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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Detecting charging state of ultra-fine particles: instrumental development and ambient measurements" *by* L. Laakso et al.

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The authors have developed a new method to study the contribution of ion-induced nucleation to atmospheric new particle formation events. For that purpose, the ordinary Differential Mobility Particle Sizer (DMPS) with a redesigned bipolar charger/neutralizer was used. The new system, called the ion-Dmps, is able to measure the concentrations of naturally positively and negatively charged atmospheric aerosols and neutralized aerosols in the size range of 3-15 nm. The ratios of naturally charged to neutralized particle concentrations of both polarities have been used to study the charged fraction on particles and gain information about the charging state of aerosol particles (overcharged or undercharged compared to the steady state charge distribution). The results of ion-Dmps laboratory tests, as well as the measurements at the Hyytiälä field station during BACCI-QUEST campaign in spring 2005 are reported and discussed. In

addition, the air ion mobility distribution measurements by Balanced Scanning Mobility Analyzer (BSMA) are used as supporting material. The results presented in this paper provide useful information about the charging state of aerosol particles during nucleation burst events that is important for understanding the role of different nucleation mechanisms in new particle formation. Therefore, the results have a substantial scientific value to the aerosol researchers' community and could be published in the ACP. However, the present paper has some shortcomings. The only innovation of the ion-Dmps system - a new redesigned bipolar charger/neutralizer, is not well described. The uncertainty estimates of the contribution of ion-induced nucleation to total nucleation rate are missing or these estimates are mainly qualitative. The paper needs proper editing and native speaker of English should correct the grammar and syntax. I recommend the publication of this paper in ACP after the following particular comments and recommendations have been taken into consideration.

Page 6402 Page 6402, lines 5-7. Concerning the following sentence in Abstarct: "We performed several laboratory tests to test the operation of the device and then we measured atmospheric new particle formation events with the instrument in a boreal forest". Probably the "events" were not measured, but the naturally and bipolar charged particle size distributions in a certain size range.

Page 6402, lines 9-11. Concerning the following sentence in Abstarct: "We also found that negative and positive ions behaved in a different manner, days with negative overcharging were more frequent than days with positive overcharging". Here it is rather unclear what the authors mean with the term "ions". In principle, the reader can think about both the cluster ions or charged nanometer particles. I am also concerned about the terms "negative overcharging" and "positive overcharging". In the case of bipolar charging/neutralization the process (charging) cannot result in "overcharge" on particles, but only the steady-state charge distribution on particles. Due to the contribution of ion-induced nucleation, the particle population can be considered as overcharged compared to the steady-state charge distribution. The latter (overcharged state) is not

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due to charging, but due to the condensation of vapors around the cluster ions. Therefore, the use of a still undefined term “overcharging” is probably not correct in Abstract. Also, the last sentence in the Abstact (lines 12-13) is trivial.

Page 6403. Insufficient credit is given to the earlier works in Introduction, e.g. by Laakso et al. (2004), Vana et al. (2006). The authors should summarize the results of their earlier works.

Page 6403, lines 5-7. Comment about the following sentence: “Recent developments in atmospheric measurements are the ion spectrometers which detect ion or charged aerosol distributions from cluster ion sizes up to the Aitken mode (Laakso et al. al., 2004)”. Such ion spectrometers are certainly not the “recent development” because the ion spectrometers were used already before the development of commercial aerosol spectrometers in the 1970s (see e.g. Misaki, 1961a, b).

Page 6403, line 11, instead of “chosen” we recommend the using of ”separated”. Page 6403, line 25. I recommend the adding of the concretization “on particles” just after the “electric charges”.

Page 6403, lines 26-28. Comment regarding the sentence: “In case of ion-induced nucleation, new particles are formed electrically charged, whereas in case of neutral nucleation particles do not initially carry any charges”. The statement is not entirely correct, because the small ion recombination, which is also considered as a new particle formation mechanism by ion-induced (or ion-mediated) nucleation (Turco et al., 1998), can result in the formation of neutral stable particles as well.

