

Uptake of neutral polar vapor molecules by charged clusters/particles: Enhancement due to dipole-charge interaction

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[1] Recently proposed ion-mediated nucleation theory suggests that the enhanced uptake of neutral polar molecules by the charged clusters as a result of dipole-charge interaction may be critical to the nucleation of particles in the atmosphere. A rigorous parameterization of the enhancement effect of dipole-charge interaction on the growth of charged clusters is presented and the important parameters controlling this enhancement factors are explored. The interaction of polar gas molecules with charges significantly enhances the growth rate of small charged clusters/particles. Polar molecules with higher dipole moment and smaller molecular size have larger enhancement factor. The enhancement factor decreases with increasing particle size and is roughly inversely proportional to temperature when the charged particles are small. At T of 300 K, the enhancement factor reaches up to 10 for the uptake of sulfuric acid molecules by ions with diameter of ~ 0.5 nm but decreases quickly to 2 for uptake by a charged particle of ~ 2 nm in diameter. For the uptake by molecular ions, the enhancement factor can reach as high as 20 for water molecules in the mesopause and as high as 15 for sulfuric acid in the polar stratosphere. The enhancement factors for the uptake of water dimers by charged clusters are consistently higher (up to 20–25%) than the corresponding enhancement factors for monomers. The hydration of sulfuric acid molecules in the atmosphere may affect the enhancement factor and hence ion-mediated nucleation rate, which remains to be investigated. **INDEX TERMS:** 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0335 Atmospheric Composition and Structure: Ion chemistry of the atmosphere (2419, 2427); 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; **KEYWORDS:** dipole-charge interaction, enhanced growth rate, ion-mediated nucleation

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1. Introduction

[2] The fine particles in the atmosphere have received increasing attention due to their possible impacts on climate and health. However, the mechanisms controlling the formation of new particles from precursor gases in the atmosphere remain unclear. Ion-mediated nucleation (IMN) theory involving $\text{H}_2\text{SO}_4\text{-H}_2\text{O-Ion}$ [Yu and Turco, 2000, 2001; Yu, 2003] and ternary homogeneous nucleation (THN) theory involving $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ [e.g., Coffman and Hegg, 1995; Korhonen et al., 1999; Ball et al., 1999; Napari et al., 2002] are the two proposed theories which have been used to explain some nucleation events observed in the atmosphere. According to the IMN theory, the charged molecular clusters, formed around air ions, are much more stable and can grow significantly faster than corresponding neutral clusters as a result of electrical interactions, and thus can preferentially achieve stable, observable sizes [Yu and Turco, 2000, 2001]. In the past, researchers in various fields have alluded to ions as poten-

tial nucleation embryos [e.g., Mohnen, 1971; Castleman et al., 1978; Arnold, 1980b; Hamill et al., 1982; Raes et al., 1986; Hoppel et al., 1994; Makela et al., 1996; Nadykto, 2001]. Recent in-situ measurements of ion clusters with very large mass may provide evidence supporting the possible involvement of ions in aerosol formation [e.g., Hörrak et al., 1998; Eichkorn et al., 2002].

[3] The IMN theory, which considers enhanced growth rate and stability of ions/charged clusters to be critical to the formation of new particles in the atmosphere, is different from the classical ion-induced nucleation (IIN) theory reported in the literature [e.g., Hamill et al., 1982; Raes et al., 1986; Laakso et al., 2002]. The IIN theory modifies the free energy needed to form the critical embryo with the Thomson term to account for the electrostatic energy of the charged body, but does not consider the kinetic interactions among sub-critical clusters and microphysical effects related to the interaction of the condensable vapor molecules with electrical field of charged cluster. Recent observations indicate that the growth rates of sub-3 nm particles (estimated from the time delay in the appearance of the peak concentrations of H_2SO_4 gas and freshly nucleated 3–4 nm particles) are a factor 2–10 higher than that can be

Table 1. Dipole Moments, Polarizabilities, and Sizes of the Molecules Considered in This Study

