Observations of positively charged nanoparticles in the nighttime polar mesosphere

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[1] We present results of in situ measurements of charged nanoparticles, electrons, and positive ions obtained during a sounding rocket flight in October 2004 from Kiruna, Sweden, under nighttime conditions. The particle measurement reveals positive charge signatures in the altitude range between 80 and 90 km corresponding to peak charge number densities of $\sim$100 e/cm^3 at around 86 km. Aerodynamical analysis of the sampling efficiency of our instrument reveals that the particles must have been larger than 2 nm assuming spherical particles with a density of 3 g/cm^3. The plasma environment of the observed particles is dominated by negative and positive ions, with only few free electrons. A calculation of the mean particle charge expected for particles in a plasma consisting of electrons and positive and negative ions shows that the presence of sufficiently heavy and numerous negative ions (i.e., $m_n > 300$ amu and $\lambda \geq 50$) can explain the observed positive particle charge. **Citation:** Rapp, M., J. Hedin, I. Strelnikova, M. Friedrich, J. Gumbel, and F.-J. Lübken (2005), Observations of positively charged nanoparticles in the nighttime polar mesosphere, *Geophys. Res. Lett.*, *32*, L23821, doi:10.1029/2005GL024676.

1. Introduction

[2] Every day, the Earth's atmosphere is hit by 10–100 tons of meteoric material which largely ablates in the altitude range between 70 and 100 km (see *Gabrielli et al.* [2004] for a recent review). Already in the beginning of the sixties, *Rosinski and Snow* [1961] considered the possibility that nanometer-scale particles form as a product of meteoroid ablation and subsequent recondensation and coagulation. Almost 20 years later *Hunten et al.* [1980] presented the first comprehensive model of the altitude and size distribution of such 'meteoric smoke particles' and predicted the occurrence of significant number densities (up to 10^4/cm^3) of particles with radii on the order of $\sim$1 nm in the upper mesosphere.

[3] Meteoric smoke particles have been proposed to play a major role in a variety of atmospheric processes such as the nucleation of ice particles in the polar summer mesopause region [e.g., *Keesee*, 1989]. Recently, it has also been proposed that the particles are transported into the winter polar vortices by the mesospheric meridional circulation and lead to a preferential deposition of meteoric material in the polar ice caps [*Gabrielli et al.*, 2004]. Despite the obvious scientific interest in meteoric smoke particles, very little is known about their properties. This is mainly because of the tiny dimensions and low number densities of the particles rendering the detection by optical methods hardly feasible. One possibility to detect such small particles, is to take advantage of the fact that they may become charged [e.g., *Rapp and Lübken* 2001]. Hence, they can be detected by in situ instruments for the measurement of charged species [*Havnes et al.*, 1996; *Gelinas et al.*, 1998; *Croskey et al.*, 2001; *Lynch et al.*, 2005]. Importantly, the measurement of charged particles does not only simplify the detection, it also provides valuable geophysical information on the charge balance of the lower ionosphere which needs to be known, e.g., to properly interpret the spectral characteristics of incoherent scatter radar spectra [*Cho et al.*, 1998]. Hence, further observations of charged particles and their plasma environment are highly desirable.

[4] In the current manuscript, we present new in situ measurements of charged particles and ambient plasma parameters in the nighttime polar mesosphere. In section 2 we describe the applied instrumentation, and continue with a detailed analysis of the aerodynamical properties of the particle detector in section 3. In section 4 we present our results, which are discussed in section 5 in terms of our understanding of particle charging and particle impact phenomena.

2. Experimental Techniques

[5] The particle detector applied for the current study is a combination of a Faraday-cup and a Xenon-flashlamp for the photo-ionization of particles. Similar instruments employing lamps to actively ionize atmospheric constituents were applied earlier [e.g., *Croskey et al.*, 2003, and references therein].

[6] The design of the Faraday cup (see Figure 1) is similar to the one described by *Havnes et al.* [1996] and comprises a collector electrode (held at payload potential by the negative feedback loop of the electrometer) for the measurement of particles of either positive or negative charge and two grids (biased at ±6.2 V relative to payload potential) to shield the collector electrode from electrons and ions. The flashlamp is operated at a repetition rate of 20 Hz. Immediately after the flash, the charge detected at the collector electrode is recorded for 48 samples at a rate of 100 kHz. After a flight time of <1 ms, the detector (which moves at a typical speed of 500–1000 m/s) has passed through the actively ionized atmospheric volume and then records naturally charged particles reaching the collector electrode at a sampling rate of 1 kHz, until the whole

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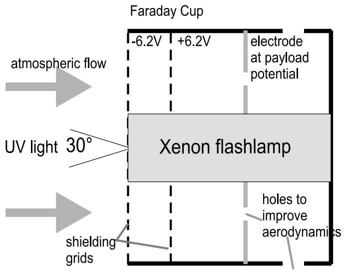

Figure 1. Schematic of the particle detector.

sequence starts again after 50 ms (see *Rapp et al.* [2003] for technical details). Unfortunately, the 100 kHz data following the flash of the Xenon-lamp were impaired by electromagnetic interference from the flash-electronics and will therefore not be discussed here any further.

