A Review of Aerosol Nanoparticle Formation from Ions[†]

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Abstract

Ion-induced nucleation (IIN) mechanism has been widely accepted as an efficient source of new particle formation in the middle and upper troposphere. However, there have been debates on its contribution to the nucleation events observed in the boundary layer. To reveal the current understanding of IINs, we here summarise investigations on microphysical mechanisms of aerosol formation from ions, i.e., ion induced homogeneous nucleation (HN). The basic formation steps of ion-induced HN include primary ion production, charged cluster formation from ions, and stable nanoparticle formation from clusters. Two essential controlling processes (ion generation and formation of condensable species) are emphasized in the viewpoint of plasma performance for three case studies, i.e., galactic cosmic ray travelling in the troposphere, lightning discharges, and charging processes by aerosol chargers. The first two cases result in IINs due to the simultaneous generation of ions and condensable species (such as H₂SO₄ and oxidized organic vapours) from oxidizing trace atmospheric molecules. The third case leads to ion-induced clustering or nucleation in aerosol chargers. Due to a relatively short residence time in chargers (normally less than 1 minute), big charged clusters often exist in the outgoing aerosol flows.

Keywords: ion-induced nucleation, charged clusters, plasmas, lightning, cosmic rays, chargers

1. Introduction

Aerosol nucleation events, frequently observed in many regions of the troposphere (Kulmala et al., 2004; Kulmala et al., 2013; Deshpande et al., 2014), may significantly influence the earth's climate (Kazil et al., 2010; Koren et al., 2012; Makkonen et al., 2012) by causing a net cooling and leading to numerous small cloud droplets, which makes cloud brighter and extends their lifetimes (Solomon, 2007; Nicoll and Harrison, 2014; Yu and Luo, 2014). This nucleation via gas-to-particle conversion, called as homogeneous nucleation (HN), is the largest source of atmospheric aerosol particles (Kulmala et al., 2004), providing up to half of global cloud condensation nuclei (Merikanto et al., 2009; Yu and Luo, 2009). Therefore HN is critical to achieve a clear physical understanding for improving our prognostic capability of aerosol influences on climate (Kerminen et al., 2012; Riccobono et al., 2014).

HN is a complex process of forming aerosol particles (solid or liquid particles) from gas-phase species, originating from both natural (such as volcano and plant emissions) and anthropogenic (such as industrial and vehicle

emissions) sources. Prevailing HN theories include binary homogeneous nucleation (BHN, e.g., H₂SO₄-H₂O) (Harrington and Kreidenweis, 1998; Kulmala et al., 1998; Vehkamäki et al., 2002; Yu, 2008; Sipilä et al., 2010) and ternary homogeneous nucleation (THN, e.g., H₂SO₄-NH₃-H₂O) (Ball et al., 1999; Kulmala et al., 2000; Merikanto et al., 2007). BHN, the nucleation mechanism primarily used in global aerosol models (Vehkamäki et al., 2002), has been widely used to explain aerosol formation in the upper troposphere, due to there's enhanced solar radiation, high relative humidity, and low aerosol surface area (Brock et al., 1995; Weber et al., 1996). In the middle and lower troposphere, especially in the boundary layer, aerosol nucleation rates have been frequently observed to be much higher than that predicted by classical BHN (Weber et al., 1996; Clarke et al., 1998; Weber et al., 2001; Vehkamäki et al., 2002). This discrepancy has led to the explanation by using THN (Marti et al., 1997; Kulmala et al., 2000), whose nucleation rate is much higher than the BHN rate due to ammonia stabilizing the critical embryos. However, the tertiary compound has not been determined, such as that amines strongly enhance nucleation rates already in low pptv range (Chen et al., 2012; Almeida et al., 2013), and oxidation products of biogenic organics at atmospheric concentrations can reproduce particle nucleation rates (Riccobono et al., 2014). Recently experimental researches suggest that the THN of including amines or biogenic organics to stabilize the sulfuric

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acid clusters can successfully explain the dominant nucleation way in the boundary layer (Chen et al., 2012; Almeida et al., 2013; Riccobono et al., 2014).

The ion-induced nucleation (IIN) (Yu and Turco, 2000, 2001), which predicts that the presence of ions can enhance the formation of aerosol particles, have also been developed to explain the high nucleation rate in the boundary layer. Recent studies (Hanson and Lovejoy, 2006; Yu, 2007; Yu and Turco, 2008) have further updated parameters in IIN such as the bounding energetics of H_2SO_4 (Lovejoy et al., 2004) and revealed that the updated IIN model can not only predict new particle formation in the colder upper troposphere (Lucas and Akimoto, 2006), but also in the warmer lower troposphere including the boundary layer (Yu and Turco, 2008; Yu, 2010). This model has been confirmed in some conditions of chamber experiments such as low nucleation rates and high ion concentrations (Almeida et al., 2013; Riccobono et al., 2014).

Although significant progress has been achieved for understanding nucleation phenomena over last decade or so, there are still uncertainties on dominant nucleation mechanism in the lower troposphere.