	Dipole Moment l , Debye	Polarizability α , \AA^3	Molecule Radius r_m , nm
Sulfuric acid	2.84	6.2	0.274
Water	1.85	1.19	0.193
Ammonia	1.46	2.31	0.206
Acetaldehyde	2.72	4.6	0.284
Acetone	2.89	6.4	0.308
Formaldehyde	2.27	2.49	0.244
Phenol	1.45	11.19	0.290

accounted for by the condensation of H_2SO_4 together with H_2O and NH_3 [Weber *et al.*, 1996, 1997; Birmili *et al.*, 2003]. A factor of 2–10 higher growth rate of sub-3 nm particles inferred from the measurements is actually consistent with the IMN theory about the enhanced growth rate of charged clusters/particles [Yu and Turco, 2000; Yu, 2003]. Another explanation for the higher growth rate is the possible involvement of species other than H_2SO_4 , H_2O , NH_3 , and ions (such as some organic compounds) in the nucleation and condensation processes [e.g., Weber *et al.*, 1996, 1997; Birmili *et al.*, 2003].

[4] To properly study the dynamic interactions among polar gas molecules and clusters of both charged and neutral, Yu and Turco [2000, 2001] developed a kinetic model which simulates a size-resolved multicomponent aerosol system via a unified collisional mechanism involving both neutral and charged particles down to molecular sizes. The purpose of this study is to investigate the enhancement factors for the uptake of different neutral polar molecules by the charged particles of various sizes and the corresponding coagulation kernels needed for the explicit kinetic simulations of the particle formation. We will also discuss the dependences of the uptake enhancement factors on both individual properties of gas molecules (such as dipole moment and size) and ambient conditions such as gas temperature. The implications of the results to the particle formation and growth under a variety of atmospheric conditions (from lower troposphere to polar stratosphere to mesosphere) will be explored.

2. Polar Molecule-Charge Particle Interactions

[5] In order to calculate the collision cross section needed for the following derivation of the enhancement factors for uptake efficiency and construction of the coagulation kernels, we used a simple model [Landau and Lifshitz, 1976], which, however, accounts for the motion of the mass centre in the polar molecule-charged particle system neglected in Hoppel and Frick [1986]. In this model both the gas molecule and particle are approximated by rigid spheres and the value of the impact parameter is given by the following equation [Landau and Lifshitz, 1976; von Schilling, 1972]

$$b_c^2 = (r_p + r_m)^2 \left(1 - 2 \left(\frac{U(r_p + r_m)}{3kT} \right) \right) \quad (1)$$

where b_c is the impact parameter, r_p is the particle radius, r_m is the radius of the gas molecule, $U(r)$ is the potential energy of the interaction of the molecular dipole with the charged

particle, k is the Boltzman constant and T is the gas temperature. Similar approach has been applied by Sutherland, who derived, accounting for the intermolecular interaction, the well-known formula for the viscosity of gases that gives excellent agreement with the experimental data [Loeb, 1961]. The potential energy of the interaction $U(r)$ can be expressed [Loeb, 1961] as,

$$U(r) = -lE(r)L\left(\frac{lE(r)}{kT}\right) - \frac{\varepsilon_0\alpha E^2(r)}{2} \quad (2)$$

where l is the dipole moment of the gas molecules, $L(z) = \left[\frac{e^z + e^{-z}}{z} \right] - \frac{1}{z}$ is the Langevin function [Loeb, 1961], α is the polarizability, $E(r) = \left(\frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_p} \right) \frac{ie_0}{4\pi\varepsilon_0 r^2}$ is the electrical field of the charged particle, ε_g is the relative permittivity of the vapour, ε_p is the relative permittivity of the particle, ε_0 is the vacuum permittivity, e_0 is the elementary charge and i is the number of the elementary charges in the aerosol particle. Function $L\left(\frac{lE(r)}{kT}\right)$ describes the average value of $\cos\theta$, where θ is the angle between dipole and electrical field. The enhancement factor EF is defined as

$$EF = \left[\frac{b_c^2}{(b_c|_{U=0})^2} \right] \quad (3)$$

where $b_c|_{U=0}$ is the impact parameter in the absence of the dipole-charge interaction. By combining Equations (1)–(3) and rearranging the terms, we get the expression for the enhancement factor EF in the final form,

$$EF = 1 + \frac{2lE(r_p + r_m)L\left(\frac{lE(r_p + r_m)}{kT}\right) + \alpha\varepsilon_0 E^2(r_p + r_m)}{3kT} \quad (4)$$

