Particle number concentrations and size distributions in the stratosphere: Implications of nucleation mechanisms and particle microphysics

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Abstract. While formation and growth of particles in the troposphere have been extensively studied in the past two decades, very limited efforts have been devoted to understanding these in the stratosphere. Here we use both Cosmics Leaving OUtdoor Droplets (CLOUD) laboratory measurements taken under very low temperatures (205–223K) and Atmospheric Tomography Mission (ATom) in-situ observations of particle number size distributions (PNSD) down to 3 nm to constrain nucleation mechanisms and to evaluate model simulated particle size distributions in the lowermost stratosphere (LMS). We show that the binary homogenous nucleation (BHN) scheme used in most of the existing stratospheric aerosol injection (a proposed method of solar radiation modification) modeling studies overpredict the nucleation rates by 3–4 orders of magnitude (when compared to CLOUD data) and particle number concentrations in the background LMS by a factor ~2–4 (when compared to ATom data). Based on a recently developed kinetic nucleation model, which gives rates of both ion-mediated nucleation (IMN) and BHN at low temperatures in good agreement with CLOUD measurements, both BHN and IMN occur in the stratosphere. However, IMN rates are generally more than one order of magnitude higher than BHN rates and thus dominate nucleation in the background stratosphere. In the Southern Hemisphere (SH) LMS with minimum influence of anthropogenic emissions, our analysis shows that ATom measured PNSDs generally have four apparent modes. The model captures reasonably well the two modes (Aitken mode and the first accumulation mode) with the highest number concentrations and the size-dependent standard deviations. However, the model misses an apparent second accumulation mode peaking around 300–400 nm, which is in the size range important for aerosol direct radiative forcing. The bi-modal structure of accumulation mode particles has also been observed in the stratosphere well above tropopause and in the volcano-perturbed stratosphere. We suggest that this bi-modal structure may be caused by the effect of charges on coagulation and growth, which is not yet considered in any existing models and may be important in the stratosphere due to high ionization rates and long lifetime of aerosols. Considering the importance of accurate PNSDs for projecting realistic radiation forcing response to stratospheric aerosol injection (SAI), it is essential to understand and incorporate such potentially important processes in SAI model simulations.

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1. Introduction

Solar radiation modification (also known as solar geoengineering) approaches are being developed in response to the climate crisis (IPCC, 2021). They would temporarily offset climate change by reducing incoming sunlight, augmenting (currently inadequate) mitigation efforts and buying time to reduce atmospheric levels of CO_2, which is the root cause of the climate crisis. A recent report by the National Academies of Sciences, Engineering and Medicine (NASEM) emphasizes the urgent need to have a comprehensive understanding of the feasibility and potential risks/benefits of solar climate intervention approaches (NASEM, 2021). Stratospheric aerosol injection (SAI) has demonstrated the most promise as proximately engineerable (Shepherd et al., 2009; Lockley et al., 2020; IPCC, 2021) and has been extensively studied using models (e.g., GeoMIP: Kravitz et al., 2011; GLENS: Mills et al., 2017; Richter et al., 2022). The NASEM report (NASEM, 2021) pointed out that "the overall magnitude and spatial distribution of the forcing produced by SAI depends strongly on the aerosol size distribution" and "One of the research priorities for SAI is thus to address critical gaps in knowledge about the evolution of the aerosol particle size distribution". In the stratosphere, sulfate aerosols are formed by nucleation, followed by condensational growth and coagulation, and lost by evaporation in the upper stratosphere and downward sedimentation into the troposphere (Turco et al., 1982). New particle formation (NPF) (or nucleation) affects not only the number abundance but also the size distributions of stratospheric particles (e.g., Brock et al., 1995; Lee et al., 2003). There is increasing evidence (Weisenstein et al., 2022, Laakso et al., 2022) that a careful treatment of microphysical processes is necessary for projecting realistic radiative forcing response to SAI.

The process of NPF under tropospheric conditions has been extensively explored over the last two decades through laboratory and field measurements, theoretical studies, and numerical simulations (e.g., Yu and Turco, 2000; Vehkamäki et al., 2002; Kulmala et al., 2004; Kirkby et al., 2011; Dawson et al., 2012; Zhang et al., 2012; Kürten et al., 2016; Yu et al., 2018; Kerminen et al., 2018; Lee et al., 2019). Although some of the advances in our understanding of nucleation gained in the last two decades can be applied to stratospheric conditions, focused studies specifically examining the mechanisms of NPF under stratospheric conditions are quite limited. Indeed, the H_2SO_4–H_2O binary homogenous nucleation (BHN) parameterization developed two decades ago by Vehkamäki et al. (2002) (named BHN_V2002 thereafter) has been widely used in SAI modeling studies when nucleation process is explicitly considered (e.g., Tilmes et al., 2015; Jones et al., 2021; Weisenstein et al., 2022). Tilmes et al. (2015) described a Geoengineering Model Intercomparison Project (GeoMIP) experiment designed for climate and chemistry models, using the stratospheric aerosol distribution derived from the ECHAM5-HAM microphysical model (Stier et al., 2005) which calculated nucleation rates with the BHN_V2002 scheme. Both models (UKESM1 and CESM2-WACCM6) employed for a recent GeoMIP G6sulfur study (Jones et al., 2021) used the BHN_V2002 scheme. In another recent SAI study based on three interactive stratospheric aerosol microphysics models (Weisenstein et al., 2022), two models (MAECHAM5-HAM and SOCOL-AER) used BHN_V2002 scheme while the other (CESM2-WACCM) used an empirical nucleation scheme to calculate nucleation rate as a function of sulfuric acid concentration only (i.e, no dependence on temperature and relative humidity). To our knowledge, the performance of this widely used BHN_V2002 under stratospheric conditions has not been carefully examined, probably due to the lack of suitable in situ measurements of freshly nucleated particles in the stratosphere for constraining the scheme. In this regard, particle size distributions down to 3 nm measured in-situ during the NASA Atmospheric Tomography Mission (ATom) in

Deleted: used in most of SAI modeling studies when nucleation mechanism is considered (e.g., Weisenstein et al., 2022, Laakso et al., 2022) the lowermost stratosphere (LMS) of both SH and NH in four different seasons (Williamson et al., 2019, 2021; Kupc et al., 2020; Brock et al., 2021) provide much-needed data to constrain our understanding of the nucleation and particle microphysics in the stratosphere. In addition, well-controlled CLOUD experiments taken under low temperature (within the range of stratosphere) can also be used to assess the performance of nucleation schemes under stratospheric conditions. Another important issue related to stratospheric particles is the role of ionization in nucleation. It is well established that nucleation of H_2SO_4–H_2O on ions is favored over homogenous nucleation (Hamill et al., 1982; Yu and Turco, 2000; Lovejoy et al., 2004; Kirkby et al. 2011; Yu et al., 2018) but the role of ionization in NPF in the stratosphere has not been considered in any previous SAI studies (to our knowledge) in spite of the very high ionization rates in the stratosphere.

