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Interactive Comment

Interactive comment on "Identification and classification of the formation of intermediate ions measured in boreal forest" *by* A. Hirsikko et al.

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I would like to comment on the authors' response (copied below in Italic) to my specific comment 1 (Atmos. Chem. Phys. Discuss., 6, S4429-S4430, 2006) about the contribution of ion-induced nucleation.

1. The authors' response: *The referee recommends us to conclude that ion-induced nucleation dominates on days with the particle formation event of subclasses Ia and Ib.1. The domination of ion-induced nucleation would mean that ion-induced nucleation makes more than 50 per cent of the new intermediate ions. Just based on the ion size distributions we can only say that ion-induced nucleation could be important on those days, but not necessarily dominating.*

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I would like to make a clarification here. When we say that ion-induced nucleation (IIN) dominates the particle formation, it means that more than 50% of newly formed particles (both charged and neutral) originate from ions. In other words, the new particle production would decrease by more than 50% if there were no ions around. It is noteworthy that most of newly formed particles (d > 3nm) could have grown from sub-3 nm neutral particles which originated from IIN but got neutralized before reaching 3 nm. These particles should be considered to be resulted from IIN. The detailed simulations based on a full kinetic model (Yu, 2006) indicate that most of intermediate ions (2.5 - 7.5 nm) are resulted from the attachment of small ions (< 1.2 nm) to neutral particles originated from IIN.

2. The authors' response: *To find out the relative contribution of ion-induced and neutral nucleation mechanisms we should apply additional measurement methods to obtain the charging state of small particles (e.g. < 6 nm in diameter) during the particle formation (see Laakso et al., 2006, reference in the manuscript) and models/calculations to obtain nucleation rates for neutral and charged particles (Laakso et al., 2006b,c). The charging state is defined as the ratio of naturally charged particles to particles charged to bipolar charge equilibrium. If the aerosol particles are overcharged (ratio over 1) it indicates the important contribution of ion-induced nucleation, whereas the undercharged state (ratio below 1) indicates the dominance of neutral nucleation mechanism. Based on their measurements in Hyytiälä, Laakso et al. (2006) found correlation between subclass Ib.2 events and the dominance of neutral nucleation (undercharged state), but there was a large variation in the contribution of ion-induced nucleation during other particle formation days (days in subclasses Ia, Ib.1 or II). The model calculations by Laakso et al. (2006b,c) showed that ion-induced nucleation clearly dominated (the fraction of ion-induced nucleation of the total nucleation rate was over 50 per cent) only on one day in Hyytiälä during one year of measurements and the corresponding calculations. In addition to that, the ion-induced nucleation was important on many days.*

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I agree with the authors that additional measurement methods and model interpretation are needed to delineate the relative contribution of IIN and neutral nucleation mechanisms. However, it is important that the measurements are interpreted properly. The authors cited their recent ACPD paper (Laakso et al., 2006a) and conference/workshop abstracts (Laakso et al., 2006b, c) in which they conclude that on average the IIN contributes only about a few percentages (range from 0.1% to 10% based on different estimation methods) to new particle formation observed in Hyytiälä. I disagree with this conclusion for the reasons given below. The conference/workshop abstracts (Laakso et al., 2006b, c) didn't provide enough details for analyzing. My discussion below focuses on the results published in Laakso et al. (2006a). Based on my analysis, the same measurements may actually indicate that the IIN dominates most of the observed nucleation events.

I would like to emphasize that both the data presented in the present paper and in Laakso et al. (2006a) indicate that ions are involved in more than 90% of the particle formation days that can be clearly identified. Subclass Ia and Ib.1 in the present paper and overcharging state of 3 nm particles (positive beita value) in Laakso et al. (2006a) can only be explained by the involvement of ions in nucleation. The key issue is what the relative contribution of IIN and neutral nucleation to particle production in such days.

Laakso et al. (2006a) used an empirical equation (equ. 1) to derive the charged fraction of 1 nm particles from the measured charging state of 3 nm particles. Based on their calculation, the median charged fraction of 1 nm particles (negative + positive) is 13%. They further analyzed the four assumptions underlying their equ. 1 and concluded that the average contribution of IIN to total nucleation rate is at most 13% but is likely to be around 4%. Both referees of the ACPD paper by Laakso et al. (2006a) pointed out that it is unclear how the equ. 1 was derived and the validity of equ.1 remains to be established. As one referee pointed out (ACPD, 6, S2873, 2006), Laakso et al. (2006a)'s analysis is likely to be flawed because the contribution of ion-ion recombination (one

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type of IIN) was not considered.

Here, I show in a straightforward way that the observed overcharging state of 3 nm particles may actually indicate the dominance of IIN.

Let us assume that positive IIN, negative IIN, and neutral nucleation rates are JP, JN, and J0, respectively, with the initial diameter of nucleated particles d = d0. It should be pointed out that the formation rate of neutral particles with d = d0 (i.e., J0) could itself a result of ion-ion recombination (Yu, 2006).

