

Interactive comment on "The metastable HCI.

6H₂*Ophase* –

-IRspectroscopy, phasetransitions and kinetic/thermodyna -205K"byS. Chiesa and M.J. Rossi

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I have just seen the manuscript by Chiesa and Rossi, which describes experiments on the HCI-ice system in the 170-205 K temperature range. The study has been done in a very careful and VERY comprehensive way. Clearly, significant achievements and significant conclusions could be made in this work.

One major achievement is the growth of a pure HCI-hexahydrate film and its extensive characterization in terms of infrared cross-sections. This has not been possible before and could only be reached because of a very clever combination of mass-spectroscopic

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observation of the gas-phase, including evaporation and condensation rates of H2O and HCI, and the FTIR observation of the thin film itself in transmission mode. By contrast to grazing angle techniques (such as RAIRS) applied in the past, the IR spectrum can be analyzed in a quantitative way when using transmission FTIR. The beauty in this approach is the possibility of evaporating excess H2O molecules from the surface to finally reach the pure hydrate phase, which is only possible because of a neat design of the reactor, which has only one single cold spot. There is one caveat, though. From the data itself the stoichiometry of the hydrate can not be determined, and also the issue of possible hexahydrate polymorphism can not be addressed. It would be the true masterpiece to recover the pure hydrate and study its stoichiometry, e.g., using calorimetric approaches, and study its crystal structure using scattering techniques such as XRD. In absence of this additional information the authors have to rely on a comparison of their peak positions with literature data and need to rely on the assignments made in earlier studies, e.g., by Devlin et al. I think it is highly likely that Chiesa and Rossi have indeed obtained the hexahydrate, rather than maybe the trihydrate, but I think a small degree of uncertainty remains. This is even more troublesome because the 6:1 ratio had to be assumed in the quantitative treatment of the data. In this context the authors state on p.17804 that they were "unable to quantitatively determine the amount of adsorbed HCI using the MS signal at m/e = 36.", which I find troublesome. What is the reason for this inability? What is the ratio of HCl to H2O that the raw MS-data would indicate? Why do the authors believe that the data can not be employed for quantitative descriptions? What is the reason for the "30% overall uncertainty" the authors claim on p.17805 for the integral of the peak at m/e=18? Furthermore, I wonder whether the HCI-hexahydrate might crystallize in two polymorphic forms, alpha and beta. Delval et al. had observed previously an IR spectrum that might be understood as a superposition of two ordered phases, maybe the alpha- and beta-hexahydrates. So, it would be of interest to nail down which polymorph was obtained, but unfortunately this could not be achieved in this work, and the authors have to assume that they are dealing with the same polymorph also obtained in earlier studies.

The second major achievement is the calculation of rates of evaporation, activation energies for sublimation and equilibrium vapour pressures, which can be used to construct the phase diagram of the HCI-H2O system and to understand the phase transitions, decomposition and/or sublimation of the hexahydrate. What I find here of great interest and novelty is the determination of the activation energies and the recognition that the rate-limiting step in the decomposition is HCl evaporation. In the quantitative treatment of the data I again would have loved to see calorimetric data for the hexahydrate, in particular because sublimation enthalpies play a crucial role, which were determined here from Van't Hoff plots in a quite narrow temperature range and by using some "empirical" correction factors to vapour pressures, e.g, 1.281 in case of water. What is good here, is that the authors have calculated the activation energies here using two different approaches, based on the decay of the FTIR absorption and also based on the relative change in evaporation rates (p.17811), and reach agreement within the error bars of about 10 kJ/mol.

The major achievements mentioned so far would make a good case for publication of this work in a spectroscopically or thermodynamically oriented journal. The main conclusion that is of relevance to our understanding of processes in the atmosphere especially the upper troposphere and lower stratosphere is that the hexahydrate of HCI only nucleates at < 173 K and so is very likely not of any importance in the atmosphere. One could argue that there is no point of publishing spectroscopic and thermodynamic information about a phase that is not relevant in our atmosphere in a journal that focusses on understanding the physical chemistry of our atmosphere. However, this point alone, that the hexahydrate is NOT of importance, is of interest to the community and second, the authors also reach important conclusions that the amorphous HCI/H2Osystem is likely of high relevance in understanding polar stratospheric ice chemistry. In this context the authors speak about liquid-like layers, the QLL, surface roughening and a highly-granular structure of the surface - in an apparently interchangeable way. It would be of interest here to clearly define what these terms stand for - which would make it easier to follow the discussion in the context of earlier literature. Finally, the

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intersection of the evaporation rates of the hexahydrate with the evaporation rates of HCI/H2O determined earlier by Flueckiger et al. just below 200 K in Fig.7 is of direct relevance. And also the recognition that initial water content is responsible in determing what happens at higher temperature to the hexahydrate is outstanding. That is, I absolutely think that the authors have made a good choice of journal and that their results are of high importance and novel, and clearly warrant publication.

However, while I congratulate the authors on their experimental achievements, I think they have not done the best job in conveying their message to the reader. The paper is very hard and very long to read and very, very technical - a nightmare for a referee. It is very difficult to follow what the main message is and not to get lost in all the equations and side-tracks about experimental details. Even the abstract is very technical rather than presenting the "big picture" that can be deduced from this comprehensive piece of work. I, therefore, suggest that the authors significantly shorten the paper itself - and focus on just the key points in the main text, whereas all the technical details and most equations should go to the supplemental information or Experimental section, which are both quite short at the moment and better places for technical information than the Results section. I do understand that this is some work to rewrite the paper with this in mind, but I think it will ultimately increase the visibility and the impact of the paper. If this is not done, the paper will probably be read, and maybe understood, exclusively by researchers studying exactly the same system, but not by the broader community.

Finally, some minor issues: p.17803: in the beginning of chap3.2 "pure HCI.6H2O" is used, four lines below (the same thing?) is called "H2O poor HH" - I do not see why two different names are used... p.17810 in eq.(16) there is an unwanted "6" p.17812: "the break around 190 K" is unclear... is this just from the literature or also found here? or was it found here, but not in literature? p.17813: a sublimation enthalpy of 65.4 kJ/mol is guoted first, and a few lines further down 65.8 kJ/mol are employed for calculations... why? Table 5: erase the word "ration" Fig.7: a second absicassa showing the absolute temperature in K on the top would be good (similar to the ones

shown in Fig.11/12); the gas-constant is 8.314, not 8.312 J/Kmol (same in Fig.5) Fig.1: some of the peaks quoted in the text are so small that they can be hardly seen; I suggest to magnify the corresponding wavenumber regions, e.g., near 1700 cm-1, so that one can also see what happens to these peaks during film evaporation Fig.2: since this is the "pure" hexahydrate spectrum no-one else was able to obtain, it would be good to indicate the wavenumbers of the peaks assigned to it, and to also clearly state what is contamination, e.g., the CO2 between 2300 and 2400 cm-1 Fig.10: temperature labels in the figure would make it easier to follow the discussion; three temperatures are quoted in the legend, but only two spectra are shown... why not include the third (170 K) spectrum? Fig.11: "HH" and "HCI.6H2O" are used interchangeably; please avoid the (less intuitive) abbreviation "HH"

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 17793, 2013.

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