Intermediate Ions in the Atmosphere

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ABSTRACT: During the last decades, intermediate ion burst events became the focus of attention due to their role in the generation of atmospheric aerosol. Measuring of intermediate ions during the quiet periods between the bursts of aerosol nucleation is difficult due to the extremely low concentration of ions. A new mobility analyzer [Tammet, 2011] is able to measure the air ions at the concentrations of about 1 cm^{-3}, which makes available new information about the intermediate ions during the quiet periods. The measurements show that the intermediate ions exist always in the atmospheric air and should be considered as an indicator and a factor of the aerosol nucleation.

1. INTRODUCTION

Intermediate ions were discovered a hundred years ago [Pollock, 1915], but knowledge about this category of atmospheric ions remained low until the last decades. The AMS Glossary of Meteorology states: "whereas small and large ions are readily detected in all localities, intermediate ions have been reported only in a limited number of cases." (http://amsglossary.allenpress.com). Hõrrak et al. [2000] distinguished the intermediate air ions in the mobility range of 0.034–0.5 $cm^2V^{-1}s^{-1}$ or the diameter range of 1.6–7.4 nm and showed that they are responsible in average only for about 2% of total air conductivity. Thus their role as carriers of electric current in the atmosphere is marginal.

Small ions are charged molecules or clusters, whose internal energy levels are not excited when encountering a molecule of the carrier gas. Intermediate ions are charged nanometer particles whose internal energy changes during impacts. This difference has an effect in the size-mobility relation [Tammet, 1995]. Contemporary interest to study the intermediate ions is driven by discussions about the role of air ions in the formation of atmospheric aerosols. The electric charge lowers the energy barrier of the particle formation, enhances coagulation, and assists in creating particle embryos (ion-induced nucleation) as well as the following growth of these embryos (ion-mediated nucleation). The hypothesis about the genesis of nanometer particles via ion induced nucleation is supported by the positive-negative asymmetry of the intermediate ion polar concentrations, which is often observed during nucleation bursts. Some authors believe that ion-induced and ion-mediated mechanisms dominate in the atmosphere [Enghoff and Svensmark, 2008], but mostly the role of electrical mechanisms is estimated to be about 5–30 % of the total nucleation [Hirsikko et al., 2011].

The burst-like generation of intermediate ions was discovered in Tahkuse, Estonia [Tammet et al., 1988] and statistically described by Hõrrak et al. [1998, 2000]. Systematic measurements of atmospheric intermediate ions in Hyytiälä, Finland, supported the development of criteria for the classification of the burst events of intermediate ions [Hirsikko et al., 2007]. The concentration of the intermediate ions during bursts is comparable with the concentration of small ions and their mobility distribution can be correctly measured with contemporary instrumentation. Thus knowledge about intermediate ions in burst periods is fairly good [Hirsikko et al., 2007, 2011]. Unfortunately, the concentration of intermediate ions during the quiet periods between bursts is below the sensitivity level of earlier instruments. A new instrument SIGMA [Tammet, 2011] allowed to obtain better information about the intermediate ions.

2. METHODS OF MEASUREMENT

Measurement of intermediate ions in natural atmospheric air is a challenge for instrument developers. The distribution of ions is described by the set of concentrations of narrow mobility fractions. The concentration of ions in some fractions may turn out to be less than 1 cm^{-3}. The classic requirement of laminar flow limits the air flow rate in a traditional mobility analyzer to about 1000 cm^3s^{-1}. This air flow is divided into deionized sheath air and sample air. If a mobility fraction contains 1 charged particle per cm^3 and the sample air flow rate is 200 cm^3s^{-1}, then the collected current of about 3×10^{-17} A turns out less than the noise level of the best electrometric instruments when applied in atmospheric conditions. Hence, the air flow rate should be much larger to make measurements possible. Another reason for having a high flow rate is the necessity to suppress the diffusion losses in the air inlet tract and the effect of the atmospheric electric field on the intake of ions.

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The control voltage required for the classification of intermediate ions at a high flow rate exceeds a thousand volts. Keeping the ion collector on high potential is technically inconvenient and can lead to usability issues. On the other hand, the inlet of the instrument must be grounded to avoid the edge effect of the electric field on the sampling of ions. Labowsky and Fernández de la Mora [2006] introduced the term *isopotential* to designate mobility analyzers where both the inlet and outlet are on the ground potential. Instruments for the research of intermediate ions in natural atmospheric air must be isopotential.

An effective way to increase the sensitivity in the mobility distribution measurements is the multichannel method [Tammet et al., 1973]. Using n simultaneous electrometers reduces the effective noise level $\sqrt{n}$ times. The multichannel method was used for measurements at Tahkuse [Hõrrak et al., 1998, 2000] and in the modern instruments AIS and NAIS [Mirme et al., 2007], which are used in many stations of atmospheric aerosol research [Manninen et al., 2010].

