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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Initial steps of aerosol growth" *by* M. Kulmala et al.

Anonymous Referee #2

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General Comments

In "Initial steps of aerosol growth" by M. Kulmala et al., measurements of aerosol growth obtained at a boreal forest site (Hyytiällä, Finland) are analyzed for insights into the mechanism by which critical clusters resulting from homogeneous nucleation grow into new particles. Key to this study are observations from ion spectrometers, which measure ambient ion size distributions down to 0.5 nm in diameter and, according to the authors, characterize the distributions of neutral post-nucleation molecular clusters. This paper makes an important contribution to the current set of observations of new particle formation. In particular, the ion spectrometer measurements show that, during most of the day, clusters with diameters between 0.5 and 1.5 nm in diameter appear to be always present (roughly corresponding to the diameter of the critical cluster). This supports the notion that nucleation may be occurring continuously, but that new particle formation only occurs when subsequent growth processes exceed the loss of

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the critical clusters to existing aerosol surfaces. Another observation is that the growth rate of aerosol over the range of diameters that extends down to 0.5 nm appears to increase as a function of size. This rules out a major role of charge-enhanced condensation, which would result in a decrease in growth rate as a function of size, and is consistent with a model of condensation by a vapor that is different from that which was responsible for nucleation.

The paper addresses scientific questions that are well within the scope of ACP, and the presentation of the work is well structured. I do, however, have some concerns that I feel need to be addressed that will strengthen the conclusions of the paper. These specific comments are presented next.

Specific Comments

1. On page 5436 the authors state (lines 9-10) the belief that observations of growth have, thus far, not been able to reconcile the observed growth rates with the model of condensation of the nucleating vapor (usually assumed to be sulfuric acid). The authors adopt the interpretation that there must be other vapors that are contributing to growth. The fact that has always puzzled me about this is that in spite of the rich variety of locales in which we have observations of aerosol growth (ranging from Macquarie Isl. near Antarctica to remote continental and urban sites, see Kulmala et al., 2004a, in manuscript), the reported under-predictions are remarkably consistent in magnitude (roughly 30%). Could this mean that there are always the same amount of condensing vapors present to make up for the other 70% of growth, or is there another explanation for this? One interesting answer to this question was presented at the recent annual meeting of AAAR (Stolzenburg et al., "Growth of the atmospheric nanoparticle mode - Comparison of measurements and theory"). That particular study of aerosol growth in urban Atlanta showed that three processes could be contributing: condensation, intramodal coagulation and differential loss by extramodal coagulation with larger particles. Only the first process, condensation of sulfuric acid monomer and its associated ammonia and water, represents true growth of individual particles. The other two pro-

ACPD

4, S2105–S2109, 2004

cesses do not involve growth of individual particles but rather apparent growth of the mode by shifting the peak toward larger particles sizes. The contributions of all three processes were calculated directly from the measurements and were found to be of similar magnitudes, and the total calculated modal growth rates were found to be in relatively good agreement with the measurements. This might be an alternative explanation for the observed discrepancy, although it is presently too early to conclude anything from this as it has not been peer-reviewed.

2. In pages 5437, line 19, and page 5438, lines 3 and 7, the authors use terms like "very sensitive," "very rapidly," and "strong size dependence" (respectively) to describe the effects aerosol diameter on various growth processes. Such phrases are subjective: different readers will likely think of different magnitudes for these effects. I suggest that the authors consider replacing these with the exact relationship if possible (e.g., for charge-enhanced condensation, I believe the enhancement factor is roughly proportional to the inverse square root of the aerosol diameter).

3. I believe that the calculation of the growth rate needs to be more clearly presented, especially for the smallest size ranges that were characterized using the ion spectrometers. Figure 1 is presented as a typical example of a day in which new particle formation and growth are observed. In the data from the ion spectrometers (lower two plots), I find it very difficult to see any evidence at all of growth of post-nucleation clusters to the sizes that are detected with the DMPS instrument (top plot). This prompts me to be concerned about the uncertainties associated with the growth rate calculations in the size range of 0.5 - 3 nm (the most critical with respect to the conclusions of the paper). Figure 2 shows a merged plot of ion mobility with aerosol mobility, and again it is difficult to interpret the uncertainty in the growth curves from the ion mobility data. While I might be satisfied that the authors applied criteria for measuring the peak that is systematic and non-biased, a clearer presentation of the uncertainty and/or counting statistics over various size ranges would remove many doubts. Such an analysis may be especially important in the 0.5 - 5 nm diameter range, since the interpretation of the

ACPD

4, S2105–S2109, 2004

ion data may be off by as much as 1.6 due to uncertainties associated with linking ion mobility spectra with those of neutral clusters (indeed, there may very well be a size dependence associated with this).

4. Figure 3 shows a summary of all data, in which the growth rates over 3 size ranges are presented as individual points over all the events in the study. The rates in each size class are then averaged, and this analysis shows that the rate increases weakly with diameter. The authors present the data in this way (averaging over all events) without providing a justification as to why each event can be treated equally. Do the events occur during similar times of day, with similar background concentrations of trace organics and sulfuric acid? Looking at the change in rate between 2 and 5 nm and the spread in the data, it's conceivable to me that some individual events might not have shown any change in rate. This is lost without lines that link data from individual events. Perhaps the authors chose not to draw the lines that connect points from individual events because the graph would appear cluttered, so an alternative way of presenting this would be as a histogram plot of the change in rate from 2 nm to 5 nm, with bin values corresponding to the difference in growth rates for individual events. This can also be done for the 5 nm to 13.5 nm size classes. This would give the reader a lot more information on the variability of these growth rates and would strengthen your conclusions regarding the increase in rate with diameter.

5. Without addressing the above concerns over the growth rate, it's still conceivable to me that the mechanism outlined by Lovejoy et al. (JGR, 10.1029/2003JD004460) might still be valid. That is, initial growth may in some instances be dominated by ion-mediated condensation, but over time these charged clusters are neutralized by recombination and continue growth by vapor condensation on neutral clusters.

Technical Corrections (capital letters emphasize suggested changes)

page 5434 line 6: role IN the growth; line 7: is diameter implied here? I recommend you state diameter; line 13: charge-enhanceD.

ACPD

4, S2105–S2109, 2004

page 5435 line 15: decoupled, i.e., different; line 27: The observed data HAVE been used to analyze four different hypotheses OF how.

page 5436 line 19: mechanism OF how.

page 5437 line 4: technically, this line should just be "charge-enhanced condensation" so that it is consistent with the other items, which all describe strictly growth processes; line 22: similar argument as for line 4: this should be changed to "Charge-enhanced condensation".

page 5438 lines 23-24: a single-sentence paragraph - recommend incorporating into previous paragraph.

page 5439 line 15: piece of evidence HAS emerged.

page 5440 line 4: used to MEASURE the particle.

page 5441 lines 12 and 19: term "electrometrical amplifier" is not a usual term to my knowledge, suggest replacing with "electrical amplifiers" or "preamplifiers"; line 14: enable ONE to record; lines 14-15: confusing ending: do you mean that the distributions actually do show considerable variation in the atmosphere? I suggest this be generalized to say "distribution under conditions where ion concentration varies over times of XX." (please provide time constant).

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ACPD

4, S2105–S2109, 2004

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