4.1 A COMPARATIVE STUDY OF HOMOGENEOUS NUCLEATION PARAMETERIZATIONS FOR 3-D ATMOSPHERIC MODELS

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1. INTRODUCTION

Homogeneous nucleation provides a significant source of new particles and affects number and mass concentrations and size distributions of fine particulate matters ($PM_{2.5}$) that have important chemical, radiative, health and visibility impacts. Occurrence of nucleation has been widely observed and well documented in a variety of environments such as marine and remote marine boundary layers (e.g., Raes et al., 1997; Clarke et al., 1998; Weber et al., 1998; McMurry et al., 2000; Pirjola et al., 2000), coastal areas (e.g., McGovern et al., 1996; McGovern, 1999; O'Dowd et al., 1999, 2002), mountains (e.g., Weber et al., 1995, 1997; Raes et al., 1997), boreal forests (e.g., Mäkelä et al., 1997, 2000; Kulmala et al., 1998a; 2001), free troposphere (Clarke et al., 1992; Raes et al., 1997; Weber et al., 1999), remote and moderately polluted continental atmospheres (e.g., Marti et al., 1997; Birmili and Wiedensohler, 1998; Birmili et al., 2000, 2003), stack plumes (e.g., Kerminen and Wexler, 1996; Brock et al., 2003), and urban atmosphere (e.g., Kerminen and Wexler, 1994; McMurry et al., 2000; Woo et al., 2001; Weber et al., 2003). New particle formation through homogeneous nucleation is typically simulated for the binary system of sulfuric acid (H_2SO_4) and water vapor (H_2O) in three-dimensional (3-D) atmospheric models with parameterizations that are based on a classical nucleation theory. Growing evidence from field studies has shown that observed nucleation rates often exceed those predicted by classic binary nucleation theory, particularly within the marine boundary layer (e.g., Cover et al., 1992; Weber et al., 1996, 1997, 1998, 1999; Clarke et al., 1998; Kulmala et al., 1998 a; O'Dowd et al., 1999; Birmili et al., 2000; McMurry et al., 2000). The participation of a third compound, such as ammonia (NH_3) (e.g., Coffman and Hegg, 1995; Weber et al., 1997, 1999, 2003; Kim et al., 1998; Korhonen et al., 1999; Kumala et al., 2000), an organic compound such as benzoic acid (e.g., Zhang et al., 2004a) and terpenes (Marti et al., 1997; Hoffmann et al., 1998), or methane sulfonic acid (MSA) (e.g., Van Dingenen and Raes, 1993) has been proposed. The H_2SO_4-NH_3-H_2O ternary nucleation formulations/modules have been developed based on either the classical theory (e.g., Korhonen *et al.*, 1999; and Napari *et al.* (2002a) or the generalized nucleation flux theory that solves the multidimensional Fokker-Planck equations for multi-component nucleation (e.g., Lazaridis, 2001). In addition to the ternary nucleation of H_2SO_4-NH_3-H_2O that is generally considered as a primary ternary nucleation pathway (Napari et al., 2002 b), ternary nucleation theory has also been developed for other systems such as H_2O-hydrochloric acid (HCl)-NH_3 and H_2O-H_2SO_4-MSA systems (e.g., Arstila et al., 1999; Van Dingenen and Raes, 1993).

Large uncertainty exists in the homogeneous nucleation parameterizations that are derived either empirically from laboratory experiments or the kinetic models that are based on classical binary and ternary nucleation theories. In this study, seven binary and one ternary nucleation parameterizations are first examined in a box model under a variety of atmospheric conditions with temperatures (T) of 240-300 K, relative humidities (RH) of 5-95%, number concentrations of sulfuric acid (N_{H2SO4}) of 10^4-10^{11} molecules cm^{-3} and mixing ratios of ammonia (C_{NH3}) of 0.1-100 ppt. Some of those parameterizations are then evaluated further in the U.S. Environmental Protection Agency (EPA) Models-3 Community Multiscale Air Quality (CMAQ) Modeling System.

2. NUCLEATION PARAMETERIZATIONS

The seven binary homogeneous nucleation parameterizations included in our test are those of McMurray and Friedlander (1979), Wexler et al. (1994), Pandis et al. (1994), Fitzgerald et al. (1998), Harrington and Kreidenweis (1998), Kulmala et al. (1998 b), and Vehkamäki et al. (2002). All these binary parameterizations have been used in 3-D air quality models such as the California/Carnegie-Mellon Institute of Technology Air Quality Model (CIT) (Griffin et al., 2002), the CMAQ (Binkowski and Roselle, 2003; Byun and Schere, 2005), the CMAQ with the Model of Aerosol Dynamics, Reaction, Ionization and Dissolution (CMAQ-MADRID) (Zhang et al., 2004b) and the Gas, Aerosol, Transport, radiation, General Circulation, Mesoscale, and Ocean Model (GATOR-GCMOM) and its predecessors (Jacobson, 1997, 2002, 2004). Use of different binary nucleation parameterizations in 3-D models introduces significant uncertainties in the predicted number production rates and number concentrations of $PM_{2.5}$, particularly in the nuclei mode (Roth et al., 2003). The binary parameterizations of Wexler et al. (1994), Pandis et al. (1994), Fitzgerald et al. (1998) and Harrington and

