**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

Interactive comment on "Prompt deliquescence and efflorescence of aerosol nanoparticles" *by* G. Biskos et al.

G. Biskos et al.

We thank the reviewer for his time and effort to prove very useful comments for the improvement of the manuscript. Below are detailed responses to each of his/her comments.

1. The first two paragraphs of the Introduction may mislead readers who are not familiar with the literature on atmospheric new particle formation:
(1) It is true that progress has been made in measuring the chemical composition of atmospheric nanoparticles, but the paper is misleading when it states "the chemical composition of atmospheric aerosol nanoparticles can now be determinedE? " The AMS does a reasonable job for particles larger than about 20 nm. For particles as small as 7 nm the TDCIMS can measure sulfates and ammonium quantitatively, and Smith and coworkers are making progress at measuring

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

organics with this instrument. The amount or composition of organics on such small particles, however, can not yet be quantified.

(2) The first paragraph points out correctly that in some locations, measurements suggest that freshly nucleated particles consist primarily of ammonium sulfate. The authors should also point out, however, that organics are also frequently important constituents. Supporting evidence for this includes direct measurements of composition by the AMS (Allan et al., 2006), indirect measurements of composition by the pulse height analysis method (O'Dowd et al., 2002), and the observation that actual growth rates are typically much higher than can be explained by the condensation of sulfuric acid vapor and its associated water and ammonia (Stolzenburg et al., 2005).

To include the two points made by the reviewer in our introduction, we have modified the two first sentences from:

"*Despite their small mass, the chemical composition of atmospheric aerosol nanoparticles can now be determined in part due to recent advances in analytical instrumentation (McMurry 2000). Observations employing this instrumentation indicate that freshly nucleated ambient particles having diameters of a few nanometers are frequently composed primarily of ammonium and sulfate ions at variable mixing ratios (Kulmala et al. 2004).*"

to:

"*Despite their small mass, the chemical composition of atmospheric aerosol nanoparticles with diameters as small as 20 nm can now be approximately determined, in part due to recent advances in analytical instrumentation (McMurry 2000). A substantial number of field studies indicate that ambient particles following nucleation events are in many location composed primarily of ammonium and sulfate ions at variable mixing ratios (Kulmala et al. 2004), although organic compounds have been identified as important constituents of atmospheric nanoparticles in some cases (O'Dowd et al. 2002;*

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

Allan et al. 2006)."

(3) "Ammonium sulfate nanoparticles form in the atmosphere by homogeneous nucleation in the presence of gas-phase sulfuric acid, water, and ammonia." In fact, the process responsible for nucleation remains a current area of research. There has been speculation that this ternary nucleation process is responsible, but no one has shown this definitively. The atmosphere contains many trace compounds that could participate in nucleation, and it is likely that the nucleation mechanism varies with time and location. To avoid misleading the reader, this language needs to be softened.

To point out the poor understanding of the mechanisms that lead to the formation of ammonium sulfate nanoparticles in the atmosphere, we have modified the sentence:

"*Ammonium sulfate nanoparticles form in the atmosphere by homogeneous nucleation in the presence of gas-phase sulfuric acid, water, and ammonia (Ball et al. 1999).*"

to:

"*Ammonium sulfate nanoparticles are believed to form in the atmosphere by nucleation in the presence of gas-phase sulfuric acid, water, and ammonia (Ball et al. 1999).*"

Also, to further highlight our poor understanding of the exact mechanisms of new-particle formation in the atmosphere, we have added the following sentence in the introduction:

"*Although the exact mechanism of new-particle formation is not yet fully understood, recent theoretical predictions indicate that ternary nucleation could explain the high particle-formation rates observed in the atmosphere (Napari et al. 2002).*"

