The authors acknowledge the referees. We modified and improved the manuscript according to comments and questions pointed by the referees and Prof. Jayaratne. We have submitted our responses to Prof. Kamra and Jayaratne during the open discussion of the manuscript. In the following we give our response to the referee 2.

Author response to referee 2:

Main comments:

1. Referee: ''The relative importance of ion versus neutral nucleation pathways in the atmosphere is controversial. This manuscript reviewed in detail a number of previous measurements of air ions and analysis (most by co-authors of this paper) that concluded the dominance of neutral nucleation (>_90%). However, the work of opposite opinion (i.e., the dominance of ion mediated nucleation over neutral nucleation) was only mentioned very briefly. As a review paper, I think that it is useful and necessary to give more in-depth discussion about the possible reasons of difference in the interpretations with regard to the importance of ion versus neutral nucleation. Are there any uncertainties/limitations in both sides of arguments? Such insights derived from a comprehensive review of related works will be useful to the readers.
Yu (JGR, 2010, section 2.2) discussed the possible causes of the controversy and argued that Kulmala and colleagues might have underestimated the importance of ionmediated nucleation, and the results of Laakso et al. (ACP, 2007) may actually support the significance of ion-mediated nucleation. The main argument of Yu (2010) is that Kulmala and colleagues assume that all neutral particles _ 2 nm or growing into 2 nm are from neutral nucleation, which may lead to significant underestimation of the ionmediated nucleation contribution because a significant fraction of neutral particles _ 2 nm and smaller may be formed from the ion-mediated nucleation. The authors should comment on these arguments.''

2. Referee: ''Equations 10 and 11. Based on Yu (2010)'s argument, many neutral particles smaller than 2 nm may form as a result of ion-ion recombination and thus should be considered as ion-mediated nucleation rather than neutral nucleation. It is apparent from Equation 11 that the ion-ion recombination contribution in authors' analysis only includes the recombination of charged particles between 2-3 nm with ions of opposite charge. It appears that the conclusions about the <10% contribution of ion-mediated nucleation are based on the assumption that all neutral clusters smaller than 2 nm are formed via neutral nucleation pathway. I don't think that this assumption is justified. If the authors consider the contribution of ion-mediated nucleation to sub-2 nm particles (including those neutral), their conclusion about the importance of ion-mediated nucleation may change significantly. At least, this implied assumption should be explicitly pointed out and possible effect on the conclusion (with regard to the importance of ion mediated nucleation) should be discussed and reflected in the summary and abstract.''

Author response to comments 1 and 2: We agree that these are very important topics, which were not explained as clearly as should have been done in the manuscript. We have corrected the manuscript accordingly.

We modified the following sentence in the abstract on page 24246, l. 16-19: '' Due to small changes in J_2[ion], the relative importance of ions in 2-nm particle formation was determined by the large changes in J_2[tot], and, accordingly the contribution of ions increased with decreasing J_2[tot].''

We have changed the sentence on page 24280, l.5-9 as follows: "This section discusses ions in association with atmospheric new particle formation events. After considering what kind of general information ion measurement can provide on atmospheric nucleation events (Sect. 5.1), we will briefly review the observed formation rates of 2-nm ions and neutral particles, as well as observed particle growth rates based on ion measurement (Sect. 5.2). The role of ions in the actual nucleation process will be discussed in section 5.3.''

We added following discussion at the end of paragraph on page 24283, l.17: '' Equations 10 and 11 describe the formation rates of total and charged 2-nm particles, as derived from measured quantities, but do not contain information on how ions and neutral particles/clusters smaller than 2 nm in diameter interact with each other below 2 nm. ''

The titles of sections 5.2.2 and 5.3 were changed into "5.2.2. Observations" and "5.3. The role of ions in atmospheric nucleation", respectively.

The paragraph discussing the observed formation rates of 2 nm ions and particles was moved from the beginning of section 5.3 (page 24287, l.9-18) to the beginning of section 5.2.2, and the whole section 5.3 on pages 24288-24289 was modified into the following form:

"The recent measurements with various ion spectrometers and Ion-DMPS have brought plenty of new insight into the role of ions in the nucleation process. Firstly, from NAIS measurements one may calculate the maximum contribution of ion-mediated nucleation to the overall nucleation rate using the following equation:

$$maximum\ ion - mediated\ fraction = \frac{J_2^+[ion] + J_2^-[ion] + J_2[rec]}{J_2[tot]} \quad (12)$$

Here J_2[tot] and $J_2^{\pm}$[ion] are given by equations (10) and (11) presented in section 5.2.1, and J_{rec} is the recombination rate of sub-2 nm ions. The corresponding minimum contribution of ion-mediated nucleation, called the "ion-induced fraction" by Manninen et al. (2010) and "ion-induced contribution" by Gagné et al. (2008), is obtained by setting J_{rec} equal to zero in equation (12). Secondly, the Ion-DMPS measures directly the charging state of particles larger than 3 nm in mobility diameter (see section 3.2), from which the contribution of ion-mediated nucleation can be estimated using the theoretical framework by Kerminen et al. (2007). Thirdly, the temporal evolution of concentrations of different-size ions during the nucleation events provides complementary, yet indirect, information on the role of ions in atmospheric nucleation.

By using the Ion-DMPS and AIS/NAIS at the SMEAR II station, Manninen et al. (2009a) studied the charging state and ratio of concentrations of total population and ions ($Conc_{tot}/Conc_{ion}$) in the 1.8-3 nm size range. They showed that the negative and positive ion overcharging was accompanied with a decrease in the ratio of concentrations on 51 % and 34 % of particle formation days, respectively. This is indicative of the importance of ions in particle formation on such days. Also Gagné et al. (2010) used the Ion-DMPS to investigate the charging state of newly formed aerosol particles. They found that overcharged particle formation events are frequent throughout the year, while undercharged events are being observed more frequently from November to January. They concluded that the overcharged days are observed typically on dryer and warmer days, with higher solar radiation than the undercharged days, and that the overcharged days are more frequent for the negative polarity than for the positive one. Additionally, the nucleation mode particle (3-25 nm) concentrations seem to be higher during undercharged days, which is in accordance with Vana et al. (2006). Gagné et al. (2010) and Nieminen et al. (2009) reported a decrease in the small ion concentrations during particle formation events. Such a decrease can be due to ion-induced nucleation or increased sink after new particle formation.

According to the observations by Hirsikko et al. (2007a) at the SMEAR II station, negative ions were sometimes favoured over the positive ones, since more particle formation events were observed in the negative polarity than in the positive one. Based on the measurements from April 2003 to March 2006, during 19 and 6 particle formation events observed for only positive and negative ions, respectively, there was a gap in the size distribution between the small and intermediate ions. This indicates the dominance of neutral mechanisms over ion-induced pathways during particle formation (see Leppä et al., 2009).

In some cases, ion-mediated processes have been observed to be important at the beginning of the events and the one ion polarity to be favoured over the otherone (Laakso et al, 2007a, c; Manninen et al., 2010). During particle formation event taking place at the SMEAR II station, small ions seem to activate earlier than neutral 2-nm particles (Laakso et al., 2007c; Manninen et al., 2009b; 2010). This is in accordance with the laboratory observations that small ions activate at lower super saturation than neutral ones (Winkler et al., 2008).

In spite of the frequent involvement of ions in the nucleation process (Manninen et al., 2009a), the ion-induced fraction has been observed to be on average 10 % of the total 2-nm particle formation at the SMEAR II station in Hyytiälä (Manninen et al., 2009b). Kulmala et al. (2010) reported that ion-induced fraction was about 10% of the 2-nm particle formation in Hyytiälä, Hohenpeissenberg and Melpitz rural continental sites, which is consistent with other studies (e.g. Kulmala et al., 2007, Manninen et al., 2010). Gagné et al. (2008) obtained similar contributions of ions in particle formation in Hyytiälä based on their charging state measurements: median value of 6.4% with range 1.7-16.5%. Similarly, nocturnal particle formation seems to be driven by neutral mechanism in Hyytiälä, Finland (Lehtipalo et al., 2010a). Iida et al. (2006) estimated that the contribution of positive ion-induced particle formation was 0-3.8 % and negative ion formation was 0-2.6 % during their measurements in Boulder, Colorado, USA.

Higher ion-induced fractions have been observed in some environments, such as in the high-altitude site Jungfraujoch and Pallas where the average ion-induced fraction was ca. 30 % and 20 %, respectively (Manninen et al., 2010). Asmi et al. (2010) observed a new particle formation event in Antrarctica using both AIS and DMPS, and during that event the ion-induced fraction was about 30 % of the total particle formation rate.

Based on aircraft measurements, Kulmala et al. (2010) and Mirme et al. (2010) concluded that the contribution of ions to 2-nm particle formation is minor for the whole tropospheric column. Contrary to this, Arnold (2008) estimated that ion-induced nucleation could be the dominant process at altitudes of ca. 8 km over Central Europe with a maximum particle formation rates of 25 $cm^{-3}s^{-1}$, which is the same as the maximum ion production rate via ionisation at 8 km (Bazilevskaya et al., 2008). Arnold (2008) concluded that neutral and ion-induced nucleation is frequent phenomena in the upper troposphere, but further growth is limited.

