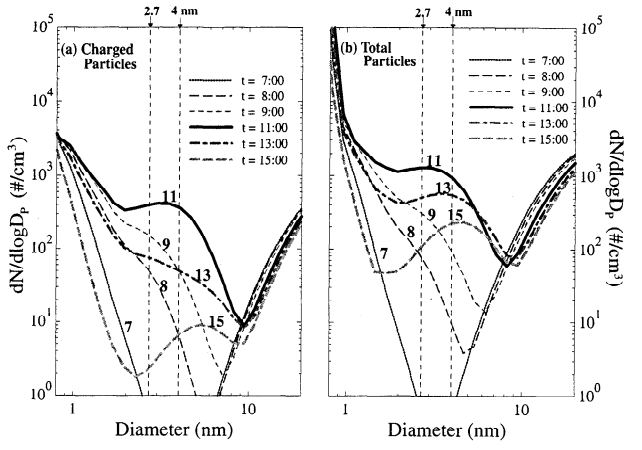

Figure 3. Simulated evolution of the size distributions of (a) the total charged particles (positive + negative), and (b) all particles, for the case in Figure 2.

Figure 3 illustrates, for the simulation depicted in Figure 2, the evolution of the size distributions of (a) the total charged (positive + negative) particles and (b) the total particle population (charged + neutral). Both panels clearly depict the growth and accumulation of nano-particles during the morning hours as the concentration of H_2SO_4 increases. The number of particles sampled (at sizes between 2.7 nm and 4 nm) rises most rapidly between ~8:00 and 11:00. Beginning at mid-morning, uncharged ultrafine particles are dominant, having been generated mainly by the neutralization of charged nano-particles (that is, primary aerosol-ions). At ≈9:00, roughly half of the total ultrafine particles are charged, while by ≈11:00, only about one-third are charged.

The number of freshly "nucleated" particles (those with d_p >1.8 nm) increases before 11:00, but decreases thereafter, owing to a change in the balance between growth and scavenging. Indeed, by 15:00, most of the new particles have been removed, since the H_2SO_4 concentration is quite low while the background aerosol surface area is relatively large (~55 $\mu m^2/cm^3$). It follows that the fraction of nucleated particles that eventually add to the population of cloud condensation nuclei (CCN), which requires growth to sizes exceeding ~80 nm, is likely to be quite small in this case. If H_2SO_4 had been higher (or other condensable species were dominant), and ambient aerosol surface areas lower, more CCN might have been expected.

To investigate particle formation in the environment of the marine boundary layer, we performed a number of simulations based on aircraft measurements published by Clarke et al. (1998). For the particular conditions encountered during one flight, the IMN model successfully predicted a major nucleation event in terms of the onset and total abundance of ultrafine particles, as well as their relative concentration with respect to the larger condensation nuclei. Detailed results will be published elsewhere.

Summary and Discussion

The present analysis suggests that, under typical atmospheric conditions, the formation of new particles is likely to be enhanced by the intervention of natural ionization (leading to ion-mediated nucleation, IMN). IMN may be important in environments where nanometer-sized clusters are marginally thermodynamically stable, and homogeneous nucleation is improbable. Because of the well known microphysical effects of electric charge, IMN offers a rational physical basis for explaining certain phenomena, including ultrafine aerosol bursts and enhanced nano-particle growth rates (by a factor as large as 10). As we have illustrated, IMN is consistent with a range of field data describing the behavior of fine aerosols (e.g., Hõrrak et al., 1998; Weber et al., 1996, 1997, 1998; Clarke et al., 1998). Thus, IMN theory may provide a quantitative means of predicting particle formation rates under typical atmospheric conditions. IMN also links traditional studies of air mobility with basic research on aerosol microphysics. Such connections may ultimately lead to novel explanations for the correlation noted between variations in galactic cosmic ray fluxes and global cloud coverage (e.g., Svensmark, 1998), thus offering a physically-based link between external forcing and Earth's climate system response.

The APM model discussed here requires further development. The parameterization of size-dependent coalescence of vapors and small molecular clusters onto charged particles needs to be validated through laboratory investigations. Moreover, the thermodynamic properties of charged molecular clusters under atmospheric conditions must be carefully characterized. Additional simulations and intercomparisons with measurements will be required to validate and eventually refine the IMN theory.

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