2. The TDMA technique (Rader and McMurry 1986) includes the TDMA apparatus (DMA1, aerosol conditioner, and DMA2) as well as the basis for analyzing data from this apparatus (i.e., for interpreting N2(V2)). Assumptions made by Rader and McMurry (1986) regarding the effect of aerosol conditioning on the mobil-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

ity distribution were subsequently relaxed to allow for the interpretation of data from particles that are not entirely uniform chemically (Stolzenburg and McMurry 1988), such as atmospheric particles. The paper under review makes use of the apparatus but neglects the subtleties of TDMA data analysis. This paper would benefit somewhat if more attention were paid to that early work. For example, by using TDMA data analysis techniques the authors could have quantified the extent to which N2(V2) measurements are broadened by overlapping peaks. Those methodologies also provide a rigorous methodology for quantifying the relative proportions (and the uncertainty in those proportions) of particles in each of the overlapping peaks. Indeed, if the full power of the TDMA technique had been employed earlier, it is possible that more skepticism might have arisen regarding claims for nonprompt deliquescence.

Indeed, algorithms for analyzing data from HTDMA measurement are powerful tools for interpreting changes in the monodisperse size distributions of the sample, especially when the particles are internally mixed and/or their exact composition is not known. In the measurements reported in this paper, however, the particles are composed of a single component (namely, ammonium sulfate). Therefore, any broadening in the monodisperse size distribution when RH increases is due to condition non-uniformities in the experimental system that causes some particles to experience higher RH conditions than others. The resulting broadening of the monodisperse size distribution is more evident at RH values close to the DRH when the RHs = RHa + 3% protocol is used (cf. Figure 2c). This is because particles in the crystalline and aqueous phase downstream of the aerosol conditioner grow to slightly different diameters within DMA-2. On the other hand, when the RHs = RHa protocol is used, particles in the crystalline and aqueous phase are distinguishing as two separate peaks of the same spread during deliquescence-mode experiments.

Our data fitting algorithm is a simplified version of the TDMAFIT. By assuming that the spread of the monodisperse sample should not change with RH because the particles

are of uniform chemical composition, the gsd of the fitted distribution is fixed, and any increases of the measured gsd are automatically accommodated by fitting two size distributions to the data. Comparison of the fitted size distributions obtained with our method and the TDMAFIT algorithm were very similar.

The importance of using a data analysis algorithm to interpret the HTDMA data has been addressed in the revised manuscript, including references to the Rader and McMurry original TDMA paper and the TDMAFIT manual (Stolzenburg and McMurry 1988).

3. When referring to the N2(V2) data shown in Figures 2 and 3 the authors use the terminology "number size distributions." This is confusing. Readers who are familiar with TDMA data analysis methodologies will think in terms of the aerosol size distribution function (dN/dDp, dN/dZp or a variant) when they read "number size distributions". The authors need to use different language when discussing the N2(V2) data.

The terminology "*number size distributions*" has been changed to "*normalized number size distributions*" in the revised manuscript.

4. In Appendix it is stated that (Zelenyuk et al., 2006) reported that ammonium sulfate has a dynamic shape factor of 1.0. In fact, Zelenyuk et al. reported that the dynamic shape factor of ammonium sulfate particles in the free molecular regime decreases from 1.07 to 1.03 as particle size decreases from 500 nm to 160 nm. Although they did not carry out measurements on nanoparticles, it would appear that their results are not inconsistent with those reported by Biskos et al.

We have changed the following sentences from:

"*Literature accounts suggest that submicron dry ammonium sulfate particles are nearly spherical and, therefore, have a shape factor χ of 1.00 (Zelenyuk et al. 2006). The restructuring shown in Figure 6 for increasing RH, however, demonstrates that shape*

ACPD

6, S3417–S3422, 2006

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

factor differs slightly from 1.00 (e.g., 1.02; see further discussion in main text)."

to:

"*Literature accounts suggest that submicron dry ammonium sulfate particles are slightly nonspherical, having a shape factor χ that ranges from 1.07 to 1.03 as particle size decreases from 500 to 160 nm (Zelenyuk et al. 2006). The restructuring shown in Figure 6 for increasing RH also demonstrates that shape factor differs slightly from 1.00 (e.g., 1.02; see further discussion in main text).*"

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7051, 2006.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU