

Enhanced growth rate of atmospheric particles from sulphuric acid

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Abstract. In the present-day atmosphere, sulphuric acid is the most important vapour for aerosol particle formation and initial growth. However, the growth rates of nanoparticles (<10 nm) from sulphuric acid vapour remain poorly measured. Therefore, the effect of stabilizing bases, the contribution of ions and the impact of attractive forces on molecular collisions are under
45 debate. Here we present precise growth-rate measurements of uncharged sulphuric acid particles in the size range 1.8-10 nm, performed under atmospheric conditions in the CERN CLOUD chamber. Our results show that the evaporation of sulphuric acid particles above 2 nm is indeed negligible and growth proceeds kinetically even at low ammonia concentrations. The experimental growth rates exceed the geometric hard-sphere kinetic limit for condensation of sulphuric acid, and reveal an enhancement resulting from van-der-Waals forces between the vapour molecules and particles. We are able to disentangle the
50 effects of charge-dipole interactions and van-der-Waals forces and observe a steep increase of particle growth rates with decreasing size. Including the experimental results in a global model, we find the enhanced growth rate of sulphuric acid particles increases predicted particle number concentrations in the upper free troposphere by more than 50%.

1 Introduction

Sulphuric acid (H₂SO₄) is the major atmospheric trace compound responsible for nucleation of aerosol particles in the present-
55 day atmosphere (Dunne et al., 2016). Sulphuric acid participates in new particle formation (NPF) in the upper troposphere (Brock et al., 1995; Weber et al., 1999; Weigel et al., 2011), stratosphere (Deshler, 2008), polar regions (Jokinen et al., 2018), urban or anthropogenic influenced environments (Yao et al., 2018) and when a complex mixture of different condensable vapours is present (Lehtipalo et al., 2018). Especially in the initial growth of small atmospheric molecular clusters, sulphuric acid is likely of crucial importance (Kulmala et al., 2013). The newly formed particles need to grow rapidly in order to avoid
60 scavenging by larger, pre-existing aerosols and, thereby, contribute to the global cloud condensation nuclei (CCN) budget (Pierce and Adams, 2007). The dynamics in this cluster size-range of a few nm therefore determines the climatic significance of atmospheric NPF, which is the major source of CCN (Gordon et al., 2017) and can also affect urban air quality (Guo et al., 2014).

65 The main pathway of cluster and particle growth is condensation of low volatility vapours, like sulphuric acid or oxidized organics (Stolzenburg et al., 2018). Nanoparticle growth rates depend mainly on the evaporation rates of the condensing vapours and on the molecular collision frequencies. On the one hand, the incomplete understanding of the evaporation and cluster processes in growth lead to the question if growth caused by sulphuric acid proceeds at the kinetic limit of condensation, where evaporation rates are negligible. It was shown in earlier laboratory measurements that bases like ammonia can have a
70 stabilizing effect for growth below 2 nm (Lehtipalo et al., 2016). If amines, which are stronger bases than ammonia, are added, nucleation itself can proceed at the kinetic limit, i.e. evaporation rates from the monomer onwards are zero (Jen et al., 2014; Kürten et al., 2014; Olenius et al., 2013). In this case, cluster coagulation also plays an important role in the growth process due to the strong clustering behaviour of sulphuric acid and amines (Kontkanen et al., 2016; Lehtipalo et al., 2016; Li and

McMurry, 2018). However, in the presence of ammonia, the evaporation rates and the magnitude of cluster coagulation remain unmeasured, although ammonia is much more important than amines globally due to its longer atmospheric lifetime. On the other hand, condensation at the kinetic limit is extremely sensitive to molecular-particle collision rates, which may be enhanced by either charge-dipole interactions (Nadykto and Yu, 2003) or van-der-Waals forces (Chan and Mozurkewich, 2001), but there are only few direct measurements of the charge effect on growth (Lehtipalo et al., 2016; Svensmark et al., 2017). Even if the charge-dipole interactions are stronger, an enhancement due to van-der-Waals forces might be more important at typical atmospheric ionization levels. Several atmospheric studies have demonstrated that sulphuric acid uptake proceeds close at a collision-limited rate (Bzdek et al., 2013; Kuang et al., 2010). However, they could not provide a measurement of a collision enhancement, which will be strongest in the free molecular regime below 5 nm, where growth measurements are affected by larger uncertainties (Kangasluoma and Kontkanen, 2017).