The ion-ion recombination taking place below 2 nm limits our ability to estimate the contribution of ion-mediated nucleation to the total nucleation rate. Lehtipalo et al. (2009) studied small neutral particles by subtracting small ion concentrations from the total small particle concentrations measured with a Pulse Height Condensation Particle Counter (Saros et al., 1996) operated at a high saturation ratio to allow the activation of sub-2 nm particles (e.g. Sipilä et al., 2008, 2009). Lehtipalo et al. (2009, 2010b) showed that ion-ion recombination can explain only a minor fraction of the high concentrations of small neutral particles that were detected in Hyytiälä, Finland, which is supported by the results of Manninen et al. (2009a). In Mace Head when the air masses came from the ocean, a significant fraction, and at night-time even all of the particles in the size range 1.3-3 nm could be ions and their recombination products (Lehtipalo et al., 2010b).

Based on above, the measurements conducted in continental boundary layers are indicative of frequent, yet moderate, ion-mediated nucleation outweighed usually by much stronger neutral nucleation events. Model studies tend to predict a large contribution of ion-mediated (or charged) nucleation to the total nucleation rate in the global troposphere (e.g. Kazil et al., 2010; Yu et al., 2010), and in some cases model simulations seem to be in conflict with deductions made from field measurements (Yu and Turco, 2008). The main reason for these apparent discrepancies is that the interactions between sub-2 to 3 nm ions and neutral particles are complicated and not yet well characterized. This results in substantial uncertainties in modeling the ion-mediated nucleation process, as well as in deriving ion-mediated nucleation rates from atmospheric observations. Furthermore, there are still considerable uncertainties in measuring the formation and growth rates of charged and neutral 2 nm particles. Resolving these uncertainties and discrepancies requires both theoretical and experimental approaches to tackle the dynamics of sub 3-nm population of ions and neutral particles. ''

At the concluding remarks on page 24292, l.2-3 the text was modified as follows: 'Atmospheric observations suggest, however, that the ion-mediated fraction of 2-nm particle formation is usually small compared to neutral pathways''

At the concluding remarks on page 24292, l.20-22 the text was modified as follows: ''Ion-mediated particle formation pathway is limited by the ion production rate, being, however an important 2-nm particle formation mechanism under certain conditions, as discussed in this review. ''

The comments 1 and 2 are also included in the new paragraph of the concluding remarks, when we discuss about the gaps in our knowledge and future plans (see our response to Dr. Kamra).

3. Referee: ''Page 24279, lines 21-25. Based on Yu (2010), the conditions for ion-mediated nucleation to be important can also be encountered in the lower troposphere (including boundary layer), especially at relatively high latitudes during the spring and fall seasons. This should be pointed out and discussed.''

Author response: We feel that this comment is nicely fulfilled when we changed the sentence on l. 24-26 as follows: '' These kinds of conditions are typically encountered in the middle and upper troposphere, and even in the lower troposphere (including the boundary layer) as well as in the lower stratosphere (Arnold, 1982; Lee et al., 2003; Kanawade and Tripathi, 2006; Manninen et al., 2010; Yu, 2010).''

Other comments:

4. Referee: ''Page 24279, lines 11-18. It will be good to list those references suggesting the role of ammonia and other bases and those references pointing to ions separately.''

Author response: We changed the sentence as follows: '' Nucleation is driven by sulphuric acid and possibly other low-volatile vapours (e.g. Clarke et al., 1999; Sihto et al., 2006; Kulmala et al., 2006; Riipinen et al., 2007, 2009; Kuang et al., 2008; Sipilä et al., 2010), in addition, it may be assisted by ammonia and other bases (e.g. Weber et al., 1996; 1997; 1998; 1999; Eisele and McMurry, 1997; Kerminen et al., 2010) as well as by ions (e.g. Froyd and Lovejoy, 2003a,b; Lovejoy et al., 2004; Nadykto and Yu, 2004; Enghoff et al., 2008; Yu, 2010).''

5. Referee: ''Page 24291, lines 19-22. Please give some details about "the opposite has been observed". Does it refer to the growth rate of particles larger than 3 nm? It is well known that the effect of ion in enhancing growth is generally very small for particles larger than _ 3 nm. What message do the authors want to convey in this sentence?''

Author response: We changed the sentence as follows: ''However, usually the growth of sub-3 nm ions is the slowest (Kulmala et al., 2004b, Hirsikko et al., 2005, Virkkula et al., 2007, Suni et al., 2008, Yli-Juuti et al., 2009; Manninen et al., 2010), indicating that ion-mediated mechanisms would be less important compared to neutral processes in particle growth (Kulmala et al., 2004b).''