MOBILITY SPECTRA OF AIR IONS

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ABSTRACT: Air ions are classified into cluster ions and aerosol ions. The aerosol ions may be subdivided into condensed ions and secondary ions. The latter subgroup is usually dominating. An annual measurement of the air ion mobility spectra has been carried out on a rural site. The examples of the spectra demonstrate the occurrence of condensed ions in the troposphere. The mobility of 0.5 $cm^2/(V \cdot s)$ seems to be a physical boundary between the cluster ions and the aerosol ions. The evolution of cluster ions has been theoretically studied. The average mobility spectrum of aerosol ions is derived from the aerosol measurement data.

INTRODUCTION

All the charged particles whose drift velocity v in the air is proportional to the electric field strength E may be called air ions. Hence, $v = kE$, where the proportionality factor k is the mobility of an air ion. In the real air there are air ions with different physical nature and with different mobilities. The distribution of air ions according to their mobilities, i.e. the mobility spectrum of air ions, describes almost entirely the electric state of air and provides information about trace gases and the particles in it.

The measurement of the mobility spectrum is relatively easy to carry out in the case of high ion concentrations or low air pressure, and thus more detailed data about air ions have been obtained by experiments in the laboratory as well as by measurements in the upper atmosphere. Still the mobility spectrum of air ions depends on their age and on the composition of the air. For that reason a direct study of natural air ions on the atmospheric surface level is necessary. The aspiration method for measuring the mobility spectrum of air ions has proved to be the most effective method for tropospheric conditions (Tammet, 1970).

To study the nature of air ions the mass-spectrometric method has lately been used on the ground level (Eisele, 1986). However, mathematical simulation of ion-molecular reactions remains still a useful instrument for investigating the evolution of ions (Kawamoto, Ogawa, 1987).

CLASSIFICATION OF AIR IONS

The classification of air ions according to mobility into small, intermediate, Langevin's (large) and ultra-large is the most familiar one (Israël, 1957). Our recent investigations enable us to add some comments and revisions to this matter. The group of small air ions is definable by taking into account the physical considerations, but lower limit of mobility is to be made more adequate. The boundaries between intermediate, large and ultra-large ions are conventional. The last 3 types of air ions, in accordance with their physical nature, are charged aerosol particles.

We have proposed another classification based on the physical nature of air ions (Tammet, Iher, Salm, 1987). Small air ions are charged

molecular clusters and therefore we recommend to call them cluster ions. Charged aerosol particles could be called aerosol ions. The most abundant aerosol ions which are charged by the attachment of cluster ions have been called secondary aerosol ions or secondary ions.

Our results of the measurements in the troposphere show that the condensation of some gases on ions sometimes plays an important role in the formation of the mobility spectrum. For that reason the aerosol ions with inherent charges which have enlarged by the condensation of matter on cluster ions can be called condensed ions.

The ranges of the mobility of cluster ions, condensed ions and secondary ions partially overlap.

CLUSTER IONS

The mobility of a cluster ion can be reduced to normal conditions according to the equation

$$k = k' \frac{p}{101325\ \mathrm{Pa}} \frac{273.15\ \mathrm{K}}{T}, \qquad (1)$$

where k' is natural mobility.

The mobility of a cluster ion is correlated with its mass. The experimental data (Kilpatrick, 1971; Meyerott, Reagan, Joiner, 1980) can be expressed by the following approximation formula

$$m \approx \frac{800\ \mathrm{amu}}{(0.3 + k:\ \mathrm{cm^2/(V \cdot s)})^3}. \qquad (2)$$

Cluster ions with fixed mass and structure have discrete mobilities. Fast ion-molecule reactions inside the mobility analyzer can modify and smooth the measured spectrum (Mohnen, 1977).

The mobility spectrum of air ions within the mobility interval of 0.32 - 3.2 $cm^2/(V \cdot s)$ has been continuously recorded in the village of Tahkuse situated 30 kilometers to NE from Pärnu, Estonian SSR, during the period of 10 June 1985 - 2 June 1986 (Tammet, Iher, Salm, 1987). The annual average spectra are shown in Figure 1. The nonzero values of the spectra, where $k > 2.5\ cm^2/(V \cdot s)$ can be explained by the apparatus dispersion. The most mobile ions $NH_4^+ \cdot H_2O$ whose occurrence in considerable amount is probable have the mobility of about 2.5 $cm^2/(V \cdot s)$. The mobility values higher than 3 $cm^2/(V \cdot s)$ given in some papers are evidently the results of apparatus distortions.

