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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Results from the CERN pilot CLOUD experiment" *by* J. Duplissy et al.

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This manuscript reports initial 2006 results of the CLOUD experiment to understand the effect of cosmic rays on particle formation, using proton synchrotron beams in an environmental chamber. The main conclusion is that this pilot study has validated the experimental setup and from some of the initial experiments, the authors also claimed that they found evidence of ion-induced nucleation or ion-ion recombination processes for sulfuric acid particle formation at the typical atmospheric conditions. While this study intended to validate this new experimental setup, experiments shown in this manuscript were conducted in not well-controlled experimental conditions and the results are not reproducible. There is also some misinterpretation of experimental results. And from these results, the main conclusion is not convincing.

A. Introduction.

The experiments shown in this manuscript were designed to study the cosmic ray ef-

fect on particle formation in the lower atmospheric region. However, Introduction is confusing, considering the current understanding of the field. It is now relatively well recognized that ion-induced nucleation is important in the upper troposphere and lower stratosphere region (as opposed to lower troposphere) where ion production rates by cosmic rays are highest, as shown by [Lovejoy et al., 2004] IIN model predictions; this IIN model was vigorously tested and constrained by in-situ observation data of SO2, OH, H2SO4 and particle size distributions in this region provided by [Lee et al., 2003]. However, both [Lovejoy et al., 2004] (laboratory observations) and [Lee et al., 2003] (field observations) did not exclude the possibility of sulfuric acid binary or ternary nucleation processes in this region. Especially when temperatures are very low, nucleation barriers of even binary homogeneous nucleation can also disappear like in IIN [Yu, 2002]. So it is likely that cosmic rays have little or no effects on particle or cloud formation even in a global scale. A new article by [Carslaw, 2009] also states the same conclusion that the effect of cosmic rays on particle formation "is smaller than thought", by summarizing recent global aerosol modeling work. As another example, [Kulmala, 2009] also state in their title, "Atmospheric data over a solar cycle: no connection between galactic cosmic rays and new particle formation". The most important question here is, what will be the homogeneous nucleation processes in the lower temperature range and at low sulfuric acid concentrations (representative of upper troposphere and lower stratosphere where IIN is most effective), in comparison to IIN, rather than the effect of cosmic rays on particle or cloud formation at room temperature.

B. Interpretation of data.

1. The "evidence of ion-induced nucleation or ion-ion recombination for sulfuric acid particle formation" (Conclusions, page 18256) is not convincing. The authors used two criteria for IIN: a high fraction of charged particles and association of enhanced particle concentrations with beam intensities (Page 18248, 1st paragraph). However, the authors also stated that high fraction of charged particles does not necessary suggest IIN involvement but lack of charged particles also do not exclude IIN (Page 18248 3rd

Paragraph; Page 18250, 4th paragraph). That is, this first criterion is not really useful. In fact, there are only 6 events showed overcharge out of 44 nucleation events (page 18248, 4th paragraph). With regard to the 2nd criterion, which is more straightforward, the experimental results do now show any consistent results (e.g., Figure 7; Section 3.2.4), except Run 35, which only showed some association of particle concentrations with beam intensities, but this Run 35 also did not have evidence of particle overcharge (Page 18250, 4th paragraph), on the other hand. From these data, it is difficult to conclude that IIN was actually involved in these nucleation events – it sounds rather that artifact particles were emitted or produced from unknown sources (likely form the wall) under uncontrolled experimental conditions (such as temperature fluctuations or by other species other than sulfuric acid).

