REPORT SERIES IN AEROSOL SCIENCE
N:o 178 (2015)

Extending fundamental knowledge on aerosol formation by measuring sub–3 nm ions and particles

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Academic dissertation

*To be presented, with the permission of the Faculty of Science of
the University of Helsinki, for public criticism in Chemicum auditorium A110,
A. I. Virtasen aukio 1, on December 4th, 2015, at noon.*

Helsinki 2015

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Extending fundamental knowledge on aerosol formation by measuring sub–3 nm ions and particles

Alessandro Franchin
University of Helsinki, 2015

Abstract

This thesis focuses on the experimental characterization of secondary atmospheric nanoparticles and ions during their formation. This work was developed in two distinct and complementary levels: a scientific level, aimed to advance the understanding of particle formation and a more technical level, dedicated to instrument development and characterization.

Understanding and characterizing aerosol formation, is important, as formation of aerosol particles from precursor gases is one of the main sources of atmospheric aerosols. Elucidating how aerosol formation proceeds in detail is critical to better quantify aerosol contribution to the Earth's radiation budget.

Experimentally characterizing the first steps of aerosol formation is the key to understanding this phenomenon. Developing and characterizing suitable instrumentation to measure clusters and ions in the sub–3 nm range, where aerosol formation starts, is necessary to clarify the processes that lead to aerosol formation.

This thesis presents the results of a series of experimental studies of sub–3 nm aerosol particles and ions. It also shows the results of the technical characterization and instrument development that were made in the process.

Specifically, we describe three scientific results achieved from chamber experiments. Firstly the relative contributions of sulfuric acid, ammonia and ions in nucleation processes was quantified experimentally, supporting that sulfuric acid alone cannot explain atmospheric observation of nucleation rates. Secondly, the chemical composition of cluster ions was directly measured for a ternary system, where sulfuric acid, ammonia and water were the condensable vapors. In these measurements we observed a decreasing acidity of the clusters with increasing concentration of gas phase ammonia, with the ratio of sulfuric–acid/ammonia staying closer to that of ammonium bisulfate than to that of ammonium sulfate. Finally, in a series of chamber experiments the ion–ion recombination coefficient was quantified at different conditions. The ion–ion recombination coefficient is a basic physical quantity for modeling ion induced and ion mediated nucleation. We observed a steep increase in the ion–ion recombination coefficient with decreasing temperatures and with decreasing relative humidity.

This thesis also reviews technical results of: 1) laboratory verification, characterization and testing of different aerosol and ion instruments measuring in the sub–3 nm range; 2) the development of new inlets for such instruments to improve the detection of sub-3 nm particles and ions.

Acknowledgements

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List of publications

This thesis consists of an introductory review followed by 6 research publications. In the introduction these publications are referred to by the following numbers. Paper I is reprinted with permission from the publisher, and all other papers are under the Creative Commons Attribution License.

I   Kirkby, J., J. Curtius, J. Almeida, E. Dunne, J. Duplissy, S. Ehrhart, A. Franchin, S. Gagné, L. Ickes, A. Kürten, F. Riccobono, L. Rondo, S. Schobesberger, G. Tsagkogeorgas, D. Wimmer, A. Amorim, F. Bianchi, M. Breitenlechner, A. David, J. Dommen, A. Downard, M. Ehn, R. C. Flagan, S. Haider, A. Hansel, D. Hauser, W. Jud, H. Junninen, F. Kreissl, A. Kvashin, A. Laaksonen, K. Lehtipalo, J. Lima, E. R. Lovejoy, V. Makhmutov, S. Mathot, J. Mikkilä, P. Minginette, S. Mogo, T. Nieminen, A. Onnela, P. Pereira, T. Petäjä , Y. Stozhkov, F.Stratmann, A. Tomé, J. Vanhanen, R. Schnitzhofer, J. H. Seinfeld, M. Sipilä, Y. Viisanen, A. Vrtala, P. E. Wagner, H. Walther, E. Weingartner, H. Wex, P. M. Winkler, K. S. Carslaw, D. R. Worsnop, U. Baltensperger & M. Kulmala: Role of Sulphuric Acid, Ammonia and Galactic Cosmic Rays in Atmospheric Aerosol Nucleation. *Nature* 476 (7361): 429–33, 2011. doi:10.1038/nature10343.

II   Schobesberger, S., A. Franchin, F. Bianchi, L. Rondo, J. Duplissy, A. Kürten, I. K. Ortega, A. Metzger, R. Schnitzhofer, J. Almeida, A. Amorim, J. Dommen, E. M. Dunne, M. Ehn, S. Gagné, L. Ickes, H. Junninen, A. Hansel, V.-M. Kerminen, J. Kirkby, A. Kupc, A. Laaksonen, K. Lehtipalo, S. Mathot, A. Onnela, T. Petäjä, F. Riccobono, F. D. Santos, M. Sipilä, A. Tomé, G. Tsagkogeorgas, Y. Viisanen, P. E. Wagner, D. Wimmer, J. Curtius, N. M. Donahue, U. Baltensperger, M. Kulmala, and D. R. Worsnop: On the Composition of Ammonia–sulfuric-Acid Ion Clusters during Aerosol Particle Formation. *Atmos. Chem. Phys.* 15 (1): 55–78. 2015. doi:10.5194/acp-15-55-2015.

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IV   Manninen, H. E., A. Franchin, S. Schobesberger, A. Hirsikko, J. Hakala, A. Skromulis, J. Kangasluoma, M. Ehn, H. Junninen, A. Mirme, S. Mirme, M. Sipilä, T. Petäjä, D. R. Worsnop and M. Kulmala: Characterisation of Corona-Generated Ions Used in a Neutral Cluster and Air Ion Spectrometer (NAIS). *Atmospheric Measurement Techniques* 4 (12): 2767–76. 2011. doi:10.5194/amt-4-2767-2011.

V   Franchin, A., A. Downard , T. Nieminen, K. Lehtipalo, J. Kangasluoma, G. Steiner, H. E. Manninen, T. Petäjä, R. Flagan and M. Kulmala: The new high-transmission inlet for the Caltech nano-RDMA for size measurements of sub-3 nm ions at ambient concentrations. *Atmos. Meas. Tech. Discuss.* 8 (6): 5847–76. 2015. doi:10.5194/amtd-8-5847-2015.

VI   Kangasluoma, J., A. Franchin, J. Duplissy, L. Ahonen, F. Korhonen, M. Attoui, J. Mikkilä, K. Lehtipalo, J. Vanhanen, M. Kulmala and T. Petäjä: Operation of Airmodus A11 Condensation Nucleus Counter at various inlet pressures, various operation temperatures and design of a new inlet system. *Atmos. Meas. Tech. Discuss.* 8 (8): 8483–8508. doi:10.5194/amtd-8-8483-2015.

1 Introduction

Nanoparticles are bits of material smaller than 100 nm in diameter (Horikoshi and Serpone, 2013). They can be deposited on surfaces, using sophisticated equipment in a laboratory facility. They can be generated as sub–products of combustion by human activities or produced by natural chemical reactions in the air. Nanoparticles can be used in nanotechnology for the synthesis of new material with unusual optical (Murray et al., 1993; Canham et al., 1990), electronic (Brust et al., 1998;), and catalytic (Iablokov et al., 2012; Turner et al., 2008; Valden et al., 1998) properties. On one hand, nanoparticles can have adverse effects on human health when inhaled (Mauderly et al., 2008). On the other hand, they can have positive effects when used to create new drug delivery to treat cancer (Ye et al., 2015) or other diseases (Huebsch et al., 2015). Nanoparticles can affect Earth's climate too (Adams et al., 2013, IPCC, 2013). They affect the scattering of sunlight and cloud properties, with a net cooling effect on the atmosphere (Strawa et al., 2010).

Nanoparticles that affect the planet's climate float in the atmosphere, suspended in the air that we breathe. Each breath of air that we take contains mostly nitrogen, oxygen and argon. These gases make up more than 99.9% of the atmosphere of our planet. The concentration of these gases does not change much on a global scale, and their presence is essential for life. Interestingly, the remaining percentage, although very small, is extremely important for life. The biggest part of this tiny fraction of air is made of water vapor, CO_2 and methane, which are greenhouse gases and allow our planet to stay warm enough to host life. An even smaller fraction of the atmosphere is composed of a very interesting entity: aerosols. Aerosols are a mixture of solid and liquid particles and the gas in which they are suspended.

Aerosols are active players in our planet's changing climate. Fossil fuel consumption has increased since. The rise in greenhouse gas emissions has continued at higher and higher rates (Boden et al., 2010), leading to Earth's climate change. The net warming effect, caused by the increase in concentrations of CO_2 and methane, triggers a temperature increase of the planet's atmosphere and oceans (NOAA, Climate at a Glance 2015). This effect is partially counterbalanced and masked by the cooling effect of aerosols (Pósfai and Buseck, 2010), which, on average scatter back part of the incoming radiation from the sun. Atmospheric aerosols affect the climate directly and indirectly, though their effects are not yet fully understood and quantified. Uncertainties about the contribution of aerosol to climate change are related to the spatial and temporal variability of aerosol particles and their sources (Kanakidou et al., 2005). Scientists have been working for decades (IPCC FAR, 1990) to reduce these uncertainties by characterizing the dynamics of aerosol formation and evolution in order to implement them in global models.

Aerosol particles in the atmosphere can be classified as natural or anthropogenic, according to their sources. Examples of natural sources are: volcanoes (Martucci et al., 2012), erosion of soil by the wind (Zender et al., 2004), sea spray (Gong, 2003), spontaneous combustion (Chakrabarty et al., 2014) and nucleation involving vapors emitted by natural sources (Spracklen et al., 2008; Ehn et al., 2014).

Examples of anthropogenic sources are: the exhaust of cars, trucks (DeWitt et al., 2015), ships (Cesari et al., 2014) and planes (Masiol and Harrison, 2014), the chimneys of factories, power plants and incinerators (Stevens et al., 2012; Zeuthen et al., 2007; Stevens and Pierce, 2014), controlled fires (Paglione et al., 2014) and all processes related to man-made combustion.

Aerosol particles that are emitted directly into the atmosphere are called primary aerosol particles. The ones formed by gas-to-particle conversion are called secondary aerosol. Particles produced by secondary sources were first observed by Aitken, in the late 1800s on the west coast of Ireland (Aitken, 1889). They are important (Merikanto et al., 2009) and difficult to study because of their small size and their spatial and temporal variability (Lack et al., 2004; Penner et al., 2011).

Aerosol particles span five orders of magnitude – from about 1 nm to about 100 μm – making it extremely challenging to cover with a single measurement instrument or working principle (Seinfeld and Pandis, 2006; Boucher, 2015). On the small side of the spectrum are molecular clusters generated by collision and attachment of trace gas molecules with low vapor pressure and high surface tension (Kulmala et al., 2013; Kürten et al., 2014). On the large side of the aerosol spectrum there are pollen particles, fungal spores, mineral dust and water droplets (Taylor et al., 2004; Heald et al., 2009; Kok, 2011).

Aerosol particles can reside in the air from a few seconds to a few weeks (Jaenicke, 1982; Williams et al., 2002; Croft et al., 2014). Small particles do not necessarily reside longer than big particles or vice versa, since aerosol particles of different sizes are subject to different generation and removal processes. Small particles will be quickly lost onto bigger particles or surfaces by Brownian diffusion, while big particles will be removed from the atmosphere by gravitational settling.

Coagulation, growth and diffusion onto surfaces are typical processes that remove small particles (<100 nm), whereas rainout, washout, gravitational settling, and impaction are processes that affect bigger particles (> 100 nm). The competition of different sources and sinks makes aerosol particles accumulate around certain diameters, forming modes: cluster mode (< 3 nm), nucleation mode (from 1 to 20 nm), Aitken mode (from 20 to 50 nm), accumulation mode (from 50 to 300 nm) and coarse mode (> 300 nm) (Raes et al., 2000; Seinfeld and Pandis, 2006).

Aerosols can be classified by size and concentration by determining their number size

distribution. The concept of diameter is traditionally used to define the size of an aerosol particle. However, it can be challenging to define. In fact, many definitions of particle diameter exist, and every definition is related to the measurement principle used to determine the diameter: geometric, optical, mass, aerodynamic, Stokes or mobility diameter (Hinds, 2012). From this point on in this thesis I will refer to mobility equivalent diameter as diameter or D_p (e.g., Mäkelä et al., 1996).

A number size distribution measurement can be very useful to characterize processes, sources and sinks of a certain location. Different sites have different size distributions that can be grouped into larger categories urban, rural, background, remote and polar (Hamilton et al., 2014; Brines et al., 2014). These same categories also have different concentrations which fall roughly in the ranges $[10^5 – 10^4]$ for urban environments, $[10^4 – 10^3]$ cm^{-3} rural, $[10^3 – 10^2]$ cm^{-3} background, $[10^2 – 10]$ cm^{-3} remote and $[10^2 – 1]$ cm^{-3} polar.

