Response to comments by anonymous referee #2:

Wang and Lei et al., present a study about the hygroscopicity of aerosol particles consisting of ammonium sulfate (AS) and phthalic acid (PA). Using a HTDMA setup, the authors study first the hygroscopicity of particles where AS and PA are present in a well-mixed, internal mixture and then particles consisting of AS core and PA shell of varying size. Later, the authors compare the hygroscopicity of internally mixed particles to those with core-shell structure.

The authors show that at RH above 80% the core-shell particles have higher hygrocopicity than the well-mixed particles. Further, a traditional ZSR-relation, coupled with an empirical growth factor fit for PA hydration curve, predicts a lower hygroscopicity than what is measured for the core-shell particles. These differences in predicted and measured hygroscopicity are attributed to particle morphology changes, i.e., the shape of the particles deviate from a spherical shape.

The manuscript is generally well written and the results increase the understanding of Atmospheric Chemistry and Physics community about the hygroscopicity of complex organic-inorganic particles. I recommend that the manuscript is published after a minor revision.

Response: We are grateful to referee #2 for comments and suggestions to improve our manuscript. We have implemented changes based on these comments in the revised manuscript. We repeat the specific points raised by the reviewer in italic font, followed by our response. The page numbers and lines mentioned are with respect to the Atmospheric Chemistry and Physics Discussions (ACPD) version.

General comments:

1. How the uncertainty of the measurements was determined? In Figures 2-5 the measured points have uncertainty both in the RH and growth factor direction. However, in the manuscript no information is given how this uncertainty was calculated.

Response: Thanks for your comment. The measured results have the uncertainty of both RH and the hygroscopic growth factor as shown in Figures 2-5. The RH uncertainty is the accuracy of RH sensor (±2 %). We calculated the uncertainty of growth factor of aerosol particles in the RH range from 5 to 90 % according to the following formula (Mochida and Kawamura, 2004):

$$\sqrt{\left(\left(g_f \frac{\sqrt{2}\varepsilon_{Dp}}{D_p}\right)^2 + \left(\varepsilon_{RH} \frac{dg_f}{dRH}\right)^2,\right)} \quad \text{(R1)}$$

Here, ε_{Dp}, ε_{RH}, and g_f are uncertainty of particle mobility diameter, relative humidity, and growth factor at different RHs, respectively. The average sizing offsets of our system is taken here as $\frac{\varepsilon_{Dp}}{D_p}$. Therefore, in our study, the calculated uncertainty of growth factor of AS/PA aerosol particles is ~1 %-2 %.

Related additions included in the revised manuscript:

Page 7 line 137: we add "Thus, the calculated uncertainty of growth factor depends on the error propagation formula by $\sqrt{\left(\left(g_f \frac{\sqrt{2}\varepsilon_{Dp}}{D_p}\right)^2 + \left(\varepsilon_{RH} \frac{dg_f}{dRH}\right)^2,\right)}$ (Mochida and Kawamura, 2004). Here, ε_{Dp}, ε_{RH}, and g_f are uncertainty of particle mobility diameter, relative humidity, and growth factor at different RH, respectively. The average sizing offsets of our system is taken here as $\frac{\varepsilon_{Dp}}{D_p}$. Also, the RH uncertainty is the accuracy of RH sensor (±2 %). In this study, the calculated uncertainty of growth factor of AS/PA aerosol particles is ~1%-2%."

Specific comments:

1. Section 2.2.2. Please explain what the different R symbols are in Eq. (2) and (3). Supposedly they refer to radii of spheres.

Response: Thanks for the comment. "R_{AS}" is the radius of core. "$R_{core\text{-}shell}$" is the radius of core-shell aerosol.

Related additions included in the revised manuscript:

Page 9 line 181: We added "R_{As} is the radius of core and $R_{core\text{-}shell}$ is the radius of core-shell-generated aerosol."

2. Lines 242–244. To me it looks like the ZSR relation does not predict the hygroscopic growth of AS/PA core-shell particles. The sentence starting from line 245 states the same ("The ZSR-based predictions are lower than...")

