

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

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We thank both referees for their careful reading of the manuscript (acp-2013-856) as well as for their thoughtful comments and criticisms. We will make every effort to take their comments into account when preparing the final revised manuscript. In the following we respond point-by-point to the raised questions. In the beginning we would like to change a detail in the title of the publication because the term “amorphous hydrates may lead to confusion. The proposed new title is: “H₂O and HCl trace gas kinetics

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on crystalline hydrates and amorphous HCl/H₂O in the range 170-205 K: the HCl/H₂O phase diagram revisited”.

Final Response to Referee #1:

1. We agree with the referee that Appendices A, B and C will be moved into the Supplemental Information (SI) section as well as parts of section 2 (Experimental Apparatus) as it is mostly description of hardware. We also propose to thin out section 3 (Experimental Methodology) in order to keep the bare essentials of the methodology that is necessary to understand the measurement strategy. We reckon that we will thereby relegate a good part of the existing length of section 3 into the SI section. 2. We will move Figures 3 and 10 into SI as suggested. 3. The legend of Figure 4 identifies the pure HCl adsorption isotherm on the stainless steel walls of the reactor as the black curve whereas the lower, blue, curve corresponds to the HCl isotherm in the presence of the partial pressure of H₂O. We will clarify this situation in the text by emphasizing that the limited amount of information on both the H₂O and HCl adsorption isotherms may only lead to a speculative interpretation. The increasing trend of H₂O adsorption in going from the pure case to H₂O in the presence of HCl (going from red to green in Figure 4) means that H₂O will unselectively adsorb on both surface (SS) sites as well as on already adsorbed HCl. More H₂O is able to adsorb on already adsorbed HCl than on SS sites. In contrast, the decreasing trend of HCl adsorption in going from pure HCl to HCl in the presence of H₂O (going from black to blue in Figure 4) may be interpreted as a displacement process: H₂O displaces already adsorbed HCl in order to reduce the adsorption capacity of HCl in the presence of H₂O. We observe some sort of “mass balance” when we consider H₂O adsorption in the presence of HCl (increasing trend, see above) and its inverse, namely HCl adsorption in the presence of H₂O. The decrease in the amount of adsorbed HCl from the pure case to the presence of H₂O should be balanced by the increase in H₂O adsorption from the pure case to the presence of HCl if the total number of adsorption sites remains constant and are identical for both HCl and H₂O. This is approximately, but perhaps not absolutely, correct

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on the basis of existing data (Figure 4) and should be further checked. The changes in the Langmuir equilibrium constant K_L are consistent with the trends of both the H₂O and HCl isotherms in the presence of each other (see Table 2). The existing data are sufficient for the interpretation of HCl kinetics in the present work and the treatment may be an “operational” application of the Langmuir isotherm. We will streamline and clarify the discussion in section 5.1 on pg. 30790 (Langmuir Adsorption isotherms). 4. This comment shows that we have failed to communicate the used measurement strategy to the reader. We will make an honest effort to emphasize the nature of both pulsed valve (PV) and steady-state measurements as they both represent the “meat” of the present study.

Final Response to Referee #2:

- Regarding the comment on the amorphous phase HCl/H₂O: This “phase” is not new by any means. Dominé and coworkers have published IR absorption spectra in the past (see Xueref and Dominé, *acp* 2003 and references therein), and all Chiesa and Rossi (*acp* 2013) recently did was to add additional IR absorption spectra pertaining to some defined HCl to H₂O mole fractions, mostly in the HCl/H₂O = 6:1 ratio. We will gladly expound on the amorphous HCl/H₂O phase in the Introduction by stressing that in this case it is a stable phase that may extend over much of the known (= published) phase diagram depending on the HCl/H₂O molar mixing ratio. Phase diagrams are usually represented in terms of thermodynamically stable phases which generally correspond to crystalline phases that are more stable than metastable phases. The present case is an exception to the rule (Chiesa and Rossi, *acp* 2013) in that the metastable crystalline HCl hexahydrate slowly converts into a stable amorphous phase at typical UT/LS relevant temperatures. In any case, the “amorphous phase” seems like a frozen glass or frozen solution when we consider the IR absorption spectra (broad, featureless IR spectrum). - Pg. 30768, lines 16-18: From the present experiments as well as from those performed by McNeill et al. we do not know whether the “disordered” regions within the crystalline H₂O existence area of the phase diagram (close to the HCl hex-