The pioneer aerosol scientists started to quantify aerosol particles by collecting them on filters, weighing them and carrying out chemical analysis of the aerosol deposited onto the filter substrate. The collection became more detailed with the introduction of a cascade impactor (May, 1945), which allowed the classification of particles in mass distributions according their size. However using mass to understand the physics and phenomenology of aerosol particles is not ideal. Few coarse particles contribute to the largest part of the mass hiding the presence of the smallest aerosol. Fine particles are more numerous and very important for many processes, like cloud formation and light scattering and absorption (Horvath, 1993).

To characterize aerosol mass size distributions, volume or surface size distributions can be used. However, number distributions are currently most used by the scientific community and are of interest in this thesis. To generate a number size distribution, it is necessary to size and count the aerosol particles, which is not an easy task. The development of the differential mobility analyzer (Rohman, 1923; Zeleny, 1929; Knutson and Whitby, 1975; Flagan, 1998; McMurry, 2000) combined with a condensation particle counter (e.g., McDermott et al., 1991) to compose a differential mobility particle sizer (or a scanning mobility particle sizer) made the measurements of number size distributions possible.

In order to characterize the physics and the chemistry of newly formed clusters/secondary aerosol particles, it is necessary to investigate the sub–3 nm range in depth, since that range is where the first steps of particle formation take place. In the last decade important advances have been made in understanding new particle formation (Kulmala et al., 2007; Metzger et al.,2010; Kuang et al., 2012; Kulmala et al., 2013; Riccobono et al., 2014; Jokinen et al., 2015). Furthermore, instrument development (Mirme et al., 2007; Iida et al., 2009; Zhao et al., 2010; Junninen et al., 2010; Jiang et al., 2011; Vanhanen et al., 2011; Mirme and Mirme 2013; Lee et al.,

2014) has played a fundamental role in the advances of understanding secondary aerosols.

Instrument development is vital to be able to measure the necessary physical and chemical characteristics of aerosol particles. The results of these measurements shine light on the properties and dynamics of aerosol particles, and thus on the formation and life cycle of aerosols. These measurements results can then be summarized in parameterizations that can be used in models that describe atmospheric processes and the climate. Model predictions are then checked against new measurements to verify our understanding of the processes. The scientific knowledge acquired in this way is invaluable for society as it can be used to guide policy decisions that directly impact society.

My thesis takes some steps towards understanding the properties of atmospheric nanoparticles, identifying their chemical composition, excluding some pathways for their formation in the troposphere, and assessing the relative role of sulfuric acid, ammonia and ions (**Paper I,II**). This doctoral work also experimentally investigates one of the processes in aerosol formation that involves ions: ion–ion recombination (**Paper III**). The results presented here help in characterizing the charging mechanisms used to measure sub–3 nm particles (**Paper V**) and improve the measurements with differential mobility analyzer techniques (**Paper IV**). In summary, this thesis aims to address the following research goals:

- investigate the relative contribution of sulfuric acid, ammonia and ions to nucleation processes (**Paper I-II**)

- determine the chemical composition of cluster ions nucleating in a ternary (H_2SO_4–H_2O–NH_4) environment (**Paper II**)

- quantify a basic physical quantity, the recombination coefficient, which is essential to model certain nucleation processes (**Paper III**)

- improve measurements of sub–3 nm aerosol particles and ions by instrument characterization (**Paper III-V-VI**)

- develop further instrumentation for measurements of sub–3 nm aerosol particles and ions (**Paper V-VI**)

More specifically this thesis answers the following scientific questions: 1) is binary nucleation enough to explain ambient observation of particle formation rates? 2)

What is the role of ions in binary and ternary nucleation? 3) What is the chemical composition of cluster ions during ternary nucleation? 4) What is the magnitude of the recombination coefficient and how does that change with temperature and relative humidity?

2 Atmospheric aerosol formation and ions

Aerosols can be formed starting from precursor vapors. During their life time, gas molecules emitted into the atmosphere can react with O_3 and radicals like OH and NO_3. Some of the products of these reactions, for example H_2SO_4 or extremely low volatile organic compounds (Ehn et al., 2014), have very low vapor pressure and can form chemical bonds with other molecules. This process is called "clustering" and it is the first step of new particle formation (NPF). Once the clusters are formed they can grow via condensation and form aerosol particles. Clustering of sulfuric acid vapor molecules, generated by photo–oxidation of SO_2, is an example of atmospheric aerosol formation (Weber et al., 1996). This kind of process is influenced by a number of factors, such as ion concentration and trace gas composition (Arnold, 1980; Arnold et al., 1982; Suni et al., 2008; Enghoff, 2008).

2.1 Aerosol formation and nucleation processes

Atmospheric aerosol formation is the production of aerosols starting from precursor molecules in the gas phase. It is a phase transition from gas to liquid/solid. During an aerosol particle formation process, molecules of gas with low vapor pressure and high surface tension collide and stick together, forming clusters that grow and form tiny droplets (Vehkamäki, 2006).

In this thesis as in much scientific literature, the terms "nucleation", "new particle formation" and "atmospheric aerosol formation" are used interchangeably (Chate et al., 2010; Zhang et al., 2012; Glasoe et al., 2015; Minguillon et al., 2015) to describe the process of phase transition from vapor to aerosol. However, strictly speaking, nucleation and aerosol formation are not equivalent terms (Kulmala et al., 2013). Nucleation implies the presence of an energy barrier that separates two phases. Usually those two phases are gas and liquid as during homogeneous nucleation of water vapor that leads to the formation of water droplets. Nucleation can only happen if the vapor (or vapors) is supersaturated meaning that the amount of vapor molecules present in the air, or in another gas, exceeds the amount of molecules that can be "hosted" in the air parcel in gas phase. The limit of how many molecules can exist in gas phase depends only on temperature and is given by the saturation vapor pressure, according to the ideal gas law. This description is valid if there is only one nucleating vapor or if, in the presence of multiple vapors, they do not interact with each other (Vehkamäki, 2006).

When the number of vapor molecules in an air parcel is larger than the number allowed by the saturated vapor pressure, the vapor molecules in gas phase start to be unstable and the air becomes supersaturated. This is equivalent to saying that the partial pressure (p_v) of the vapor in question is larger than the saturated vapor pressure
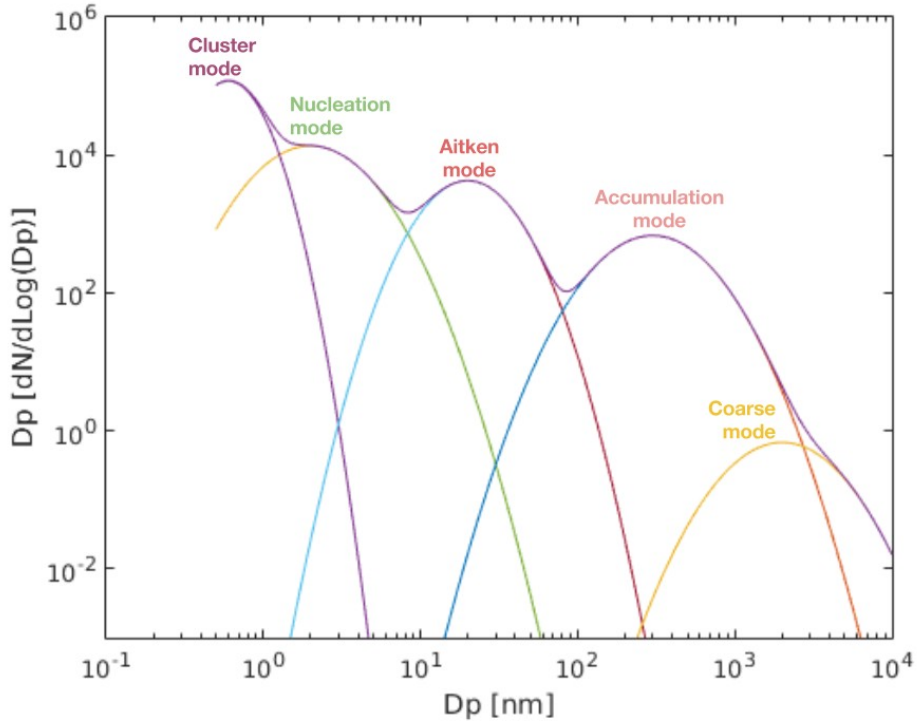
Figure 1. Idealized examples of number size distributions

(p_s). For the vapor molecules to change phase from gas to liquid, an energy barrier must be overcome. The energetic cost of forming a new interface between liquid and solid phase for a one component system is expressed as:

$$\Delta G = -n k_b T \ln(S) + A\sigma \quad , \tag{1}$$

where n is the number of molecules, k_b is the Boltzmann constant, T is the temperature, S the saturation ratio, A the area of the newly formed cluster and σ the surface tension. The first, negative term represents the gain in energy of the molecules that form the cluster. The second positive term represents the energy paid for building the surface that divides the air from the newly formed cluster. The higher the supersaturation is, the lower the barrier, and the easier it is for the vapor molecules to become a critical cluster. Only when a cluster reaches a critical size can it grow into a liquid droplet. The size of a cluster is defined as critical when the probability of its molecules evaporating equals the probability of gaining one more molecule after a collision. A critical cluster is in a metastable phase (Curtius, 2006).

However, sometimes there is no energy barrier involved in the process, each collision adds a molecule to the cluster and no molecule evaporates from it. In this case, the

clusters form at the kinetic limit (e.g., Laakso et al., 2004). Instead, in ion induced nucleation, the starting point of the clustering is not a single molecule but a small charged cluster (Lovejoy et al., 2004). If the starting nucleus for the clustering is electrically neutral the nucleation process is called "activation nucleation" (Kulmala et al., 2006). If the initial growth is enhanced as a function of size the phenomenon is called "nano–Köhler" (Kulmala et al., 2004). Therefore, the term "aerosol formation" is a more general term referring to the cluster formation and growth of stable aerosol particles.

Although processes of phase transition are well understood for macroscopic systems (Imry and Wortis, 1979) and nucleation is understood for specific systems, such as homogeneous nucleation of N-Nonane and N-Propanol mixtures (Gaman et al., 2005), many details still remain unclear about atmospheric particle formation (e.g., Andreae, 2013). There are three main limitations to fully understanding such processes. First, the low concentrations of precursor vapors that is sufficient to initiate the process makes it difficult to detect them. Precursors vapors are just of the order of a part per quadrillion in volume (ppq_v) with respect to the number of air molecules, one molecule of vapor per one quadrillion molecules of air. Second, the kind of precursor vapors involved in particle formation and how they interact still present some uncertainties, despite that it is known that sulfuric acid plays a key role (Weber et al., 1995; Kulmala et al., 2004; Sihto et al., 2006; Kuang et al., 2008; Erupe et al.,2010; Petäjä et al., 2011), iodine participates in aerosol formation in coastal areas (O'Dowd et al., 2002; Huang et al., 2010; McFiggans et al., 2010), and in many cases, ammonia and other basis (Kulmala et al., 2000; Erupe et al., 2011; Glasoe et al., 2015) and organic vapors are also involved (Kulmala et al., 1998; Na et al., 2007; Smith et al., 2008; Jimenez et al., 2009; Wyche et al., 2014).

Of all the gases present in the air during particle formation, it is not totally clear which ones contribute to nucleation and to what extent (**Paper I, II**). The role of different trace gases in different parts of the globe, in the troposphere and stratosphere is also debated. The role of ions in atmospheric nucleation is also a controversial topic (Enghoff and Svensmark, 2008; Kazil et al., 2008; Yu et al., 2010; Kulmala et al., 2010; Mirme et al., 2010; Gagné et al., 2012). It is known that ions contribute to nucleation in simple systems, lowering the energy barrier and creating a stable local minimum (Thomson, 1906), but is that directly transferable to the atmosphere? (**Paper I, III**).

2.2   Binary and ternary nucleation

It is known that sulfuric acid plays a key role in aerosol particle formation (Weber et al., 1995; Sipilä et al., 2010). Sulfuric acid concentrations strongly correlate with nucleation rates with a linear dependency on a logarithmic scale, following the relationship

$$J = K\left[H_2SO_4\right]^a \quad ,$$ (2)

with the pre–factor K ranging from 10^{-5} to 10^{-14} and the exponent a from 1 to 2 (Sipilä et al., 2010). In atmospheric systems where sulfuric acid is the main nucleating vapor, water is always present and participates. Therefore, new particle formation is called "binary", as it involves two species: sulfuric acid and water.

Binary systems are not the only possible systems. There are a variety of other compounds that can contribute to new particle formation in the boundary layer, including ammonia, amines and organic vapors (**Paper I**; Almeida et al., 2013; Riccobono et al., 2014). We speak of ternary systems when three compounds participate in new particle formation: typically one of the bases mentioned above, together with sulfuric acid and water. In polluted area within the boundary layer it is very likely that the contribution to new particle formation comes from more than three compounds or that more than one kind of nucleation process takes place at the same time (Kulmala et al., 2013; Yu et al., 2014). Atmospheric ions are other controversial players in new particle formation.