1.1 Debate between IIN and NCN

A lively discussion on the dominant nucleation pathway in the lower atmospheric layer is the relative importance of IIN versus neutral cluster nucleation (NCN) under various atmospheric conditions. The argumentation is mainly among results from the direct charged aerosol ratio measurement of freshly nucleated particles in atmospheric observations (Iida et al., 2006; Kulmala, 2007; Kulmala et

al., 2010), predicted results from the IIN simulations (Yu and Turco, 2008; Yu et al., 2008; Yu and Turco, 2011), and results from laboratory experiments (Enghoff et al., 2008; Kirkby et al., 2011; Almeida et al., 2013; Riccobono et al., 2014).

Table 1 lists some main supporting evidences for the debate between IIN and NCN. In a series of studies, NCN has been claimed to be identified as the main nucleation pathway, with only a small contribution of about 10 % or less from IIN in a boreal forest (Kulmala et al., 2007; Laakso et al., 2007; Manninen et al., 2009; Gagne et al., 2010; Kulmala et al., 2010; Kulmala et al., 2013). By contrast, a different conclusion has been made by using a different analytical methodology to the same atmospheric data, with IIN to be clearly dominant (Yu and Turco, 2008; Yu et al., 2008; Yu, 2010; Yu and Turco, 2011). Furthermore, recently several laboratory experimental results have simulated the IIN and NCN processes in the upper and lower troposphere, especially in the boundary layer (Kirkby et al., 2011; Chen et al., 2012; Almeida et al., 2013; Riccobono et al., 2014). The relative importance of IIN versus NCN under different atmospheric conditions remains unresolved.

1.2 Laboratory experiments on the role of IIN

To address the long-standing controversy, recent CLOUD experiments in CERN (under well controlled laboratory conditions) have been performed to reveal the role of IIN and NCN in atmospheric condition (Kirkby et al., 2011; Almeida et al., 2013; Riccobono et al., 2014). Their results show that ion-induced BHN of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$

Table 1 Evidence comparison for the two most likely mechanism candidates of ion-induced nucleation (IIN) and neutral cluster nucleation (NCN) in the lower atmosphere

	Ion-induced nucleation	Neutral cluster nucleation
Atmospheric observations:	<p>(i) Ions have been confirmed to participate in many boundary layer nucleation events (Hirsikko et al., 2007; Laakso et al., 2007; Tammet, 2009; Manninen et al., 2010).</p> <p>(ii) Observational parameters in 6-typical nucleation events in the boreal forests have been reproduced by IIN model (Yu and Turco, 2008; Yu, 2010).</p>	<p>(i) Field measurements taken in the boreal forests suggest that the contribution of IIN is about 10 % or less of the total nucleation events (Kulmala et al., 2010; Kulmala et al., 2013) and less than 5 % during summertime events in Boulder (Iida et al., 2006).</p> <p>(ii) Estimated nucleation rates ($\sim 1\text{--}10^3$ numbers$\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$) in the polluted boundary layer (e.g., Atlanta and Mexico city) were often much greater than typical ion production rates ($\sim 2\text{--}30$ numbers$\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$) (Chen et al., 2012).</p>
Laboratory experiments:	<p>(i) An increase in ionization by a factor of 10 increases the production rate of stable clusters by a factor of about 3 in chamber experiments (Enghoff et al., 2008).</p> <p>(ii) Ions increase the nucleation rate by an additional factor of between 2 and more than 10 at ground galactic-cosmic-ray level in the Cloud experiments (Kirkby et al., 2011).</p>	<p>(i) The role of amines in particle formation was examined in Minnesota laboratory chamber and suggested that amines enhanced sulfuric acid NCN rates (Chen et al., 2012; Titcombe, 2012).</p> <p>(ii) Sufficient nucleation rate in the Cloud experiment can be explained by a base-stabilization mechanism involving $\text{H}_2\text{SO}_4\text{-dimethylamine}$ pairs, with small influence from galactic-cosmic-rays (Almeida et al., 2013).</p>

nucleation proceeds at a significant rate in cool temperatures (such as in the middle troposphere) at atmospheric concentrations of H_2SO_4 , but may be unimportant when ternary vapor concentrations are high (such as in the boundary layer) (Kirkby et al., 2011). Comparing to neutral BHN, the nucleation rate of ion-induced BHN can be enhanced roughly two times at 292 K with ground level galactic-cosmic-rays. However, both rates from the neutral and ion-induced BHNs are too low to explain the nucleation rate in the boundary layer, especially in the polluted regions (Chen et al., 2012).

To explain the high nucleation rate in the boundary layer, further experimental results reveal that a base-stabilization mechanism involving pairs or H_2SO_4 -dimethylamine and H_2SO_4 -oxidation products of biogenic compounds, strongly decreasing evaporation, can provide high enough nucleation rate in the boundary layer (Almeida et al., 2013; Riccobono et al., 2014). The high nucleation rate in the boundary layer is highly sensitive to the trace amine and organic vapor (or other highly oxidized organic species) levels, which are more tightly bound than with ammonia for H_2SO_4 . However, in most of the atmospheric conditions, the nucleation is limited by the concentration of H_2SO_4 and not that of amine and organic vapors. Concentrations of H_2SO_4 and oxidized organic vapors highly depend on $\cdot\text{OH}$ radical level, because it accounts for the oxidation both of organics to oxidation products and of SO_2 to H_2SO_4 (Riccobono et al., 2014). These Cloud experimental results suggest that IIN can be significant when (i) the associated neutral particles have appreciable evaporation, and (ii) the overall nucleation rates are low (lower than about $0.1 \text{ numbers}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$) and below the ion-pair production rate (around $2 \text{ numbers}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$) (Reiter, 1992).

