Enhanced growth rate of atmospheric particles from sulfuric acid

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40   **Abstract.** In the present-day atmosphere, sulfuric acid is the most important vapour for aerosol particle formation and initial growth. However, the growth rates of nanoparticles (<10 nm) from sulfuric 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 debate. Here we present precise growth-rate measurements of uncharged sulfuric 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 sulfuric acid

45   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 sulfuric acid, and reveal an enhancement resulting from dipole-induced dipole interactions between the vapour molecules and particles. We are able to disentangle the effect 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 sulfuric

50   acid particles increases predicted particle number concentrations in the upper free troposphere by more than 50%.

1 Introduction

Sulfuric acid (H_2SO_4) is the major atmospheric trace compound responsible for nucleation of aerosol particles in the present-day atmosphere (Dunne et al., 2016). Sulfuric 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),

55   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, sulfuric acid is likely of crucial importance (Kulmala et al., 2013). The newly formed particles need to grow rapidly in order to avoid scavenging by larger pre-existing aerosol and so to 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

60   atmospheric NPF, which is the major source of CCN (Gordon et al., 2017) and can also affect urban air quality (Guo et al., 2014).

The main pathway of cluster and particle growth is condensation of low volatility vapours, like sulfuric acid or oxidized organics (Stolzenburg et al., 2018). Nanoparticle growth rates depend mainly on the evaporation rates of the condensing

65   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 sulfuric 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 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;

70   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 sulfuric 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 hence also the magnitude of cluster coagulation remain unmeasured, although globally ammonia is much more important than amines due to its longer atmospheric lifetime. On the other hand, condensation at the kinetic limit is extremely sensitive to molecular and particle collision rates.

75   These can be subject to enhancement due to 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 than van-der-Waals forces, an enhancement due to Debye-type permanent dipole-induced dipole van-der-Waals forces might be more important at typical atmospheric ionization levels. A measurement of such a collision enhancement for neutral sulfuric acid molecules and particles for the free

80   molecular regime has not yet been presented, due to large uncertainties in determining growth rates at small sizes.

Here, we address the questions of sulfuric acid evaporation, cluster contribution and collision enhancement in sulfuric 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 infer the Hamaker constant for sulfuric acid particles, which

85   describes the magnitude of the collision enhancement due to attractive van-der-Waals forces (Hamaker, 1937) and show its global atmospheric impact by implementing the resulting growth parametrization in a global climate model (Walters et al., 2019) with detailed aerosol microphysics (Mann et al., 2010).

2 Results

We performed measurements of particle growth from sulfuric acid and ammonia in the 26.1 m³ stainless-steel CLOUD

90   chamber, at either +20 °C or +5°C with the relative humidity kept constant at either 38% or 60%. SO_2 (5 ppb), O_3 (~120 ppb) and ammonia (varied between 3 and 1000 pptv) were injected into the chamber and UV lights induced the formation of sulfuric acid (varied between 10^7 and 10^9 cm^{-3}) and subsequent particle formation. A typical experiment and the methodology on determining particle growth rates with the appearance time method are described in the Supplement and presented in Fig. S1.

2.1 Collision enhancement in sulfuric acid growth

95   Figure 1 shows the particle growth rates for two size-intervals (1.8-3.2 nm, Fig. 1a and 3.2-8 nm, Fig. 1b) versus the sulfuric 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 unmeasurable 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

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the lower size range for the growth-rate measurements (1.5-2.5 nm) in that study due to a different set of instrumentation. For smaller sizes and at low ammonia, sulfuric acid evaporation most likely still plays a role due to an increased Kelvin term. The

105   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 Figure 2. It demonstrates that, in the absence of gas-phase sulfuric acid, the loss rates of particles in the chamber are not affected by evaporation effects but are completely dominated by wall, dilution and coagulation losses. 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

110   is inferred from the sulfuric acid monomer decay. Any signs of evaporation of the sulfuric acid particles would have introduced another loss term. Moreover, the insignificant effect of ammonia on growth (Fig. 1) and the same high ratio (>100) between sulfuric acid monomer and dimer concentrations for all experiments, point towards a negligible clustering effect, which could have influenced our measured growth rates (Li and McMurry, 2018). Additionally, in Fig. S3 in the Supplement, we find excellent agreement with a recent modelling study, which includes a sulfuric acid/ammonia clustering and evaporation (Kürten,

115   2019).