2 Results

Here, we address the questions of sulphuric acid evaporation, cluster contribution and collision enhancement in sulphuric acid driven growth with precision measurements (Stolzenburg et al., 2017) at the CERN (European Organization for Nuclear Research) CLOUD experiment (Duplissy et al., 2016). We performed measurements of particle growth from sulphuric acid and ammonia at either +20 °C or +5°C with the relative humidity kept constant at either 38% or 60%. SO₂ (5 ppb), O₃ (~120 ppb) and ammonia (varied between 3 and 1000 pptv) were injected into the chamber and UV lights induced the formation of sulphuric acid (varied between 10⁷ and 10⁹ cm⁻³) and subsequent particle formation. A typical experiment and the approach used to measure particle growth rates with the appearance time method (Dada et al., 2020) are described in the Supplement and presented in Fig. S1.

2.1 Collision enhancement in sulphuric acid growth

Figure 1 shows the particle growth rates for two size-intervals (Fig. 1a, 1.8-3.2 nm mobility diameter and Fig. 1b, 3.2-8.0 nm mobility diameter) versus the sulphuric acid monomer concentration, correlating linearly. No significant dependencies on temperature, ionization levels in the chamber or the concentration of ammonia are evident. While the effect of temperature expected from theory is small and cannot be discerned within the statistical uncertainties of our measurements (Nieminen et al., 2010), the insignificant influence of ammonia and ionization level on the growth rate differs from previous findings (Lehtipalo et al., 2016).

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We compare the measured growth rates of this study with the results from Lehtipalo et al. (2016) in Fig. S2 in the Supplement. In contrast to our results, elevated ammonia (~ 1000 pptv) led to increased growth rates in that study. The major difference is the narrower size range for the growth-rate measurements (1.5-2.5 nm mobility diameter) due to a different set of instrumentation. For smaller sizes and at low ammonia, sulphuric acid evaporation likely still plays a role due to an increased

105 Kelvin term. The stabilizing effect of ammonia is certainly relevant at the sizes of the nucleating clusters (Kirkby et al., 2011).
For our results, we confirm the absence of significant evaporation rates above 2 nm by an independent experiment presented
in Fig. 2. It demonstrates that, in the absence of gas-phase sulphuric acid, the coagulation and dilution corrected loss rates of
particles ($k_{tot}^{meas} - k_{dil} - k_{coag}^{avg}$) over all sizes follow the expected size-dependence of wall losses which is inferred from the
sulphuric acid monomer decay. Evaporation would cause another term distorting the balance equation (also depending on the
110 relative abundances of the particles during the decay), causing a deviation from the expected wall loss rate.
The insignificant effect of ammonia on growth (Fig. 1) and the same high ratio (>100, Fig. S3a in the Supplement) between
sulphuric acid monomer and dimer concentrations for all experiments, point towards a negligible clustering, possibly
influencing our measured growth rates (Li and McMurry, 2018). Moreover, in Fig. S3b in the Supplement, we show with a
model including sulphuric acid/ammonia clustering and evaporation, that no cluster contribution is indeed expected even at
115 elevated ammonia concentrations (Kürten, 2019).

In the absence of evaporation and strong clustering, our growth-rate data provide a direct measurement of the condensational
growth at the kinetic limit caused by sulphuric acid monomers only. We find the measured growth rates both with and without
addition of ammonia to be significantly above the geometric hard-sphere limit of kinetic condensation (Nieminen et al., 2010).
120 For this comparison we adjusted the measured dry mobility diameters by -0.3 nm to actual mass diameters (Larriba et al.,
2011) and then assumed an average hydration of the monomer based on quantum chemical calculations (Henschel et al., 2014)
together with a size-dependent most probable water content for the growing particles (see Fig. S4a) based on the SAWNUC
code (Ehrhart et al., 2016). The derivation of the growth rates from theory and the used parameters are in detail described in
the Supplement and listed in Table S1. The observed enhancement is similar to Lehtipalo et al. (2016) in the case when
125 evaporation was suppressed by ammonia (see Fig. S2). We also measure a growth-rate enhancement for the larger size-range
(Fig. 1b), which should be less sensitive to evaporation. The faster growth rates might be due to an enhanced collision
frequency which can be attributed to van-der-Waals forces, either permanent dipole-(induced) dipole interactions between
polar sulphuric acid molecules and particles or London dispersion forces (London, 1937). We therefore adjusted the
condensation equations of Nieminen et al. (2010) with a kinetic collision frequency k_{coll} accounting for an enhancement due
130 to van-der-Waals forces (Chan and Mozurkewich, 2001) (see Supplement). The magnitude of the enhancement is described
by the Hamaker constant A (Hamaker, 1937), which we use as the single free parameter to fit a collision enhanced kinetic limit
(see Eq. (S9)) to the measured growth-rate data. We find $A = (5.2 \pm 1.5 (stat.) \pm_{4.4}^{8.1} (syst.)) \cdot 10^{-20} \text{ J} (\pm 1\sigma \text{ uncertainty})$ in
good agreement with previous results (Chan and Mozurkewich, 2001; McMurry, 1980). While this result uses a Brownian
coagulation model to calculate the collision enhancement (Sceats, 1989), we also applied a ballistics approach for the free
135 molecular regime (Fuchs and Sutugin, 1965; Ouyang et al., 2012), and derive a slightly higher value of $1.3 \cdot 10^{-19} \text{ J}$ (see
Supplement). For both approaches, the enhancement factor for the free molecular regime (2.2 and 2.6, respectively) is
comparable to previous experimental results (Kürten et al., 2014; Lehtipalo et al., 2016) and in agreement with quantum
chemical calculations (Halonen et al., 2019). The relatively large systematic uncertainties on the Hamaker constant estimate

are connected to the systematic uncertainty of the sulphuric acid measurement and to the assumptions on the water content of
140 condensing clusters and growing particles (see Fig. S4b in the Supplement).

An enhancement due to charge-dipole interactions between the polar sulphuric acid monomers and charged particles is not
significant in our total (neutral plus charged particle) growth rate measurements, as shown in Fig. 1, where we observe no
145 difference between growth rates under neutral and galactic cosmic ray ionization levels. From average-dipole-orientation
theory (Su and Bowers, 1973), a small enhancement in collision frequency even for charged particles above 2 nm is expected
(Nadykto and Yu, 2003) affecting the growth rate (Laakso et al., 2003; Lehtipalo et al., 2016). We find an enhancement factor
of 1.45 by comparing the total to the ion growth rate as shown in Fig. 3, which is in good agreement with theory. However,
the total growth rate is influenced on a minor level by the faster ion growth because at the representative galactic cosmic ray
ionization levels (ion production rate: $\sim 2\text{-}4$ ion pairs $\text{cm}^{-3} \text{s}^{-1}$) and sulphuric acid concentrations in our experiments, most (more
150 than 75%) of the growing particles are neutral (see Fig. 3). However, effects of ion condensation and charge-dipole
enhancement might be stronger at lower sulphuric acid concentrations (Svensmark et al., 2017).

2.2 Size-dependency of sulphuric acid growth

Condensational growth at the geometric kinetic limit predicts increasing growth rates with decreasing particle sizes due to the
non-negligible effect of vapour molecule size on the collision cross-section (Nieminen et al., 2010), which, was not yet shown
155 experimentally. Furthermore, the collision enhancement due to van-der-Waals forces and the collision enhancement due to
dipole-charge interactions also depend on the comparative size of the condensing vapour and the growing particle. Fig. 4a
illustrates the theoretical predictions of the size-dependency of the collision rate of sulphuric acid monomers with larger
particles, including van-der-Waals forces and dipole-charge interactions.

160 Fig. 4b shows the measured size-dependence of all growth-rate measurements normalized to a sulphuric acid concentration of
 10^7 cm^{-3} . In addition we calculated the growth rates using the time- and size-resolving growth rate analysis method INSIDE
(Pichelstorfer et al., 2018), which accounts for the effects of coagulation and wall losses. Both methods clearly show increasing
growth rates towards smaller sizes and agree remarkably well, demonstrating that we are not biased by the approach in growth
rate determination. The experimental results have a stronger size-dependence than the predicted in the hard-sphere limit. They
165 follow the theoretical predictions including van-der-Waals forces up to 10 nm, with the approach of Fuchs and Sutugin (1965)
slightly better reproducing the measured size-dependency. Charge-dipole interactions are not considered here because the
charged fraction of the growing particle population is small (Fig. 3) and charge effects only start to dominate below 2 nm (Fig.
4a).

2.3 Global implications

170 Due to this steep increase of particle growth rates with decreasing size, the collision enhancement due to van-der-Waals forces is especially important for the smallest particles. As these are the most vulnerable for losses to pre-existing aerosols, their survival probability in the atmosphere is directly affected, altering the CCN budget (Pierce and Adams, 2007) or promoting new particle formation in urban environments (Kulmala et al., 2017). In order to test the effects of collision enhancement in sulphuric acid growth on a global scale, we use the atmosphere-only configuration of the United Kingdom Earth System Model
175 (UKESM1) (Mulcahy et al., 2018; Walters et al., 2019) which includes the GLOMAP aerosol microphysics module describing nucleation and growth (Mann et al., 2010). Figure 5 illustrates the global model results comparing the baseline case (no collision enhancement) with a collision enhancement simulation for the present-day atmosphere (see Supplement for details). The absolute particle number concentrations averaged over all longitudes are shown in Figure 5a, indicating changes of more than 50%, especially at high altitudes (>10 km; Figure 5b), where most aerosol particles originate from pure sulphuric-acid
180 driven NPF. The importance of the nucleation process, and therefore the growth-rate enhancement, is lower at lower altitudes and in the northern hemisphere, mainly due to the higher condensation sink and the restriction of the model to only sulphuric acid-water binary nucleation. However, the significant enhancement of sulphuric acid driven nanoparticle growth in the upper troposphere may be important in quantifying sources of stratospheric aerosols and cirrus cloud condensation nuclei (Brock et al., 1995; Deshler, 2008) and needs to be accounted for in future model development.

185 3 Discussion

Understanding nanoparticle growth driven by sulphuric acid is extremely important for modelling the present-day atmosphere. Our measured growth rates cover a wide range of representative atmospheric conditions below 20 °C and reveal that sulphuric acid growth proceeds faster than the geometric hard-sphere kinetic limit. Such faster growth rates in the cluster size range could be in part responsible for the occurrence of NPF in polluted environments (Kulmala et al., 2017). Our results suggest
190 that for sizes larger than 2 nm this collision enhancement due to van-der-Waals forces can be more important than dipole-charge interactions or base-stabilization by ammonia.

For smaller sizes, evaporation of sulphuric acid and charge effects need to be considered (Lehtipalo et al., 2016), but the size-range covered by our measurements is sufficient for the used global model, which nucleates particles at 1.7 nm. We find
195 significantly increased upper tropospheric aerosol concentrations, but the global impact of van-der-Waals forces in nanoparticle growth might be even higher due to the model limitations to binary sulphuric-acid water nucleation.

Our results should therefore be considered in future model development, especially when discussing the importance of changing sulphuric acid levels due to reduced anthropogenic emissions of SO₂. Moreover, our parametrization of pure
200 sulphuric acid growth rates will help to identify the contribution to growth of other co-condensing vapours in ambient and

laboratory experiments, as they set a new baseline for kinetic condensation of sulphuric acid. Several simplifications have often been applied to kinetic particle growth, including hard-spheres collision based on bulk density and neglect of vapour size to the collision cross section; our results provide clear experimental verification that these simplifications are no longer fit for increasingly accurate measurements at these tiny yet critical sizes.

205 *Data availability:* All presented datasets are available from the corresponding author upon reasonable request.

