Response to referee # 2：

We are grateful for the reviewer's comments. Those comments are all valuable and helpful for improving our paper. Our response to the comments and changes to the manuscript are included below. We repeat the specific points raised by the reviewer in bold font, followed by our response in italic font. The pages numbers and lines mentioned below are consistent with those in the Atmospheric Chemistry and Physics Discussions (ACPD) paper.

Major comment:

The authors mention that the chemical interactions between the species can affect the hygroscopic growth or phase transition of the mixed aerosols throughout the manuscript. For example, in the abstract, "For the internal mixture of oxalic acid with levoglucosan or succinic acid, there is enhanced water uptake at high RH due to positive chemical interactions between solutes." It is not clear what kinds of chemical interactions are referred to and how these interactions enhance the hygroscopic growth of the mixed aerosols. The authors should explain and address how and what kinds of interactions between the species alter hygroscopicity of the mixed aerosols in details.

Reply: *We appreciate the reviewer's comments. The chemical interactions mentioned in the manuscript are related to the ZSR assumption. The ZSR relation is based on the assumption that each component in the mixture takes up water independently without interactions between species. As a result, the ZSR rule could well describe the hygroscopic behaviors of mixtures if no obvious interactions between components exist. The discrepancies between ZSR predictions and measurements can be attributed to the significant interactions between components. Chan and Chan (2003) have introduced a parameter* ξ_w' *based on ZSR assumption to quantify the effect of chemical interaction between species on the water uptake of the mixtures. The enhancement (*$\xi_w' > 1$*, measurements greater than predictions) and reduction effects (*$\xi_w' < 1$*, measurements less than predictions) indicate that the water uptake of the mixture is larger and smaller than the sum of water uptake of individual component following the ZSR relation, respectively. This is likely due to the fact that the interactions between the species enhance (*$\xi_w' > 1$*) or reduce (*$\xi_w' < 1$*) water uptake of the mixtures compared to ZSR predictions. Neutral effect (*$\xi_w' \sim 1$*, measurements close to predictions) indicates that the water uptake of the mixtures is close to the ZSR predictions, suggesting no* *interactions exist or the chemical interactions between species have no effect on the water uptake of the mixtures. It was found that the effect of chemical interactions on the water uptake of mixtures was related to the component type and RH (Chan and Chan, 2003). According to the method proposed by Chan and Chan (2003), we also attributed the large discrepancies between measurements and ZSR predictions to chemical interactions.*

For organic compounds with polar functional groups such as OH and COOH, hydrogen bonding is the most probable interaction related to the hygroscopicity of organic aerosols. In present study, the hydrogen bonding interaction between organic mixtures containing oxalic acid with levoglucosan or other dicarboxylic acid could enhance the solubility of each organic composition, which may even make the organic fractions stay in liquid irrespective of various humidity (Hemming and Seinfeld, 2001;Marcolli et al., 2004). One previous study also suggests that the solubility of each component is enhanced in the fructose and citric acid mixture by some intermolecular interactions relevant to hydrogen bonding between the hydroxyl groups of the two components (Kwok et al., 2010).

These organic acids as well as levoglucosan molecules possess a large number of polar functional groups that promote the formation of hydrogen bonding with water molecules and enhance intra- and intermolecular interactions. UNIFAC does not account for hydrogen bonding interactions between the polar groups that can occur within the small, polyfunctional oxygenated organics, which often leads to underprediction of the water uptake by individual organics (Peng et al., 2001). It suggests that the polar functional groups promote formation of hydrogen bonding with water molecules may enhance the hygroscopic growth of some organic aerosols. Due to the technology and literature limitation, the detailed mechanism for the effects of chemical interactions on the hygroscopicity of the submicron mixed aerosols has not been well captured. In the future, measurement techniques with high size resolution are needed to explore the chemical interactions mechanism.

Related changes included in the revised manuscript:

Page 23365 line 12: We add some discussion after ZSR method description, "Due to its simple assumption that each component in the mixture takes up water independently without interactions between species, the ZSR rule could well describe the hygroscopic behaviors of mixtures if no obvious interactions between components exist. Thus, the large discrepancies *between ZSR predictions and measurements can be attributed to the significant interactions between components.”*

The other changes related to interactions can be seen in response to minor comments. In addition, page 23358 line 17: “positive chemical interactions” is revised to “chemical interactions such as hydrogen bonding”. Page 23378 line 15: after the sentence “interactions between it and oxalic acid could induce significant water uptake after 70 % RH”, we add “The hydrogen bonding interaction between organic mixtures containing oxalic acid with levoglucosan or other dicarboxylic acid could enhance the solubility of each organic composition which may even make the organic fractions stay in liquid irrespective of various humidity. The polar functional groups can promote formation of hydrogen bonding with water molecules. It may enhance the hygroscopic growth of some organic aerosols at medium and high RH.” Page 23378 line 26: “positive chemical interactions” is revised to “chemical interactions such as hydrogen bonding”.