Our growth-rate data provide a direct measurement of the condensational growth at the kinetic limit caused by sulfuric 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 based on bulk density (Nieminen et al., 2010). This is similar to Lehtipalo

120   et al. (2016) in the case when evaporation was suppressed by ammonia (see Fig. S2). We also observe the growth-rate enhancement for the larger size-range (Fig. 1b), which should be even less sensitive to evaporation effects. The faster growth rates might be due to an enhanced collision frequency which can be attributed to Debye-type van-der-Waals forces between the permanent sulfuric acid dipoles and induced dipoles on the particles. We therefore adjusted the condensation equations of Nieminen et al. (2010) with a kinetic collision frequency k_{coll} accounting for an enhancement due to van-der-Waals forces

125   (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. (S6)) to the measured growth-rate data. We find $A = (6.6 \pm 0.2 \, (stat.) \, {}^{+8.5}_{-4.2} \, (syst.)) \cdot 10^{-20}$ J ($\pm 1\sigma$ uncertainty) in excellent agreement with previous results (Chan and Mozurkewich, 2001; McMurry, 1980) but directly probing the collision enhancement in the free molecular regime. The systematic uncertainties are almost completely dominated by the uncertainty in the sulfuric acid

130   measurement, which is demonstrated in Fig. S4 in the Supplement.

An enhancement due to charge-dipole interactions between the polar sulfuric 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 difference between growth rates under neutral and galactic cosmic ray ionization levels. From average-dipole-orientation

135   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 barely influenced by the faster ion growth because at the representative galactic cosmic ray ionization levels (ion production rate: ~2-4 ion pairs cm^{-3} s^{-1}) and sulfuric acid concentrations in our experiments, most (more than 75%) of the growing particles are neutral in the investigated size-range (see Fig. 3). However, effects of ion condensation and charge-dipole enhancement might be stronger at lower sulfuric acid concentrations (Svensmark et al., 2017).

2.2 Size-dependency of sulfuric acid growth

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

Fig. 4b shows the measured size-dependence of all growth-rate measurements normalized to a sulfuric acid concentration of 10^7 cm^{-3}. In addition we also 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 systematic effects in the growth rate determination. The experimental results have a stronger than the predicted size-dependence from the hard-sphere limit, which can be explained by the collision enhancement due to van-der-Waals forces. Charge-dipole interactions are not considered here because the charged fraction of the growing particle population is small (Fig. 3) and charge effects only dominate below 2 nm (Fig. 4a).

An analytical approximation of the growth rates as given in Nieminen et al. (2010) is not possible for the more complex collision enhanced collision kernel. We therefore parametrize the size- and sulfuric acid dependency of growth rates from 2-100 nm and 278-293 K by the equation (maximum 8% discrepancy):

$$GR(nm\ h^{-1}) = \left[2.73 \cdot d_p(nm)^{-0.75} + 0.54\right] \cdot \left[H_2SO_4(cm^{-3}) \cdot 10^{-7}\right] \tag{1}$$

2.3 Global implications

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

sulfuric acid growth on a global scale, we use the atmosphere-only configuration of the United Kingdom Earth System Model (UKESM1) (Mulcahy et al., 2018; Walters et al., 2019) which includes the GLOMAP aerosol microphysics module describing

170 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 sulfuric-acid driven NPF. The importance of the nucleation process, and therefore the growth-rate enhancement, is lower at lower altitudes

175 and in the northern hemisphere, mainly due to the higher condensation sink and the restriction of the model to only sulfuric acid-water binary nucleation. However, the significant enhancement of sulfuric 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.

