

Answer to referees regarding “The Influence of HCl on the Evaporation Rates of H₂O over Water Ice in the Range 188 to 210 K at small Average Concentrations by C. Delval and M.J. Rossi, Atmospheric Chemistry and Physics Discussions (<https://doi.org/10.5194/acp-2018-238-RC2>, and - RC1, 2018)

We would like to thank both referees for their comments, questions and remarks. We have taken into account all questions and comments of both referees to various degrees of implementation in the revised version of above-referenced paper thereby wanting to avoid unnecessary duplication of text in relation to previous papers dealing with the same subject. We have outlined our actions on the manuscript point-by-point and will highlight the added/modified text in “track change” format once we will have the encouragement for submission of the revised version of the manuscript by the acp editors. We report the questions/comments of the referees in *italics* followed by our answer in straight font.

Answer to Dr. J.P. Devlin (referee 2):

We would like to address our sincere thanks to this referee for pointing out the inconsistencies in the assignment of the IR reflection-absorption (RAIR) spectra in the work of Parent and coworkers as stated in your comment. We did indeed miss these author’s reassignment in their recent 2011 work and are grateful for your astute observations. We cannot contribute much to confirm or deny their assignment from our own chemical kinetic work, but like to agree with you that the conversion usually follows the route “molecular” to “ionic” with increasing temperature and not the inverse, akin to the results on N₂O₅ deposition on ice films in the seminal work of John Sodeau and Andy Horn some time ago (J. Phys. Chem. 98, 946-951, 1994). However, what we may contribute are some shortcomings in the Parent and coworker’s study of 2011 (Parent et al., Phys. Chem. Chem. Phys. 13, 7142-7148, 2011) from our point of view:

- Their value for a monolayer is a factor of approximately four too high compared to the consensus value of 2-3 10¹⁴ molecule cm⁻². Although most of the early work resulted in distinctly larger values, probably owing to the phase transition to amorphous, the newer studies under stricter experimental control all settle around the indicated value according to Table 1 below. Although not explicitly stated, the conversion of their exposure to coverage values makes use of 8.0 10¹⁴ molecule cm⁻² as a molecular monolayer. Using a factor of four lower value surely will affect the calculated surface concentrations.
- Somewhat related, the derived concentrations in Figure 3 (XPS, 50 and 90 K concentrations) and Figure 4 (FT-RAIR) do not have any uncertainty limits which has apparently slipped the attention of the competent editor! The reader does not have a clue regarding uncertainties and sensitivities/limits of detection.
- The deposition of CRYSTALLINE Ice at 150 K (for the NEXAFS experiment) is doubtful! In order to make sure that one has indeed I_h ice one must anneal the deposit up to 190 K in order to be sure of the structure and subsequently cool down! What they most probably have is a disordered I_h ice phase that mimicks the often sought but so far elusive atmospheric cubic ice phase (I_c), probably together with amorphous domains (see work by W. Kuhs and co-workers).
- The authors deposit 4 ML’s of amorphous ice at 110-120 K for XPS, UPS and FT-RAIR and compare it to 100 ML’s amorphous ice deposited at 150 K for NEXAFS experiments. Most likely, the density of the “amorphous ice” is different following astrochemical work (high density vs. low density amorphous). Even though the species observed are qualitatively similar in both environments, the question of comparability of results must be posed. As long as it cannot be

shown that the transformation/conversion rates are not identical in both ice films no statement about relative abundances may be made. IR or RAIR is probably not an ideal monitoring technique for radiation damage of a sample (disparate beam diameters!). It seems to us that Parent and coworkers cannot assert that the ice substrate is identical for all spectroscopic experiments reported, and this will have consequences for HCl deposition.

- We are critical of the “dangling” H (dH) results in Figure 4 in terms of “negative” IR absorption peaks. Following our own unpublished work dH disappears at 220 K both in the presence and absence of HCl without apparent kinetics/reactivity at lower temperature that would manifest itself as a decrease of dH abundance upon HCl exposure. We reckon that the abundance of these sites is low enough such that HCl may interact with other sites on the existing ice surface. We note the absence of a correlation between the decrease of the number of dH sites with the appearance of “new” IR absorptions up to 220 K.
- Comparing the 50 K results in Figure 3 from 0 to 3 L exposure with the calculated concentrations in mol % (right ordinate) and coverage in ML (left ordinate), it is not obvious to us how these results were derived and how sensitive they are to calibration (see above under HCl monolayers). Uncertainty limits would be quite helpful in this instance, especially so as these data are the cornerstone of their conclusions. The same goes for the correspondence between exposure and concentrations displayed in Table S1.

