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Comment

Interactive comment on “H₂O and HCl trace gas kinetics on crystalline and amorphous HCl hydrates in the range 170 to 205 K: the HCl/H₂O phase diagram revisited” by R. Iannarelli and M. J. Rossi

Anonymous Referee #2

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This manuscript describes a detailed laboratory investigation of HCl-ice interactions, specifically hydrate formation, under conditions relevant to (or close to) polar stratospheric conditions. The data presented are novel and valuable to our understanding of trace gas-ice interactions and stratospheric chemistry. However, the presentation needs clarification in order to increase the potential impact of this work and make it suitable for publication in ACP.

There was some fundamental confusion on the part of this reviewer regarding what

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the authors termed “amorphous HCl/H₂O,” that probably could have been remedied with more description in the introduction of the manuscript. This seems to be a new proposed phase of the HCl/H₂O system, and it is central to the authors’ interpretation of their data. I think that this idea was initiated in a recent paper from this group (Chiesa and Rossi, 2013), and later in the discussion section of this paper they provide FTIR spectra characterizing this new phase. But, to be kind to the reader and add the proper emphasis to this new concept, more explanation is needed, starting in the introduction of the paper, of what is this new phase and how is it related to previous representations of the HCl-ice phase diagram.

Specific comments:

p. 30768, Lines 16-18: The connection between the amorphous HCl/H₂O mixtures described by the authors and the work of McNeill et al. (2006, 2007) isn’t clear. I believe that the authors may be trying to make an interesting point but it needs much more explanation (see my related comment above). McNeill et al. (2007) studied HCl-ice interactions within the HCl-ice coexistence envelope, as well as HCl hexahydrate formation. They found that, even at temperatures and HCl partial pressures within the region of the phase diagram where HCl hexahydrate is believed to be the stable phase, with rough, vapor deposited ice samples they didn’t see sufficient HCl uptake for the formation of HCl hexahydrate. The uptake was more consistent with the (sub)monolayer HCl uptake they observed within the HCl/ice coexistence envelope for non-disordered conditions. They did see enhanced HCl uptake consistent with HCl hexahydrate formation at the expected conditions for smooth ice samples. They interpreted this to mean that there is a kinetic barrier to formation of the crystalline HCl hexahydrate phase, and the roughness of the vapor-deposited ice inhibited growth of that crystalline phase. Are the authors suggesting that the state observed by McNeill et al. on vapor deposited ice is an amorphous solid? (This is really just a guess since it is not clear from the text what was meant). If that is what was meant, the authors should explain why that condition should be interpreted as formation of an amorphous phase rather than the

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way it was interpreted by those authors: primarily (sub)monolayer uptake to hexagonal ice as observed within the HCl/ice coexistence envelope, with a minor population of HCl hexahydrate nuclei, which were not extensive or abundant enough to affect the magnitude of HCl uptake as detected by CIMS.

p. 30770, Lines 8-9: Can the authors comment on the smoothness of the ice samples? Vapor deposited ice can be rough, and the smoothness of the ice sample has been observed to affect HCl hexahydrate formation (see comment above, and McNeill et al., 2007). This is mentioned later in the discussion but it would be helpful to hear more about these ice samples in the experimental section.

p. 30771, Line 25: The nomenclature "Stirred flow" is misleading here. The word "Stirred" implies that an impeller is used to actively stir the reactor and eliminate concentration gradients. This is not the case with this experimental setup. Please use a different term.

Section 4.1/Figure 6: the panels of Figure 6 are introduced in the text in reverse order (C, B, A). Please invert the panels in the figure so that the flow is logically consistent with the text.

Section 4.1/Figure 6: Why is $P_{eq}(H_2O)$ consistent with Marti and Mauersberger but $Rev(H_2O)$ is not? What is the implication? I could not find an explanation for this discrepancy in the text.

Section 4.2/Figure 8: like Figure 6, the panels of Figure 8 are introduced in the text in reverse order (C, B, A). Please invert the panels in the figure so that the flow is logically consistent with the text.

Section 5.1/Figure 4: Figure 4 is introduced here out of order. It's confusing for the reader. I also suggest that Figure 4 may be moved to supporting online information (see comment below).

Section 5.3 – discussion of the dynamic experiments needs a summary statement,

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perhaps before the discussion begins, explaining the motivation behind these experiments. The procedure is described in detail but it's not clear what we are supposed to conclude from the results.

Figure 1: The location of the ice film in the reactor should be indicated on the diagram.

Figure 2, Figure 3, and Figure 4: These figures belong in supporting online information. The paper is too long and moving this kind of diagnostic/technical data (along with the text describing it) to the SI will help that problem.

Figure 6: Panels should be reordered (see comment above). Need units for panels (a) and (b). Please show error bars on these points that reflect the full propagation of errors, starting from noise the experimental date, through eq. 13 and similar calculations.

Figure 7 – I recommend combining this with Figure 9 and Figure 12.

Figure 11 – this color code used in this figure doesn't make sense.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 30765, 2013.

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