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Atmospheric
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Discussions

Interactive comment on "Hygroscopicity of the submicrometer aerosol at the high-alpine site Jungfraujoch, 3580 m a.s.l., Switzerland" *by* S. Sjogren et al.

Anonymous Referee #3

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Review of "Hygroscopicity of Submicrometer Aerosol at the High-Alpine Site...." (ACPD MS # acpd-2007-0350)

1. Recommendation The study presented here addresses an important issue in aerosol science, characterization of the hygroscopicity of ambient, atmospheric aerosol and the link between that hygroscopicity and the aerosol chemical composition. Furthermore, measurements are presented with some size resolution, a relatively rare and valuable elaboration. The approach to the measurements is generally sound and the presentation mostly fairly clear. Hence, I feel that eventual publication is well merited. On the other hand, there were several instances in which I found the authors' argu-

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ments less than decisive and/or unclear, calling for possibly more circumspection and certainly more clarity. It is noteworthy, for example, that chemical composition data are given in this study only in a form (time series plots in a very small format) that render them hard to quantitatively assess. Similarly, the synthetic GF's are difficult to collate with the corresponding chemical composition data. My comments in support of these reservations are given below.

2. Comments 2.1 Page 13704, line 14. The assertion concerning the sampling efficiency of the inlet, an important parameter in the study (whether acknowledged as such or not), is not well supported. The given citation does not supply any data or detail concerning the estimated passing efficiency, which is in any case poorly characterized (e.g., what is the 50% cut point, what is the kurtosis of the presumably sigmoid efficiency curve, etc.). Mind you, there is noting intrinsically improbable about the somewhat vague, given efficiency for a stationary inlet but I have seen plenty of such inlets with 50% cut points well below 40 microns for wind speeds of 20 m/s. The authors must simply provide better support here.

2.2 Page 13706, lines 2-4 I find it at least mildly surprising that the hygroscopicity is insensitive to the BC concentration to within a factor of two (essentially the impact of varying the specific absorption by about a factor of two) and to the size distribution of that BC. After all, one can easily envision situations where there would be sensitivity (e.g., BC dominating the mass in a particular size range). The text suggests that authors have done sensitivity studies on this issue. They should report the results explicitly to support this claim.

2.3 Page 13706, line 13. This is a minor organizational comment. One would normally expect temperature gradients in a TDMA system and such gradients in principle would produce errors in RH measurements. Hence, the assumption made here seems questionable. On the other hand, the authors DO provide good support for the assertion a bit further on (page 13707, lines 13-23). I would suggest a bit of a rewrite to more nearly juxtapose the assertion and its defense. Perhaps the insertion of a "see below for justification" would suffice.

2.4 Page 13708, lines 3-13. The inversion technique used here is not really clearly delineated. The reference to a manuscript in preparation is, of course, not adequate and, recognizing this, the authors have tried to characterize their procedure by comparison with Cubison et al(2005). However, the characterization is a bit obscure. They say that the inversion has "similarities" to Cubison et al. This is not very enlightening since it does not preclude quite substantial differences between the two approaches. The only difference apparently given is the non-linearity of the inversion function. Is this all that differs? If not, what else is different? The authors need to clearly show exactly how the procedure they employ here differs from the only actual literature reference they supply.

2.5 Page 13708, lines 17-26. I found the discussion of the "ensemble mean growth factor" a bit confusing. This apparently refers to the mass mean GF, important since the AMS was used in scanning mode. The authors then state that this corresponds to the GF if water were "equally distributed among all particles." This will be true only if the particles are both of the same composition and size. Of course, this is all one can really get from a bulk measurement. On the other hand, it is not the same as the average of the hygroscopicities (and mass hydration) of individual particles of differing composition and size. I THINK that the authors are trying to say this but I am not sure. The discussion needs to be clarified.