3 Discussion

180 Understanding nanoparticle growth driven by sulfuric 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 sulfuric 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). We demonstrate that for sizes larger than 2 nm this collision enhancement due to van-der-Waals forces between the permanent sulfuric acid dipoles

185 and induced dipoles on the growing particles is more important than dipole-charge interactions or base-stabilization by ammonia.

For smaller sizes, evaporation of sulfuric 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

190 significantly increased upper tropospheric aerosol concentrations, but due to the model limitations to binary sulfuric-acid water nucleation the global impact of van-der-Waals forces in nanoparticle growth might be even higher.

Our results should therefore be considered in future model development, especially when discussing the importance of changing sulfuric acid levels due to reduced anthropogenic emissions of SO_2. Moreover, our parametrization of pure sulfuric

195 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 sulfuric 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.

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

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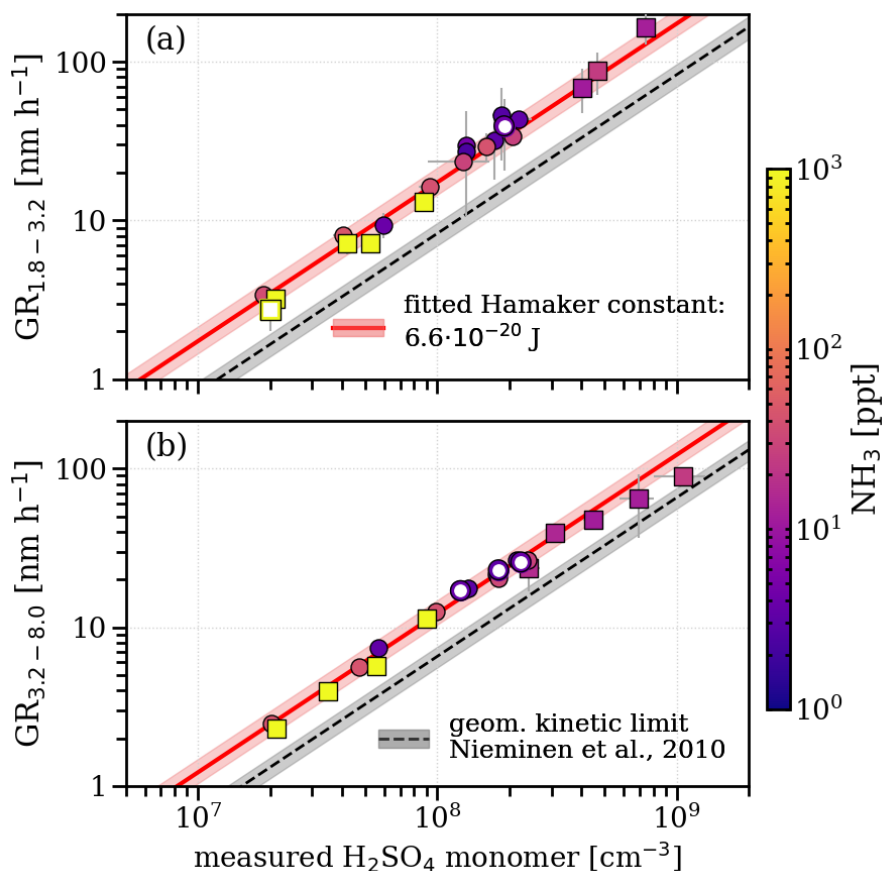290   under atmospheric conditions, P. Nat. Acad. Sci. USA, 111(42), 15019–15024, doi:10.1073/pnas.1404853111, 2014.

