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Effect of Ionic Pollution on Aerosol Nucleation And Cloud Formation

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ABSTRACT: Atmospheric aerosol particles have a strong impact on the global climate and that is the main reason for many observed events of new aerosol formation being not understood. Forwarding, to explain these events one of the theory put is that the presence of ions can enhance the formation of aerosols in the atmosphere. This theory is called ion induced nucleation and in this paper, the state of observations and theory within the field is reviewed. While evidence for ion induced nucleation is accumulating the exact mechanism is still not known and more research is required to understand and quantify the effect.

KEYWORDS: Atmospheric aerosols, climate change, ion nucleation, nucleation rate, bulk nucleation

I. INTRODUCTION

The role of ions in the production of aerosols is among the least understood, but potentially is an important process in the Earth's atmosphere. Observation has shown that the nucleation of aerosol particles can occur under conditions that cannot be explained by classical nucleation theory [8]. Several ideas have been put forward to solve this nucleation problem, e.g. ion-induced nucleation [11, 13]. However, experimental investigations exploring the role of ions in particle production are scarce and often at conditions far removed from those relevant for the lower part of the atmosphere [1]. Since production rates at the size of 3 nm were observed to be $1-10 \text{ cm}^{-3}\text{s}^{-1}$, and numerical simulations yielded nucleation rates of initial stable clusters (approx. 1 nm) around $0.1-1 \text{ cm}^{-3}\text{s}^{-1}$, it is suggested that ions are active in continuously generating a reservoir of small thermodynamically stable clusters that can then rapidly grow in the presence of condensable vapours [9, 10, 12]. These results demonstrate that ions probably play an important role in the production of new aerosol particles in the Earth's atmosphere.

The chemical composition of aerosols is widely varied from largest size of fine mineral dust, to soot, to sulphate and nitrate salts. Human activities, especially fossil fuel burning, produce a lot of aerosols. In general, aerosols are more abundant over continents than over the oceans, which have consequences in form of the clouds that form there. Because aerosols interact with radiation and are crucial to cloud formation, they can strongly affect climate. Not all aerosol particles can be used to form a cloud droplet: certain criteria apply. Those aerosols meeting these criteria are called cloud condensation nuclei (CCN). There are 2 types of aerosol which can act as CCN:

1. The aerosol is insoluble but wettable (or hydrophilic), and sufficiently large. A surface is wettable when water collects on it in a thin film rather than bunching into drops (the opposite of a wettable surface is called hydrophobic, the classic example being a well-waxed car).
2. The other way for an aerosol to act as a CCN is for it to be soluble and large enough. Though there is still a size restriction, it is much less stringent than in the previous case. Because there are many more small aerosols than larger ones, this is the most common way for cloud droplets to form.

Aerosols are present throughout the atmosphere and affect Earth's climate directly through backscattering of sunlight and indirectly by altering cloud properties [4]. A ternary nucleating agent such as ammonia has been proposed to enhance the nucleation process by stabilizing early cluster formation [14]. Another possibility is that ions, produced mainly by galactic cosmic rays, can play an important role to give out the observed nucleation rates [13].



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In this paper the role of ions in aerosol nucleation is reviewed. Two areas: Theory and Experimental studies are described in separate sections. In theory section, the various theories are mentioned to understand the nucleation. Experimental studies

covers all measurements performed in the atmosphere from studies of the general behaviour of ions to particle nucleation observations where the role of ions is considered. This section also describes laboratory measurements from nucleation events to investigations of single reactions. Finally the state of the field is summarized.

II.THEORITICAL APPROACHES

A competition between the growth and evaporation of molecular clusters is called as Nucleation. For a stable cluster to be formed an initial energy barrier must be overcome – this barrier is due to the surface tension of the cluster. The height of this barrier is determined by the temperature and concentration of the nucleating species. There are several good introductions to nucleation theory as mentioned by Curtius [2]. This section deals with how the addition of an electrical charge alters the nucleation process.

Thermodynamic theory

The classical approach to bi- molecular homogeneous nucleation uses thermodynamics for the nucleation rate J is given as

$$J = J_0 \exp(-\Delta G^*/kT) \quad (1)$$

where the pre exponential factor

$$J_0 = (2 \sigma / \pi m)^{1/2} \rho_v^2 / \rho_l$$

depends upon the kinetics of the system and ΔG^* is the free energy of formation of the critical cluster (the required cluster size to overcome the energy barrier), k is the Boltzmann's constant, T the temperature, ρ_v is the density of the supersaturated vapour, m is the mass of monomer molecules, ρ_l the bulk liquid density.