[6] It is clear from equation (4) that EF depends on temperature, size of charged particles, and microphysical properties (dipole moment, polarizability, and size) of vapor molecules. From the well-known Fuchs' equation for Brownian coagulation [Fuchs, 1964], we obtain the coagulation kernel (K_{mp}) between polar molecules and charged particles in the free molecular regime,

$$K_{mp} = EF\pi(r_p + r_m)^2 C_{stick} \sqrt{\bar{V}_p^2 + \bar{V}_m^2} \quad (5)$$

Here \bar{V} is the mean thermal velocity with subscripts p and m referring to the particle and vapour molecule respectively. C_{stick} is the sticking coefficient [e.g., Yu and Turco, 2001]. With equations (4) and (5), we can obtain the interaction rates among neutral polar molecules/clusters and charged clusters/particles of various sizes under different atmospheric conditions. Such information is important to simulate kinetically the cluster growth and nucleation.

3. Results

[7] Calculations were performed using equations (4) and (5) for the following polar vapours nucleating: sulfuric acid, water, ammonia, acetone, acetaldehyde, formaldehyde, and phenol. The substances have been chosen in such a way as to represent not only so-called key substances for the

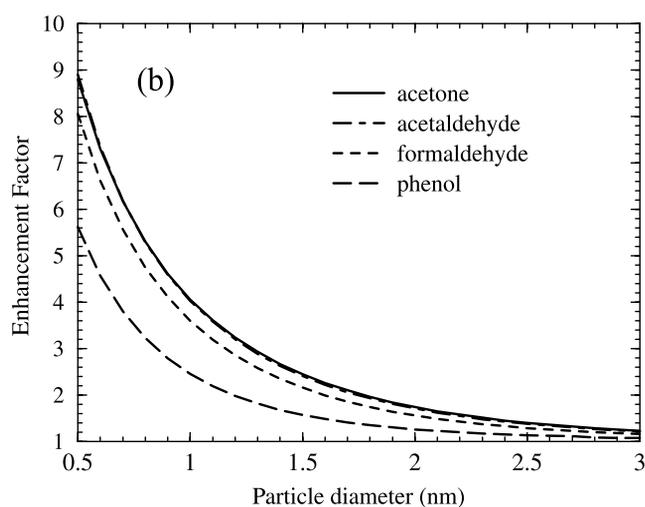
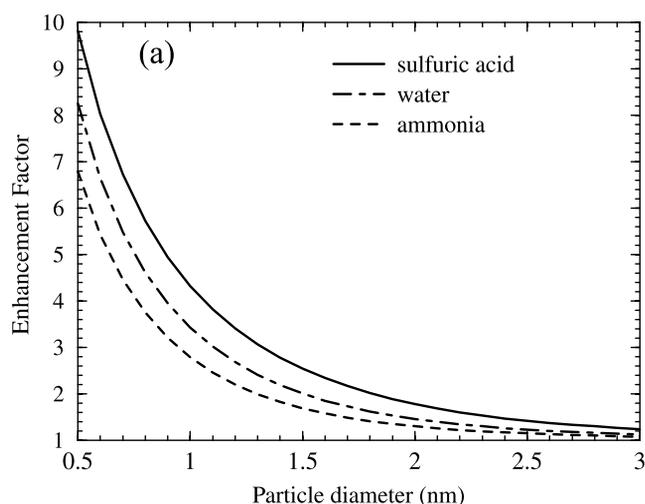


Figure 1. The enhancement factors for the uptake of (a) sulfuric acid, ammonia, water; (b) phenol, formaldehyde, acetaldehyde, and acetone by charged particles ($T=298$ K). See color version of this figure in the HTML.

atmospheric aerosol formation such as water, sulfuric acid and ammonia but also pollutants from different sources [Finlayson-Pitts and Pitts, 2000]. Values of dipole moments and polarizabilities adopted from CRC [2002] and equivalent sizes of the vapor molecules are given in Table 1. The equivalent molecular radius is calculated from the mass of the vapor molecule and the density of corresponding liquid at room temperature.