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Figure 1: Growth Rate Measurements. Growth rates of nanoparticles in two size-intervals versus measured gas-phase sulfuric acid monomer concentration. (a) shows growth rates for the size-interval between 1.8-3.2 nm, while (b) shows the growth rates for the size-interval 3.2-8.0 nm. The colour code represents the measured NH3 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 and the sulfuric acid measurement. The dashed black line and shaded grey area show the geometric limit of kinetic condensation and the corresponding systematic uncertainty interval based on uncertainties of the density and water content of the condensing cluster (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 London-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. The systematic uncertainty for the fit result (red area) is dominated by the systematic uncertainties of the sulfuric acid measurement (+50/-33 %, see Supplement).
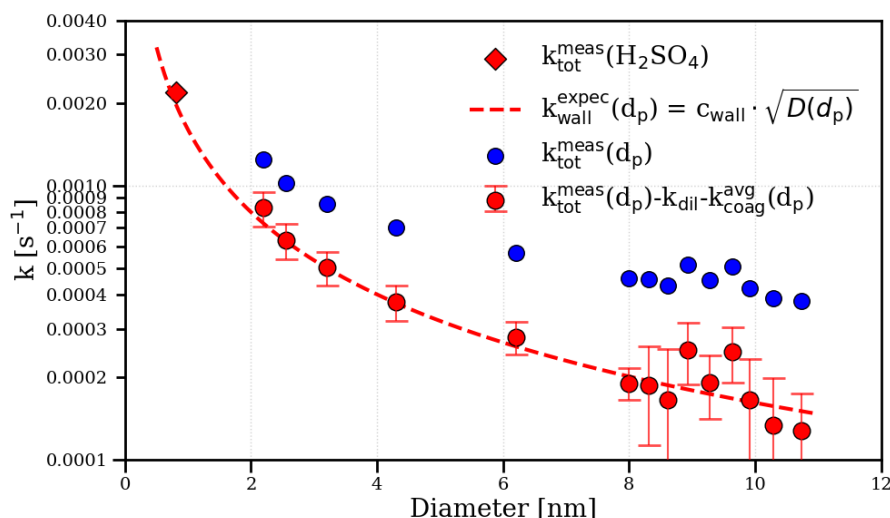
Figure 2: Measurement of zero sulfuric acid evaporation rates. Total loss rates of sulfuric acid and ammonia particles measured during a decay experiment (5°C, 60% relative humidity, 1000 pptv NH$_3$), by switching off the UV lights after a particle growth stage, which stops the production of sulfuric acid and subsequently nucleation and growth. After sulfuric acid is reduced to background level, the exponential decay of the remaining particles in the chamber is measured (k_{tot}^{meas}, blue circles). Decay of particles in the chamber is dominated by three loss mechanisms, wall loss, dilution loss and coagulation loss to other particles. Particle loss rates are corrected for an averaged coagulation loss during the decay (k_{coag}^{avg}) to