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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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This paper shows that previous measurements suggesting that the deliquescence of ammonium sulfate nanoparticles is "nonprompt" are an artifact of experimental protocol. The authors show clearly that deliquescence of ammonium sulfate particles in the 6 to 60 nm range is "prompt" (i.e., occurs at a well defined relative humidity rather than over a range of relative humidities.) This is a very nice result that brings closure and clarity to an important fundamental question of aerosol science. The paper also provides guidance for improving TDMA measurement protocols. The paper is clearly written and is suitable for publication in Atmospheric Chemistry and Physics. I recommend that it be accepted after the authors respond to the following comments.

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 determinedĚ” 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 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).

(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.

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 mobility distribution were subsequently relaxed to allow for the interpretation of data from particles that are

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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.

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.

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.

Allan, J. D., M. R. Alfarra, K. N. Bower, H. Coe, J. T. Jayne, D. R. Worsnop, P. P. Aalto, M. Kulmala, T. Hyotylainen, F. Cavalli and A. Laaksonen (2006). "Size and composition *measurements* of background *aerosol* and new particle growth in a Finnish forest during QUEST 2 using an Aerodyne *Aerosol* Mass Spectrometer." Atmospheric Chemistry and Physics 6: 315-327. O’Dowd, C., P. Aalto, K. Hämeri, M. Kulmala and T. Hoffmann (2002). "Atmospheric particles from organic vapours." Nature 416: 497-498. Rader, D. J. and P. H. McMurry (1986). "Application of the Tandem Differential Mobility

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Analyzer to Studies of Droplet Growth or Evaporation." J. Aerosol Sci. 17(5): 771-787. Stolzenburg, M. R. and P. H. McMurry (1988). TDMAFIT User's Manual. Minneapolis, MN 55455, Particle Technology Laboratory, Department of Mechanical Engineering, U of Minnesota. Stolzenburg, M. R., P. H. McMurry, H. Sakurai, J. N. Smith, R. L. Mauldin, F. L. Eisele and C. F. Clement (2005). "Growth rates of freshly nucleated atmospheric particles in Atlanta - art. no. D22S05." Journal of Geophysical Research-Atmospheres 110(D22): S2205. Zelenyuk, A., Y. Cai and D. Imre (2006). "From agglomerates of spheres to irregularly shaped particles: Determination of dynamic shape factors from measurements of mobility and vacuum aerodynamic diameters." Aerosol Science and Technology 40(3): 197-217.

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