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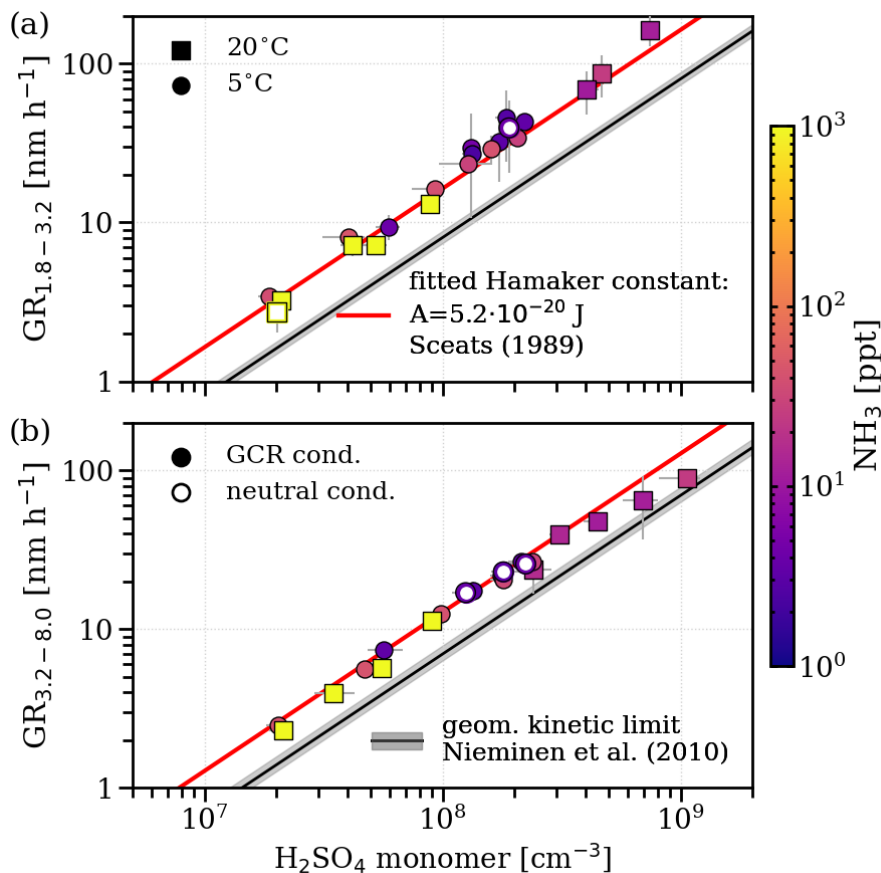
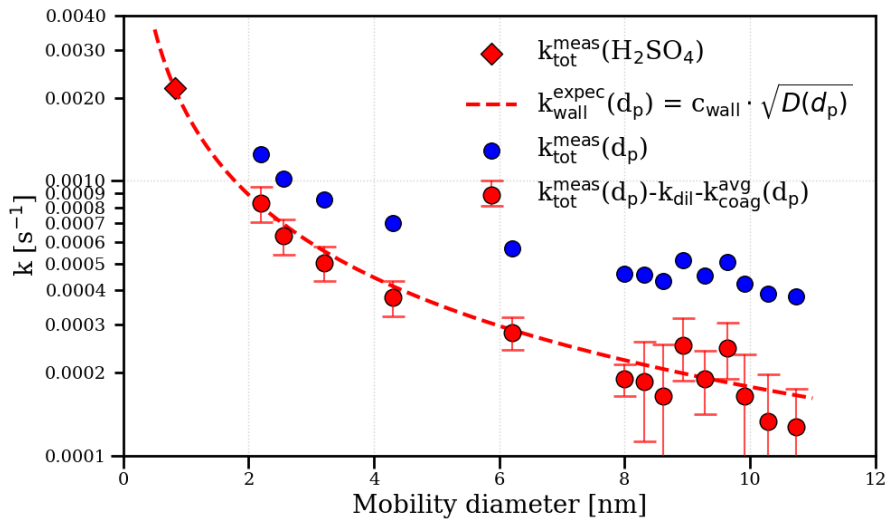
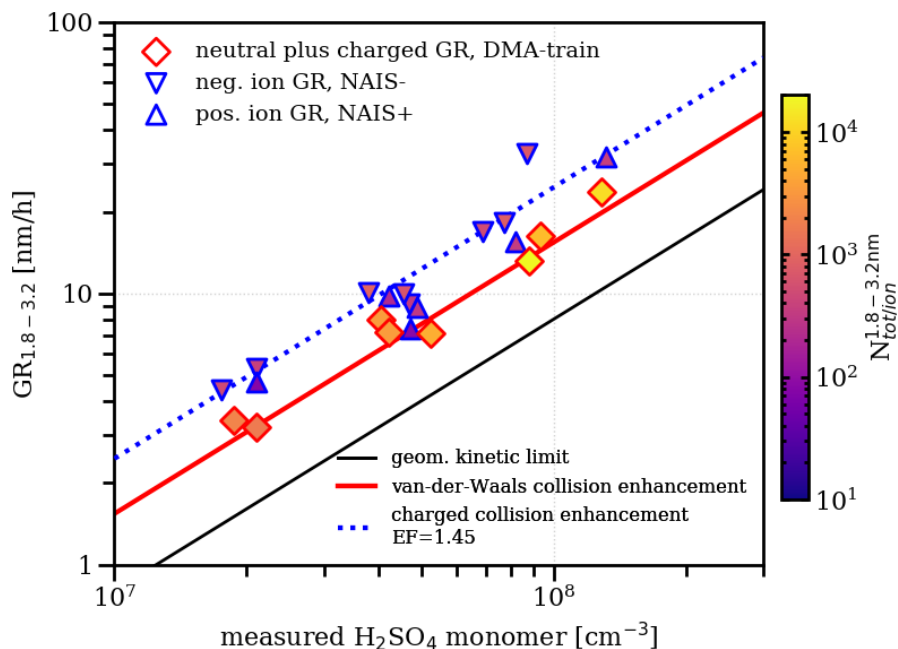


