Ion-mediated nucleation in the atmosphere: Key controlling parameters, implications, and look-up table

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Abstract. Nucleation is an important source of atmospheric particles and ubiquitous ions in the atmosphere have long been known to promote nucleation. An ion-mediated nucleation (IMN) mechanism based on a kinetic model is supported by recent measurements of the excess charge on freshly nucleated particles and ion cluster evolution during nucleation events. Here we investigate the dependence of steady state IMN rate ($J_{IMN}$) on key controlling parameters. We find that sulfuric acid vapor concentration, temperature, relative humidity, ionization rate, and surface area of pre-existing particles have profound and non-linear impacts on $J_{IMN}$. The sensitivities of $J_{IMN}$ to the changes in these key parameters may imply important physical feedback mechanisms involving climate and emission changes, solar variations, nucleation, aerosol number abundance, and aerosol indirect radiative forcing. We also describe a five-dimensional $J_{IMN}$ look-up table derived from the most recent version of IMN model, with the key parameters covering a wide range of atmospheric conditions. With the look-up table and a multiple-variable interpolation subroutine, $J_{IMN}$ and the properties of critical clusters can be determined efficiently and accurately under given atmospheric conditions. The look-up table reduces the computational costs of the IMN rate calculations significantly (by a factor of around $\sim 8000$), and can be readily incorporated into multi-dimensional models to study the secondary particle formation via IMN and associated climatic and health effects.
1. Introduction

The magnitude of the aerosol indirect radiative forcing is poorly constrained in climate models, and this is the dominant uncertainty in assessing climate change [IPCC, 2007]. The aerosol indirect radiative forcing is largely determined by the number abundance of particles that can act as cloud condensation nuclei (CCN) [e.g., Twomey, 1977; Albrecht 1989]. New particle formation, which has been frequently observed throughout the troposphere [Kulmala et al., 2004a; Yu et al., 2008], is an important source of atmospheric CCN. To accurately assess the influences of aerosols on climate, interpret past climate, and project future changes, the contribution of secondary particle formation and growth to CCN abundance have to be understood and properly incorporated in the large scale models. In this regard, it is critical to achieve a clear physical understanding of atmospheric particle nucleation mechanisms, especially the dependence of nucleation rates on key atmospheric parameters.

Based on an up-to-date kinetically consistent ion-mediated nucleation model (IMN) incorporating recently available thermodynamic data and schemes, Yu [2006] showed that ions can lead to significant particle formation not only in the upper troposphere but also in the lower troposphere (including boundary layer). The involvement of ions in many boundary layer nucleation events has been confirmed by measurements of the evolution of charged clusters during nucleation events and the observed overcharge of freshly nucleated nanometer-sized particles [Iida et al., 2006; Hirsikko et al., 2007; Laakso et al., 2007; Gagné et al., 2008]. Both three-year records of ion mobility measurements [Hirsikko et al., 2007] and one-year overcharging ratio measurements for freshly nucleated particles [Gagné et al., 2008] indicate that ions are involved in more than 90% of the particle formation events that can be clearly identified, although the relative contribution of ion and neutral nucleation remains controversial [see
Section 2.2 for more discussion on this]. Detailed case studies [Yu and Turco, 2008] indicate that, for most of well-defined nucleation events observed in Hyytiälä, Finland, the predictions based on the ion-mediated nucleation (IMN) model are in good agreement with field data for a range of variables, including critical nucleation sizes, size-dependent overcharging ratios, and the concentrations of 1.8-3 nm stable clusters and 3-6 nm particles, as well as their diurnal variations. Thus, we have experimental evidence that IMN may be important in the atmosphere.

In this paper we study the dependence of IMN rates on key parameters and derive an IMN look-up table from the detailed kinetic IMN model. An overview of the IMN mechanism is given in section 2. The dependence of IMN rates on key parameters and associated implications are discussed in Section 3. Section 4 describes the IMN look-up table, which can be used for a quick and accurate calculation of IMN rates at given conditions. Lastly, section 5 is the summary.

2. Overview of ion-mediated nucleation (IMN) mechanism

2.1. The kinetic IMN model: Physics, features, and recent development

Ions, which are generated continuously and ubiquitously in the atmosphere by cosmic radiation and radioactive decay, have long been suggested to promote nucleation [Castleman et al., 1978; Arnold, 1980; Chan and Mohnen, 1980; Hamill et al., 1982; Raes et al., 1986]. Yu and Turco [1997, 2000, 2001] developed a comprehensive approach for studying nucleation processes involving ion clusters. They utilized a kinetic model that explicitly treats the complex interactions among small air ions, neutral and charged clusters of various sizes, precursor vapor molecules, and pre-existing aerosols. Compared to homogeneous nucleation, which involves the formation of small, transient neutral molecular clusters, nucleation onto ions is favored because: (1) small charged clusters are typically much more stable thermodynamically than their neutral counterparts [Yu, 2005, 2006]; (2) the initial growth rates of small ion clusters are enhanced by
the dipole-charge interaction between the core ion and the strongly dipolar condensing molecules [Nadykto and Yu, 2003]; and (3) there is a continuous and ubiquitous supply of stable, fast growing ionic embryos. Yu and Turco [2000] refer to the coupled formation and evolution of cluster size distributions, including both charged and neutral clusters, under the influence of ionization, recombination, neutralization, condensation, evaporation, coagulation, and scavenging as ion-mediated nucleation (IMN).

The IMN theory differs substantially from classical ion-nucleation theory, which is commonly adopted in the literature [e.g., Hamill et al., 1982; Raes et al., 1986; Laakso et al., 2003]. Classical “ion-nucleation” is based on a simple modification of the free energy associated with the formation of a “critical nucleation embryo” in which the electrostatic potential energy induced by the embedded charge is included. However, this classical approach does not properly account for the kinetic limitation to embryo development imposed by the typically low atmospheric concentrations of precursors, especially sulfuric acid. In addition, the important contribution of neutral clusters resulting from ion-ion recombination to nucleation is not considered in the classical ion-nucleation theory. By contrast, in IMN theory, the kinetic effect of charge on cluster growth rates and the contribution of neutral clusters resulting from the neutralization of charged clusters are explicitly considered.

IMN explains the rapid initial growth of small clusters, as a result of the charge-neutral interactions. This initial growth phase (to sizes of ~1.5 nm diameter) is not to be confused with later stages of stable nanoparticle growth (from ~2-3 nm and larger). In the initial phase, ion-molecule interactions greatly accelerate the kinetics of molecular association – by up to an order of magnitude. However, by the time the nucleating embryos are larger than ~1.5 nm in diameter, the charge-enhanced growth effect becomes quite small due to the inverse relationship between
charge effect and embryo size [Nadykto and Yu, 2003] and rapid neutralization of ion embryos [Yu, 2006; Yu and Turco, 2008]. Subsequently, the growth rate is dominated by the vapor pressure of the major condensing species. In the case of organic condensates, for example, the normal Kelvin effect would predict that the growth rate accelerates as the particles size increases, opposite to the effect produced by a fixed particle charge. This predicted pattern of growth is consistent with observations [e.g., Kulmala et al., 2004b].