Response: Thanks for comment. The predicted growth factor of core-shell-generated AS/PA aerosol particles by the ZSR relation is lower than the measured results, suggesting an unfavorable assumption of ZSR relation (i.e., additivity of water uptake by the different mixture components according to their individual hygroscopicity). The range of measurement–model comparisons presented in this study indicates that providing accurate thermodynamic model predictions of the hygroscopic growth behavior of core-shell systems remains a challenging problem.

3. Lines 338–342. I do not understand this sentence. Please rephrase it. Do you mean that in the future you will explore why the ZSR relation predicts lower growth factors than what is measured for the core-shell particles?

Response: Thanks for comment. No, "The low mass fraction of PA will be explored in future" means: "In the sect. 3.3, we have measured and compared the hygroscopic growth factor of core-shell-generated AS/PA particles with that of initially well-mixed aerosol particles with the same mass fraction of PA (46-68 wt %). Next, the hygroscopic growth factor of core-shell AS/PA particles containing less than 46 wt % PA (e.g., 20, or 10 wt % PA in the core-shell) would be investigated and compared to that of well-mixed particles, and ZSR relation prediction."

Related additions and changes included in the revised manuscript:

Page 16 line 338-342: we revised sentences as "In addition, for the AS/PA mixture aerosol particles containing 46-68 wt % PA, the measured growth factors of well-mixed AS/PA particles are in good agreement with the ZSR relation prediction comparing with that of core-shell-generated AS/PA particles."

4. The manuscript contains several typographical or grammar errors.

Response: Thanks for the comment. We have carefully revised the whole manuscript regarding language issues, including grammar, wording, and sentence structure, following the reviewer's suggestions, we have rewritten Sect. 4 (Summary and conclusion) they now reads as:

Page 16 line 345-Page 18 line 381: "In this study, we focused on PA to represent common organic compounds produced by various sources (e.g., vehicles, biomass burning, photo-oxidation). It is found that PA aerosol particles uptake water continuously as RH increases. We further investigated the effect of PA coating on the hygroscopicity of core-shell-generated aerosol particles. As PA coating thickness increases, the hygroscopic growth factor of AS/PA core-shell-generated particles increases prior to the deliquescence of AS, but the water uptake decreases at RH above 80 %. Furthermore, we compared the hygroscopic behavior of AS/PA core-shell-generated particles with that of AS/PA initially well-mixed particles. Due to mixing state effects, higher hygroscopic growth factors of AS/PA core-shell-generated particles, compared to that of initially well-mixed particles, were observed in this study at RH above 80 %. In addition, the ZSR relation prediction is in good agreement with measured results of AS/PA initially well-mixed particles, but leads to the underestimation of the hygroscopic growth factor of AS/PA core-shell-generated particles at RH above 80 %. We attribute these discrepancies to the morphology effect when AS deliquesces in the core-shell-generated particles.

There are a vast number of internally mixed organic-inorganic aerosol particles existing in the atmosphere. The hygroscopicity behavior of mixture particles exhibits variability during RH cycles depending on the chemical composition, size, and mixing state. Humidity cycles may lead to liquid-liquid phase separation, e.g., in the form of core-shell aerosol particles, including at higher RH or in the salt-supersaturated concentration range. Also, due to the different physicochemical properties of organic compounds (e.g., viscosity, solubility, physical state, and morphology), the equilibrium time varies for these organic coated with inorganic aerosol particles. Therefore, potential kinetic limitations in the HTDMA-measured hygroscopicity of core-shell aerosol particles is to be investigated in both humidification and dehumidification conditions."

Related changes included in the revised manuscript:

In this study, we have systematically investigated the hygroscopicity of AS/PA aerosol particles with different mass fractions of PA in the different mixing states in terms of initial particle generation. Therefore, we revised "well mixed" as "initially well-mixed" in the response to referee files and the whole paper, including figures. Also, we added the explanation for the term "initially well-mixed aerosol particles". To further avoid the misleading terminality "core-shell", we revised "core-shell" as "core-shell-generated" in response to referee files and the whole paper, including figures.

Page 3 line 58-61: "Most of the previous studies on the hygroscopic behavior of multi-components aerosol focus on the well-mixed particles generated from initially well-mixed solutions (Miñambres et al., 2010; Shi et al., 2014; Gupta et al., 2015; Jing et al., 2016; Lei et al., 2014; 2018).

