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Mobility spectrum of air ions at Tahkuse Observatory

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Abstract. Mobility spectra of air ions have been measured at a rural site in Estonia during several periods. The annual average mobility spectrum of natural small air ions is presented. The concentrations of two groups of air ions with mobilities 0.32-0.5 $cm^2/(V\ s)$ and 0.5-2.5 $cm^2/(V\ s)$ are not correlated; this fact indicates the different nature of the ions of the two groups. The air ions with mobilities 0.5-2.5 $cm^2/(V\ s)$ are interpreted as cluster ions and the air ions with mobilities 0.32-0.5 $cm^2/(V\ s)$ as charged aerosol particles that can be created in the process of ion-induced nucleation. A half-year average mobility spectrum of the large ions with mobilities 3.2×10^{-4} - 1.5×10^{-1} $cm^2/(V\ s)$ is presented. The spectrum is well interpreted on the basis of the average size distribution of aerosol particles and on the theory of diffusion charging of the particles.

Introduction

Despite the long history of atmospheric ion measurements, many problems of fundamental importance have not been solved up to now: for example, the chemical composition of small air ions, conditions and mechanism of generation of intermediate air ions, and mobility distribution of ultralarge air ions. There are a few systematic observations of air ions in a wide range of mobility and no long-termed measurements of detailed mobility spectra in atmospheric air. The aim of this work is to obtain some information for solving the above problems.

Location, Apparatus, and Measurement Techniques

The air ion observatory is located in the village of Tahkuse, in a sparsely populated rural region, 27 km northeast of the city of Pärnu, Estonia. The geographical coordinates of the observatory are 58°31'N 24°56'E. The most accessible experimental technique of air ion analysis is the mobility spectrometry. The authors have accepted aspiration spectrometers as the most suitable for measurements in the troposphere.

The first measurements of air ions at this place have been performed in summer 1984 [*Tammet et al.*, 1985]. A mobility spectrometer of special design (with a built-in corona ionizer) was used [*Tammet et al.*, 1977]. The air intake was at a height of 3 m from ground level. A computer-controlled equipment provided measurement and storage of mobility spectra of both negative and positive ions every 2 min. At the end of every hour the hourly average spectra with standard deviations of the signals were computed and saved on a compact cassette.

The mobility spectrum of natural small air ions was recorded in 1985-1986 [*Tammet et al.*, 1992]. An original mobility spectrometer has been designed and built for these measurements [*Tammet et al.*, 1987]. The air intake was at a height of 5 m. The complete information about mobility spectra of negative and positive ions with zero-level signals of each channel was obtained and stored every 5 min. The hourly averages and standard deviations of spectral components and meteorological parameters were saved on a compact cassette.

In 1988 an extended system for routine measurements in a wide range of mobility was set into operation [*Hõrrak et al.*, 1990]. The system has been designed for continuous measurement of atmospheric electrical and meteorological parameters. The mobility spectrum of air ions is measured by two original multichannel spectrometers in a range of 3×10^{-4}-3 $cm^2/(V\ s)$. The air intake is at the same height as in 1985-1986. The whole range of mobility is logarithmically divided into 20 intervals: 9 intervals for subrange of 3×10^{-4}-0.25 $cm^2/(V\ s)$ and 11 intervals for 0.25-3 $cm^2/(V\ s)$. The procedures of measurement and of data management described in the paper [*Tammet*, 1990] are similar to that of the above period 1985-1986.

The results primarily saved on compact cassettes are subsequently rewritten on a hard disk of a laboratory computer. The first stage of data processing includes an analysis of measurement errors and the elimination of failures. The analysis is based on the recordings of zero levels when the driving voltage of the spectrometers is switched off every 5 min. Statistical criteria are used to eliminate the incorrect measurements.

Mobility Spectrum of Small Ions Generated in Natural Air

Artificially generated small air ions were measured in the city of Tartu and at the Tahkuse observatory (for 2 months) in the summer of 1984 [*Tammet et al.*, 1985]. The ions were generated by corona discharge and measured after an aging of 1 s. During the aging the composition of the ions changes due to ion-molecular reactions. The result of the reactions depends on the contents of various trace gases in the air.

The mobility spectra of both negative and positive ions in urban air (city of Tartu) were unimodal (Figure 1a). The peak of negative ions was at 1.8 $cm^2/(V\ s)$ and that of positive ions at 1.1 $cm^2/(V\ s)$. Additional measurements in the same place during March 1986 confirmed the stability of these shapes of spectra.

The measurements at the Tahkuse observatory were carried out from June 27 to August 29, 1984; 160 hourly average spectra have been recorded. The measurement hours were distributed stochastically in the interval from 0500 to 2300 LT. According to statistical criteria, 39 spectra were rejected, and 121 spectra both of negative and of positive ions remained for further analysis.

