5. BURSTS OF INTERMEDIATE IONS

Certain thermodynamical causes hinder the formation of nanometer particles via gas-to-particle conversion mechanism, as well as the growth of cluster ions in ordinary environmental conditions, keeping the concentration of intermediate ions (0.034–0.5 $cm^2V^{-1}s^{-1}$; 1.6–7.6 nm) at a low background of about 50 cm^{-3}. Enhanced concentrations of intermediate ions up to about 900 cm^{-3} (bursts) are observable in the mobility spectra in fine weather conditions during daytime. Intermediate ions are probably formed by diffusion charging of nanometer aerosol particles generated by photochemical nucleation process. At the same time, cluster ions can also grow up to intermediate ion size range.

The number of burst events recorded during 14 months was 101 (about 80 per year); polar concentration over 100 cm^{-3} was observed during 14% of the measurement time. A typical time variation is shown in Figure 14.

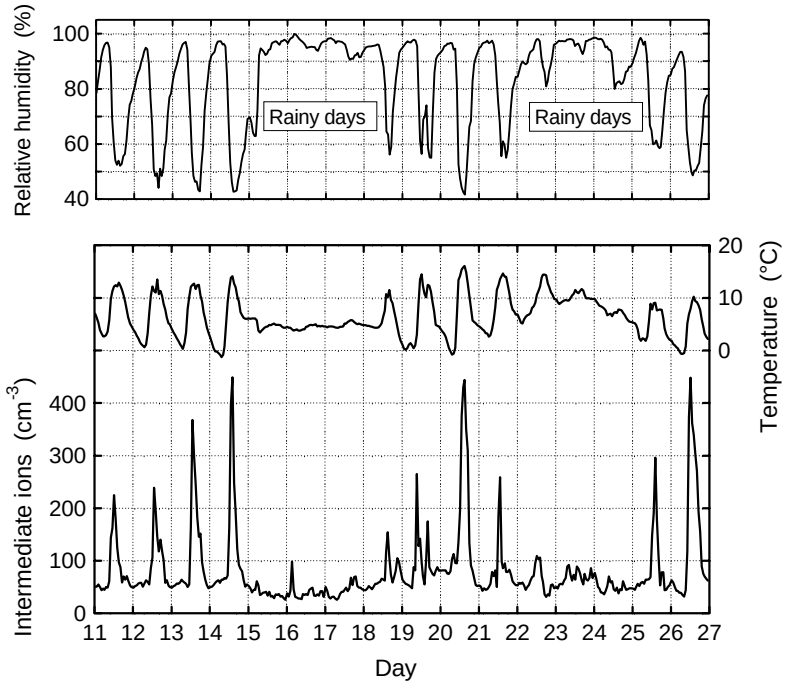

Figure 14. Variation in the concentration of positive intermediate ions (0.034–0.5 $cm^2V^{-1}s^{-1}$), air temperature, and relative humidity at Tahkuse, September 11–27, 1993.

On the background the of concentration of about 50 cm^{-3}, bursts up to 10 times above the background are noticeable. As a rule, a burst occurs around noontime. The solar radiation is considered as an essential factor of a burst. Commonly, an enhancement of the concentration of intermediate ions was recorded with a delay of about 3 hours after sunrise, at the time of quick development of the boundary layer (increase in the depth of well mixed layer). Therefore, the bursts of intermediate ion concentration are closely correlated with meteorological parameters during the diurnal cycle (positively with air temperature and negatively with relative humidity).

As a rule, the extensive variations of temperature and relative humidity during diurnal cycle are present at the time of bursts (Figure 14). There are no bursts in cloudy and rainy days. Bursts occur when relative humidity is less than 70%. The concentration of intermediate ions is negatively correlated with relative humidity (e.g. linear correlation coefficient of about –65% in September). Consequently, the humidity (pure H_2O as a condensable vapor) is not a factor of generating intermediate air ions.

The bursts of intermediate ions are related to the changes in the mobility spectrum of small ions (0.5–3.2 $cm^2V^{-1}s^{-1}$); during the burst the changes take place mainly in the low-mobility wing of the spectrum (below 1 $cm^2V^{-1}s^{-1}$). The bursts coincide with the minima of the mean mobility of small ions in the diurnal cycle (Figure 15).