2.3   Atmospheric ions

The pioneers of electricity defined ions as carriers of electric charge floating in the air (Thompson and E. Rutherford 1896; Rutherford, 1897). Later, they were better identified by aerosol scientists and described according to their mobility or their mobility equivalent diameter (Tammet 1995; Hõrrak et al., 2000; Hirsikko et al., 2011). Ions are currently classified in terms of D_p as: small ions (< 1.9 nm), intermediate ions (1.9–7.7 nm) and large ions (> 7.7 nm). In terms of mobility ranges they are classified as: small ions (> 0.57 $cm^2V^{-1}s^{-1}$), intermediate ions (4.3×10^{-2} –0.57 $cm^2V^{-1}s^{-1}$) and large ions ($<4.3\times10^{-2}$ $cm^2V^{-1}s^{-1}$). Intermediate and large ions are also called "charged aerosols", allowing the word "ion" to be reserved for small ions composed of charged clusters or charged molecules. Small ions can play a role in new particle formation (Hirsikko et al., 2011).

Atmospheric ions are generated in the atmosphere mostly by natural sources. Radon decay and gamma rays from the soil are the dominant sources in the lower troposphere (Zhang et al., 2011). Galactic cosmic rays are dominant above the oceans and in the upper troposphere (Kazil and Lovejoy, 2004). Lightning and the ionizing radiation emitted by lightning are also sources of ions although very localized and highly variable in time and space and therefore extremely difficult to characterize. Another interesting local source of ions is splashing water, for example in waterfalls or during heavy rain episodes (Laakso et al., 2007; Tammet et al., 2009; Kolarz et al., 2012).
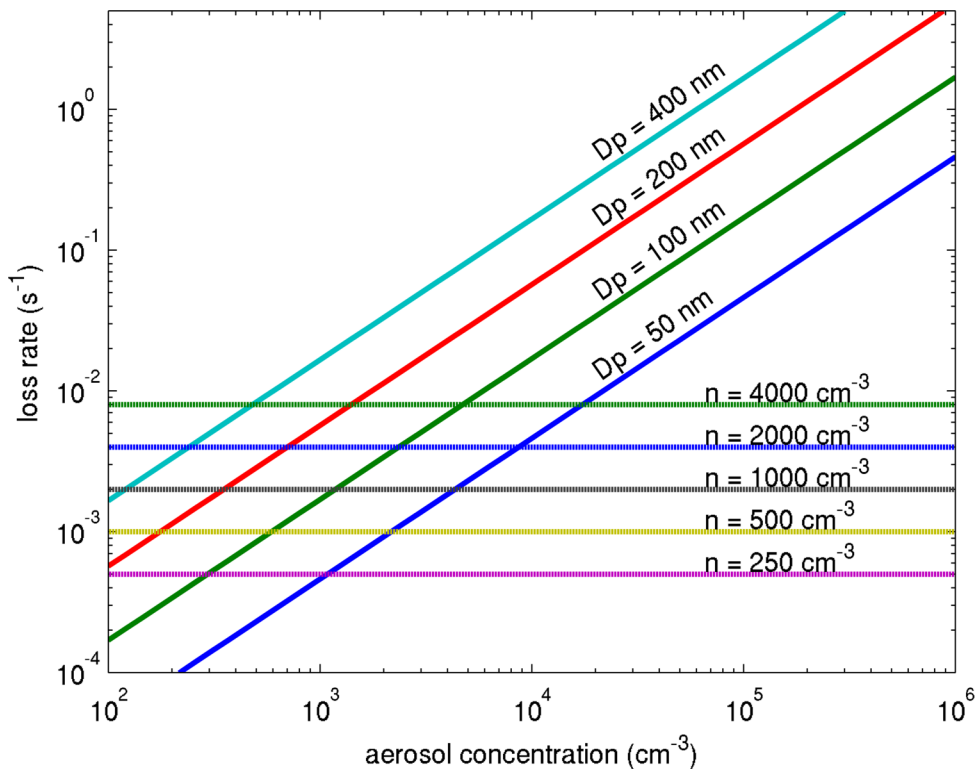
Figure 2. Comparison between losses due to ion attachment and losses due to ion–ion recombination as a function of aerosol concentration. The solid lines are loss rates due to ion–aerosol attachment calculated assuming an ion of 1 nm in mobility diameter and a neutral aerosol particle of 50, 100, 200, 400 nm. The dashed lines are loss rates due to ion–ion recombination. The concentration is assumed to be equal for positive and negative. Ion–ion recombination dominates at low aerosol concentrations.

2.4   Ions and nucleation

The effect of ions increasing nucleation rates has been known since the beginning of the 1900s. Wilson (1900) demonstrated experimentally that in a simple system involving only a single supersaturated vapor, the presence of ions increased the rate at which aerosol droplets were formed. These experiments confirmed the predictions by Thomson (1906). Thomson's theory, further developed by Tohmfor and Volmer (1938) into the classical ion-induced nucleation theory (CIINT) showed how an electrical charge lowers the Gibbs free energy barrier, increasing homogeneous nucleation rates.

Interestingly, Wilson observed a sign preference that was not predicted by the CIINT. This fact hinted to a more complex explanation of the phenomenon, related to the chemistry of ions (Kathmann, 2005) and also observed also by Adachi et al. (1992) and Winkler et al. (2008). In addition to the effect of ions in accelerating rates of vapor condensation, ions are thought to be able to produce neutral embryos via charge recombination. The combination of the two phenomena is referred to as "ion mediated nucleation". The growth of sub–3 nm particles and ions is thought to be accelerated up to a factor of 10. This effect is due to the charge of the seed ion that accelerates the condensation rate of the vapor molecules (Yu and Turco, 2000).

When moving from a system with only one supersaturated vapor to mixtures, as is the norm in ambient conditions, the processes become even more complicated. The details of ion-induced nucleation are not clear and are under debate (Enghoff, 2008; Yu et al., 2012; Gagné et al., 2012; Gonser et al., 2014), especially on the relative contribution of the electrical charge compared to chemistry.

2.5   Chemical composition of ions

Recently, technological developments in the field of mass spectrometry have made it possible to directly measure the chemical composition of atmospheric ions. Their chemical composition varies according to the presence of trace gases with high electronegativity and proton affinity. Some of the negative ions that are commonly present in the air are I^-, HSO_4^-, NO_3^-, organic acids and their clusters. Common atmospheric positive ions are H_3O^+, NH_4^+, amines (e.g., dimethylamine ion, $C_2H_8N^+$), nitrogen-containing compounds, such as pyridine ions ($C_6H_8N^+$), quinoline ions ($C_9H_8N^+$) and their clusters (**Paper II, IV**).

2.6   Ion sources and ion production

The typical ion production rate q in the troposphere ranges from about 2 to about 100 $cm^{-3}s^{-1}$. The minimum ion production rate is found above the oceans, where the contribution of radon and gamma radiation from the soil is zero and the galactic cosmic ray contribution is minimal, as most of them interact with the highest part of the atmosphere and their flux is attenuated at ground level. Man-made sources are very localized and despite they can emit high concentrations in their vicinity, they are of minor concern for atmospheric studies. Anthropogenic sources are mainly corona discharge from high voltage power lines (Wright et al., 2014) and combustion engines (Eichkorn et al., 2002; Sorokin and Arnold, 2006; Lahde et al., 2009).

Within the troposphere, the maximum ionization rate can be found at the top, where the flux of ionizing particles is the highest, or at ground level, in environments with stagnant air and soil rich of radioactive minerals, like in mountain valleys and in granite caves.

The concentration of atmospheric ions in a certain location is variable in time and space and depends on the balance between sources and sinks according to the balance equation

$$\frac{dn}{dt} = q - \alpha n^2 - \beta_{eff} n \quad , \tag{3}$$

where n is the number concentration of air ions (cm^{-3}), $\frac{dn}{dt}$ is the variation of ion concentration per unit time (cm^{-3}s^{-1}), q is the source term, i.e. the ion production rate (cm^{-3}s^{-1}). The other two are sink terms. α is the recombination coefficient (cm^{3}s^{-1}) describing how fast two ions of opposite polarity neutralize each other and β_{eff} (s^{-1}) is a first order sink that is related to the losses of ions onto surfaces that can be macroscopic, for example, tree leaves; or microscopic, for example, the surfaces of an aerosol particle or coagulation sink (*CoagS*). Typical ion concentrations are of the order of a few hundred cm^{-3} and can vary from just a few cm^{-3} to a few thousand cm^{-3} (Hirsikko et al., 2011).

2.7   Ion–ion recombination

The ion–ion recombination coefficient α appears in the ion balance equation (3). It describes the process of neutralization of two ions of opposite charge by collision. Ion–ion recombination is the main sink of ions wherever coagulation sinks are low (Fig. 2), for example in the upper troposphere, and in pristine environments.

In the troposphere, the most common recombination process is the three body process

$$A^+ + B^- + M \Rightarrow A + B + M \quad , \tag{4}$$

introduced by Thomson (1924), who hypothesized that recombination takes place via collisions with neutral atoms that reduce the kinetic energy of the system, minimizing the probability that the two ions will separate after exchanging the charge (Bates and Flannery 1969; Volland, 1995). The recombination coefficient is dependent on size, chemical composition, temperature and pressure. Recombination can also be a pathway for new particle formation when the reaction (4) becomes:

$$A^+ + B^- + M \Rightarrow AB + M \quad . \tag{5}$$

The significance of ion–ion recombination in atmospheric particle formation, however, remains controversial (Yu and Turco, 2008; Manninen et al., 2010; Yu et al., 2012; Gagne et al., 2012; Kontkanen et al., 2013; **Paper III**).

3   Experimental methods

Measuring is a way to increase our scientific understanding and to prove that a model or a theoretical prediction is correct. If atmospheric models predict the presence of a certain physical quantity at a certain location and time, but solid ambient measurements do not confirm it, then the theory must be modified.

There are many ways to carry out experimental work via measurements in atmospheric sciences. Experiments can be done in a laboratory, where a carefully controlled environment and set up allows the measurement of a property of a specific system, or the response of a new instrument. They can also be carried out in aerosol chambers, where a portion of the atmosphere is simulated at the desired conditions, changing the conditions one at a time to determine the importance of each parameter. Ultimately, measurements can be done in the atmosphere. Ambient measurements give us the most important information on the level of understanding of a natural phenomenon or process. They show if there is closure in our scientific understanding, or if there is a gap, and if a new instrument is needed to measure a physical quantity suspected to play a role in the atmospheric process under study.

Ambient measurement should ideally involve the largest amount of instruments possible, measuring all the quantities of interest, maybe even with redundant measurements, monitoring the same physical quantity using different measurement principles, for the largest amount of time possible. Unfortunately, this is rarely the case. It is often impossible to deploy a large number of instruments for a long time due to costs and organization problems. Usually a choice is made between short, intensive campaigns or long term campaigns. During intensive measurement campaigns a relatively large number of instruments, often including the state–of–the–art ones, are employed for a short time. Instead, in long term measurements, a more limited selection of more established instruments is used to monitor the changes of the physical quantities under observations over the years. Both approaches are important and contribute in different ways to scientific knowledge of the atmosphere.

Laboratory experiments, including instrument characterization, chamber measurements and ambient measurement support and complete each other, allowing a complete picture of the life cycle of aerosol particles in the atmosphere to be gathered.

3.1   Aerosol and ion instrumentation

The physical quantity that allows the classification of particles at atmospheric pressure is electrical mobility, hereafter referred simply as "mobility". Mobility is

defined by the relationship

$$\vec{v}_d = Z\vec{E} \quad , \tag{6}$$

where $\vec{v}_d$ is the drift velocity of a particle of mobility Z moving in a viscous medium, immersed in a uniform electric field $\vec{E}$.

On a more fundamental level, Z depends on the number of elementary charges on the aerosol particle (ne), its diffusion coefficient (D) and the temperature of the gas (T) time the Boltzman constant (k_B):

$$Z = \frac{ne}{k_B T} D \quad . \tag{7}$$

Assuming that the aerosol particle is of spherical shape and unity density, mobility is proportional to the particle size and can be measured with a mobility spectrometer. Throughout this work I will refer to mobility spectrometer with a specific subset in mind: differential mobility analyzers (Reischl, 1991; Reischl et al., 1997). References to mass spectrometers will refer specifically to time of flight mass spectrometers. The two types of instruments involved in this PhD work were differential mobility analyzers and time of flight mass spectrometers.

The operating principle of a mobility spectrometer can be schematically summarized in three steps: charging, selecting and counting. Once the sample air enters the instrument, most of the particles carry no electrical charge. In order to analyze them aerosol particles and clusters need to be charged in a known, predictable way. Having a known amount of charge on a particle or cluster is also key also in detecting them, if the detection is done electrically. Charging can be done in several different ways, for example using radioactive sources (Hoppel and Frick, 1990), corona discharges (Stommel and Riebel, 2004), ultraviolet lamps (Li and Chen, 2011) or electrospray (Liu and Chen, 2014). Charging becomes more and more challenging the smaller the aerosol particles are. Larger particles can carry more than one elementary charge, as the larger they are the more charges can exist on a particle. Correcting for multiple charges is essential to ensure unique proportionality between mobility and size. However for particles smaller than 10 nm the probability of having more than one elementary charge is negligible (Stommel and Riebel, 2007), making the correction unnecessary. A fraction of aerosols and clusters are naturally charged, and therefore don't need to be charged to be classified, making their measurement easier. Once the charging has happened, the mobility selection in the analyzer takes place via an electric field that pushes the aerosol particles with the desired mobility towards the outlet of the instrument. After selection, aerosol particles or clusters are counted with a condensation particle counter or with an electrometer.