Kinetic theory

One of the first kinetic models was developed by Yu et al. [17] in order to simulate exhaust plumes from aeroplanes. Coagulation processes were so fast that the thermodynamic solution did not apply and the evolution of heat in the plumes resulted in very high ion concentrations. Coagulation, condensation and evaporation were treated, and neutral, positive, and negative clusters were examined from 0.56 nm up to 0.56 μm size with individual bins for the first five molecules and bin sizes increasing by 20% per bin. All the parameters used were calculated from theory. It was concluded by the theory that the effect of changing ion concentration is highest when the ion production and



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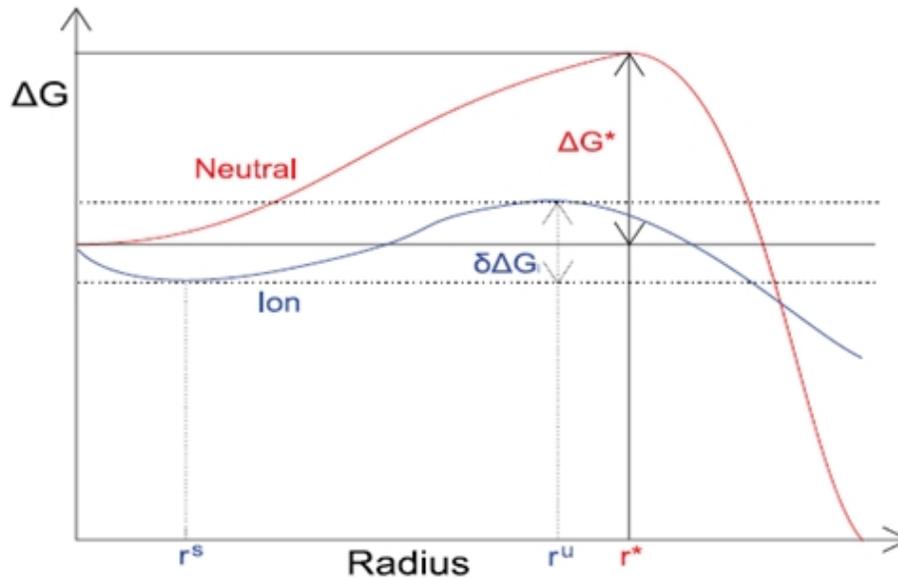


Fig. 1- Gibbs free Energy barrier (Curtius, [2])

the pre-existing aerosol surface are low to begin with and when condensable gas concentrations are high.

III. EXPERIMENTAL STUDIES

Ion nucleation

A review of atmospheric ion formation and different mechanisms for nucleation via ions was given by Harrison [6]. Large positive cluster ions (mass 2500 amu) were detected in the upper troposphere for the first time in 2002 using a large ion mass spectrometer [3]. The most common ions measured were composed of water, acetone, and a proton. Two larger modes were also detected. The lesser of these could be explained by the uptake of sulphuric acid but there were insufficient amounts of condensable gases to explain the largest measured particles by any other means than attachment of small aerosols to the ion clusters. The required concentration of these aerosols was $2.5 \times 10^4 \text{ cm}^{-3}$ and their presence could not be explained by homogeneous nucleation, which strongly indicated that the ions participated in the formation of clusters.

The particles formed during a nucleation event were overcharged with negative ions indicating the participation of negative ion chemistry in the nucleation process. However little change in the number of small cluster ions (stable ions with a diameter of $\sim 1.5 \text{ nm}$) was observed during the events, contrary to what would be expected from ion-induced nucleation (INU). This was possibly due to mixing of air parcels or a decrease in the ion condensation sink to other particles previous to the events.

An instrument to measure the charged fraction of particles in nucleation events has been developed by Laakso et al. [7]. Particles were passed through a charger that could be turned on and off, and the size distribution was then determined by a differential mobility particle size counter with a switchable polarity to measure either positive or negative ions. A charged fraction above the expected equilibrium was detected in many cases indicating a contribution from INU. Negative overcharging was more common than positive.

In order to test the theories and understand what to look for in field studies it is necessary to do experiments under controlled conditions. There are three main approaches to experimental investigation of INU. One approach explains the ion nucleation. Second approach operates on a macroscopic level trying to determine the influence of ions on bulk nucleation. The second approach is to investigate the molecular reactions taking place in an attempt to understand each step in the mechanism of particle formation.

Bulk nucleation



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The first of this kind of experiments are the ones conducted by Wilson [16] where an expansion chamber was exposed to various kinds of ionizing radiation, and an increase in density of the resulting fog was reported. With the advent of particle counters more detailed studies became possible, and the relation between generated particles and radiation doses of alpha rays, beta rays, and x-rays were reported [10]. The doses used were from 1 to 15 rads forming ion concentrations orders of magnitude above atmospheric levels, and using this span of doses the particle production rate was increased by more than a factor of 100.