all particles larger than d_p and for the dilution loss (k_{dil}, total chamber flow divided by total chamber volume) (red circles). They agree well with the expected wall loss rate $k_{wall}(d_p) = C_{wall} \cdot \sqrt{D_p(d_p)}$ (red dashed line) with $C_{wall} = 0.007$ s$^{-0.5}$ cm^{-1} inferred from an independent sulfuric acid decay experiment in the absence of a particle sink (red diamond). This indicates that there is no evaporation from the sulfuric acid particles above ca. 2 nm under the above mentioned experimental conditions, which would introduce another loss term and disturb the agreement of measured and expected decay rates. 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.
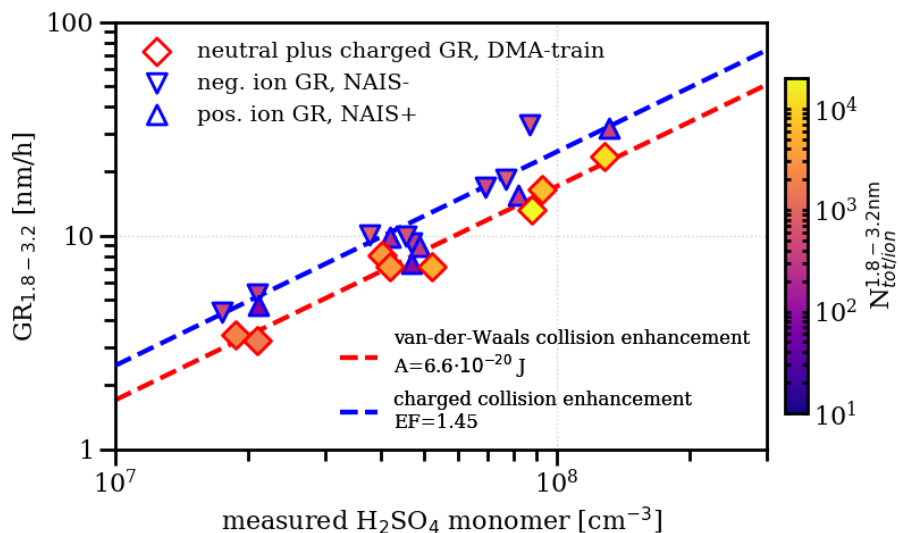
Figure 3: The effect of charge on growth. Measured growth rates of 1.8-3.2 nm particles and ions in experiments with ammonia above 10 pptv. The DMA-train measures both neutral and charged particles (diamonds with red contours) whereas the NAIS+/- (Manninen et al., 2009) measures purely charged particles (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 1.45 in this size range (blue dashed line), which is consistent with estimates from average dipole orientation theory for the mean diameter of 2.5 nm of our growth rate measurements (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 is between 5 and 25%. This is demonstrated by the colour code of the growth rate measurements 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 barely affected by the small earlier appearing charged fraction.
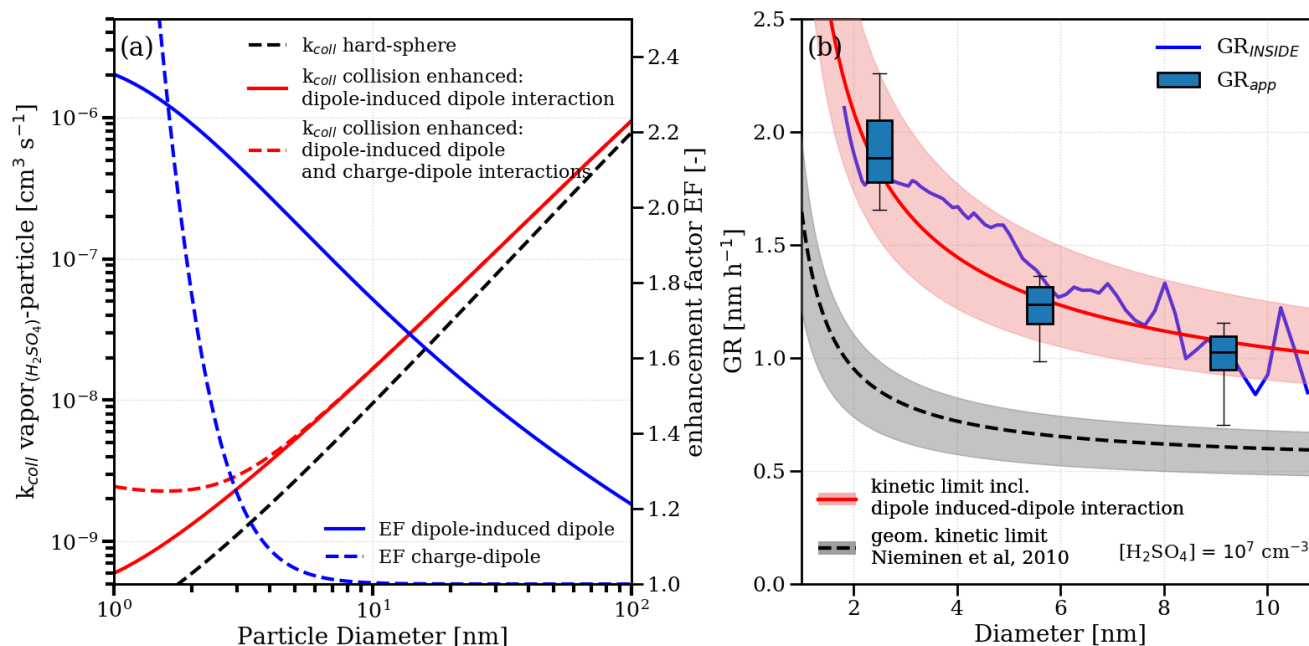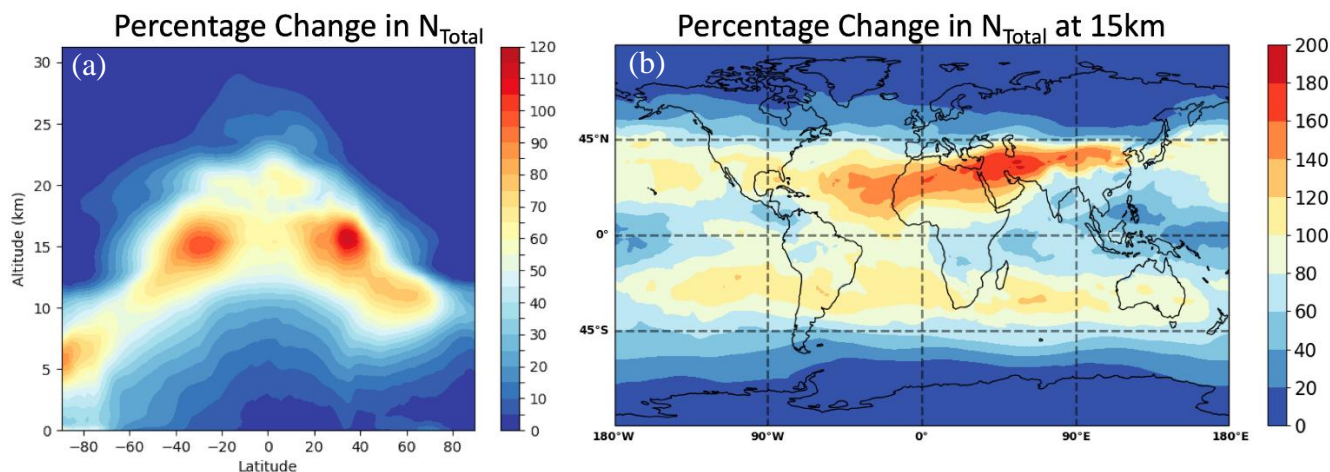
Figure 4: The size-dependency of sulfuric acid growth. Measured and modelled size-dependency of growth rates. (a) shows