Built upon an earlier version of the IMN model [Yu and Turco, 1997, 2000, 2001], Yu [2006] developed a second-generation IMN model which incorporates new thermodynamic data [Froyd, 2002; Wilhelm et al., 2004] and physical algorithms [Nadykto and Yu, 2003; Yu, 2005] and explicitly treats the evaporation of neutral and charged clusters. The uncertainty in the IMN model has been further reduced by using two independent measurements to constrain monomer hydration in the H$_2$SO$_4$-H$_2$O system, and by incorporating recently determined energetics of small neutral H$_2$SO$_4$-H$_2$O clusters [Yu, 2007]. It should be pointed out that the present IMN model is for the H$_2$SO$_4$-H$_2$O binary system. In the atmosphere, species other than H$_2$SO$_4$ and H$_2$O (such as NH$_3$, amines, HNO$_3$, and some organics) may be involved in the IMN process under some conditions. Obtaining necessary thermodynamic data and extending the IMN model for a multiple-component nucleation system will be the subject of future research.

Based on the most comprehensive and well-constrained case studies of atmospheric nucleation processes to date (at least to our knowledge), Yu and Turco [2008] concluded that, beyond a reasonable level of uncertainty, IMN appears to be the dominant nucleation mechanism in at least a large fraction of nucleation events observed during an intensive field campaign in boreal forests. In addition, the global nucleation spatial patterns and absolute magnitude predicted using the IMN mechanism is reasonably consistent to land-, ship-, and aircraft-based
observations [Yu et al., 2008]. More recently, Yu and Luo [2009] used global size resolved aerosol microphysics modeling to show that IMN is able to account for (within a factor of two) the annual mean particle number concentrations observed in many parts of troposphere.

2.2. Controversy with regard to the importance of IMN in the atmosphere

While our analyses indicate that the ion mobility data and the measurements of excess charge on freshly nucleated particles in the boreal forest support the dominance of the IMN mechanism [Yu and Turco, 2007, 2008], Kulmala and colleagues concluded that, based on their analysis of the same dataset, IMN contributes only up to ~10% to the boreal forest nucleation [Laakso et al., 2007; Kulmala et al., 2007; Gagné et al., 2008; Boy et al., 2008; Manninen et al., 2009]. Given such discrepancies, we discuss these studies here along with possible reasons for the differences.

Kulmala and colleagues’ studies concluding the dominance of neutral nucleation process include: (1) Laakso et al. [2007] and Gagné et al. [2008] extrapolated measured charging states of nucleation mode particles (~3 - 7 nm) down to smaller sizes (1-2 nm) and concluded that the contribution of IMN to total nucleation rate was either negligible or relatively small in a large fraction of days considered. (2) Kulmala et al. [2007] and Manninen et al. [2009] calculated the formation rate of total and charged 2 nm particles from the particle concentrations detected in the size range of ~2–3 nm, and concluded that IMN contributes ~10% to the boreal forest new particle formation events. (3) Boy et al. [2008] simulated 4 days of nucleation events using atmospheric input data from the SMEAR II station. They calculated the IMN rate based on the model of Kazil and Lovejoy [2007], and used the empirical activation (\(J_{\text{act}} = A [\text{H}_2\text{SO}_4]\)) and kinetic nucleation formulas (\(J_{\text{kin}} = K [\text{H}_2\text{SO}_4]^2\)) to represent neutral nucleation. By comparing their calculated ion and neutral nucleation rates, Boy et al. [2008] concluded that IMN
contributes between <0.5 to 12% to the total number of particles nucleated inside the mixed layer in the boreal forests.

Yu and Turco’s studies pointing out the dominance of the IMN process include: (1) Yu and Turco [2007] showed, based on a conservative analytical analysis of the neutralization of charged particles, that the observed charging states of nucleated particles (~ 3 - 7 nm) reported in Laakso et al. [2007] are fully consistent with the dominance of IMN in most of the nucleation events. (2) Based on the well-constrained case studies of nucleation events characterized in Hyytiälä, with a kinetic nucleation model accounting for the size-dependent microphysics of neutral and charged clusters, Yu and Turco [2008] demonstrated a good agreement between the IMN predictions and field data for a wide range of the key parameters including the overcharging ratio (OR) of 3-7 nm particles and concluded that IMN is likely to be the dominant nucleation mechanism in at least a large fraction of nucleation events in boreal forests.

One possible cause of such different conclusions is that Kulmala and colleagues’ analyses focused on 2-3 nm particles while Yu and Turco’s kinetic modeling considered the actual dynamics of the formation of clusters with diameters ranging from ~0.5 nm to >3 nm. Kulmala and colleagues assume that all neutral particles ~ 2 nm or growing into 2 nm are from neutral nucleation. This may lead to significant underestimation of the IMN contribution because a significant fraction of neutral particles ~ 2 nm and smaller may be formed from the IMN [Yu and Turco, 2008]. Yu et al. [2007] have demonstrated that Laakso et al. [2007]’s conclusion that IMN has a negligible or small contribution to new particle formation is inconsistent with their own analysis of the charging state (Sc) of 1 nm particles. Laakso et al. [2007]’s conclusion appears to be based on Sc values of 2 nm particles. However, it is more appropriate to use Sc at 1 nm because neutral particles at 1-2 nm may actually be produced by the neutralization of
particles formed on ions and thus are a direct result of IMN [Yu and Turco, 2008]. Based on Sc at 1 nm given in Laakso et al. [2007], a large fraction (60%) of the days have either a significant or dominant (Sc>50) contribution from IMN, while only a small fraction (13%) of days have either negligible (Sc<1) or small (Sc<10) contributions from IMN [Yu et al., 2007]. These considerations lead us to conclude that Laakso et al.’s analysis may actually support Yu and Turco’s conclusion. Similarly, we think that Kulmala et al. [2007] and Manninen et al. [2009] underestimated the importance of IMN because they assumed all neutral particles growing to ~ 2 nm were produced via neutral nucleation, while in the reality these particles may have been formed via the neutralization of particles formed on ions. The conclusion of Boy et al. [2008] is not surprising because they used the ion nucleation model similar to that of Lovejoy et al. [2004], which under-predicts ion nucleation rate by several orders of magnitude [Yu and Turco, 2008]. In addition, Boy et al. [2008] used empirical activation and kinetic nucleation formulas to represent neutral nucleation. It remains to be established whether the empirical formula indicates a new nucleation mechanism or if it simply represents an empirical fitting of exiting nucleation process such as IMN [Yu and Turco, 2008].

While more comprehensive studies are needed in order to more clearly resolve the IMN controversy, our analyses given above indicate that Kulmala and colleagues might have underestimated the importance of IMN, and the results of Laakso et al. [2007] may actually support the significance of IMN. It should be emphasized that the dominance of the neutral nucleation process will lead to the undercharging of freshly nucleated particles. Laakso et al. [2007] and Gagne et al. [2008] showed that ion-DMPS detected substantial undercharging of freshly nucleated particles in only ~ 10% of nucleation event days. The undercharging could be
an indication of the dominance of neutral nucleation; however it may also be a result of air mass
inhomogeneity and uncertainties in measurements [Yu and Turco, 2008].

