The role of ions in the formation and evolution of particles in aircraft plumes

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Abstract. We consider the effects on aircraft plume microphysics of ions generated by chemiionization processes within the engine combustors. Ions provide centers around which molecular clusters rapidly coalesce, thus promoting the formation of electrically charged sulfuric acid/water aerosols. The resulting charged micro-particles exhibit enhanced growth due to condensation and coagulation aided by electrostatic effects. Simulations with a plume microphysics code show that volatile particles observed behind aircraft may be explained by such processes, as long as initial ion concentrations in the exhaust exceed ~$10^8/cm^3$. This analysis also suggests that the primary emissions of sulfuric acid (plus sulfur trioxide) should amount to at least 20-30% of the fuel sulfur to explain the observed number of volatile particles >9 nm in diameter. Ionized plume simulations reveal a distinct bimodal aerosol distribution, in which an "ion" mode constitutes the larger "activated" volatile sulfuric acid particles, while a smaller "neutral" mode comprises the residual slowly-growing neutral molecular clusters formed in the highly supersaturated region of the plume.

Introduction

The formation of aerosols in jet engine plumes at high altitudes represents a potentially important perturbation of the lower stratosphere and upper troposphere associated with a fleet of advanced commercial aircraft. Up to 500 high-speed civil transport (HSCT) planes may be operating in the stratosphere in the future (NASA, 1995). Jet engines are known to generate substantial quantities of sulfate and soot aerosols, which might affect both stratospheric chemistry and climate (e.g., Turco et al., 1980; Weisenstein et al., 1996).

Recent *in situ* sampling in the wake of a Concorde aircraft (Fahey et al., 1995) found particle concentrations (for diameters $d\geq9$ nm) of ~1.6–4.8 $\times 10^4/cm^3$, of which 70-90% were volatile (here, a "volatile" particle is one that, upon evaporation at elevated temperatures, does not leave a residual refractory core of sufficient size to be detected as a condensation nucleus, or CN; hence, a "nonvolatile" particle is one that contains a detectable solid core). These measurements also suggest that at least 12% of the fuel sulfur had been converted into H_2SO_4. Such observations indicate efficient gas-to-particle conversion in aircraft plumes (Zhao and Turco, 1995), leading to relatively large volatile particles, presumably $H_2SO_4 - H_2O$ droplets under stratospheric conditions.

Kärcher et al. (1995) considered the subsequent growth of plume aerosols due to condensation and coagulation and found that the resulting properties of the large particles (for example, with sizes >40 nm) were very sensitive to the initial homogeneous nucleation rate (where values as large as $10^{12}/cm^3$-sec are theoretically possible with high-sulfur fuels). Similarly, Brown et al. (1996a) carried out detailed microphysical simulations of aerosol formation and evolution in the near-field (for plume ages of up to ~10 seconds). Their calculations indicated that condensation and coagulation would not be sufficiently rapid to generate particles large enough to act as water conden-

sation nuclei for contrail formation, although high levels of small (3-6 Å radius) sulfuric acid embryos were predicted to form by homogeneous nucleation.

On the basis of simulations assuming different critical embryo sizes for homogeneous nucleation, Kärcher and Fahey (1997) concluded that roughly 25-60% of the fuel sulfur would need to be converted to S(VI) (here, sulfur trioxide plus sulfuric acid vapor) to reproduce observed aerosol properties. The assumption of large critical embryos was made to compensate for mechanical inefficiencies in the formation and growth of very small particles, brought to light when predictions were compared to observations.

We propose that many of the difficulties with the classical model of aircraft aerosol formation can be overcome by introducing the effects of ionization on molecular clustering, nucleation, coagulation, and condensation rates. Key aspects of this new conceptual model for aircraft plume particle evolution are described below.

Ionized Plume Microphysics

The effects of charge on atmospheric fine aerosols are generally ignored because of the improbability of very small particles collecting a net charge from the background atmospheric plasma, a conclusion that is based on the reasonable assumption of a Boltzmann charge distribution (Twomey, 1977). However, in aircraft exhaust, very high concentrations of ions may be present that significantly modify the microphysics of the aerosols formed in the wake.