[7] In addition, we applied a spherical fixed biased DC-probe for the measurement of positive ions, and a four frequency Faraday rotation experiment (using frequencies of 1.3, 2.2, 3.8, and 7.8 MHz) to derive the absolute electron number density [e.g., *Mechtly et al.*, 1967]. The positive ion probe was mounted on a 40 cm-long boom on the front deck of the payload which after its sidewards deployment following nosecone ejection guaranteed that the measurement was performed outside the main shock front of the payload.

3. Aerodynamical Considerations

[8] The aerodynamics of particle sampling by rocket borne detectors moving at supersonic speeds was studied by *Horanyi et al.* [1999]. They found that the density enhancement in front of supersonically moving instruments on sounding rockets leads to a size-dependent detection efficiency for the measurement of particles embedded into the flow. In order to estimate the detection efficiency of our own instrument, we repeated the simulations described by *Horanyi et al.* [1999] for the particular geometry of our detector and the conditions during the sounding rocket flight discussed in this paper. First calculating the density fields inside and in the vicinity of our detector, and then simulating the trajectories of particles of an assumed mass density of 3 g/cm^3 and given radius in this density field, we determined the minimum particle radius r^* needed to allow the particles to reach the collector electrode (see *Hedin et al.* [2005] for technical details). We have determined r^* at altitudes between 70 and 90 km, where we have also distinguished between cases of (singly) negatively and

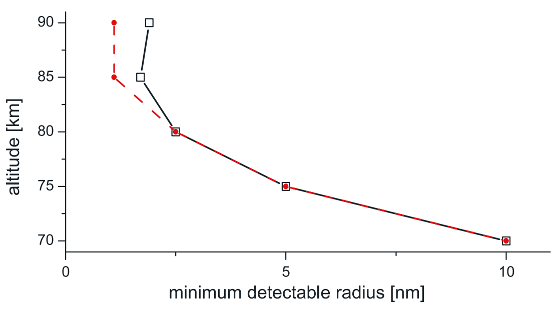

Figure 2. Minimum detectable radius of negatively (red line) and positively (black line) charged particles as a function of altitude.

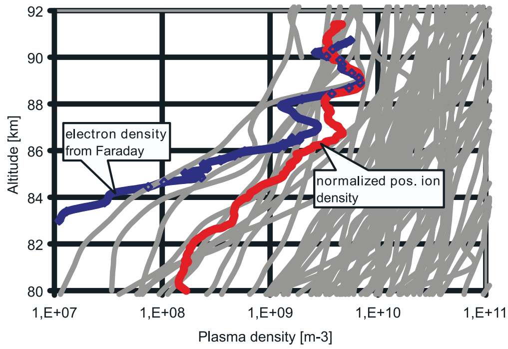

Figure 3. Measured plasma densities. The electron densities n_e are based on Faraday rotation of the lowest (most sensitive) frequencies, the positive ion density is normalized to the absolute n_e near apogee. Other night-time measurements from the auroral zone are indicated by gray lines.

positively charged particles in order to investigate the effect of the electric field inside the detector.

[9] Figure 2 shows that r^* is ~2 nm above 80 km and increases up to 10 nm at 70 km. These values are probably lower estimates of r^* since our analysis assumes spherical solid spheres while meteor smoke particles have probably grown by coagulation and should have a larger surface area than solid spheres with the consequence of a larger drag coefficient. We also note that r^*-values would have been even larger without the holes in the collector electrode and the wall of the detector (see Figure 1) which were added to improve the detection efficiency for small particles [*Hedin et al.*, 2005].

4. Results

[10] On 28 October 2004, 21:49 LT, a sounding rocket carrying the above described instruments was launched from the Swedish rocket launch site ESRANGE (68°N, 21°E). The instruments were exposed to the ambient atmosphere at an altitude of ~55 km on the ascent of the rocket which reached an apogee of 91.4 km. In Figure 3 we show the measured profiles of electron and positive ion number densities, n_e and n_i. Currents measured with the positive ion probe were converted to number densities and then normalized to n_e at 90 km altitude. Below 88 km altitude, n_i is significantly larger than n_e, providing evidence for significant abundances of negative ions. Deriving the negative ion number density from $n_i - n_e$ (i.e., assuming local charge neutrality), the ratio between negative ions and electrons, λ, becomes as large as ~40 (10) at an altitude of 83 (85) km. Note, that these λ-values must be considered as lower limits, because of their dependence on the normalization altitude which we had to choose at ~90 km due to the low apogee of this rocket flight.