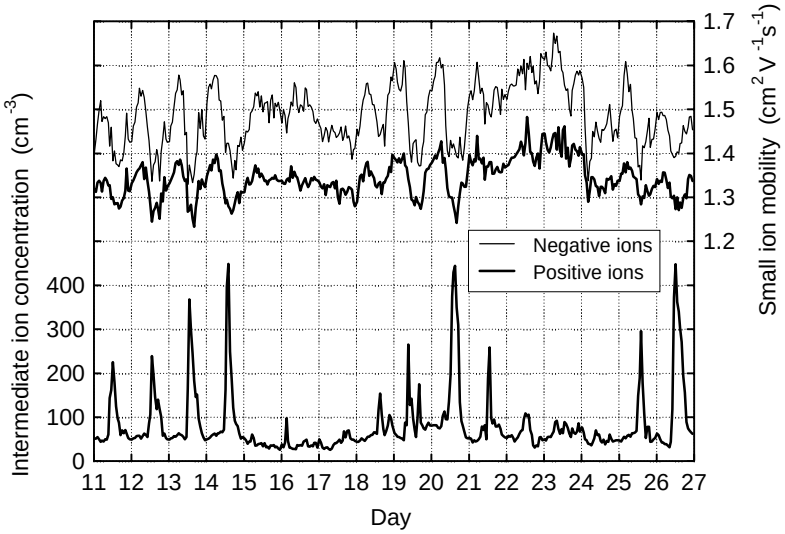

Figure 15. Variation in the concentration of positive intermediate ions (mobility 0.034–0.5 $cm^2V^{-1}s^{-1}$) and the mean mobility of negative and positive small ions (0.5–3.2 $cm^2V^{-1}s^{-1}$) at Tahkuse, September 11–27, 1993.

The diurnal variation of the mean mobility of small air ions was a more frequently recorded phenomenon than the burst of intermediate ion concentration. Only in certain cases the burst followed the decrease in the mean mobility. We suppose that the changes in the mobility spectrum of small ions are due to the changes in the chemical composition and concentration of some

trace gases or vapors in the air probably generated by photochemical reactions.

The examination of the time series of intermediate ion concentration and meteorological parameters enables to conclude that sometimes series of bursts followed drastic changes (decrease) in air temperature and relative humidity. The drastic changes of meteorological parameters in their turn are related to the exchange of air masses. On the basis of daily weather maps [*Berliner Wetterkarte*, 1993–1994] we can conclude that almost all the bursts are recorded in cool Arctic or Polar high-pressure air masses. These air masses are comparatively clean of accumulation mode particles (100–200 nm) that considerably decreases the removal rate of vapors produced by photochemical reactions. The low condensational sink of vapors together with characteristic nighttime temperature inversions and intensive mixing of boundary layer air at daytime, provide conditions necessary for nucleation [*Kulmala et al*., 1998; *Nilsson and Kulmala*, 1998; *Clement et al*., 2001].

The burst of intermediate ions is a factor that considerably changes the general shape of the mobility spectra. It can initiate a process of the evolution of aerosol ion spectra, generating new aerosol particles that grow toward large sizes [*Hõrrak et al.*, 1995, 1998b]. An example is presented in Figure 16. The first hourly average spectrum of positive air ions at 10–11 LST is similar to the long time average and can be considered as an undisturbed spectrum of air ions. During the next hour a considerable amount of intermediate ions had arisen in the depressed region of the spectrum and a spectral peak appeared in the diameter range of 2–4 nm. Henceforth, the peak in the spectrum of intermediate ions gradually shifted toward lower mobility and larger size up to a size range of 9.7–15 nm (mobility range of 0.0091–0.021 $cm^2V^{-1}s^{-1}$). This first stage of the process looks like a triggering of a nucleation process with the accumulation of particles in the nucleation mode size range of 9.7–15 nm. The process of evolution from the intermediate ion size range to the nucleation mode size range took about 3 hours. During the next 3 hours, the intermediate ion concentration decreased simultaneously with a decrease in the nucleation mode size range. The nucleation mode disappeared after a sudden increase in the Aitken mode size range of 22–79 nm (mobility range of 0.00041–0.0042 $cm^2V^{-1}s^{-1}$). The evolution of the spectrum of negative ions was similar. The weather was sunny and almost calm, with weak wind from the south.

The variations in air temperature, relative humidity, wind speed, and NO_2 concentration are presented in Figure 17. Sunrise was at about 7 LST and sunset at 17 LST. The variation of the concentrations of intermediate, small, and large ions is shown in Figure 18. An enhancement of the concentration of intermediate ions began at about 11 LST with the delay of about 3 hours after sunrise. The decreased concentration of heavy large ions (charged Aitken particles with the diameters of 22–79 nm) during the burst of intermediate ions from 11 to 18 LST probably refers to the increasing rate of atmospheric mixing processes (atmospheric exchange).