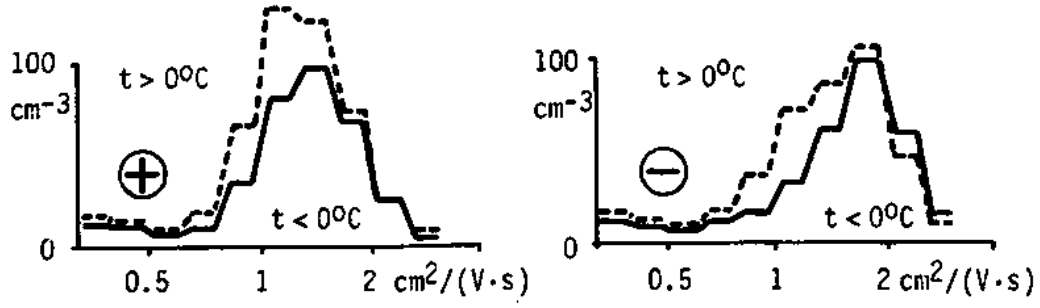

Fig. 1. Annual average spectra of air ions

The statistical analysis of the spectra showed that the concentrations of two different spectral fractions are positively correlated if the mobilities of both fractions are either higher or lower than

0.5 $cm^2/(V \cdot s)$. Otherwise there is no essential correlation. This phenomenon can be explained by different physical nature of ions on both sides of the value mentioned above. The value 0.5 $cm^2/(V \cdot s)$ corresponds to the mass of 1500 amu. If the mass of a cluster ion exceeds the boundary value, the cluster turns into an aerosol particle. On the basis of measurements and theoretical considerations we can state that the reduced mobility of the majority of cluster ions on the atmospheric surface level is found in the range of 0.5-2.2 $cm^2/(V \cdot s)$. Henceforth we reserve this range as inherent for cluster ions.

The analysis of the measurement results shows that the mobility spectrum essentially depends on the temperature of the air. For example, the average mobility of cluster ions considerably decreases with an increase in temperature, especially in summer. The wind direction also has an effect on the spectra. These phenomena may be explained by the dependence of the amount of various trace gases in the atmosphere on the temperature and other meteorological parameters.

The annual average of reduced mobilities of cluster ions were $k_- = 1.56$ $cm^2/(V \cdot s)$ and $k_+ = 1.36$ $cm^2/(V \cdot s)$. They correspond to the masses of about 130 amu and 175 amu.

NUMERICAL SIMULATION OF THE EVOLUTION OF CLUSTER IONS

Several authors have made use of numerical simulation of ion-molecular reactions (Mohnen, 1977; Huertas, Fontan, 1982; Kawamoto, Ogawa, 1987). We have found some effective methods of calculation and we have somewhat increased the number of ions, neutrals and reactions under consideration.

The model for negative ions contains 60 ions, 20 neutrals and 200 reactions. The predominant ions in the steady state are $O_2^- \cdot (H_2O)_4$, $O_2^- \cdot (H_2O)_5$, $NO_3^- \cdot (HNO_3) \cdot H_2O$, $NO_2^- \cdot SO_2$ and $CO_3^- \cdot (H_2O)_4$. The corresponding mobilities from Formula (2) are 1.7, 1.6, 1.5, 1.6 and 1.5 $cm^2/(V \cdot s)$ which do not disagree with the observed average value of 1.56 $cm^2/(V \cdot s)$.

An analogous calculation for 250 positive ions, 120 neutrals and 1200 reactions reveals the predominant ions $H_3O^+ \cdot (H_2O)_6$, $H_3O^+ \cdot (H_2O)_5$, $NH_4^+ \cdot NH_3 \cdot H_2O$, $NH_4^+ \cdot H_2O$ and $NH_4^+ \cdot (H_2O)_3$ with the mobilities of 1.5, 1.6, 2.2, 2.5, and 1.9 $cm^2/(V \cdot s)$ which cannot explain the observed average value of 1.36 $cm^2/(V \cdot s)$. Probably some essential components are missing in the model, for example the pyridine bases (Eisele, 1986; Сальм и др., 1987) and water clathrates (Siksna, 1973).

CONDENSED IONS

The air ions with the mobility lower than 0.5 $cm^2/(V \cdot s)$ are secondary aerosol ions or condensed ions, the latter being related with the upper end of the mobility range. The condensed ions are of great interest in connection with gas-to-particle conversion in the atmosphere (Kojima, 1984).