[11] We further compare the measured electron number density profile to a compilation of previous absolute electron number density measurements in the auroral zone under nighttime conditions [*Friedrich and Kirkwood*, 2000]. The comparison shows that the ionization level during our rocket flight was exceptionally low.

[12] The measurements obtained with the particle detector are presented in Figure 4 showing the current

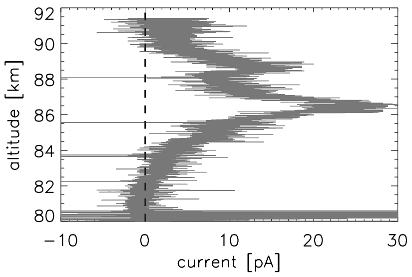

Figure 4. DC current measured with the particle detector as a function of altitude (in gray). The vertical dashed line indicates a current of 0 pA for orientation. The disturbances seen below 80.5 km were caused by a transient data transmission problem.

measured with the slow data channel described above. Our measurements show a positive current between ~82 and 90 km with a maximum of +25 pA at 86 km. Note that this positive current cannot have been caused by the short Xe-flashes because in the relevant altitude range, the payload moved at a speed of ~500 m/s and hence passed the artificially ionized atmospheric volume within less than one millisecond [*Rapp et al.*, 2003]. Interestingly, the current shows a double peak structure similar to the wave-like structures observed in the electron and positive ion profiles. Assuming that the observed current is given by $I = N\,Z\,e\,v_pA$ (with N the particle number density, Z the number of elementary charges per particle, e the elementary charge, v_p the rocket velocity perpendicular to the detector surface, and A the area of the collector electrode), our peak current corresponds to a maximum positive charge number density of $N\,Z\,e \sim 100\ e/\mathrm{cm}^3$ produced by particles with radii $\geq$2 nm (see Figure 2). This value is surprisingly close to the few available previous measurements of heavy charge carriers in the upper mesosphere outside the polar summer [e.g., *Lynch et al.*, 2005], i.e., during conditions with no ice particles present (though admittedly in these cases the particles were negatively charged, not positive).

5. Discussion

[13] According to usual charging models, particles are expected to be negatively charged except under conditions of significant photo-emission or secondary electron emission [e.g., *Rapp and Lübken*, 2001]. This is because capture rates are proportional to the thermal velocity of the species to be captured, which is ~300 times larger for electrons than for positive ions. For our observing conditions, photo-emission can be excluded as a source of positively charged particles because the solar zenith angle χ was 124.4° leaving the D-region in darkness for more than 4 hours. In addition, secondary electron emission due to the bombardment of particles by energetic electrons can also likely be excluded given the very low ionization level of the D-region evident in Figure 3. Current charging models, however, do not consider the effect of significant number densities of negative ions, which were a major plasma constituent at the time of our measurement (see Figure 3).

[14] In order to investigate whether the presence of negative ions can lead to a net positive particle charge, we have calculated the average charge of a 2 nm particle immersed in a plasma consisting of electrons, positive ions (of mass 50 amu), and negative ions. Following the work by *Draine and Sutin* [1987] we derive the probability $f(Z)$ to find a particle having a net charge Ze due to collisions with electrons, positive ions, and negative ions as

$$f(Z>0) = f(0)\cdot\prod_{Z'=1}^{Z}\left(\frac{J_i(Z'-1)}{J_e(Z')+J_n(Z')}\right) \tag{1}$$

$$f(Z<0) = f(0)\cdot\prod_{Z'=Z}^{-1}\left(\frac{J_e(Z'+1)+J_n(Z'+1)}{J_i(Z')}\right) \tag{2}$$

