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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Influence of the ice growth rate on the incorporation of gaseous HCl” *by* F. Domine and C. Rauzy

Anonymous Referee #1

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Referee comment on the paper Influence of the ice growth rate on the incorporation of gaseous HCl by F. Dominé and C. Rauzy. For the reminder of this text, I will refer to the refereed paper as DR.

General comments

The paper they impressively demonstrate that change in supersaturation will alter the amount of HCl built into the vapor grown ice. The paper aims to test the incorporation model as published previously by Dominé and Thibert (1996). This model distinguished a fast and a slow growth regime, as given by equation (1) and (2) respectively in the submitted paper. The authors claim that the presented measurements are consistent with their previously published growth model.

As natural ice and snow undergoes continuous morphological changes by evaporation and condensation, this is a very important topic of the research on trace gas uptake on ice. The addressed problem falls well into the scope of Atmospheric Chemistry and Physics.

The description of the experimental setup is vague. Important open questions remain: What is the total pressure in the system - I guess one atmosphere ? What is the temperature stability? How homogeneously grows the ice? Are there regions of fast and slow ice growth? What is the temperature stability? What is the temperature of the ball in the cell, where the gases are flowed through into the growth cell? Could ice grow on the ball as well? How much HCl is adsorbed on the ball, if it is cold? Is the flow turbulent or laminar?

There have been many studies on ice growth in the past. Results are conflicting and often hard to compare. One reason for this, as I suspect, is the often incomplete description of the experimental procedures and conditions. Therefore it should be a request to newly published studies to describe experimental procedures especially carefully

Specific comments

Low mass accommodation of HCl on ice and definition of mass accommodation coefficient

A key parameter is the sticking coefficient or mass accommodation coefficient. When comparing their experimental results with the model they find interesting results for the mass accommodation coefficient α_c for HCl and water, i.e. $\alpha_{HCl}/\alpha_{H2O} = 0.0014$. This value implies that if the water molecule sticks with unity probability to the growing ice, roughly every 1000^{th} HCl molecule is taken up onto the ice surface. This is a very exiting result, as all previous studies found a very high affinity of HCl to ice. One would rather expect a mass accommodation coefficient in the range of 0.2 to unity. The authors acknowledge this discrepancy themselves in the draft (p.4724, line 23 - p. 4725 line 3) and present arguments why their results are not invalidated by the unusual low value for the mass accommodation coefficient of HCl on ice.

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When talking about mass accommodation and sticking coefficients it is important to note that different definitions are being used in the literature, which might be a reason for discrepancies between different studies. I like to urge the authors to think and define what their real definition of the sticking/mass accommodation coefficient is and what they believe the observed uptake is. There are several possible definitions. To make my point I like to recall various definitions as used in the literature.

1. **Surface accommodation coefficient (S_0) = probability of a molecule to hit a surface and leave it after a very short time without any memory of it incoming path (thermal desorption)**. This encounter with the interface may be very, very short, depending on the binding energy to the substrate (ns to s). According to this definition, the surface accommodation coefficient is often close to unity on liquids, but can be much less on solids. The surface accommodation coefficient separates those encounters with the surface, which result in thermal desorption from the pure scattering processes (time scale of ps). This definition is supported by molecular beam experiments which can actually distinguish between these two and also by MD simulations. Hanson [Hanson 1997] and many solid state physicists have called S0 sticking coefficient or also surface trapping coefficient.

2. The term **mass accommodation coefficient** and the symbol α have been used with different meanings. When describing condensation and growth of ice crystals, the mass accommodation coefficient or condensation coefficient α_c is used to describe the probability of a water molecule to stick on the ice surface within the framework of the Hertz-Knudsen equation (see for example [Pruppacher and Klett, 1997, p.164], or the work of Libbrecht, which is cited by DR). Here, the net flux jnet of water molecules during growth of the ice is given by matching condensation and evaporation fluxes: $j_{net} = \alpha n_g \omega/4 - \alpha n_{vap} \omega/4$ (with: α mass accommodation coefficient or condensation coefficient, n_g, concentration in the gas phase, ω mean thermal velocity, and n_{vap} is the concentration in the gas phase partial pressure equals the vapor pressure above the solid. Here I assume the accommodation coefficient equals the evaporation coefficient.

