SPIN modification for low temperature experiments.

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Summary

This study introduces a new design that allows the Spectrometer for Ice Nuclei, SPIN, to investigate ice nucleation at colder temperatures. The demonstrated technique involves using one refrigerant loop to cool both walls of the chamber. The authors demonstrate that their simple design modification extends the temperature range by approximately 20 degrees below the range traditionally used by the SPIN community. The performance of the new design is evaluated using ammonium sulfate ($(NH_4)_2SO_4$) and silver iodide (AgI).

General Comments

The paper summarizes a design modification that will be of significant interest to other SPIN users and most likely other continuous flow diffusion chamber (CFDC) designs as well. Their technique has several demonstrable benefits. The authors note that the SPIN can now operate within the full set of conditions relevant to cirrus formation in the upper troposphere. One additional benefit not explicitly highlighted by the authors is the reduced number of compressors. Previous attempts to operate CFDCs at cold temperatures have resulted in the damage of compressors, and reducing the number of compressors used in the design will likely reduce instrument down-time due to repairs.

This paper is therefore well-suited for publication in AMT. Below, I provide a few questions and comments to strengthen the paper and clarify the interpretation of the SPIN results. The authors will note that most of these are minor points. I therefore recommend the paper be accepted for publications after the authors have adequately addressed or responded to them.

Major Comments

1. My only major comment concerns the interpretation of the apparent early-onset of homogeneous freezing of ($(NH_4)_2SO_4$). The authors note that the ($(NH_4)_2SO_4$) solution droplets appear to nucleate at a lamina RH lower than that expected for homogeneous freezing ((Koop et al., 2000)). The authors claim a discrepancy between their data and the Koop parameterization. However, I would venture a guess that their data actually presents no discrepancy if the uncertainty in lamina RH is taken into account.
    a. I believe Fig. 4 reports the average lamina conditions. However, at high RH and cold temperatures, CFDCs (and I would guess SPIN) generally show a few % uncertainty in the lamina RH. This uncertainty is caused by variability in the wall temperatures. Colder regions of the wall – for example, where refrigerant is injected – can cause certain areas of the lamina to experience a higher RH than the average. See e.g. Kulkarni and Kok, 2012, for a simple method and pre-written code to calculate the variability in lamina RH for a CFDC with SPIN's geometry.
    b. If this is lamina range is taken into account, does the onset of ($(NH_4)_2SO_4$) nucleation more closely align with the Koop homogeneous freezing parameterization?

Minor Comments

Abstract

2. Page 1 Lines 4-5: "*The modification extends the measurement range of SPIN by more than 20 K to the temperature regime relevant for ice formation in cirrus clouds*." Can the authors specify in the abstract the lower temperature range now achievable with their design modification?

Introduction

3. Page 1 Lines 13-15: "*Tropospheric ice nucleation at low temperatures (T < 236 K), typical for cirrus clouds, proceeds at water sub-saturated conditions by homogeneous nucleation of aqueous aerosol or heterogeneous nucleation from the vapour phase.*" The authors should briefly mention the possibility that heterogeneous nucleation below water supersaturation could be due to the pore-condensation freezing mechanism. E.g. (David et al., 2019; Marcolli, 2014)

Operating Principles

4. Page 2 Lines 17-18: "*For an explicit derivation of the linear temperature and vapour pressure field in a CFDC we refer to Rogers (1988); Lüönd (2009).*" I recommend also citing here Kulkarni and Kok, 2012 – it specifically discusses calcualtion of lamina conditions for the parallel plate (SPIN) design.
5. Page 2 Line 21: "…*a lamellar sample, which is confined by a sheath flow to a narrow position between the ice covered wall plates*…" The authors should briefly note here recent work that demonstrates aerosol samples are *not* constrained by sheath flows but rather spread outside the lamina. See e.g. DeMott et al., 2015; Garimella et al., 2017. This fact should not much change the author's results or interpretation, but it is important for the field of CFDC users to start to acknowledge.

Modified Cooling System

6. Page 3 Line 31: "*To reach lower temperatures, the SPIN cooling system has been modified by reconnecting the cold wall, cascade compressor system to deliver R116 refrigerant to both wall plates.*" The authors may know that R116 is a HFC whose use is being phased out in the European Union as per the Kigali Amendment to the Montreal Protocol. At this time, do the authors have knowledge of any non-HFC refrigerant (e.g. hydrofluoroolefin, CO_2) that might be an acceptable substitute in the future? The authors might note that if HFC refrigerants are banned, a new overall to the SPIN or other CFDC instruments' refrigeration loops may be needed anyways.
7. Page 3 Lines 4-6: "*A consequence of using only one instead of two compressors to deliver the refrigerant for both walls, is a reduction in the achievable cooling rate from approximately 2 K min^{-1} to 1 K min^{-1} above 233 K and decreasing to < 0.5 Kmin−1 towards the lowest temperatures.*" Please comment on the circumstances when both walls need to be cooled concurrently (i.e. during cooling down to start experiment).
8. Page 3 Lines 11-13: "*The range of the original SPIN setup is calculated with the cold wall varying from 273.15 K-194.95 K and the warm wall between 273.15 K-226.65 K (boiling point of R404A).*" The authors should note how this range compares to the coldest temperatures previously achieved for SPIN experiments. The coldest I can find published are ~-58 ˚C (Wolf et al., 2019) and ~-56 ˚C (Nichman et al., 2019).
9. Page 4 Lines 7-8: "*Conditions for ice crystals to grow to a diameter of 0.5 µm, 1 µm, 2 µm and 4 µm in ∼ 10 s residence time in the ice super-saturated section of SPIN are calculated according to Rogers and Yau (1989)*…" Can the authors please include the ice crystal growth equation in the manuscript? This will help readers understand the important point they are raising about the kinetic-limitations of the new instrument setup.