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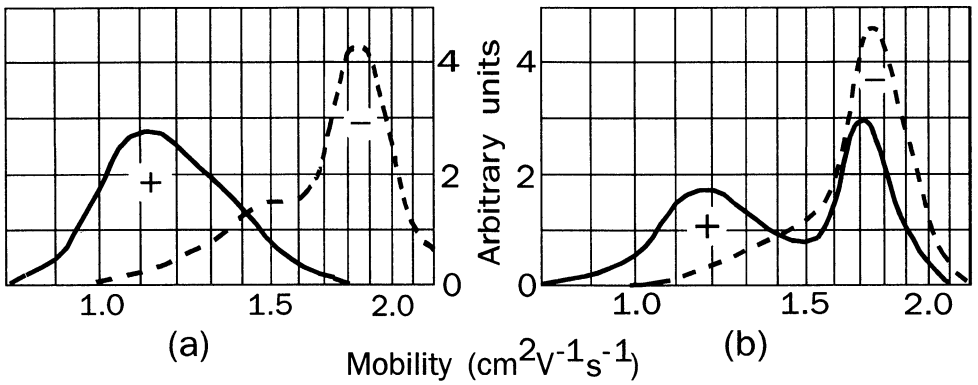

Figure 1. Average mobility spectra of 1-s-aged air ions: (a) in the city of Tartu and (b) at the Tahkuse observatory [*Tammet et al.*, 1985].

In the rural air the spectrum of negative ions remained almost the same, but the spectrum of positive ions acquired another peak at 1.7 $cm^2/(V\ s)$ (Figure 1b) that was never met in urban air. The heights of the peaks of positive ions varied, but the peak at 1.7 $cm^2/(V\ s)$ dominated statistically in more than 90% of the spectra.

The origin of the previously mentioned effect was not determined. A laboratory experiment proved that the addition of amines, especially diamines, into the air generated positive ions with higher mobilities [*Parts*, 1992]. In special cases the mobility of about 1.7 $cm^2/(V\ s)$ was found. The amines are typical trace gases in rural air.

Natural Small Air Ions

Continuous measurements of the mobility spectra of natural small air ions were carried out from June 10, 1985, to June 2, 1986. About 16% of the total number of hours was lost due to technical reasons (power cutoff, check and adjustment of apparatus, etc.). Almost the same percentage of spectra was eliminated within data processing. The reason of data elimination was the deterioration of the electrometric insulation that was detected according to anomalous high variations of zero levels or overloading of electrometers. The lost and eliminated hours were uniformly distributed over the year; 6053 hourly average spectra of negative and positive ions remained for further analysis. The fraction concentrations were directly averaged without any normalization of the spectra. The average spectra for this period are depicted in Figure 2. Average spectra for a period from July 21, 1988, to January 31, 1989, are given in the same figure with a dashed line.

Almost all the small air ions are concentrated in the interval of mobility from 0.6 to 2.5 $cm^2/(V\ s)$. The occurrence of a small amount of ions above 2.5 $cm^2/(V\ s)$ in the measurement results can be explained as an effect of a low resolution of the apparatus. Probably, there are no real ions with mobility more than 2.5 $cm^2/(V\ s)$ in the near-ground air. The lower boundary of the mobilities of small air ions is about 0.5 $cm^2/(V\ s)$. A statistical analysis shows that there is no correlation between the concentrations of fractions situated on either side of this boundary [*Tammet et al.*, 1992]. The value of 0.5 $cm^2/(V\ s)$ corresponds to an ion diameter of 1.3-1.4 nm and to a mass of about 1500 amu. This boundary obviously separates molecular clusters and macroscopic particles.

There is a quantitative difference between the spectra measured during the two periods. The total concentration of small air ions was about 1.4 times lower in 1988-1989 compared with 1985-1986. This can be a consequence of a higher aerosol load or of a lower radioactivity of the atmosphere. The average mobility of small air ions is also slightly reduced.

The first measurement period includes the date of the accident in the nuclear power plant at Chernobyl (April 26, 1986) and the following month. The concentration of both negative and positive small air ions was about 300 cm^{-3} for many weeks till April 27. Then it began to increase rapidly and reached a maximum 800 cm^{-3} on May 1. After that the concentration slowly decayed during a month to a value of about 400 cm^{-3}. Although the melting of soil (and the eventual release of radon) occurred roughly at the same time, probably the radioactive contamination caused by the accident was essential. However, the contribution of this additional ionization to the yearly average concentration of small air ions cannot exceed a few percent.