As a result we will briefly summarize the situation in the introduction of the manuscript in the revised version. By the same token we will attenuate the significance of the work of Parent et al. in light of the obvious shortcomings pointed out above and made worse by the recent reversal of vibrational assignments occurred in their most recent (2011) compared to previous (2005) work.

Table 1: Brief Summary of the Amount of a Molecular Monolayer of HCl adsorbed on H₂O ice

Value / (molecule cm ⁻²)	Temperature / K	Bibliographic Reference
5.0 10 ¹⁵	200	Hanson, D. R., Mauersberger, K., HCl/H ₂ O Solid Phase Vapor Pressures and HCl Solubility in Ice, <i>J. Phys. Chem.</i> , 94, 4700–4705, 1990
1.0 10 ¹⁵	200	Abbatt, J.P.D., Beyer, K. D., Fucaloro, A. F., McMahon, J. R., Wooldridge, P. J., Zhang, R., Molina, M. J., Interaction of HCl vapor with water ice: implications for the stratosphere, <i>J. Geophys. Res.</i> , 97, 15819–15826, 1992
(2.0 – 3.0) 10 ¹⁴	191	Hanson, D., Ravishankara, A.R., Investigation of the Reactive and Nonreactive Processes Involving ClONO ₂ and HCl on Water and Nitric Acid Doped Ice, <i>J. Phys. Chem.</i> 96, 2682-2691, 1992
(7.3 ± 0.5) 10 ¹⁵	183	Foster, K. L., Tolbert, M. A., George, S. M., Interaction of HCl with Ice: Investigation of the Predicted Trihydrate, Hexahydrate, and Monolayer Regimes, <i>J. Phys. Chem. A</i> , 101, 4979–4986, 1997
2.5 10 ¹⁴	208	Interaction of HNO ₃ with water-ice surface at temperatures of the free troposphere, Abbatt, J.P.D., <i>Geophys Res. Lett.</i> 24, 1479-1482, 1997
3.1 10 ¹⁴	185	Flückiger, B., Thielmann, A., Gutzwiller, L., Rossi, M. J., Real time kinetics and thermochemistry of the uptake of HCl, HBr and HI on water ice in the temperature range 190 to 210 K, <i>Ber. Bunsenges. Phys. Chem.</i> , 102, 915–928, 1998
(1.1 ± 0.6) 10 ¹⁴	201	Lee, S.-H., Leard, D. C., Zhang, R., Molina, L. T., Molina, M. J., The HCl + ClONO ₂ reaction on various water ice surfaces, <i>Chem. Phys. Lett.</i> 315, 7–11, 1999
(2.0 ± 0.7) 10 ¹⁴	2001	Hynes, R. G., Mössinger, J. C., Cox, R. A.: The interaction of HCl with water-ice at tropospheric temperatures, <i>Geophys. Res. Lett.</i> 28, 2827–2830, 2001
1.7 10 ¹⁴ 1.3 10 ¹⁴ 6.7 10 ¹³	190 200 210	Flückiger, B., Rossi, M.J., Common Precursor Mechanism for the Heterogeneous Reaction of D ₂ O, HCl, HBr, and HOBr with Water Ice in the Range 170-230 K: Mass Accommodation Coefficients on Ice, <i>J. Phys. Chem. A</i> 197, 4103-4115, 2003
2.3 to 2.7 10 ¹⁴	180 to 200	Henson, B. F., Wilson, K. R., Robinson, J. M., Noble, C. A., Casson, J. L., Worsnop, D. R.: Experimental isotherms of HCl and H ₂ O ice under stratospheric conditions, Connections between bulk and interfacial thermodynamics, <i>J. Chem. Phys.</i> , 121, 8486– 8499, 2004

In summary, the work of Parent et al. (2011) glosses over the properties of the ice substrate itself that may be different for different experiments, such as NEXAFS, XPS, UPS and RAIR spectroscopies. It behooves the authors to search for a relevant experimental marker that pinpoints the properties of the ices investigated as a function of temperature and mode of deposition. There is room for improvement.

The additional questions posed by the referee may be answered in the following:

1. Perhaps it should be clarified that RAIR FTIR data often cannot be compared directly with absorbance data

The discrepancy between RAIR and FTIR absorption data will be pointed out in the main text although the interfacial character of the obtained data is emphasized in polarized (s and p-type) RAIR data which is desirable if you are interested in the composition of the interface. In all honesty, we would have liked to record our recent NAT and NAD data in polarized RAIR fashion if it were not for the missing capability to measure quantitative absorption cross sections (R. Iannarelli and M.J. Rossi, J. Geophys. Res. Atmos., 120, 11,707–11,727, doi:10.1002/2015JD023903).