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Kreidenweis (1998) are based on the same set of calculations of nucleation rates performed by Jaecker-Voirol and Mirabel (1989), which calculates the absolute nucleation rates based on heteromolecular homogeneous nucleation theory of the H_2SO_4–H_2O system. Therefore, discrepancies in the nucleation rates from these parameterizations originate from the algorithms used to parameterize them. The parameterizations of Kulmala et al. (1998) and Vehkamäki et al. (2002) are derived based on the classical binary homogeneous nucleation model that simulates nucleation kinetics and accounts for hydration. McMurry and Friedlander (1979) use an approach that partitions gas-to-particle conversion between nucleation of new particles and condensation on existing particles, which is a more realistic approach than one based on the absolute prediction of a nucleation rate. The ternary nucleation parameterization of Napari ***et al.*** (2002 b) is derived based on a detailed numerical model of ternary nucleation with the largest deviation of no more than one order of magnitude. This parameterization is valid for atmospheric conditions with temperature of 240-300 K, RH of 0.05-0.95, H_2SO_4 number concentration of 10^4-10^9 molecules cm^{-3}, NH_3 mixing ratio of 0.1-100 ppt and nucleation rate of 10^{-5} – 10^6 cm^{-3} s^{-1} (Napari ***et al.***, 2002 c). If C_{NH3} exceeds 100 ppt, nucleation rate calculated with C_{NH3} of 100 ppt should be used.

3. BOX MODEL COMPARISONS

Figure 1 shows the calculated nucleation rates from these binary and ternary parameterizations as a function of RH at T = 298.15 K and as a function of T at RH = 80% under the hazy condition with a condensational rate of H_2SO_4 of 1.65 $\mu gm^{-3} h^{-1}$, C_{NH3} of 0.1, 1, 10, and 100 ppt, and a time step of 5 minutes (A condensational rate of H_2SO_4 of 1.65 $\mu gm^{-3} h^{-1}$ for a time period of 5 minutes is equivalent to an ambient N_{H2SO4} of 8.45 × 10^8 cm^{-3}). The maximum H_2SO_4 nucleation rate (labeled [H_2SO_4]) allowed from the H_2SO_4 production rate is also shown in the figure. Therefore, in an air quality model, nucleation rates will be capped at that maximum H_2SO_4 nucleation rate due to mass conservation constraints. The nucleation rate that corresponds to 1% of the maximum nucleation rate is also shown (labeled 1% [H_2SO_4]). If the calculated nucleation rate is less than 1% of that value, then, nucleation is a negligible pathway for H_2SO_4 gas-to-particle conversion because condensation on existing particles would dominate in a pristine environment. Therefore, the range between these two lines, [H_2SO_4] and 1% [H_2SO_4] represents the range of relevant nucleation rates.

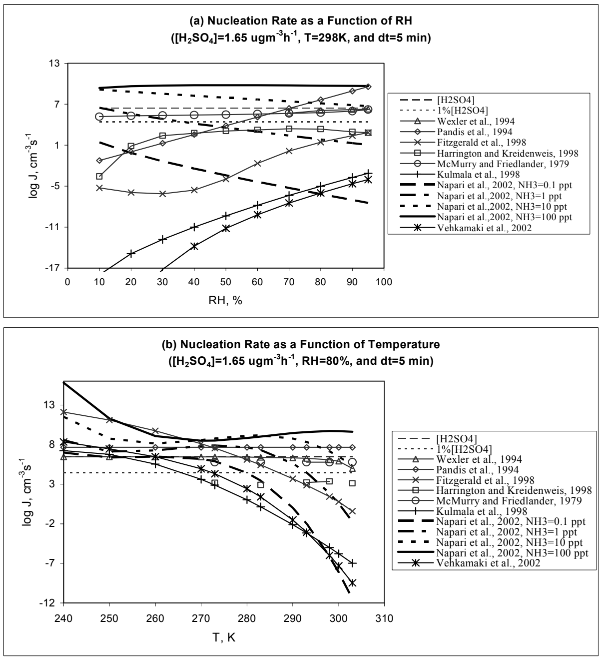

Figure 1. Nucleation rate as a function of (a) RH at T = 298.15 K and (b) temperature at RH=80%, both under the conditions of [H_2SO_4]=1.65 $\mu gm^{-3}h^{-1}$ and dt=5 minutes for all binary parameterizations and for mixing ratios of NH_3 of 0.1-100 ppt for the ternary parameterization. The results for Wexler et al. (1994), Pandis et al. (1994), Fitzgerald et al. (1998), Harrington and Kreidenweis (1998) were taken from Zhang et al. (1999).