In this study, we use both CLOUD laboratory measurements taken under very low stratospheric temperatures and ATom PNSD measurements in LMS to constrain nucleation mechanisms and model simulated particle size distributions. For 3-D simulation of size-resolved stratospheric aerosols, we use the GEOS-Chem with the unified tropospheric-stratospheric chemistry-transport model with the size-resolved advanced particle microphysics (APM) package.

2. Model and data

2.1 GEOS-Chem/APM

The GEOS-Chem model is a global 3-D model of atmospheric composition (e.g., Bey et al., 2001) and is continuously being improved (e.g., Luo et al., 2020; Holmes et al., 2019; Keller et al., 2014; Murray et al., 2012; Pye and Seinfeld, 2010; van Donkelaar et al., 2008; Evans and Jacob, 2005; Martin et al., 2003). The GEOS-Chem tropospheric–stratospheric unified chemistry extension (UCX; Eastham et al., 2014), now the standard GEOS-Chem configuration, implements stratospheric chemistry, calculation of J-values for shorter wavelengths, and improved modeling of high-altitude aerosols. Extension of the chemistry mechanism to include reactions relevant to the stratosphere enables the capturing of stratospheric responses and troposphere–stratosphere coupling. UCX adds 28 species and 104 kinetic reactions, including 8 heterogeneous reactions, along with 34 photolytic decompositions. Atomic oxygen [both $O(^3P)$ and $O(^1D)$] is explicitly modeled; although also of short lifetime in the stratosphere, these species are important in correctly modeling stratospheric chemistry. Photochemistry is extended up to the stratopause to high-energy photons (177 nm) using the Fast-JX model, which includes cross-section data for many species relevant to the troposphere and stratosphere. Photolysis rates respond to changes in the stratospheric ozone layer. Additional heterogeneous reactions (Kirner et al., 2011, Rotman et al., 2001, Shi et al., 2001) are included to capture seasonal ozone depletion. H_2O is treated as a chemically-active advected tracer within the stratosphere. These permit chemical feedbacks between stratospheric ozone and aerosols and tropospheric photochemistry. The improved GEOS-Chem with coupled stratospheric–tropospheric responses has been evaluated with sonde and satellite measurements of O_3, HNO_3, H_2O, HCl, ClO, NO_2 and stratospheric intrusions (Eastham et al., 2014; Gronoff et al., 2021; Knowland et al., 2022). Yu and Luo (2009) incorporated a size-resolved (sectional) APM package into GEOS-Chem, henceforth referred to as GC-APM. The APM separates secondary particles from primary particles, uses 40 bins to represent secondary particles with high size resolution for the size range important for the growth of nucleated particles to accumulation mode sizes, and contains options to calculate nucleation rates based on different nucleation schemes. In GEOS-Chem/APM, nucleation is calculated before condensation using a time-splitting technique. Therefore, no competition between nucleation and condensation for sulfuric acid vapor is considered. In most conditions, nucleation consumes only a very small fraction (<1%) of sulfuric acid vapor in the air and the time splitting does not affect the results. When nucleation rate is high, reduced time step for nucleation and growth is used to ensure that the fraction of sulfuric acid vapor consumed by nucleation each time step is small. The GC-APM uses a semi-implicit scheme to calculate sulfuric acid condensation together with sulfuric acid gas phase production to ensure that the change of sulfuric acid vapor concentration is smooth. APM is fully coupled with GEOS-Chem in both the troposphere and stratosphere, and is employed for the present study.

In the present study we have carried out GEOS-Chem-UCX/APM global simulations from 01/2015 to 05/2018, with the first 17 months as spin-up and the remaining period covering ATom 1-4 periods (06/2016–05/2018). The horizontal resolution is $4^{o}\times5^{o}$ and there are 72 vertical layers. Emissions from different sources, regions, and species are computed via the Harvard-NASA Emissions Component (HEMCO) on a user-defined grid (Keller et al., 2014). Historical global anthropogenic emissions are based on the Community Emissions Data System (CEDS) inventory (Hoesly et al., 2018). Regional anthropogenic emissions over the United States, Canada, Europe, and East Asia are replaced by regional emission inventories of the National Emissions Inventory (NEI, https://www.epa.gov/air-emissions-inventories/2017-national-emissions-inventory-nei-data), the Air Pollutant Emission Inventory (APEI, https://www.canada.ca/en/environment-climate-change/services/pollutants/air-emissions-inventory-overview.html), the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP, https://www.emep.int/index.html), and the MIX Asian emission inventory (Li et al., 2017), respectively. Monthly mean aircraft emissions are generated based on the Aviation Emissions Inventory v2.0 (Stettler et al., 2011). The aircraft particle emissions include nucleation mode sulfate particles (Emission index = 2×10^{17} /kg-fuel, mean diameter = 9 nm, based on Kärcher et al., 2000), and black carbon and primary organic carbon (POC) particles. Global biomass burning is taken from Global Fire Emissions Database version 4 (van der Werf et al., 2017). The volcanic emissions of SO_2 are taken from AeroCom point-source data (Carn et al., 2015). Fixed global surface boundary conditions are applied for N_2O, CFCs, HCFCs, halons, OCS and long-lived organic chlorine species (Eastham et al., 2014).

2.2 Airborne ATom measurements of PNSD

Measurements are essential in advancing our understanding of stratospheric aerosol properties and the fundamental processes governing these properties. NASA's Atmospheric Tomography Mission (ATom; Wofsy et al., 2021; Thompson et al., 2022) is a multi-agency effort that provides global in situ aircraft observations of the vertical structure of aerosols from near surface to ~12 km altitude. PNSDs are measured using the NOAA Aerosol Microphysical Properties (AMP) package (Brock et al., 2019) comprising nucleation-mode aerosol size spectrometer(s) (NMASS) (Williamson et al. 2018), ultra-high-sensitivity aerosol spectrometer(s) (UHSAS) (Kupc et al. 2018), and a laser aerosol spectrometer (LAS) covering aerosol sizes from 3 nm to 4.5 µm. The aerosol number abundance can be obtained by integrating the PNSD measurements.

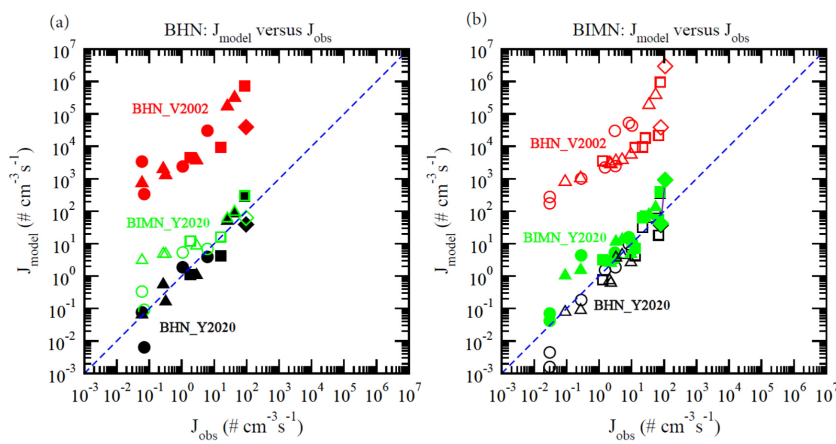
2.3 The CLOUD (Cosmics Leaving OUtdoor Droplets) measurements

Laboratory measurements of nucleation rates as a function of key controlled parameters have been carried out in a 26.1 m^3 stainless steel cylinder chamber at the European Organization for Nuclear Research (CERN), in the framework of the CLOUD experiment (Cosmics Leaving OUtdoor Droplets) (e.g., Kirkby et al., 2011; Kürten et al., 2016; Dunne et al., 2016). Some of these experiments were conducted at the temperature in the range of those in the stratosphere (Kirkby et al., 2011; Dunne et al., 2016) which are used in this study to evaluate nucleation schemes under stratospheric conditions.