The above example was selected as the most expressive from seven bursts during the period of October 16–23. This period began with the inflow of a cool Arctic high-pressure air mass; the daily average temperature suddenly decreased from 8ºC to 0.3ºC, remained roughly on this level during the whole period, and raised to 7.2ºC on October 24.

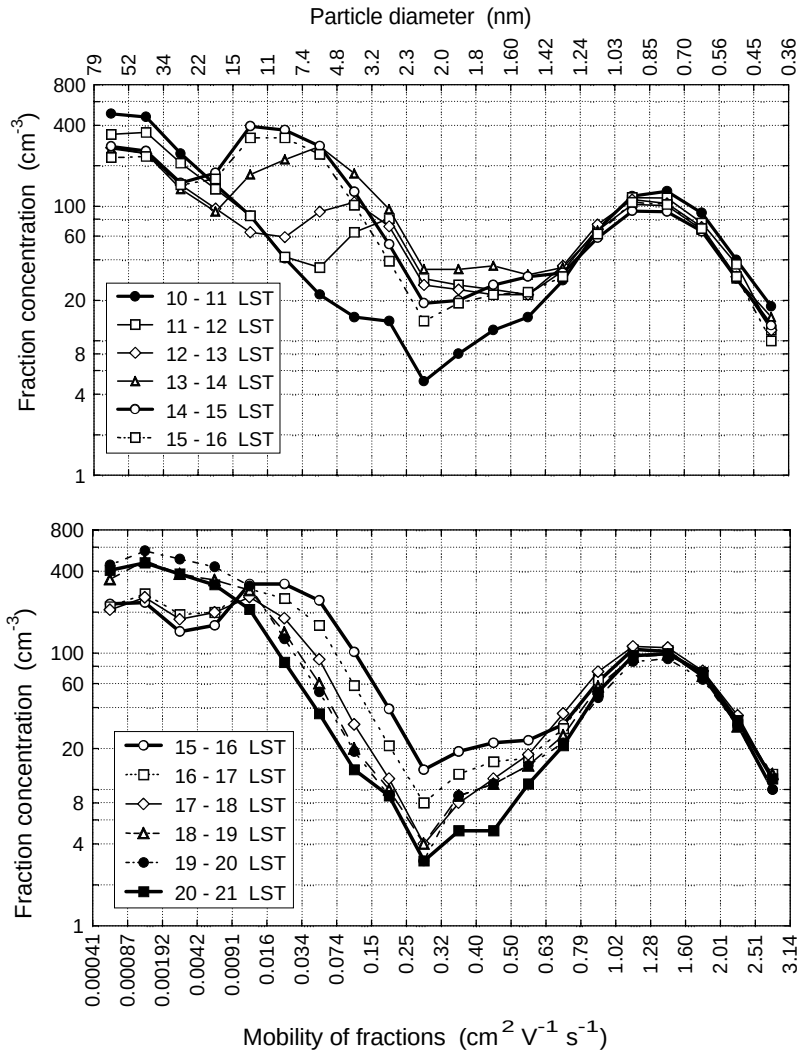

Figure 16. Evolution of positive ion mobility spectra at Tahkuse, October 20, 1994.

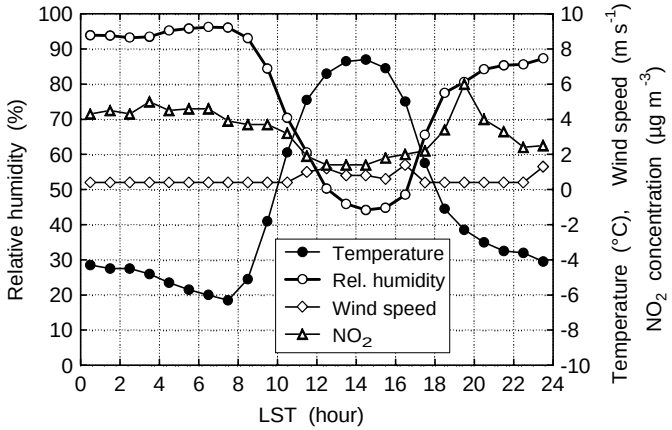

Figure 17. Variation in air temperature, relative humidity, wind speed, and NO_2 concentration at Tahkuse Observatory, October 20, 1994.