Molecular reaction

By investigating directly the molecules involved in the nucleation process more information about details of the mechanism may be revealed. It was found that the mole fraction of sulphuric acid approached that of neutral clusters with increasing cluster size [15]. Small negative clusters had more sulphuric acid than neutrals and the small positive clusters had less. The clusters did not grow to the sizes expected from the rate of collision between clusters and sulphuric acid, meaning that detachment of sulphuric acid played an important role. It was also shown that growth was more effective for negative than for positive clusters. A later study using the same setup determined the hydration constants for the clusters and using the obtained data together with data from Froyd et al. [5], the authors simulated the obtained mass spectra.

IV. SUMMARY

Evidence for the importance of ions in aerosol nucleation is accumulating. We have shown above experimental studies, as well as the theoretical formulations which indicate that INU is a real effect, even under atmospheric conditions. In some studies the effect of ions is seen directly [12].

Some of the studies presented here indicate that the contribution from INU is just a few percent, compared to other nucleation mechanisms [7]. On the other hand there are also studies which point to ions as being a dominant source of new particles [18]. Models also do not agree where in the atmosphere INU can take place [9]. The main question being whether it can happen in the boundary layer or not, and more data is required to improve the theories. One major obstacle to overcome in order to quantify the effect of INU is to determine the exact mechanism. It is well established that sulphate species play an important role, however the participation of other compounds cannot be ruled out. However, more investigations under atmospheric conditions are required to confirm and quantify the effect at varying temperatures and pressures. To further elucidate the potential impact on cloud formation, growth from freshly nucleated particles to cloud droplets must be investigated.

REFERENCES

- [1] Bricard, J., F. Billard, G. Madelaine: Formation and evolution of nuclei of condensation that appear in air initially free of aerosols, *J. Geophys. Res.* **73**(1968) 4487– 4496.
- [2] Curtius, J.: Nucleation of atmospheric aerosol particles, *C. R Phys.* **7**(2006), 1027-1045.
- [3] Eichkorn, S., F. Arnold, R. Busen: Massive positive and negative ions in the exhaust of an aircraft jet engine at ground-level: mass distribution measurement and implications for aerosol formation, *Atmos. Environ.* **36** (2002), 1821–1825.
- [4] Forster, P., V. Ramaswamy, P. Artaxo: Changes in atmospheric constituents and in radiative forcing in climate change, Cambridge Univ. Press, 2007, 171–180.
- [5] Froyd, K. D. and E. R. Lovejoy: Experimental Thermodynamic of Cluster ions, *J. Phys. Chem. A* **107**(2003 a), 9812–9824.
- [6] Harrison, R. G.: Cloud Formation and the possible significance of charge for atmospheric condensation and ice nuclei, *Space Sci. Rev.* **94** (2000), 381–396.
- [7] Laakso, L., A. Hirsikko, M. Kulmala: Detecting charging state of ultra-fine particles: instrumental development and ambient measurements, *Atmos. Chem. Phys.* **7**(2007), 1333– 1345.
- [8] Lee, S.H., J. M. Reeves, J. C. Wilson: Particle formation by ion nucleation in the upper troposphere and lower stratosphere, *Science* **301** (2003), 1886–1889.
- [9] Lovejoy, E. R., J. Curtius, K. D. Froyd: Atmospheric ion induced nucleation of sulfuric acid and water, *J. Geophys. Res.* **109 D** (2004), 8204–8214.
- [10] Megaw, W. J. and R. D. Wiffen: The generation of condensation nuclei by ionizing radiation, *Pure Appl. Geophys.* **50**(1961), 118–128.
- [11] Raes, F., A. Janssens, R. Van Dingenen: The role of ion-induced aerosol formation in the lower atmosphere, *J. Aerosol Sci.* **17** (1986), 466–470.
- [12] Svensmark, H., J. Pedersen, M. B. Enghoff: Experimental evidence for the role of ion in particle nucleation under atmospheric conditions, *Proc. Roy. Soc. A* **463** (2007), 385–396.
- [13] Turco, R., P. Zhao, F. Yu: A new source of tropospheric aerosols: Ion-ion recombination, *Geophys. Res. Lett.* **25** (1998), 635– 638.
- [14] Weber, R. J., P. H. McMurry, L. Mauldin: A study of new particle formation and growth involving biogenic and trace gas species, *J. Geophys. Res.* **103**(1998), 16385–16396.



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- [15] Wilhelm, S. D. and F. Arnold: Ion-induced aerosol formation: new insights from laboratory measurements of mixed cluster ions, Atmos. Environ. **38**(2004), 1734–1744
- [16] Wilson, C. T. R.: The Effect of Röntgen's Rays on Cloudy Condensation, Proc. Roy. Soc. **59** (1895), 338–339.
- [17] Yu, F. and R. P. Turco: The formation of aerosols in stratospheric aircraft plumes: Numerical simulations and comparisons with observations, J. Geophys. Res. **103**(2008), 25915– 25934.