Figure 1: Growth Rate Measurements. Growth rates of nanoparticles in two size-intervals versus measured gas-phase sulphuric acid monomer concentration. (a) shows growth rates for the size-interval between 1.8-3.2 nm (mobility diameter; 1.5-2.9 nm in mass diameter), while (b) shows the growth rates for the size-interval 3.2-8.0 nm (mobility diameter, 2.9-7.7 nm in mass diameter). The colour code represents the measured NH_3 concentration during the growth period. Squares are measurements at 20°C , circles at 5°C . Filled symbols represent runs under ambient galactic cosmic ray ionization levels, and open symbols under neutral conditions. Error bars for the data points represent the statistical uncertainty in the appearance time growth rate measurements in y-direction. In x-direction, they represent the maximum variation of the sulphuric acid concentration during the growth period in the corresponding interval, also explaining the slight deviations from linearity at high sulphuric acid concentrations, where stable conditions are not fully reached. The dashed black line and shaded grey area show the geometric limit of kinetic condensation and the corresponding systematic uncertainty based on the assumed water content of the condensing cluster and growing particles (Nieminen et al., 2010), while the red line shows the fit of Eq. (1) to the data with the Hamaker constant as free parameter. The enhancement factor due to van-der-Waals forces compared to the geometric kinetic limit is 2.1 for the interval 1.8-3.2 nm and 1.9 for the interval 3.2-8 nm.



425 **Figure 2: Measurement of zero sulphuric acid evaporation rates.** Total loss rates of sulphuric acid and ammonia particles
with mobility diameter shown on the x-axis measured during a decay experiment (5°C, 60% relative humidity, 1000 pptv
NH₃), by switching off the UV lights after a particle growth stage, which stops the production of sulphuric acid and
subsequently nucleation and growth. After sulphuric acid is reduced to background level, the exponential decay rate of the
remaining particles in the chamber is measured ($k_{\text{tot}}^{\text{meas}}$, blue circles), which was not possible for the 1.8 nm channel due to
430 low statistics. Decay of particles in the chamber is dominated by wall loss, dilution loss and coagulation loss to other particles.
Particle loss rates are corrected for an averaged coagulation loss during the decay ($k_{\text{coag}}^{\text{avg}}$) to all particles larger than d_p and for
the dilution loss (k_{dil}) (red circles). They agree well with the expected wall loss rate $k_{\text{wall}}(d_p) = C_{\text{wall}} \cdot \sqrt{D_p(d_p)}$ (red dashed
line) with $C_{\text{wall}} = 0.0077 \text{ s}^{-0.5} \text{ cm}^{-1}$ inferred from an independent sulphuric acid decay experiment in the absence of a particle
sink, where the mobility diameter is assumed to be 0.82 nm (Ehrhart et al., 2016) (red diamond). This suggests that there is
435 negligible evaporation from the sulphuric acid particles above ca. 2 nm under the above mentioned experimental conditions,
which would introduce another term disturbing the balance equation at each size. As all our growth-rate measurements,
independent of the ammonia concentration and temperature, fall on the same line (see Fig. 2), this also points towards
negligible evaporation effects at reduced ammonia levels (below 10 pptv) and up to 20°C.