At a constant temperature of 298.15 K, only three binary parameterizations, namely, Wexler et al. (1994), Pandis et al. (1994), and McMurray and Friedlander (1979), predict nucleation rates that exceed the 1% maximum rate level for RH > 70%. The nucleation rates predicted by Pandis et al. (1994) are significantly higher than those of Wexler et al. (1994) and McMurray and Friedlander (1979) for RH > 70%. The parameterizations of McMurray and Friedlander (1979), Wexler et al. (1994), and Harrington and Kreidenweis (1998) show a relatively weak dependence on RH. While other binary parameterizations show a strong dependence on RH with a positive correlation between the nucleation rate and RH (namely, nucleation rates increase by 9-21 orders of magnitudes when RH changes from 10% to 95%), the ternary parameterization shows an opposite correlation between the nucleation rate and RH for NH_3 levels $\leq$ 10 ppt (nucleation rates decrease by 9, 5, and 3 orders of magnitudes for NH_3 levels of 0.1, 1, and 10 ppt respectively, when RH changes from 10% to 95%) but little dependence on RH at higher NH_3 levels. Compared with the ternary nucleation parameterization, binary nucleation parameterizations tend to underestimate nucleation rates at high NH_3 levels (> 10 ppt) for all RHs (except for that of Pandis et al. (1994), which gives rates comparable to those of ternary nucleation parameterization for RH $\geq$ 80%) and overestimate nucleation rates for medium-to-high RHs (> 50%) for NH_3 levels < 1 ppt under this test condition (as a result of an opposite RH-dependence used in those binary parameterizations).

At a constant RH of 80%, all parameterizations, except that of Harrington and Kreidenweis (1998), predict nucleation rates that exceed the 1% maximum rate level for some temperatures; they also differ significantly for the range of temperatures over which nucleation rates are non-negligible. The parameterization of Pandis et al. (1994) does not include temperature dependence, it predicts a maximum nucleation rate for the whole T range among all binary nucleation parameterizations.

The parameterizations of McMurray and Friedlander (1979), Wexler et al. (1994) and Harrington and Kreidenweis (1998) show little or a weak T-dependence, whereas those of Fitzgerald et al. (1998), Kulmala et al. (1998), and Vehkamäki et al. (2002) show a strong T-dependence with a negative correlation between nucleation rate and T (i.e., nucleation rates decrease by 12-18 orders of magnitudes when T changes from 240.15 K to 303.15 K). The ternary nucleation parameterization shows a very strong T-dependence at low NH_3 levels (nucleation rates decrease by 18.5, 10.3, and 6.2 orders of magnitudes for NH_3 levels of 0.1, 1, and 10 ppt, respectively, when T changes from 273.15 K to 303.15 K). For an NH_3 level of 100 ppt, the ternary nucleation parameterization shows a strong T-dependence for T< 273.15 K (i.e., nucleation rates decrease by 7.3 orders of magnitudes when T changes from 240.15 K to 273.15 K) but a weak T-dependence with an opposite correlation (i.e., nucleation rates increase by 1.1 orders of magnitudes when T changes from 273.15 K to 303.15 K). Compared with the ternary nucleation parameterization, binary nucleation parameterizations tend to give lower nucleation rates at high NH_3 levels (> 10 ppt) for all temperatures (except for that of Fitzgerald et al. (1998), which gives rates larger than or comparable to the ternary nucleation rates for T ≤ 273.15 K, and Pandis et al. (1994), which gives rates higher than the ternary nucleation rates for T > 298.15 K). All binary nucleation parameterizations except those of Kulmala et al. (1998) and Vehkamäki et al. (2002) tend to give higher nucleation rates for T > 298.15 K at NH_3 levels ≤ 1 ppt under this test condition.

Figures 2 (a) and (b) show the calculated nucleation rate as a function of total H_2SO_4 concentration at RH = 50% and T = 258.15 K and T = 298.15 K, respectively, from those parameterizations. The ternary nucleation rates at two NH_3 levels are shown. At RH = 50% and T = 258.15 K, all parameterizations except Wexler et al. (1994) show a strong dependence on N_{H2SO4}. The parameterization of Wexler et al. (1994) gives zero rates for $N_{H2SO4} < 5 \times 10^7$ cm^{-3} and a relatively weaker dependence on N_{H2SO4} for higher N_{H2SO4} values. For higher NH_3 levels (≥ 10 ppt), all binary parameterizations give rates that are lower than those from the ternary nucleation parameterization for $N_{H2SO4} < 9 \times 10^7$ cm^{-3}. For $N_{H2SO4} > 9 \times 10^7$-$3 \times 10^8$ cm^{-3}, Wexler et al. (1994) and Fitzgerald et al. (1998) give rates that are higher than the ternary nucleation rates. For NH_3 = 0.1 ppt, the parameterization of McMurray and Friedlander (1979) gives rates within 1-2 orders of magnitude of the ternary nucleation rates for $N_{H2SO4} > 3 \times 10^5$ cm^{-3}. The parameterizations of Fitzgerald et al. (1998) and Wexler et al. (1994) give rates within 1-2 orders of magnitude of the ternary nucleation rates for certain ranges of N_{H2SO4} (i.e., 7×10^7 - 3×10^8 cm^{-3} and 5×10^7 - 2×10^8 cm^{-3}, respectively). The parameterizations of Pandis et al. (1994) and Kulmala et al. (1998) show the largest and the second largest deviations from the ternary nucleation rates among all binary parameterizations tested. At RH = 50% and T = 298.15 K, the parameterization of Wexler et al. (1994) gives zero rates for the N_{H2SO4} range of 1×10^4 -1×10^9 cm^{-3}. All other binary parameterizations show a strong dependence on N_{H2SO4}. Note that the parameterizations of Kulmala et al. (1998) and Vehkamäki et al. (2002) give rates that are below 1×10^{-8} cm^3 s^{-1}, thus they are not shown in Figure (b). While the binary parameterizations of Fitzgerald et al. (1998) and McMurray and Friedlander (1979) show large deviations in either directions (lower or higher, respectively) from the ternary nucleation rates for NH_3 = 100 ppt, the parameterization of Pandis al. (1994) gives a very close agreement to the ternary nucleation rates for NH_3 = 1 ppt. For nucleation rates > 1×10^{-8} cm^3 s^{-1}, the nucleation rates predicted by Kulmala et al. (1998) are lower by 1-2 orders of magnitude compared with that of Vehkamäki et al. (2002) and by 1-9 and 3-6 orders of magnitude, respectively, as compared with those of McMurry and Friedlander (1979) and Fitzgerald et al. (1998). The differences between nucleation rates predicted from Kulmala et al. (1998) and Vehkamäki et al. (2002) can be attributed to the fact that the parameterization of Kulmala et al. (1998) was derived based on a classical nucleation model that contains mistakes in the kinetic treatment for hydrate formation and several approximations (Vehkamäki et al. 2002; Noppel et al., 2002).