3. Results

3.1 H_2SO_4–H_2O binary homogeneous nucleation (BHN) and binary ion-mediated nucleation (BIMN) under stratospheric conditions

Nucleation is one of the microphysical processes influencing particle size distributions in the stratosphere (Turco et al., 1982) The CLOUD measurements under a wide range of well-controlled conditions (Kirkby et al., 2011; Dunne et al., 2016) provide a unique set of data to evaluate the nucleation theories. Yu et al. (2020) compared nucleation rates calculated based on a number of commonly used aerosol nucleation parameterizations with the CLOUD measurements. Here we specifically examine the comparison under stratospheric conditions where temperature is below ~ 230 K. Since ammonia concentrations in the stratosphere are generally negligible, we focus on binary nucleation in the present study. The contribution of organics to particle formation, growth, and compositions in the upper troposphere and LMS has been investigated in several studies (Kupc et al., 2020; Murphy et al., 2021; Williamson et al., 2021). Because of the lack of information with regard to the low volatile gaseous organic species, the possible role of organics in new particle formation in LWS is not considered in the present study.



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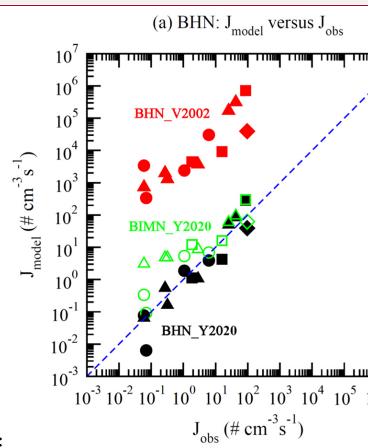

Figure 1. Comparison of nucleation rates based on three different schemes with CLOUD measurements within the low temperature range (T = 205–223 K) as that in the stratosphere for (a) binary homogeneous nucleation (no ionization) and (b) ion nucleation (at the presence of ionization rates 2.51 – 110 ion-pairs $cm^{-3}s^{-1}$). The different nucleation schemes shown are: BHN

of Vehkamäki et al. (2002) (BHN_V2002), BHN of Yu et al. (2020) (BHN_Y2020), and BIMN of Yu et al. (2020) (BIMN_Y2020). For comparison, under binary condition of (a), BIMN rates at Q = 20 ion-pairs $cm^{-3}s^{-1}$ are given while under binary ion nucleation condition of (b), BHN rates are also given. Values of H_2SO_4 vapor concentration ([H_2SO_4]) range from 10^6 to 3×10^7 cm^{-3} and are separated into four groups in the plots (Circles: $10^6 – 5\times10^6$ cm^{-3}; triangles: $5\times10^6 – 10^7$ cm^{-3}; Squares: $10^7 – 1.5\times10^7$ cm^{-3}; Diamonds: $1.5\times10^7 – 3\times10^7$ cm^{-3}).

Figure 1 compares nucleation rates based on the following three different schemes with CLOUD measurements under stratospheric temperature range (T = 205–223 K): BHN of Vehkamäki et al. (2002) (BHN_V2002), BHN of Yu et al. (2020) (BHN_Y2020), and BIMN of Yu et al. (2020) (BIMN_Y2020). BHN_V2002 and BHN_Y2020 differ in term of thermodynamic data and nucleation approach used (Yu et al., 2020). To show the relative importance of homogeneous versus ion nucleation, BIMN rates at Q = 20 ion-pairs $cm^{-3}s^{-1}$ were given under binary homogeneous condition in Fig. 1a and BHN rates were also given under binary ion nucleation condition in Fig. 1b. Nucleation rates based on BHN_V2002 are consistently 3–5 orders of magnitude higher than those observed under H_2SO_4–H_2O binary nucleation conditions without (Fig. 1a) and with (Fig. 1b) the effect of ionizations, while those based on BHN_Y2020 and BIMN_Y2020 are close to the observed values. It should be noted that similar to the CLOUD measurements with the effect of ionization, BHN rates are included in the BIMN rates (Yu et al., 2018) and the difference between BIMN and BHN rates indicates the contribution of ion mediated or induced nucleation. Under the conditions of Fig. 1a, assuming ionization rate of 20 ion-pairs $cm^{-3}s^{-1}$ (within the range of its typical value in the stratosphere) the BIMN rates are about one order of magnitude higher than BHN rates when the nucleation rates are below ~ 5 $cm^{-3}s^{-1}$ but close to BHN rates when nucleation rates are above ~ 5 $cm^{-3}s^{-1}$. Similar difference between BHN_Y2020 and BIMN_Y2020 can also be seen in Fig. 1b, indicating the importance of ion nucleation at relatively lower nucleation rates (mostly associated with relatively lower [H_2SO_4]) and dominance of homogeneous nucleation at higher nucleation rates (associated with larger [H_2SO_4]). As we show next, [H_2SO_4] in the background stratosphere is generally quite low and thus ion nucleation dominates but BHN can become important in the SO_2 plumes injected into the stratosphere.

3.2 Nucleation rates and particle number concentrations in the stratosphere

Figure 2 shows the zonal mean SO_2 emission (SO_2_emit), particle number emitted by aviation (PN_aviation), temperature (T), relative humidity (RH), ionization rate (Q), and [H_2SO_4] averaged during the two-year period (06/2016–05/2018) covering ATom 1-4. To focus on lower stratosphere (LS), only the values of these variables in the stratosphere (grid boxes with more than 50% time above tropopause) are shown. The SO_2 emissions include all sources including volcanos and aviation. During this period, there was one relatively strong volcanic event, the Bezymianny volcano (55.98˚N, 160.59˚E), on December 20, 2017 that injected 5×10^6 kg S into an altitude of ~ 14–18 km (Carn et al., 2015). Aviation emission is generally limited to below ~ 12.5 km altitude. Based on MERRA2 meteorology data, which is used to drive GEOS-Chem, almost all of grid boxes at 12 km are under the tropopause in the tropics (30°N-30°S), most of grid boxes at 12 km in the high latitude regions (60°N–90°N, 60°S–90°S) are above tropopause, and some fractions of grid boxes at 12 km in the middle latitude regions (30°N–60°N, 30°S–60°S) are above tropopause.

