Comment on “On the discrepancy of HCl processing in the dark polar vortices”

Alexander D. James

School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

The authors present a useful summary, and thought-provoking new ideas, relating to a relatively well-known problem in stratospheric chemistry. This is likely to provoke future research and certainly merits publication following some revision.

The reference to the “dark polar vortex” in the title seems misleading given that the authors show an apparent correlation of the HCl discrepancy to hours of sunlight.

The reviews presented in RC1 and RC2 detail a number of additional processes which should be discussed in the text. In particular the paper lacks a discussion of the possible role of solid PSC. The loss of HCl is known to proceed rather differently on nitric acid hydrate (NAX) or ice surfaces compared to liquid PSCs (Chu et al., 1993). Hoyle et al. (2013) recently showed a good agreement between CLAMS and CALIPSO data on PSC type when a heterogeneous nucleation scheme was implemented, leading to a sharp onset in NAX nucleation below 195 K. In James et al. (2018) we then showed, based a study in our laboratory, that such heterogeneous nucleation can be caused by meteoric smoke or fragmented meteoroids, and can occur at temperatures as high as 197 K for typical stratospheric abundances of HNO_3, H_2SO_4 and H_2O.

In figure 7 of the current text, the discrepancy is shown not to relate to temperatures below 194 K. I would like to make several points about this approach. Firstly, there is not only a lack of correlation between the model and observations, but in fact the general trend of HCl concentrations is rather different. The model shows a gradual increase in HCl at lower temperatures, whereas the observations show a significant increase below 186 K. This temperature is consistent with the formation of water ice PSC. It would also be informative for the reader if data were included to higher temperatures, to include the formation of possible NAX between 197 and 194 K.

In producing Figure 8 (setting to one side the concerns raised by the reviewers), a cut-off temperature of 195 K is used. This is reasonable if the growth of liquid PSC through deposition of H_2O is the determining factor; however, it is known that significant nucleation of NAX can occur above 195 K (Peter and Grooß, 2012). A more appropriate approach might be to examine the difference between the nucleation scheme used in each model (presumably the same as the Hoyle et al. (2013), Carslaw et al. (2002) and Brakebusch et al. (2013) schemes for CLAMs, SLIMCAT and WACCM respectively) and the more recent literature. In James et al. (2018) we showed that different parameterisations of nucleation give rather different results in terms of particle concentrations and therefore surface area.

A simple and informative experiment would be to correlate the HCl discrepancy to the difference between the onset of nucleation (e.g. time spent between 197 and 195 K for models using a constant volume nucleation rate, see Figure 6 in James et al. (2018)). Since MIPAS data are used extensively another obvious approach would be to relate the HCl (or $ClONO_2$) discrepancy to the data on PSC type which MIPAS provides.

It is not possible given the present text to assess whether the presence of solid PSC could explain the discrepancies; however, with the inclusion of the references mentioned above and the subsequent suggestions (see above), this could prove an important process contributing to the HCl discrepancy.

Brakebusch, M., Randall, C. E., Kinnison, D. E., Tilmes, S., Santee, M. L., and Manney, G. L.: Evaluation of Whole Atmosphere Community Climate Model simulations of ozone during Arctic winter 2004–2005, J. Geophy. Res.: Atmos., 118, 2673-2688, 10.1002/jgrd.50226, 2013.

Carslaw, K. S., Kettleborough, J. A., Northway, M. J., Davies, S., Gao, R.-S., Fahey, D. W., G., B. D., Chipperfield, M. P., and Kleinböhl, A.: A vortex-scale simulation of the growth and sedimentation of large nitric acid hydrate particles, J. Geophys. Res.: Atmos., 107, SOL 43-41-SOL 43-16, doi:10.1029/2001JD000467, 2002.

Chu, L. T., Leu, M. T., and Keyser, L. F.: Uptake of hydrogen chloride in water ice and nitric acid ice films, J. Phys. Chem., 97, 7779-7785, 1993.

Hoyle, C. R., Engel, I., Luo, B. P., Pitts, M. C., Poole, L. R., Grooß, J. U., and Peter, T.: Heterogeneous formation of polar stratospheric clouds – Part 1: Nucleation of Nitric Acid Trihydrate (NAT), Atmos. Chem. Phys., 13, 9577-9595, 2013.

James, A. D., Brooke, J. S. A., Mangan, T. P., Whale, T. F., Plane, J. M. C., and Murray, B. J.: Nucleation of nitric acid hydrates in polar stratospheric clouds by meteoric material, Atmos. Chem. Phys., 18, 4519-4531, 10.5194/acp-18-4519-2018, 2018.

Peter, T., and Grooß, J. U.: Chapter 4: Polar stratospheric clouds and sulfate aerosol particles: Microphysics, denitrification and heterogeneous chemistry, in: Stratospheric Ozone Depletion and Climate Change, The Royal Society of Chemistry, 108-144, 2012.