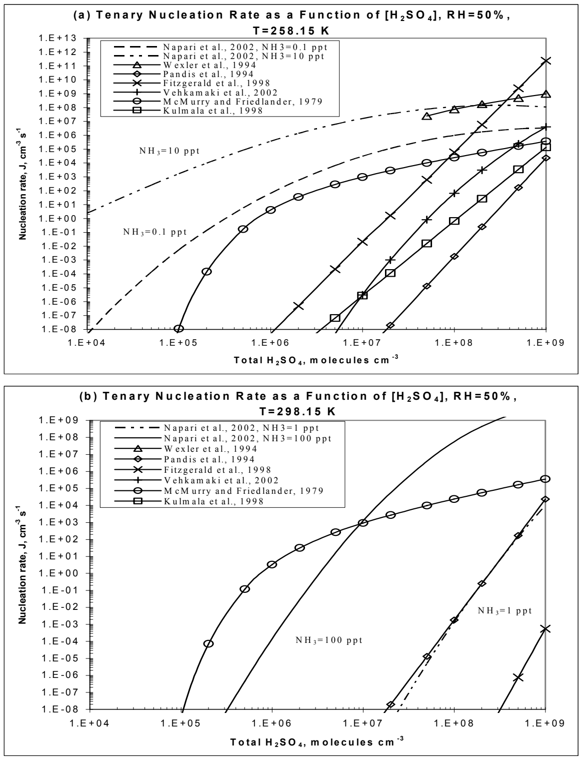

Figure 2. The calculated nucleation rate as a function of total H_2SO_4 concentration at RH = 50% and (a) T = 258.15 K and (b) T = 298.15 K from binary and ternary nucleation parameterizations.

Figures 3 (a) and (b) show the calculated nucleation rates as a function of RH at two conditions. At $N_{H2SO4} = 10^4$ cm^{-3} and T = 258.15 K, all parameterizations except Fitzgerald et al. (1998) for RH ≤ 10% give rates that are lower than 10^{-8} cm^{-3} s^{-1}, which are significantly lower than the ternary nucleation rates. At $N_{H2SO4} = 10^7$ cm^{-3} and T = 298.15 K, the parameterization of McMurry and

Friedlander (1979) gives binary nucleation rates of $2.6 \times 10^2 - 9.7 \times 10^3$ cm^{-3} s^{-1}, which lie between the ternary nucleation rates predicted with C_{NH3} of 10-100 ppt for RH < 51% and within 3 orders of magnitude higher than the ternary nucleation rates predicted with C_{NH3} =100 ppt for higher RH values. All other binary parameterizations except Fitzgerald et al. (1998) for RH ≤ 12% and Pandis et al. (1994) for RH > 70% give rates that are lower than 1×10^{-8} cm^{-3} s^{-1}. The ternary nucleation rates show much stronger RH-dependence at both temperatures for C_{NH3} =1-10 ppt than that for C_{NH3} =100 ppt.

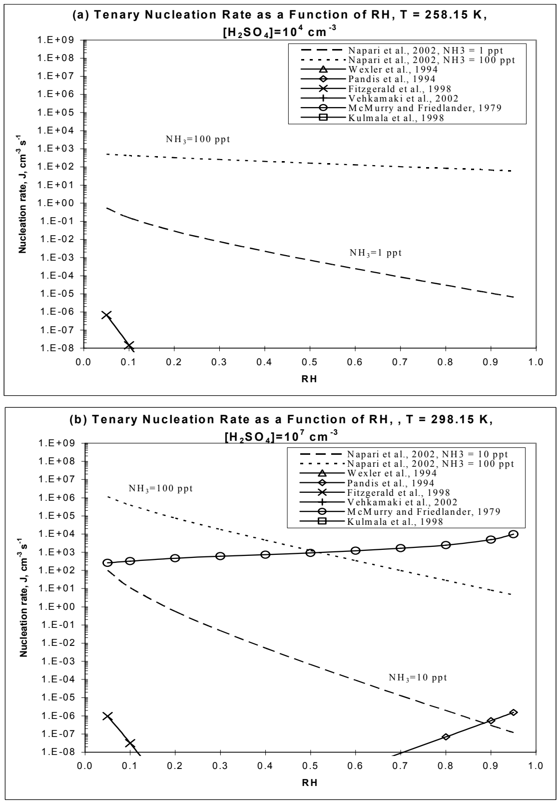

Figure 3. The calculated nucleation rates as a function of RH at (a) $N_{H2SO4} = 10^4$ cm^{-3} and T = 258.15 K, (b) $N_{H2SO4} = 10^7$ cm^{-3} and T = 298.15K.