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As can be seen from Fig. 2b, some of aviation emissions in the middle and high latitude regions are in the LMS, and the amount emitted into NH LMS is much higher (by several orders of magnitude) than that in SH. The temperature in the LS ranges from 190–225K, with the lowest value in the region just above tropical tropopause (Fig. 2c). RH in LS has highest values near tropopause but drops quickly with increasing altitude, from ~30–50% near tropopause to ~0.1–1% at ~ 25 km in the tropical and middle latitudes (Fig. 2d). The spatial variations of T and RH have important effects on nucleation in LS. The cosmic ray induced ionization rate in LS has large latitudinal gradient, ranging from ~40–100 ion-pair std. $cm^{-3}s^{-1}$ (here "std. cm^{-3}" refers to per cubic centimeter at standard temperature and pressure, 273 K and 1013 hPa respectively) in the tropics to 100–400 ion-pair std. $cm^{-3}s^{-1}$ in middle and high latitude region (Fig. 2e). The high ionization rates may have important implication for particle microphysics in LS, which will also be discussed in Section 3.3. H_2SO_4 is the most important aerosol precursor in LS and its concentration depends on SO_2 concentrations and oxidation, condensation sink, and its vapor pressure that depends on T and RH. The annual mean [H_2SO_4] (Fig. 2f) has large spatial variations, ranging from a minimum of ~ 1–2 ×10^5 std. cm^{-3} at altitudes of ~ 12–15 km in polar regions to ~ 4–20 ×10^5 std. cm^{-3} close to the tropopause. From ~ 18–25 km (well above the ATom measurement altitude), [H_2SO_4] increases with altitude, mainly due to the increasing H_2SO_4 vapor pressure associated with vertical changes of T (Fig. 2c) and RH (Fig. 2d).

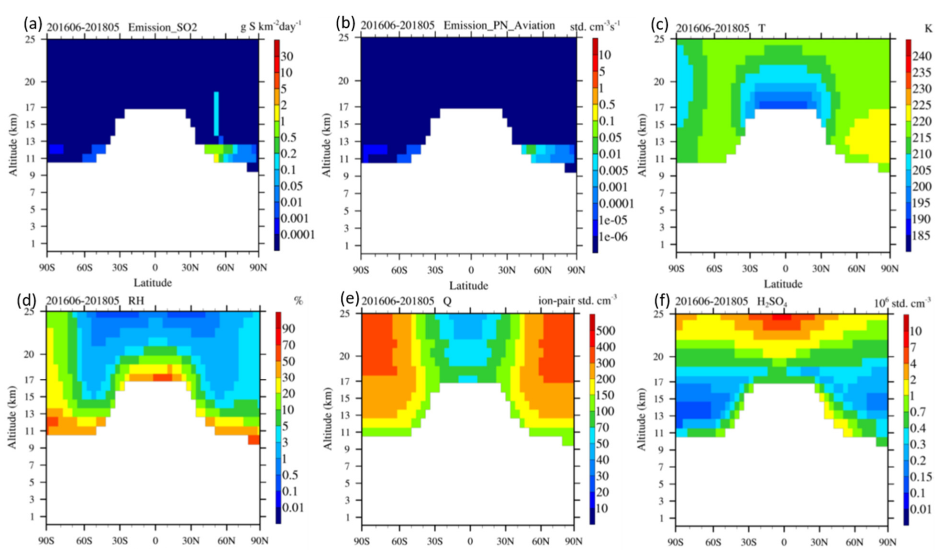
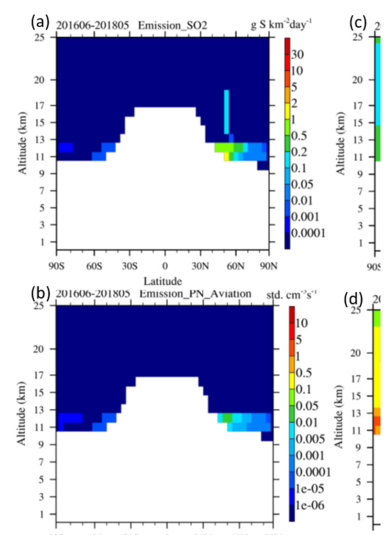


Figure 2. Zonal mean SO_2_emit, PN_Emit, T, RH, Q, and [H_2SO_4] averaged during the two-year period (06/2016-05/2018) covering ATom 1-4. To focus on the lower stratosphere, only the values of these variables in grid boxes with more than 50% time above tropopause and below 25 km are shown.



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To demonstrate the effect of nucleation schemes on simulated aerosol properties, we compare in Fig. 3 zonal mean and vertical profiles of nucleation rates (J) and number concentrations of condensation nuclei larger than 3 nm (CN3) simulated based on the three nucleation schemes: BHN_V2002, BHN_Y2020, and BIMN_Y2020. In all three schemes, the aviation emissions of both SO_2 (Fig. 2a) and particle numbers (Fig. 2b) are the same. The model simulations indicate that NPF occurs in the lower stratosphere but is mostly confined to LMS except in the area of volcano injection (for example, above ~ 14 km around ~ 52ºN). There exist large differences in the nucleation rates predicted by the three schemes (noting the logarithmic color scale), with BHN_V2002 rates generally 1–4 orders of magnitude higher while BIMN_Y2020 rates ~ one order of magnitude higher than those based on BHN-Y2020. The difference between BIMN_Y2020 and BHN_V2002 rates are smaller in the LMS over tropics (30°S-30°N) where temperature is the lowest (see Fig. 2c). The magnitudes of differences are consistent with comparisons with CLOUD measurements (Fig. 1). The difference in nucleation rates leads to substantial difference in CN3 in LMS, with those based on BHN_V2002 a factor 2–5 higher than those based on BHN_Y2020 in LMS. LMS CN3 based on BIMN_Y2020 is about 50% higher than that of BHN_Y2020. Compared to the difference in nucleation rates, the differences in CN3 is much smaller. This is expected because on one hand only a small fraction of nucleated particles survive the coagulation scavenging and grow beyond 3 nm, and on the other hand direct emission of particle numbers from aviation (Fig. 2b; treated as direct emission but most of these are actually nucleated on chemi-ions in the exhaust plume shortly after emission) (Brock et al., 2000) and transport provide substantial amount of CN3 even without nucleation. Nevertheless, nucleation is still significant enough to affect the CN3. It is interesting to note that CN3 based on BIMN_Y2020 is higher at altitudes > ~ 22 km (Fig. 3h), which is associated with higher nucleation rates based on BIMN_Y2020 than those based on BHN_V2002 and BHN_Y2020 within the altitude range of 35-55 km. Another interesting point is that there is a much smaller vertical gradient in BHN_V2002 nucleation rates in the tropical region (30S-30N) within ~ 17-20 km (see Figs. 3a and 3d), likely a result of different dependences of nucleation rates based on different schemes on T, RH, and [H_2SO_4] which have large vertical variations (see Fig. 2). It can be seen from Fig. 3 that the simulations based on three nucleation schemes all show large hemispheric difference in particle number concentrations (by a factor of ~3-6) in LMS at middle and high latitudes, consistent with the ATom measurements (Williamson et al., 2021). Our sensitivity study (by turning off aviation emission, not shown, to be reported in a separate study) indicates this large hemispheric difference is largely caused by aviation emissions, confirming the analysis of Williamson et al. (2021).