For the polluted regions, such as in the ambient conditions of cities, a kinetic model based on a sequence of acid-base reactions (including efficient stabilization of the acids by a tertiary compound such as amines) has been proposed to explain the high nucleation rates without involving ions (Chen et al., 2012). Laboratory chamber studies in the University of Minnesota and ambient measurements in Atlanta and Mexico City have shown a reasonable agreement of predicted nucleation rates (Stolzenburg et al., 2005; Iida et al., 2008; Smith et al., 2008; Chen et al., 2012; Kuang et al., 2012; Titcombe, 2012).

Suggestions from the overlap between laboratory experiments and atmospheric observations in diverse locations are briefly summarized in **Fig. 1**. The schematic shows the main nucleation pathways in the troposphere: (i) IIN in the upper and middle troposphere, (ii) IIN (most reports believed in IIN) or THN in free troposphere, and (iii) IIN or THN (most reports believed in THN) in the boundary layer, where acid-base chemical reaction model

can explain nucleation events in polluted regions.

A clear physical understanding of nucleation processes is critical in explaining nucleation events and assessing the influences of aerosols on climate. The precise mechanism of IIN, as one of the most likely candidates for field observations, is still unclear (Svensmark et al., 2007).

2. How do ions induce aerosol formation in the atmosphere?

Lots of efforts to model HN basic processes have focused on simulating the dynamics of a nucleating aerosol particle growing through condensation and coagulation (McMurry, 1983; Lehtinen and Kulmala, 2003; Korhonen et al., 2004; Kulmala et al., 2004; Gaydos et al., 2005; McMurry et al., 2005; Yu, 2006; Kuang et al., 2010; Yu and Turco, 2011; Kulmala et al., 2013). Here we present a brief analysis for the “development process”, growing from sub-1 nm ions to stable aerosol particles and partially to cloud droplets ($\sim 10\text{--}20 \mu\text{m}$).

2.1 Development process of nucleation from ions

Fig. 2 shows the schematic illustration of development process for IIN from a negative ion ($<0.36 \text{ nm}$, one molecule in mass diameter) to a stable heavy aerosol particle ($> 22 \text{ nm}$). The process for originating from a positive ion would be similar (Yu and Turco, 2011). The new particle formation in the atmosphere is a dynamic process involving various interactions between precursor gas molecules (including primary ions), clusters (including charged and neutral ones), and aerosol particles (including pre-existing ones) (Horrak et al., 2000).

The initial primary ions (or atmospheric ions near ground), concentrations of about several hundreds to thousands up to $5000 \text{ numbers}\cdot\text{cm}^{-3}$ in the boundary layers (Dhanorkar and Kamra, 1993; Aplin and Harrison, 2000; Vartiainen et al., 2007), are continuously generated by galactic cosmic rays at the rate of about $4 \text{ numbers}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$ at ground level and up to $40\text{--}60 \text{ numbers}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$ in the upper troposphere (Thomas, 1974; Reiter, 1992; Volland, 1995). Below approximately 80 km, primary ions are mainly lost by the recombination between positive and negative ions (including electrons) with rate constant of about $5 \text{ to } 8 \times 10^{-8} \text{ numbers}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$ (Smith et al., 1981). In the boundary layer, other ion loss processes are attachment both onto aerosol particles (i.e., aerosol charging process) and onto the ground.

The initial primary ions quickly react with common trace air constituents such as H_2O , H_2SO_4 , HNO_3 , NH_3 and organic species to form more stable ions such as HSO_4^- , called as small cluster ions with mass diameter in range $0.36\text{--}0.85 \text{ nm}$ (Horrak et al., 2000). The following

Fig. 1 Schematic of aerosol formation in the troposphere. The red words on the left denote the nucleation pathways including binary homogeneous nucleation (BHN) and ternary homogeneous nucleation (THN), according to the atmospheric observations and simulation analysis (Yu and Luo, 2009; Kirkby et al., 2011; Chen et al., 2012; Almeida et al., 2013; Riccobono et al., 2014). Heterogeneous nucleation commonly occurs in cases where there are pre-existing nuclei present of high concentration (McMurry, 1983; McMurry et al., 2005; Kuang et al., 2010), such as in the top of anthropogenic emission sources. Organic compounds and iodine oxides emitted from trees and marine are thought to participate in aerosol nucleation and growth (Riccobono et al., 2014).

big cluster ions with mass diameter in range 0.85–1.6 nm would be typical in the troposphere (Luts and Salm, 1994; Volland, 1995; Beig and Brasseur, 2000; Eichkorn et al., 2002; Harrison and Tammet, 2008):

where n and m are small integers (about 5–7 for water molecule in hydrated proton ions), and OM denotes organic matters (such as CH_3CO and CH_3CN). The size and mobility distributions of these big cluster ions (0.85–1.6 nm) depend on the minor contaminants present in the atmosphere. Commonly, their lifetime in the lower atmosphere is about one minute (Rosen and Hofmann, 1981). Most cluster ions will be lost through condensation to pre-existing aerosol particles (McMurry et al., 2005; Kuang et al., 2010) or recombination with ambient ions.