3.1. Enhancement Factors

[8] Figure 1 shows the comparison of the enhancement factors as a function of the particle diameter for (a) sulfuric acid, water, ammonia, and (b) acetone, acetaldehyde, formaldehyde, and phenol at the ambient gas temperature of 298 K. It is clear that significant enhancement of the uptake rates has been achieved for the entire group. The enhancement factors decrease quickly as the sizes of charged particles increase. The enhancement factor reaches up to 10 for uptake of sulfuric acid molecules by ions with diameter of ~ 0.5 nm but decreases quickly to 1.8 for uptake

by a charged particle with diameter of 2 nm. The biggest enhancement has been obtained for sulfuric acid, which has smaller dipole moment than that of the acetone but sulfuric acid molecule is smaller in size. Acetone and acetaldehyde have very close enhancement factor though acetone molecules has higher dipole moment but its size is also larger. The dipole moment of phenol and ammonia molecules is much smaller than other ones in the group; however, the enhancement for them is still significant when the sizes of charged particles are small ($< \sim 1.5$ nm). Effect of the polarizability, which consistently does not exceed 2%, may be neglected in all the cases studied here.

3.2. Coagulation Kernels (or Uptake Coefficients)

[9] It is helpful to compute the absolute values of coagulation kernels for polar molecules and ions/charged particles, which are important for kinetic calculations.

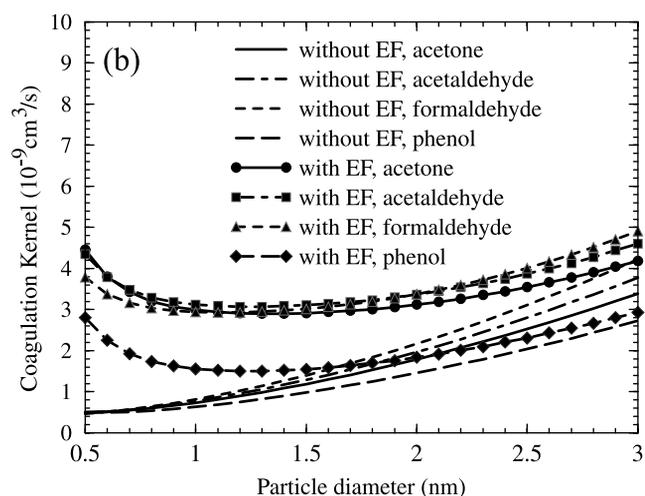
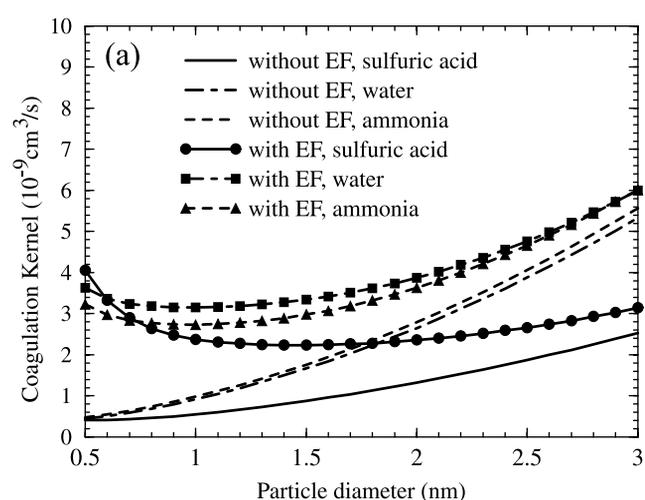


Figure 2. The coagulation kernels or collision rates of polar molecules with charged particles (curves with enhancement factor) and neutral particles (curves without enhancement factors). A unity sticking coefficient is assumed for all the curves which means that the shown values are the upper limits. See color version of this figure in the HTML.