Ion Emissions: It is well known that chemiionization generates ions and electrons in hydrocarbon flames according to the reactions (Calcote 1962, 1983),

$$CH + O \rightarrow CHO^+ + e$$
$$CH(^2\Sigma^+) + O \rightarrow CHO^+ + e \tag{1}$$
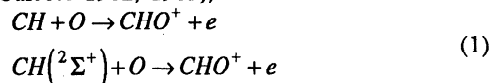
The primary positive ions quickly undergo a proton-exchange with water,

$$CHO^+ + H_2O \rightarrow H_3O^+ + CO \tag{2}$$
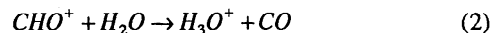
with a rate coefficient of $>10^{-9}$ cm^3/sec (Calcote, 1962). The resulting hydronium core ion then rapidly clusters with water vapor and other polar molecules, with typical rate coefficients $\geq10^{-9}$ cm^3/sec (Beig et al., 1993). Electrons produced by chemiionization rapidly form O_2^-, which subsequently reacts with nitrogen and sulfur species to create the stable terminal negative ions, NO_3^- and HSO_4^-. These ions further cluster with H_2SO_4 to produce species such as $HSO_4^- \cdot (H_2SO_4)_n$, with ion-molecule reaction rate coefficients exceeding 10^{-9} cm^3/sec (Viggiano et al., 1980; Beig et al., 1993).

Ion concentrations of 10^8-$10^{11}/cm^3$ have been reported in hydrocarbon flames (Calcote 1962; Keil et al., 1984). The charge concentration falls off quickly with increasing distance from the combustion source due to ion-ion recombination. For the molecular ions of interest, the recombination coefficients are ~2x10^{-7} cm^3/sec (Calcote, 1962). The associated charge recombination leads to maximum ion concentrations of ~$10^8/cm^3$ roughly 0.1 second after expansion from the combustion zone. While ions have not been directly measured in aircraft combustors, the thermochemistry is similar enough to flames to expect substantial ion emissions. Below, we predict the evolution of electrical charge in the wake to provide a benchmark for future observations.

Molecular Aggregation: In aircraft exhaust, ions generated by the engines will quickly form charged molecular clusters that represent nascent plume particles. Owing to the high supersaturation of H_2SO_4 in the expanding plume, it can be assumed that all of these ions are effectively "nucleated" in the jet regime and continue to grow by condensation and coagulation (e.g., Hamill et al., 1982). Accordingly, the initial stages of cluster growth are expected to be greatly accelerated in an ionized plume as compared to a neutral one.

A recent measurement of the emission of an aircraft engine found the expected sulfuric acid-based cluster ions (Frenzel and Arnold, 1994). Based on ion-molecule kinetics, the collection of sulfuric acid and water vapors around ions occurs with an effective collision kernel of the order of $\sim 10^{-9}$ cm^3/sec. At the vapor concentrations present in the early plume, large ions composed of sulfuric acid and water will form within milliseconds once the temperature drops to several hundred Kelvin.

For neutral molecules, by contrast, typical collision/aggregation kernels are in the range of 10^{-10}-10^{-12} cm^3/sec. The former value represents an upper-limit corresponding to the molecular collision rate at normal temperatures, while the latter is a typical high-pressure-limited third-body-stabilized association rate coefficient, which reflects the mechanical barrier to the formation of aggregates by encounters in a warm gas (equivalently, the smaller kernel can be considered the result of a collisional "sticking coefficient" of less than unity). The uptake of neutral molecules by very small uncharged particles may also be less than perfectly efficient. As an example, the effective accommodation coefficient for the condensation of sulfuric acid vapor on 0.05 μm to 0.5 μm $H_2SO_4 - H_2O$ particles has been estimated experimentally to lie in the range of 0.02-0.09 (Van Dingenen and Raes, 1991).