Small aerosol particles will be formed when the cluster ions can successfully continue their growth. This is

known as ion-induced homogeneous nucleation or IIN for simplification (Yu and Turco, 2001; Yu, 2006; Yu and Turco, 2011). The formed particles encounter further small ambient ions, and will be neutralized or recharged on timescales of minutes (Harrison and Tammet, 2008) by collisions (a proposed charging mechanism by collisions can be seen in **Fig. 3**) (Pahtz et al., 2010) or ion attachments.

HN is commonly considered to form a “critical nucleus” firstly, and then grows to a larger size (Kulmala et al., 2000; Sipila et al., 2010; Zhang, 2010; Kulmala et al., 2013). Commonly, the lifetime of clusters (0.36–1.6 nm) is extremely short (a few or ten minutes) (Tammet et al., 2014), and only a few can reach the critical size to form aerosol particles. Classical nucleation theory reveals that when the critical nucleus forms, the free energy of the nucleating cluster reaches a maximum, called as “the nucleation barrier”, beyond which the formed small aerosol

Fig. 2 Schematic illustration of the IIN kinetic processes for aerosol formation from a negative ion (as an example). The terminal aerosol particle can be negatively and positively charged, and can also be *neutralized* (see Fig. 3). The nucleation is processing in the atmosphere, where concentration of ambient ions is about several hundreds or thousands of numbers·cm⁻³. Particles larger than 1.6 nm in mass diameter are defined as aerosol particles according to their physical nature, while smaller ones are called as clusters or primary ions (Tammet, 1995; Horrak et al., 2000; Ehn et al., 2010). Clusters and aerosol particles are easy to be charged or neutralized due to the kinetic processes evolve in the quasi-electroneutrality environment with high charge concentrations (Vartiainen et al., 2007). Condensable species can condense onto clusters and aerosol particles, but also can evaporate from their surfaces. Thus the kinetic processes include condensation, evaporation, coagulation, charging, and neutralized reactions (NR), and recombination (Yu and Turco, 2011). A small fraction of freshly formed particles, mostly lost through scavenging by pre-existing aerosol particles (McMurry, 1983; McMurry et al., 2005; Kuang et al., 2010), will grow to cloud condensation nuclei (~ 50–100 nm diameter) and further become cloud droplet (~10–20 μm) (Dusek et al., 2006; Kuang et al., 2009; Westervelt et al., 2013).

particle growth become spontaneous (Zhang, 2010; Zhang et al., 2012). This critical diameter can be calculated and predicted to be about 1.6 nm at standard atmospheric condition, detail of the calculation as shown in other reviews such as Harrison R.G. and Tammet H. (2008). This diameter has been identified in the atmosphere observations (Sipila et al., 2010). Thus the small clusters (0.36–0.85 nm), too small to overcome the nucleation barrier (Mcgraw and Zhang, 2008), need continually growth to big clusters (0.85–1.6 nm), and then become stable aerosol particles, whose molecules of more than hundreds are held together by noncovalent van der Waals interactions (Castleman and Bowen, 1996; Zhang et al., 2012).

The above discussion on the development process is mainly for nucleation and growth, however, loss of clusters and aerosol particles onto the pre-existing aerosol surfaces should also be noted, especially in polluted atmospheric boundary layer. An aerosol population balance model, considering the ratio of the particle scavenging loss rate to the particle growth rate, has been developed to determine whether or not aerosol nucleation would occur in diverse conditions since 1983 (McMurry, 1983; McMurry et al.,

2005; Kuang et al., 2010; Kuang et al., 2012). The model proposes that aerosol nucleation events in the boundary layer can occur and be suppressed when the ratio is lower and higher than 0.7, respectively (McMurry et al., 2005; Kuang et al., 2010).

2.2 Two essential controlling processes

Generations of ions and condensable species are the two key controlling processes for IIN in the atmosphere. Generation of ions, the origin of the subsequent formed clusters and further aerosol particles, is an apparent key progress. We will mainly focus on generation of condensable species from atmospheric trace gas molecules. The clustering and condensable species are often trace gas molecules in the atmosphere, such as H₂SO₄, HNO₃, NH₃, amines, and oxidized organic vapors. These molecules have large dipoles and hydrogen atoms connected with electronegative atoms (such as N, S, and O). Their electrostatic properties and hydrogen-bonding interactions have been recognized to play a significant role in HN (Zhang et al., 2012). These species also commonly have

Fig. 3 Schematic illustration for the proposed charging and neutralizing mechanism of colliding particles in a local electric field. The local electric field is denoted as E_0 , which is ubiquitous in the atmosphere, especially in the free troposphere (Carslaw et al., 2002). The black bold arrow denotes the direction of particle movements, while the colors denote the polarity of charges on particles. For simplification, the polarized charge is assumed to be one unit charge. Initially a pair of particles polarized by an external electric field collides to neutralize adjoining hemispheres. Once separated, the particles again become polarized by the external field. In this way, initially neutral ((a) and (b)) but polarized particles gain one unit of charge following every collision. The charged ones with opposite polarities collide and lose their charges (i.e., recombination process). Adapted from Pahtz et al. (2010).

