

A possible new molecular mechanism of thundercloud electrification

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SUMMARY

It is well established that electrification occurs when charge is transferred between small and large ice particles colliding in a thundercloud that contains strong updrafts. The small ice particles rise with one type of charge and the large ice particles (graupels) fall and carry with them downward the other type of charge, which is most often negative, so that normally lightning lowers negative charge from cloud to the ground. Currently, the nature of the charge transfer between the colliding ice particles is not very well understood on the atomic level, and no present microscopic theory can explain fully the charge transfer, or even the sign of the charging. Here we propose a new charge separation mechanism that is based on molecular simulations of the collisions, keeping track of the individual charges as they move in the form of salt ions from one ice particle to another. This mechanism invokes charge separation at the surface of a thin layer of salt solution covering the graupel (the salt originates from the cloud condensation nuclei and is rejected to the surface during freezing of the droplets). Under normal conditions, when sulfates dominate as cloud condensation nuclei, this ionic mechanism is consistent with the prevailing negative lightning in thunderclouds. Moreover, with dearth of sulfate anions, the present mechanism predicts a shift towards positive charging. This fits well to a large range of observations of enhanced positive lightning, connected with smoke rich in chlorides and nitrates, that could not be explained satisfactorily previously.

MOLECULAR MODELLING

The suggested ionic mechanism of electrification relies on the fundamental difference in the composition of the ice crystal and the graupel. Ice crystals grow directly by

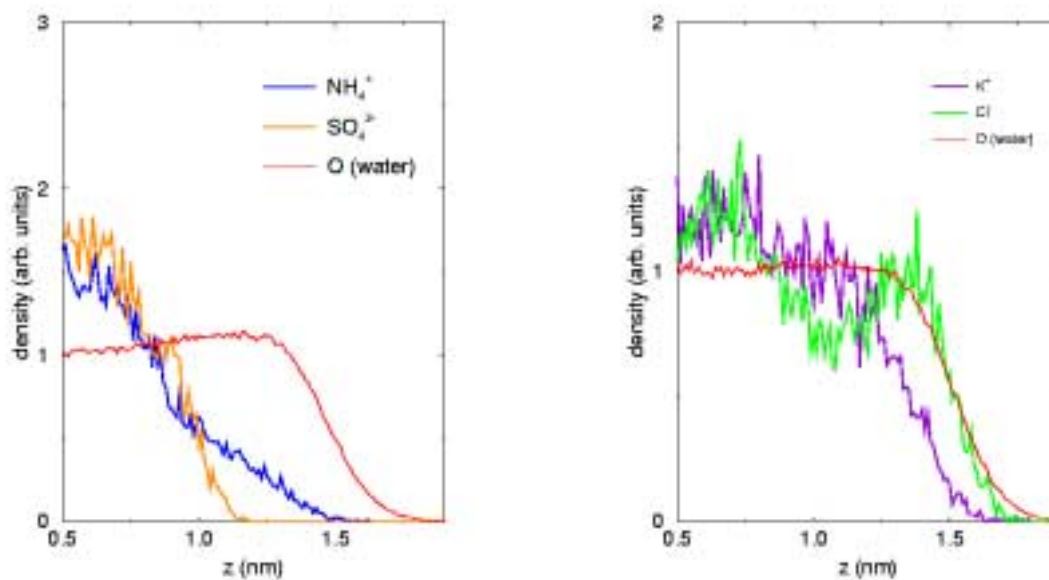
deposition of water vapor, forming a neat ice surface. The graupel surface is formed by frozen cloud droplets, which originally nucleated on pre-existing soluble aerosol particles - the cloud condensation nuclei (CCN). The surface of these frozen droplets is covered by a thin liquid layer containing soluble salts, primarily ammonium sulfate (which forms the most abundant CCN under normal conditions). The mechanism of the appearance of a concentrated solution at the surface during freezing of accreted water droplets can be viewed as a micro-analogue to salt rejection from ice during freezing of sea water above the eutectic point.