A proof of the existence of condensed ions on the atmospheric surface level may be the rare appearance of high ion concentrations in the mobility range of 0.3-0.5 $cm^2/(V \cdot s)$ in our observations. Let us present two particular spectra:

Date	Time	$n_-(0.3\text{-}0.5)$	$n_-(0.5\text{-}3.2)$	$n_+(0.3\text{-}0.5)$	$n_+(0.5\text{-}3.2)$
13.06.85	03-04	15	300	394	616
05.09.85	17-18	510	701	39	391

The concentrations and the mobilities are given accordingly in cm^{-3} and

$cm^2/(V \cdot s)$. These spectra cannot be explained by the attachment of cluster ions to neutral aerosol particles. But the condensation of different components of air on negative or positive cluster ions can serve as an explanation.

As a rule, the concentration of condensed ions in the mobility range of 0.3-0.5 $cm^2/(V \cdot s)$ does not exceed a few tens of cm^{-3} and it is difficult to distinguish them from the secondary ions.

SECONDARY AEROSOL IONS

Despite the long history of ion measurements the picture of the mobility spectrum of aerosol ions is still unsatisfactory over the whole range, especially in the regions of ultra-large and intermediate ions. At present the number of measured size spectra of aerosols considerably exceeds the number of the measured mobility spectra of aerosol ions. This adds importance to indirect methods for the estimation of ion mobility spectrum.

If the charging conditions are sufficiently well known, the mobility spectrum of secondary ions can be calculated starting from the size spectrum of aerosol particles. The necessary equation may be expressed as follows

$$\rho(k) = e \sum_{i=1}^{\infty} iz(r_i)p_i(r_i) \left| \frac{dr}{dk} \right|_{r_i}, \qquad (3)$$

where $\rho(k)dk$ is the polar charge density carried by ions in the interval from k to $k+dk$, e is the elementary charge, i is the charge number, $z(r)dr$ is the numerical concentration of aerosol particles in the interval of radius from r to $r+dr$, $p_i(r)$ is the probability to carry i elementary charges for an aerosol particle with the radius of r, $|dr/dk|_{r_i}$ is the Jacobian of the transform of spectra from r-space to k-space, r_i is determined by the pre-assigned values of k and i.

We took the assumptions of stationarity and charge symmetry and applied the recognized theories of aerosol charging (Fuchs, 1963) and the mobility of ions (Israël, 1957). The average particle size spectrum of tropospheric aerosols can be approximated with the Smerkalov's (1984) model obtained by generalization of about 250 empiric distributions. The corresponding average mobility spectrum was calculated and is shown in Figure 2.

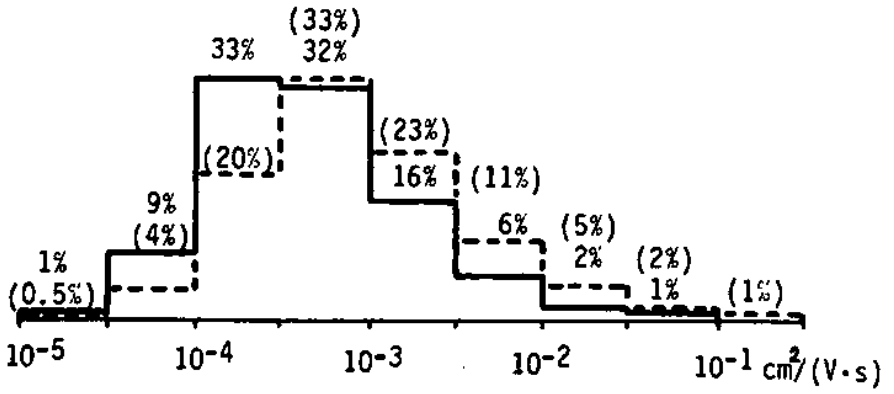

Fig. 2. Average mobility spectra of secondary aerosol ions.
—— Smerkalov's average, ---- example of observation.

The figure also gives the average spectrum based on a particular

series of observations in a rural site during a week in late spring. It is obvious that the aerosol ion mobilities in clean rural air are slightly higher than those calculated from the Smerkalov's average spectrum. The calculated spectra of secondary ions are in satisfactory agreement with the results of direct measurements (Misaki, Ohtagaki, Kanazawa, 1972; Salm, Reinart, 1983).

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