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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Impact of H_2SO_4/H_2O coating and ice crystal size on radiative properties of sub-visible cirrus" *by* P. Räisänen et al.

P. Räisänen et al.

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We thank the Referees for their constructive comments. Point-by-point responses to the referee comments are provided below.

REREFEE #1: . . . The originality of the study is that the authors focused on the impact of ice particles coated with an H_2SO_4 over-layer. The authors also revisit the impact of small ice particles. It has been already treated without the assumption that the ice crystals are spheres.. . .

REPLY: It is true that the impact of small ice crystals has been discussed by previous authors, but few have considered as small particle sizes as we consider here (down to micrometer size). In fact, we are not aware of any other studies demonstrating that even for very thin high clouds, the SW CRE (cloud radiative effect) at the top-of-the-atmosphere can exceed the LW CRE when the particles are small enough.

We agree that the use of spherical particles is somewhat unrealistic. To probe the sensitivity of the results to particle shape, we have added calculations for spheroidal particles (aspect ratio of 2) to Section 4. Although this may not provide a comprehensive evaluation of the impacts of non-sphericity, the similarity of the results to the spherical case suggests that the conclusions of Section 4 are largely independent of particle shape. If anything, it seems that the range of particle size with SW CRE dominating over LW CRE is slightly broader for non-spherical particles, which would make our case stronger.

Please see our reply to comment 2) for further discussion.

REFEREE #1: 1) . . . These laboratory experiments are referred in proceedings that is difficult to consult. This is an important point that should be developed in the present paper to convince the readers that the H_2SO_4/H_2O over-layer is realistic.

REPLY: Citing two conference papers in the Discussion paper may have given the impression that the laboratory work has only been documented in conference abstracts with no intent of peer-reviewed publication. This is, however, not the case. After the submission of the original manuscript to ACPD, a peer-reviewed paper (Letter) by A. Bogdan has been published in *Journal of Physical Chemistry*:

Bogdan, A.: Reversible formation of glassy water in slowly cooling diluted drops. J. Phys. Chem. B, 110, 12 205–12 206, 2006.

Although the emphasis of this paper is on a slightly different topic, it also documents the existence of the H_2SO_4/H_2O over-layer and the general setting of the laboratory

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measurements. In addition, the following paper, which focuses specifically on the H_2SO_4/H_2O over-layer, has been recently submitted:

Bogdan, A., Molina, M. J., Sassen, K. and Kulmala, M: Low-temperature cirrus clouds. J. Phys. Chem. A (submitted), 2006.

However, we only cite the Bogdan (J. Phys. Chem. B. 2006) paper and one of the abstracts (Bogdan et al. 2004) in the revised manuscript, owing to the fact that the last-mentioned paper has not been approved yet.

REFEREE #1: 2) The second part of the study deals with the impact of very small ice particles. The assumption that very small ice particles may persist in such clouds is not well established. Is it based on the hypotheses that sulphuric acid coating could reduce the growth of the ice particles as mentioned at the end of page 5238? This should be discussed more precisely.

REPLY: While the sulfuric acid coating could help to keep the crystals small for a longer time, perhaps enhancing the relevance of the cases with very small size, it was not our purpose to imply that it would keep the crystals small through the lifecycle of the subvisual cirrus (SVC) clouds. Rather, we tend to think that effective diameters d_e of a few microns probably occur in SVCs in the initial phase, while for mature SVC clouds, $d_e \sim 10$ μm is probably more typical, based on in situ observations. This is stated more explicitly in section 3 of the revised version of the paper. Note, however, that the available information about particle size in SVCs is somewhat controversial (p. 5233 in the Discussion paper), the satellite-based study of Wang et al. (1995) suggesting that very small particles are typical.

Apart from young SVCs, cases with very small particle size could also be relevant for contrails and some orographic clouds (as mentioned on p. 5240 in the Discussion

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paper). Even if/when cases with effective diameters of a few μm are an exception rather than the rule, we think that the analysis of the impact of particle size serves a useful purpose: it demonstrates very explicitly the strong dependence of LW CRE on particle size. This is not a strictly new scientific result in the sense that the underlying physics is old and “well-known to those who know it well”; however, it is our impression that the notion that LW CRE automatically dominates for high thin clouds is accepted by most people without further thought.