Page 6404. Page 6404, line 2. Here I recommend the adding of “steady-state” before the term “charging probability”. In principle, the charging probability can be found also for an evolving system in any time (e.g. aerosol population growing towards large sizes).

Page 6404, line 7. Concerning the end of the sentence: “ the charging state of the

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particles is undercharged". I recommend the adding of "called" just before the "undercharged". Otherwise the sentence is not correct.

Page 6404, line14. I recommend the adding of the term "study" just after "to", otherwise the sentence is not correct. Page 6404, line 25. I recommend the using of "positively and negatively charged particles" instead of "positive and negative particles".

Page 6404, line 25-26. Regarding the sentence: "The DMA was operated with a closed loop flow ". Here, "sheath air flow" should certainly be instead of "flow".

Page 6405 Page 6405, lines 2-4. Regarding the sentence: "Given the maximum voltage, flow rates, and counting efficiency of the CPC, this corresponded to a size range approximately from 3 to 15nm in electrical mobility equivalent diameter". Probably, the sentence should start with the fragment "Given the minimum and maximum voltage", because the maximum voltage applied in the DMA can determine only the minimum of the measured size range, but not the maximum. The sheath flow rate and aerosol sample flow rate of the DMA of ion-Dmps should also be given.

The bipolar charger (or neutralizer), which can be switched ON and OFF, is the only innovation in the ion-Dmps system, but unfortunately this innovation is not described in the paper. Thus, we recommend adding a principal scheme (or photos) of the bipolar charger, including dimensions and the following parameters: sample flow rate through the charger, residence time of particles in the charging zone and the concentration of polar charger ions. The data about the mean mobility of polar charger ions or mobility distribution is also highly recommended. Reading the caption of Fig. 1 I found that the aerosol sample is "either directed to the Differential Mobility Analyzer (DMA) via bipolar charger" or "the charger is bypassed". If there are two different pathways for naturally charged particles and artificially charged particles, then the losses can also be different. Therefore, a more detailed description of the bipolar charger/neutralizer of the ion-Dmps system is certainly needed to avoid misunderstandings in the interpretation of the results. A good example of charger description can be found in paper by Hoppel

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and Frick (1990).

In the section “2.1.1 Laboratory verification of Ion-DMPS”, the authors have described a lab setup for the generation of test aerosols. However, the description of the setup for the generation of ammonium sulphate particles is missing. Here I also recommend the presenting of some data concerning the sensitivity (the minimal concentration of ions in different size ranges, which can be reliable detected) and measurements uncertainty of the ion-Dmps. This additional information is required to understand how reliable are the measurements made with instrumentation, the cut-size (the diameter at which the transport efficiency is 50%) of which is 7.2 nm, and which has the CPC3025 with the 50% cutoff-size about 3 nm.

Page 6406 Page 6406, line 10. The diameter of the tube is missing.

Page 6406, lines 11-13. Regarding the sentence: “In the ion-DMPS, the desired information is the ratio between the concentrations, which are exposed to the same losses despite their polarities or the number of charges”. First, I recommend the adding of a concretization “of particles measured in four different operation modes” just after the word “concentrations”. Second, I am concerned about the statement that “the concentrations are exposed to the same losses despite their polarities or the number of charges”. Did the authors estimated experimentally or theoretically the rate of diffusion losses of neutral and charged particles (3-15 nm), as well as the recombination/coagulation losses of charged particles in the inlet of ion-Dmps?

Page 6406, section 2.1.3 Charge balance and neutralization efficiency. The lab setup of these experiments is not well described. Should we assume here that in all experiments the setup was exactly the same as shown in Figure 1?

NB! Regarding the figure captions of Figures 2 and 3 (see pages 6420-6421). According to the paper text, there should be only one figure, Figure 2 with lower and upper panel instead of Figures 2 and 3. Please correct it by deleting the superfluous figure caption (Fig. 3) and changing the numbers of the following figures. Hereinafter, to

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avoid misunderstandings, we make reference to figures as they are in the paper.