Figures 4 (a) and (b) show the nucleation rates as a function of T at RH = 50% and total N_{H2SO4} of 10^4 and 10^7 cm^{-3}, respectively. At RH = 50% and N_{H2SO4} of 10^4 cm^{-3}, all binary parameterizations give negligible rates (< 1×10^{-8} cm^{-3} s^{-1}) that are significantly lower than the ternary nucleation rates. At RH = 50% and a total N_{H2SO4} of 10^7 cm^{-3}, while the parameterization of Pandis et al. (1994) gives negligible rates, the parameterizations of Kulmala et al. (1998), Vehkamäki et al. (2002), and Fitzgerald et al. (1998) give rates up to 0.6, 21.3, and 1.2×10^4 cm^{-3} s^{-1} for T < 265 K, 263 K, and 273 K, respectively and the parameterization of Wexler et al. (1994) gives a rate of 5.8×10^6 cm^{-3} s^{-1} at T = 240 K. The parameterization of McMurray and Friedlander (1979) gives a nearly constant rate of ~1×10^3 cm^{-3} s^{-1}, which is lower than the ternary nucleation rates for T < 285 K. All binary nucleation parameterizations (except that of Kulmala et al. (1998) at T = 240 K and that of McMurray and Friedlander (1979) at T > 285 K) give rates that are significantly lower than the ternary nucleation rates for all temperatures. The ternary nucleation rates and the binary nucleation rates predicted from Kulmala et al. (1998), Vehkamäki et al. (2002), and Fitzgerald et al. (1998) show a strong negative T-dependence under these test conditions.

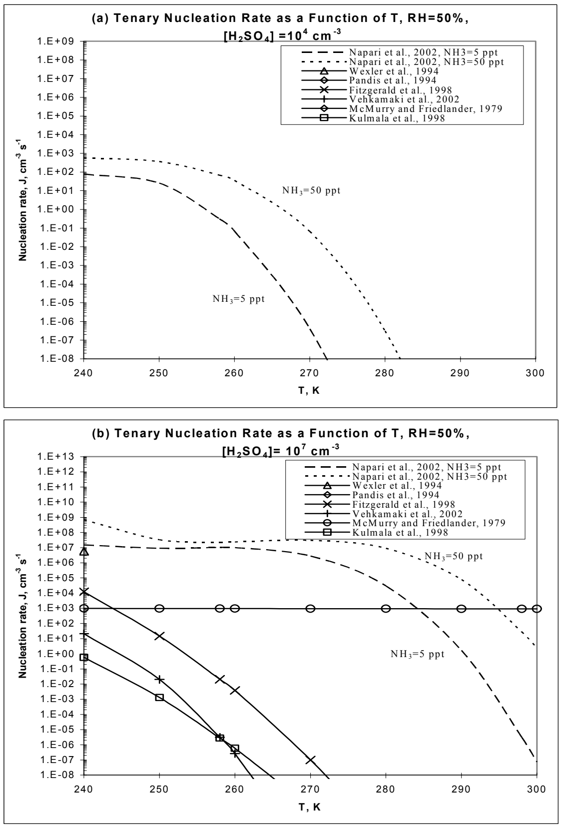

Figure 4. The nucleation rates as a function of temperature at RH = 50% and total H_2SO_4 concentrations of (a) 10^4, and (b) 10^7 cm^{-3}.

Figures 5 (a) and (b) show the nucleation rates as a function of C_{NH3} at two conditions. At RH=50%, T = 258.15 K, and a total N_{H2SO4} of 10^6 cm^{-3}, only the parameterization of McMurry and Friedlander (1979) gives non-negligible rates (4 cm^{-3} s^{-1}), which is lower by 2-6 orders of magnitude than the ternary nucleation rates. At RH = 50%, T = 298.15 K, and a total N_{H2SO4} of 10^9 cm^{-3}, three binary parameterizations, namely, Pandis et al. (1994), Fitzgerald et al. (1998), and McMurry and Friedlander (1979), give non-negligible rates but differ by up to 8 orders of magnitude. The binary nucleation rates predicted by McMurry and Friedlander (1979) and Pandis et al. (1994) are comparable to or higher than the ternary nucleation rates for C_{NH3} < 2 ppt. The ternary nucleation rates show a strong dependence on C_{NH3} under both conditions.

The comparison between binary and ternary nucleation parameterizations under the test conditions in this work has shown that the binary nucleation parameterizations tend to give lower rates at lower temperatures (< 273.15 K), lower RH values (≤ 70%) for lower N_{H2SO4} (generally < 10^7 cm^{-3}) and all ranges of NH_3 (0.1-100 ppt). At lower temperatures (< 273.15 K), the binary nucleation rates can be higher or comparable to the ternary nucleation rates given higher N_{H2SO4} (generally ≥ 10^7 cm^{-3}), or higher RH conditions. At higher temperatures (≥ 298.15 K), higher RH values (≥ 80%) for most ranges of N_{H2SO4} (10^5 – 10^9 cm^{-3}) and low ranges of C_{NH3} (0.1-10 ppt), some binary parameterizations such as Pandis et al. (1994) and McMurry and Friedlander (1979) can give rates that are higher than or comparable to the ternary nucleation rates.

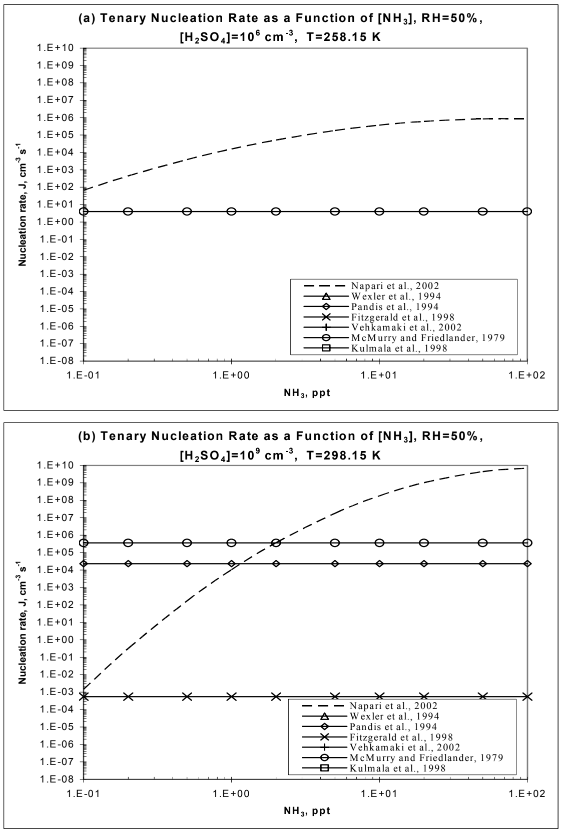

Figure 5. The nucleation rates as a function of NH_3 concentration at (a) RH=50%, T=258.15 K, and a total H_2SO_4 concentration of 10^6 cm^{-3}, (b) RH=50%, T=298.15 K, and a total H_2SO_4 concentration of 10^9 cm^{-3}.

4. THREE-DIMENSIONAL MODEL COMPARISONS

Several nucleation parameterizations are being tested in the U.S. Environmental Protection Agency (EPA) Models-3 Community Multiscale Air Quality (CMAQ) Modeling System (version 4.4, released in October 2004) for its application to the summer 1999 Southern Oxidants Study (SOS99) episode. The particle number concentrations and size distributions predicted with different nucleation formulations were compared with available observations in the southeastern U.S. Several special field studies were carried out in Atlanta, GA to study atmospheric particle formation, evolution, and health effects. These include the Aerosol Research Inhalation Epidemiological Study (ARIES) (Van Loy et al., 2000; Woo et al., 2000) during 1998-2000 and an intensive study of nucleation in August 2002 (Peter H. McMurry, University of Minnesota, personal communication, 2005). The total particle number in multiple size sections was measured during ARIES and then segregated into three size ranges (i.e., Stokes diameter < 10 nm, 10-100 nm, and 0.1-2 μm) at Jefferson Street (JST), Atlanta, GA (Woo, 2003). High concentrations (up to 2.7 × 10^5 number cm^{-3}) of freshly nucleated 3-10 nm particles have been frequently observed in summer in Atlanta, GA (McMurry et al., 2000; Woo et al., 2001). The enhancement of ultrafine particle concentrations often occurred near noontime and was associated with high solar radiation. It was suggested that these nanoparticles were formed through a photochemically-driven collision-controlled nucleation process involving H_2SO_4 (McMurry et al., 2000). In this study, the CMAQ predictions of particle number concentrations and size distributions are compared with observations from ARIES. The observed data are available for the accumulation-mode size range of 0.1-2 μm during the period of 1 June to 30 August, 1999 and for all three modes during the period of 5-28 June, 29 July to 6 August and 19-20 August, 1999 at JST, Atlanta, GA.

The modeling domain covers the contiguous U.S. and a small portion of southern Canada and northern Mexico, with a horizontal resolution of 32-km. The vertical resolution includes 19 layers from the surface to the tropopause, corresponding to sigma levels of 1.00, 0.998, 0.995, 0.990, 0.985, 0.980, 0.970, 0.960, 0.945, 0.930, 0.910, 0.890, 0.865, 0.840, 0.810, 0.740, 0.650, 0.500, 0.200, and 0.00. The meteorological fields were generated by the Tennessee Valley Authority (TVA) using the Pennsylvania State University (PSU) / National Center for Atmospheric Research (NCAR) Mesoscale Modeling System Generation 5 Version 3.4 (MM5) with four-dimensional data assimilation (FDDA). The EPA's National Emissions Trends (NET) 96 emission inventory was used to generate a gridded emission inventory for the contiguous U.S. This emission inventory was processed with the Sparse Matrix Operator Kernel Emissions system (SMOKE1.4) for the U.S. sources and for the Canadian non-point sources (i.e., area, mobile and biogenic sources). A separate processor from TVA was used to incorporate Canadian point sources and Mexican sources from a global inventory. The CMAQ default values were used for initial conditions (ICONs) and boundary conditions (BCONs). A spin-up period of two days (June 29-30) was used to minimize the influence of ICONs. More detailed information on meteorology, emissions, ICONs and BCONs can be found in Zhang et al. (2004 c and 2005 c).

Particles are simulated in CMAQ with three lognormally-distributed modes: Aitken, accumulation, and coarse modes (correspond to particles with diameters up to approximately 0.1 μm, between 0.1 and 2.5 μm, and between 2.5 and 10 μm, respectively, for mass distribution). The binary nucleation parameterization of Kulmala et al. (1998) is used in CMAQ version 4.4 to simulate new particle formation. A baseline simulation with this parameterization has been conducted by Zhang et al. (2005 a, b, c). Additional simulations with several binary nucleation parameterizations such as Harrington and Kreidenweis (1998) and Vehkamäki et al. (2002) and the ternary nucleation parameterization of Napari et al. (2002 c) are being conducted.

The number concentrations predicted by the nucleation parameterization of Kulmala et al. (1998) for Aitken-mode particles during 1-10 July at JST, Atlanta range from 188 to 1590 cm^{-3}, which are significantly lower than the measured values at JST during the summer 1999 (i.e., 1.3×10^{3} - 1.0×10^{5} cm^{-3}). Those for accumulation-mode particles at JST, Atlanta range from 702 to 6440 number cm^{-3}, which are higher than the measured values (i.e., 370 - 4764 cm^{-3}). The overprediction in accumulation-mode particle number concentrations can be attributed to an overestimation of the PM number emission rates (by a factor of 3-5.3) and several model assumptions/uncertainties in PM treatments in CMAQ (Zhang et al., 2005 c). The underprediction in Aitken-mode particle number concentrations is due to the incorrect nucleation parameterization of Kulmala et al. (1998) used in CMAQ v4.4. This parameterization was derived based on the classic binary nucleation theory but its derivation contained mistakes in the kinetic treatment for hydrate formation, resulting in binary nucleation rates 1-3 orders of magnitude lower than those observed and predicted by most other binary nucleation parameterizations (Noppel et al., 2002; Figure 2 in this work). A recent comparison of Elleman et al. (2004) has also shown that the number concentrations for Aitken-mode particles predicted by CMAQ were underpredicted by a factor of 10-100, as compared with observations obtained for the Pacific Northwest U.S.

Figure 6 shows the number concentrations of Aitken-mode particles at JST, Atlanta and Great Smoky Mountains (GRSM), TN predicted with three binary nucleation parameterizations: Kulmala et al. (1998), Harrington and Kreidenweis (1998), and Vehkamäki et al. (2002). At JST, the number concentrations predicted by the nucleation parameterization of Vehkamäki et al. (2002) range from 190 to 1682 cm^{-3}, which are similar to those predicted by Kulmala et al. (1998). Those predicted by Harrington and Kreidenweis (1998) range from 426 to 3688 cm^{-3}, which are closer to the observed values. Compared with the predictions by Kulmala et al. (1998), those predicted by Harrington and Kreidenweis (1998) and Vehkamäki et al. (2002) are higher by up to a factor of14.4 and 25.7%, respectively, at JST. At GRSM, the number concentrations of Aitken-mode particles predicted by the nucleation parameterizations of Kulmala et al. (1998), Harrington and Kreidenweis (1998), and Vehkamäki et al. (2002) during 1-10 July at JST, Atlanta range from 113 to 1372, 421 to 2510, and 114-1937 cm^{-3}, respectively. Compared with the predictions by Kulmala et al. (1998), those predicted by Harrington and Kreidenweis (1998) and Vehkamäki et al. (2002) are higher by up to a factor of 8.6 and 65.7%, respectively, at GRSM.

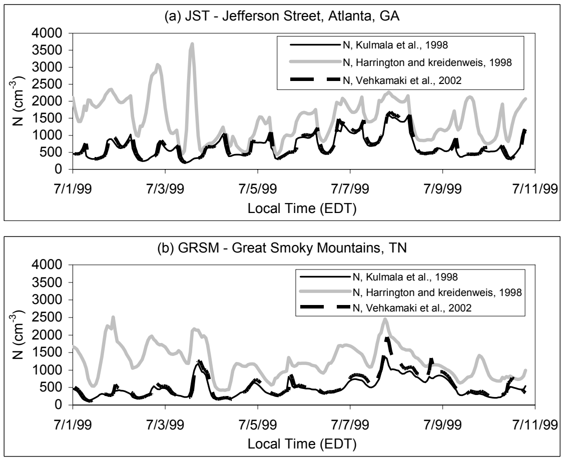

Figure 6. the number concentrations of Aitken-mode particles at JST, Atlanta, GA and GRSM, TN predicted with three binary nucleation parameterizations: Kulmala et al. (1998), Harrington and Kreidenweis (1998), and Vehkamäki et al. (2002).