The single-channel scanning intermediate ion mobility analyzers should employ an extra high air flow rate of up to 40 liters per second. This is implemented in the instruments BSMA [Tammet, 2006] and SIGMA [Tammet, 2011], which are optimized for measuring intermediate ions with mobility down to 0.032 $cm^2V^{-1}s^{-1}$. The SIGMA allows for measuring the fraction concentrations of ions below 1 cm^{-3} as required for studying the intermediate ions during quiet periods between burst events.

3. INTERMEDIATE IONS DURING THE QUIET PHASE OF AEROSOL NUCLEATION

The measurements of intermediate ions in the mobility range of 0.032–0.50 $cm^2V^{-1}s^{-1}$ by SIGMA were made in Tartu, Estonia, during 2010–2011. The average concentration of positive intermediate ions was 35 cm^{-3} and the concentration of negative intermediate ions was 33 cm^{-3}. This is about 60% of the values measured earlier by Hõrrak et al. [2000] in the rural station at Tahkuse. Distribution of the measurements according to the concentration classes shown in Figure 1 is very much asymmetric. The concentration of less than 50 cm^{-3} can be considered as a distinctive characteristic of the quiet phase of aerosol nucleation.

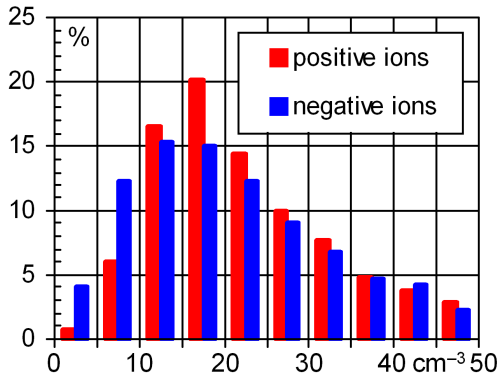

Figure 1. Histogram of the intermediate ion concentration in Tartu, Estonia, 2010–2011. About 14% of the measurements exceed the diagram limit of 50 cm^{-3}.

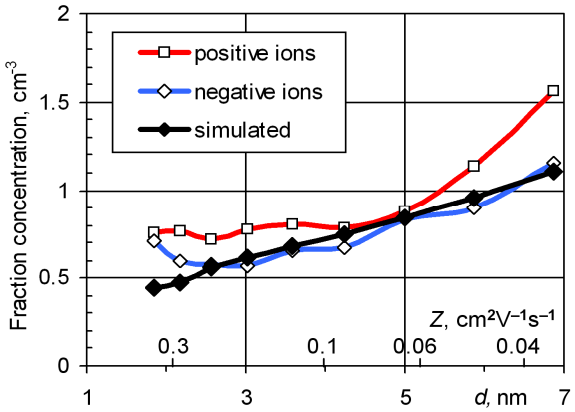

Figure 2. Distribution of air ions according to the mobility Z and the diameter d during quiet periods of aerosol nucleation. The markers on the curves point the centers of the mobility fractions.

The distribution of intermediate ions measured in Tartu 2010–2011 according to the mobility and the diameter of the particles is shown in Figure 2, which is compiled according to the average of the 48 selected hours when the concentration of intermediate ions was extra low.

Intermediate ions are created in the initial stage of aerosol nucleation. They cannot immediately act as condensation nuclei due to the small size, but can be considered to be the germs of the condensation nuclei. The genesis and following evolution of the nanoparticles is an essential subject of the research of atmospheric aerosols. The evolution of the intermediate ions during burst events can be estimated according to the growth of the mean diameter of ions in time during the burst [Hirsikko et al., 2007]. The mean diameter does not grow during quiet periods. Nevertheless, the individual intermediate ions always grow while some atmospheric trace substances are condensing on the particles. Unlike during the burst events, the growth in the quiet phase is not immediately visible in the diagrams. However, the growth rate can be estimated using numerical models of nanoparticle evolution e.g. the model proposed by Tammet and Kulmala [2005] for simulating the nanoparticle bursts. This model takes into consideration the ion-induced and homogeneous nucleation, the charging and neutralization of nanoparticles with small ions, the growth of nanoparticles as influenced by different factors,

and the depletion of nanoparticles and ions on pre-existing background aerosol. The model can be easily modified for the study of steady distributions. A numerical experiment showed that the measurements like those presented in Figure 2 can be approximated with simulated curves without including the ion-induced nucleation. The black simulated curve in Figure 2 corresponds to a nucleation rate of 1.5 $cm^{-3}s^{-1}$ at a particle birth diameter of 1.65 nm and a flat growth rate of 3.2 nm/hour. This growth rate is of the same magnitude as during typical burst events. The nucleation rate in the simulation experiment is presented for a very small size and the apparent nucleation rate (see Kerminen and Kulmala, 2002) at the traditional initial size of 3 nm is 0.15 $cm^{-3}s^{-1}$. This is 10–30 times less than the typical nucleation rate during bursts. The total duration of the quiet periods exceeds the duration of the burst periods by about 20 times, which compensates for a low nucleation rate. Thus the quiet nucleation is a considerable source of ultrafine particles of atmospheric aerosol.

