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Interactive comment on "Phase transitions and hygroscopic growth of aerosol particles containing humic acid and mixtures of humic acid and ammonium sulphate" *by* C. L. Badger et al.

C. L. Badger et al.

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Response to Referee #2

The authors thank the referee for his/her constructive comments and have amended the manuscript accordingly. Specific points are addressed below.

1. In p.9584 l.4-5 is mentioned that 'only one study considered the effect of these humic and fulvic acids'. Which study is that? A reference would be helpful at this point.

This reference has been added to the revised manuscript.

2. In section 2.1 the authors state that particles for both the FTIR and the TDMA

method were generated by atomizing bulk solutions. They do not specify, however, if the solutions used for atomization were also the same. From their discussion of the results it is evident that the compositions used in the two experiments were different. Also, it is not very clear whether in the discussion on the variation of the pH of some solutions the authors refer to aerosols generated for the FTIR or the TDMA experiments.

Different solutions were used for the different experiments (as the FTIR experiments were carried out in the University of Toronto whereas the TDMA experiments were carried out in the University of Cambridge). The dependence of the phase transitions and water content on aerosol pH was only studied with FTIR and the manuscript has been amended to reflect this. See also our response to the comments from Referee #1 on the effect of pH.

Characteristic information of the typical size distribution of the polydisperse aerosols (e.g., mean diameter, gds, and total number concentration) would be helpful in this discussion.

This information has been added to the revised manuscript.

3. No efflorescence-mode TDMA measurements are provided parallel to the FTIR measurements, making the TDMA work seem somehow incomplete. Was there a specific reason that TDMA efflorescence measurements were not made? I would strongly encourage the authors to add these measurements in the revised version of the manuscript.

The current TDMA set-up does not allow efflorescence measurements to be made (as this would involve the use of two Nafion humidifiers). Although it would be interesting to see whether there was a change in particle size at the same RH as the NH_4^+ mode shifts, these changes in particle size are likely to be quite small (as the change in aerosol water content at this RH is also small) and may not be seen above the noise in the data.

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4. The residence time in the conditioner of the FTIR apparatus was between 6-8s whereas in the TDMA apparatus that was approx. 3 min. What was the reason or maintaining different conditioning times in the two experiments? Given the high sensitivity of organic particle growth on their exposure time to the humid environment, shouldn't the two measurements be consistent in this respect?

As in our response to the comments of Referee #1, we agree that the issue of mass transfer affects could potentially be important. This could be addressed more systematically in future studies. The residence times in this study were chosen to match the experimental conditions that have been validated in past studies with these experimental systems.

5. Some more information of the TDMA experimental setup would be helpful for the readers that might want to perform similar measurements in the future. For example, the authors mention that they get a monodisperse size distribution downstream of DMA 1 (p.9588 l.4), but do not provide any information on the geometric standard deviation of this distributions, or the DMA settings (mainly sheath to aerosol flow ratio). A reference of the Hauke DMA and also information on whether the authors use a recirculation or an open sheath-flow system would be helpful in this discussion.

Further details of the Hauke DMA and references have been added to the revised manuscript.

6. From Fig. 2 it seems that the permapure humidifier downstream of DMA 1 was operated using a controlling flow parallel to the aerosol flow. This is not recommended by the manufacturer because it can result in a non-uniform humidification of the aerosol sample along the nafion humidity exchanger. This can possibly cause measurements of lower DRH values with the TDMA.

The authors were not aware of this and thank the referee for bringing this to our attention. We recognise that this could be an important effect in studies were mass transfer effects are being investigated. Future experiments will be carried out with the control-

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ling flow anti-parallel to the aerosol flow. However, the aerosol particles are expected to equilibrate to the same RH in the conditioner so non-uniform rates of humidification in the humidifier should not be an issue in the work presented here.

7. The authors define the hygroscopic growth factor as the ratio of the median diameter at the RH of the measurement over the median diameter of the dry aerosol (p.9588 l.20-23). It should be stressed that the TDMA measurements provide the growth factor based on the mobility-diameter, and not the physical (or volume-equivalent) diameter. Therefore, the definition of the growth factor the authors provide does not fully describe what is presented as TDMA measurements. It is accurate only if the shape correction factor of the dry particles is unity (assuming that the deliquesced particles are spherical). It would be more accurate if the authors refer to the growth factor as mobility-diameter based since no information is provided, or is available in the literature for the shape of the particles studied in this paper.

This has been noted in the revised manuscript.

8. The authors perform TDMA measurements for two sizes (50 and 100 nm mobility diameter) to investigate any effect of particle size. The results show that 50 and 100 nm particles behave very similarly, indicating that size does not have any effect. This corroborates the TDMA studies provided by Hameri et al. (2000) who investigated the size effect on the deliquescence of AS nanoparticles. The authors might want to mention that at some point.

This is an interesting point has been included in the revised manuscript.

9. It seems that by measuring the size distribution of the polydisperse aerosol used in the FTIR experiments and using the water uptake measurements presented for the different compositions, the growth factor of the particles can be estimated. This should be a rather easy calculation to compare with the TDMA measurements.

To date, the water contents in FTIR experiments of this type have been uncalibrated in

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an absolute sense. However, work is ongoing in our laboratory to develop a technique to calibrate the absorption due to condensed-phase water using a combined FTIR-SMPS system. This has been used to calculate the absolute water content of humic acid aerosol and is described in a paper recently submitted to the Journal of Physical Chemistry [Badger et al. 2006].

References: C.L. Badger, P.T. Griffiths, I. George, J.P.D. Abbatt and R.A. Cox 'Reactive uptake of N_2O_5 by aerosol particles containing humic acid and mixtures of humic acid and ammonium sulphate', Journal of Physical Chemistry A, (2006). Submitted.

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