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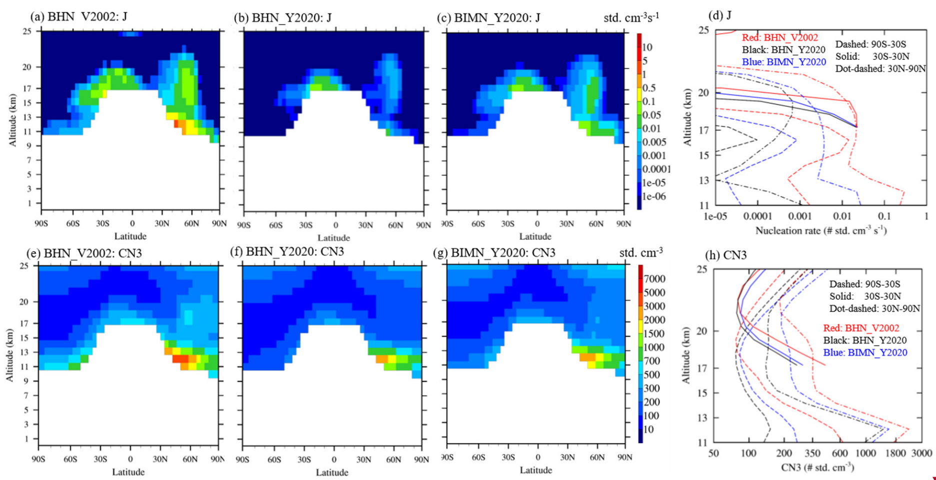

Figure 3. Model simulated zonal mean and vertical profiles of nucleation rates (J; upper panels) and number concentrations of particles larger than 3 nm (CN3; lower panels) in the stratosphere during the two-year period covering ATom 1-4 (06/2016- 05/2018), based on three nucleation schemes (a&e: BHN_V2002, b&f: BHN_Y2020, and c&g: BIMN_Y2020). The vertical profiles in (d) and (h) are averaged for three latitude zones (90S-30S, 30S-30N, and 30N-90N). The values for those grids with at least 50% of time above the tropopause are shown.

While it is difficult to observe nucleation rates in the stratosphere, the measurement of freshly nucleated nanoparticles can be used to constrain nucleation schemes. Figure 4a compares the model simulated CN3 (all particles with diameter larger than 3 nm, with the upper size limit of 12 µm corresponding to the size of last model bin) based on the three nucleation schemes at altitudes of around 12 km in SH middle and high altitudes during four seasons with the corresponding ATom 1–4 observations. As an example, Figures 4b–d show the model simulated horizontal distributions of CN3 at 12 km altitude during ATom 4 with the values and locations of ATom4 CN3 data overlaid. We choose SH for comparison, as it represents the background stratosphere with minimum influence of anthropogenic emissions (i.e., aviation) (Fig. 2b), to avoid the uncertainty associated with aviation emissions. In Figure 4, the model results are two-month average corresponding to the flight months of each ATom campaign while the measurement data points shown are those sampled within the altitudes range of 11.5–12.5 km, in the stratosphere (ozone>250 ppbv and RH<10%, following the same stratosphere definitions as in Murphy et al. (2021) and Williamson et al. (2021)), and averaged to a 4°x5° gridbox for comparison with modeled results. The impact of nucleation scheme on CN3 can be clearly seen: BHN_V2002 overpredicted CN3 by a factor of 2–4, BHN_Y2020 slightly underpredicted CN3, and BIMN_Y2020 slightly overpredicted CN3. The larger vertical spread in CN3 from BHN_V2002 is caused by the large CN3 latitude gradient associated with higher nucleation near tropopause

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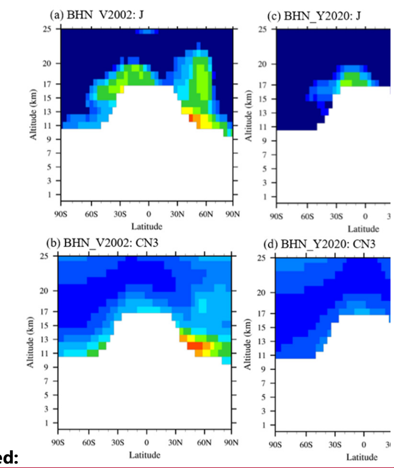

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(Fig. 3). The comparisons above show that the ATom measurements provide a good constraint on our understanding of the processes controlling CN3 in the LMS at mid-high latitudes.

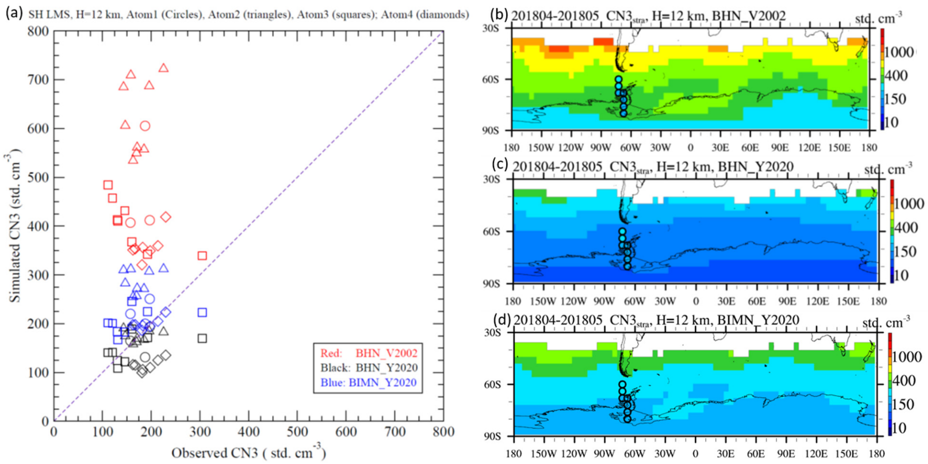

Figure 4. CN3 at altitudes of around 12 km in SH middle and high latitudes: (a) Model simulated versus observed during ATom 1-4 (Circles: ATom1; Triangles: ATom2; Sqaures: ATom3; Diamonds: ATom4); (b-d) model simulated horizontal distributions corresponding to ATom 4 based on three different nucleation schemes (BHN_V2002, BHN_Y2020, and BIMN_Y2020), with the values and locations of ATom 4 CN3 measurements shown in the circles.

3.3 PNSDs in the stratosphere

Figure 5 shows the model simulated evolution of PNSDs at an altitude of 12 km over a site in SH (70°S, 60°W) during the two-year ATom period based on the three different nucleation schemes. The PNSDs shown in Fig. 5 are averaged into four different seasons corresponding to the months of ATom 1-4 field campaigns and are presented in Fig. 6 for comparison with the observed mean PNSDs in SH LMS (Williamsons et al., 2021). It should be noted that modeled PNSDs in Fig. 6 are two-month average at one fixed site at an altitude of 12 km (in the region where many of SH LMS measurements were taken, see Fig. 4) while the observed ones are averaged over all SH LMS air mass sampled during the corresponding ATom campaign. While the comparison in Fig. 6 is not exactly coterminous, it allows us to make quantitative comparisons of modeled and observed PNSDs. To take into account the variations in both model and observed PNSDs, standard deviations are shown as error bars in the measured and modeled curves based on BIMN_Y2020.