2.6 Page 13710 - 13711, section 2.6 (ZSR relationship) A major assumption is implicit in the adoption of the ZSR mixing rule, namely the independence of organic and inorganic effects on water activity. The authors do state this (essentially) but do not discuss it at all adequately, in my view. First, of course, such independence is not generally correct, even as an approximation, it is simply difficult to deal with the alternative. Perhaps the best attempt at incorporating organic-inorganic ion interactions into a prognostic model was the modified UNIFAC model of Ming and Russell (JGR, 106, 28259-28274,2001). This effort suggests that substantial errors may be incurred using

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an approximation such as ZSR, perhaps 30% or so. Similarly, even studies that do indicate that the ZSR relationship can be useful, suggest errors on the order of 20% or so due to organic-inorganic interactions (cf. Cruz and Pandis, Environ. Sci. Technol., 34, 4313-4319, 2000). Furthermore, it is not simply the presence of organics that can invalidate the mixing rule. Aklilu et al (Atmos. Environ., 40, 2650-2661, 2006) have found that high nitrate levels will also render the ZSR mixing rule suspect. Of course, there is relatively little nitrate in the aerosol presented here (at least ostensibly), but there is certainly plenty of organic matter, typically at or in excess of a 50% mass fraction according to Figure 4. As noted by the authors, the ZSR mixing rule is relatively insensitive to this large organic fraction due to the cubic weighting of the GF's - and the assumed relatively low hygroscopicity of the organic fraction. However, this is not true of less approximate methods and the high organic mass fraction dictates that this issue be explored. I am not unalterably opposed to the use of the ZSR rule but its use needs to be justified here.

2.7 Page 13712, lines 1-11. I am not sure I follow the argument here concerning the partitioning of NH3 in solution. Thermodynamic equilibrium for the nitrate-sulfate-ammonia-water system has been studied for some time (cf. Seinfeld and Pandis, Atmospheric Chemistry and Physics, 2nd ed, Wiley InterScience,1998). The relative concentrations of the various aqueous ionic species will be determined by the absolute masses in the system (i.e., masses per unit volume of sampled air) together with the RH and temperature. Presumably, the authors have this information and there should therefore be no ambiguity in the speciation. Are there substantial organic acids present to complicate matters? Is there some question as to the validity of the nitrate measurements? Again, it has been known for sometime that one can evaporate nitrate particles in DMA's - and thus presumably in HTDMA's (cf., Khlystov et al, J. Aerosol Sci., 28, S1, s59-s60, 1997). If there is an issue here, it must be discussed. The Gysel et al citation simply, in so far as I can tell, reiterates the statement already in the text that the given choice of partitioning yields the best closure. I do not find this very satisfying. Why not do the detailed thermodynamic calculation and put the issue to rest?

2.8 Page 13714, lines 11-20. In the abstract to this study, the authors state that hygroscopic closure was done using the HTDMA and AMS data by means of the ZSR mixing rule and that, "in general, a good agreement between measured and modeled data was found." One would expect that this apparently major theme would be reflected in the content of the paper but this does not seem to be the case. Here, we finally return to this topic but in a very vague and indecisive manner. Firstly, the closure is not actually presented except in a form that is difficult to quantitatively assess (the time series of Figure 4). Indeed, no quantitative assessment is given, at least in so far as I can see. There is nothing at all wrong with showing the time series of Figure 4 (though the figure should really be a bit larger). However, in addition, standard regression plots of the observed vs predicted values of GF should be given, showing the regression line(s). The R2 value(s) for the regression(s) should also be given, together with the regression coefficients and their uncertainties. Furthermore, I would have expected to see some discussion of the chemical composition characteristic of both good and bad closure. There IS some discussion of poor closure on page 13715, vis a vis nitrate evaporation as examined by Gysel et al but it is, again, non quantitative. This should be rectified.

2.9 Page 13714, lines 20-23. The authors state that the absence of the m/z=57 peak indicates that there is little unprocessed, primary organic material present and that the majority of the organics are oxidized. I think that these assumptions are not warranted. The 57 peak is certainly associated with a commonly occurring hydrocarbon fragment - essentially a CH3CH2CH2CH2 group - but there are plenty of other fragment of different m/z associated with HC's (e.g., 41, 43, 55, 69, 71, etc.). Similarly, I do not understand at all the reasoning that says that the absence of this peak implies that the bulk of the organic material present is oxidized. The references cited certainly do not claim this. It may well be true, of course, that the organic matter present IS mostly oxidized, but the presence or absence of the 57 peak does not in itself determine this. The authors need to supply more support for their assertion.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 13699, 2007.

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