Particle Coagulation: The influence of electrical charge on the coagulation of fine particles is quite strong (Twomey, 1977). Our calculations indicate that the coagulation enhancement factor, β (which multiplies the coagulation kernel for a pair of otherwise neutral particles), can have values of up to 800 for molecular-sized particles ($d\sim 0.5$ nm) with opposite charges, and up to 8 for one charged and one neutral particle. Note that any neutral aerosols formed by the recombination of two oppositely charged particles will be stable against evaporation because of the high supersaturation of sulfuric acid vapor in this region of the plume (Zhao and Turco, 1995). The entrainment of ambient ions will have a negligible effect on the ionization levels in the early plume.

Physically, the limit of the effect of electrical charge on coagulation at small sizes is consistent with the observed kinetics of charged molecular species. For example, the enhanced coagulation kernel predicted for oppositely-charged molecular-sized particles is comparable in magnitude to measured molecular ion-ion recombination coefficients (that is, $\sim 10^{-7}$ cm^3/sec). Moreover, the coagulation kernel for a charged-neutral pair of monomer-sized particles is comparable to a typical ion-neutral reaction rate coefficient ($\sim 10^{-9}$ cm^3/sec). It follows that, if ion concentrations in the exhaust stream are very high, then molecular clusters formed preferentially upon ions will accelerate the overall growth of the embryonic particles.

Aerosol Formation and Evolution: The microphysical code we have developed to study aircraft wakes treats sulfuric acid/water solution droplets, solid soot particles, core ionic charge, and mixtures of these components. Aerosol formation (nucleation) and growth from microscopic (atomic) to macroscopic dimensions are incorporated as kinetic processes equivalent to molecular "coagulation." Clustering of vapors onto core ions, and charge-enhanced condensation and coagulation, are treated by adjusting the coagulation kernels and accommodation (or "sticking") coefficients appropriately (e.g., for charged-particle interactions, as noted above). In the case of charged aerosols, a unit accommodation coefficient for coagulation is consistent with the stabilization of collision complexes by attractive electrostatic forces. For coagulation between electrically-neutral particles, the accommodation coefficient is taken to increase linearly with particle size from 0.01 at molecular sizes, to 1 at a collision diameter of 20 nm. This replicates the observed kinetic behavior of H_2SO_4 condensation on particles of molecular dimensions, as well as on fine aerosols (Van Dingenen and Raes, 1991). A complete de-

scription of the microphysics of ionized aerosol plumes is provided elsewhere (Yu and Turco, manuscript to be submitted).

Simulations

Plume Behavior: Two plume dilution rates have been adopted for the present work, as discussed by Turco and Yu (1997) and Yu and Turco (manuscript to be submitted). As a baseline, relatively "slow" plume growth is assumed in the vortex regime, owing to the confining effect of the descending vortex pair (Miake-Lye et al., 1993, Schilling et al., 1996). In the alternate dispersion scenario, the rate of plume expansion is taken from early studies of the Concorde wake (CIAP, 1975), and is relatively "fast" in the vortex regime. The former "slow" dilution model is preferred. In either case, the overall expansion has been calibrated against CO_2 concentrations measured in aged plumes (Fahey et al., 1995). All of the simulations were initiated at the exit plane of the engine combustors, subsequent to the initial adiabatic expansion of the exhaust. The ions injected into the airstream were allowed to recombine from this initial time, However, aerosol growth occurred only after sulfuric acid vapor had become supersaturated, with an initial ion diameter of about 0.65 nm (assumed to be achieved within a millisecond after the onset of supersaturation).

Emission Parameters: The emission index for soot particles is, $EI_{soot}=0.5g/kg$; the size distribution is taken to be log-normal with $\sigma=1.4$, and a mean diameter of $\bar{d} \approx 20$ nm (Pueschel et al., 1992). The adopted soot size distribution agrees well with measurements at 16 minutes (Fahey et al., 1995) in terms of the concentration of nonvolatile particles ($\sim 4800/cm^3$) and their size dispersion (where no refractory particles were detected at diameters >80 nm). A key source of uncertainty in this study is the fraction, S_C, of the fuel sulfur that is converted to S(VI) in the combustors and emitted within milliseconds into the wake. Brown et al., (1996b) estimated this fraction to be at most 10%. However, some aircraft plume observations suggest a higher number (Fahey et al., 1995). In the wake, conversion of SO_2 to H_2SO_4 is relatively slow because the concentrations of OH, while higher than ambient levels, are still quite low. Owing to the large uncertainty in S_C, we consider direct sulfuric acid emission fractions in the wide range of 2-90% (equating S_C with the H_2SO_4 emission fraction in these simulations).