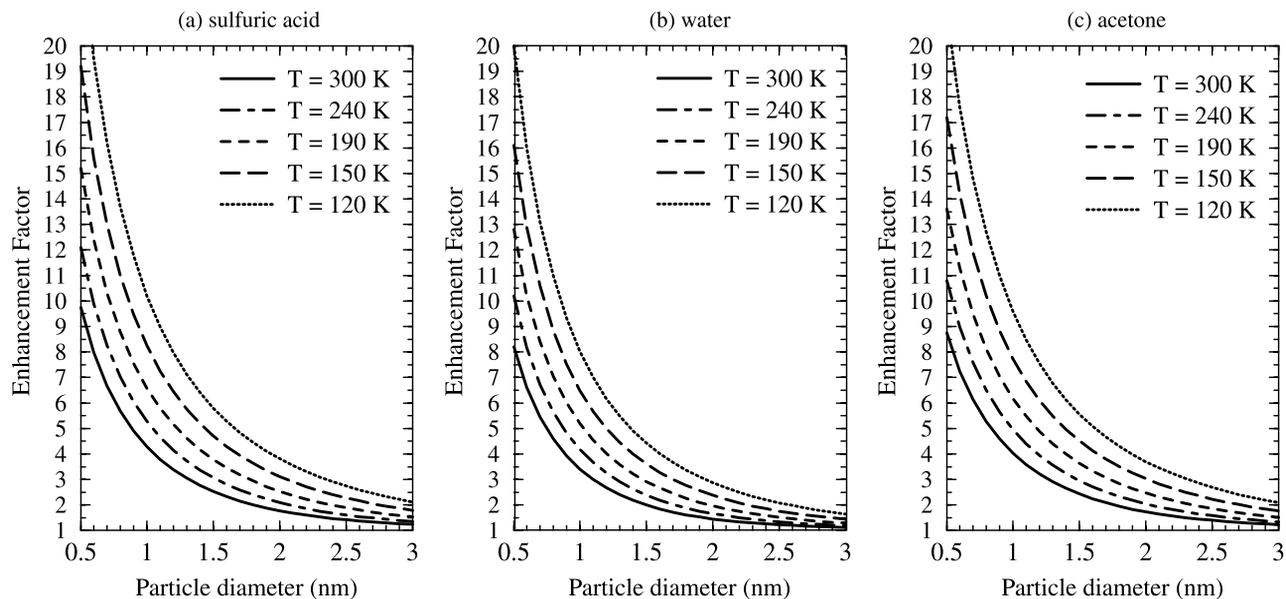


Figure 3. The effect of temperature on the enhancement factors for the uptake of (a) sulfuric acid, (b) water, and (c) acetone molecules by charged clusters/particles. See color version of this figure in the HTML.

Figure 2 presents the Brownian coagulation kernels K_{mp} calculated using Equation (5) with and without enhancement factors. The charged particles are assumed to have density of water. The curves without enhancement factors correspond to the collision rates between the polar molecules and neutral clusters/particles. A unity sticking coefficient is assumed for all the curves which means that the shown values are the upper limits. As the sizes of particles increase, the coagulation kernels of polar molecules with neutral particles (no enhancement) increase as a result of increasing collision cross section. For the uptake of polar molecules by charged particles when the enhancement factors (which decrease with increasing particle sizes) are taken into account, the uptake rates (or coagulation kernels) decrease slightly and then increase slowly as the sizes of charged particles increase.

[10] The collision rates of polar molecules with molecular ions (diameter $< \sim 0.7$ nm) are in the range of $1.8\text{--}4.5 \times 10^9$ cm^3/s , which are about a factor of 2–4 larger than the typical ion reaction rates of $1.0\text{--}2.5 \times 10^9$ cm^3/s measured in the laboratory. The difference is not surprising as the values shown in Figure 2 assume a unity sticking coefficient and do not consider the dissociation (or evaporation) of small ions/charged clusters while the measured reaction rates are overall rates. To account for the difference, Yu and Turco [2001] used a size-dependent sticking coefficient of less than unity for the collision of polar molecules with small ions. The sticking coefficients for the collision of polar molecules with small neutral clusters are likely much smaller than that of polar molecules with small charged clusters. Therefore the differences between the uptake rates of polar molecules by neutral particles and by charged particles are likely much bigger than that shown in Figure 2.