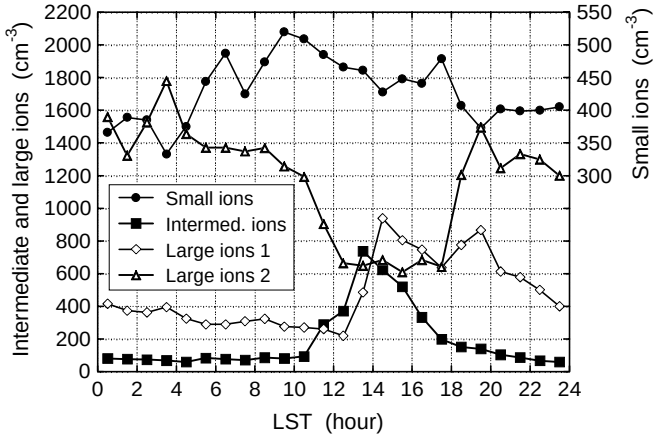

Figure 18. Variation in the concentration of positive intermediate ions (mobility 0.034–0.5 $cm^2V^{-1}s^{-1}$), small ions (0.5–3.2 $cm^2V^{-1}s^{-1}$), large ions 1 (0.0042–0.034 $cm^2V^{-1}s^{-1}$), and large ions 2 (0.00041–0.0042 $cm^2V^{-1}s^{-1}$) at Tahkuse, October 20, 1994.

Besides the process of evolution described above, a process of another character was also observed: a spectral peak suddenly appeared in the nucleation mode size range of 9.7–15 nm (mobility range of 0.0091–0.021 $cm^2V^{-1}s^{-1}$) or 15–22 nm, and remained there for 4–8 hours (during the time of intensive sunlight), slightly changing in height. The shape of the spectrum was similar to that presented in Figure 16 at 14–15 LST. Sometimes a spectral peak at 9.7–15 nm slowly continued to rise towards large sizes and the spectrum formed one broad peak at about 34–52 nm. Sometimes the peak at 9.7–15 nm dominated over the whole spectrum. The reduction of the concentration of heavy large ions of 22–79 nm (0.00041–0.0042 $cm^2V^{-1}s^{-1}$) was observed at the first stage of the process. Several such events have been observed when an anticyclonic air mass of good visibility has come over the Baltic Sea to inland areas.

During the both processes described above, the enhanced concentrations of intermediate ions were recorded as a result of nucleation phenomena, depending on the intensity and development stage of the process. In the following, we do not distinguish between these two situations, because the time resolution of the data mostly used in the present thesis (1 hour) is not sufficient enough. Considering also our recent measurements, it takes about 2–3 hours for the particles of 2–3 nm to grow (by condensation and self-coagulation) into the nucleation mode size range of 9.7–15 nm, as it results from the shift of a spectral peak. This is consistent with the nanometer particle growth rates observed at clean continental sites [*Weber et al.*, 1997; *Mäkelä et al*., 2000a]. The peak of intermediate ions was never recorded below 2.3 nm. The following shift of the peak beyond 23 nm was observed only sometimes in the case of intensive burst events. The most reasonable explanation is that the increased surface area of newly formed particles provided an effective sink for nucleating vapor (e.g. H_2SO_4), considerably decreasing its concentration [*Clement et al*., 2001] and thereby decreasing the nucleation rate and also the growth rate of particles. Also, as particles reach the diameter of the order of the mean free path of the gas molecule (about 60 nm), condensation becomes diffusion-limited and slows down. To maintain a nucleation and the growth of particles by condensation, it is necessary that the production rate of nucleating vapour also increases compared to the removal rate [*Clement et al*., 2001; *Yu and Turco*, 2000]. The correlation between ultrafine particle generation and H_2SO_4 concentration is confirmed by field measurements [*Weber et al.*, 1997; *Birmili et al.*, 2000].

The lack of information about particles large than 90 nm, as well as the measurements at a single fixed point (Eulerian experiment) cannot explain the evolution process in detail. The latter restriction could be ignored if the process took place in the air mass of considerable horizontal extent. The measurements of intermediate ions and nanometer particles at Tahkuse and at different locations in Estonia showed that concentration bursts can be recorded nearly simultaneously at stations separated by 100–150 km [*Vana et al*., 2000].

The average spectra of positive air ion number concentration in the case of the bursts of intermediate ions (hourly average concentration is more than 100 cm^{-3}) versus non-burst situations are presented in Figure 19. The results for negative ions are similar. The disturbed region of air ion mobility spectra affected by the bursts of intermediate ions is from about 0.002 to 1.0 $cm^2V^{-1}s^{-1}$ (from 1.1 to 34 nm), including the groups of big cluster ions, intermediate and light large ions.