The differences in the predicted number concentrations shown in Figure 6 can be qualitatively explained by differences in the meteorological and chemical conditions at the two locations. Figure 7 shows the predicted T, RH, SO_2 mixing ratios, and sulfate concentrations at JST and GRSM from the baseline simulation. The predicted temperatures and RHs at JST and GRSM range from 294.3 to 307.6 K and 30.2 to 94.3%, respectively. In this T and RH range, the nucleation of Harrington and Kreidenweis (1998) gives rates that are significantly (e.g., by up to 12.6 orders of magnitude at $N_{H2SO4} = 8.45 \times 10^{8}$ cm^{-3}, see Figure 1) higher than those predicted by Kulmala et al. (1998) and Vehkamäki et al. (2002), resulting in a much higher number concentrations for Aitken-mode particles at both locations. In this T and RH range, the difference in the nucleation rates between the parameterizations of Kulmala et al. (1998) and Vehkamäki et al. (2002) is relatively small (e.g., by a factor of 1.3 to 318 and 8 to 2.3×10^{4} at $N_{H2SO4} = 8.45 \times 10^{8}$ cm^{-3}, respectively, see Figure 1). The number concentrations for Aitken-mode particles predicted by the two parameterizatrions are quite similar except the time period between evening July 7 and evening July 8, during which the number concentrations predicted by Vehkamäki et al. (2002) are much larger than those predicted by Kulmala et al. (1998). This significant increase in the particle number concentrations predicted by Vehkamäki et al. (2002) is due mainly to its stronger N_{H2SO4}-dependence at higher N_{H2SO4} levels, as indicated by the elevated amounts of SO_2 and H_2SO_4 during this time period (see Figures 7 (c) and (d)). In the parameterization of Vehkamäki et al. (2002), the nucleation rate is given by an exponential of a third order polynomial of Ln (N_{H2SO4}), whereas that in Kulmala et al. (1998) is given by an exponential of first order polynomial of Ln (N_{H2SO4}).

4. SUMMARY

Significant differences are found among the binary nucleation rates calculated with different parameterizations (e.g., by 7 orders of magnitude under a temperature of 258 K, a relative humidity of 50%, and an ambient sulfuric acid concentration of 10^9 molecules cm^{-3}) and between the binary and ternary nucleation rates (e.g., by 3-4 orders of magnitude under a temperature of 258 K, a relative humidity of 50%, an ambient sulfuric acid concentration of 10^9 molecules cm^{-3}, and an ambient ammonia concentration of 10 ppt).

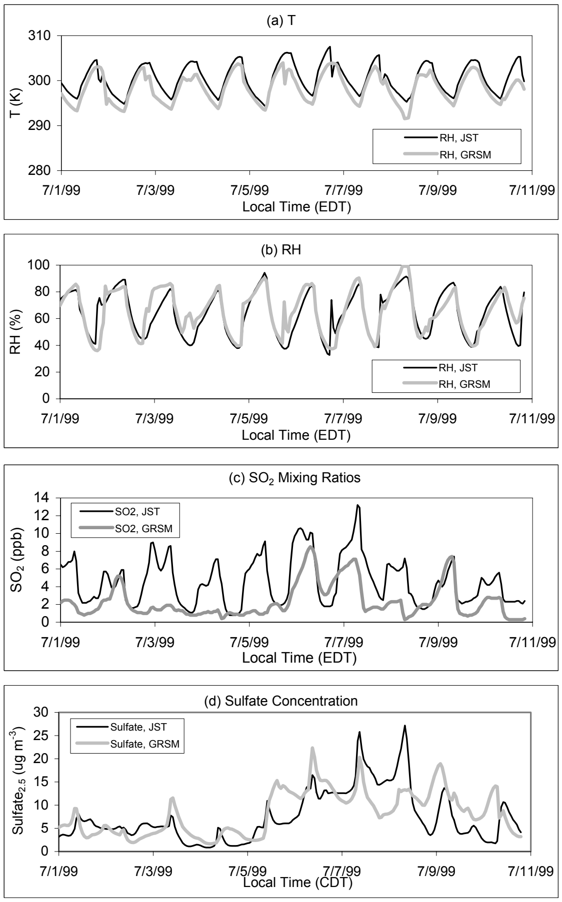

Figure 7. The predicted T, RH, SO_2 mixing ratios, and sulfate concentrations at JST and GRSM from the baseline simulation.

These binary and ternary nucleation parameterizations are being evaluated in 3-D CMAQ with available observations from ARIES. Our evaluation has shown that the parameterization of Kulmala et al. (1998) significantly underpredicts (by 1-3 orders of magnitude) the number concentrations for Aitken-mode particles, due to mistakes in its kinetic treatment for hydrate formation. Under similar T and RH conditions, Vehkamäki et al. (2002) gives higher number concentrations than does Kulmala et al. (1998) at higher NH_2SO_4 levels. The parameterization of Harrington and Kreidenweis (1998) gives much higher nucleation rates thus particle number concentrations for Aitken-mode particles than do those of Kulmala et al. (1998) and Vehkamäki et al. (2002). Additional parameterizations are being evaluated in CMAQ using available measurements to assess the appropriateness of these parameterizations in reproducing number concentrations and size distributions of $PM_{2.5}$, the associated uncertainties, and implications.

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