3. Dependence of IMN rates on key parameters and implications

The IMN model explicitly solves the dynamic equations governing the size distribution
evolution of neutral, positively charged, and negatively charged cluster/particles. The IMN rates
(denoted as $J_{IMN}$) are calculated based on the net fluxes of particles across the critical size of
neutral embryos. Under a given condition, cluster distribution and nucleation rate reach steady
state after a certain amount of time. Detailed information about the IMN model and how IMN
rates are determined can be found in Yu [2006]. All the IMN rates presented in this paper are the
steady state values, and the steady state apparent IMN rates across the clusters containing 10
sulfuric molecules (around 1.5 nm) are used for the conditions that give very small critical size
(containing less than 10 sulfuric molecules). The current version of the IMN model only
considers the binary H$_2$SO$_4$-H$_2$O system, and there are five key parameters controlling $J_{IMN}$:
sulfuric acid vapor concentration ([H$_2$SO$_4$]), temperature (T), relative humidity (RH), ionization
rate (Q), and surface area of pre-existing particles (S). Figures 1-5 show the dependence of $J_{IMN}$
on these parameters, based on the calculations from full IMN model (solid lines) and IMN look-
up table detailed in Section 4 (dashed lines).

3.1. Sulfuric acid vapor concentration ([H$_2$SO$_4$])

Figure 1 gives $J_{IMN}$ as a function of [H$_2$SO$_4$] for four different atmospheric states. There is no
doubt that [H$_2$SO$_4$] is a key parameter controlling $J_{IMN}$. To achieve a nucleation rate of 1 cm$^{-3}$s$^{-1}$
under typical values of Q (10 ion-pairs cm$^{-3}$s$^{-1}$), RH (50%), and S (100 μm$^2$ cm$^{-3}$), [H$_2$SO$_4$] has
to be around $6 \times 10^6$, $9 \times 10^6$, $2.5 \times 10^7$, and $10^8$ cm$^{-3}$ for T = 265, 275, 285, and 295 K, respectively.
Nucleation events have been frequently observed in boreal forests during the spring season when $T \approx 270 - 285$ K and peak $[\text{H}_2\text{SO}_4]$ is in the range of $5 \times 10^6 - 3 \times 10^7$ cm$^{-3}$. It has been shown by Yu and Turco [2008] that the IMN mechanism appears to be able to account for at least a large fraction of these nucleation events and is supported by the observed overcharging of freshly nucleated particles.

Under the conditions considered in Fig. 1, $J_{\text{IMN}}$ is very sensitive to $[\text{H}_2\text{SO}_4]$ when $[\text{H}_2\text{SO}_4]$ is relatively low and $J_{\text{IMN}}$ is relatively small, and becomes insensitive at higher $[\text{H}_2\text{SO}_4]$, because of the limitation of nucleation by ionization rate. For low $T$, $J_{\text{IMN}}$ becomes sensitive to $[\text{H}_2\text{SO}_4]$ when $[\text{H}_2\text{SO}_4]$ is high (for example, see the curve with $T=230$ K when $[\text{H}_2\text{SO}_4] > \sim 2 \times 10^7$/cm$^3$) because of the dominance of binary homogeneous nucleation (BHN) under such conditions. It should be noted that BHN is an integrated part of IMN [Yu, 2006].

The importance of $[\text{H}_2\text{SO}_4]$ in controlling $J_{\text{IMN}}$ can also be seen from the global spatial distribution of $J_{\text{IMN}}$ presented in Yu et al. [2008], showing that high nucleation zones are generally confined to high sulfur source regions. The sensitivity of $J_{\text{IMN}}$ to $[\text{H}_2\text{SO}_4]$ implies that future changes in anthropogenic and natural emissions of sulfur species may have important impacts on new particle formation, aerosol abundance, and radiative forcing. For example, Charlson et al. [1987] proposed that a warmer climate would increase dimethylsulphide (DMS) emissions which in turn leads to higher formation rates of sulfate aerosols and CCN abundance. The resulting increase in cloud albedo should reflect more sunlight back to space and thus cool the Earth. On the other hand, the pollution controlling strategies aimed to reduce anthropogenic sulfur emissions may significantly decrease aerosol number abundance in the atmosphere and thus diminish the cooling effects of atmospheric aerosols.

3.2 Temperature ($T$)
Figure 2 illustrates the dependence of $J_{IMN}$ on $T$ under four different ambient conditions. Similar to $[H_2SO_4]$, $T$ has a strong effect on $J_{IMN}$. Under a variety of conditions given in Fig. 2, $J_{IMN}$ is very sensitive to $T$ when $J_{IMN}$ increases from insignificant ($< ~0.01$ cm$^{-3}$s$^{-1}$) to significant ($> ~1$ cm$^{-3}$s$^{-1}$) as $T$ decreases. After $J_{IMN}$ reaches a significant level, further decreases of $T$ (with other parameters fixed) have relatively small effects because nucleation under such conditions is limited by ionization rates. When $T$ is very low, BHN becomes dominant and the nucleation rates become sensitive to $T$ again. Under typical values of $Q$ (10 ion-pairs cm$^{-3}$s$^{-1}$), RH(50%), and $S$ (100 μm$^2$ cm$^{-3}$), to achieve a nucleation rate of 1 cm$^{-3}$s$^{-1}$, $T$ should be around 268, 277, 286, and 291 K, for $[H_2SO_4]$=5×10$^6$, 10$^7$, 3×10$^7$, and 6×10$^7$ cm$^{-3}$, respectively. Clearly, much higher $[H_2SO_4]$ is needed to achieve a similar level of nucleation rate at higher temperature.

Based on mass-resolved ion cluster distributions measured in the summer of 2002 at an urban site in Atlanta, Georgia, and in the late summer/fall of 2004 at the National Center for Atmospheric Research (NCAR)’s Marshall Field Site, Eisele et al. [2006] concluded that ion-induced nucleation was unlikely to have contributed significantly to the new particle formation observed on some days during the study period. Under the atmospheric conditions corresponding to the days that Eisele et al. [2006]’s measurements were made ($T > ~290$ K, RH $< ~40\%$, $[H_2SO_4]<4\times10^7$/cm$^3$), the IMN model would likewise predict a negligible rate of nucleation ($<10^{-3}$/cm$^3$s, see Fig. 2). Thus, the IMN mechanism does not directly conflict with these measurements. It is possible that additional species may be involved and enhance nucleation in urban and other disturbed environments. By analyzing the charged fractions (CFs) of 3-5.5 nm particles measured at NCAR’s Marshall Field Site, Iida et al. [2006] concluded that, while obviously involved in nucleation on some days, ions overall contributed insignificantly to new particle formation observed at the site. Our model predicts negligible IMN rates on days with
high temperature (>~290 K). However, the model also suggests that IMN can become significant during periods of relatively lower temperatures (<~285 K). Iida et al. [2006] derived their CFs at 1 nm by extrapolating from observed CFs for 3-5.5 nm particles, and the interpretive analysis is likely subject to large uncertainties. For example, during a nucleation period on June 1, 2004, the 3-5.5 nm particles were clearly overcharged, with ORs above 2 (Fig. 5 of Iida et al., 2006).