3.3. Effect of Temperature

[11] Both air ions and polar molecules (for example, water molecules) exist ubiquitously in the atmosphere from

Earth's surface to mesosphere. The temperature in the atmosphere varies widely. In the low troposphere, temperatures can reach over 300 K. Temperature can drop to 180 K in the polar stratosphere and as low as 120 K in the mesopause, where polar stratospheric clouds (PSCs) and noctilucent clouds have been observed respectively. While the possible effects of ions on aerosol and cloud microphysics in polar stratosphere are unknown, many studies and observations suggest that the uptake of water molecules by ions might be one of the main mechanisms leading to the formation of noctilucent clouds [e.g., Arnold, 1980a; Sugiyama, 1994]. It would be useful to look into the effect of temperature on the uptake enhancement factor.

[12] Figure 3 shows the enhancement factors for the uptake of sulfuric acid, water, and acetone molecules by charged clusters/particles at 5 different temperatures. Ion clusters containing H_2SO_4 are known to exist both in the troposphere and in the stratosphere, and recent measurements indicate that ions containing acetone are abundant in the upper troposphere [Arnold *et al.*, 1997]. It is clear from Figure 3 that enhancement factors increase as temperatures decrease. Actually, the enhancement factor is roughly inversely proportional to temperature when the sizes of charged particles are small. Thus the charge enhancement effect for uptake of polar molecules by charged clusters/particles is much significant in the mesopause and polar stratosphere than in the lower troposphere. The enhancement factor can be as high as 20 for water molecules in the mesopause ($T = 120$ K) and as high as 15 for sulfuric acid in the polar stratosphere ($T = 190$ K). One has to take into account the effect of temperature on the uptake enhancement factor when investigating the role of ions in the formation of small particles in the upper troposphere, polar stratosphere and mesosphere.

[13] Since very few data are available about the dependence of dipole moment, polarizability, and size of the vapour molecules on temperature, we assume these molec-

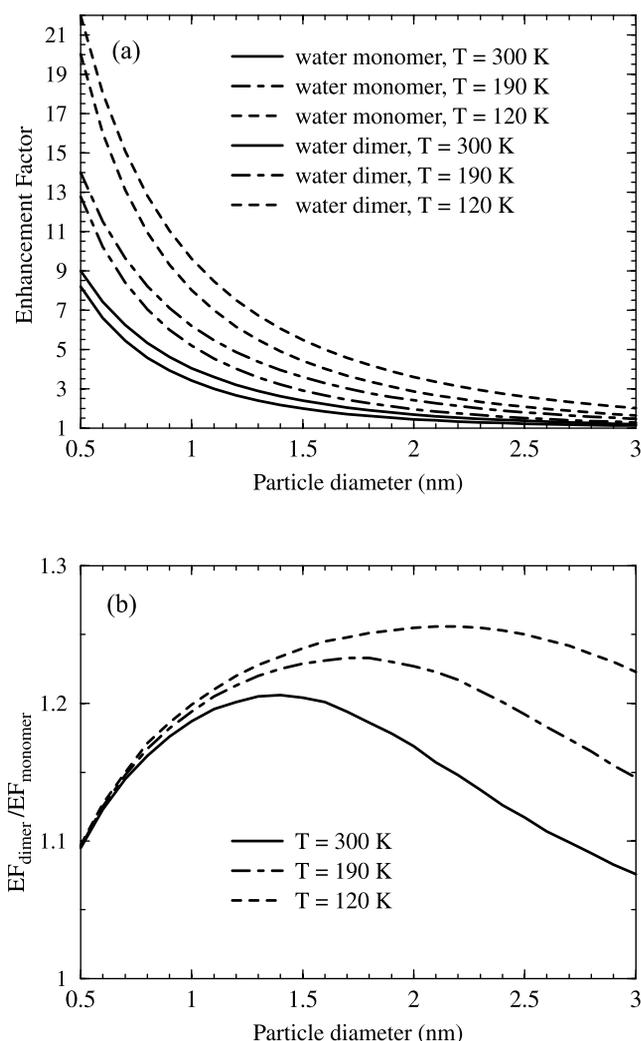


Figure 4. (a) Enhancement factors for both water monomer and dimer, (b) the ratios of enhancement factors for water dimer to that for water monomer at $T = 300$ K, 190 K, and 120 K. See color version of this figure in the HTML.

ular properties to be constant in above calculation. However, one has to keep in mind that, generally, dipole moment and polarizability increase and size of the vapour molecules decreases as the temperature decreases [Gubskaya and Kusalik, 2002], and thus the actual effect of temperature can be bigger than that shown in Figure 3.