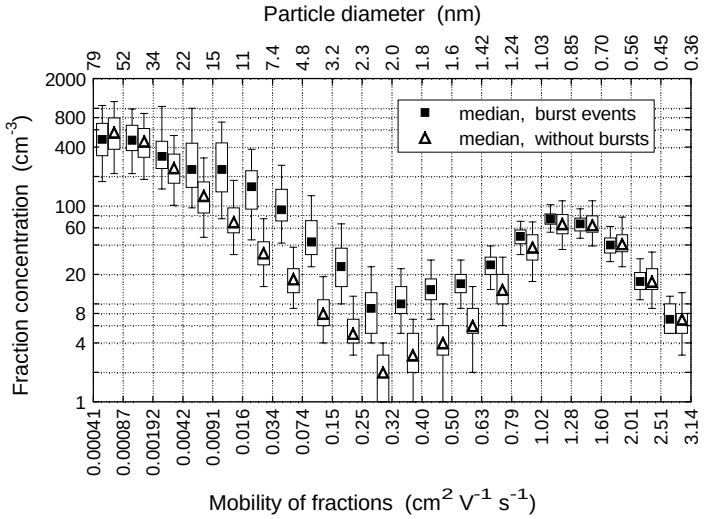

Figure 19. The box plot of average spectra of positive air ions; burst events of intermediate ions versus the common situation. Tahkuse, September 1993–October 1994. Descriptive statistics: median, box (25% and 75%) and whiskers (5% and 95% quantiles). The spectra are shifted by little.

As a rule, the concentration of heavy large ions varies oppositely to that of intermediate ions during the bursts (see Figure 18). Considering all the burst events, only the fraction concentration of heavy large ions (0.00041–0.00087 $cm^2V^{-1}s^{-1}$; 52–79 nm) showed a distinct opposite diurnal variation. These particles are close to the critical size of particles (about 80 nm) that can act as cloud condensation nuclei in the atmosphere [*Hoppel et al*., 1990; *Raes et al*., 2000]. The low concentration of heavy large ions (charged Aitken particles) is considered as a factor that favors the bursts of intermediate ions. On the contrary, the high concentration of preexisting particles are likely to deplete the nucleating species.

The process of the evolution of a mobility spectrum is similar, as observed by *Misaki* [1964] in the New Mexico semidesert for large air ions in a mobility range of 0.00032–0.01 $cm^2V^{-1}s^{-1}$ (diameter 14–100 nm). He observed a gradual shift of a spectral peak toward larger sizes up to about 40 nm during several hours in daytime; the weather was fine at that time.

Some indications on the phenomenon of the same physical nature as the bursts of intermediate ions are known and described in the literature.

The short measurement campaign near Zvenigorod in June 1986 showed several events, when at first the concentration of air ions in the range of 0.32–0.5 $cm^2V^{-1}s^{-1}$ arose, and then after 1–2 hours, an enhancement of the concentration of aerosol particles in the diameter range of 10–18 nm (measured by EAS) followed [*Kikas et al.*, 1990].

Covert et al. [1992] have found local mesoscale bursts of new particle production in a size range less than 15 nm in the marine boundary layer (MBL) along the coast of Washington State in 1991. The generation of particles was favored in the conditions of low particulate surface area, intensive solar radiation, and high concentration of SO_2. Similar nucleation bursts have been observed by *Aalto et al.* [1995] at the Värriö environmental measurement station in Finland and by *McGovern et al.* [1996a, b] at the Mace Head Atmospheric Research Station in 1991.

Covert et al. [1996] made aerosol measurements onboard the Swedish icebreaker *Oden* during the International Arctic Ocean Expedition in 1991. They measured aerosol number size spectra in a range from 3 nm to 500 nm and recorded three simultaneously existing distinct number modes with mean geometric diameters of around 170 nm, 45 nm, and 14 nm, referred to as accumulation, Aitken, and ultrafine modes, respectively. They concluded that the generation of ultrafine particles is not associated with the MBL, but occurs near the top of the MBL or in the free troposphere. The air parcels containing a high concentration of ultrafine particles are mixed into the MBL with Aitken and accumulation mode particles.