It is interesting to note that charging, selecting and counting works for differential mobility analyzers (Hinds, 2012), as well as for mass spectrometers (De Hoffmann and Stroobant, 2007). One main difference between mobility and mass spectrometers is that mobility spectrometers work at ambient pressure all the way from

charger to counter, while mass spectrometers have inlets at ambient pressure and the spectrometer and the counting unit (an electron multiplier or a microchannel plate detector) at vacuum pressure (~10^{-6}mbar). The primary fiscal quantity measured by mass spectrometers is the mass over charge ratio (m/z) measured in Thomson (Th). The charging in mass spectrometers can be done via electron impaction (Koontz and Denton, 1981), laser desorption (Morrical et al., 1998) or chemical ionization (Hearn and Smith, 2004). Naturally charged ions and clusters can be detected too, if the transmission of the inlet is high enough to allow them to reach the mass analyzer. In this case a charger is not necessary.

With both mobility and mass spectrometers the information about concentration and size is retrieved after accounting for the charging state of the aerosol/clusters, the internal transmission and detection efficiency of the instrument. In the case of a mobility spectrometer inverting the signal using transfer functions is required (Stolzenburg and McMurry, 2008). In the case of time of flight mass spectrometry a conversion from time– of–flight to mass–to–mobility is necessary.
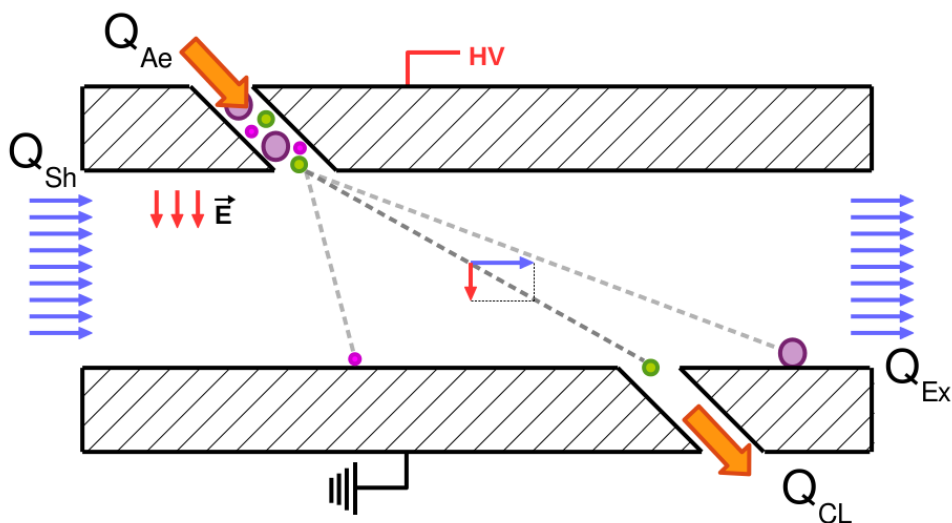
Figure 3. Operating principle of a differential mobility analyzer. Here is shown a planar DMA. The ion clusters/ charged aerosol enters the classification region from a narrow entrance slit (top right). In the classification region the flow field and the electric field determine the trajectory of the ion clusters/ charged aerosol that have a certain electrical mobility (Z). The flow field is generated by the aerosol–free sheath gas (Q_{sh}) and the elctric field is generated by a voltage difference (ΔV) between the top plate (at voltage HV, in the picture) and the bottom plate (at ground potential in th picture). At a given Q_{sh} only one ΔV will allow the ion clusters/ charged aerosol particle with an electrical mobility Z to reach the exit slit (bottom right).
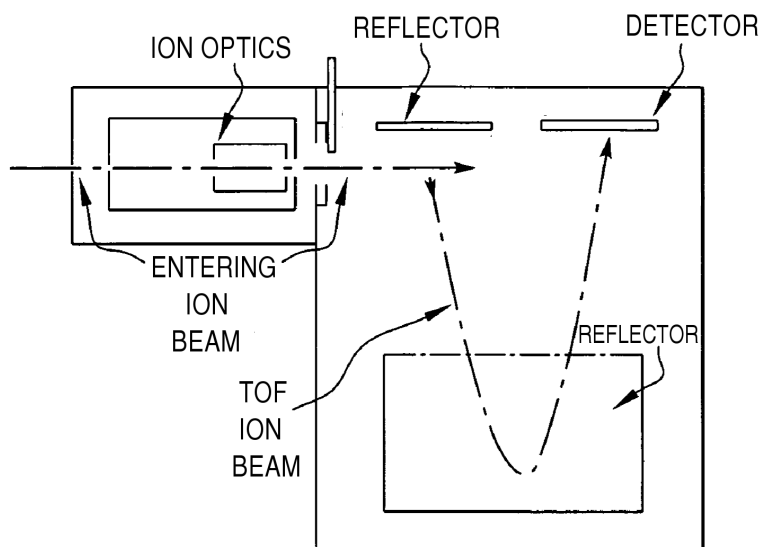
Figure 4. *S*chematics of the operating principle of a time of flight mass spectrometer (TOF). The charging unit is not present in this case. The ions are carried from ambient pressure to the TOF region (left to right in the picture) via the ion optics that keep them focused along their path. In the TOF region they are pushed perpendicularly to their path by the first reflector. The second reflector push the ions back to the detector where they are counted. The time lapsed between the pulse of the first reflector and the moment when the ions are counted is proportional to the mass to charge ratio of the ions.

The two configurations present advantages and disadvantages related to the total transmission and resolution. In both cases, when the goal is to measure aerosol and clusters composed only of a few molecules, as in our case, the inlet has to be carefully designed to avoid diffusion losses in the line that would hinder the signal. Additionally, in the case of mass spectrometers, additionally, it is necessary to confine and concentrate the ions using appropriate electrostatic lenses and focusing quadrupoles, while the surrounding air is pumped away. The fact that the ions have to undergo such a huge change in pressure causes more uncertainty on their original hydration state and it is hard to exclude that some fragmentation, condensation or evaporation might happen before detection. In the case of mobility spectrometers, the pressure is constant from inlet to counter, causing less perturbation of the sample. Nevertheless the extremely high resolution achieved with the time of flight (TOF) and the possibility to integrate spectra over time, allows an unprecedented insight on the cluster composition.

For both mobility and mass spectrometers, size selection is done by applying an appropriate electric field that guides the desired aerosol particle/cluster from the inlet to the counter. In the case of mobility spectrometers, the trajectories are the result of

the superposition of the constant velocity of the particle traveling into a laminar flow and the electric field constant but not necessarily uniform in space. In the case of mass spectrometers, the trajectories are the result of the sum of the initial velocity of the ion and the perpendicular impulse generated in the extraction region.

Counting for mobility spectrometers can be done with electrometers at atmospheric conditions. Another way to count particles is a combination of condensation and optical methods. After the particles are grown to sizes large enough to scatter light (500 – 1000 nm), they can be counted with an optical particle counter. The light from a source is deflected towards a photodiode and a pulse is generated every time a particle passes in front the light source.

Electrometers measure the current of charges that reaches their Faraday cup. The current is proportional to flow and concentration. The sensitivity of the electrometers is limited by their electronic noise. The best electrometers built nowadays (add reference) have noise levels of the order of a fraction of a fA (say 0.1 to 0.5 fA). Typical flows in aerosol instruments vary from 1 to 10 $Lmin^{-1}$. Therefore detection limits for the concentrations are between 20 and 1000 cm^{-3}.

3.1.1 The Neutral cluster and Air Ion Spectrometer (NAIS)

The Neutral cluster and Air Ion Spectrometer (Mirme et al., 2012) is manufactured by Airel Ltd in Estonia. It measures atmospheric ions in the range [0.8 - 42] nm and total aerosol particles in the range [2.5 – 42] nm (**Paper IV**, Mirme and Mirme 2013). It consists of two cylindrical Differential Mobility Analyzers (DMAs) working in parallel. One analyzer classifies ions of negative polarity and the other ions of positive polarity (Manninen et al., 2009). The ions are classified simultaneously, according to their mobility and their concentration is determined using a stack of 21 electrometer rings for each analyzer. The closer the electrometer to the inlet the more mobile the ions. The NAIS can also measure size distribution of neutral particles using a unipolar charging unit for each analyzer. The charging unit can be switched on and off, allowing the measurement of ions only when switched off, and neutral particles when switched on.
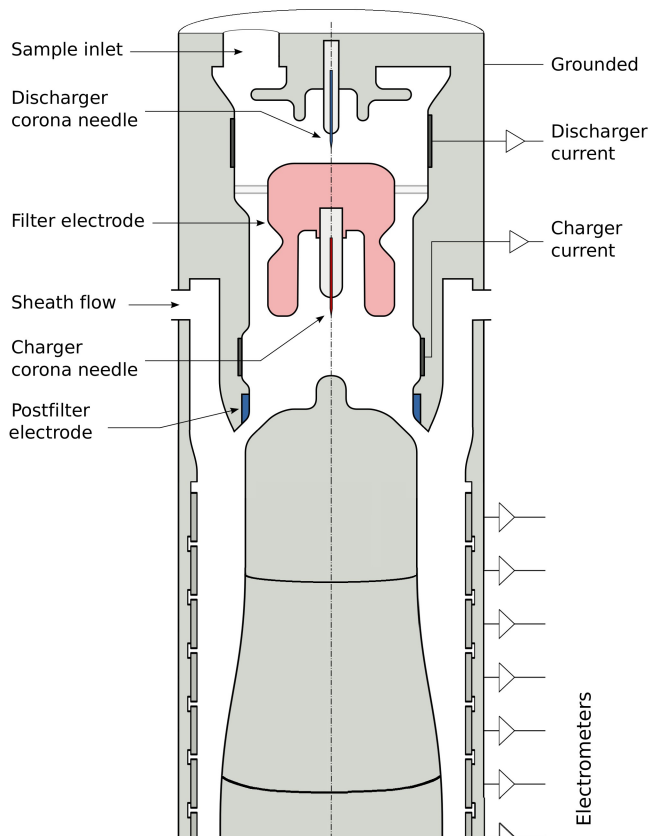
Figure 5. *S*ection of a NAIS charger unit and mobility analyzer
(adapted from Mirme and Mirme 2013).

The ions produced by the charging unit have a size range below 1.7 nm (0.7 cm^2V^{-1} s^{-1}) and they overlap with the measurement range of the NAIS (0.8 − 42 nm) (Asmi et al., 2009; **Paper IV**). For this reason it is necessary to filter the charger ions in a way that leaves unaltered as much as possible the aerosol in the sample (**Paper IV**). The filtering, a very delicate step, is done by the post filter and managed automatically by a feedback loop.

3.1.2 The nano Radial Differential Mobility Analyzer (nRDMA)

The nano Radial Differential Mobility Analyzer is a DMA with a radial geometry, optimized for sampling particles smaller than 10 nm (Brunelli et al., 2009; Jiang et al., 2011).

In general terms, a differential mobility analyzer classifies charged aerosols by electrical mobility (Knutson and Whitby, 1975). The simplest DMA configuration consists of two flat, parallel electrodes positioned at a distance h from each other. Within the two plates runs a clean aerosol–free laminar flow (sheath flow). Aerosol

particles are transported by the sample flow and enter the classification region from a slit through the first electrode, upstream from the sheath flow. The sample flow is merged with the sheath flow so that the flows remain laminar and the aerosol-laden flow runs following the streamlines furthest from the second electrode. A potential difference is applied between the two electrodes, generating an electric field that drives the charged particles towards the second electrode. Only one combination of
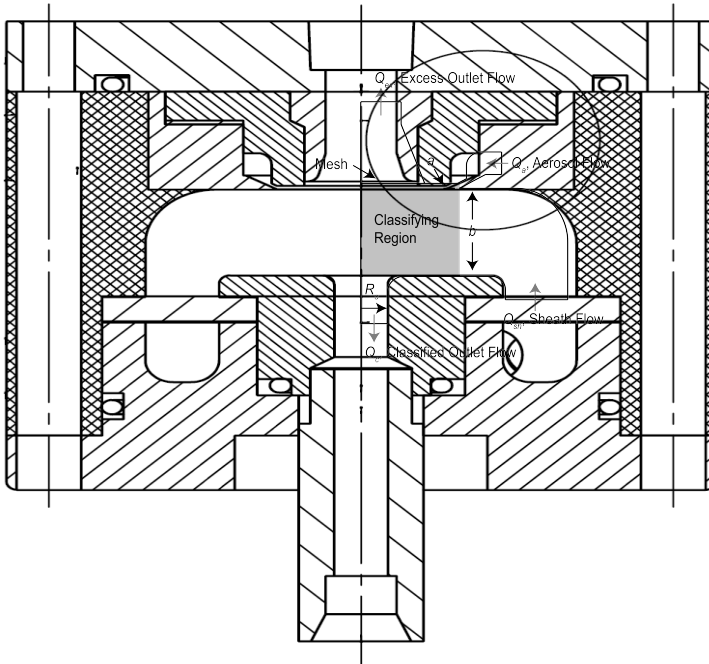
Figure 6. Side view of the nano radial DMA (adapted from Brunelli et al., 2009)

flow velocity (horizontal) and electrostatic velocity (vertical) make a particle with a certain mobility Z* drift to the outlet slit, which is situated at a certain length (L) downstream from the inlet (Fig. 5).