Case Studies and Variations: Three basic microphysical scenarios are treated (see Table 1). The "Baseline" case (Case 1) assumes that ions are present, and aerosol evolution is calculated using the molecular aggregation approach. The equivalent scenario without the effects of ionization is Case 2 ("No Ions"). Finally, a standard microphysical treatment based on the classical theory of nucleation, condensation, and coagulation (Toon et al., 1988)—rather than a molecular clustering

Table 1. Parameters and Variations for Sensitivity Analysis

Parameter	Reference Value (Variations)	Case 1 (Baseline)	Case 2 (No Ions)	Case 3 (Classical)
Plume Mixing Rate	Slow	x	x	x
	(Fast)	x	x	x
S_C	30%	x	x	x
	(2–90%)	x	x	x
n_i	$10^8/cm^3$	x		
	($10^7, 10^9/cm^3$)	x		
β_{OC}	Variable, 1–800	x		
β_{CN}	Variable, 1–8	x		
α_{NN}	Variable, 0.01–1.0	x	x	
	(Fixed, 1.0)			x
α_{CN}/α_{OC}	Fixed, 1.0	x		

Symbols are: S_C, H_2SO_4 [S(VI)] emission fraction; n_i, initial ion concentration; β_{OC}, β_{CN}, coagulation enhancement factor for oppositely charged and charged-neutral particles, respectively; α_{NN}, α_{CN}/α_{OC}, coagulation accommodation coefficient for neutral-neutral and charged-neutral/oppositely charged particles, respectively.
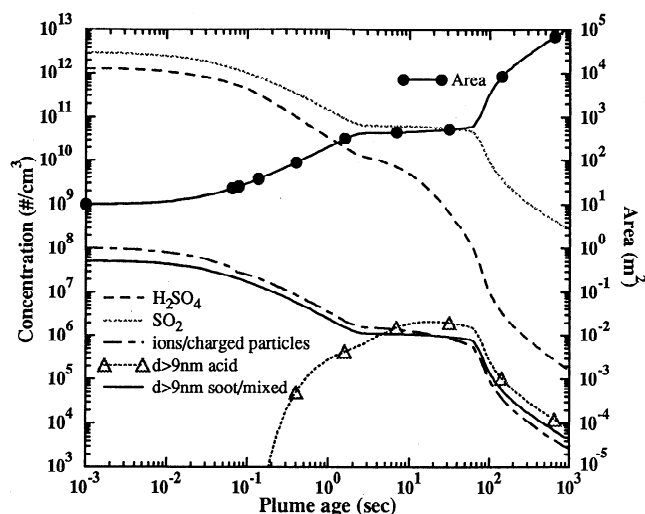
Figure 1. Predicted evolution of plume properties for Case 1 (using reference value for all parameters, see Table 1). Results are shown for the plume cross-sectional area, concentrations of gaseous constituents, total charge concentrations (positive or negative, including ions and charged particles), and total number densities of volatile (acid) and nonvolatile (soot and mixed soot/acid) particles having diameters greater than 9 nm.

model—is adopted as Case 3 ("Classical"). In Case 3, only the neutral mechanics of the aerosols are considered (Zhao and Turco, 1995; Yu and Turco, manuscript to be submitted), and a unit accommodation coefficient is assumed for both coagulation and condensation. For each of the three conceptually distinct cases, reference values are specified for the key parameters, while variations in these parameters comprise a set of sensitivity studies to probe uncertainties inherent in the physical models (see Table 1).