Page 6406, lines 16-17. Concerning the sentence: “All the ratios were normalized with respect to the concentration of negative, non-neutralized particles”. It is not clear for the reader without reading the figure caption (Fig. 2), what are the ratios the authors mean here, why just the concentrations of negative, non-neutralized particles were selected for the normalization, how many lab measurements were done and how the normalization was done. We can only guess that the mean values of the concentrations of “non-neutralized particles” have been used for that purpose.

By the way, the using of terminology “neutralized” and “non-neutralized” is not correct (it is even confusing) in the section “2.1.3 Charge balance and neutralization efficiency” and also in Figure 2 caption, because in lab experiments all the particles were neutralized by the first bipolar charger/neutralizer (see Fig. 1). So, in the lab the ion-Dmps measured neutralized or doubly neutralized particles. I have understood that under the terms “neutralized” and “non-neutralized” the authors mean the different operation modes of the ion-Dmps system, but it is not explained anywhere in the text in this section.

Page 6406, lines 17-18. Is it correct to use the term “polydisperse particles” here? It is not clear for the reader whether the first DMA (see Figure 1) was also used in these lab experiments with test aerosols or not. Please add a comment in the text.

Page 6406, line 19. I recommend to specify, which one of the two chargers/neutralizers (see Fig.1) was switched ON by adding the term “ion-Dmps” just before the word “charger”.

Page 4606 in line 20. The authors have estimated the increase in the concentration of sub-10 nm particles by approximately 10% after switching on the ion-Dmps charger compared to the corresponding “non-neutralized” negative particle concentration. However, in the Fig. 2 (upper panel), one can find the ratios above 1.1.

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Page 4606 in lines 22-24. The authors have stated that the “Absolute concentrations were higher in the case of negative polarity. This is due to higher mobilities of negative cluster ions, which attach to the sampled particles in the ion-DMPS charger”. However, it seems to me that the differences more than 2 times in the positively charged particle (ion) concentrations compared to “non-neutralized” negative ones in Figure 2 is hard to explain by the differences in the charging efficiencies due to different mean mobilities of positive and negative small ions in the charger. Also, the latter parameters are not known for the charger used in the experiment. In accordance with the data given by Reischl et al. (1996), the ratio of positively to negatively charged particles (2-10 nm) in steady state conditions is about 0.6-0.7. Therefore, we have a reason to suppose that due to some unknown reason the positively charged particles had extra losses compared to negatively charged particles, or the concentrations of bipolar charger ions were significantly different.

Page 6407 Page 6407, lines 8-11. Here the authors are using very approximate estimates like “higher than atmospheric concentrations” and “agreed well” to characterize the concentration of aerosol particles used in lab experiments to test the bipolar charger/neutralizer and the charge distribution on aerosol particles, respectively. I recommend to be more specific and to give some numerical estimates. Also, the authors have made conclusions about the functioning of the charger based only on negatively charged particles data (lines 10-12), but unfortunately forgot to give a comment about positively charged particles, which seem to deviate much from the parameterization given by Wiedensohler (1988) and Reischl (1996) (see Fig. 2). Also, the test of neutralization efficiency carried out is sufficient only if the chargers/neutralizers have similar characteristics.

Page 6407, lines 13 and 15. According to Tammet (Tammet, 2004), the device used in measurements is called the Balanced Scanning Mobility Analyzer (BSMA). Here the authors have probably by mistake called it the Balanced Scanning Mobility Sizer.

Page 6408 Page 6408, lines 5-8. The authors have not mentioned here that one of

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the ion-induced nucleation mechanisms, the small ion recombination, is also resulting in the production of neutral particles similarly as neutral nucleation. Unfortunately, the latter mechanism was not discussed in the paper at all.