2. This current review of the data convinces me that at least between 40 and 130 K the Bartels-Rausch recent HCl-on-ice publication may be right about the presence of molecular HCl on ice surfaces to some extent at most temperatures (but not all conditions). Is there a reason that paper was not included?

The Bartels-Rausch paper on HCl-ice was not included in the first place because the evidence the authors present is not ultra-strong. However, for completeness sake, we will list it in the bibliographic references being a newer piece of work recorded using a synchrotron.

3. The Zundel ion is important in understanding the evolution of the changes that follow warming after HCl has been adsorbed on ice at low levels at low T. Also the basic characteristics of the Zundel ion vs its environment have been thoroughly examined in the last 10 years. I particularly recommend an older joint review paper of Buch, Parrinello and others on the hydrates of HCl; J. Phys. Chem. A 2008, 112, 2144-2161 that highlights the Zundel ion.

We will make mention of the importance of the Zundel IR absorption continuum in the revised text in relation to its temperature dependence. The reason we did not consider it was that the present study focused on higher temperatures and on thermochemical kinetic aspects rather than on IR vibrational assignments.

4. On page 5 the authors question the importance of the dangling O-H bonds during the early uptake of HCl at low temperature. Is this consistent with the Parent infrared data in their 2011 paper in which they show/remark that the dH-band is gone after 0.15 ML at 50 K. Why did you make the statement WITHOUT GIVING A REASON?

We refer to the point raised above in relation to the dangling (isolated) –OH bond. In our hands the behavior of the dH bonds was different, most probably owing to the higher temperatures used. We do not want to get involved in discussions in view of our unpublished results at variance with Parent et al. (2011).

Answer to referee 1:

Most of the points raised by referee 1 have already been mentioned in the original text. However, the referee questions/comments show us where we could have been clearer in our explanations, and we nevertheless thank the referee for his diligence and attention to detail. We will emphasize or complete our original text, as the case may be. Here, we will give brief answers to the specific questions raised by the referee.

o Limited Discussion: The manuscript tends to stop at the level of reporting the results without relating them to the results by other groups or lifting them to a more general level

There are simply no other measurements of absolute desorption rates of molecules constituting the components of contaminated ices of atmospheric relevance. All existing reports on desorption rates $J_{\text{des}}(\text{M})$ of H_2O , HCl , HNO_3 , adsorbed organics and the like make the assumption of unity accommodation coefficients which may be wrong by up to three orders of magnitude, whereas the present results were obtained without the incidence of readsorption owing to the small absolute pressures used. The only other study with which to compare the results of HCl is our own dealing with HNO_3 absolute rate of desorption referenced in the bibliography (Delval and Rossi, 2005). We will therefore emphasize this point in the discussion section.

o No Relevance Given: The introduction is very interesting to read and reveals a detailed discussion on key-topics relevant to the ice-HCl system. However, questions key to this study are not covered:

+ Why do we need to know $J(\text{des})$?

The value of $J_{\text{ev}}(\text{H}_2\text{O})$ ($J_{\text{des}}(\text{H}_2\text{O})$) is directly related to the net evaporative lifetime once the relative humidity (rh in %) is known, or in the present case, to lifetime prolongation of contaminated atmospheric ice particles with respect to pure water ice. The reciprocal value $1/J_{\text{ev}}(\text{H}_2\text{O})(100-\text{rh})$ scales with the time it takes to evaporate a given mass of water ice at a given temperature and rh value. As pointed out above, there are no measured lifetimes of ice particles except those based on vapor pressures in conjunction with a unity accommodation coefficient that lead to significantly shortened lifetimes of ice particles.

+ Where and when is the lifetime of ice particles critical and is the water flux the determining factor?

Lifetimes are important when gauging heterogeneous chemistry on ice particles with reactive “reservoir” species in the UT/LS region of the atmosphere as is the case in polar stratospheric chemistry (ozone hole), polar boundary layer ozone disappearance (so-called bromine explosions) or global heterogeneous ozone disappearance on sulfate aerosols in the UT/LS region of the atmosphere. This region of the atmosphere is subject to frequent under- and sometimes oversaturation because the stratosphere is often “dry”, that is undersaturated in water vapor.

+ How relevant are the non-equilibrium desorption processes described here to the environment? Please, do not get me wrong. I do believe this lists topics that are nicely addressed by this study and are highly relevant to the environment. It is primarily the question of discussing those in the text.