3.4. Effect of Dipole Moment and Size of Polar Molecules

[14] We have shown in Figure 1 that different vapour molecules have different dipole moment and size, which result in different enhancement factor. The dipole moment and size of same vapor molecules may also change on one hand due to the changes in temperature [Gubskaya and Kusalik, 2002] and on the other hand due to the formation of clusters (dimers, trimers, etc.). For example, the dipole moment of water dimer was measured to be 2.6 Debye [Dyke et al., 1977], which is $\sim 40\%$ higher than that of water monomer. The equivalent radius of water dimer is $\sim 26\%$ larger than that of water monomer. Compared to that of water monomer, the higher dipole moment of water dimer

will increase the enhancement factor, however, the larger size of dimer will reduce the enhancement factor. Figure 4 shows (a) the enhancement factors for both water monomer and dimer at $T = 300$ K, 190 K, and 120 K, (b) the ratios of enhancement factors for water dimer to that of water monomer. The enhancement factors for the uptake of water dimers by charged clusters are consistently higher than the corresponding enhancement factors for monomers. The differences depend on the sizes of the charged particles, and are bigger at lower temperature. The maximum difference can reach up to 25% at $T = 120$ K and 20% at $T = 300$ K.

[15] Since most of sulfuric acid molecules are likely to be hydrated in the atmosphere [Jaeger-Voirol and Mirabel, 1989; Noppel, 1998] and some of hydrates (probably monohydrate and particularly bihydrate [Ding et al., 2003]) are highly polar, it is important to understand how the hydration of sulfuric acid molecule will affect its dipole moment and equivalent size, and, consequently, the uptake rates by ions/charged clusters. While the equivalent size of hydrated sulfuric acid molecules can be readily calculated, the dipole moment of the hydrated sulphuric acid molecules is currently not available. Here we do a simple sensitivity calculation to see how sensitive is the enhancement factor to dipole moment and size of vapor molecules.

[16] Figure 5 presents the enhancement of the uptake coefficient as a function of particle sizes at five different values of (a) dipole moment and (b) size of condensing molecules/clusters. The properties of sulfuric acid molecules are assumed for the baseline case ($l = 2.84$ Debye, $r_m = 0.274$ nm), and the variations in dipole moment and size can be considered as a result of clustering or hydration. While understanding that dipole moment and size are likely to change simultaneously due to hydration or clustering of polar molecules, for simplicity we fix one of the two parameters to study the effect of the change in the other parameter on enhancement factor. The enhancement factors depend strongly on the dipole moment and the size of condensing molecules (or clusters). While the enhancement factor increases as the dipole moment increases (Figure 5a), it decreases as the size of condensing molecules increases (Figure 5b). The net effect of hydration on the enhancement factor depends on the relative changes in dipole moment and equivalent size. Since the uptake of sulfuric acid molecules by ions/charged clusters may be critical to formation of new particles in the atmosphere, it is important to understand how the hydration will affect the uptake rates.

4. Summary and Discussion

[17] Ion-mediated nucleation theory involving H_2SO_4 - H_2O -Ion [Yu and Turco, 2000] is one of theories recently proposed to explain the observed formation of ultrafine particles in the atmosphere. According to the theory, the charged molecular clusters/particles may have great growth advantage over corresponding neutral clusters as a result of electrical interactions of polar molecules with charges. In this paper, the microphysics of electrical interactions of neutral polar molecules of condensable vapor with the charged clusters is considered and the enhancement effect of dipole-charge interaction on the uptake of vapor molecules by the charged clusters/particles and its dependence