440 **Figure 3: The effect of charge on growth.** Measured growth rates of 1.8-3.2 nm (mobility diameter) particles and ions in
 experiments with ammonia above 10 pptv. The DMA-train measures both neutral and charged particles (diamonds with red
 contours) whereas the NAIS+/- (Manninen et al., 2009) measures purely charged particles (triangles with blue contours). Both,
 the positively and negatively charged particle population have a faster apparent growth rate than the total particle population
 due to an enhanced collision rate from dipole-charge interactions. We measure a multiplicative charge enhancement factor of
 445 1.45 in this size range with a combined fit to both polarities (blue dashed line), which is consistent with estimates from average
 dipole orientation theory (Nadykto and Yu, 2003). At galactic cosmic rays ionization levels in the chamber, the charged fraction
 of the growing particles in the size-range 1.8-3.2 nm (mobility diameter) is between 5 and 25%. This is demonstrated by the
 colour code which indicates the integrated total or ion number concentration over the growth rate size interval averaged during
 the growth period. The fit of the appearance time for the total particle population is therefore affected on a minor level by the
 450 small earlier appearing charged fraction.

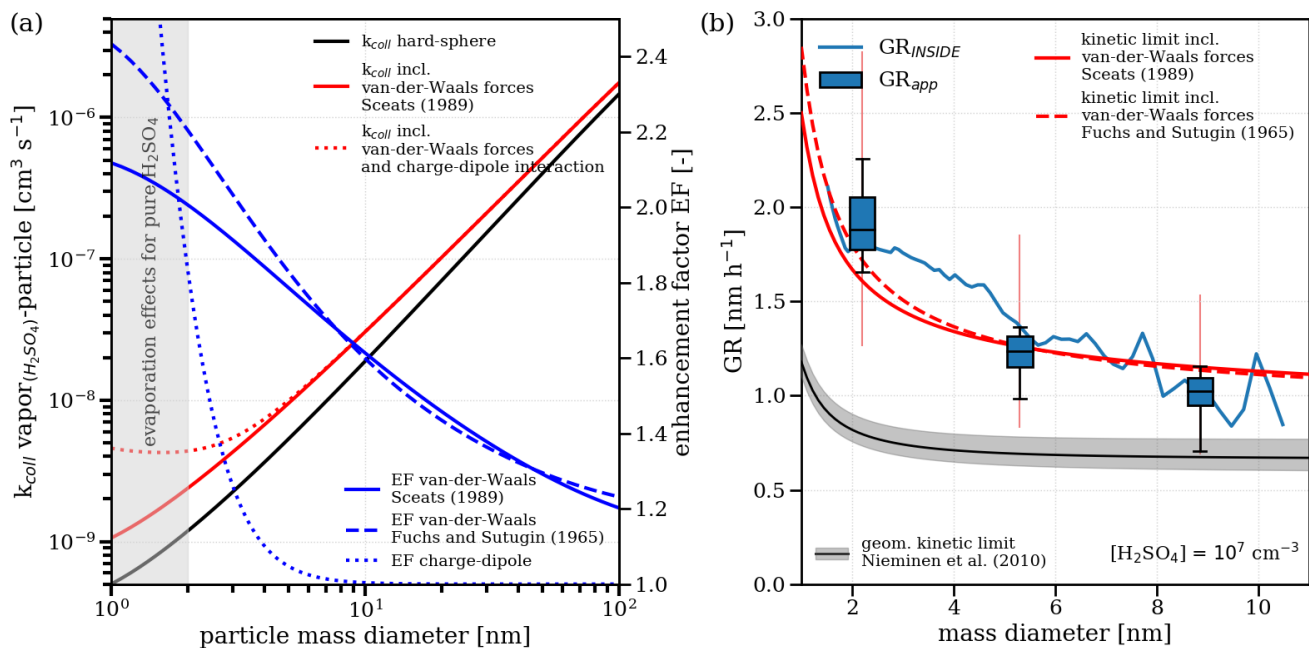
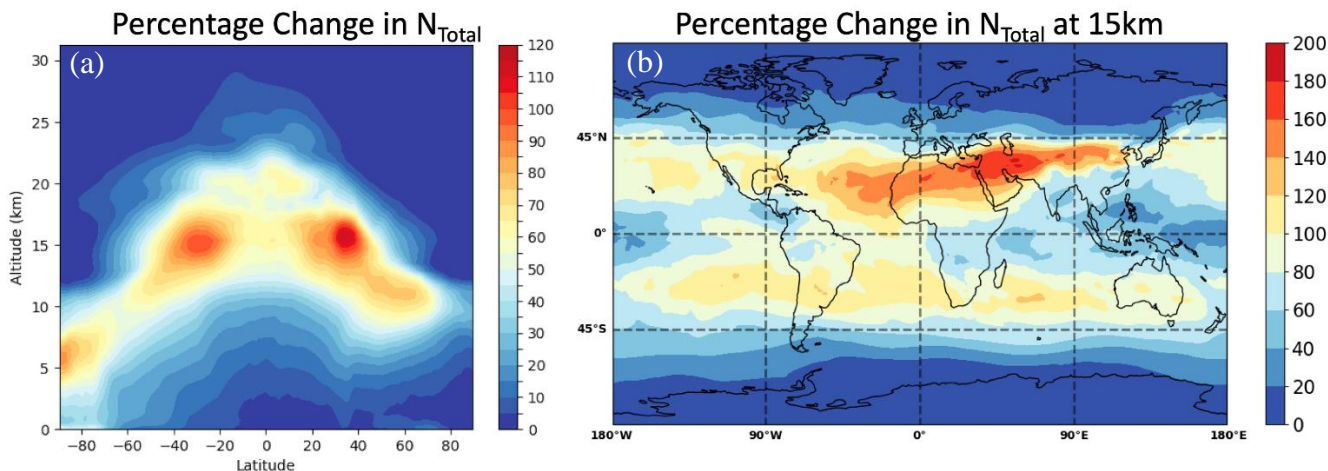