We have modelled the interfacial salt solution layer using molecular dynamics simulation in a slab arrangement. This principal result of the simulation is that aqueous ammonium cations and sulfate dianions have different interfacial concentrations. While in the bulk solution, the concentration ratio between the two ionic species, ammonium cations and sulfate dianions, equals to 2:1, we see an enhanced propensity of ammonium for the solution/air interface. The fact, that ammonium cations reside up to 0.5 nm closer to the solution/air interface than sulfate dianions has direct consequences for the charge transfer during collisions between ice crystals and graupels. Namely, as the neat quasi-liquid interfacial layer of the ice crystal gets in touch with the thin layer of ammonium sulfate solution covering the graupel, ammonium cations are preferentially transferred along the concentration gradient. This leads to positive charging of the rising ice crystals and negative charging of the falling graupels, in accord with the polarity evolution in standard thunderclouds, with the main positive charge pocket being situated above the negative charge region.

Under specific atmospheric conditions (e.g., forest fires or biomass burning) a large amount of aerosols containing other soluble ions, such as potassium cations and chloride and nitrate anions is released into the atmosphere. We have modelled this situation at a molecular level by simulating liquid slabs of a solutions of potassium chloride and potassium nitrate. The resulting density profiles for KCl are compared to those for in Fig. 1. We conclude that for aqueous KCl, the polarity of the interfacial layer is opposite to that of aqueous ammonium sulfate. As a matter of fact, KCl and behave similarly as the majority of inorganic salts (with the exception of salts containing polyvalent anions such as sulfate) creating an interfacial layer of negative polarity, i.e., with anions penetrating significantly closer to the solution/air interface than cations [1]. Thus, the present simulations indicate that replacing the sulfate dianion with monovalent anions such as chloride or nitrate leads to an opposite polarity of charging during graupel-ice crystal collisions, due to a polarity reversal at the interface of the salt solution covering the graupel.

We have also modelled a direct collision between an ice crystal and graupel particle. It follows from the present molecular dynamics simulations that during a single collision 1 - 3 elementary charges ($1.6-4.8 \times 10^{-4}$ fC) can be transferred per 10 nm^2 of contact area. This is equivalent to a charge transfer of 16-48 fC per collision, which is of the same order of magnitude or larger than values reported from laboratory studies [2].

Fig. 1: Density profiles at the air solution interface of 1.2 M aqueous ammonium sulfate and potassium chloride. Note the positive (negative) charge at the interface in the former (latter) case.



ATMOSPHERIC OBSERVATIONS

Sulfate is the most common anion in CCN, which is consistent with the observations that negative lightning prevail in ordinary thunderstorms. However, this negative charging is described also by the previously proposed mechanisms, so that solely this observation cannot lend support to the role of the present ionic mechanism. It is more instructive to examine below the relation between the ionic composition of aerosols and the polarity of lightning, exploring whether a greater fraction of non-sulfate anions is related to a greater percentage of positive lightning. Positive anomalies in the percentage of positive lightning that amounted to triple the climatological norm were observed over the USA in smoke plumes from forest fires in southern Mexico [3]. Chemical analysis of the smoke that reached the USA, which was associated with the enhanced percentage of positive lightning, showed that the fraction of nitrate and organic anion was greater than in the ambient aerosols [4]. Conversely, the highly sulfatic urban air pollution over Houston, Texas, was observed to have exactly the opposite effect on the lightning [5]. A decrease of 12% in the percentage of positive flashes is observed over the city. Higher negative median peak currents were also observed. In non-urban areas, smoke from tropical forest fires has the largest fraction of sulfate anions and hence a reduced potential to induce positive lightning compared to smoke from temperate forests or grasslands [6]. The sulfate content of the smoke typically increases as it matures because of deposition

and oxidation of SO₂ on the smoke particles [7]. This might explain why positive lightning does not dominate the thunderstorms that develop in the extensive mature smoke from the Amazon rain forest.

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