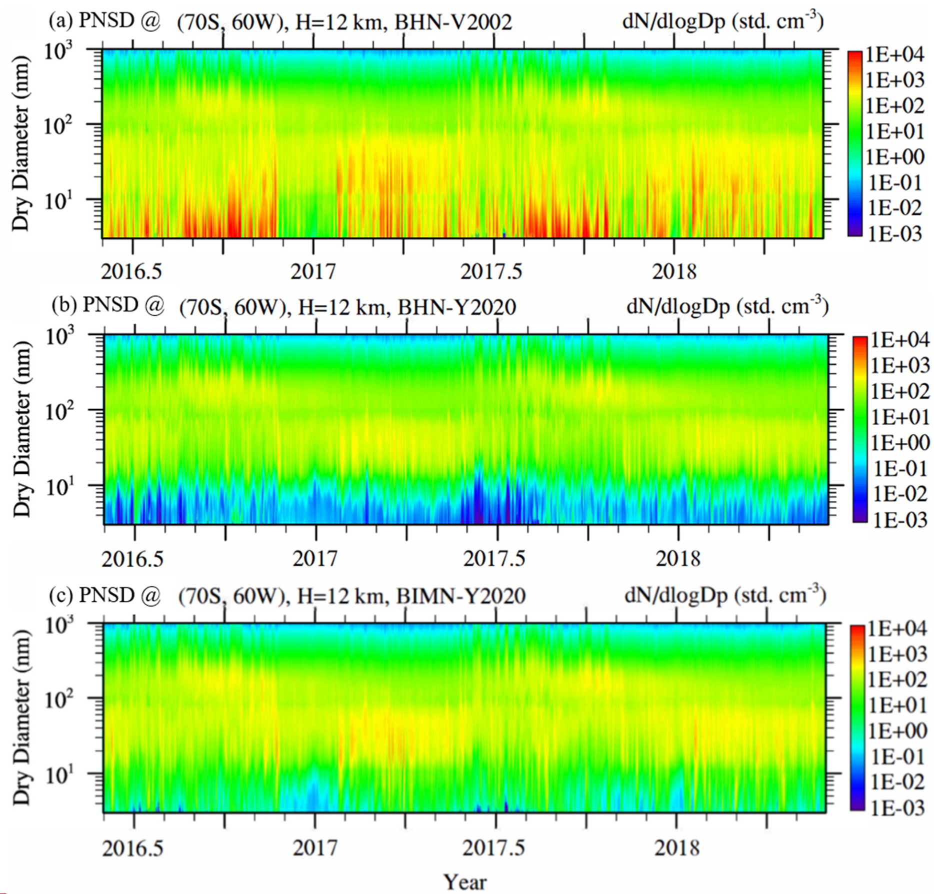

Figure 5. Model simulated evolution of PNSDs at a site in SH (70S, 60 W) at altitude of 12 km based on three nucleation schemes (BHN_2002, BHN_Y2020, and BIMN_Y2020).

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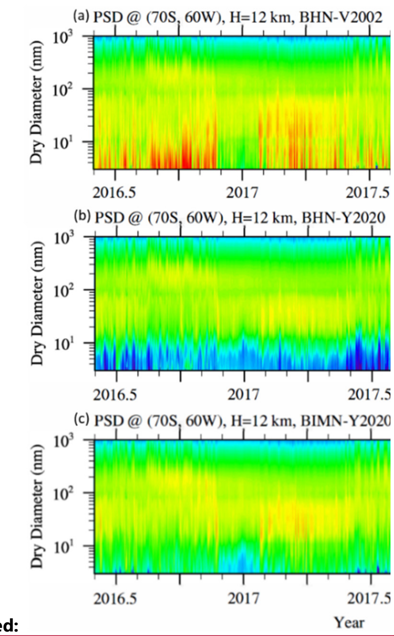

Figure 6 shows that PNSDs measured in the background LMS have multiple modes: a nucleation mode (NuclM: ≲ 10 nm), an Aitken mode (AitkenM: ~10 – 80 nm), and two accumulation modes (AccuM1: ~ 80 – 250 nm and AccuM2: ~ 250 – 700 nm). It should be noted that these modes are not the same size limits as those presented in the public ATom dataset. As shown in Figures 5 and 6, the model based on all three nucleation schemes generally captures the AitkenM and AccuM1 and the existence of a minimum in PNSDs around 80 nm, although there exist differences. Interestingly, the relative height (or peak values of dN/dlogD$_p$) of AitkenM and AccuM1 has strong seasonal variations. The model captures a relatively higher AitkenM in SH Summer and Fall and a higher AccuM1 in SH Spring. The model simulated PNSDs also agree

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well with the measurements in term of the size-dependent normalized standard deviation (σ_N, i.e., the standard deviation σ divided by the mean): relatively smaller σ_N for AccuM1 and larger size part of AitkenM and much larger σ_N for NuclM, smaller size part of AitkenM, and AccuM2. While the larger σ_N for NuclM is understandable because of NPF, it is surprising for AccuM2. The AccuM2 particles have relatively long lifetime and are expected to be well-mixed (and thus have small variations) in LS. The transport of AccuM2 particles from UT may contribute to the larger variations. Murphy et al. (2021) showed the chemical signature of this transported mode, and here we show that the variation in the size distribution may also contain information about the mixing of UT particles into LMS. Compared to the observations, the model simulated AccuM2 σ_N are larger in SH Winter and Spring but are smaller in SH Summer and Fall. The possible reasons for the large variations of AccuM2 in LMS and the differences between model simulations and measurements remain to be studied.

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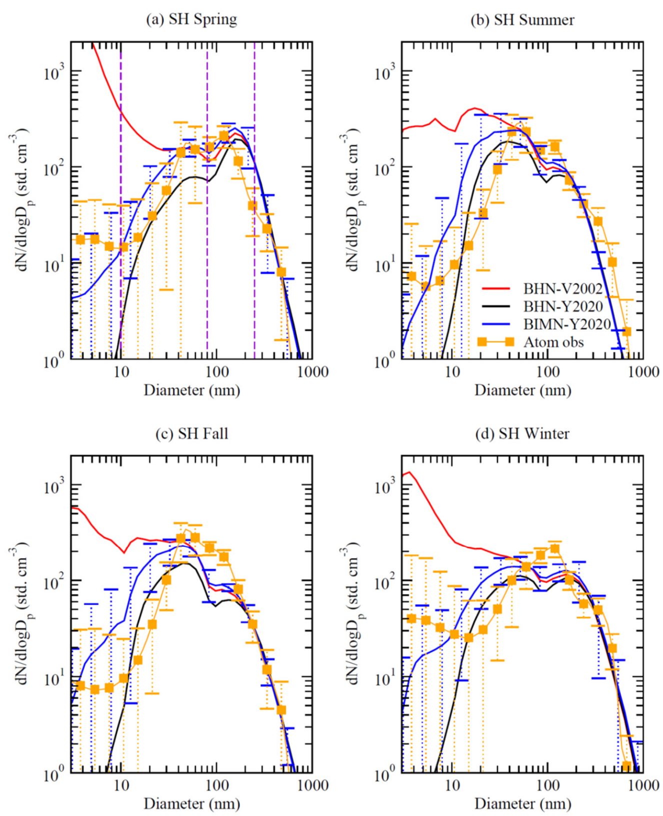

Figure 6. Model simulated seasonal mean PNSDs at a site in SH (70ºS, 60ºW) at altitude of 12 km based on three nucleation schemes and comparisons with the corresponding ATom measurements (a: SH Spring 09–10/2017, b: SH Summer 01–02/2017, c: SH Fall 04–05/2018, and

d: SH Winter 06–07/2016). To take into account the variations in both model and observed PNSDs, standard deviations are shown as error bars in the measured and modeled curves based on BIMN_Y2020. Three vertical dashed lines at 10 nm, 80 nm, and 250 nm are drawn in (a) to guide the eye to the four modes discussed in the text.