In 1929 Zeleny had already adopted a cylindrical geometry, using two concentric cylinders as electrodes, instead of two flat parallel electrodes. The design was later developed by Hewitt, 1957.

In 1963 Hoegl, and Knutson and Whitby designed the modern DMA, commercialized by TSI. Interestingly, Pourprix et al. (1990, 1992) introduced the radial design, later developed by Zhang (1995), Fissan (1998), Brunelli et al. (2009). The radial design can be easily understood as rotation of the cross section of a planar design. In fact, if we imagine the cross section of a planar DMA and we rotate it around the axis along

the second electrode we obtain the cylindrical design. However, if we rotate it along the axis that runs through the end point of the planar DMA, perpendicular to the two electrodes we obtain the radial design. After such a rotation the upper and lower electrodes become discs. The aerosol inlet is now a circular slit that runs around the periphery of the upper electrode and the aerosol outlet is located at the center of the second electrode. The sheath gas flow runs from the outside to the center of the two electrodes, and exits from a hole at the center of the upper electrode (Fig. 5).

This geometry turns out to be very convenient for classifying nanoparticles. The main problem in classifying particles below 10 nm is Brownian diffusion onto the walls of the instrument (Chen et al., 1998). The radial design allows inlets and outlets to be very short, therefore minimizing internal diffusion losses.

All DMA designs have to face the voltage transition from a grounded electrode to one at potential. This potential difference is necessary to generate the electric field needed to classify the charged aerosol particles. For this reason an unfavorable potential gradient at the outlet (e.g. long column, Vienna type) or at the inlet (nano-radial DMA) is always present. This adverse gradient is not critical for particles bigger than 3 nm, where $Z\bar{E}$ almost always $\ll v_{flow}$, but for the smallest nanoparticles $Z\bar{E} > v_{flow}$ prevents a good transmission efficiency. **Paper VI** describes the development of a new, high transmission efficiency inlet that reduces the impact of this adverse gradient.

3.1.3 The Particle Size Magnifier (PSM)

The particle size magnifier (PSM), combined with a Condensation Particle Counter, allows the detection and counting of single aerosol particles as small as 1 nm in diameter with an efficiency higher than 50% (Vanhanen et al., 2011).

The PSM was built following a mixing type design based on Sgro and Fernandez de la Mora (2004) and uses diethylene glycol as working fluid (Iida et al., 2009). A detailed description of the first prototype version of the instrument is given in (Vanhanen et al., 2011). Here we give a brief description.

The PSM is composed of an inlet, a saturator, a mixing region and growth tube. The 2.5 Lmin⁻¹ aerosol flow enters from the inlet and is mixed with the 1 Lmin⁻¹ saturator flow in the mixing region. The merged flows then go through the growth tube after which 2.5 Lmin⁻¹ are discarded and the remaining 1 Lmin⁻¹ flow, laden with the activated aerosol particles feeds a CPC. The saturator flow is saturated with diethylene glycol vapor at a temperature that ranges from 70 to 85 °C. When the cold inlet flow is mixed with the hot saturator flow the temperature drops and a region of supersaturation is created. The temperature is cooled further in the growth tube where supersaturation is maintained high. At the end of the growth tube the activated

particle reach sizes around 80 – 90 nm, dimensions that are too small to allow counting with optical methods. Therefore, a CPC is needed to grow them further using butanol vapors in order to count them optically.
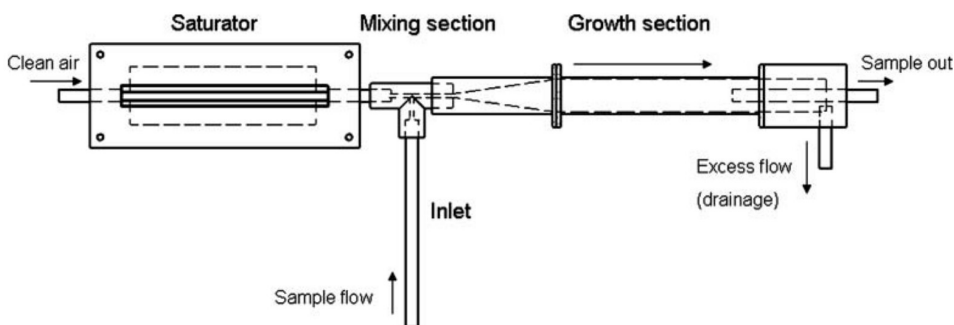
Figure 7. Schematics of the particle size magnifier (Vanhanen et al., 2011)

3.1.4 The Atmospheric Pressure interface Time of Flight Mass Spectrometer (ApiTOF)

The APi-TOF consists of: 1) a time of flight unit that classifies the ions at 10^{-6} mbar, and 2) an inlet that gradually guides the ions from atmospheric pressure to the low pressure of the TOF.

The APiTOF is not equipped with a charger, therefore it measures molecules and clusters that already exist in the atmosphere in the form of ions. The APiTOF measures the mass-to-charge m/z, in Thomson (Th).The size range covered by the APiTOF goes from 50 Th to ~3000 Th, corresponding to mobility equivalent diameters smaller than $0.2 - 2.25$ nm (Junninen et al., 2010).

The ions are sampled through a critical orifice of 300 μm in diameter. The inlet flow through the orifice is 0.8 Lmin^{-1}, although an extra flow on the order of 10 L min^{-1} is often used, in a core sampling configuration, to reduce diffusion losses in the sampling line.

The vacuum is achieved by pumping the air differentially in three stages: 2, 10^{-2} and 10^{-4} mbar. At each stage, the ions are kept in the desired trajectory with 2 quadrupoles and a set of electrostatic lenses, respectively.

A key feature of the APiTOF is its high resolution. The resolution (R) is defined as the mass (M) of the compound divided by the full width at half maximum (Δm) of the peak in the mass space $R = \dfrac{m^*}{\Delta m}$. The resolution of the APiTOF is as high as 5000 Th/Th allowing the isotopic pattern of a given compound to be resolved, acting an

extra tool for a more certain peak identification.
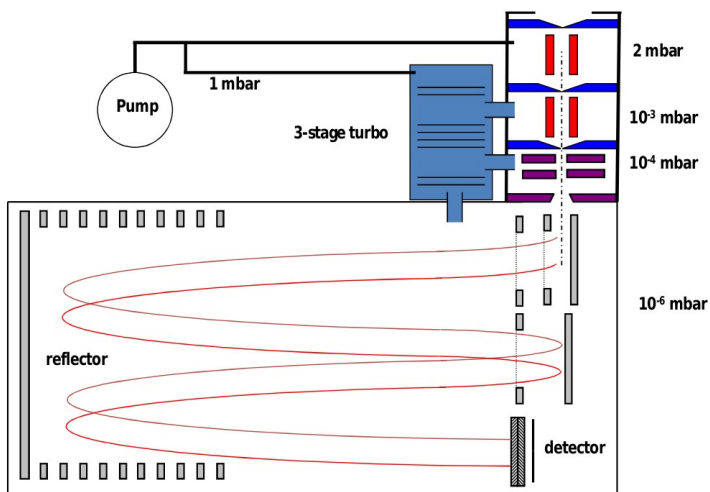
Figure 8. Schematics of the atmospheric pressure interface
mass spectrometer (Junninen et al., 2011).

DMA	Transmission (%)	Resolution (@1.47 nm)	Qae/Qsh (lpm)/(lpm)	Max Dp (nm)
TSI	6.8	3.9	2.0/20	150
Grimm	3.1	5.4	2/21.9	350
Caltech	14	6	1.5/15	10
Karlsruhe-Vienna	2.7	5.2	6/61.4	350(?)
Hermann	1	30	10/400(?)	6
Half Mini	5(?)	25	5/200(?)	6
ApiTOF-MS	0.1 – 0.5	3000	–	–

Table 1. Summary of resolution and transmission of two commercial DMAs (TSI,
Grimm), the Caltech nRDMA, and Karlsruhe-Vienna DMA. The Hermann and Half
Mini DMA are high resolution DMAs. In last row the same values for the
atmospheric pressure interface time of flight mass spectrometer.

3.2   The CLOUD chamber

Studying atmospheric processes is complicated. Not only are the quantities we want to measure hard to measure, but they also tend to be strongly correlated with each other. An example is particle formation and growth, which is deeply intertwined and correlated with vapor concentration, solar radiation, temperature and dilution via the evolution of the planetary boundary layer (Nilsson et al., 2001; Kulmala et al., 2001).

Aerosol chambers allow us to decouple the processes of interest and change one parameter at a time, while maintaining the experimental conditions relevant to the atmosphere. The dimensions of a chamber are important because they are related to the residence time of a compound in the chamber. If the surface-to-volume ratio of the chamber is too low, the compounds do not spend enough time in the chamber to react. This situation forces the scientists to use higher concentrations to achieve measurable results.

Uniformity is very important to ensure an easy interpretation of the results. The concentrations measured by the instruments need to be representative of the ones inside the chamber. Mixing the gases inside the chamber is one way to ensure uniformity and representative sampling.

The CLOUD (Cosmics Leaving OUtdoor Droplets) aerosol chamber has many unique characteristics that make it an extremely valuable tool to investigate atmospheric processes (Kupc et al., 2011; Voigtländer et al., 2012). It is big, clean and equipped with state of the art instruments.

The CLOUD chamber is a cylindrical stainless steel vessel, with a diameter of 3 m and a volume of 26.1 m^3. Located at the Centre Européen pour la Recherche Nucléaire (CERN), the CLOUD chamber has a very high standard of cleanliness and can use the proton syncroton (PS) to ionize the air inside, using a 3.5 GeV/c pion (PI$^+$) beam (Duplissy et al., 2010).

Its stainless steel walls are electropolished, therefore conductive and very smooth. These characteristics make it possible, for small ions, to have a lifetime on the order of several minutes. In this way it is possible for them to be measured and to interact with vapor molecules and aerosol particles inside the chamber. In contrast, traditional aerosol chambers are made of polytetrafluoroethylene (PTFE) that removes ions in less than 1 second, by generating parasitic electric fields (McMurry et al., 1985). This rapid removal makes the conditions of study in these chambers electrically neutral.

The CLOUD chamber can be operated in three modes: neutral, galactic cosmic ray (GCR) and with a pion beam (PI$^+$).
   1. In neutral mode, two circular metallic grids, one at the top and one at the bottom of the chamber, are put at a potential of +30 kV and -30 kV, generating an electric field that is able to sweep small ions in less than 0.2 s, allowing for experiments to be conducted in electrically neutral conditions.

2. In GCR mode, the two grids are grounded, allowing the ions generated by the natural ionization coming from space to reside in the chamber for several minutes before they attach to the walls, to aerosol particles or to other surfaces inside the chamber.

3. In PI+ mode, the two grids are grounded, similarly to GCR mode, but the PS increases the ion production rate (q) in the chamber from the 2 cm^{-3}s^{-1} of GCR to almost 100 cm^{-3}s^{-1}. This increase in q boosts the number of ions from a few hundred at GCR up to several thousand.

In the CLOUD chamber, sulfuric acid is produced in situ, using ultraviolet (UV) light, O_3 and SO_2. The UV light system consists of a bundle of optic fibers that channel the lights from the lamps, away from the chamber, to the top end of the chamber, where a system of optical fibers feed through fittings guarantees a uniform distribution of the UV light inside the chamber (Kupc et al., 2011). The O_3 is generated by illuminating an oxygen flow with a UV lamp ($\lambda > 320$ nm). The SO_2 flow, as well as a number of other trace gas flows (ammonia, amines, organic vapors) are fed with dedicated lines from the bottom of the chamber.

The chamber is kept at a constant pressure (+5 mbar above ambient) and is filled with air generated from evaporation of liquid O_2 and N_2, then humidified with a heated Nafion system that uses water purified by recirculation through Millipore Super-Q filters and by UV radiation.

