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Atmospheric Chemistry and Physics Discussions
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Interactive comment on "Estimating the contribution of ion–ion recombination to sub-2 nm cluster concentrations from atmospheric measurements" *by* J. Kontkanen et al.

Anonymous Referee #2

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<General Comments>

This study investigates the role of ion-ion recombination on the formation of sub-2nm particles by comparing the calculated concentration of the recombination products with the measured concentration of total sub 2nm clusters. Authors conclude that the contribution is highest at 1.5-1.9 nm diameter range, and their results shows that ~10% of the total electrically neutral particles is produced by the recombination within 1.5-1.9 nm diameter range. The authors analysis clearly shows that the neglecting the particle growth overestimates the concentration of recombination products. The authors describes a new method for obtaining the collision pair among oppositely charged ions from different mass classes. I believe that this study satisfies the requirements on the scientific quality of the ACP journal; therefore, this paper deserves to be published in ACP. However, authors need to add some discussions on the assumptions they made in their analysis. In addition, the value of this paper would greatly increase if authors can explain the reasons for the vastly different conclusions made by this study and some previous theoretical studies which claim that ion-mediated nucleation can have significant contribution to the new particle formation.

<Technical Comments>

1. Authors assume the same relationship between the electrical mobility and mass for both positive and negative ions. Chemical identities of atmospheric positive and negative ions are different. For example, Figure 2 of (Swider 1988) shows the different trend between positive and negative small ions. Mass mobility relation for tropospheric positive ions are also given by (Dolezalek et al. 1977). Authors should discuss how the proposed approach needs to be modified if the mass-mobility relation is polarity dependent.

2. Authors assumes the same recombination rate (1.6*10ˆ-6 cmˆ3/s) for all collision pairs. (Natanson 1959) shows the theoretical expression for the recombination coefficient between two ions having different mass. The expression can also be found and explained well in (Gringel et al. 1978). Authors should discuss how the results would change if the mass of the collision pair, which affects the relative velocity of colliding ions, was included in the calculation of the recombination rates.

3. Authors should add some discussion on the effect of the size-mobility relation on the calculated concentration of recombination products since the scavenging rate is sensitive to the particle size of the recombination products. It is not clear why authors chose not to use the more recent size-mobility relation such as Equation 1 in (Ehn et al. 2011). Since authors also has information on the ion mass the expression given in (Ehn et al. 2011) should give better estimate of the true particle diameter. (Tammet

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1995; Okada et al. 2011) also discuss that for a given value of mobility the size of an electrically neutral particle is larger than the size of an electrically charged particle since the polarization effect reduces the mobility of the charged particle.

4. It is not clear how the rjk are evaluated when the size range shown in Table 3 do not fall nicely within one of the size ranges shown in Table 4. For example, the upper and lower sizes of the recombination products of N3+P3 are 1.20 and 1.42 nm, respectively. How they will be distributed between two size ranges which is separated at 1.3 nm.

5. Page 9 line 1∼4. Authors may be able to discuss more on the difference between their results and Manninen et al (2009a). After reading this paper I thought that the results of Manninen et al (2009a) most likely over-estimated the concentration of recombination products if they did not account for the particle growth.

<Pure Technical Correction>

1. Page 8 line 2, "to" is repeated twice

2. The contents of Figure 6(a) and 6(b) probably needs to be switched. Figure 6(a) which accounts for the effect of particle growth show larger concentrations of the recombination products, which is inconsistent with the arguments in the paper.

<References>

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