**Atmospheric
Chemistry
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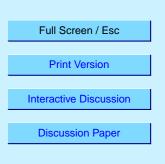Discussions**

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Interactive comment on "Ice nucleation in sulfuric acid/organic aerosols: implications for cirrus cloud formation" *by* M. R. Beaver et al.

Anonymous Referee #2

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The formation of ice in the atmosphere is an important topic as it is highly relevant to cloud formation and, thus, climate change. The authors correctly explain that the organic aerosol fraction remains highly unknown as is the resulting effect on cloud formation. This is, as far as I know, a unique data set to elucidate the role of mixed sulfuric acid/organics on aerosol freezing using a conventional low temperature flow tube coupled to FTIR. It is highly suitable for publication in ACP.

There is some important information lacking from this manuscript, however, and the following issues should be addressed by the authors in a revision of their work. The foremost of these is a lack of a comprehensive error estimation in the data presented in the manuscript figures and how it relates to data uncertainty. A secondary issue is

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how the uptake of the organics affects the water activity.

1. The most significant shortcoming in this manuscript is that there are no error bars presented in any figure. A number of uncertainties are mentioned in the text but it is not clear what the result is on the figures and thus the data interpretation. For example: A) The uncertainty in temperature is 0.6 deg C; the difference in freezing point for 15wt % H2SO4 versus similar experiments is about 1 deg C. This should be reflected in Figures 4 - 8. B) The uncertainty in H2SO4 wt% is 2%, please add to the figures. C) See point 6 regarding the uncertainty in Mie calculation; this should set error bars in Figure 3. 2. A description of the work of Koop et al. (2000) is made. This is discussed throughout the manuscript until the statement on page 2072 'Ěa direct comparison to Koop et al. (2000) Ě is not possible in this case' due to the lack of water activity data for the mixed organic/sulfuric acid aerosols. It is clear that this is true but two questions results: A) Why are there references throughout the text to water activity if this comparison can not ultimately be made with these data? B) More importantly, Figure 8, which is arguably the central figure of this paper, compares all data to the freezing point of 15wt% sulfuric acid. This should only be done if the water activity of all points is the same otherwise there is no reason to assume the freezing temperature would be the same. One can imagine this is a reasonable comparison in cases where only small amounts of organic is in solution but it is clear that this comparison is essentially meaningless in cases where significant organic is involved (i.e., the shorter chain organics which exhibit significant uptake); it would be analogous to putting a point for 50wt% H2SO4 on the plot. It should be made clear in the text and the figure caption what the limitations of this comparison are. 3. It would be useful to put both the calculated and NIST data in Table 1 and then the differences between them. There is reference to solubility data for organics on page 2070 for bulk data and from this experiment. These should both be shown in Table 2 along with differences. 4. Are the lines in Figures 3, 5, 6 and 7 fits to the data or from some theory? This should be explained in the figure captions or the lines should be removed. 5. The attribution of homogeneous or heterogeneous freezing appears to be inferred based on a difference

from the freezing point of 15wt% H2SO4 (Figure 8). The authors' group has used FTIR to observe phase changes (e.g., efflorescence) in past publications. Thus I wonder if it is not possible to show if a second phase (i.e., a pure organic) is present? Figures 5 and 6 are consistent with the formation of a second phase and no second phase, respectively, but it would seem the authors should see this formation in the FTIR spectra. Is this the case? 6. Given point 5 the sentence in the Implications and Conclusions 'Ěby a homogeneous mechanism Ě via a heterogeneous mechanism Ě' would seem to be too definitive a statement. Please change the wording throughout the paper to make it clear that heterogeneous/homogeneous mechanisms are inferred, not directly observed. 7. Section 2.2 describes the use of Mie scattering to obtain the organic content. If I understand correctly the aerosol size change between just sulfuric acid and acid and organic aerosol is differenced and this is attributed to the amount of organic uptake. This section should be expanded as this is an interesting method to obtain organic uptake but it is not clear how accurate these data are. Specifically: A) What is the variability in the produced sulfuric acid aerosol? Typical atomizers have an output that is variable in both radius and total number. Is this uncertainty larger or smaller than the observed uptake? B) What is the uncertainty in the Mie scattering fit? Mie fits are not normally single valued; several choices of r and GSD normally return good fits. What is the range in suitable fit choices and how does this relate to the observed uptake? 8. On page 2068 the term 'a similar diameter increase was observedĚ' for ammonium sulfate as for sulfuric acid. It is then assumed that the uptake of organics is the same for neutral and acidic species. Please state the observed increase ratios as it pertains to the uncertainty in this measurement. For how many of the organic species was this experiment performed? 9. On page 2072 reference is made to the use of lambda as a model for supercooling of aerosols (equation 1). The original work using this sensitivity parameter is by Rasmussen, for example Rasmussen, D. H., and A. P. MacKenzie. Water Structure at the Water Polymer Interface, New York, Plenum, 1972; Prenni et al. (see following points) and Demott are only recent users of this concept. 10. Lambda is not defined as the authors use it here. Lambda is the factor by which

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the melting point depression at a given concentration is multiplied by to obtain the observed freezing points after subtraction of the supercooling of pure water supercooling. Observations give the typical values between 1.4 and 2.2 that are referenced using this concept. Thus a lambda equal to unity is a constant depression of the melting line by the amount that pure water supercools (Ÿ-38 deg C) NOT an 'absence of supercooling'. 11. It is not clear what the source of equation 2 is. Kf is referenced as the freezing point depression constant for '15wt% H2SO4' and then 1.86 deg C m-1 is the value for 'water'. Is m the molality? Is this a fit to this data? I should note that after looking at Prenni et al. (2001a) I can find neither equation and Demott (2002) only has equation 1 so what is the source? 12. Is it known that pure externally mixed organic particles are not formed in the experiment (i.e., in addition to organic vapor partitioning to the sulfuric acid aerosol)? If the impurity level in the organics is up to 5% is it known what the impurities are? Could they be a species that promotes ice nucleation in the longer chain organics?

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 2059, 2006.

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