Page 7 line 141: "2.1.1 Initially well-mixed AS/PA Aerosol particles"

Page 7 line 154: "2.1.2 Core-shell-generated AS/PA aerosol particles"

Page 9 line 188: "3.1 Hygroscopic growth of initially well-mixed aerosol particles"

Page 13 line 281-282: "3.3 Comparison of core-shell-generated and initially well-mixed AS/PA aerosol particles"

Page 14 line 291-293: "At 75 % RH, the measured growth factor value of core-shell-generated particles is lower than that of initially well-mixed mixtures in the PA mass fraction range from 68 to 46 wt % due to the mass transfer limitations of water vapor transport to the AS core in the core-shell particles."

Page 2 line 29-30: "For the AS/PA initially well-mixed particles, a shift of deliquescence relative humidity (DRH) of AS (~80 %, Tang and Munkelwitz (1994)) to lower relative humidity (RH) is observed due to the presence of PA in the initially well-mixed particles."

Page 3 line 61-64: "For example, Choi and Chan (2002) studied on the effects of glycerol, succinic acid, malonic acid, citric acid, and glutaric acid on the hygroscopic properties of sodium chloride and AS in the initially well-mixed aerosol particles, respectively, using an electrodynamic balance."

Page 14 line 288-290: "However, compared to Fig 5a-b, Fig. 5c shows the hygroscopic growth factors of initially well-mixed AS/PA is slightly higher than that of AS/PA core-shell-generated particles with 46 wt % PA."

Page 14 line 293-294: "For the initially well-mixed AS/PA particles, however, partial dissolution of AS into the liquid AP phase may lead to more water uptake by initially well-mixed particles."

Page 31 line 660-662: "In comparison, the E-AIM model, the fitted expression Eq. (1), and the ZSR relation predicted growth factors of ammonium sulfate (AS), PA, and initially well-mixed particles with different mass fractions of PA, respectively."

Page 34 line 694-697: "In comparison, the E-AIM model, the fitted expression Eq. (1), and the ZSR relation predicted growth factors of ammonium sulfate (AS), PA, and initially well-mixed particles with different mass fractions of PA, respectively."

Page 3 line 54-58: We revised as "The initially well-mixed aerosol particles may be divided into homogeneous and heterogeneous internally mixed aerosol particles (Lang-Yona et al., 2009), which could, in turn, strongly influence the water uptake, optical properties, and the cloud condensation nuclei (CCN) ability of the particles (Lesins et al., 2002; Falkovich et al., 2004; Zhang et al., 2005; Schwarz et al., 2006; Su et al., 2010)."

Page 4 line 69-72: We revised as "However, to date, few laboratory studies have been investigated on the influence of organic coatings on the hygroscopic behavior of core-shell particles and the difference of mixing state effects on the hygroscopicity of aerosol particles (Zhang et al., 2008; Pagels et al., 2009; Xue et al., 2009; Lang-Yona et al., 2010; Ditas et al., 2018)."

Page 4 line 76-77: We revised as "They suggest that different organic coatings lead to changes in the hygroscopic properties of core-shell-generated particles."

Page 5 line 92-94: We revised as "The organic PA can have a profound effect on light scattering, hygroscopicity, and phase transition properties of multicomponent atmospheric aerosols."

Page 8 line 161: We added "The temperature required for vaporizing PA is between ~100 and ~130°C, which corresponds to coating thickness between 10 and 50 nm."

Page 8 line 166-167: We revised as "After core-shell-generated particle-sizing, aerosols were pre-humidified in a Nafion tube and flowed into the second Nafion humidifier at the set RH2 to reach equilibrium for growth of aerosol particles."

Page 8 line 167-168: We revised as "Finally, the humidified core-shell-generated particles were detected by a DMA3 and a CPC at ambient temperature."

Page 10 line 209-212: We revised as "For example, in the case of 1:3 mixtures of AS:PA (by mass), 75 wt % PA in the initially well-mixed particles suppresses the deliquescence of AS, i.e., AS in the initially well-mixed particles slowly dissolves into the liquid phase due to continuous water uptake of PA prior to DRH of AS (80 % RH)."