A special study of the dependence of mobility spectra on temperature showed some distinct relationships [*Salm et al.*, 1992]. The reduced average mobilities of both negative and positive air ions decrease about 20% according to the increase in temperature from -5°C to 25°C. This phenomenon has not yet been sufficiently explained by a certain physical-chemical model. As a working hypothesis, we suppose that the concentration of active trace gases rises when temperature is increased, and it follows the formation of larger clusters.

Intermediate Air Ions

The problem of intermediate air ions was raised as far back as in 1915 [*Pollock*, 1915], but it is still problematic up to the present. The fraction of ions from 0.32 to 0.5 $cm^2/(V\ s)$ (see Figure 2) was measured together with more mobile ions in 1985-1986. The fraction has a quite different behavior in comparison with the small air ions [*Tammet et al.*, 1988a, b, 1992; *Hõrrak et al.*, 1988]. Enhanced concentrations of these ions occurred rarely (4% of the whole period); their variations were not correlated with the variations of small air ions. In extreme cases the concentration of intermediate air ions exceeded that of the small air ions. Not any clear dependence on seasons was established, but the diurnal variation has an expressive shape: enhanced concentrations of intermediate ions took place mainly at local midday [*Hõrrak et al.*, 1988]. In 1988-1989, enhanced concentrations of intermediate ions were observed less frequently.

The mechanism of the generation of intermediate air ions was

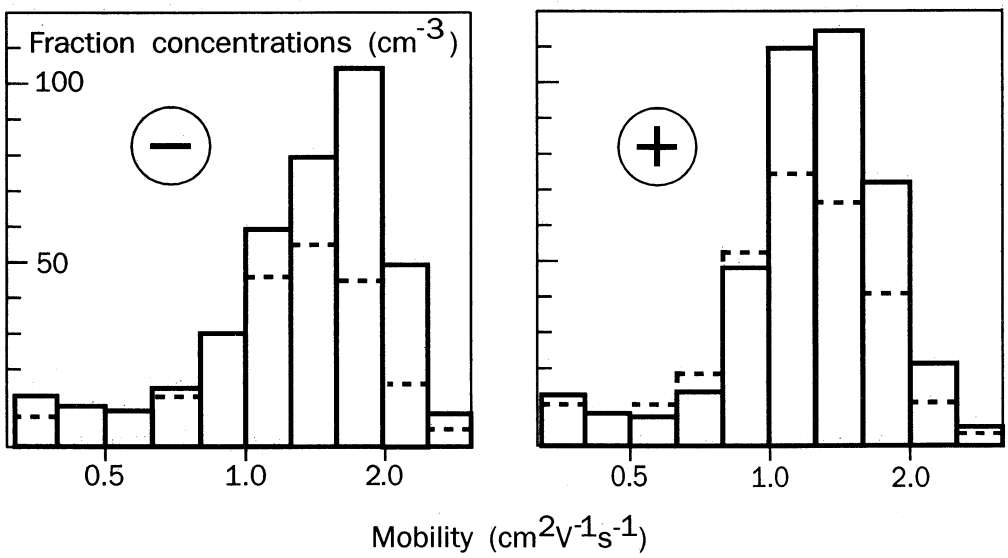

Figure 2. Annual average mobility spectra at Tahkuse observatory in 1985-1986 (solid line) and in 1988-1989 (dashed line). In the case of 70% of measurement hours the hourly average fraction concentrations remain between 40% and 200% of the annual averages. For details of statistical distributions, see *Tammet et al.* [1992].

discussed but has not yet been established [*Tammet et al.*, 1988a, b, 1992]. The standard hypothesis is that neutral particles are charged by the attachment of small ions, but at least three objections can be made:

1. If the hypothesis is true, the concentration of neutral particles in the size range of 1.4-1.9 nm should be tens of thousands in cubic centimeters.

2. The high concentrations of neutral particles should suppress the concentration of small ions, but no considerable suppression was observed.

3. It is difficult to explain the charge asymmetry of the concentrations of intermediate ions that was often observed.

Therefore we suppose that the generation of intermediate air ions is due to the ion-induced gas-to-particle conversion process [*Tammet et al.*, 1988a] depending on the concentrations of some special trace gases.

Mobility Spectrum of Large Air Ions

The conception that Langevin (large) ions are aerosol particles charged by attachments of small ions was commonly accepted but not explicitly proved by direct measurements in atmospheric air. The quantitative proof needs, on the one hand, theoretical calculations of the mobility spectrum and, on the other hand, systematic measurements of the mobility spectrum of air ions and of the size spectrum of aerosol particles in natural conditions.