4. INTERMEDIATE IONS DURING BURSTS OF AEROSOL NUCLEATION

The atmospheric chemical processes always produce a lot of nanometer size clusters. Most of these clusters are quickly adsorbed by background aerosol during the quiet periods and only few of them will grow into detectable particles. When the concentration of background aerosol particles is extra low and cluster formation is enhanced, new intermediate ions will extensively grow and transform to the Aitken and accumulation mode aerosol particles. A favorable situation for a burst event in the hemiboreal and boreal zone is sunny and cold weather, when the air mass is from the Arctic region and contains few background aerosol particles. A burst event can usually be explained with the simultaneous decrease of the background aerosol concentration and an increase in the concentration of sulfuric acid molecules that is an important factor of new particle formation. Other contributing compounds may be ammonia and some volatile organic compounds. The model calculations showed that the transfer from the quiet situation to the burst situation is abrupt. Thus the burst events are usually clearly distinguished from the quiet phase. According to the year-round measurements in Tartu, Estonia, the 100 cm^{-3} level of the one-polarity intermediate ion concentration is surpassed in about 5% of the measurements. Measurements in other locations in the hemiboreal and boreal zone show similar results as in Tartu. According to a rough criterion a burst is reliably identified when the concentration of intermediate ions of one polarity in the mobility range of 0.032–0.50 $cm^2V^{-1}s^{-1}$ exceeds the value of 100 cm^{-3}. Events with a concentration in the range of 50–100 cm^{-3} can be qualified as weak bursts or a quiet phase after learning the details of the size-time distribution of the intermediate ions.

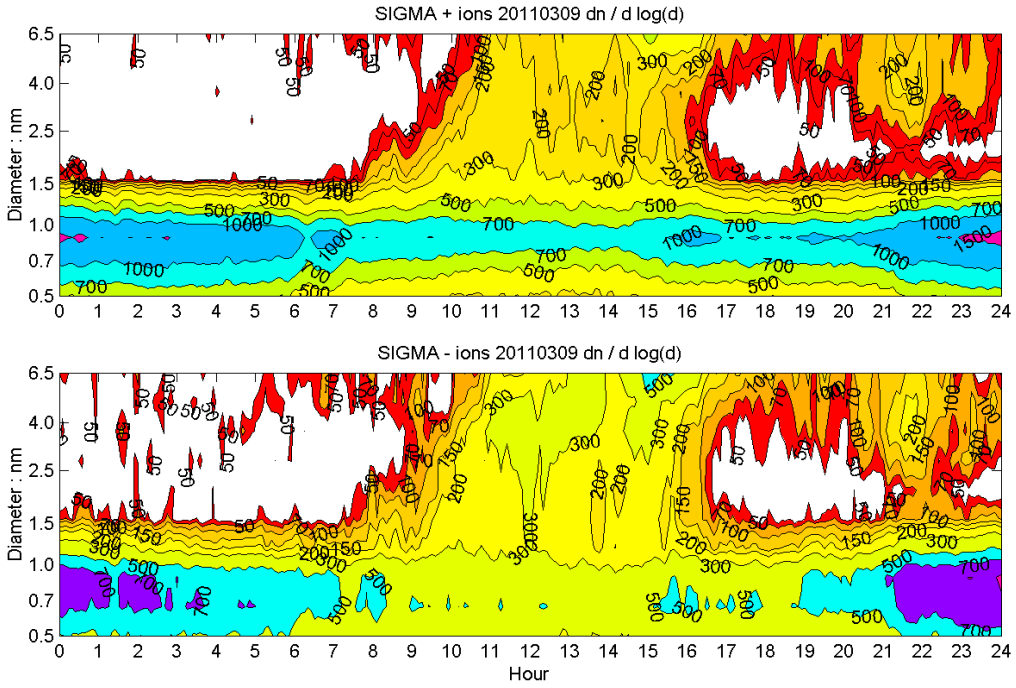

Figure 3. Example of the evolution of intermediate ions during a burst day in the city of Tartu, Estonia. Concentrations of measured size fractions were 8 times less than the numbers at the isolines.

An example of the evolution of the size distribution of intermediate ions during a day is illustrated by a contour plot in Figure 3. The first 7 hours of the day qualifies as a quiet phase of aerosol nucleation when the concentration of the intermediate ions is mostly less than the level of the first contour line. A typical fair weather

burst event follows around noon. A weak burst of a different shape is seen in the same diagram around hour 22. Main classes of aerosol nucleation burst events are thoroughly described by Hirsikko et al. [2007]. The existing classification is based on the visual analysis of the diagrams of burst events. Unfortunately, the physical-chemical mechanisms of the different burst events are not reliably known and the peculiarities of specific classes are mostly explained only by hypotheses.

A considerable part of intermediate ion bursts in the real atmosphere is caused by the generation of negative intermediate ions during rain by the splashing of water [Tammet et al., 2009], which is known as the balloelectric effect. These particles will not grow up to condensation nuclei and the rain-time balloelectric generation of nanoparticles is not considered to be aerosol nucleation.

5. CONCLUSIONS

Intermediate ions are often recorded during bursts of atmospheric aerosol nucleation. The concentration of intermediate ions during quiet periods between the bursts is below the sensitivity level of earlier instruments. A new instrument allowed to show that the intermediate ions exist always in the atmospheric air and should be considered as an indicator and a factor of the aerosol nucleation during nucleation bursts as well as during quiet periods. The annual average concentrations of intermediate ions in Tartu, Estonia, were about 34 cm^{-3}.

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REFERENCES

Enghoff, M.B. and H. Svensmark, The role of atmospheric ions in aerosol nucleation – a review, Atmos. Chem. Phys., 8, 4911–4923, 2008.

Hirsikko, A., Bergman, T., Laakso, L., Dal Maso, M., Riipinen, I., Hõrrak, U., and M. Kulmala, Identification and classification of the formation of intermediate ions measured in boreal forest, Atmos. Chem. Phys., 7, 201–210, 2007.

Hirsikko, A., Nieminen, T., Gagné, S., Lehtipalo, K., Manninen, H.E., Ehn, M., Hõrrak, U., Kerminen, V.-M., Laakso, L., McMurry, P.H., Mirme, A., Mirme, S., Petäjä, T., Tammet, H., Vakkari, V., Vana, M., and M. Kulmala, Atmospheric ions and nucleation: a review of observations, Atmos. Chem. Phys., 11, 767–798, 2011.

Hõrrak, U., Salm, J., and H. Tammet, Bursts of intermediate ions in atmospheric air, Journal of Geophysical Research 103 (D12), 13909–13915, 1998.

Hõrrak, U., Salm, J., and H. Tammet, Statistical characterization of air ion mobility spectra at Tahkuse Observatory: Classification of air ions, J. Geophys. Res. Atmospheres, 105, 9291–9302, 2000.

Kerminen, V.-M. and M. Kulmala, Analytical formulae connecting the “real” and the “apparent” nucleation rate and the nuclei number concentration for atmospheric nucleation events, J. Aerosol Sci., 33, 609–622, 2002.

Labowsky, M. and J. Fernández de la Mora, Novel ion mobility analyzers and filters, J. Aerosol Sci., 37, 340–362, 2006.

Manninen, H.E. et al., EUCAARI ion spectrometer measurements at 12 European sites – analysis of new particle formation events, Atmos. Chem. Phys., 10, 7907–7927, 2010.

Mirme, A., Tamm, E., Mordas, G., Vana, M., Uin, J., Mirme, S., Bernotas, T., Laakso, L., Hirsikko, A., and M. Kulmala, A wide-range multi-channel Air Ion Spectrometer, Boreal Environ. Res., 12, 247–264, 2007.

Pollock, J.A., A new type of ion in the air, Philos. Mag., 29, 636–646, 1915.

Tammet, H., Continuous scanning of the mobility and size distribution of charged clusters and nanometer particles in atmospheric air and the Balanced Scanning Mobility Analyzer BSMA, Atmos. Res., 82, 523–535, 2006.

Tammet, H., Hõrrak, U., M. Kulmala, Negatively charged nanoparticles produced by splashing of water, Atmos. Chem. Phys., 9, 357–367, 2009.

Tammet H. and M. Kulmala, Simulation tool for atmospheric aerosol nucleation bursts. J. Aerosol Sci., 36, 173–196, 2005.

Tammet, H., Salm, J., and H. Iher, Observation of condensation on small air ions in the atmosphere, In Atmospheric Aerosols and Nucleation, Lecture Notes in Physics, Springer-Verlag, Vienna, 309, pp. 239–240, 1988.

Tammet, H., Size and mobility of nanometer particles, clusters and ions, J. Aerosol Sci., 26, 459–475, 1995.

Tammet, H., Symmetric inclined grid mobility analyzer for the measurement of charged clusters and fine nanoparticles in atmospheric air, Aerosol Sci. Technol., 45, 468–479, 2011.

Tammet, H.F., Jakobson, A. F., and J.J. Salm, Multi-channel automatic air ion spectrometer (in Russian), Acta Comm. Univ. Tartu, 320, 48–75, 1973.