Based on our size-dependent kinetic modeling, an OR above 2 for 3-5 nm particles should indicate the dominance of IMN [Yu and Turco, 2008], whereas Iida et al. [2006] inferred that IMN only contributed ~ 0.4% of the nucleation. A more detailed case study of measurements reported in Iida et al. [2006] may shed new light on the mechanisms of particle nucleation.

In the atmosphere, nucleation events typically last for several hours only and there exist clear seasonal variations in the frequency of nucleation events. According to IMN mechanism, temperature and \([\text{H}_2\text{SO}_4]\) are the two most important factors controlling the start and end of nucleation events, although other parameters also contribute to the changes in nucleation rates. The optimum conditions for IMN are relatively high \([\text{H}_2\text{SO}_4]\) and relatively low T, which may explain (at least partially) why nucleation generally occurs in the morning and why nucleation event frequency peaks in the Spring and Fall [e.g., Stanier et al., 2004; Laaksonen et al., 2008].

Figure 2 shows that, within the T range that \(J_{\text{IMN}}\) changes from insignificant (< ~0.01 cm\(^{-3}\)s\(^{-1}\)) to significant (> ~1 cm\(^{-3}\)s\(^{-1}\)), a 2 K difference in T causes up to around one order of magnitude difference in \(J_{\text{IMN}}\). Such high sensitivity of \(J_{\text{IMN}}\) to temperature may have important implications. For example, future global warming may significantly suppress new particle formation in the atmosphere, reduce CCN abundance and aerosol indirect radiative cooling, and thus may imply a positive climate/nucleation feedback mechanism. The magnitude of this new positive feedback
mechanism proposed here should be assessed with global climate models that incorporate the IMN mechanism and proper size-resolved aerosol microphysics. It is also clear from Figure 2 that, at a constant level of [H$_2$SO$_4$], nucleation is more favored in air with slightly lower temperature. One example is that under some conditions, nucleation is favored in the top of boundary layer instead of surface because of the temperature difference. Actually, many of the nucleation events observed at the surface may be associated with the mixing of particles nucleated aloft (especially particle size distribution evolutions exhibiting the "apple" shape rather than the "banana" shape [Yu et al., 2008]). The high sensitivity of J$_{IMN}$ to T may also imply large inhomogeneities in nucleation rates due to temperature fluctuation in different air masses. Airborne measurements of nucleation-mode aerosol concentrations over boreal forests reveal significant variability in nucleated particle concentrations attributable to variability in land coverage between forests and lakes [O’Dowd et al., 2008], and temperature difference could be one of the factors contributing to the variability.

3.3 Relative Humidity (RH)

The effects of RH on J$_{IMN}$ under four atmospheric conditions are shown in Figure 3. With all other parameters fixed, J$_{IMN}$ increases with increasing RH until J$_{IMN}$ reaches a level that is limited by ionization rates. The effect of RH on J$_{IMN}$ can be very significant under some conditions. For example, J$_{IMN}$ increases by about three orders of magnitude when RH increases (1) from 60% to 90% under one shown condition (T=290 K, [H$_2$SO$_4$]=2x10$^7$ cm$^{-3}$, Q=10 ion-pairs cm$^{-3}$s$^{-1}$, and S=100 $\mu$m$^2$ cm$^{-3}$) and (2) from 20% to 30% under another condition (T=285 K, [H$_2$SO$_4$]=5x10$^7$ cm$^{-3}$, Q=10 ion-pairs cm$^{-3}$s$^{-1}$, and S=100 $\mu$m$^2$ cm$^{-3}$).

In the real atmosphere, RH has clear diurnal variations which are associated with T changes. The increase of temperature generally leads to the decrease of RH which in turn enhances the
effect of T on nucleation rates. *Yu and Turco* [2008] showed in the well-constrained case studies that the increase in T and decrease in RH are the main reasons for the shut-off of nucleation events around noontime observed in boreal forests.

Most climate models predict little change in global RH as a result of projected global warming associated with greenhouse effect. Nevertheless, some observations and modeling analysis indicate that RH may decrease as T increases, especially in the middle and upper troposphere [*Minschwaner and Dessler*, 2004]. For each degree of surface warming, absolute RH could decrease 3%–5% in the upper troposphere and 3–10% in the middle troposphere [*Minschwaner and Dessler*, 2004]. The possible decrease in RH associated with global warming could further inhibit the nucleation and thus enhance the positive climate/nucleation feedback mechanism proposed above in section 3.2.

It should be noted that RH variations may lead to changes in the surface area of pre-existing particles which is also one of the parameters controlling nucleation rates. Due to the uptake of water by aerosols, an increase in RH will generally increase the size and hence surface area of pre-existing particles, reducing nucleation rates (see Section 3.5 for details). The effect of RH on particle size depends on the composition of particles. To properly assess the combined effects of RH changes on nucleation, a size- and composition- resolved aerosol microphysics model is needed.

### 3.4 Ionization rate (Q)

The dependence of \( J_{IMN} \) on ion production rate is presented in Figure 4 for a number of atmospheric conditions. \( J_{IMN} \) is sensitive (almost proportional) to Q when \([H_2SO_4]\) is large and Q is relatively low. \( J_{IMN} \) generally increases with Q when \([H_2SO_4]\) is above around \(10^7\)cm\(^{-3}\). However, \( J_{IMN} \) decreases with increasing Q when Q is relatively big and \([H_2SO_4]\) is low.
The non-linear dependence of $J_{IMN}$ on $Q$ is a result of the competition between the time needed to grow ion clusters to a stable size ($t_g$) and the neutralization time ($t_n$) of charged clusters. The neutralization by ion-ion recombination will cause the growing charged clusters to lose their growth advantage and the resulting neutral clusters may dissociate if smaller than the critical size [Yu, 2006]. $t_g$ is inversely proportional to $[H_2SO_4]$ while $t_n$ is inversely proportional to the concentration of small opposite ions ([ion]), which is directly related to $Q$.