Figure 4: The size-dependency of sulphuric acid growth. Measured and modelled size-dependency of growth rates. (a) shows the theoretical collision rate of hydrated sulphuric acid vapour molecules with particles of a certain mass diameter. The black line represents the hard-sphere limit, the red line also includes a collision enhancement due to van der Waals forces based on the approach of (Sceats, 1989), while the red dashed line is based on the approach of (Fuchs and Sutugin, 1965). The red dotted line additionally includes charge-dipole interactions based on average-dipole-orientation theory. The blue lines show the enhancement factor of a single attractive force (charge-dipole interaction or van-der-Waals forces) compared to the hard-sphere limit. The measured size-dependency is shown in (b). The growth rates were inferred with two different methods, the appearance time method (GR_{app}) and the INSIDE method (GR_{INSIDE}). Growth rates are normalized to a sulphuric acid concentration of $10^7 cm^{-3}$. For the appearance time growth-rate results, the thick black line inside the boxes show the median of the results for a given size, the boxes indicate the 50% interquartile range of the data and the whiskers represent the 90% quantile. The red small errorbars indicate the -33%/+50% systematic uncertainty in the sulphuric acid measurement. Also shown are the modelled growth rates for the geometric hard-sphere kinetic limit (solid black line) or the collision enhanced growth rates according to Eq. (S9) (solid and dashed red line). The grey shaded area includes the systematic uncertainty due to the assumed hydration of vapour and particles.



465 **Figure 5: Increased global aerosol number concentrations due to the collision enhancement.** Results from a global modeling study of the present-day atmosphere. (a) shows the relative change in total aerosol number concentration (particles larger 3 nm) averaged over all longitudes in a vertical profile if a collision enhancement is considered in sulphuric acid growth. (b) shows the relative increase at 15 km altitude on a global scale where the effects are most significant. Higher relative changes would be expected also at lower altitudes, if the model is adjusted for ternary sulphuric acid-water-ammonia nucleation.