The large impacts of nucleation schemes on PNSDs, especially those smaller than 100 nm, can be seen in Fig. 6. The formation rates and concentrations of nucleation mode particles are very high based on BHN_V2002 (peak dNdlogDp values reaching well above 10^3 std. cm^{-3}), negligible based on BHN_Y2020 (dNdlogDp values for particles <10 nm are generally below 1 std. cm^{-3}), and moderate based on BIMN_Y2020. When compared to the observed values, the number concentrations of particles within 3–10 nm based on BHN_V2002 are 1–2 orders of magnitude too high but those based on BHN_Y2020 are 1–2 orders of magnitudes too low, while those based on BIMN_Y2020 are of the same order of magnitude. The impact of nucleation schemes on NuclM propagates into the AitkenM and AccuM1, with BHN_Y2020 giving the lowest number concentrations while BHN_V2002 gives the highest AitkenM and BIMN_Y2020 gives the highest AccuM1. It should be noted that, while the line of BHN-Y2020 is lower than that of BIMN and BHN-V2002 for particles of smaller sizes (<~ 300 nm), it is slightly higher for larger particles (>~ 300 nm). This is consistent with the competition of sulfuric acid gas between pre-existing larger particles and nucleated smaller particles. It is interesting to note that AccuM1 based on BIMN_Y2020 is higher than that based on BHN_V2002 although BHN_V2002 predicts higher NuclM and AitkenM, indicating a non-linear interaction among nucleation, growth, and coagulation. The competition between nucleation and condensation for available sulfuric acid gas has been shown to be important for SAI studies (Laakso et al., 2022).

There exist a number of differences in the simulated and observed PNSDs. Firstly, measurements indicate a slight increase of dNdlogD_p with decreasing sizes for particles < 10 nm but the simulated PNSDs based on BIMN_Y2020, the scheme mostly consistent with CLOUD measurements and predicting NuclM concentrations closest to those observed, decreases with decreasing sizes for particles < 10 nm. The possible reasons of the difference remain to be investigated but probably are associated with uncertainty in nucleation rates and size-dependent growth rates of freshly nucleated particles, and/or the fact that ATom observations are bias towards daytime. In addition, the small number of particles in this mode is likely within the uncertainty in the ATom measurements (about 7% of the total number of particles), so that this measured mode may not be significant. Secondly, the model appears to overpredict the smaller size part (~10–40 nm) of AitkenM although it is close to the larger part of the mode (~40–80 nm). The overprediction may be a result of the underestimated growth rates or coagulation scavenging rates of these particles or overpredicted growth rates of NuclM particles. Thirdly, the model generally overpredicts the mean mode sizes of AccuM1 and underpredicts the concentrations of the mode except in SH Spring. The nucleation schemes have observable effects on the concentrations and mean sizes of AccuM1 and overall the simulations based on BIMN_Y2020 are in stronger agreement with measurements. Finally, the observed PNSDs show a clear AccuM2 in all seasons except Fall but such a mode cannot be clearly seen in the model simulated PNSDs, indicating that the model underpredicts the concentrations of AccuM2 mode particles. AccuM2 particles are

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As pointed out earlier, the comparison in Fig. 6 does not exactly match in terms of time and location, which likely contributes to some of the differences shown in Fig. 6. Some of the differences can also be caused by the uncertainties in the model in term of emissions, transport, chemistry, aerosol microphysics, and deposition. Nevertheless, some of these differences, especially the shape of PNSDs (AccuM2, NuclM, etc.), are unlikely to be fully accounted for by the above-mentioned possible mismatch or model uncertainties and thus may indicate that some fundamental processes are not represented in the model. One possible cause of the differences is that the transport of organic-sulfate particles from UT (Murphy et al., 2014, 2021) is not properly simulated by the model. Based on size-resolved particle composition measurements, Murphy et al. (2021) showed that the LMS accumulation mode particles (diameter ~ 0.1 and 1.0 µm) have at least two modes: the larger mode consists mostly of sulfuric acid particles produced in the stratosphere, and the smaller mode consists mostly of organic-sulfate particles transported from the troposphere. Murphy et al. (2014) showed that the fraction of organic-sulfate aerosols above tropopause decreases quickly with altitudes. While the organic-sulfate mode aerosols from UT may contribute to the bi-modal structure of accumulation mode particles in the LMS observed during ATom, it is unlikely to contribute to the bi-modal structure of particles larger than ~200 nm observed at altitude above ~20 km both in the background and in volcano perturbed stratosphere (Deshler et al., 2013, 2019; also see Fig. 7). Here, we suggest that the role of charges on coagulation and growth of particles in the stratosphere could be another process causing the bi-modal of large particles in the stratosphere.

As shown Fig. 2e, ionization rates are high in LS, ranging from ~ 40–100 ion-pair std. $cm^{-3}s^{-1}$. Due to their low number concentrations (~100–1000 std. cm^{-3}) but long lifetime, particles in the stratosphere are expected to be in charge equilibrium. Figure 7 shows mean particle number size distribution (PNSD) and particle volume size distribution (PVSD) observed during ATom 1-4 in SH LMS and measured within 20-25 km altitude over Lararie WY in 1992, and fraction of particles carrying *n* charges based on the modified Boltzmann equilibrium equation (Clement and Harrison, 1992). The bi-modal structure of accumulation mode particles can be clearly seen in both background and volcano perturbed stratosphere. It should be noted that while the smaller mode generally dominates the number concentrations, the larger mode dominates mass concentrations. Under equilibrium more particles are charged (i.e., $1\text{-}f_0 > 50\%$) than neutral (f_0) for particles with diameter larger than ~80 nm and a significant fraction (> 25%) of particles larger than 300 nm carrying multiple charges. While the equilibrium charge fraction is small for NuclM particles (≲ 10 nm), this fraction can be much larger when nucleation on ions occurs, which is consistent with the observed overcharging of freshly nucleated particles (Laakso et al. 2007; Yu and Turco, 2008). Particle coagulation rates are influenced by forces exerted between colliding particles, including van der Waals and electrostatic forces, which can modify the effective collision cross section and sticking coefficient. The van der Waals force has been shown to be important in the stratosphere (English et al., 2011, 2012) and has been considered in the simulations shown above. The effects of charges on coagulation and implications for PNSDs in the stratosphere have not yet been studied (to our knowledge). Since coagulation is a dominant process for the growth of accumulation mode particles in the stratosphere, we hypothesize that differential coagulation rates for neutral and

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charged particles in accumulation modes can potentially act as a physical process separating the modeled single accumulation mode (Fig. 6) into two modes (AccuM1 and AccuM2) as observed. Further research is needed to test this hypothesis. In addition to affecting coagulation, charge on small particles can also enhance the growth rate due to ion-dipole interactions of condensing molecules with charged particles (Nadykto and Yu, 2005). This enhancement is expected to be stronger in the stratosphere because of lower temperature (Nadykto and Yu, 2005). Beside these, Svensmark et al. (2020) showed that the condensation of ion clusters can enhance particle growth rates. How much the enhanced coagulation and growth rates of charged particles may shape PNSDs and modes in the stratosphere remains to be investigated.