Page 8 line 156-158: We revised as "After a passage through a silica gel diffusion dryer and a neutralizer, the AS core aerosol particles with a certain diameter (100, 150, and 200 nm, respectively) were firstly selected by a DMA1 and then exposed to organic vapors in a coating system."

Page 9 line 193-195: We revised as "However, an abrupt increase in the hygroscopic growth factor is observed at 75 % RH for initially well-mixed particles containing 50 and 75 wt % PA, of which the growth factor is higher than that of pure PA aerosol particles (1.09 ± 0.01 nm from measurements shown in Fig. 2) at the same RH."

Page 10 line 201-204: We revised as "For example, the measured growth factors for initially well-mixed containing 25, 50, and 75 wt % PA are 1.36, 1.28, and 1.19 at 80 % RH, respectively, lower than the growth factor of 1.45 for pure deliquesced AS particles (value from measurements shown in Fig. 2) at the same RH."

Page 11 line 230-231: We revised as "Here, we investigated the hygroscopic behavior of samples of various AS core particle sizes (AS particle dry diameter of 100, 150, and 200 nm) and coating (PA coating of 10, 20, 30, and 50 nm), respectively."

Page 11 line 237-239: We revised as "For example, the measured growth factor value at 80 % RH is 1.45, 1.40, 1.32, and 1.28 for core-shell-generated particles containing 100 nm AS and 10, 20, 30, and 50 nm coating PA shell, respectively."

Page 12 line 265-Page 13 line 268: We revised as "In the case of 50-nm PA shell coated with a certain size of the AS core (100, 150, and 200 nm) with respect to 68, 55, and 46 wt % PA in the core-shell-generated particles, it exhibits an increase in hygroscopic growth factor of core-shell-generated particles at RH below 80 % as the size of AS core decreases."

Page 12 line 246-247: We revised as "The underprediction of the ZSR relation was also observed in the literature (Chan et al., 2006; Sjogren et al., 2007)."

Page 12 line 246-247: We revised as "Sjogren et al. (2006) observed an enhanced water uptake of mixtures consisting of AS and adipic acid with different mass ratios (1:2, 1:3, and 1:4) at RH above 80 % compared with ZSR relation in the hydration condition."

Page 13 line 276-278: We revised as "For ZSR prediction, it is assumed that volume fraction of AS components is constant according to the ratio of the volume of AS core in the sphere to the volume of a core-shell sphere based on Eq. (3)."

Page 14 line 288-290: We revised as "However, compared to Fig 5a-b, Fig. 5c shows the hygroscopic growth factors of initially well-mixed AS/PA are slightly higher than that of AS/PA core-shell-generated particles with 46 wt % PA."

Page 14 line 293-294: We revised as "For the initially well mixed AS/PA particles, however, partial dissolution of AS into the liquid PA phase may lead to more water uptake by initially well-mixed particles."

Page 14 line 293-294: We revised "Core-shell-generated particle morphology may experience the restructuring and associate size change of particles." as

"Accordingly, at high RH, the occurrence of microscopic restructuring of core-shell-generated particles may affect their size."

Page 14 line 301-304: We revised as "Chan et al. (2006) investigated hygroscopicity of 49 wt % glutaric acid coated on AS core during two continuous hydration cycles. They observed that the experimental growth factor of the fresh core-shell of AS and glutaric acid in the first hydration cycle is slightly higher than those in the second hydration cycle with the same mass fractions of glutaric acid."

Page 14 line 309-Page 15 line 310: We revised as "However, a contrasting phenomenon was observed in the previous study (Maskey et al., 2014)."

Page 14 line 332-334: We revised as "they found that the slightly higher growth factors of initially well-mixed particles are than that of core-shell-generated aerosol particles (12-nm levoglucosan coated 88-nm AS)."

Page 16 line 338-342: We revised as "In addition, for the AS/PA mixture aerosol particles containing 46-68 wt % PA, the measured growth factors of initially well-mixed AS/PA particles are in good agreement with the ZSR relation prediction comparing with that of core-shell-generated AS/PA particles."

Reference:

Mochida, M. and Kawamura, K.: Hygroscopic properties of levoglucosan and related organic compounds characteristic to biomass burning aerosol particles, Journal of Geophysical Research-Atmospheres, 109, 2004.