Results and Discussion

Figure 1 illustrates the evolution of the plume cross-sectional area, and gaseous and particulate components, including the charge density, for times up to 1000 seconds in Case 1 (baseline) with reference parameters. The limited mixing in the vortex regime has a substantial effect on the evolving aerosol properties at early times, including the size distribution, total concentration, and surface area. Mixing with ambient air causes the concentrations of the vapors, ions, and

volatile and nonvolatile (pure "soot" and mixed soot/sulfuric-acid particles) particles to decrease rapidly. According to the results in Figure 1, with 30% of the sulfur emitted in highly oxidized states, the abundance of volatile acid droplets with diameters >9 nm is $\sim 10^4/cm^3$ after 16 minutes, representing about 70% of the particles at these sizes. Sensitivity studies show that, after a few seconds, the charge concentrations—clearly associated with aerosols—have become relatively insensitive to the initial ion abundance (for ion concentrations exceeding $\sim 10^8/cm^3$). While dilution has an important influence on the evolving charge concentration, recombination can reduce the overall charge level by up to one more order of magnitude over the first ten minutes, during which ion concentrations approach background values.

Figure 2 summarizes the volatile particle size distributions for a number of simulations corresponding to Case 1 (using reference value for all parameters except S_C). Size distributions are shown after about 1 second and after 16 minutes of evolution. The ion-induced size distributions are distinctly bimodal in nature. Further analysis reveals that the larger size mode is associated with the charged particles, while the smaller mode is related to the neutral clusters that form during the period of high supersaturation in the plume. Subsequently, the growth of the smaller-mode particles is inhibited—even beyond the normal kinetic limitations to neutral aggregation—because H_2SO_4 vapor is more efficiently scavenged by the ionized particles. The mean size of the ion-mode aerosols depends on the initial H_2SO_4 vapor concentrations as well as the initial ion concentration (since the available vapor must be shared among the "activated" ions).

In the ion-assisted aerosol growth case, volatile particles have already achieved substantial dimensions by 1 second. This rapid growth occurs in a region where the concentrations of condensing vapors are highest, and the ion effects in accelerating aggregation are greatest. In this regime, neutral species react with ions within milliseconds, and hence very large molecular clusters quickly build up. Further, once the fraction of sulfur emitted as H_2SO_4 surpasses a certain value (for example, about 20% for an initial ion concentration of $10^8/cm^3$), the fraction of measurable volatile particles (those having diameters >9 nm) at 16 minutes is relatively insensitive to S_C, since most of the surviving charged particles have grown into this size partition, while the neutral-mode particles remain too small to contribute to the observed volatile fraction.

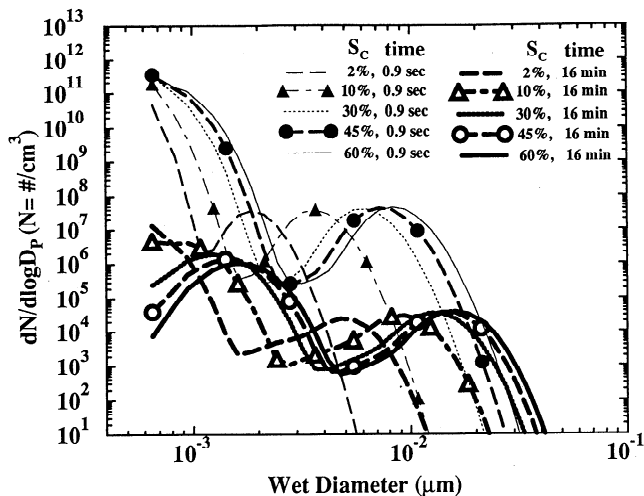A number of the simulations are summarized in Figure 3 in

Figure 2. Size distributions of acid (volatile) particles at two times during plume evolution for Case 1, using reference value for all parameters except S_C.
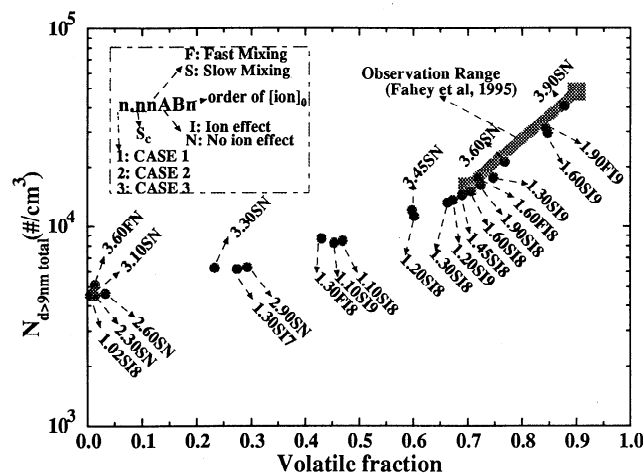