The steady-state $J_{IMN}$ is limited by the local ionization rate except under the conditions that BHN becomes dominant. Ambient ions are continuously generated by galactic cosmic rays at the rate of $\sim$2 ion-pairs cm$^{-3}$s$^{-1}$ at Earth’s surface and up to $\sim$20-30 ion-pairs cm$^{-3}$s$^{-1}$ in the upper troposphere. Other localized sources (such as radioactive emanations, corona discharge, combustion, lightning, nuclear waste, etc.) can also generate ions. Owing to natural radioactivity from soils, the ionization rate in the continental surface layer can reach up to $\sim$10 ion-pairs cm$^{-3}$s$^{-1}$ [Reiter, 1992]. Some measurements indicate that ionization rates near the surface can exceed 100 ion-pairs cm$^{-3}$s$^{-1}$ due to the accumulation of radon gas in the nocturnal boundary layer [Dhanorkar and Kamra, 1994]. Vartiainen et al. [2007] detected exceptionally high ion production rates of up to 30 ion-pairs cm$^{-3}$s$^{-1}$ during some measurement periods. In urban zones, corona discharge may generate high concentrations of small ions as well. Small ion concentrations of up to $10^4$–$10^5$ cm$^{-3}$ have been observed near and downwind of high voltage Transmission lines [Carter and Johnson, 1988; Suda and Sunaga, 1990]. Under favorable conditions, these localized ion sources may lead to the formation of large concentrations of ultrafine particles. In-situ measurements indicate that $[H_2SO_4]$ can reach as high as $2\times10^8$ cm$^{-3}$ in Atlanta, Georgia [McMurry et al., 2005]. Higher ion production rates coupled with higher
[H$_2$SO$_4$] can lead to significant nucleation, even when the concentration of pre-existing particles is very high (see the top curve in Fig. 4).

The effect of ionization rate on aerosol production in the troposphere may have important implications to the possible mechanisms amplifying the impact of solar variations on Earth’s climate [Yu, 2002]. During a solar cycle, the values of $Q$ vary by ~20-25% in the upper troposphere and ~5-10% in the lower troposphere at high latitudes, and by ~4-7% in the upper troposphere and ~3-5% in the lower troposphere at low latitudes [Ney, 1959]. Such variations in GCR-induced ionization rate associated with solar activities will cause substantial systematic changes in IMN rates which may have important climatic effects [Yu, 2002]. The physically-based IMN mechanism presented in this paper can be applied in global aerosol models to study how solar variations may influence the abundance of climatic effective aerosols. The IMN mechanism can also be applied to study how emission of radioactive species associated with civil and military nuclear activity may affect the atmospheric ionization (especially near the source regions) and thus the new particle formation rate.

3.5 Surface area of pre-existing particles (S)

Figure 5 shows the dependence of steady state IMN rates on the surface area of the pre-existing particles under four ambient conditions. When [H$_2$SO$_4$] is fixed, pre-existing particles affect the nucleation by scavenging small ions and pre-critical clusters. The magnitude of the effect depends on the time needed to grow the molecular clusters to critical clusters ($t_g$) and the lifetime of these clusters due to scavenging by pre-existing particles ($t_s$). Therefore, the effect of pre-existing particles on $J_{IMN}$ depends not only on concentration or surface area of pre-existing particles, but also on the sizes of critical clusters (controlled by [H$_2$SO$_4$], T, and RH) and growth rates of pre-critical clusters (determined mainly by [H$_2$SO$_4$] and to a lesser degree by T and RH).
Due to the scavenging, apparent $J_{\text{IMN}}$ (i.e., nucleation rate calculated at particle sizes larger than critical sizes, for example 3 nm) decreases with increasing sizes where the apparent nucleation rates are calculated. As mentioned earlier, we use the steady state apparent IMN rates across the clusters containing 10 sulfuric molecules (around 1.5 nm) for the conditions that give very small critical size (containing less than 10 sulfuric molecules).

It should be noted that the effects of pre-existing particle surface area on atmospheric particle formation rates should be stronger than those shown in Fig. 5 for two reasons: (1) pre-existing particles have a significant effect on $[\text{H}_2\text{SO}_4]$ to which the nucleation rate is very sensitive, (2) observed particles are generally larger than 3 nm, and the scavenging of clusters/particles smaller than 3 nm but larger than critical sizes will enhance the effect of S. One implication of the effect of S on nucleation is that the emission controlling strategy aimed to reduce particulate mass (and thus surface area) may lead to the increase in new particle formation and thus particle number concentration.

An additional point to note from Fig. 5 is that nucleation rate can still be very high even when $S > 500 \mu m^2 cm^{-3}$ in polluted areas as long as $[\text{H}_2\text{SO}_4]$ is high enough ($> \sim 10^8 cm^{-3}$). Measurements indicate that $[\text{H}_2\text{SO}_4]$ can reach above $10^8 cm^{-3}$ in polluted urban areas [McMurry et al., 2005]. This may explain why nucleation rates can still happen in some highly polluted regions.

4. IMN Look-up Table

In order to study aerosol nucleation in the context of 3-dimensional models, the nucleation calculations must be simplified to reduce computing costs. In the past, various versions of parameterizations have been derived for binary, ternary, and ion nucleation. The parameterization formulas become complex and very lengthy as the number of parameters
determining nucleation rates increases [Modgil et al., 2005]. Furthermore, it is hard to obtain accurate parameterization for all the possible ranges of input parameters. For example, the ion nucleation rates calculated with the parameterization of Modgil et al. [2005] can deviate by more than one order of magnitude from those calculated by the nucleation model under some parameter spaces.

Yu [2008] developed an alternative approach – look-up tables – to reduce the computing costs for 3-D nucleation rate calculations. With the pre-generated look-up table and a simple interpolation subroutine, nucleation rates under given conditions can be calculated accurately (compared to the results from full model simulation) and efficiently. One advantage of the look-up table is that it can cover any needed variable ranges and provide nucleation rates with good accuracy for all the parameter spaces. Another advantage is that it is capable of handling five or more input variables, which is difficult to obtain via parameterizations.

Here we describe the look-up table of steady state ion-mediated nucleation rates under a wide range of atmospheric conditions. The table is derived by running an updated version of the kinetic IMN model. The tabulated ion-mediated nucleation rates ($J_{IMN}$) depend on $[\text{H}_2\text{SO}_4]$, RH, $T$, $Q$, and $S$, and thus the look-up table is five-dimensional. The number of sulfuric acid molecules in the critical cluster ($n_a^*$), the acid mole fraction (AMOLF*, defined as the relative mole fraction of $\text{H}_2\text{SO}_4$ in the system of $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}$), and diameter ($d^*$) of the critical cluster are also included in the look-up table.

Table 1 shows the range of each dependent variable dimension, total number of points in each dimension, and values at each point for the look-up table. In the IMN look-up table, $T$ ranges from 190 K to 302 K with a resolution of 2 K and RH ranges from 0.5% to 99.5% with a resolution of 2%. $[\text{H}_2\text{SO}_4]$ ranges from $5 \times 10^5$ – $5 \times 10^8$ cm$^{-3}$ with a resolution of 10 values per
decade (geometric), Q ranges from 1.5 – 60 ion-pairs cm$^{-3}$s$^{-1}$ with a resolution of 5 values per
decade (geometric), and S ranges from 10 – 1000 μm$^{2}$cm$^{-3}$ with a resolution of 2.5 values per
decade (geometric) plus one point at S=1 μm$^{2}$cm$^{-3}$. These parameter ranges should cover almost
all the possible conditions in the troposphere relevant to atmospheric nucleation. The range and
resolution in each parameter space can be extended in the future if needed. The look-up table is
composed of J, $n_{a}^{*}$, AMOLF*, and d* values at 31x57x51x9x7 = 5,677,371 points, and has a
total size of ~50 MB in the text format. The look-up table, along with a FORTRAN code to read
and interpolate the tables, is given in the AGU auxiliary material or electronic data supplements¹.
For quick application, one can obtain $J_{IMN}$ using an online nucleation rate calculator
(http://www.albany.edu/~yfq/YuOnLineNucleation.html) developed by the author.