Under the steady state condition, we can assume that the total particles at a given size is proportional to JP+JN+J0. The fractions of particles charged positively (CFP) and negatively (CFN) at d=d0 can be approximated as

CFP(d0) = JP/(JP+JN+J0)

CFN(d0)= JN/(JP+JN+J0)

The particles nucleated on ions are neutralized quickly due to recombination with small ions during the growth process. As the particles grow from d0 to d1, the contribution of particles originally nucleated on ions at d=d0 (i.e., JP and JN) to the charged fraction of particles at d=d1 is

CFP(d1) = CFP(d0) * exp(-alpha*Cn*t) = CFP(d0) / exp(t/tao)

CFN(d1) = CFN(d0) * exp(-alpha*Cp*t) = CFN(d0) / exp(t/tao)

where alpha is the ion-ion recombination coefficient. Cn and Cp are total concentrations of small negative ions and positive ions, respectively. tao=1/(alpha*Cn) or 1/(alpha*Cp) is the lifetime of intermediate ions due to recombination. t = (d1-d0)/GR is the time needed to grow particles from d=d0 to d=d1 with a growth rate of GR.

The attachment of small ions to neutral particles (either from neutralization of charged particles or neutral nucleation) also contribute to the charged fractions. Here we use CFP'(d) and CFN'(d) to represent such contribution. CFP'(d) and CFN'(d) are always

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smaller than the corresponding equilibrium charged fractions CFP0(d) and CFN0(d).

The charging state of particles (as defined in Laakso et al., 2006a) is

Positive: CSP = (CFP+CFP')/CFP0

Negative: CSN = (CFN+CFN')/CFN0

Since in general CFP'< CFP0 and CFN'< CFN0,

CSP< 1+CFP/ CFP0

CSN<1+ CFN/ CFN0

If CSP (or CSN) > 1, the particles are overcharged.

If CSP (or CSN) < 1, the particles are undercharged.

Here I give the estimated values of charged fractions and charging state for particles at d=3 nm under several nucleation scenarios.

Under typical conditions, alpha = 1.5E-6 cm3/s, Cn=Cp=750/cm3, then tao = 900 s. CFP(d) and CFN(d) depend strongly on the growth rate (GR) and particle size (d). The growth rates of sub-3 nm intermediate ions in Hyytiälä have been estimated from ion mobility spectrum to be in the range of 0-4 nm/hour (Kulmala et al., 2004). If we assume d1=3 nm, d0=1.0 nm, GR=2 nm/hr (for sub-3 nm particles), we get

CFP(3 nm) = CFP(1.0 nm) /57

CFN(3 nm) = CFN(1.0 nm) /57

The equilibrium charged fractions CFP0(d) and CFN0(d) at d= 3nm are around 1%.

Case 1: All ion nucleation, no neutral nucleation: CFP(1.0 nm)=80%, CFN(1.0 nm)=20%.

CFP(3 nm) = 1.4%

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CFN(3 nm) = 0.35%

CSP(3 nm) = (CFP(3 nm)+CFP'(3nm))/ CFP0(3nm) < 2.4

CSN(3 nm) < 1.35

Case 2: 50% ion nucleation, 50% neutral nucleation: CFP(1.0 nm)=40%, CFN(1.0 nm)=10%.

CFP(3 nm) = 0.7%

CFN(3 nm) = 0.17%

CSP(3 nm) < 1.7

CSN(3 nm) < 1.2

Case 3: 10% ion nucleation, 90% neutral nucleation: CFP(1.0 nm)=8%, CFN(1.0 nm)=2%.

CFP(3 nm) = 0.14%

CFN(3 nm) = 0.04%

CSP(3 nm) < 1.14

CSN(3 nm) < 1.04

From the 27 nucleation event days presented in Laakso et al. (2006a) in which CFP(3nm) values are given,

CSP(3nm) > 2 in 20 days (74%),

1<CSP(3nm) < 2 in 5 days (18.5%),

CSP(3nm) < 1 in 2 days (7.5%)

Thus, based on my analysis given above, the measurements presented in Laakso et al. (2006a) may actually indicate that IIN dominates the nucleation in most of the days.

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Of course, our conclusion may change if the GR is larger than 2 nm/hour used above. A larger GR will give a higher CSP(3 nm). Growth rate of 2 nm/hour for sub-3nm particles is reasonable although a higher value is possible (Kulmala et al., 2004). It is important to point out that GR for particles > 3 nm derived from SMPS measurements is generally larger than GR for sub-3 nm particles (due to condensation of organic species on large particles) and thus can't be used in the above equations for calculating CFP(3 nm). Also, alpha and Cn (and Cp) may differ from the values used in above estimation. However, the simple estimation given here is consistent with the simulation based on full kinetic model that treats explicitly the size-dependent growth of neutral and charged ion clusters, recombination, ion attachments, and scavenging (Yu, 2006). Under a realistic atmospheric condition, Yu (2006) showed that the charged fraction of 3 nm particles is around 3% even all the particles originally form via ion-induced nucleation(i.e., no neutral nucleation).

In summary, the 3 nm particles are clearly overcharged (negatively) in most (>90%) of the nucleation event days based on the data given in the present paper (subclasses Ia and Ib.1) and in Laakso et al. (2006a). Based on my analysis given here, these measurements may indicate that IIN dominates the nucleation. My conclusion is opposite to the one offered in the authors' reply. I think that it will be interesting and useful to discuss these different interpretations in the paper.

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