very low vapor pressure at typically atmospheric temperatures, especially H_2SO_4 , whose vapor pressure is further reduced in the presence of H_2O (Ayers et al., 1980; Marti et al., 1997; Sipila et al., 2010). H_2SO_4 is therefore considered to be a key precursor for atmospheric HN (Weber et al., 1996; Kuang et al., 2008; Riccobono et al., 2014). Its value higher than $10^5 \text{ numbers}\cdot\text{cm}^{-3}$ (commonly $10^6\text{--}10^8 \text{ numbers}\cdot\text{cm}^{-3}$) (Nadykto and Yu, 2007; Zhao et al., 2009) has been identified to be necessary condition for HN in the atmosphere (Niemininen et al., 2009). Thus the key process for IIN is the generation of such high concentrations of condensable species.

The condensable species should be efficiently produced, since they can rapidly (within about one hour in typical atmosphere conditions) condense onto pre-existing aerosol particles as heterogeneous nucleation (see Fig. 1), especially in the polluted boundary layers (Kuang et al., 2010; Chen et al., 2012). Thus geographical regions of low concentration aerosol particles are the most favorable locations for HN, such as in the boreal coniferous forest in Helsinki, Finland. The cold upper troposphere also tends to be a region for new particle formation and growth due to relatively lower surface area of pre-existing aerosol particles and low ambient temperature (Heitmann and Arnold, 1983; Lee et al., 2003). In the boundary layer, where HNs are strongly suppressed by both primary aero-

sol emissions and entrainment of particles nucleated in the free troposphere (Merikanto et al., 2009; Kuang et al., 2010), however, sometimes HN can still occur as an “aerosol burst”, a brief period of rapid production and growth lasting a few hours, such as in the polluted Beijing (Yue et al., 2011), Mexico City (Iida et al., 2008; Smith et al., 2008), and Atlanta (Stolzenburg et al., 2005; Kuang et al., 2010; Kuang et al., 2012). During aerosol bursts, as shown in Jiang et al. (2011c), the clusters measured by the cluster chemical ionization mass spectrometer (Zhao et al., 2010) overlapping in size with the smallest nano condensation nuclei (Jiang et al., 2011b) have provided valuable new information about the mechanism of neutral nucleation and growth.

The detailed for the importance of producing condensable species has been given in other reviews (Arnold, 2008; Zhang et al., 2012), and case discussions will be presented in the next section, based on the two essential controlling processes.

2.3 Charged ratio of nucleated aerosol particles

Information on the electric charge distribution carried by the nucleating clusters is one key for identifying the relative contributions of neutral and ion-induced processes. Fortunately, measurements of the charged states

or fractions of ambient freshly nucleated and undergoing particles have been available to help resolve the main pathway of aerosol nucleation in the past several years (Kuang et al., 2012). Some studies (see **Table 1**) basing on the atmospheric observations have concluded that the overall contribution of IIN to the atmospheric aerosol formation is typically much less than 10 % (Kulmala et al., 2007; Kulmala et al., 2010) and less than 5 % during summertime events in Boulder (Iida et al., 2006). Responding to the direct measurement results of the low charged ratios, some simulation studies have explained by assuming that IIN aerosol particles neutralized and collided during growth and movement in the environment with ambient ions (Yu and Turco, 2011).

Figs. 2 and 3 show the complex processes for charging and neutralization reactions in the atmosphere, which is actually a quasi “plasma environment” with non-negligible concentration of ions and reactive species (Rycroft and Harrison, 2012). Ion-ion recombination has been considered as an important channel for IIN (see **Fig. 2** and **Fig. 3(c)**) (Turco et al., 1998; Yu and Turco, 2008). The importance of IIN will be systematically underestimated if all neutral sub-2 nm particles are attributed to a purely NCN. Due to these complex evolution processes, it is difficult to make interpretation for the origin of aerosol particles and assessing the role of IIN directly. However, the size dependent evolution of freshly formed aerosol particles can carry the electrical signature of the nucleation pathway (Gagne et al., 2010; Yu and Turco, 2011). By considering complex interactions among ions, molecular clusters of various sizes and charges, vapor molecules, and pre-existing aerosol particles, the relatively low charged ratios of atmospheric observations from state-of-the-art multi-instrument field measurements have been explained in a recent IIN simulation (Yu and Turco, 2011).

A precise estimation for the contribution of IIN is difficult from directly analyzing observational data in the atmosphere. While evidence for the effect of IIN is accumulating, the exact mechanism is still not known and more research is required to understand and quantify this effect (Enghoff and Svensmark, 2008; Riccobono et al., 2014).