For any given values of [H$_2$SO$_4$], T, RH, Q, and S within the ranges specified in Table 1, $J_{IMN}$
and properties of critical clusters ($n_{a}^{*}$, AMOLF*, and d*) can be obtained using the look-up table
with an efficient multiple-variable interpolation scheme described in the Appendix. In Figures 1-5,
the values of $J_{IMN}$ interpolated from the look-up table ($J_{IMN}^{LT}$) are plotted along with those
calculated with the full model ($J_{IMN}^{FM}$) and we can see that $J_{IMN}^{LT}$ is very close to $J_{IMN}^{FM}$ under the
shown conditions. To explore the accuracy of the interpolated values under other conditions, we
randomly generated 30,000 combinations of [H$_2$SO$_4$], T, RH, Q, and S within the specified
ranges. It should be noted that many of those combinations are very unlikely to happen in the
atmosphere. $J_{IMN}$ is between $10^{-5}$ and $10^{4}$ cm$^{-3}$s$^{-1}$ in about 18,000 out of these 30,000 conditions.
A comparison of $J_{IMN}$, $n_{a}^{*}$, AMOLF*, and d* interpolated from the look-up table (LT) with those
calculated with full model (FM) are given in Figure 6. The average absolute deviations (AAD)
marked in each panel are defined as,

¹ Supporting materials are available via Web browser or via Anonymous FTP from ftp://ftp.agu.org/apend/
(Username = "anonymous", Password = “guest”).
AAD = \sum_{i=1}^{N} \left( \frac{X_{i}^{\text{LT}} - X_{i}^{\text{FM}}}{X_{i}^{\text{FM}}} \right) \frac{X_{i}^{\text{FM}}}{N}

where X = J_{IMN}, n_{a}^{*}, AMOLF*, and d* and N is the total numbers of cases with $J_{IMN}$ between $10^{-5}$ and $10^{4}$ cm$^{-3}$s$^{-1}$.

It is clear from Figure 6 that the differences between the interpolated values and those corresponding values calculated with full IMN model are generally within a few percentages (AAD $\leq ~ 4\%$). The cases with relatively large deviations are those cases falling into the parameter spaces where nucleation rates are sensitive to the changes in the parameters (i.e., the steepest part of curves shown in Figures 1-5). The deviations can be reduced if we increase the resolution of the look-up table. Considering the current uncertainty in the IMN model [Yu, 2006], we think that the results from the present look-up table are acceptable.

The application of the look-up table significantly reduces the computing time needed to calculate large numbers of IMN rates, such as required in 3-dimensional modeling. In a unix workstation we tested, it takes about 0.3 sec CPU time to calculate $J_{IMN}$, $n_{a}^{*}$, AMOLF*, and d* for 30,000 randomly selected cases using the look-up table while it takes about 2350 sec CPU time when we use the full IMN mode. Thus, the look-up table reduces the computing time by a factor of $\sim 8000$. The IMN look-up table has been successfully incorporated into a global chemical transport model [Yu et al., 2008; Yu and Luo, 2009] and the nucleation rate calculation has a very small effect on the overall global simulation computing time.

5. Summary

The primary mechanisms of particle nucleation – which control aerosol number concentrations to a significant degree – remain elusive, despite decades of intensive study. An ion-mediated nucleation (IMN) mechanism based on a kinetic model, which incorporates new
thermodynamic data and physical algorithms and explicitly treats the evaporation of neutral and
charged clusters, is supported by long-term measurements of cluster ion spectrum evolution
during nucleation events and the excess charge on freshly nucleated particles. With the kinetic
IMN model that explicitly resolves the size-dependent microphysical processes among precursor
gases and charged and neutral clusters/particles ranging from molecular sizes to several
micrometers, we systematically investigate the key parameters controlling IMN rate ($J_{IMN}$).

We show that sulfuric acid vapor concentration ([H$_2$SO$_4$]), temperature (T), relative humidity
(RH), ionization rate (Q), and surface area of pre-existing particles (S) have profound and non-
linear impacts on $J_{IMN}$. Generally, $J_{IMN}$ is larger when [H$_2$SO$_4$] and RH are higher, and T and S
are lower. $J_{IMN}$ generally increases with Q unless Q is large and [H$_2$SO$_4$] is relatively small. With
other parameters fixed, $J_{IMN}$ may be insensitive to some parameters under certain conditions
when $J_{IMN}$ is limited by other parameter(s). According to the IMN mechanism, T and [H$_2$SO$_4$]
are the two most important factors controlling the start and end of nucleation events, although
other parameters also contribute to the changes in nucleation rates. The implications of such
dependences are discussed. The critical impact of T and [H$_2$SO$_4$] on $J_{IMN}$ may explain the general
occurrence of nucleation in the morning hours and peak of nucleation frequency in the Spring
and Fall. More importantly, systematic changes in T and [H$_2$SO$_4$] associated with future climate
and emission changes may substantially affect nucleation rates and aerosol indirect radiative
forcing and thus may imply important climate feedback mechanisms. In addition, the dependence
of $J_{IMN}$ on ionization rates may provide a physical mechanism amplifying the effect of solar
variations on Earth’s climate.

An IMN look-up table derived using the most recent version of the IMN model is presented.
The look-up table is five-dimensional with the key parameters covering almost all the
tropospheric conditions relevant to atmospheric nucleation. With the look-up table and a multiple-variable interpolation subroutine, one can calculate the IMN rates and the properties of critical clusters under given conditions efficiently and accurately. The usage of the look-up table reduces the computational costs of the IMN rate calculations by a factor of ~8000 and requires negligible computing resources in multi-dimensional simulations.

Appendix. Multi-variable linear interpolation scheme

The tabulated ion-mediated nucleation rates (JIMN) depend on \([\text{H}_2\text{SO}_4]\), RH, T, Q, and S, and thus the look-up table is five-dimensional. The properties of critical clusters (n\(_a^*\), AMOLF\(^*\), and d\(^*\)) depend on \([\text{H}_2\text{SO}_4]\), RH, and T, and thus the corresponding look-up table is three-dimensional. For any set of \([\text{H}_2\text{SO}_4]\), RH, T, Q, and S, JIMN along with n\(_a^*\), AMOLF\(^*\), and d\(^*\) can be calculated efficiently based on a multiple-variable linear interpolation scheme described below. We use JIMN as example.