Page 6408, line 6. The correct reference is Fig. 4, second row. So, instead of “first row” there should be “, second row”. Page 6408, line 8. Similarly, instead of “Fig. 4, second row “ there should be “Fig. 4, first row”. Otherwise the figures in the first and second rows in Fig. 4 should be exchanged.

Page 6408, line 21. Instead of “negative natural particles” I recommend using of “naturally charged negative particles”. The particles measured in the field experiments are certainly natural, but the charges on particles can be natural or artificial (bipolar charger). Also, please indicate the size range of nanometer particles, where the concentration of naturally charged negative particles was higher.

Page 6408, line 23. The reference to figures (Fig. 5c and d) is not correct. The proper reference is “Fig. 5c and b, respectively” or “Fig. 5b and d, respectively” depending on the context the authors would like to point out.

Page 6409 Page 6409, line 7. The term “neutralized ion concentration” is certainly incorrect here, the authors probably mean “the ion concentration after the neutralization of particles in the ion-Dmps”.

Page 6409, line 8. The term “nucleation period” is not defined anywhere. If we assume that the growth rate of newly formed particles is about some nanometers per hour, then the nucleation (the formation of particles from the gas phase) can already be over when the new particles grow above the 3 nm, and it is the most probably over, when the particles grow above about 10 nm. Perhaps the “particle formation period” should be used instead of “nucleation period”.

Page 6409, line 10. Please consider the revision of the fragment “an overcharged nucleation event” using correct English. Page 6409, line 13. Instead of “7 m particles”

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there should be “7 nm particles”.

Page 6409, line 13. The authors stated that “the charging states of 5 nm and 7 nm particles are pretty constant”. However, in Figure 8 we can see that the ratio can vary from values close to zero up to about 2-3. As no uncertainty estimates have been given, nobody can realize whether these changes (variations) are within instrumental uncertainties or whether they have also some physical background.

Page 6409, last paragraph (lines 21-23). The authors inform the reader about the testing of the ion-Dmps with test aerosols (ammonium sulphate particles) during the field campaign. However, the results of the ion-Dmps tests are not discussed anywhere in the paper.

Page 6410 Page 6410, lines 11-13. Regarding the sentence: “One must remember, however, that the charging state of sub-5nm particles could not be determined during the non-event days due to absence of these particles from the measured size spectra”. This should be emphasized already in the beginning of the paper, and the uncertainty estimates of the ion concentration measurements, as well as the ratios should be given in the section “Instrumentation”.

Page 6410, line 22. The derivation of Equation 1 from the analytical formulae given by Kerminen and Kulmala (2002) is not straightforward. The latter formula was derived assuming neutral particles. Taking into account also the charging/neutralization processes, the particles can be as in neutral as in charged state during the growth. In principle, the growth rate for neutral and charged clusters and nanometer particles can be different. The growth rate is also one of the parameters in the analytical formulae given by Kerminen and Kulmala (2002), but its value (or values) used in the present model remains unknown. So, more information is needed to explain the derivation of the Equation 1. Also, the accuracy of Eq. (1), as well as its sensitivity to input parameters are not discussed in the paper, for example, the uncertainty due to neglecting the size dependence of the ion-aerosol attachment coefficients. The attachment coeffi-

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cients for the charging of neutral particles are increasing about 5-6 times if to compare 3 nm particles with 10 nm particles. In the present model it is assumed as a constant, but its value (or corresponding particle size) also remains unknown.

Page 6411 Page 6411, line 25. The order of magnitude of uncertainty estimates should be given for the average contribution of ion-induced nucleation to the total new particle formation rate.

Page 6411, line 22 and 28. Instead of “over charging” should be “overcharging” or “overcharging rate”.

Page 6412 Page 6412, line 21. The reference to paper by Hirsikko et al. (2005) is probably not correct. Perhaps the correct reference is the following: Hirsikko, A., Laakso, L., Hõrrak, U., Aalto, P.P., Kerminen, V-M., and Kulmala, M.: Annual and size dependent variation of growth rates and ion concentrations in boreal forest, Boreal Environment Research, 10, 357-369, 2005.