The CLOUD chamber has an inflow of air that varies between 100 and 150 L min^{-1} and replaces the content of the chamber in about 3 hours. Its temperature range spans from -80 to 100 ^{o}C, with a stability of about 0.1 ^{o}C (**Paper I**).
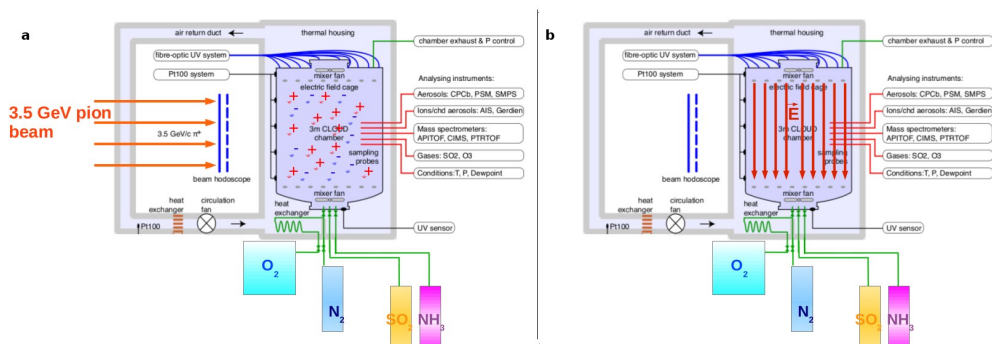
Figure 9. Schematics of the CLOUD chamber. In panel a) is represented the PI+ mode. In panel b) is represented the neutral mode (adapted from **Paper I**, SI).

3.3 Laboratory measurements

My PhD work focused mainly on lab characterization and design of aerosol instruments, as well as on chamber measurements. Characterizing instruments for field studies is necessary to interpret field measurements, where often little is known about the processes involved and the scientist needs to be sure that the instrument is measuring something that is happening in the environment, as opposed to an artifact generated by the instrument itself (e.g., lower concentrations measured with a PSM at low pressure).

Instrument characterization is often challenging, as the laboratory environment can be very different from ambient conditions. It is often necessary to make some compromises when attempting to mimic the environment, with an understanding of how the instrumental setting can be simplified, and the associate divergence from ambient conditions.

Instrument characterization in laboratory and chamber measurements need to be in synergy with the other components of the scientific process: ambient observations and modeling. The iteration of these four steps increases the understanding of a complex system such as the Earth's atmosphere and no single step can be neglected.

4   Results and discussion

The experimental results summarized in this PhD thesis (sections 4.4 to 4.7) answer the following scientific questions: 1) Is binary nucleation enough to explain ambient observation of particle formation rates? 2) What is the role of ions in binary and ternary nucleation? 3) What is the chemical composition of cluster ions during ternary nucleation? 4) What is the magnitude of the recombination coefficient and how does it change with temperature and relative humidity?

All those experimental results have been possible thanks to aerosol and ion instruments that were characterized in the laboratory. Results of some of the laboratory verifications and tests on the instruments are presented in the chapter below from section 4.1 to 4.3. We also show developments of new inlets that have improved the detection of sub–3 nm particles and ions.

4.1   Characterization of the NAIS corona charger

The charger unit of the NAIS consists of a corona charger made of a platinum needle (0.08 mm in diameter and 4 mm in length) maintained at positive/negative high-voltage at 2.5 cm from a counter electrode at ground potential. The charger unit produces ions from a corona discharge in the carrier gas. The aerosol is transported through the charging unit where it gets charged by ions that move by Brownian motion and attach to the aerosol particles. The ion production is kept constant by a feedback loop that changes the applied voltage to the corona needle keeping the ion current constant.

In the charger region, charger-generated ions coexist with sampled aerosol to be charged and detected. The concentration of corona-generated ions is kept much larger (10^4 to 10^7 ions cm^{-3}) than the concentration of the aerosol to be charged. In order to avoid ions and charged aerosol entering the analyzer together, it is necessary to filter the ions produced inside the instrument. Ideally, the charger ions should consist of a very stable peak, with a high mobility and a narrow distribution, that could be easily identified in a number–mobility spectrum and subtracted or filtered from the real signal of the charged aerosol.

Unfortunately, this is not the case, and an easy subtraction or filtering is not possible because the air next to the corona is the same as the air of the aerosol we want to measure. The number–size distribution of the charger ions can be very similar to – or sometimes even overlap with – the number-size distribution of the aerosol that we want to measure. In order to use the NAIS properly and interpret the results correctly it is important to know: 1) How the charger-generated ion number size distribution changes for different carrier gas mixtures and 2) What is the chemical composition of the ions and how the ion filter downstream of the charger acts on the charged sample

aerosol.

We found that the spectra of the charger ions differs from negative to positive. The positive presents 2 peaks at 1.1 and 1.2 nm and the negative presents four peaks in the range 1 to 1.3 nm. The positive spectra have no ions at sizes larger than 1.4 nm while the negative spectra have a tail that decrease to zero at around 1.7 nm. We observed variation with applied voltage and RH in the carrier gas, but we never saw peaks exceeding 1.7 nm.

The chemical composition of the positive ions showed two dominant masses: 100 and 199 Th, which correspond to $C_5H_{10}NO^+$ and $C_{10}H_{19}NO_2^+$, respectively, with the 199 Th peak being the dimer of the 100 Th peak. The molecular composition of $C_5H_{10}NO^+$ is not known, but could be either protonated piperidone or protonatedmethyl-pyrrolidone. It is tricky to identify the chemical composition of masses above 200 Th. However, we could identify a spacing of 74 Th for peaks at high m/Q, i.e. 610, 684, and 758 Th. These compounds arise from silicone polymers, most likely originating from conductive silicone tubing, a common contaminant in these types of measurements.

The negative ion spectrum was dominated by different acids, ionized by donating a proton. The largest contribution was from the nitrate ion NO_3^- at 62 Th and its dimer $(HNO_3)NO_3^-$ at 125 Th. NO_3^- is a usual terminal ion, also in ambient air, due to its low proton affinity. It also clusters with carbonic acid $(H_2CO_3)NO_3^-$, 124 Th, and probably other, stronger acids as well. Other acids identified in the negative ion spectra were e.g. pyruvic acid, lactic acid and benzoic acid. Strong acids, by definition, are more likely to donate an H^+ and become negatively charged.

The experiments relative to particle charging and filtering of the corona-generated ions showed that when the post filters are set at +/-50 V all the corona generated ions are removed, while only a portion of the test WOx particles is removed. This result is not ideal but is a good compromise that allows the corona-generated ions to be filtered out and still leave some of the initially neutral particles at the 2–3 nm size to be detected by the electrometers in the instrument (**Paper IV**).

4.2 Developing the nRDMA inlet

The nRDMA has been reported to be the best DMA for measuring sub-10 nm particles (Jiang et al., 2011). However, during the CLOUD 7 campaign at CERN in Switzerland in 2012 we deployed the nRDMA, combined with a PSM to form a nano ion differential mobility particle sizer, and, unexpectedly, we observed a low transmission efficiency for ions smaller than 3 nm.

Subsequently, we investigated the transmission of the nRDMA in the laboratory, using an electrospray (ES) to generate aerosols with well-defined mobility (Ude and Fernández De La Mora, 2005). Varying the configuration of the ES electrodes we

found an increase in transmission when the counter electrode was at an intermediate voltage between the high voltage of the ES solution and the ground potential of the nRDMA inlet. A very low transmission was found when the ES counter electrode, as well as the nRDMA inlet, were kept at ground potential. The smaller the particles used (higher mobility), the lower the transmission was.

We related this low transmission to the low transmission efficiency obtained in the chamber measurements and we attributed this change in transmission to a change in electrostatic losses in the region between the inlet and the counter electrode of the ES. Hence we designed an inlet to apply to the nRDMA to circumvent the problem. Our high transmission inlet design consists of two parts: a segmented tube and a coaxial core sampling probe (**Paper V**).

The segmented tube consist of 20 alternating rings of conductive and insulating material of 2 mm thickness, with conductive rings connected by 1 MOhm resistors. The function of the new inlet is to reduce the potential gradient, while the coaxial core sampling at the end serves to extract the flow at the center of the segmented tube, where the population of charged particles is nearly unperturbed.

Thanks to this design the transverse component of the drift velocity is small compared to the flow velocity, resulting in an improved overall ion transmission efficiency. The new high transmission inlet design improves the detection of ions with diameters as small as 1.3 nm. Now, the performance of the updated system allows its use in chamber measurements and in field studies. We made it possible to use the nRDMA-PSM system to investigate the onset of new particle formation and to determine nucleation and growth rates of freshly formed particles with a higher size resolution than a traditional DMA.

4.3   PSM characterization and new inlet design

We characterized the PSM, investigating the effect of varying the pressure at the inlet and exploring the changes in detection efficiency at different temperature settings. We also designed and tested an inlet that increases the transmission efficiency of the inlet line and it is suitable for long term field measurements.

To simulate PSM measurements at higher altitudes we measured the detection efficiency of the PSM from ambient pressure down to 50 kPa, which corresponds approximately to 4000 m in altitude. We used 50 nm ammonium sulfate particles, a valve to constrict the inlet flow and decrease the pressure and an electrometer as reference instrument. We found that the PSM-CPC system underestimates the real aerosol number concentration due to changes in the mass flows inside the PSM and due to CPC undercounting. Therefore, we assessed the corrections needed to obtain a correct evaluation of concentration data. It is necessary to apply a correction for different values for the dilution inside the mixing region of the PSM (inlet flow + saturator flow) as well as for the different CPC counting efficiency.

We investigated the detection efficiency of the PSM for different temperature settings. In order to detect aerosol particles and clusters as low as 1 nm in size the PSM is operated at the limit of homogeneous nucleation. The activation efficiency is governed by the temperature difference inside the PSM. We found that when the PSM is operated using a low inlet temperature (<5 ºC) and a high growth tube temperature (>30 ºC) the activation tends to occur mostly inside the mixing region. The aerosol particle residence time in this region, however, is not enough to activate most of the sub–3 nm particles, leading to a sub-optimal supersaturation and detection efficiency.

However, when the inlet temperature is higher and the growth tube temperature is lower, the activation occurs mostly in the growth tube, where the residence time is longer with respect to the mixing region. The supersaturation formed in the growth tube leads to a better activation off the smallest clusters. Additionally, we tested the maximum detectable size range by scanning the growth tube temperature, instead of by scanning the saturator flow. Scanning the growth tube temperature, the PSM can potentially measure size distributions up to 6 nm. This is an advantage as it would expand the size range of the scanning and give information over a larger size range, as currently the size range is limited from about 1.1 to about 2.5 nm.

With our new sampling inlet, it is possible to measure automated background and charged fraction, and to achieve a transmission efficiency close to 100 % for 40 cm of inlet line.

4.4 Binary Nucleation. The importance of contaminants

Sulfuric acid (H_2SO_4) has been known for a long time to have a major role in new particle formation (Weber et al., 1995; Sipilä et al., 2010). Above a certain concentration threshold ($\sim 5 \times 10^5$ cm^{-3}) of sulfuric acid, the production of particles can be observed and nucleation rates (J) increase with the increasing concentration of H_2SO_4. The first results of the CLOUD experiments (**Paper I**) contributed to clarifying the role of H_2SO_4 in particle formation.

The two main hypotheses on its role are well represented by the work of Sipila et al. (2010) and of Metzger et al. (2010). The first was a study done using a flow tube, where the authors managed to reproduce nucleation rates comparable to the ones measured in different ambient locations, using only sulfuric acid as precursor vapor. The authors supported the idea that other vapors, like organic compounds or ammonia, were participating only in the growth of freshly formed atmospheric particles, in a sort of two stage process: first a core particle is made, exclusively formed of sulfuric acid, then organic compounds started to condense. Metzger et al. (2010), instead, performed a chamber study where a mixture of organic compounds and sulfuric acid vapors were used as precursors. The authors concluded that it was very likely that both organic compounds and sulfuric acid were initiating the nucleation process and contributing to the growth.

The main limitation in both works was the control of the contaminant level, which prevented both studies from drawing conclusive statements. This limitation was overcome with the work presented in **Paper I**, where binary (sulfuric acid and water) and ternary (sulfuric acid, water and ammonia) nucleation were investigated. The results of the experiments in **Paper I** confirmed that binary nucleation is not enough to explain ambient nucleation, supporting the interpretation of Metzger et al. (2010).

We obtained nucleation rates on the order of unity for temperatures of 5 and 20 ℃ at sulfuric acid concentrations of 2×10^7 and 5×10^8, one order of magnitude higher than the onset measured in Sipilä et al. (2010) for the same particle size. This discrepancy allowed us to understand that pure binary experiments performed in other facilities were contaminated. Nucleation rates comparable to those in ambient conditions were obtained because contaminants were present, despite remarkable efforts to keep the unwanted trace gas concentrations as low as possible. We also observed that, even in the CLOUD chamber, despite the high level of cleanliness, some level of contaminants were present and influenced our results.

The important difference was that, not only did the materials of the CLOUD chamber minimize the level of contaminants, but also that we were able to quantify the extent of the contamination, thanks to novel instrument techniques (Schnitzhofer et al., 2014; **Paper I**).

The theoretical onset of nucleation for a binary system at T = 25 ℃ and RH = 38% is around 5×10^9 molecule of sulfuric acid per cm^3 (Clegg et al., 1995; Noppel et al., 2002). In CLOUD, at similar conditions (T = 20 ℃, RH = 38%) we obtained a J of 1 $cm^{-3}s^{-1}$ at 5×10^8 cm^{-3}. The fact that the concentration of sulfuric acid necessary to produce a J of 1 in the CLOUD chamber is at around one order of magnitude lower than the theory hints to the fact that we have a certain amount of contaminants present in the chamber.