3. Ion-induced aerosol formation in three most common cases

The most important trace gas for aerosol nucleation has been thought to be H_2SO_4 (sometimes including amine, ammonia, or oxidized organic vapors) (Weber et al., 1996; Chen et al., 2012; Riccobono et al., 2014). These condensable species are favorable to condense onto the pre-existing aerosol surfaces, especially in the polluted regions (Kuang et al., 2010). Their pre-existing concentrations are

generally too low to drive nucleation and subsequent growth for a nucleation event in the lower atmosphere if they cannot be efficiently generated in local regions. Ion generation should be together with generation of condensable species for IIN (see **Fig. 4**).

Fig. 4 shows the schematic illustration for the general nucleation process including ion generation and the induced generation of condensable species. Input energy (such as cosmic rays and lightning) can create a plasma region, which contains reactive radical species, electromagnetic radiation, and ions. These plasma species further react with trace gas molecules in the atmosphere to generate condensable species, such as H_2SO_4 , HNO_3 , and oxidized organic vapors. These locally generated species and ions, or stabilized by tertiary species such as amine and NH_3 , can continue clustering and nucleation.

Basing on the above discussion on the basic processes and the two essential controlling processes, we will briefly review three common IIN cases, i.e., cosmic rays,

Fig. 4 Schematic illustration for the nucleation process including ion generation and induced generation of condensable species in the case of low pre-existing aerosol concentration. The energy input on air results in a local plasma region containing electromagnetic radiation, reactive radicals, and primary ions. The radiation and radicals can induce the oxidation-reduction reactions with trace gas molecules such as organics, SO_2 , and NO_x to be oxidized into condensable species such as oxidized organics (e.g., organic acids), H_2SO_4 , and HNO_3 . The generated primary ions react with the oxidation products to form cluster ions, sometimes stabilized by tertiary species such as amine and NH_3 (Chen et al., 2012; Riccobono et al., 2014), and then further grow to aerosol particles by the generated condensable species, following the kinetic processes for aerosol formation in **Fig. 2**. A small fraction of these formed aerosol particles can even grow to cloud droplets, and contribute to the cloud formation.

lightning, and aerosol charger. The first two cases are always linked with the kinetic process of cloud formations and evolutions (Kirkby, 2007), while the third one resulting in nano-scale clusters is a frequently encountered problem for aerosol measurements (Jiang et al., 2011b; Steiner and Reischl, 2012).

3.1 Cosmic ray-induced nucleation

Intensive studies have been conducted on the correlations between cosmic rays and cloud formation. Excellent reviews have also been published (Carslaw et al., 2002; Kirkby, 2007; Bazilevskaya et al., 2008; Williams and Mareev, 2014). It has been proposed and confirmed that the Earth's climate could be affected by changes in cloudiness caused by variations in the intensity of galactic cosmic rays (Nicoll and Harrison, 2010; Harrison et al., 2011; Rycroft and Harrison, 2012; Bennett and Harrison, 2013). Two microphysical mechanisms have been proposed to explain how cosmic rays could affect clouds: i.e., (i) presence of ions from cosmic rays enhances the production of cloud condensation nuclei (Yu and Turco, 2001; Yu et al., 2008), and (ii) influence of cosmic rays on the global electric current flowing between the atmosphere and the ground surface affects ice nucleation and other cloud microphysical processes (Tinsley, 2000; Harrison and Carslaw, 2003; Harrison et al., 2011). In the second mechanism, the current flowing in the global circuit is generated by disturbed weather such as lightning (Rycroft and Harrison, 2012), which will be briefly reviewed in the next subsection. Corresponding to the first mechanism, here we only briefly describe the basic process for cosmic ray-induced nucleation, since this topic is rather complicated and still unclear.

Cosmic rays contain the lowest energies ($\sim 10^7$ – 10^{10} eV), mainly attributed to solar cosmic rays, intermediate energies ($\sim 10^{10}$ – 10^{15} eV) of galactic cosmic rays, and the highest energies ($> \sim 10^{15}$ eV) of extragalactic cosmic rays. The low energy rays are deflected by the Earth's and Sun's magnetic fields, while only high energy rays ($> \sim 1$ GeV) can enter the Earth's atmosphere. When primary cosmic ray particles (about 90 % are protons) (Beringer, 2012) enter the atmosphere, collision with air molecules (nuclear collision) produces a cascade of lighter particles and leads to a number of chemical reactions, a so-called air shower (see Fig. 5).

Cosmic ray is an ionizing radiation with sufficient energy to knock electrons out of atoms or molecules, and produces Cherenkov radiation during secondary particles' travelling. A plasma region is actually produced by the shower particles. In the air shower, the generated photon radiations of high energy and reactive radicals have high potentials to effectively oxidize atmospheric trace species, such as organics, SO_2 , and NO_x (Harris et al., 2013;

Schobesberger et al., 2013). Some of these oxidized trace species turn out to be condensable species. Most of the condensable species will condense onto pre-existing aerosol particles such as in the top region of aerosol sources, and result in their growth (McMurry et al., 2005; Ehn et al., 2014). However, cosmic rays can lead to the aerosol formation, especially in the middle and upper troposphere (Kirkby et al., 2011). Although no direct connection between cosmic rays and aerosol nucleation was reported (Kulmala et al., 2010), the above basic analysis indicates that the air shower of cosmic rays contributes to the formation of global cloud condensation nuclei (Yu et al., 2008; Kirkby et al., 2011).