415   the theoretical collision rate of sulfuric acid vapour molecules with particles of a certain size. The black dashed line represents

the hard-sphere limit based on bulk-density, the red solid line also includes a collision enhancement due to dipole-induced

dipole interactions (based on a Hamaker constant of $A=6.6 \cdot 10^{-20}$J), and the red dashed line also includes charge-dipole

interactions based on average-dipole-orientation theory, which agrees with our experiments. The blue lines show the

enhancement factor compared to the hard-sphere limit. The results for the enhancement due to van-der-Waals forces for the

420   free molecular regime (at 1 nm, i.e. E(∞) in Eq. (S3)) is very similar for this study (2.3) and the dimethylamine and sulfuric

acid case (2.3 (Kürten et al., 2014) or 2.7 (Lehtipalo et al., 2016)). 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}, blue

solid line), which accounts for coagulation and wall losses during the experiments. Growth rates are normalized to a sulfuric

acid concentration of 10^7 cm^{-3}. For the appearance time growth-rate results, the thick black line inside the boxes show the

425   median of all growth rate results for a given size, the boxes indicate the 50% interquartile range of the data and the whiskers

represent the 90% quantile. Modelled growth rates for the geometric hard-sphere kinetic limit or the collision enhanced growth

rates according to Eq. (S6) are calculated with a Hamaker constant of $A = 6.6 \cdot 10^{-20}$ J, $m_v = 142.5$ amu and $T = 278.15\ K$

are shown as dashed black line or red line, respectively. The corresponding systematic uncertainties are represented by the

coloured areas.

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430 **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 sulfuric 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 sulfuric acid-water-ammonia nucleation.