Homogeneous freezing of freezing of Ammonium sulfate solution

10. Should "*Ammonium*" be capitalized in this section title?
11. In this section title you say "*ammonium sulfate solution*," but you introduced dried particles into the SPIN. The $(NH_4)_2SO_4)$ particles obviously deliquesced; please briefly report the deliquescence RH in the text, or show it in Figure 4.
12. Page 6 Lines 13-15: "*Possible reasons for the discrepancy between the measurements in this study and the Koop-parametrisation are time dependent effects, i.e. aqueous aerosol do not reach equilibrium before freezing in SPIN.*" See my Major Comment (#1) above. Could the apparent early onset of homogeneous freezing be due to heterogeneities in wall temperature, leading some sections of the aerosol lamina to experience homogeneous freezing conditions while the mean conditions are below homogeneous freezing? Tt would help to report the standard deviation of lamina supersaturation here or show it in Figure 4.

Discussion

Page 8 Lines 3-5: "*While the data are generally consistent, the measurements of this study show systematic discrepancies in T-RH dependance both from the predicted heterogeneous ice nucleation of CNT (Fletcher, 1962) and from the widely used parametrisation of homogeneous ice nucleation of solution droplets by Koop et al. (2000). Apart from differences in the method of particle generation, size segregation and detection, it is unclear why partly systematically deviating T-RH dependencies were observed in similar experiments.*" Again, see my comments above about whether uncertainty/variability in the average lamina RH could be responsible for discrepancies in the onset of homogeneous freezing.

Figure 1

Caption: The citation here is Murphy and "Koop," not "*Kopp*." Koop's name is also misspelled in the references (Page 11 Line 15).

Figures 4-5

The coverage of T and RH space for these experiments is impressive!

References

David, R. O., Marcolli, C., Fahrni, J., Qiu, Y., Perez Sirkin, Y. A., Molinero, V., Mahrt, F., Brühwiler, D., Lohmann, U. and Kanji, Z. A.: Pore condensation and freezing is responsible for ice formation below water saturation for porous particles, Proc. Natl. Acad. Sci., 116(17), 8184–8189, doi:10.1073/pnas.1813647116, 2019.

DeMott, P. J., Prenni, A. J., McMeeking, G. R., Sullivan, R. C., Petters, M. D., Tobo, Y., Niemand, M., Möhler, O., Snider, J. R., Wang, Z. and Kreidenweis, S. M.: Integrating laboratory and field data to quantify the immersion freezing ice nucleation activity of mineral dust particles, , 15(1), 393–409, doi:10.5194/acp-15-393-2015, 2015.

Garimella, S., Rothenberg, D. A. D. A., Wolf, M. J. M. J., David, R. O. R. O., Kanji, Z. A. Z. A., Wang, C., Rösch, M. and Cziczo, D. J. D. J.: Uncertainty in counting ice nucleating particles with continuous flow diffusion chambers, Atmos. Chem. Phys., 17(17), 10855–10864, doi:10.5194/acp-17-10855-2017, 2017.

Koop, T., Luo, B., Tsias, A. and Peter, T.: Water activity as the determinant for homogeneous ice nucleation in aqueoussolutions, Nature, 406(6796), 611–614, doi:10.1038/35020537, 2000.

Kulkarni, G. and Kok, G.: Mobile Ice Nucleus Spectrometer, Pacific Northwest Natl. Lab. Richland, WA, 2012.

Marcolli, C.: Deposition nucleation viewed as homogeneous or immersion freezing in pores and cavities, Atmos. Chem. Phys., 14(4), 2071–2104, doi:10.5194/acp-14-2071-2014, 2014.

Nichman, L., Wolf, M., Davidovits, P., Onasch, T. B. T. B., Zhang, Y., Worsnop, D. R. D. R., Bhandari, J., Mazzoleni, C. and Cziczo, D. J. D. J.: Laboratory study of the heterogeneous ice nucleation on black-carbon-containing aerosol, Atmos. Chem. Phys., 19(19), 12175–12194, doi:10.5194/acp-19-12175-2019, 2019.

Wolf, M. J., Coe, A., Dove, L. A., Zawadowicz, M. A., Dooley, K., Biller, S. J., Zhang, Y., Chisholm, S. W. and Cziczo, D. J.: Investigating the Heterogeneous Ice Nucleation of Sea Spray Aerosols Using Prochlorococcus as a Model Source of Marine Organic Matter, Environ. Sci. Technol., 53(3), doi:10.1021/acs.est.8b05150, 2019.