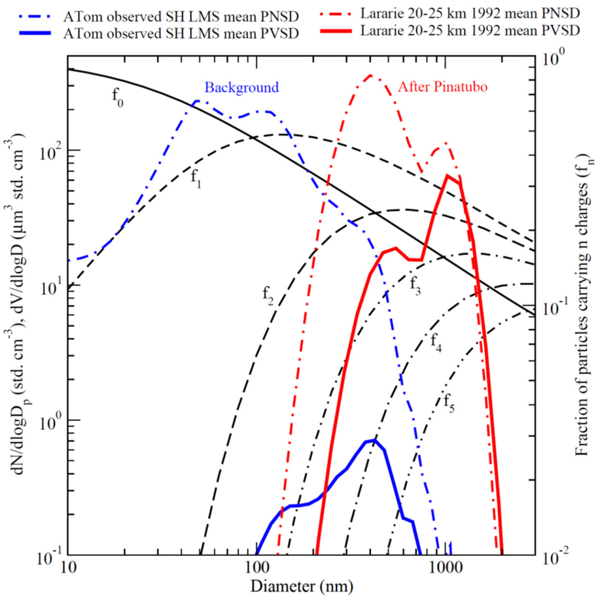

Figure 7. ATom 1-4 mean observed particle number size distribution (PNSD, or dN/dlogDp) and particle volume size distribution (PVSD, or dV/dlogDp) in SH LMS, balloon-borne measured mean PNSD and PVSD within 20-25 km altitude over Lararie WY in 1992, and fraction of particles carrying *n* (n = 0, 1, 2, 3, 4, and 5) charges based on the modified Boltzmann equilibrium equation (Clement and Harrison, 1992). Note that f_n with $n \geq 1$ including both positive and negative charges, i.e., for example, half of f_1 carrying one negative charge while the other half positive.

4. Summary and Discussions

Interest in stratospheric aerosols has been increasing in recent years, due to the ongoing discussion about the plausibility, potential benefits and risks of offsetting climate change through stratospheric aerosol injection (SAI) to buy time for reduction of CO_2 in the atmosphere. Recent studies indicate the dependence of SAI radiative efficacy (Dai et al., 2018) on the particle size distribution (NASEM, 2021) and thus it is critical to improve foundational understanding and

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model representation of aerosol microphysics processes controlling the evolution of stratospheric aerosols, both under background conditions and perturbed scenarios. While formation and growth of particles in the troposphere have been extensively studied in the past two decades, very limited efforts have been devoted to understanding these in the stratosphere.

In the present study we use both CLOUD laboratory measurements taken under very low stratospheric temperatures and ATom in-situ observations of particle number size distributions (PNSD) down to 3 nm to constrain nucleation schemes and model-simulated particle size distributions in the lowermost stratosphere (LMS). We show that the binary homogenous nucleation scheme used in most of the existing SAI modeling studies overpredicts the nucleation rates by 3–4 orders of magnitude (when compared to CLOUD data), leading to significant overprediction of particle number concentrations in the background stratosphere (by a factor of 2–4 in SH LMS, compared to ATom data). Based on a recently developed kinetic nucleation model which provides rates of both ion-mediated nucleation (IMN) and BHN at low temperatures in good agreement with CLOUD measurements, both BHN and IMN occur in the stratosphere but IMN rates are generally more than one order of magnitude higher than BHN rates and thus dominate nucleation in the background stratosphere.

In the SH LMS that has minimal influences from anthropogenic emissions, our analysis shows that ATom-measured PNSDs generally have four apparent modes: a nucleation mode (NuclM: $\lesssim$ 10 nm), which may not be statistically significant, an Aitken mode (AitkenM: ~10–80 nm), and two accumulation modes (AccuM1: ~ 80–250 nm and AccuM2: ~ 250–700 nm). The model generally captures the AitkenM and AccuM1 and the existence of a minimum in PNSDs at ~ 80 nm, although there are differences. The model captures a relatively higher AitkenM in SH Summer and Fall and a higher AccuM1 in SH Spring. The model simulated PNSDs also agree well with the measurements in term of the size-dependent standard deviations: relatively smaller standard deviations for AccuM1 and larger size part of AitkenM and much larger standard deviations for NuclM, smaller size part of AitkenM, and AccuM2.

A detailed comparison indicates the existence of a third PNSD mode peaking around 300–400 nm in the ATom measurements that are not captured by the model. Compared to the observations, the model-simulated AccuM2 standard deviations are larger in SH Winter and Spring but are smaller in SH Summer and Fall. In addition, the model overpredicts the number concentration of particles in the size range of 10–50 nm. These differences may indicate that, in addition to nucleation, the model may be missing some fundamental microphysical processes of stratospheric aerosols. Our analysis shows that, in the stratosphere, more particles are charged (positive + negative) than neutral for particles with diameter larger than ~80 nm and a significant fraction (> 25%) of particles larger than 300 nm carrying multiple charges. We propose that the role of charges on coagulation and growth of particles in the stratosphere, where ionization rates are high and particles have very long lifetime, is likely one of such processes. Considering the importance of accurate particle size distributions (especially the accumulation mode particles) for projecting realistic radiative forcing response to stratospheric aerosols, it is essential to understand and incorporate such potentially important processes in model simulations of future changes in the stratosphere. It should be noted that the ATom measurement period does not have a high stratospheric aerosol loading (i.e., no major volcano eruptions). It remains to be investigated if previous assessments of volcanic aerosol microphysics missed something important. We expect the uncertainties in the nucleation schemes and unknown cause of the bi-modal structure of accumulation mode particles will affect particle optical properties and surface area and thus radiative forcing or chemistry. The present work highlights the importance of advancing scientific understanding of processes controlling properties of stratospheric particles as well as further development, improvement, and validation of models for reducing uncertainties of SAI simulations (e.g., Golja et al., 2021, Sun et al., 2022).

Conflict of interest: The authors declare that they have no conflict of interest.

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Data availability. The GEOS-Chem model is available to the public at https://geos-chem.seas.harvard.edu/. Simulation output in this analysis is available at https://doi.org/10.5281/zenodo.6909944. The ATom dataset is published as Wofsy et al., (2021, https://doi.org/10.3334/ORNLDAAC/1925) and is also available at https://espoarchive.nasa.gov/archive/browse/atom (last access: June 2022).

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