Figure 3. The total concentration of particles (volatile + nonvolatile) with diameters exceeding 9 nm $(N_{d>9nm})$ versus the fraction of these particles that are volatile. Simulations corresponding to cases described in Table 1 are compared to observations taken by Fahey et al. (1995) in a stratospheric plume (the bar in the upper right-hand area of the plot identifies the range of observational values for $N_{d>9nm}$ versus volatility). The individual simulations are identified by a coded label explained in the inset (S_C is given as a percentage, and the initial ion concentration, n_i, is specified by its log_{10}).

terms of the total concentration of observable aerosols (>9 nm) and the fraction of those particles that are volatile. The predictions are given at 16 minutes after emission, corresponding to the series of measurements reported by Fahey et al. (1995) in a Concorde plume. The three cases and their variations are coded in the graph (refer to the inset). It can be seen that Case 1 (with ion effects) clearly reproduces the observational results when primary sulfate emissions (H_2SO_4 plus SO_3) represent 20-30% or more of the fuel sulfur (with an initial ion concentration of 10^8-$10^9/cm^3$). Case 2, in which the underlying physics is comparable to that of Case 1 except that charge influences are neglected, does not reproduce the measurements for any reasonable parameter variations. In effect, few large volatile particles are generated through neutral molecular aggregation.

The simulations for Case 3 in Figure 3 reproduce observations when high S(VI) emission fractions are adopted. However, the classical approach assumes optimum conditions for the production of large volatile aerosols in the plume. For example, the formation of nucleation embryos occurs essentially instantaneously, H_2SO_4 vapor collection (which controls the condensational growth rates) occurs with a unit accommodation coefficient, and coagulating particles are always assumed to stick regardless of size. As discussed earlier, all of these assumptions are doubtful. Indeed, in contrasting the results of Case 3 with those of Case 2, the likely limitations of the classical approach are revealed. Thus, when particle formation and growth rates are based on kinetically-controlled aggregation processes without ionization effects, and more conservative accommodation efficiencies are adopted, the predicted volatile fraction of the aerosols >9 nm is negligible after 16 minutes.

In Case 3, aerosol concentrations above 9 nm are also sensitive to the initial sulfuric acid concentration, because homogeneous nucleation—which provides, artificially, a nearly instantaneous pathway from the vapor to the condensed phase—is very sensitive to this parameter. Coagulation subsequently reduces the aerosol population so that no memory remains of the high initial particle concentrations (Turco and Yu, 1997). The coagulation of nucleation embryos therefore dominates the growth of volatile particles under these conditions.

Conclusion

We have shown that ions generated in aircraft engines may control the short-term evolution of aerosols in the wake. Further, we have demonstrated that standard approaches to plume microphysical modeling have difficulty reproducing *in situ* measurements of aerosol properties. The present simulations also suggest that, even with ion enhancement, at least 20-30% of the fuel sulfur must be oxidized to sulfuric acid to produce the number of large volatile particles detected experimentally. Many uncertainties in these predictions remain, however, including the impacts of chemical processing in the early plume, the effects of turbulence on the microphysics, and the true nature of molecule-particle interactions in the jet regime. Nevertheless, based on the sensitivity analysis presented here, it follows that ionization is likely to play a key role in determining aircraft aerosol characteristics. Specific experiments could be carried out to confirm the contribution of ionization to aerosol formation, including the direct measurement of charge levels in the exhaust of engine combustors, and the detection in the wake of a bimodal aerosol distribution consisting of an ion mode and a neutral mode, as predicted here.

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