Page 6413 Page 6413, line 7. Instead of “device” should be “divide”.

Page 6413, second paragraph (lines 4-12). It is not clear why the model results about the contribution of ion-induced nucleation to the total new particle formation rate should be divided by a factor 3. If this is due to the fact that the maximum contribution should be 100%, but the model gives the maximum of 300%, then such a rough approach is certainly not correct, because the uncertainty estimates of the model are rather qualitative than quantitative.

Page 6413, third paragraph (lines 14-17). Here I recommend indicating also the mobility/size range of particles used for the fitting of data points.

Page 6413, last paragraph (lines 25-27) and Page 6414, first paragraph (lines 1-3). It should be kept in mind that much time (hours) is needed for the charging of nanometer size particles in the atmosphere (due to low charging probability) to reach the situation close to steady state condition. So, I guess that in atmospheric conditions the negative

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slope in the mobility/size distribution of ions above 2 nm due to neutral nucleation is mostly improbable.

Page 6413, line 27. Instead of “part of particles are charged” should be “minor part of particles get charged”, otherwise the sentence is not correct.

Page 6414 Page 6414, Cases 2 and 3 (lines 4-7). To draw any conclusions about the nucleation mechanism, it should be kept in mind that the charging of initially neutral particles in the atmosphere to obtain the steady state charge distribution on particles is many times slower process (more time consuming) than discharging of charged particles (ions). Thus, the residence time of new particles in the atmosphere before the measuring should be known.

Page 6414, lines 14-16. Regarding the following sentence: “Some of the days were clearly overcharged which indicates contribution of ion-induced nucleation on new particle formation whereas some days were undercharged and thus neutral nucleation dominates”. The days cannot be overcharged or undercharged, but the charging state of particles can be considered as overcharged or undercharged compared to the steady state charge distribution.

Page 6414, line 22. In Conclusions the average contribution of ion-induced nucleation to total new particle formation rate was estimated to be 4%. In the section “4.2 Contribution of ion-induced nucleation to the total nucleation rate” at first the number 10% was given and then the corrected value 3%. In my point of view this correction was still arbitrary to some extent. Therefore, I recommend presenting both of the estimates in Conclusions. The authors should also emphasize that the estimates are valid in the case if the four assumptions outlined in page 6410 hold, i.e. the processes of growing the particles and carrying them towards the charge equilibrium are similar between the size ranges 1-3nm and 3-15 nm.

Page 6414, lines 22-23. Regarding the following sentence: “Minimum contribution was found to be close to 0% and maximum close to 100%”. This result is trivial and

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can be concluded without any measurements, and, therefore, it is recommended to be dropped out from the conclusions.

Page 6418, Table 1. The heading of Table is not as informative as it should be. The foreword is missing, as well as the units of the BSMA data. It is not possible to understand what is presented in Table 1 without reading the paper text. One negative value (-0.1) found in the third column of the table, representing the charging state of negatively charged particles should be corrected. In the preface, instead of "using minimum concentration of 0.1 cm-3" it is recommended to use "using the concentrations above 0.1 cm-3". I also recommend adding of one extra parameter (e.g. the concentration of ions or neutralized particles above about 2-3 nm) to gain more information about the nucleation event strength.

Page 6419, Figure 1. In figure caption (line 5) I recommend the using of "measurements of ion concentration of both negative and positive polarities" instead of "measurements of both negative and positive polarities".

Page 6420, Figure 2. It is not clear what is presented in Figure 2, whether there are the mean values and the "whiskers" correspond to a standard deviation, or whether the "whiskers" are measurement uncertainty estimates. In figure caption (line 5) please consider using of "decreasing as" instead of "decreases as". Please correct the sentence "Ratios are normalized with negative concentration", see recommendations given above. The term "negative concentration" is certainly not correct. Hereinafter, if possible please consider the using of different data labels, so that the figures were understandable also if printed out in black and white.