Let x=[H\(_2\)SO\(_4\)], y=RH, z=T, u=Q, v=S, and J=JIMN, then J = f(x, y, z, u, v). To find J\(_0\) value at the point (x\(_0\),y\(_0\),z\(_0\),u\(_0\),v\(_0\)), we first need to locate the closest set of grid points surrounding the point (x\(_0\),y\(_0\),z\(_0\),u\(_0\),v\(_0\)) in each look-up table dimension: x\(_1\)≤x\(_0\)<x\(_2\); y\(_1\)≤y\(_0\)<y\(_2\); z\(_1\)≤z\(_0\)<z\(_2\); u\(_1\)≤u\(_0\)<u\(_2\); v\(_1\)≤v\(_0\)<v\(_2\). The values of points of look-up table given in Table 1 are designed in a way that x\(_1\), x\(_2\), y\(_1\), y\(_2\), z\(_1\), z\(_2\), u\(_1\), u\(_2\), v\(_1\), and v\(_2\) can be determined quickly with a simple calculation (based on the analytical formula given in the last column of Table 1).

(1) Linear interpolation: J = f(x).

Let J\(_1\) = f(x\(_1\)), J\(_2\) = f(x\(_2\)), and dx=x\(_2\)-x\(_1\), dx\(_1\)=x\(_0\)-x\(_1\), dx\(_2\)=x\(_2\)-x\(_0\), then

\[
J_0 = f(x_0) = J_1 + (J_2 - J_1)dx_1/dx = (J_1 dx_2 + J_2 dx_1)/dx \quad (A1)
\]

(2) Bi-linear interpolation: J = f(x, y).

\[
J_0 = \left. f(x, y) \right|_{x_0, y_0} = \left. \frac{\partial^2 f}{\partial x \partial y} \right|_{x_0, y_0} dx dy + \left. \frac{\partial f}{\partial x} \right|_{x_0, y_0} dx + \left. f \right|_{x_0, y_0} \]

\[
= f(x_0, y_0) + \left. \frac{\partial f}{\partial x} \right|_{x_0, y_0} dx + \left. \frac{\partial^2 f}{\partial x^2} \right|_{x_0, y_0} dx^2 + \left. \frac{\partial^2 f}{\partial y^2} \right|_{x_0, y_0} dy^2 + \left. \frac{\partial^2 f}{\partial x \partial y} \right|_{x_0, y_0} dx dy
\]

\[
= \left. \frac{\partial f}{\partial x} \right|_{x_0, y_0} dx + \left. \frac{\partial^2 f}{\partial x^2} \right|_{x_0, y_0} dx^2 + \left. \frac{\partial^2 f}{\partial y^2} \right|_{x_0, y_0} dy^2 + \left. \frac{\partial^2 f}{\partial x \partial y} \right|_{x_0, y_0} dx dy
\]

\[
= f(x_0, y_0) + \left. \frac{\partial f}{\partial x} \right|_{x_0, y_0} dx + \left. \frac{\partial^2 f}{\partial x^2} \right|_{x_0, y_0} dx^2 + \left. \frac{\partial^2 f}{\partial y^2} \right|_{x_0, y_0} dy^2 + \left. \frac{\partial^2 f}{\partial x \partial y} \right|_{x_0, y_0} dx dy
\]

\[
= f(x_0, y_0) + \left. \frac{\partial f}{\partial x} \right|_{x_0, y_0} dx + \left. \frac{\partial^2 f}{\partial x^2} \right|_{x_0, y_0} dx^2 + \left. \frac{\partial^2 f}{\partial y^2} \right|_{x_0, y_0} dy^2 + \left. \frac{\partial^2 f}{\partial x \partial y} \right|_{x_0, y_0} dx dy
\]

\[
= f(x_0, y_0) + \left. \frac{\partial f}{\partial x} \right|_{x_0, y_0} dx + \left. \frac{\partial^2 f}{\partial x^2} \right|_{x_0, y_0} dx^2 + \left. \frac{\partial^2 f}{\partial y^2} \right|_{x_0, y_0} dy^2 + \left. \frac{\partial^2 f}{\partial x \partial y} \right|_{x_0, y_0} dx dy
\]

\[
= f(x_0, y_0) + \left. \frac{\partial f}{\partial x} \right|_{x_0, y_0} dx + \left. \frac{\partial^2 f}{\partial x^2} \right|_{x_0, y_0} dx^2 + \left. \frac{\partial^2 f}{\partial y^2} \right|_{x_0, y_0} dy^2 + \left. \frac{\partial^2 f}{\partial x \partial y} \right|_{x_0, y_0} dx dy
\]

\[
= f(x_0, y_0) + \left. \frac{\partial f}{\partial x} \right|_{x_0, y_0} dx + \left. \frac{\partial^2 f}{\partial x^2} \right|_{x_0, y_0} dx^2 + \left. \frac{\partial^2 f}{\partial y^2} \right|_{x_0, y_0} dy^2 + \left. \frac{\partial^2 f}{\partial x \partial y} \right|_{x_0, y_0} dx dy
\]

\[
= f(x_0, y_0) + \left. \frac{\partial f}{\partial x} \right|_{x_0, y_0} dx + \left. \frac{\partial^2 f}{\partial x^2} \right|_{x_0, y_0} dx^2 + \left. \frac{\partial^2 f}{\partial y^2} \right|_{x_0, y_0} dy^2 + \left. \frac{\partial^2 f}{\partial x \partial y} \right|_{x_0, y_0} dx dy
\]
For any given point \((x_0, y_0)\), there are \(2^2=4\) surrounding points. Let \(J_{11} = f(x_1, y_1), J_{12} = f(x_1, y_2)\), \(J_{21} = f(x_2, y_1), J_{22} = f(x_2, y_2)\), \(dy = y_2 - y_1, dy_1 = y_0 - y_1, dy_2 = y_2 - y_0\).

First, obtain \(J_{10}\) and \(J_{20}\) based on linear interpolation (Eq. A1),

\[
J_{10} = f(x_1, y_0) = \frac{(J_{11} dy_2 + J_{12} dy_1)}{dy}
\]

\[
J_{20} = f(x_2, y_0) = \frac{(J_{21} dy_2 + J_{22} dy_1)}{dy}
\]

Then use linear interpolation (Eq. A1) again to get

\[
J_{00} = f(x_0, y_0) = \frac{(J_{10} dx_2 + J_{20} dx_1)}{dx} = \frac{(J_{11} dx_2 dy_2 + J_{12} dx_2 dy_1 + J_{21} dx_1 dy_2 + J_{22} dx_1 dy_1)}{dxdy}
\]  

(A2)

(3) Tri-linear interpolation: \(J = f(x, y, z)\).

For any given point \((x_0, y_0, z_0)\), there are \(2^3=8\) surrounding points. Let \(J_{111} = f(x_1, y_1, z_1), J_{112} = f(x_1, y_1, z_2), \ldots, J_{222} = f(x_2, y_2, z_2)\), \(dz = z_2 - z_1, dz_1 = z_0 - z_1, dz_2 = z_2 - z_0\). We can get \(J_{000}=(x_0, y_0, z_0)\) by reducing the tri-linear interpolation to bi-linear interpolation.