Weber et al. [1997] experimentally studied nucleation and particle growth in the free troposphere on Mauna Loa and at a remote continental site at Idaho Hill in the Colorado Rockies. New particle formation (nominally 3–4 nm) showed clear diurnal pattern with maximum at noon and was correlated with high sulfuric acid (H_2SO_4) and OH concentration, low relative humidity and low particle surface area concentration. The observed rates of particle formation in these measurements exceeded the values predicted by the theory (expected binary H_2SO_4-H_2O nucleation) by 5–10 times. The measurements revealed that the growth of 3 nm particles up to 20 nm requires about 2.5 hours.

Mäkelä et al. [1997] and *Kulmala et al*. [1998] observed nanoparticle formation at the sizes of about 5–6 nm and the subsequent gradual growth during 6–12 hours, reaching the Aitken size range (60–70 nm) in the evening, at a boreal forest site in Finland in fine weather conditions.

Birmili [1998] observed the same phenomenon in densely populated Central Europe an area near Leipzig. *Birmili and Wiedensohler* [2000] have found that in 80% of the significant nucleation events, SO_2 concentration increased by a factor of 7, most likely by the entrainment from aloft. The growth rate of particles in the size range of 3–10 nm was estimated to be 4.1±2.3 nm h^{-1}. The growth rate at a rural site was 2.1±0.1 nm h^{-1} [*Birmili et al.*, 2000].

Schröder and Ström [1997] have found that during the passage of a cold front in free troposphere, ultrafine condensation nuclei (UCN, 7–18 nm) concentration doubled and occasional burst events with several thousands of UCN cm^{-3} were observed.

The monitoring of ultrafine aerosol formation at widely spaced stations (Tahkuse in Estonia, Hyytiälä and Värriö in Finland) showed that the nucleation events may occur almost simultaneously over hundreds up to a thousand kilometres during the same cold air outbreak from the Arctic [*Mäkelä et al*., 1998; *Nilsson et al*., 2001]. The nucleation was found to take place in Arctic and to some extent in Polar air masses, but never in Subtropical air masses.

For the explanation of the bursts of intermediate air ions, several hypotheses can be advanced. The two alternative mechanisms are as follows:

1. The nanometer particles are generated in a neutral state by the homogeneous nucleation of binary H_2SO_4/H_2O or ternary $H_2SO_4/NH_3/H_2O$ system (e.g. *Kulmala et al*., 1998; 2000). Then particles get charged by the attachment of small air ions. This is the same process of charging that is responsible for generating large air ions. In this case, the concentration of nanometer particles during a burst is estimated to be tens of thousands per cm^3.

2. A burst of intermediate ions is a result of an enhanced ion-induced nucleation following the bursts of some (still unknown) trace gases involving H_2SO_4-H_2O in atmospheric air (see e.g. *Raes and Janssens*, 1985; *Hoppel et al*., 1994; *Noppel*, 1996; *Yu and Turco*, 2000). These gases are not emitted by a local anthropogenic source (not at least near Tahkuse), because the long duration of the evolution process shows evidence that it is running in an air mass of a considerable horizontal size.

Alternative ion-induced gas-to-particle conversion mechanism is expected to proceed via ion-ion recombination of cluster ions with the subsequent formation of nucleus above the critical size for nucleation [*Arnold*, 1980; *Smirnov*, 1983; *Turco et al*., 1998, 2000; *Yu and Turco*, 2001].

The ion-induced nucleation rates (heterogeneous nucleation on the preexisting species – small ions) are many orders of magnitude (about 10^8 times) higher than the homogeneous nucleation rates, however limited to the ionization rate [*Raes and Van Dingenen*, 1992]. The ionization rate in atmospheric air at 1 m height commonly varies in the range of 1–10 ion pairs $cm^{-3}\,s^{-1}$ [*Hoppel et al*., 1986]. An additional argument against the diffusion-charging hypothesis is the charge asymmetry of the concentrations of intermediate air ions which was sometimes observed [*Tammet et al.*, 1988].

Kulmala et al. [2000] ruled out the ion-induced nucleation as probable aerosol formation route, because a nucleation rate of about 50–100 $cm^{-3}\,s^{-1}$ is needed in ternary nucleation model to explain the observed number concentrations in the atmosphere. However, it was noted that the observed formation rate of 3 nm size particles in the boreal forest was in the range of 0.001–1 $cm^{-3}\,s^{-1}$, which never exceeded the ion-pair production rate typical for continental areas [*Mäkelä et al*., 2000b]. The ion-mediated nucleation model developed by *Yu and Turco* [2000] provides a consistent explanation to a variety of tropospheric observations of the new particle formation (e.g. *Weber et al.*, 1997; *Hõrrak et al.*, 1998b).