Authors reply

The metastable HCI•6H₂O phase - IR spectroscopy, phase transitions and kinetic/thermodynamic properties in the range 170-205 K

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We would like to thank both Referee's for their careful reading of the extensive manuscript and the corresponding constructive remarks that will form the basis of submitting an improved and amended version in the near future. We admit that the present manuscript is longish, and perhaps "technical" and therefore more difficult to read than others. However, it has the merit to shed some light on the metastability of the title HCl hydrate. Historically, we and others have searched for the existence of crystalline HCl hexahydrate, and initially failed. Now we know under which conditions we have to look for this elusive hydrate that turns out to be less relevant than expected for the planetary (polar) atmosphere. Of course we will make every effort to streamline the manuscript in order to please as many people interested in heterogeneous processes in the UT/LS in addition to the hard-core specialists by making the text as "digestible" as possible.

We would like to answer both referees as follows:

Anonymous Referee #1:

- Regarding the occurrence of the term "Quasi Liquid Layer" (QLL): It means many things to many different people and is in fact ambiguous, especially when applying to ice or binary cryogenic mixtures. We will delete this term throughout the manuscript (called seven times towards the end of the text) and replace it with "disordered structure" that opposes it to "non-disordered structure" (McNeill et al.) or crystalline structure. This point has also been raised by Referee #2. At the outset QLL meant absence of closerange structural order (or amorphous state) as viewed by X-Ray diffraction or other structural analysis technique, and was used to differentiate from the true (thermodynamically stable) liquid phase, for instance in the HCl/H₂O phase diagram. Regarding the difference between interface and phase we are clearly dealing with phases despite the thin film nature of the sample. A 1μ m thin H₂O ice film still represents 4000 H₂O monolayers which correspond to bulk compared to interfaces that usually comprise a few formal monolayers, depending on the method of investigation. We would like to make it clear that QLL was never meant to be an interface, it is used here to denote a phase. A "layer" is a phase once it exceeds a few monolayers. We will modify the phase diagram in Figures 11 and/or 12 in order to display details on the corresponding "disordered" fringe region that surrounds the "ice" phase according to the work of McNeill et al. However, we propose to leave the phase diagrams at the end of the manuscript because they serve to orient the results of the present study and serve as cornerstones for the purpose of discussion.
- We will try to refocus the Abstract and rewrite part of the text. However, we say very clearly that we perform two kinds of experiments using a new multidiagnostic apparatus and thereby emphasize the **kinetics**, mostly evaporation rates. It is impossible to cover the many aspects of research that a new experiment offers, in a single paper dealing with as complicated a situation as a metastable phase.
- We will delete the summary of some of the results in the Introduction and will clearly state which experiments (out of many possible ones) have been performed in this study.

We will also emphasize the role of HCl electrolytic dissociation in the Discussion section: HCl is dissociated in both the HCl hexahydrate as well as the amorphous liquid, and we admit that this has not been pointed out in the manuscript. The studies of Parent et al. (NEXAFS) belong to the finest experiments on the properties of HCl/H₂O ice that there are, and so we are reluctant to remove this reference.

- The Referee proposes to start the presentation of results with HH nucleation. However, this is our weakest point as we have performed only a few quantitative experiments displayed in Figure 12. Except for the nucleation we follow the sequence suggested by the Referee in terms of properties, decomposition and phase transition. Nucleation conditions are key to the metastable nature of HCl hexahydrate, agreed, but this paper does not deal with it in depth. The current knowledge (or sate-of-the-art) should be found in the Introduction.

Referee #2 (T. Loerting):