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ahydrate and “ice” coexistence line) called “QLL” (quasi-liquid layer) by McNeill et al. and the amorphous phase treated here are identical or not. Based on the IR absorption spectra I would guess that they are not. Thermodynamic stability of a phase does not depend on the morphology of the substrate (rough vs. smooth), amount of HCl (sub-monolayer or multilayer) or HCl accommodation coefficient. “Amorphous” just means that there is no short-range order on the scale of the performed X-Ray diffraction experiment that corresponds to a few Å. We certainly do not want to imply that the phase grown on vapor-deposited ice by McNeill et al. is an amorphous solid as long as we do not have any structural information. However, adsorbed HCl induces surface disorder (“amorphization”) and surface roughening according to McNeill et al. HCl partial pressure and flow rate at deposition conditions are important parameters as well, such as noted by Delval et al. (*acp* 3, 1131-1145, 2003; see Table 4). (N.B.: We have not been able to duplicate this work, most likely because the deposition geometry was significantly different. In the referenced work of 2003 the deposition area was enclosed by a PTFE housing whereas the current work was performed by dosing into the free volume of the stirred flow reactor). We will introduce a paragraph that explicitly describes the HCl dosing parameters in our effort to generate crystalline hexahydrate at $T > 173$ K. However, we will not comment on the interpretation of experiments performed by McNeill et al. (2007) for obvious reasons, the most important one being that both experiments are complementary, and not exclusive. At variance with McNeill et al., we are able to grow crystalline HCl hexahydrate on vapor-deposited iced at $T < 172$ K, a temperature not considered by McNeill and colleagues. If we exclude this low temperature we agree with McNeill et al. because vapor-deposited ice was the only substrate that we have investigated. - Pg. 30770, lines 8-9: We would like to avoid the term “smooth” ice as it is solely based on visual inspection of the ice sample. This attribute is meaningless in terms of molecular structure and/or morphology. Samples of 1 to 2 micro m are thin compared to “smooth” ice (200-500 micro m) so that we are unable to gauge the “smoothness” of the ice. More important than the morphology seems to be the deposition parameters such as temperature, flow rates and partial pressure at

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deposition which are given in the text (page 30774, lines 18-27 and page 30775, lines 1-14). The referee is correct in that vapor-deposited ice may be rough at times, especially when deposited close to 200 K: This has been observed by B. Flückiger using the experimental equipment at hand (unpublished). - Pg. 30771, Line 25: "Stirred Flow" is a standard denomination in gas kinetics for a certain type of reactor/pressure regime combination. "Stirred" stands for molecular stirring and means that the mixing time is on the order or shorter than the gas residence time in the reactor. - Section 4.1/Figure 6 and 8: This will be done as the referee suggests. - Section 4.1/Figure 6: Marti and Mauersberger do not provide values of $Rev(H_2O)$. The implication of the Rev values is that they are approximately a factor of ten lower than the theoretical maximum which is given when the accommodation coefficient is set to $\alpha = 1.0$ which clearly is not the case here (see Figure 6 and 8). - Section 5.1/Figure 4: Will do (see answer to Referee #1). - Section 5.3: A short programmatic paragraph will be inserted into the text. However, the most suitable location of a summary statement would probably be at the beginning of Section 3.1 or 3.3 as a strategic statement. - Figure 1: Given the scale of the Figure we reckon that the best solution would be to include a sentence regarding the location of the ice film in the figure caption of Figure 1. - Figures 2, 3 and 4: We will move Figures 2, 3 and 5 into the SI section. However, we will keep Figure 4 in the main text in order to drive home the point on the importance of the Langmuir adsorption isotherms for the pulsed valve experiments. - Figure 6: See above. Units will be added to panels a, b (old notation). Errors will be reevaluated in a realistic manner. - Figure 7: The combination of Figures 7, 9 and 12 into a single Figure is not advisable and leads to data-overcrowding so that one finally can't see a thing considering that all Figures will be reduced to fit the text. Below you may find an embodiment of your suggestion as we have pondered your question quite carefully. We continue to think that our solution is best in the present case which is the reason that these three mentioned Figures are drawn exactly on the same scale such that one may superimpose them and address them visually. - Figure 11: We can't find anything wrong with the color code of Figure 11: We even are proud to have stumbled on this smart solution!

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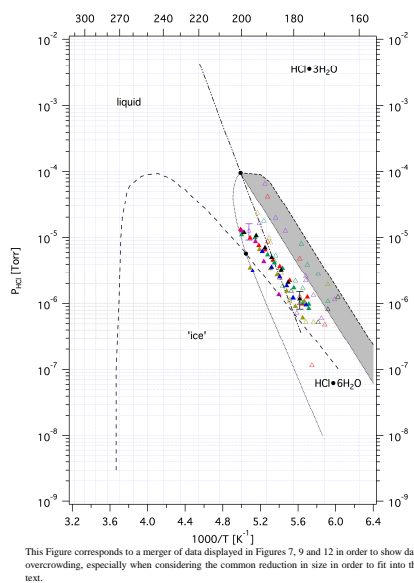


Fig. 1. This Figure corresponds to a merger of data displayed in Figures 7, 9 and 12 in order to show data overcrowding, especially when considering the common reduction in size in order to fit into the text.

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