where the multiplicative constant $f(0)$ is determined by the normalization condition $\sum_{-\infty}^{\infty} f(Z) = 1$. The charging rates J_j are given by $J_j = n_j\, s_j\, c_j \pi r^2 \sigma(Z)$ where s_j is the sticking coefficient (assumed to be 0.1 for electrons and 1.0 for ions; see *Draine and Sutin* [1987] for details), c_j is the mean thermal velocity of species j, and $\sigma(Z)$ is an efficiency factor describing the interaction between the electron or ion and the Z-times charged particle by considering both the direct Coulomb interaction as well as the polarizability of the particle [*Draine and Sutin*, 1987]. j can be either e, i, or n denoting electrons, positive ions, and negative ions, respectively. According to *Draine and Sutin* [1987], the charge on an individual dust grain fluctuates, with a time-averaged value $\langle Z\rangle = \sum_{-\infty}^{\infty} f(Z)\cdot Z$. In Figure 5 we present calculations of $\langle Z\rangle$ as a function of the parameter $\lambda = n_n/n_e$ for different negative ion masses. While for $\lambda \to 0$ $\langle Z\rangle \sim -1$ as expected from earlier calculations [e.g., *Rapp and Lübken*, 2001], Figure 5 shows that for sufficiently heavy negative ions (i.e., $m_n \geq 300$ amu), the net particle charge can become positive provided that λ becomes larger than ~50. At this point we need to consider *Gabrielli et al.*'s [2004] model results regarding the size distribution of meteoric smoke particles at an altitude of ~85 km: they predict several thousand particles/cm^3 with a radius between 0.4–1 nm (corresponding to masses between ~300 and 10,000 amu), and only some hundreds of particles/cm^3 with radii $\geq$2 nm. Assuming that this size distribution is representative for our observations, it is conceivable that the small sub-nm particles efficiently captured the majority of free electrons. In accordance with Figure 5, these very heavy negative 'ions' then led to a net positive charge of particles with a radius larger than 2 nm. Since our

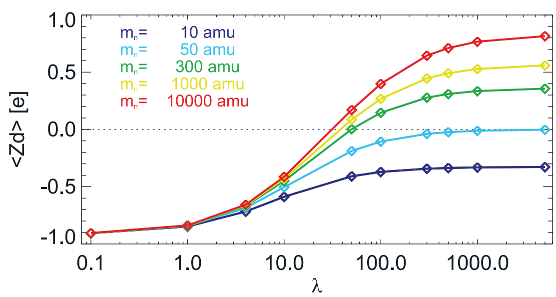

Figure 5. Mean particle charge (particle radius = 2 nm) as a function of the parameter $\lambda = n_n/n_e$ for different assumed negative ions masses m_n.

instrument is not capable of measuring particles smaller than ∼2 nm (see Figure 2), this can indeed explain our observations.

[15] Finally, we also consider whether the observed charge signature could be a consequence of secondary charging effects due to particle fragmentation or impact ionization.

[16] *Tomsic* [2001] shows for the case of impacting ice particles that negatively charged particle fragments may leave the surface. However, for the particle size of interest here ($r \sim 2$ nm), the probability for this charging process to occur is less than 10^{-4} per particle impact. *Baragiola* [1994] shows that impacting meteoric particles with sufficient kinetic energy can result in the emission of an electron from the collector electrode material. However, for the particle size and speed of interest here, the probability for this charging process to occur is less than 10^{-5} per particle impact. These ionization efficiencies would require an unreasonably large number density of $\sim 10^6 - 10^7$ particles/cm^3 with radii larger than ≥ 2 nm in order to explain our observed peak current. Hence, these secondary effects can be confidently ruled out as the cause of the observed positive charge signature.

6. Summary

[17] We have presented new in situ measurements of the charge number density of nanoparticles in the nighttime polar mesosphere. We observed positive charge signatures in the altitude range between 80 and 90 km corresponding to peak charge number densities of ~ 100 e/cm^3 at around 86 km in close agreement with previous measurements employing different techniques [e.g., *Lynch et al.*, 2005]. An aerodynamical analysis of the particle sampling efficiency of our instrument reveals that the observed particles must have been larger than ∼2 nm assuming spherical particles with a mass density of 3 g/cm^3. Measurements of electrons and positive ions conducted in the same atmospheric volume showed that our observations were performed under conditions of small number densities of free electrons and in the presence of significant numbers of negative ions. We have then calculated the average particle charge in a plasma consisting of electrons and positive and negative ions. Based on the principle that charge capture rates are determined by the mobility of the various charge carriers in the dusty plasma, we have found that the presence of sufficiently heavy and numerous negative ions (i.e., $m_n > 300$ amu and $\lambda \geq 50$) leads to the observed positive particle charge. Assuming that the observed particles are size-distributed as suggested by recent theoretical investigations, our observations can be explained if particles with radii smaller than 1 nm were negatively charged. As our calculations in Figure 5 show, this leaves the remaining larger particles in a plasma environment dominated by positive ions and the smaller negatively charged particles (or heavy negative ions) that will indeed give rise to a positive charge on the larger particles.

