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Atmospheric
Chemistry
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Discussions

Interactive comment on "Influence of the ice growth rate on the incorporation of gaseous HCl" *by* F. Domine and C. Rauzy

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Response to the comments of referee 1

To begin with, we would like to extend our grateful thanks to referee 1 for taking the time to perform a long, thorough and very constructive review, that we found to be very helpful to write an improved version of our paper. Before we explain in detail the changes that we have made following his/her comments, we would like to remind the main objectives of our paper, as these condition the way it is written. * First of all, we present here a limited amount of data, with experiments performed at one temperature and with one value of PHCl, and the main objective is to test whether the ice growth rate in the presence of dopants has any influence on the final concentration of the dopant in the ice. * Given the limited amount of data, it appears to us that only a short paper is warranted. Detailed conclusions and extended quantitative treatment on this topic are indeed highly desirable, as stressed by both referees, but we feel that our limited data only allow us to go so far. More experiments would indeed be nice, but as in many cases, this project was funded for a given duration, it is now terminated, and it cannot be pursued at this time. * In conclusion, our goal was to write a short paper that demonstrates that ice growth rate does impact dopant uptake, to derive some quantitative aspects such as the height of the growth step in ice, to point out remaining unknowns that deserve further work, and in particular to stress the need to understand the surface structure of ice to predict quantitatively its dopant uptake. The limitations of our objectives have been more clearly stated in the last pargraph of the introduction. With these limitations in mind, we have made the following changes, in response to referee 1.

Referee's comment: A better description of experimental conditions is needed. Our response: We have mentioned that the pressure in our system was around 960 mbar, and have given the temperature stability (0.01°C). We have reported our limited observations on the ice morphology. The temperature of the inlet ball could not be measured, but we deduce that it was $>$-8.4°C, as ice never did grow on it. Regarding the adsorption of HCl on the ball, we did not measure it but the system was conditioned prior to the start of experiments, so that the surface coverage of the ball was in steady state. Whatever HCl was on the ball was never sampled, so it did not interfere with the analysis of the ice. We also mention that given its geometry, our reactor (the crystallization tube) had necessarily a turbulent flow.

Referee's comment: A more accurate definition of a, the accommodation coefficient, is needed, and a more thorough discussion of this variable is also needed. Our response: We thank the referee for the details given. We do agree that our treatment and discussion of a was incomplete and may even have been in a way misleading. It is clear that the variable of interest to our system is probably not the mass accommodation coefficient, a, as defined by Ammann et al. (2003) and by Hanson (1997). In our system, many processes contribute to uptake, as suggested by the referee. These include surface processes, but also gas phase diffusion limitations, desorption of HCl,

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volume uptake, etc. Hence, the appropriate parameter would rather be g, the uptake coefficient. To address this point properly, we first have changed the formulation of the subject problem of the paper in the introduction and used g instead of a in equation (1), and we have also mentioned that this would have been more appropriate to use by Domine and Thibert (1996). In the “Results and discussion” section, we make a comparison of our g values with a values measured by others, to conclude, in line with the referee’s recommendation, that what we are measuring is indeed an uptake coefficient that results from several physical processes, and not just surface processes. Following the recommendation of referee 1, we also pursue some ideas to determine which process other than surface processes may be rate limiting in the uptake of HCl. One idea put forward by the referee is that gas phase transport may be the limiting step. We study that avenue, but conclude that since diffusion limitations did not affect H2O, as all the excess H2O condensed as ice, it most likely did not affect HCl either, as PHCl/PH2O is always around 10-5, while XHCl is about 10-8, meaning that near surface depletion due to condensation would affect HCl less than H2O. We then conclude that either HCl desorbs, or that surface processes are not what they are expected to be. This last aspect is addressed subsequently, in response to the referee’s next comment.

Referee’s comment: The discussion on the dependence of a on surface state is speculation. Our response: Despite our respect for the referee and his very useful comments, we feel that we have to disagree with him on this point. Of course, our initial writing did leave room for criticism, and we have now modified our text to address the referee’s legitimate concerns. It is now well known that the state of the surface of a solid has an extremely strong impact on the adsorption energy and mechanism, and hence on the mass accommodation coefficient. A well know example is the adsorption of H2O on MgO. On MgO surfaces cleaved under vacuum, H2O physisorbs reversibly with a low energy, while on powdered MgO, with a lot of surface defects such as step edges, H2O chemisorbs irreversibly with ionic dissociation. This of course results in different a values. Molecular dynamics and quantum calculations have confirmed experimental results. This example, and countless others, are detailed in the recent 300+ pages

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review of Henderson (2002). We then refer the readers and the referee to this paper and references therein, so they may convince themselves that surface state and detect density simply cannot be ignored in any discussion of a. We could, as suggested by the referee, cite studies other that those of Libbrecht to discuss aH2O, but again, this is intended to be a short paper, not a review, and Libbrecht's recent data serve our point sufficiently. In any case, this part of the discussion has been significantly rewritten to make it clearer and to refer to those many studies, and we hope that the referee will find the new version more convincing.

Referee's comment: Trend of aHCl and aH2O with growth rate, and the role of transport as a limiting step. Our response: Regarding the role of transport, we have mentioned that we had a turbulent reactor at essentially atmospheric pressure, and since we observed that all excess water condensed as ice, we deduced that transport in the gas phase was not a rate limiting step. We hope that this extra information will satisfy and convince the referee (who mentioned that his "objection may become obsolete, once the experiment is described in better detail"). Regarding the trends of aHCl and aH2O with growth rate, the recent work of Libbrecht clearly indicates that aH2O does increase with growth rate. It is true that the growth rate of Libbrecht were probably lower than those observed in our supersaturation of 82.5%, but at least qualitatively, our statement holds. From this argument, and all of our previous arguments about surface state, we speculate that aHCl may also vary with growth rate. There is no reason why the variations of aHCl and aH2O with growth rate would be equal, and we suggest here that if aHCl were to increase slower than aH2O with growth rate, or even decrease, this would explain the low observed gHCl/gH2O ratio. In the revised version, this is mentioned twice with the word "possible", clearly implying that there is some speculation attached to this. The referee again objects to our citing only Libbrecht, but again other (previous) studies do not bring any crucial new elements. Since this is intended to be a short paper, we also want to keep the reference list to a minimum.

Minor comments have been taken care of. We have nevertheless not added the reference of Hynes et al. (2001) because we feel that they do not add any novel data. Again, we do not want to review all the relevant work, but rather select those studies that are necessary for our discussions. This again, is to keep the paper length down.

In summary, the comments by referee 1 were most helpful is writing what we hope to be a significantly improved version of our short paper. In particular, we have clarified our experimental setup, and we hope we have removed the confusion between a and g, that indeed was an important point. We did not agree with the referee regarding the impact of surface conditions on accommodation coefficient, but have attempted to provide the reader and the referee with references that should be convincing. Again, we believe that the main interest of this short paper is to demonstrate that the growth rate impacts dopant uptake, to propose a value of the growth step height under our conditions, and to suggest that these effects may help explain the chemical composition of atmospheric ice crystal and of snow.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 4719, 2004.