2. While the authors claim that particle formation was seen at H2SO4 around e6 cm-3 or less – when beams were either on or off, in both cases (e.g., Table 1, Figures 4 and 5; page 18250, 1st paragraph). Note, the particle concentrations and nucleation rates reported here in both cases are very high at such low sulfuric acid conditions and the differences in particle concentrations between neutral and IIN processes are very small (e.g., 3,600 cm-3 vs 4,300 cm-3; Page 18250, 2nd paragraph). The authors then conclude that these results are consistent with Figure 2 in [Laaksonen et al., 2008] which summarized that field and laboratory studies show nucleation takes place in this H2SO4 range. [Laaksonen et al., 2008]'s conclusion is, however, that HSO5 radicals (which are not mentioned in the current manuscript) contribute to SO2 + OH reaction so homogeneous nucleation (without ions) to make sulfuric acid nucleation threshold very low. Also, Figure 2 of [Laaksonen et al., 2008] specifically showed that threshold of ion nucleation from the same SO2 + OH reaction by [Sorokin, 2007] is very high (>e9 cm-3) – on contrary to the current manuscript conclusion. Also, it is noted that even though using the same SO2 + OH reaction, other laboratory studies do not show this low threshold for H2SO4 nucleation [Benson et al., 2008; Benson, 2009; Young et al., 2008]. I also want to point out that formation of particles by IIN at 20-28 C temperatures with sulfuric acid around e6 cm-3 or less quite contradicts [Hanson

and Lovejoy, 2006]'s cluster thermodynamics measurements and [Lovejoy et al., 2004] IIN laboratory observations. So either neutral or IIN nucleation is not explained well from these experiments – and this brings to technical issues such as not-controlled experimental conditions and reproducibility (also see Technical issues: C).

3. Growth rates reported here in general are also much higher than those reported in most of atmospheric observations, except only one report (Iida et al., 2008) so the 1st paragraph in Section 3.2.2 is misleading. Also with regard to this high growth rates, the authors state that artifact organic compounds (at 20 pptv levels) emitted from the chamber wall during temperature fluctuations are responsible (Section 3.2.2. 2nd paragraph). However, this 20 pptv of additional organic compounds still cannot explain 2-37 nm per hour growth rates. In addition, most of organic compounds either do not participate in sulfuric acid nucleation at all ([Berndt et al., 2006] or some HC alkene compounds can even completely suppress particle formation by consuming OH radicals [Kiendler-Scharr et al., 2009; Wolf, 2009].

C. Technical issues. Most of experiments shown in this manuscript lack proper controlling or monitoring of experimental condition. Considering nucleation is a highly non-linear process, under these conditions, it will be difficult to correctly evaluate and interpret experimental results.

1. Temperature was controlled only for the second half of the experiments and for the first part, temperature varied from 20-28 C (Page 18254, Section 4.2, first paragraph), while IIN process is very sensitive to temperature [Lovejoy et al., 2004].

2. For the most of time (except the final 3 runs), SO2 background concentration in the chamber was between 0.1-0.2 ppb (similar to typical atmospheric conditions seen in rural, remote or less polluted environment), emitted from un-determined sources in the chamber. (Page 18252, last paragraph).

3. For the final days when SO2 was raised, however, no H2SO4 measurements were available. Considering IIN is highly sensitive to H2SO4 concentrations ([Lee et al.,

2003] SOM), without direct measurements of H2SO4, there will be large uncertainties in interpretation of the cosmic ray effect on particle formation via IIN. In addition, with regard to H2SO4 concentrations, the authors state that experiments were conducted typically at e6 cm-3 or less (Abstract), while they used a CIMS that can measure as low as 5e5 cm-3 (Section 2.3, 2nd paragraph).

4. Ammonia contamination. While ammonia is not mentioned in this article, it is likely that there are also quite significant ammonia left in the chamber (some of the parts consisted of stainless steel which can absorb ammonia most efficiently below 40 C), considering even less-sticky SO2 gasses (sub-ppbv) remained in the chamber for the most of the part of experimental runs. Note, deionized water also produces high concentrations of ammonia even at low relative humidity (sub-ppbv level).

5. Wall effects. Wall loss of aerosol precursors and vaporization of precursors and particles from the wall is tremendous for this kind of environmental chamber but it is not analyzed how sulfuric acid, ammonia or organic compounds are lost to the wall and how long these processes can be stabilized. Especially, sulfuric acid has high wall loss factors. It is also not clear whether experiments were conducted in a steady state condition, especially considering poor reproducibility (also see B1).

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