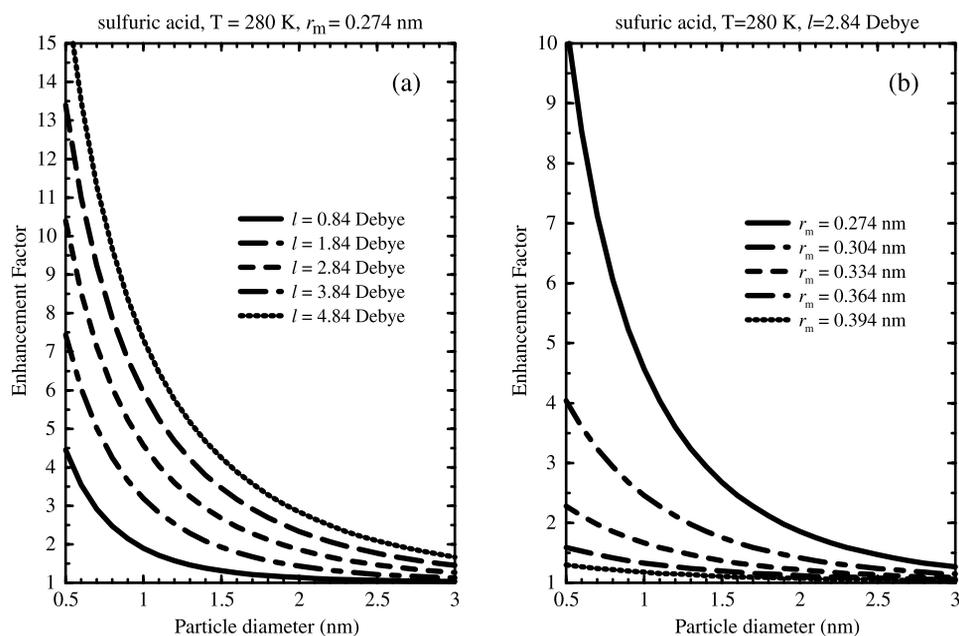


Figure 5. The enhancement factors as a function of particle sizes at five different values of (a) dipole moment and (b) size of condensing molecules/clusters. The properties of sulfuric acid molecules are assumed for the baseline case ($l = 2.84$ Debye, $r_m = 0.274$ nm). See color version of this figure in the HTML.

on various parameters are investigated. On the basis of the analytical expression derived, we calculate the enhancement factor of the uptake rates of common polar gas molecules on charged particles of various sizes and the corresponding coagulation kernels needed for the explicit kinetic simulations of the particle formation. The considered polar gas molecules include several key substances for the atmospheric aerosol formation such as water, sulfuric acid and ammonia and some organic species from different sources such as acetaldehyde, acetone, phenol, and formaldehyde. We have also studied the dependence of enhancement factors on the size of the particle, the ambient gas temperature and such microscopic properties of condensable vapor molecules as size and dipole moment.

[18] The interaction of the charges with polar gas molecules significantly enhances the growth rate of small charged clusters/particles. The enhancement factor decreases with increasing particle size. Among the species considered in this study, sulfuric acid has the biggest enhancement. At temperature of 300 K, the enhancement factor reaches up to 10 for uptake of sulfuric acid molecules by ions with diameter of ~ 0.5 nm but decreases quickly to around 2 for uptake by a charged particle with diameter of 2 nm. The enhancement factor is bigger at lower temperatures. For example, the enhancement factor can reach up to 20 for water molecules in the mesopause ($T = 120$ K) and up to 15 for sulfuric acid in the polar stratosphere ($T = 190$ K). Thus it is important to consider the effect of temperature on the uptake enhancement factor when investigating the role of ions in the formation of small particles in the upper troposphere, polar stratosphere and mesosphere.

[19] The enhancement factors depend strongly on the dipole moment and the size of condensing molecules (or clusters). The clustering among neutral polar molecules will

change both the size and dipole moment of the neutral cluster. While the enhancement factor increases as the dipole moment increases, it decreases significantly as the size of condensing molecule/cluster increases. The enhancement factors for the uptake of water dimers by charged clusters are consistently higher (up to 20–25%) than the corresponding enhancement factors for monomers. Since sulfuric acid molecules play an important role in the formation of atmospheric particles and most of sulfuric acid molecules are likely to be hydrated in the atmosphere, it is important to understand the difference in the uptake enhancement factor between hydrated and non-hydrated sulfuric acid molecules. The information on the dipole moment of the hydrated sulfuric acid molecules is needed to calculate the net effect of sulfuric acid hydration on the enhancement factor.

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