The theory of charging aerosol particles has been developed by many authors; we confine ourselves to a few essential references, e.g. *Lissowski* [1940], *Fuchs* [1947, 1963], *Hoppel and Frick* [1986]. *Hoppel* [1978] analyzes a differential mobility chamber and gives an iterative scheme for converting the mobility distribution to a size distribution. *Salm* [1988] proposed a theoretical model of the formation of the mobility spectrum in typical natural conditions of the lower troposphere, considering the preceding theory of charging aerosols for a wide range and the average size spectrum of aerosol particles by *Smerkalov* [1984].

Based on the data for the 6-month period (July 21, 1988, to January 31, 1989), the average mobility spectrum with the estimates of natural variations and of measurement errors was calculated; 2669 hourly samples of the signals in all have been recorded for this period, but 2232 spectra for negative and 2633 spectra for positive ions remained for analysis after the elimination of technically incorrect measurements.

The directly measured average mobility spectrum for the above period is presented in Figure 3. A mobility spectrum of air ions calculated from aerosol data is depicted by a dotted curve in the same figure. The spectrum was calculated using the theoretical model by *Salm* [1988]. The size distribution of aerosol particles was accepted as a worldwide average by *Smerkalov* [1984]. It is suitable to present the size spectrum of aerosol particles by the KL model [*Tammet*, 1992]:

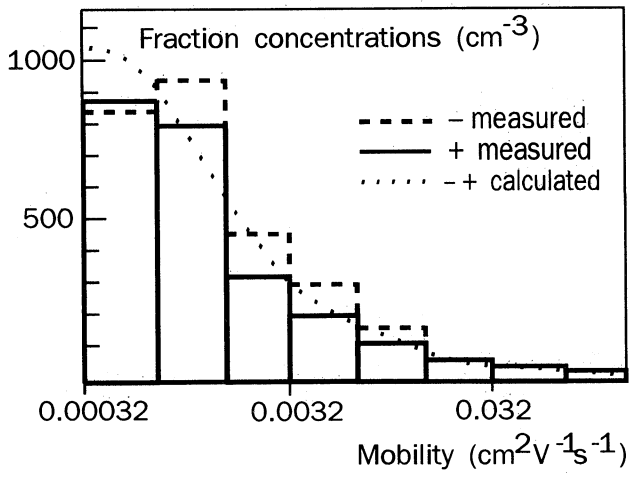

Figure 3. Calculated and measured average mobility spectra of large air ions (Tahkuse, 1988-1989). The relative variations are roughly the same as in the case of small air ions.

$$\frac{dZ}{d(\ln r)} = r\frac{dZ}{dr} = \frac{a}{[(r/r_x)^K + (r_x/r)^L]} \quad (1)$$

where r is the radius, dZ is the concentration of aerosol particles in an interval $(r, r + dr)$, and a, r_x, K, and L are parameters. The total concentration of aerosol particles in the range of radii $1\text{-}10^4$ nm is preassigned 10,000 cm^{-3} in Figure 3. Typical direct measurement data in rural regions give lower average values of the concentration (about 6000-7000 cm^{-3}), for example [*Kikas et al.*, 1990], but in those measurements the smallest particles ($r < 5$ nm) were neglected. The parameters corresponding to the Smerkalov distribution with the above total concentration are as follows: $a = 5200$ cm^{-3}, $r_x = 72$ nm, $K = 3.15$, and $L = 0.44$. The mean radius of the particles (for the above range of radii) is 33 nm.

Changing the parameters of the KL model and calculating the corresponding mobility spectrum, it is possible to better fit the experimental mobility spectrum. The best fit was reached by the following values of parameters: $a = 8400$ cm^{-3}, $r_x = 41.7$ nm, $K = 2.68$, and $L = 0.82$. The corresponding mean radius of the particles is 29 nm and the calculated concentration of aerosol particles in the range of radii $1\text{-}10^4$ nm is 10,750 cm^{-3}.

On the Classification of Air Ions

On the basis of the above measurement results and speculative argumentation the traditional classification of air ions into small, intermediate, and large ions can be completed with adjacent classification according to the physical nature of air ions [*Tammet et al.*, 1992, 1988a, b]. The latter classification first distinguishes cluster ions and aerosol ions.

The cluster ions are formed from primary ions through a chain of ion-molecular reactions. In the steady state of the troposphere they are concentrated in a mobility interval of 0.5-2.5 $cm^2/(V\ s)$ and traditionally they are called small ions.

The aerosol ions are macroscopic aerosol particles carrying an electric charge. There are two ways of charging the particles. Most of the particles get a charge by diffusion attachment with cluster ions. Such particles can be called secondary aerosol ions (the traditional synonym is large ion).

A few aerosol ions may also arise on cluster ions in the process of ion-induced nucleation. They carry an inherent charge and could be called primary aerosol ions. The primary aerosol ions can be found in the mobility interval of intermediate ions.

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