- Regarding the stoichiometry of the HCl hydrate: The reason for this "inability" is the fact that the stainless steel vessel walls adsorb HCl to a small extent, however owing to the large internal surface of the reaction chamber (2350 cm^2) compared to the small cold sample surface (0.78 cm^2) the quantity of wall-adsorbed HCl is significant, on the order of 10 to 15%. The kinetic experiments have been performed under conditions of H_2O and HCl-saturated reactor walls. However, the measurement of absolute amounts of HCl always resulted in values that were too small. This may be seen in the (bracketing) mass balance displayed in Table 4 which will be expanded in order to arrive at a better display of the uncertainties in HCl hexahydrate concentration. The Referee raises an important point which we have addressed in work following the present paper and which will be presented in Iannarelli (2013) (referenced in manuscript) to be submitted shortly to acp. In the most recent work we obtain excellent mass balance owing to the fact that we take into account both HCl and H₂O adsorption on the reactor walls using a Langmuir isotherm that we have measured for Stirred Flow Reactor (SFR) conditions used in this and Iannarelli's work. This wall adsorption correction was mandatory in the new work owing to time-resolved studies of adsorption and evaporation processes. Coming back to the present work, HCl was recovered to about 50% upon evaporation during approximately 20 minutes. The remainder of the adsorbed HCl desorbed overnight because the baseline returned to its usual value only after 8 hours or so (next morning). We therefore undercounted HCl by approximately 50%.
- The reason for the 30% uncertainty in the IR absorption cross section has entirely to do with the measurement of the HCl hexahydrate concentration and the absolute amount of HCl that we are able to measure (see above). Owing to the error in the adsorbed HCl displayed in Table 4 between the two methods (columns 4 and 5) we arrive at the 30% overall uncertainty because the mass balance is only bracketed (= determined to lie between two limiting values), therefore the accuracy is fairly low. We will revise Table 4 by adding two columns listing the relative deviation between measured HCl dose (column 2) and measured HCl adsorbed on the ice (columns 4 and 5).
- Regarding possible hexahydrate polymorphs: The HH spectrum published by Delval (2003) shows an additional high frequency IR absorption at 3549 cm⁻¹ and a symmetric split of the 1635 cm⁻¹ band. Delval had a tightly fitted dosing chamber around the Si window whereas we currently have an open configuration with the end of the dosing tube pointing towards the Si window, but at a distance of approx. 5-7 cm from the Si window. We have tried many times to reproduce the Delval spectrum of HH, but failed under all conditions explored. We therefore believe that the present HH absorption spectrum is

directly comparable to the literature (see Table 2) and that Delval's result is connected to the confinement (high HCl partial pressure, molecular beam or jet) geometry used at that time.

- Regarding the "empirical" correction of the factor 1.281: There is nothing empirical about this because it is given by equation (11) based on measured rate constants. We decided to ignore the correction factor of 1.055 for pure ice, but apply this correction to HCl/H₂O because we want to consider equilibrium concentrations derived from steady-state (= experimental) ones.
- Regarding the "technical difficulty" for reading: we will certainly streamline the Abstract (see also remark by Referee #1) and focus the text a bit more. We will forego any derivation in the text and delete equations (7) to (9). However, as for the other equations we are reluctant to relegate them into an Appendix because they "feed" the argument and belong in the text. We present quantitative arguments that may appear "technical", but are life-supporting when it comes to arguments and reasons. We will, however, relegate some non-essential parts of the discussion into an Appendix in order to alleviate the main text.
- Regarding minor issues raised at the end of last § on pg. C6637: (a) "H₂O-poor" which we will call "H₂O-deficient". "Pure" HCl hexahydrate does not exist, we can only come infinitesimally close to 100% pure HH owing to the metastable nature of that phase. Essentially, when HCl evaporates the recondensation cannot regenerate the crystalline phase owing to the nucleation (temperature) barrier; (b) The "break" around 190 K for pure ice concerns the rate or evaporation flux $J_{ev}(H_2O)$ for pure ice. This has been described by Pratte (2006) and Delval (2004). Both references are given in the paper, but we will refer the reader to them when it comes to discuss the "break" (discussed in connection to Figure 7); (c) Regarding the two values of the HCl standard enthalpy of sublimation in HCl hexahydrate: 65.4 kJ/mol applies to 300 K and 65.8 to 200 K; (d) We agree with Referee and add a top abscissa to Figure 7 in terms of the temperature scale; (e) The gas constant R = 8.314 J/K mol will be used throughout the paper; (f) We will blow up the 1700 cm⁻¹ region in Figure 1 and add labels to the main features of the HCl hexahydrate spectrum in Figure 2; (g) Temperature labels will be added to Figure 10 for easier comparison. However, the absorption spectrum of HCl hexahydrate at 170 and 192 K are very similar such that we will have to find a suitable format in order to highlight/superimpose both spectra; (h) The less intuitive label "HH" has been used in addition to the longer term HCl• 6H₂O because of its suitability as a subscript in formulas such as in equations (9), (10) and (11). By the same token, HCl trihydrate is sometimes called "TH" for handy use in equations (10) and (11). This should not be a significant obstacle as "HH" and "TH" are both defined in the text.