3.2 Lightning-induced nucleation and oxidation: a natural way to clean our sky

Lightning is one of the most impressive and commonly-experienced geophysical phenomenon. The current related researches have mainly focused on thunderstorm electrification and lightning formation as meteorological phenomena (Paluch and Sartor, 1973a, b; Bazilian and Raizer, 2000; Williams, 2005; Williams and Mareev, 2014). The electrification of cumulonimbus clouds has been proposed to be charged by three mechanisms, i.e., (i) diffusion of air ions to attach onto cloud droplets (Millikan R.A., 1911), (ii) polarization (similar as Fig. 3) (Frenkel J., 1944), and (iii) convective motion (Gish and Wait, 1950). In general, the collisions between cloud droplets transfer negative charge to larger particles, which then separate gravitationally to produce intense large-scale electric dipoles, carrying negative charge downwards and positive charge upwards (Kirkby, 2007). The lightning occurring in cloud-to-ground is the main pathway for the carried charges to transfer between clouds and ground (see Fig. 6). Lots of interesting works have been done on the lightning activities and its contribution to the global atmospheric electric circuit operation. Excellent reviews on this topic have also been reported (Kirkby, 2007; Rycroft and Harrison, 2012; Rakov, 2013; Williams and Mareev, 2014). However, the most basic questions of how lightning is initiated, how it then propagates for many tens of kilometers, and what's effects on atmospheric aerosol particles have only begun to be addressed (Pawar et al., 2011; Dwyer and Uman, 2014). The following discussion is some like a hypothesized process due to rare reports on the direct observation of lightning-induced nucleation.

Fig. 6 shows a schematic illustration for a simplified lightning process and its-induced nucleation and oxidation reactions. The example shows a descending lightning with negatively-charged leaders outgrowing from a cloud toward the ground, though active lightning can be very complicated (Stolzenburg and Marshall, 2008). The elec-

Fig. 5 Schematic illustration for cosmic rays-induced aerosol formation via generating ions and condensable species. Primary cosmic rays interact with air molecules in the atmosphere to create secondary particles, including γ -rays, leptons (such as muons), and hadrons (such as proton and mesons). These secondary particles continue to collide with air molecules to produce a cascade of lighter particles and decay to stable particles such as protons and electrons, thereby producing “primary ions”. Ion-pair production rates are about $2 \text{ numbers} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$ at ground level, $10 \text{ numbers} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$ at 5 km altitude, and $20\text{--}50 \text{ numbers} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$ at 15 km altitude (Volland, 1995). Secondary particles can travel faster than the speed of light in air with causing “Cherenkov radiation”, which can effectively oxidize the atmospheric trace species, such as organics, SO_2 , and NO_x . Thus cosmic rays can induce nucleation by simultaneously generating ions and condensable species. However, IIN is very hard to occur if the concentration of pre-existing aerosol particles is very high to consume almost all the generated condensable species (Memurry et al., 2005).

tric fields of these leader heads are the source of the runaway electrons that produce ultra-violet radiation (Dwyer et al., 2005). When the leader header contacts their induced electron avalanches (Li et al., 2011), current and luminosity waves transfer through the leader channel. These self-sustained processes complete the leader step process (Dwyer and Uman, 2014). Regions of surrounding leader heads and ionization channels are filled with generated ions (including electrons) and reactive radicals with high concentrations. These species can effectively oxidize atmospheric trace gases such as organics, SO_2 , and NO_x . Since the initiation and dissipation stage of lightning is under some IIN favorable atmospheric conditions, like low temperature, high relative humidity, high ion production rate, and sometimes low concentration of pre-existing aerosol particles (such as after a heavy rain-fall) (Pawar et al., 2011). These generated condensable

species and primary ions can result in further condensation to droplets or IINs, depending on the pre-existing aerosol concentration, or even both processes occur simultaneously.

As discussed above, the lightning may serve as an effective and natural way to oxidize and remove atmospheric trace gases such as organics, SO_2 , and NO_x . The condensation and nucleated species will be scavenged to the ground by rains and removed from the sky. Thus lightning is a natural way to clean our sky through induced oxidation, condensation, and nucleation.

3.3 Aerosol charger-induced clustering and nucleation: a limitation for nanoparticle sizing

Charging of nanoparticles by aerosol chargers is an important process in aerosol particle sizing and electrical

mobility analysis (Jiang et al., 2011a; Jiang et al., 2014). The objective of aerosol chargers (also called as neutralizers) is to impose a known stationary state charge distribution on incoming aerosol particles. Charging efficiency of nano-scale aerosol particles (especially for diameter between sub-1 nm and 3 nm) is the major limitation for their accurate measurements (McMurry, 2000; Jiang et al., 2011b; Kulmala et al., 2012), which are required to understand these particles' property and dynamics (Intra and Tippayawong, 2011). The precise determination of these small particles is especially important for fundamental investigations of nucleation and subsequently growth in the atmosphere (Winkler et al., 2008).