REFEREE #1: 3) Authors conclude that over-layer impact is small on the radiative fluxes at the top of the atmosphere. This conclusion is right if H_2SO_4/H_2O coating does not modify the life cycle of such clouds. There is however a direct potential impact on the microphysics of the clouds since the over-layer can slow down the growth of the crystals. There is also a potential impact on the radiative budget in the vicinity of the cloud. These two impacts can in return modify the dynamics of the cloud and its lifespan. The authors should show and discuss the vertical profiles of heating rates (or the vertical profiles of radiative fluxes) modified by the presence of H_2SO_4/H_2O coating. Then they will be able to discuss these potential impacts.

REPLY: We have checked the impact of the coating on the radiative heating rates. It seems too small (a warming effect of up to 0.025 K d^{-1} for Case 2) to influence the development of the cloud appreciably. This result is mentioned in the revised manuscript, but it hardly warrants an extra figure.

The two other referees also mention the impact of the over-layer on cloud microphysics through alteration of deposition/sublimation processes. This is a potentially important point, and we have somewhat expanded the discussion about it in the revised manuscript. However, at this point it remains as speculation: these ideas are mentioned, but assessing them quantitatively is clearly beyond the scope of the present paper, which is about the direct radiative impact of the over-layer.

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REFEREE #2: I object to the use of non-standard references . . . Not only are these publications difficult to find, but they are not very well-arbitrated. Given that the study in this manuscript hinges to a large extent on the validity of the lab results that are in these non-standard references, I think that much more needs to be presented of these laboratory studies than in the current manuscript. The laboratory studies are actually more instructive than the radiative effects since it seems that probably only a fraction of thin cirrus actually have the coating. . . . To me, what is much more interesting is the microphysical process by which a droplet freezes and is subsequently coated with the sulfuric acid. As eluded to by the authors, this might have the effect of suppressing the growth of the particles, in a similar way that nitric acid has been hypothesized as a coating that suppresses growth or evaporation.

REPLY: As regards the documentation of the laboratory work, see our response to comment 1) by Referee #1. The possibility that only a fraction of SVCs might actually consist of coated crystals is mentioned explicitly in the revised manuscript. (We expect that it is mainly small young ice particles that have a noticeable over-layer.) At any rate, we believe that a study focusing on the radiative effects is warranted, notwithstanding the fact that they actually prove to be small. The speculation regarding the impact of coating on the growth of the particles is expanded somewhat in the revised manuscript.

REFEREE #2: The authors fail to acknowledge work that has been done with calculating the radiative properties of small crystals; in particular there is the study by Arnott et al., 1994, . . .

REPLY: Arnott et al. (1994) is a relevant reference and is cited in the revised manuscript. However, in our view their conclusions differ from ours. While their analysis indicates that ice crystal absorption efficiency decreases with decreasing particle size, they emphasize that even the "small" particles (with maximum dimensions of a few tens of micrometers) are important for longwave radiative transfer. Our analysis extends to even smaller sizes, down to micrometer size, and shows that for such small particles, the LW effects become small in comparison to the SW effects.

REFEREE #2: If these results are to be compared with observations, the temperatures and humidity with respect to ice should be specified.

REPLY: Cloud mid-point temperatures (196 K and 232 K for clouds at 16.5–17 km and 10.5–11 km, respectively) are mentioned in the revised manuscript. As stated already in the Discussion paper (p. 5236, line 25), saturation conditions with respect to ice (i.e., relative humidity of 100%) were assumed in the cloud layers.

REFEREE #3: I think the authors do not discuss how the coating might have the biggest impact on the CRE . . . if the coating impacts the lifetime of the sub-visible cirrus by altering the rates at which sublimation or deposition occurred. . . .