The hint becomes a certainty when we look at the ionic cluster composition in the range [0.5 – 2.5] nm (**Paper I, Paper II**). In fact, the presence of several chemical species, not introduced in the chamber deliberately, was found in the ionic clusters. Ammonia, amines and urea were the main compounds found, attached to sulfuric acid clusters. The presence of contaminant levels of ammonia was observed to be the highest at 20 ℃ (estimated to be ~4 ppt_v), the highest temperature used for the experiments in the chamber, and it decreased with decreasing temperatures. At -25 ℃ no contaminants were present, with the exception of tiny concentrations of ammonia (estimated to be ~0.4 ppt_v).

The main explanation for the presence of these compounds is related to the interaction with the wall of the chamber with the water molecules. The highest the concentration of water molecules in the chamber is, the higher is the likelihood that water molecules, bouncing to the walls, strip out some trace compounds. This process increases the presence of contaminants from the walls into the chamber. Although the

RH seemed clearly connected with the amount of contaminants in the chamber. The possibility that the humidifier or the water were responsible was explored. We excluded this hypothesis, since for producing 100 ppt_v of ammonia at 20 ^{o}C the MilliQ water should have contained 93 ng L^{-1} of ammonia per liter of water, which seemed implausibly high (NWRI, 1990).

4.5   Binary, ternary and ion induced nucleation

In the first set of CLOUD experiments we investigated the role of ions in binary and ternary nucleation. The key to interpreting the CLOUD results is in understanding what "high" and "low" concentrations (defined in the section below) of trace gases mean in terms of atmospheric values, and how these influence the possible nucleation pathways.

Our results showed that the contribution of ions to NPF is strongly dependent on trace gas composition and concentration levels in the chamber. Our conclusions can be extended to the atmosphere, as the vapor concentrations that were used are representative of the ones found in ambient conditions.

Ions seem to matter only in binary nucleation, increasing nucleation rates by up to tenfold. As soon as ammonia was added, the increase due to ion contribution became negligible. In both cases, if the concentration of condensable vapors is "high", nucleation in the neutral pathway prevails. If the concentration of condensable vapors is "low" the presence of ions strongly increases nucleation rates.

In the case of binary nucleation we observed a strong increase in the nucleation rates in the presence of ions only at sulfuric acid concentrations below $\sim 5\times10^8$ cm^{-3}. The presence of ions was no longer relevant for sulfuric acid concentrations above 5×10^8 cm^{-3}, as most of nucleating particles followed the neutral pathway. Typical sulfuric acid concentrations in the atmosphere range from 10^4 to 10^7 (Berresheim et al., 2002; Iida et al., 2008; Petäjä et al., 2009), therefore we can conclude that ions play an important role in enhancing new particle formation in sulfuric acid and water binary systems at atmospheric concentrations of sulfuric acid.

Stratospheric nucleation, as observed by Arnold et al. (1982) is a good example of such a binary system. However, it is fundamental to note that such binary systems are rare in in the boundary layer. Binary systems are more common in the upper troposphere, and in extremely clean environments (Lee et al., 2003; Kyrö et al., 2013). It is more common, however that a variety of trace gases is present in the boundary layer (Ehn et al., 2010). One of the most abundant and long suspected vapor to have a role in NPF, along with sulfuric acid, is ammonia, (Kulmala et al., 1995; Korhonen et al., 1999).

In experiments where the ammonia concentration was varied in the CLOUD chamber,

while keeping sulfuric acid concentration, relative humidity and temperature constant, we observed that ions increased nucleation rates, only for [NH3] $<\sim$ 10 ppt$_v$. The variation decreased rapidly for [NH3] >10 ppt$_v$, and saturated at 100 ppt$_v$ and above (**Paper I, II**). Interestingly, typical ambient concentrations of ammonia range from few ppt$_v$ to a few ppbv in the boundary layer (Norman and Leck, 2005; Pandolfi et al., 2012; Sander et al., 2013). Therefore, we can conclude that the effect of ions is not crucial in the boundary layer.

In further experiments at CLOUD, that are not part of this thesis, we investigated the contributions of other vapors to nucleation rates. Dimethylamine was studied, finding that it stabilizes clusters more efficiently than ammonia (Almeida et al. 2013; Kürten et al., 2014; Rondo et al., 2015), confirming previous studies (Bzdek et al., 2011; Chen et al., 2012; Kupiainen et al., 2012) and extending their conclusions showing that trace amine levels of only a few ppt$_v$ increase nucleation rates of several order of magnitude, up to values close to those reported in ambient concentrations, at a given sulfuric acid concentration. Sulfuric acid clusters are stabilized by one, occasionally two base molecules. The role of ions is negligible in presence of amines and their effect on nucleation rates saturates at 5 ppt$_v$ (Almeida et al., 2013).

Organic vapors were also subsequently studied. The result of those experiments are summarized in Riccobono et al. (2014). In these experiments pinanediol, a first-generation oxidation product of a-pinene, was used as nucleating vapor and it was shown that oxidized organic together with sulfuric acid play a major role in boundary layer nucleation. In presence of pinanediol it was not possible to work out the precise nucleation pathway, however the key role of naturally charged, large, highly oxidized organic molecules, was observed and hypothesized to resemble the neutral pathway (Schobesberger et al., 2013). Concerning the role of ions the fraction of ion induced nucleation seemed to be important (60%) at low nucleation rates ($J_{1.7} \leq 0.01$ cm^{-3}s^{-1}), dropping below 10% at high nucleation rates (>10 cm^{-3}s^{-1}).
Currently in the CLOUD chamber it has been investigated the role of a-pinene and its oxidation products.
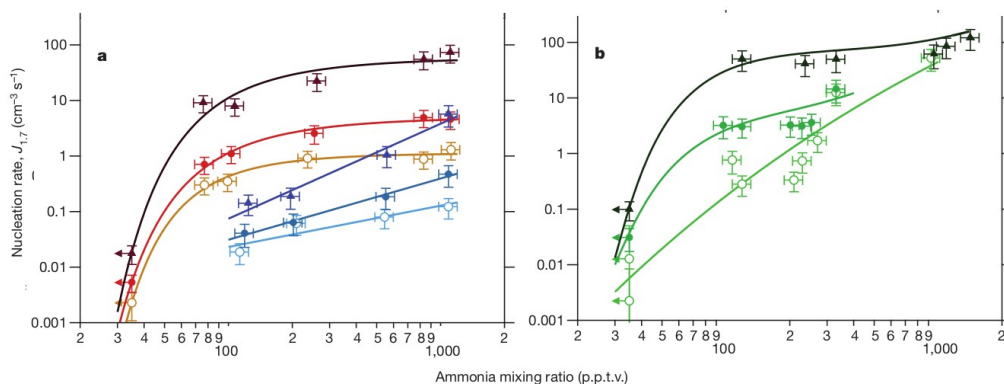
Figure 10. Nucleation rates as function of ammonia mixing ratio. The temperature of the chamber for the point in panel a) was 19°C, gradients of red represent $[H_2SO_4] = 1.5 \times 10^8$, gradients of blue represent $[H_2SO_4] = 4.3 \times 10^7$. In panel b) T = 5 °C, $[H_2SO_4] = 6.3 \times 10^7$. The RH was kept in all the experiments at 38%. Empty circles were taken with the chamber operated in neutral mode, full light circles in gcr more and dark full circles in PI+ mode. (Adapted from **Paper I**).

4.6   Chemical composition of ions

The chemical composition of the cluster ions in a ternary system was also investigated as a function of the concentrations of precursor vapors ($[NH_3]$ and $[H_2SO_4]$) and temperature.

We found that the clusters have a composition close to that of ammonium bisulfate. We varied the relative amounts of gas phase NH_3 and H_2SO_4 in the chamber, for ratios of $[NH_3]/[H_2SO_4]$ going from 0.09 to 700. The amount of added NH_3 molecules per added H_2SO_4 in the clusters increases rapidly and it saturates for $[NH_3]/[H_2SO_4]$ between 1 and 2, and we observed that the clusters were more acidic at the beginning of the nucleation event and became slightly less acidic as they grew (**Paper II**).
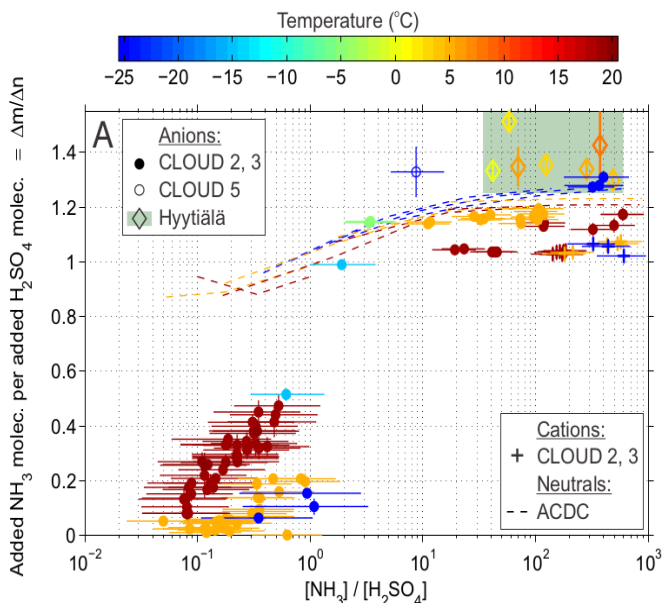
Figure 11: composition of negative cluster ions, $(NH_3)_m \cdot (H_2SO_4)_n \cdot HSO^-$, during new-particle formation experiments in the CLOUD chamber, shown as circles. RH was in the range 37–41 %; temperature is given by the color scale. The y-axis is the number of gained NH_3 molecules per gained H_2SO_4 molecule, the x-axix is the ratio of $[NH_3]$ and $[H_2SO_4]$ in the gas-phase. The green box and diamond markers show the corresponding results from ambient observations in the boreal forest. Dashed lines are ACDC model calculations for neutral clusters. (Adapted from **Paper II**)

4.7 Ion–ion Recombination

The pathways that lead to formation of new atmospheric particles depend on many factors, such as the availability of vapor molecules, oxidation state, ionization rates and ionization potentials of the trace gases.

For nucleation processes involving ions it is challenging to understand whether the ions act as nuclei for neutral vapor molecules (ion induced nucleation) or if they enhance the first step of the clustering attracting ions of opposite charge (ion mediated). For this reason it is necessary to understand and characterize all the physics processes involved as well as possible. The recombination coefficient is an important piece of the puzzle. Using the CLOUD chamber, we explored the ion-ion recombination coefficient at different temperatures, relative humidities,

concentrations of ozone and SO_2.

The measured ion-ion recombination coefficient in our experimental investigation was $2.3\times10^{-6} \pm 0.7$ cm^3s^{-1} for RH = 40% and T = 20 ºC. Our value agrees, within the measurement uncertainty, with the most commonly used recombination coefficient (Israël, 1970; Laakso et al., 2002).

We didn't find any clear dependence on ozone and only a weak variation with varying concentrations of sulfur dioxide. However we found a strong dependency of the ion–ion recombination coefficient on temperature and relative humidity. The ion–ion recombination coefficient varied more than fourfold, increasing from $(2.3\pm0.7)\times10^{-6}$ to $9.7\pm1.2)\times10^{-6}$ cm^3s^{-1} for temperature decreasing from 20 to -55 ºC.

Temperature is taken into account in many models of the ion–ion recombination coefficient, however we compared the results of those models found in the literature and, while they all agree with each other and to the experimental data for T >0 ºC, there is no good agreement for T < 0 ºC with our experimental data.

We think that our results are not biased by the effects of evaporation in the inlet line. The sampling line was kept thermally insulated to maintain the sample temperature as close as possible to the temperature inside the chamber. Although we cannot exclude some extent of evaporation, its effect would have to be very high in order to be on the same magnitude of the observed variation of the ion–ion recombination coefficient. More than 80% of the ions should have evaporated to give such an effect.

We also think that a variation in the wall loss rate at varying temperature or RH mislead our conclusions. In fact, even if the wall losses would decrease by 8 times the variation of the retrieve recombination coefficient would be less than the observed one.

The dependence of the recombination coefficient on RH hasn't been reported previously. We observed an increase in the ion–ion recombination coefficient from $(2.0\pm0.7$ to $9.9\pm3.0)\times10^{-6}$ cm^3s^{-1} as the RH decreased from 70% to 0%.