these ionization sources emit energetic particles, such as α , electrons, and photons, to generate plasmas. The plasmas contain ions, electrons, light radiation, and reactive radicals (such as $\cdot\text{O}$ and $\cdot\text{OH}$). In addition to charging the incoming aerosols with electrons and ions, the radiation and radicals can oxidize trace components (such as SO_2 and organics) of the incoming gases, and further induce the formation of charged clusters (possible neutral clusters in partially) or aerosol particles, which partially condense onto the incoming aerosol particles and partially survive a long time in the downstream of the aerosol flows (see **Fig. 7**). The condensation may change the size and property of the incoming aerosol particles. The survival clusters and nucleated aerosol particles can cause an error in aerosol nanoparticle counting by using a differential mobility analyzer (Winklmayr et al., 1990; Romay et al., 1994; Yun et al., 2009; Jiang et al., 2011b), while the condensation onto the incoming aerosol particles can cause an error in analyzing aerosol size distribution and property.

The ion-induced clustering in the chargers has been investigated in cases of corona based charger (Romy et al., 1994), radioactivity based ^{241}Am charger (Luts et al., 2011; Steiner and Reischl, 2012; Steiner et al., 2014), and soft X-ray photoionization based charger (Yun et al., 2009). Though not reported, in principle induced cluster-

Fig. 7 Schematic illustration for possible mechanism of charger-induced clustering and nucleation processes in aerosol chargers with different ionization sources such as corona discharges, surface-discharge micro-plasmas, radioactive sources, UV-light radiations, and soft X-ray sources. Energetic particles (such as α , electrons, or photons) emitted from ionization sources generate plasmas inside charger chambers. The plasmas can induce complex kinetic processes (see Fig. 4). The trace components (such as organics and SO_2) of the incoming gases can be oxidized by light radiation and reactive radicals to be condensable species, which can form charged clusters (and possible neutral ones). Since the residence time in the charger is always much shorter (commonly less than 1 minute) than the stable aerosol formation time (~ 1 h or more time) in direct atmospheric observations (Spracklen et al., 2008; Kulmala et al., 2013). The formed clusters partially condense onto the incoming aerosol particles, and partially survive for a long time in the downstream. The ratio of the survived clusters depends on the residence time (Yun et al., 2009) and pre-existing aerosol concentration (Kuang et al., 2010).

ing or nucleation may also occur in surface-discharge micro-plasma based chargers.

As an example, Fig. 8 shows a typical induced-clustering effect of a laboratory soft X-ray charger (model 3087, TSI Inc.). The incoming ambient air (summer in Beijing) was filtered by a high efficiency particulate air (HEPA) filter. There were no aerosol particles and clusters observed at the outlet of the charger when soft X-ray was turned off. However, cluster ions (both positive and negative ones) with mass diameters between 0.36–1.6 nm (see Fig. 2) existed in the outgoing gas of the charger when soft X-ray was turned on. The result is consistent with the kinetic processes of generating charged clusters, as shown in Fig. 7. The clustering effect is sensitive to the residence time and concentration of the aerosol particles in the neutralizers (Yun et al., 2009). However, basing on the clustering and nucleation effect, the charger is a ready-made instrument for investigating IIN in atmospheric condi-

tions, such as a simulated system of $\text{SO}_2/\text{H}_2\text{O}/\text{N}_2$ gas mixture irradiated by soft X-ray (Munir et al., 2010, 2013).

The charger-induced clustering or nucleation is an obstacle for nanoparticle sizing, especially for analyzing sub-2 nm aerosol particles and for sizing aerosols in flue gases which often contain relatively high concentration of trace gas species. This effect results in challenges for charging ultrafine particles and for monitoring the new particle formation process in the ambient air.

4. Summary

The kinetic processes of ion-induced clustering and aerosol formation are briefly reviewed in the viewpoint of plasma physics. The current debates on the IIN contribution to nucleation events observed in the lower tro-

Fig. 8 Size distribution functions of air ions measured with the half-mini differential mobility analyzer (De La Mora and Kozlowski, 2013) at a 40:1 sheath-to-aerosol flow ratio. Following Larriba et al. (2011), mobility diameter was converted to mass diameter by reducing 0.3 nm. The result is showed in the case of ambient air (filtered by a HEPA filter) overpassing the soft X-ray neutralizer (model 3087, TSI Inc.). Aerosol particles and clusters in the incoming gas were removed by the HEPA filter. The incoming air contains SO_2 of $\sim 30 \mu\text{g}/\text{m}^3$ and NO_2 of $\sim 12 \mu\text{g}/\text{m}^3$ with the relative humidity of 16 % and the temperature of 21 °C. Size distribution of air ions suggests that the neutralizer produces ion clusters in its chamber.

posphere are comparatively described. Simultaneous generations of ions and condensable species are emphasized as the essential processes of nucleation and clustering in addition to relatively low pre-existing aerosol concentration. While considering these essential processes, IIN for three most-encountered ion sources, i.e., cosmic rays, lightning discharges, and aerosol chargers, are discussed. The first two ion sources are ubiquitous in the atmosphere. They are often linked with cloud formations and movements and global climate. The third one is a common ion source mostly used in aerosol studies. The charger-induced clustering (or nucleation) leads to challenges for charging ultrafine particles and monitoring new particle formation events in the atmosphere.

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