

Interactive comment on “Trapping of HCl and oxidized, organic trace-gases in growing ice at temperatures relevant for cirrus clouds” by Matthias Kippenberger et al.

Anonymous Referee #1

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The authors present measurements of the uptake flux of HCl vapor (and other gases) to growing ice surfaces. The experiments were conducted under cirrus cloud conditions of temperature and ice particle growth rate, and the findings are that HCl may become buried by growing particles potentially immobilizing it from heterogeneous activation reactions. The uptake appears to be due to the need to hydrate dissociated ions, given that non-dissociating gases did not exhibit enhanced uptake under growing conditions.

Experiments are conducted in a new cylindrical dual-chamber through which a mixture of H₂O and HCl in He is flowing in a warm section. At the bottom of the chamber is ice that has formed by freezing liquid water. A glass plate separating the warm and ice-

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filled sections of the chamber is removed, allowing for exposure of the gases to the ice surface. The gas-phase water partial pressure is sufficient that water condenses, forming ice at a known rate based on the supersaturation. A mass spectrometer monitors the gas-phase composition. The data appear to be of very high quality, for example of uptake flux as a function of growth rate (Fig 3 and 4). The execution of the experiments and the interpretation of the data, done in the context of a trapping model developed by B. Karcher, are clearly described. There is good qualitative agreement between the model and the measurements. This is high quality work. I recommend publication with very few comments:

It is not clear to me how the gas-phase diffusion limitation for HCl uptake to the ice is accounted for. In particular, in a Knudsen Cell, which resembles the current cell in some respects, the diffusion constraint is minor because the pressure is kept quite low (about 10^{-3} mbar). But in this experiment the pressure is quite high, about a mbar. Shouldn't there be a large mass transfer limitation for getting the HCl to the ice surface under such conditions, when the intrinsic HCl uptake coefficient/mass accommodation coefficient to the ice is large? The authors say that such effects kick in at very high gamma values (top of page 6) and that they restrict their expts to gammas smaller than 0.018, but I would have guessed the effect is still important at much lower gammas. How was this value of 0.018 chosen? A full discussion of this mass transfer effect is warranted given how central it is to the measurements, and that this is a new experimental approach. On this topic, why is the chamber designed to operate at 1 mbar total pressure? Wouldn't it have been better to run at lower pressure to lessen the diffusion limitation?

I will be up-front and say that I have not worked through the Karcher trapping model in depth. But my impression is that it is based on a Langmuir adsorption isotherm, as a starting point. If so, to what degree does dissolution in the ice crystals themselves play a role in the uptake, both in the model and in the experimental data? Are thermodynamically stable solutions forming (see work by Domine), or are metastable

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mixtures forming? If metastable, how long would it take for the enhanced "dissolved" HCl to diffuse out, under non-growth conditions? Also, is there uptake along the grain boundaries that may affect the (model or experimental) results?

How pure is the water that is condensing? Is there any potential for trace ammonia, for example, to be interacting with the sorbed HCl, so enhancing the uptake?

Not much experimental work has been done on uptake of gases to growing ice in the last few years, and the quality of the earlier studies is not nearly as high as in this work. Nevertheless, I suggest that a brief summary of past studies, upon which this work is somewhat based, could be presented in the Introduction.

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