Minor comments

Page 23362, line 10, “The dry polydisperse aerosol particles were then charged and passed through the first differential mobility analyzer (DMA1), where nearly monodisperse aerosol particles with the desired initial particle diameter of 100 nm were selected.” Given that some species are non-crystallizing, how could the author ensure that initial dry aerosols are generated for all investigated systems?

Reply: *We agree with reviewer’s viewpoint. Some organic particles may always contain some residual water even under very low RH conditions. Hence the RH<5% in our study does not warrant that the initial organic particles are completely dried.*

Related changes included in the revised manuscript:

To avoid the misunderstanding, the word “dry” has been changed into “initial” in the revised manuscript.

Page 23362, line 15, “The residence time of aerosol particles at a given RH before entering into DMA2 was about 5 s in the humidification section.” How could the authors ensure that the single component and multicomponent aerosols reach their

equilibrium states within this timescale (5 s)?

Reply: *Kerminen (1997) estimated the residence time for achievement of water equilibrium to be between 8 × 10^{-6} s and 0.1 s for 100 nm and 500 nm particles. Therefore, the typical residence time of a few seconds in the humidification section in DMA measurement is sufficient for most equilibrium hygroscopic measurements. In this study, the measured GFs for the single component at certain RH agree well with literature values within measurement uncertainty. In addition, the residence time (5 s) in our measurement is consistent with that reported in previous single component and multicomponent organic hygroscopic growth studies (Koehler et al., 2006;Moore and Raymond, 2008).*

Page 23368, line 16 "Predictions from UNIFAC model based on MA liquid assumption have a good agreement with measured GF above 50% RH while slightly overestimate hygroscopic growth at lower RH." Based on MA liquid assumption, what the composition of MA aerosols is predicted by the model? Does the model predict that MA aerosols retain water or have no residual water at low RH?

Reply: *Based on MA liquid assumption, the model predictions indicate MA aerosols contain residual water at low RH.*

Related changes included in the revised manuscript:

Page 23368 line 15: the sentence "Such hygroscopic behavior indicates MA particles are in a liquid state even at RH ~ 5 % (Peng et al., 2001)." is revised to "Such hygroscopic behavior indicates MA particles are in a liquid state and still retain some water even at RH~ 5 % (Peng et al., 2001)."

Page 23370, line 18, "For the 1 : 1 mixed Lev/OA particles (Fig. 3a, b), no deliquescence behavior is observed and the continuous water uptake starting at low 20 RH ~ 10% indicates the initial particles appear to be in a liquid state." What is the composition of the mixed Lev/OA particles at low RH? Any residual water present in the mixed particles?

Reply: *The model predictions indicate 1 : 1 Lev/OA aerosols contain residual water at low RH, which is also suggested by the continuous water uptake starting at low RH.*

Related changes included in the revised manuscript:

Page 23369 line 18: the sentence "For the 1 : 1 mixed Lev/OA particles (Fig. 3a, b), no deliquescence behavior is observed and the continuous water uptake starting at low RH ∼ 10 % indicates the initial particles appear to be in a liquid state." is revised to "For the 1 : 1 mixed Lev/OA particles (Fig. 3a, b), no deliquescence behavior is observed and the continuous water uptake starting at low RH ∼ 10 % indicates the initial particles appear to be in a liquid state and retain some water."

Page 23372, line 17, " Both ZSR and ideal solution model could well describe the hygroscopic behavior of this mixture within experiment uncertainty, indicating that no interactions related to hygroscopicity exist and the droplets behave like ideal solution" Please elaborate what is meaning of "there is no interactions related to hygroscopicity exist".

Reply: *As shown in Fig.5, the hygroscopic growth of Lev/PA mixture (1:1, mass) is well described by ZSR predicted-curve. According to the discussions in the major comment, this consistency indicates no interactions exist or the chemical interactions between species have no effect on the water uptake of the mixtures.*

Related changes included in the revised manuscript:

To avoid confusion, Page 23372 line 18 "no interactions related to hygroscopicity exist and" will be deleted in the revised manuscript.

Page 23373, line 9, "Due to the influence of MA, the OA may also exist in a liquid state at low RH." What is the composition of mixed particles at low RH? Do the mixed particles are completely dried? Any FTIR data or model results to support the presence of dry particles? If not, how the residual aerosol phase water at low RH affects the Gf calculation and the data analysis?