First, get \(J_{110}, J_{120}, J_{210}, J_{220}\) based on Eq. (A1):

\[
J_{110} = f(x_1, y_1, z_0) = \frac{(J_{111} dz_2 + J_{112} dz_1)}{dz}
\]

\[
J_{120} = f(x_1, y_2, z_0) = \frac{(J_{121} dz_2 + J_{122} dz_1)}{dz}
\]

\[
J_{210} = f(x_2, y_1, z_0) = \frac{(J_{211} dz_2 + J_{212} dz_1)}{dz}
\]

\[
J_{220} = f(x_2, y_2, z_0) = \frac{(J_{221} dz_2 + J_{222} dz_1)}{dz}
\]

Then, obtain \(J_{000}=(x_0, y_0, z_0)\) with Eq. (A2),

\[
J_{000} = \frac{(J_{111} dx_2 dy_2 dz_2 + J_{112} dx_2 dy_2 dz_1 + \ldots + J_{221} dx_1 dy_1 dz_2 + J_{222} dx_1 dy_1 dz_1)}{dx dy dz}
\]  

(A3)

(4) Multi-variable linear interpolation

The above derivation of linear interpolation can be generalized to a system with \(N\) variables.

The strategy is to reduce the number of variables by 1 with Eq. A1, and then apply (\(N-1\))-linear interpolation formula to get the final interpolation expression.
For the 5-D look-up table $J = f(x, y, z, u, v)$, there are $2^5 = 32$ grid points surrounding any given point $(x_0, y_0, z_0, u_0, v_0)$. The formula for determining $J_{00000} = f(x_0, y_0, z_0, u_0, v_0)$ can be expressed as,

$$J_{00000} = (J_{11111} \frac{dx}{dx} \frac{dy}{dy} \frac{dz}{dz} \frac{du}{du} \frac{dv}{dv} + J_{11112} \frac{dx}{dx} \frac{dy}{dy} \frac{dz}{dz} \frac{du}{du} \frac{dv}{dv} + \ldots + J_{22221} \frac{dx}{dx} \frac{dy}{dy} \frac{dz}{dz} \frac{du}{du} \frac{dv}{dv} / (dx \cdot dy \cdot dz \cdot du \cdot dv)$$

(A4)

where $J_{11111} = f(x_1, y_1, z_1, u_1, v_1), J_{11112} = f(x_1, y_1, z_1, u_1, v_2), \ldots, J_{22221} = f(x_2, y_2, z_2, u_2, v_1), J_{22222} = f(x_2, y_2, z_2, u_2, v_2), \frac{du}{du} = u_2 - u_1, \frac{du}{du} = u_0 - u_1, \frac{dv}{dv} = v_2 - v_1, \frac{dv}{dv} = v_0 - v_1, \frac{dv}{dv} = v_2 - v_0$.

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**Figure Captions:**

**Figure 1.** Ion-mediated nucleation rate as a function of sulfuric acid vapor concentration ([H$_2$SO$_4$]) under four different ambient conditions, calculated with the full IMN model (solid lines) and IMN look-up table (dashed lines). In the legend, read T295Q10RH50S100 as T=295K, Q=10 ion-pairs cm$^{-3}$s$^{-1}$, RH=50%, and S=100 μm$^2$ cm$^{-3}$.

**Figure 2.** The dependence of predicted ion-mediated nucleation rate on T for four different ambient conditions, based on the full IMN model (solid lines) and IMN look-up table (dashed lines). In the legend, read A3E7Q10RH50S100 as [H$_2$SO$_4$]=3x10$^7$ cm$^{-3}$, Q=10 ion-pairs cm$^{-3}$s$^{-1}$, RH=50%, and S=100 μm$^2$ cm$^{-3}$.

**Figure 3.** The dependence of predicted IMN rate on RH under four selected conditions, based on the full IMN model (solid lines) and IMN look-up table (dashed lines). In the legend, read A1E7T275Q10S50 as [H$_2$SO$_4$] = 3x10$^7$ cm$^{-3}$, Q=10 ion-pairs cm$^{-3}$s$^{-1}$, T=275 K, and S=50 μm$^2$ cm$^{-3}$.

**Figure 4.** The dependence of predicted IMN rates on Q under four selected conditions, based on the full IMN model (solid lines) and IMN look-up table (dashed lines). In the legend, read A1E7T275RH50S50 as [H$_2$SO$_4$]=3x10$^7$ cm$^{-3}$, Q=10 ion-pairs cm$^{-3}$s$^{-1}$, T=275 K, RH=50%, and S=50 μm$^2$ cm$^{-3}$.

**Figure 5.** The dependence of predicted IMN rates on S under four selected conditions, based on the full IMN model (solid lines) and IMN look-up table (dashed lines). In the legend, read A1E7T275Q10RH50 as [H$_2$SO$_4$]=3x10$^7$ cm$^{-3}$, Q=10 ion-pairs cm$^{-3}$s$^{-1}$, T=275 K, and RH=50%.
Figure 6. Comparisons of $J_{\text{IMN}}$, $n_a^*$, AMOLF*, and $d^*$ interpolated from the IMN look-up table with those calculated with full IMN model. See text for the definition of the average absolute deviations (AAD) given in each panel.

Table 1. The range of each dependent variable dimension, the total number of points in each dimension, and the values at each point for the IMN look-up table.

<table>
<thead>
<tr>
<th></th>
<th>Range</th>
<th>Total # of points</th>
<th>Values at each point</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{H}_2\text{SO}_4]$ (cm$^{-3}$)</td>
<td>$5 \times 10^5 - 5 \times 10^8$</td>
<td>31</td>
<td>$<a href="i">\text{H}_2\text{SO}_4</a> = 5 \times 10^5 \times 10^{(i-1)/10}, i = 1, 31$</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>190 – 302</td>
<td>57</td>
<td>$T(j) = 190 + 2 \times (j -1), j =1, 57$</td>
</tr>
<tr>
<td>RH (%)</td>
<td>0.5 – 99.5</td>
<td>51</td>
<td>RH(1) = 0.5, RH($k$) = $2 \times (k-1), k = 2, 50$; RH(51) = 99.5</td>
</tr>
<tr>
<td>$Q$ (ion-pairs cm$^{-3}$s$^{-1}$)</td>
<td>1.5 – 60</td>
<td>9</td>
<td>$Q(l) = 1.5 \times 10^{(l-1)/5}, l = 1, 9$</td>
</tr>
<tr>
<td>$S$ (μm$^2$ cm$^{-3}$)</td>
<td>1 – 1000</td>
<td>7</td>
<td>$S(1) = l, S(m) = 10 \times 10^{(m-2)/2.5}, m = 2, 7$</td>
</tr>
</tbody>
</table>
Yu, JGR, Figure 1

Yu, JGR, Figure 2
Yu, JGR, Figure 3

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Yu, JGR, Figure 5

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