[18] Our results demonstrate that the charging processes of mesospheric nanoparticles are much more complicated that hitherto assumed. Clearly, more in situ, laboratory, and model investigations are needed to study the distribution and charging properties of mesospheric nanoparticles and clarify their significance for the propagation of radio waves and other intriguing geophysical phenomena.

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References

Baragiola, R. A. (1994), Electron emission from surfaces by impact of polyatomic ions and cosmic dust, *Nucl. Instrum. Methods Phys. Res., Sect. B*, *88*, 35–43.

Cho, J. Y., M. P. Sulzer, and M. C. Kelley (1998), Meteoric dust effects on *D*-region incoherent scatter radar spectra, *J. Atmos. Sol. Terr. Phys.*, *60*, 349–357.

Croskey, C. L., J. D. Mitchell, M. Friedrich, K. M. Torkar, U. Hoppe, and R. A. Goldberg (2001), Electrical structure of PMSE and NLC regions during the DROPPS program, *Geophys. Res. Lett.*, *28*, 1427–1430.

Croskey, C. L., J. D. Mitchell, M. Friedrich, F. J. Schmidlin, and J. W. Meriwether (2003), Initial results of a rocket-based study of gravity wave effects on photoionization in the middle atmosphere, *Adv. Space Res.*, *32*, 741–746.

Draine, B. T., and B. Sutin (1987), Collisional charging of interstellar dust grains, *Astrophys. J.*, *320*, 803–817.

Friedrich, M., and S. Kirkwood (2000), The *D*-region background at high latitudes, *Adv. Space Res.*, *25*, 15–21.

Gabrielli, P., et al. (2004), Meteoric smoke fallout over the Holocene epoch revealed by iridium and platinum in Greenland ice, *Nature*, *432*, 1011–1014.

Gelinas, L. J., K. A. Lynch, M. C. Kelley, S. Collins, S. Baker, Q. Zhou, and J. S. Friedman (1998), First observation of meteoritic charged dust in the tropical mesosphere, *Geophys. Res. Lett.*, *25*, 4047–4050.

Havnes, O., J. Trøim, T. Blix, W. Mortensen, L. I. Nsheim, E. Thrane, and T. Tønnesen (1996), First detection of charged dust particles in the Earth's mesosphere, *J. Geophys. Res.*, *101*, 10,839–10,848.

Hedin, J., J. Gumbel, and M. Rapp (2005), The aerodynamics of smoke particle sampling, in *Proceedings of the 17th ESA Symposium on European Rocket and Balloon Programmes and Related Research, Sandefjord, Norway, Eur. Space Agency Spec. Publ.*, *ESA SP-590*, 145–150.

Horanyi, M., J. Gumbel, G. Witt, and S. Robertson (1999), Simulation of rocket-borne particle measurements in the mesosphere, *Geophys. Res. Lett.*, *26*, 1537–1540.

Hunten, D. M., R. P. Turco, and O. B. Toon (1980), Smoke and dust particles of meteoric origin in the mesosphere and stratosphere, *J. Atmos. Sci.*, *37*, 1342–1357.

Keesee, R. G. (1989), Nucleation and particle formation in the upper atmosphere, *J. Geophys. Res.*, *94*, 14,683–14,692.

Lynch, K. A., L. J. Gelinas, M. C. Kelley, R. L. Collins, M. Widholm, D. Rau, E. MacDonald, Y. Liu, J. Ulwick, and P. Mace (2005), Multiple sounding rocket observations of charged dust in the polar winter mesosphere, *J. Geophys. Res.*, *110*, A03302, doi:10.1029/2004JA010502.

Mechtly, E. A., S. Bowhill, L. Smith, and H. Knoebel (1967), Lower ionosphere electron concentrations and collision frequency from rocket measurements of Faraday rotation, differential absorption, and probe current, *J. Geophys. Res.*, *72*, 5239–5245.

Rapp, M., and F.-J. Lübken (2001), Modelling of particle charging in the polar summer mesosphere: Part 1: General results, *J. Atmos. Sol. Terr. Phys.*, *63*, 759–770.

Rapp, M., et al. (2003), A new detector for the in situ measurement of meteoric dust particles in the middle atmosphere, in *Proceedings of the 16th ESA Symposium on European Rocket and Balloon Programmes and Related Research, St. Gallen, Switzerland*, *Eur. Space Agency Spec. Publ.*, *ESA SP-530*, 379–384.

Rosinski, J., and R. H. Snow (1961), Secondary particulate matter from meteor vapors, *J. Meteorol.*, *18*, 736–745.

Tomsic, A. (2001), Collisions between water clusters and surfaces, Ph.D. thesis, Gothenburg Univ., Gothenburg, Sweden.

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