You can easily convince yourself of the variability of water vapor saturation by looking at contrails that sometimes persist only for a second or so before evaporation (atmosphere heavily undersaturated) or persistent for many hours (atmosphere close to equilibrium w/r to water vapor pressure). What is relatively new is the fact that the UT/LS region is finely structured in that strata (atmospheric layers)

of only a few hundred meters thickness change between undersaturation and saturation in water vapor. The balloon-sonde measurements of Terry Deshler some time ago revealed this fine structure in a clear manner. We are refraining from going into meteorology in the present paper that deals with fundamental physical chemistry of evaporation of H₂O and HCl from model atmospheric ice particles.

o Structure: For my feeling, the manuscript jumps to much back and forth between the topics. It is rather difficult to follow. I'd kindly ask you to address these issues and would welcome a revised version. In the following, I give some detailed questions that aim at guiding you. This is not a complete list, and I kindly ask to address the major topics first. A new review can then address the details.

Here we take exception to the first statement made by referee 1. We cannot and will not rearrange the structure of the paper without more specific advice from this referee. I can assure the referee that much thought has gone into the planning and structuring of the present paper.

Detailed comments:

Introduction, p2: The molecular and dynamic details of crystallization are mentioned. Could you give details on what this would mean for your experiment. What the role of eventually slow formation dynamics in the preparation of your samples, where apparently you start with pure ice to which to dope HCl.

The structural nature of the ice substrate has some incidence on the chemical kinetics of adsorption/desorption of polar molecules as documented in Figure A3 and A4. On a very fundamental base different pure water ices have different values of $J_{ev}(H_2O)$ and water accommodation coefficient $\alpha(H_2O)$. This has been published in the literature many times, and also by us (see for instance Pratte et al., 2006). See also our comments above in response to referee 2. However, the referee is correct in pointing out this weakness from which many published studies suffer and which should be the starting point of more careful investigations in the laboratory. It turns out that the molecular structure and morphology of the ice generated in the laboratory is very important to adsorption/desorption processes, and this has not always been recognized.

Introduction, p3: Where is the paragraph starting with Fourier-Transform IR heading? What is the take home message with respect to your work?

Regarding the first part of the question we have no clue what the reviewer is referring to. For the take-home lesson please refer to the "Conclusions" section at the end of the manuscript.

Introduction, p3: "Regarding the nature of HCl-ice adsorbate, " What has ionisation to do with your study? This is a long and detailed description in the introduction to which you never return in the discussion.

"Ionisation" is not at stake here, it is rather electrolytic dissociation that is at the centerpoint of the discussion on HCl-contaminated ices. The goal here is to introduce the reader to a problem in the description of the HCl/ice interface that has motivated countless researchers in the past. We do not mention this in the discussion because we have nothing to contribute to this topic in the present study.

Experimental: Please specify how did you quantify HCl? How did you derive the mole fraction, i.e. how did you get the volume of ice? Did you assume homogeneous mixture in the total volume of ice? Why is that appropriate?

For further experimental details please see Delval et al. (2005). The amount (number) of HCl molecules lost to the ice surface was measured at the outset upon exposure of the ice to HCl. After total evaporation of the ice film HCl was monitored quantitatively with a mass balance closed to 80% after recovery as a check. The mole fraction was determined from the number of moles of HCl and H₂O because both were monitored quantitatively, thus this method is independent of the volume of ice. As mentioned in the manuscript our method is unfortunately not able to determine concentration profiles such that we cannot comment on concentration gradients upon HCl doping. However, we have measured the self-diffusion coefficient of HCl and HBr in ice some time ago at low temperature as described in the work of Aguzzi et al. (Phys. Chem. Chem. Phys. 5, 4157-4169, 2003) and Flückiger et al. (J. Phys. Chem. 104, 11739-11750, 2000).

Could you specify on mixing and diffusion times? What is the error on the mole fraction? Results, p 7 The average mole fraction should be called “apparent”? Discussion: Please add discussion of other work on H₂O Fluxes from ice in presence of acidic gases. Can your findings be related to water fluxes from other surfaces? Is this result part of a larger picture?

Regarding diffusion times see reference given above. The error/uncertainty on the mole fraction is estimated at 10%, mostly coming from the determination of the loss of HCl on the walls of the reaction vessel. We are opposed to calling the mole fraction “apparent” and will continue to use “average” because we would like to emphasize the average nature! As stated above with insistence there are no other studies dealing with H₂O fluxes from water ice in the presence of acidic gases. It turns out that the behavior of $J_{\text{ev}}(\text{H}_2\text{O})$ from HCl-doped ice is complex which at this time precludes the transfer of knowledge to other substrates. A larger picture will certainly emerge once more studies on other aspects of evaporation/condensation will have performed.