REPLY: This is a potentially important point, and, as suggested by the Referee, we have expanded the discussion in the revised manuscript. However, at this stage, we can only mention these speculative ideas, not address them properly.

REFEREE #3: Many previous observations in sub-visible cirrus show pristine particle shapes or quasi-spherical shapes, not spheres . . . . Hence, most studies that have examined the cloud radiative effects of sub-visible cirrus have used single-scattering properties of non-spherical ice crystals rather than the spherical crystals used in this paper . . . this limitation should be clearly explained (in the abstract in addition to the main body of the text). I would also recommend replacing Figure 4 with a Table similar to Table 1 to examine how the coating affects the CRE when a constant optical depth is assumed . . . Given that sub-visible cirrus almost certainly does not consist of spherical ice particles, it is really a comparison between simulations with and without coatings that is unique to this paper. Prior papers have done better computations with more realistic shapes on cloud radiative effects for clouds consisting of pure ice.

REPLY: For the most part, we agree with this comment. The use of spherical particles is mentioned in the abstract in the revised manuscript. Similarly, the fact that non-spherical (i.e., more realistic) particle shapes have been used by other authors (in particular, McFarquhar et al. 2000) to compute the radiative properties of SVCs consisting of pure ice is also acknowledged in the revised text. Moreover, we have added calculations for non-spherical particles (spheroids) for the uncoated case in Section 4. The reason for us using spherical particles in the coated cases is simple: we are not aware of any computer code that would provide single-scattering properties of coated non-spherical particles, for the range of size parameters and refractive indexes (in particular, non-zero imaginary part of the refractive index for both particle core and coating) considered here. This is stated explicitly in the revised manuscript.

We do not, however, agree with the suggestion of replacing Fig. 4 with another table about the impact of coating. Note that Fig. 4 is related to the impact of particle size for uncoated particles. As regards the use of fixed particle number vs. optical depth, see below.

REFEREE #3: The authors state that the over-layer is thickest for young freshly formed ice particles and becomes thinner as they grow due to water vapor deposition. Given that sub-visible cirrus are nearly ubiquitous in the Tropics and persist so long, would the impact therefore expected to be reduced? I would recommend that the authors add some comments on the potential origin of sub-visible cirrus (perhaps Boehm and

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Verlinde paper) to expand upon this point a little.

REPLY: In an *absolute* sense, it appears that the impact of coating does not change very much when the particle size increases with time (e.g., the impact on total CRE at the TOA for Case 2 remains close to 0.02 W m^{-2} for $d_{\rm tot}$ = 4–10 μm in Table 1). Of course, most people would consider that a small impact. In a *relative* sense, the impact of coating decreases with increasing particle size, and we agree it is most probably small for mature SVC clouds. This was already implied in the Discussion paper (p. 5238, lines 19–22), but the point is made more explicitly in the revised manuscript.

We now also cite the Boehm and Verlinde (2000) paper in the Introduction to mention the link of SVC clouds to tropical waves.

REFEREE #3: Page 5233, line 19: If the effective diameter of sub-visible cirrus is 2 microns, is this still cirrus? It would seem that you would almost be looking at aerosols in this case.

REPLY: What Wang et al. (1995) regard as subvisual cirrus clouds appear as a clearly distinct population from aerosols in their Plate 2. The values of effective diameter (or radius) are derived indirectly, based on the ratio of extinction coefficient at 0.525 μm and 1.02 μm (Fig. 11 of Wang et al.). The results suggest that effective radius (diameter) below 1 μm (2μm) is common particularly for the thinnest clouds, with some tendency toward increasing particle size for the thicker SVCs (optical depth $\sim$0.01–0.02).

Although the results of Wang et al. (1995) deviate surprisingly much from in-situ measurements, we do not find obvious flaws in the analysis performed by these authors. Therefore, we consider it best to keep this part of the paper unchanged: the different measurement values are reported at face value, without taking an explicit

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position on which values should be trusted.

REFEREE #3: Page 5234, line 13: Can you specify pressure, temperatures and dew-points that you are referring to when you say conditions resembling those found in the uppermost troposphere?