Page 6421, Figure 3. Instead of Figure 3, there should be Figure 2, lower panel. In some cases there are two data-points with the same color label corresponding to a certain size of particles. What are these extra data-points? No explanation can be found in figure caption or in the paper text.

Page 6422, Figure 4. The meaning of the symbols "0" and "-1 or +1" in the left column

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is probably not clear for the reader and should be explained in the figure caption. Also, the “pink box” indicating the measuring range of ion-Dmps should be explained in the figure caption.

Page 6424, Figure 6. The figure caption is not as informative as it should be. Also, the authors should explain in the paper text why the fitting does not follow the data-points above about 6 nm and the ratio is less than 1 (the particles are undercharged compared to equilibrium state) in the size range of 6-12 nm. The error bars or uncertainty estimates for the ratio should be given here to interpret the results. Why are there “negative values” and “positive values” in the legend instead of “negative ions” and “positive ions”? The same is valid regarding Figure 7 in page 6425.

Page 6425, Figure 7. Almost all the comments (excluding that of about the fitting and particles in the size range of 6-12 nm) can be found above.

Page 6426, Figure 8. Unfortunately, the time series of the ratio for positively charged particles is not indicated in the figure, but only one data-point.

Page 6427, Figure 9. The classification of the measurement data into “class 1 and class 2 days” cannot be found anywhere, also the reference to an appropriate paper is missing in the text.

Page 6428, Figure 10. The scale values on x-axis are mostly missing.

Page 6429, Figure 11. What is indicated in the y-axis of Figure 10? If it is really a parameter beta of Eq.1, then its maximum value is smaller than that (5.4) presented in Table 1. If it is the parameter C(dp), as explained in figure caption, then the corresponding diameter of the particles remains unknown. Please indicate also the size range of particles measured by the BSMA, which data were used for linear fittings.

References

Hoppel, W.A. and Frick, G.M.: The nonequilibrium character of the aerosol charge distributions produced by neutralizers, Aerosol Sci. Technol., 12, 471-496, 1990.

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Kerminen, V. M. and Kulmala, M.: 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.

Laakso, L., Anttila, T., Lehtinen, K., Aalto, P., Kulmala, M., Hõrrak, U., Paatero, J., Hanke, M., and Arnold, F.: Kinetic nucleation and ions in boreal particle formation events, Atmos. Chem. Phys., 4, 2353-2366, 2004.

Misaki, M.: Studies on the atmospheric ion spectrum (I). Procedures of experimental and data analysis, Pap. Meteorol. Geophys., 12, 247-260, 1961a.

Misaki, M.: Studies on the atmospheric ion spectrum (II). Relation between the ion spectrum and the electrical conductivity, Pap. Meteorol. Geophys., 12, 261-276, 1961b.

Reischl, G.P., Mäkelä, J.M., Karch, R. and Necid, J.: Bipolar charging of ultrafine particles in the size range below 10 nm, J. Aerosol Sci., 27, 931-949, 1996.

Tammet, H.: Balanced Scanning Mobility Analyzer, 16th International Conference on Nucle-ation & Atmospheric Aerosols (ICNAA) in Kyoto, 294-297, 2004.

Turco, R.P., Zhao, J.-X. and Yu, F.: A new source of tropospheric aerosols: Ion-ion recombination, Geophys. Res. Lett., 25, 635-638, 1998.

Vana, M., Tamm, E., Hõrrak, U., Mirme, A., Tammet, H., Laakso, L., Aalto, P., and Kulmala, M.: Charging state of atmospheric nanoparticles during the nucleation burst events, Atmos. Res., in print 2006.

Wiedensohler, A.: An approximation of the bipolar charge distribution for particles in the submicron range, J. Aerosol Sci., 19, 387-389, 1988.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 6401, 2006.