Reply: *For the 1:1 OA/MA mixture, the model predictions indicate the mixed particles contain residual water at low RH, also suggested by the continuous water uptake starting at low RH. In other words, if the mixed particles are completely dried the deliquescence transition may occur during the humidification. Obviously, the 1:1 OA/MA mixed particles* *are not completely dried. In fact, the GFs reported from HTDMA measurements are effective growth factors based on particle diameter at the lowest RH (~4%) measured which need not to ensure the particles are completely dried. As for the model calculations, the predicted GFs are also obtained based on particle diameter at the same lowest RH as in the measurement. Both measured and predicted GFs are obtained based on the same calculation method. Thus the residual aerosol phase water at low RH has no obvious effects on the GF calculation and the data analysis. To explore the influence of residual aerosol phase water, we carefully checked the difference of predicted GF based on particle diameter at the lowest RH(~4%) and dry condition (0% RH). It was found that the residual water at the lowest RH(~4%) was so slight that it could hardly result in significant difference between the predicted GFs based on particle diameter at the lowest RH(~4%) and dry conditions (0% RH). Even at 90% RH, this difference is not larger than 0.02.*

Related changes included in the revised manuscript:

Page 23373 line 9: the sentence "Due to the influence of MA, the OA may also exist in a liquid state at low RH." is revised to "Due to the influence of MA, the OA may also exist in a liquid state at low RH thus the mixed particles still contain some water retained from these two components."

Page 23366 line 2: after the sentence "Here the UNIFAC model with parameters modified by Peng et al. (2001) was used for WSOCs studied in this work.", we add "Considering the measured GFs are calculated from the lowest RH~4%, the predicted GFs from E-AIM are also obtained from the same lowest RH. It should be noted that the residual water in the particles at the lowest RH~4% are so slight that it could hardly result in significant difference between the predicted GFs from the lowest RH(~4%) or dry condition (0% RH)."

Page 23373, line 25, "The water uptake by the OA/SA mixture may be contributed to OA. It seems can be explained by the strong interactions among OA, SA and water molecules upon hydration." Please elaborate what are the strong interactions among OA, SA and water molecules and how the interactions affect the hygroscopic growth.

Reply: *It suggests that the polar functional groups within OA and SA may promote formation of hydrogen bonding with water molecules resulting in enhanced hygroscopic growth at high*

RH, indicated by the comparisons of measurements and ZSR predictions assuming OA and SA in a solid state.

Related changes included in the revised manuscript:

Page 23373 line 26: the sentence "It seems can be explained by the strong interactions among OA, SA and water molecules upon hydration." is revised to "It seems to be explained by the hydrogen bonding interactions within polar functional groups of OA, SA and water molecules upon hydration which promote the water association with submicron OA/SA mixed particles at moderate RH."

Page 23374, line 21, "It is clearly that phase behavior of OA is strongly influenced by the coexisting organic species, thus resulting in enhance of interactions between water and organic mixtures containing OA." Please elaborate how strong interactions between the species enhance the hygroscopic growth.

Reply: *The hydrogen bonding interaction between organic mixtures containing oxalic acid with phthalic acid could enhance the solubility of each organic composition which may even make the organic fractions stay in liquid irrespective of various humidity. As a result, the organic mixtures show more water uptake compared to the solid counterparts.*

Related changes included in the revised manuscript:

Page 23374 line 21: the sentence "It is clearly that phase behavior of OA is strongly influenced by the coexisting organic species, thus resulting in enhance of interactions between water and organic mixtures containing OA." is revised to "It is clear that phase behavior of OA is strongly influenced by the coexisting organic species, thus resulting in enhanced hygroscopic growth of organic mixtures containing OA." After this sentence, we add "The hydrogen bonding interaction between organic mixtures containing OA with PA could enhance the solubility of each organic composition which may even make the organic fractions stay in liquid irrespective of various humidity (Hemming and Seinfeld, 2001;Marcolli et al., 2004). Consequently, the organic mixtures show more water uptake compared to the solid counterparts, also suggested by model predictions based on various phase assumption."

Page 23376, line 23, "The enhanced hygroscopicity of mixed particles may be attributed to the chemical interactions between levoglucosan and OA." Please explain why interactions between levoglucosan and OA enhance the hygroscopic growth of mixed particles.

Reply: *The polar functional groups within levoglucosan and OA may promote formation of hydrogen bonding with water molecules resulting in enhanced hygroscopic growth at high RH, which is indicated by comparisons of measurements and ZSR predictions at high RH.*

Related changes included in the revised manuscript:

Page 23376 line 23: the sentence "The enhanced hygroscopicity of mixed particles may be attributed to the chemical interactions between levoglucosan and OA." is revised to "The enhanced hygroscopicity of mixed particles is likely due to the fact that the polar functional groups within levoglucosan and OA may promote formation of hydrogen bonding with water molecules resulting in more water uptake at high RH, which is indicated by the comparisons of measurements and ZSR predictions."

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