REPLY: This comment exposes a misleading wording in the Discussion paper. What we described as “conditions resembling those in the uppermost troposphere” refers to temperature (190–210 K) and size and composition (i.e., concentration) of the H_2SO_4 droplets. This is made clear in the revised manuscript. However, we cannot specify pressure or dew-point temperature. They are not relevant for a differential scanning calorimeter (it is not a “cloud chamber” like instrument).

REFEREE #3: Page 5236, last line: Have you done any sensitivity studies to see how your results differ if saturated conditions are not assumed in the cloud layer?

REPLY3: We repeated the calculations using McClatchey et al. (1971) standard tropical humidity profiles. The differences to the results reported in the manuscript were negligible. This is not surprising given that especially for a cloud height of 16.5–17 km, the water vapour content is very small due to the cold temperature. For brevity, this issue is not discussed in the revised manuscript.

REFEREE #3: Page 5237, line 10: In these sensitivity studies with varying diameters, I fear that almost all of the differences you will see will be due to varying the optical depth of the cirrus. Why not keep the optical depth fixed and adjust the effective diameter?

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REPLY: Differences in optical depth (or in the spectrally varying extinction efficiency Q_{ext}) account for roughly half of the shortwave CRE differences (with substantial case-to-case variation) and most of the longwave CRE differences between clouds consisting of coated and uncoated ice crystals. This is mentioned in the revised manuscript. However, the idea of adjusting the cloud physical properties (either effective diameter or particle concentration) so that the optical depth is the same for "coated" and "uncoated" SVC clouds is problematic. The optical depth is spectrally varying, which means that it can never be the same for the coated and uncoated cases for all spectral bands. We tested fixing the optical depth for the visible spectral band. This reduced the shortwave differences for Case 1 up to 30%, but for Case 2, it sometimes enhanced the differences! The explanation for these surprisingly small changes is that the difference in Q_{ext} between coated and uncoated particles is smaller than average in the visible spectral band, and in some cases, anomalously, Q_{ext} is smaller for coated than for uncoated particles.

Thus, while fixing optical depth could perhaps be motivated on the grounds that optical depth is probably the most readily retrievable parameter for SVC clouds, we find it physically simpler and less arbitrary to assume the same particle number concentration and total diameter for the coated and uncoated cases.

REFEREE #3: Page 5238, line 11: Note also that the cases with smaller diameters have smaller optical depths. Typically, whenever you have smaller optical depths, and adjustments will cause a larger relative change in the cloud optical properties. If you keep optical depth constant between the simulations, would you still see the largest change in CRE for the smallest particle size?

REPLY: The "saturation" (smaller changes for larger optical depths) suggested by the Referee is not an issue for the cases considered in this manuscript because the optical depth is very small in all cases. As stated already in the Discussion paper (p. 5237,

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lines 13–15), for such optically thin clouds, the CRE scales, to a very good approximation, linearly with optical depth (or particle number concentration).

To verify this, we performed tests in which the ice crystal number concentration was chosen separately for each crystal diameter considered, so that the visible optical depth was fixed at 0.01 for the case with uncoated crystals. The relative changes in CRE caused by the coating were virtually identical to those reported in Table 1. However, the absolute changes in CRE related to the coating *increased* strongly with decreasing particle size (e.g., for Case 2 and d_{tot}=2.0 μm, the SW (LW) effect was $-$0.08 W m^{-2} (0.17 W m^{-2})). We do not consider these results very realistic because for a fixed optical depth, ice crystal number concentration and the mass of H_2SO_4 incorporated in the cloud become very large for the smallest sizes. Although fixing the particle concentration is also an idealization, we consider it more realistic.

REFEREE #3: Page 5239, bottom: Can you comment or speculate on any differences you would have in the Qe plots if you were using non-spherical rather than spherical particles?

REPLY: In the revised manuscript, we represent and discuss computational results for spheroidal ice particles (both the Q_{ext} plots and the radiative transfer tests), in addition to spheres. Please see our response to Referee #1.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 5231, 2006.