We speculated that the cause of this dependency is due to the different size of the ions, which are larger and less mobile at higher RH and smaller and more mobile at lower RH. We were not able to confirm this hypothesis experimentally because the size resolution of the NAIS is not high enough to detect such a small variation We calculated that the ions should grow on average from 0.9 nm to 1.1 nm when going from 0% RH to 70% RH. Despite that the temperature was kept constant and that the extent of the dependency might be different at different temperatures our result shows that more research has to be carried out to characterize the ion–ion recombination coefficient at atmospherically relevant conditions.
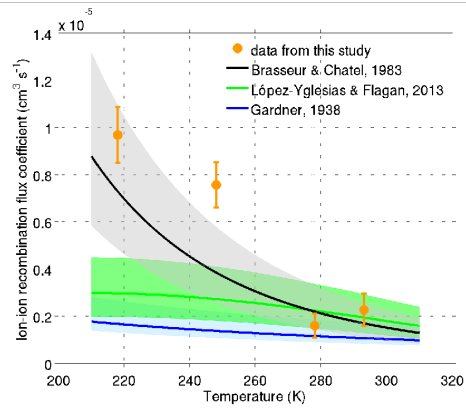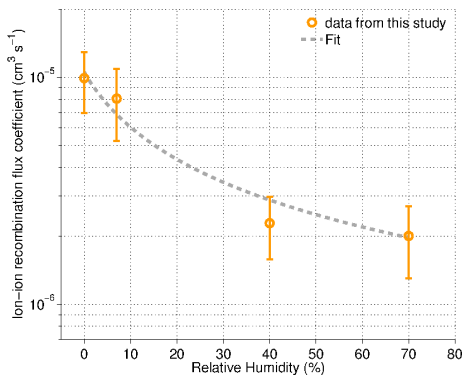
Figure 12: measured ion–ion recombination coefficient as function of relative humidity (left panel) and as finction of tempreature (right panel). The solid lines are models from the literature and the shaded lines are their respective 50% uncertainty. (Adapted from **Paper III**)

5 Review of the publications and author's contribution

Paper I presents the findings of the first CLOUD experiment, where the role of sulfuric acid, ammonia and ions on nucleation were investigated. The main result was that sulfuric acid and water alone cannot explain the magnitude of ambient nucleation rates. Similarly, neither could the addition of ammonia in the chamber. The role of ions was found to be relevant in binary systems, particularly at $[H_2SO_4]<5\times10^7$. For ternary systems, ions are relevant for $[NH_3]< 100$ ppt$_v$ and do not increase nucleation rates at $[NH_3]>100$ pptv.

I conducted measurements of number size distribution ions in the rage [0.8 – 42 nm] in the CLOUD chamber and the data analysis for several measurement campaigns (from CLOUD1 to CLOUD5 and CLOUD7). I participated in planning and conducting the setup of the instruments (NAIS, PSM, APiTOF, nRDMA and others) around the chamber. I carried out a large number of experiments (runs) monitoring the evolution of the particle formation and growth, and making sure that the experiments were successful. I gave my input for the drafting of the paper and subsequently provided my critical comments on the draft.

Paper II examines the chemical composition of the charged clusters during ternary nucleation experiments in the CLOUD chamber. It compares the experimental findings with the results of quantum chemical calculations. The main result was that the ratio of gaseous H_2SO_4 and NH_3 in the chamber determines the cluster composition. When the ratio $[H_2SO_4]/[NH_3]$ in the gas phase goes from 10 to at least 500 the clusters of both positive and negative polarity grow by addition of 1 to 2 ammonia molecules, per added sulfuric acid molecule. Interestingly, the resultant molar ratio is closer to ammonium bisulfate than to ammonium sulfate. I contributed in designing the measurements and the instrumental setup, in interpreting the results and in writing part of the manuscript.

Paper III reports on the results of the experimental investigations of the ion–ion recombination coefficient. The recombination of ions smaller than 1.9 nm mobility diameter was measured for different concentrations of ozone, sulfur dioxide, temperature and relative humidity. The main findings were that: 1)the ion–ion recombination coefficient decreases from $(2.0\pm0.7$ to $9.9\pm3.0)\times10^{-6}$ cm^{3}s^{-1} for relative humidity ranging from 0 to 70%; 2)the ion–ion recombination coefficient increases from $(2.3\pm0.7$ to $9.7\pm1.2)\times10^{-6}$cm^{3}s^{-1} for temperatures going from 20 to -55 °C; 3) and 4) small or no variation were observed for the explored ranges of concentrations of O_3 and SO_2. I contributed to the experimental design, performed most of the measurements, conducted the data analysis and wrote most of the manuscript.

Paper IV investigates the performance of the corona charger used in the Neutral clusters and Air Ion Spectrometer (NAIS). We characterized chemically and physically the ions produced by the unipolar charger applying different voltages at the

corona needle and changing the composition of the carrier gas. We also investigated the filtering efficiency of the corona generated ions after the charger unit, determining to what extent the smallest neutral aerosol particles measured are perturbed. The results showed that: 1)the size of the corona ions produced in the charger were always below 1.7 nm (positive) and 1.6 nm (negative) in mobility diameter; 2)size and concentration of the ions generated in the corona charger varied, depending on the corona voltage, but more strongly on the physical and chemical properties of the carrier gas (chemical composition and relative humidity); 3)the electrical filtering of the charger ions allows neutral particles starting from 2.5 nm in mobility diameter to be measured with reasonable confidence. For this paper I conducted and designed some of the experiments, analyzed part of the data and wrote part of the manuscript.

Paper V presents the results of the development, characterization and application of a new high transmission inlet for the Caltech nano-radial DMA (nRDMA). With the new inlet we increased the transmission efficiency of the nRDMA from a fraction of a percent to 12% for 1.5 nm ions, allowing the measurements of ion size distributions between 1.3 and 6 nm. We achieved a higher size resolution than techniques currently used in field measurements, and maintained a good transmission efficiency at moderate inlet and sheath air flows. I co-designed the new inlet, conducted most of the measurements and the data analysis, and did most of the writing.

Paper VI advances the current understanding on the operation of Airmodus A11. The Airmodus A11 consists of a Particle Size Magnifier (PSM) and a A20 Condensation Particle Counter (CPC). In this paper we explored the effect of low pressure in the inlet line on the measured particle concentration. We identified two different regions inside the PSM where supersaturation of working fluid can take place. We showed the possibility of varying the cut-off of the instrument from 1 to 6 nm, a size range wider than the one usually covered by the PSM (1 to 2.5 nm). We also presented a new inlet system that allows automated measurements of the background, minimizes the diffusion losses in the sampling line and is equipped with an electrostatic filter to remove ions. I contributed to the experiments that clarified the presence of two regions of supersaturation in the PSM, and to the design and laboratory characterization of the new inlet. I wrote part of the paper.

6   Conclusions

This thesis develops on two complementary levels: a scientific level (**Papers I, II, III**) aimed to advance the understanding of particle formation, and a more technical level (**Papers IV, V, VI**) dedicated to instrument development and characterization.

This thesis enhances the scientific understanding of atmospheric particle formation, contributing to ruling out some hypotheses about the mechanisms that dominate boundary layer aerosol particle formation. We investigated particle formation rates in a controlled chamber environment using different gas mixtures by evaluating the role of sulfuric acid, ammonia and ions. We characterized the ions' chemical and physical properties investigating their chemical composition as well as of their recombination rate at different conditions. The three primary findings of this thesis are described below.

1) The contribution of sulfuric acid and water to particle formation is not sufficient to explain atmospheric nucleation rates. In the same way, the addition of ammonia to the sulfuric acid-water vapor mixture increases the nucleation rates, but not enough to explain the observations of boundary layer atmospheric nucleation (**Paper I-II**).
We also highlight how contaminant levels of impurities can have an important impact on the actual composition of sub–3 nm aerosol particles and clusters and on nucleation rates.

The role of ions was found to be relevant for binary mixtures, at concentrations of sulfuric acid that can be found in the atmosphere. However, with the addition of ammonia, a strong base, in concentrations higher than 100 ppt$_v$, the role of ions was negligible.

2) The chemical composition of ion clusters in a ternary mixture is closer to ammonium bisulfate than to ammonium sulfate. The ion clusters tend to become slightly less acidic as they grow, gaining from 1 to 2 ammonia molecules for each sulfuric acid molecule gained. At ratios of [H_2SO_4]/[NH_3] < 500 in the gas phase in the chamber the composition of the ion clusters of size smaller than 2.5 nm is close to the composition of ammonium bisulfate: [H_2SO_4]/[NH_3] between 1 and 2 (1.4 on average).

3) The recombination of small ions (D_p< 1.9 nm in mobility diameter) is strongly dependent on temperature and relative humidity. Interestingly, both of these dependencies are either under-estimated by several models found in the literature, as in case of temperature, or even not explored at all, as in the case of relative humidity. In particular we found that the recombination coefficient increases at decreasing temperatures and increase at decreasing relative humidity. We speculate that this latter dependence is related to the change in mobility of the cluster ions (**Paper III**). The relative humidity dependency should be investigated further with varying

temperature, in order to determine if there is a variation in the extent of the change in recombination coefficient.

4) On a more technical level we were able to improve the detection of sub–3 nm ions and aerosol particles characterizing the NAIS charger unit, designing high transmission inlets for the nRDMA and the PSM, and characterizing the instruments with the new inlets at different conditions to test their performances and reliability.

We verified the role of the ions generated by the NAIS corona charger in the aerosol charging mechanisms finding that the NAIS charger unit does not generate ions larger than 1.6 nm in the negative polarity and 1.7 nm in the positive polarity. We explored the detection of neutral particles and determined that in neutral mode there is little interference of the charger ions down to 2.5 nm in mobility diameter (**Paper IV**). We also measured the chemical composition of the corona-generated ions and found that a large portion of ions is made of contaminants. Moreover, we observed a dependency of the charger ions on chemical composition of the carrier gas.

We investigated the performance of the PSM to low pressure and determined the corrections to apply to the counter in order to determine the real concentration of the aerosol particles in the air sample. We investigated the supersaturation inside the instrument finding that the PSM likely has two regions of supersaturation, one in the mixing region and one in the growth tube, and that they can vary according to the inlet and growth tube temperature settings chosen by the user. We recommend using an inlet temperature around 30 ºC and a growth tube temperature of around 2 ºC in order to maximize the PSM operation.

We explored the PSM response for varying growth tube temperatures and found that scanning the growth tube temperature allows the cut off to vary from 1 to 6 nm, a larger dynamic range than the current one. This range extension was achieved by changing the saturator flow. We suggest more study on operation mode based on varying growth tube temperature.

5) We improved the measurements of sub–3 nm aerosol particles and ions (**Paper V-VI**) by designing two different inlet for the nRDMA and the PSM. We improved the performances of the nRDMA enabling measurements of ions at atmospheric concentration. We identified a critical feature in the inlet of the nRDMA design that prevented the sampling of ions smaller than 2.5 nm. We solved the issue by designing a modular inlet that could be applied to the DMA, thus avoiding the need to redesign the inlet region inside the instrument. The transmission for 1.5 nm ions improved from a fraction of a percent to 12%. We were able to deploy the nRDMA in the chamber measurements at the CLOUD 7 campaign and measure negative ions with a good agreement compared to the NAIS.

In the case of the PSM with our new inlet increased the transmission for sampling lines as long as 80 cm is higher than 75%. The transmission efficiency achieved is

constant within +/-15% as a function of particle size making it possible to apply the inversion algorithm correctly, without introducing systematic errors due to the uncertainty of the sampling efficiency, a parameter that is often poorly characterized and difficult to correct for in field measurements.

We also equipped inlet system with an automatic zeroing unit and an ion filter. the automatic zero was included to facilitate the monitoring of the correct operation and the data quality of the PSM. The ion filter provides the possibility to alternatively sample only neutral or neutral and charged sub–2.5 nm particles. A useful feature to investigate the role of ions at early stage of particle formation.

7 Outlook

The future steps in solving boundary layer aerosol formation, as far as chamber studies are concerned, will be to find which combination of precursor vapors produces a match with ambient observations. In order to achieve this goal, the future natural steps are to systematically change the mixture of precursor gases. Amines, α–pinene and pinanediol have already been tried. It is important to continue with other monoterpenes that are commonly present in the boundary layer, such as β–pinene, 3-carene and limonene, whose oxidation product could be interacting with each other. NO_x and isoprene would need to be tested too, as they are commonly present in the boundary layer and could play a role in increasing or inhibiting the production of oxidized organic vapors. Iodide-containing hydrocarbons would be of interest as well, as they would allow the simulation of aerosol formation in coastal areas and over the sea. Finally experiments using anthropogenic organic compounds (e.g., benzene, toluene) would allow the simulation of aerosol formation in urban areas.

Concerning measurements of ion clusters during aerosol formation, the next step is to measure and identify neutral cluster during aerosol formation. Measurements have already been made using chemical ionization mass spectrometry. So far, mainly using NO_3^- as reagent ion, sometimes iodine clusters or acetate ions, however always once at a time. Measurements of neutral clusters using several mass spectrometers and different reagent ions would give a more complete picture of the first steps of aerosol formation.

So far, the knowledge of the initial steps of aerosol formation has been gathered using the output of different instruments, and using different working principles and measurement techniques. The possibility to have a single instrument, or at least a set of instruments based on the same working principle is thrilling. Differential mobility analyzers seem to be the best candidates to achieve this goal. However, for the sub–3 nm range two big challenges need to be solved: the chemical dependency on detection efficiency for condensation based counters and, even more importantly, the chemical dependency on the charging probability.

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