Now α is the probability of a water molecule which hits the surface to stick on the surface. This definition is of course somewhat ambiguous, as it does not tell how long the molecule should stay on the interface to be considered as 'being accommodated' and also does not tell where it is accommodated (is it only adsorbed on the surface? Is it dissolved into the bulk? Is it built in to the crystal matrix at upper crystal surface layer?). From a kinetic point of view, this definition of the 'quantity α' corresponds the sticking coefficient as defined above ([Hanson, 1997; Ammann, 2003]).

In contrast, α has been also used to describe the net flux of trace gas molecules onto a liquid in absence of diffusive transport limitations in the gas and liquid phase phase [Jayne, 1991; Hanson, 1997]. According to this nomenclature, the mass accommodation coefficient α is defined by the net flux onto the surface: $j_{net} = \alpha n_g \omega/4 = S_0 n_g \omega/4 - S_0 n_{vap} \omega/4$. The important issue is that the desorbing flux is now included into the definition of α. The uptake coefficient γ which is the experimentally measurable quantity, may be lower than the α, if diffusive transport limitations occur. Thus, uptake into liquids can be described as the series of surface accommodation (into an adsorbed state) and solvation at the interface (without diffusion) (Hanson, 1997; Ammann et al. 2003). Therefore, total mass accommodation may be formulated by the sum of the resistances associated with surface accommodation and solvation. In the present situation of HCl on ice, those HCl molecules, which made it into the bulk of ice must have passed through surface accommodation, solvation (equivalent to formation of a water shell?), and a further process to incorporate the HCl molecule into the solid ice, which is then rather an uptake coefficient as all these processes are associated with equilibria, and a net process is observed. The definition used in the paper should be explicitly given in the text. Given the extraordinary small value for the mass accommodation coefficient for HCl in the presented study, I suspect, that the measured HCl uptake coefficient by DR reflects several combined processes: sticking to the surface (Sticking coefficient S), the building into the ice crystal and may also be affected from the desorption of HCl from the ice surface during the ice growth.

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Thus, the mass accommodation coefficient, as used by DR might be given by this definition: mass accommodation coefficient= probability of an HCl molecule, which hits the surface to be build into the crystal after adsorbing on the interface. HCl molecules which adsorb on the surface and desorb without being taken up into the bulk of the growing ice are not considered as accommodated.

Within this definition there will be HCl adsorbing and desorbing from the surface, but only a small part of the adsorbed HCl will be build into the crystal during growth. Thus, the sticking coefficient S_0 (or α_s in the picture of the Hertz-Knudsen equation) may be close to unity, while the measured HCl uptake into the ice will much lower. This would be in accordance with the observation. It should be noted that Hynes et al. [Hynes et al. 2001] found in flow tube experiments a decreasing initial uptake coefficient of HCl on ice with rising temperature, which they explained by the increase of the HCl desorption from the ice surface. (Note that the α in Hynes *et al.* corresponds to the sticking coefficient S_0 of the Hanson/Jayne and Ammann formalism, and that γ in Hynes corresponds to α in the Jayne paper!).

The key question I like to pose to DR is: Which of the individual steps is the kinetically limiting one? Is the HCl uptake onto the ice during the growth so dominant that the evaporation of adsorbed HCl molecules can be neglected under the present conditions? Can the authors answer this question quantitatively? Again, only if the desorbing HCl fluxes are small compared to the adsorbing ones, the measured total HCl uptake into the ice would correspond to α_c as used in the Hertz-Knudsen equation (or as the sticking coefficient S in the framework as used by Hanson, Jayne or Ammann).

This may explain why the mass accommodation coefficient for HCl in a flow tube or Knudsen cell study is different from the one measured in the presented study. In a flow tube experiment, mass accommodation coefficients are derived from the very initial uptake onto fresh, unexposed ice (for example by considering only the initial part of the breakthrough curve in a flowtube experiment). Under these conditions, no HCl is adsorbed on the ice surface, thus there is no desorbing HCl, and the net flux of HCl onto

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the surface equals the first term in the Hertz-Knudsen equation (only then we have: $S = \alpha = \gamma$. However, this statement is only valid in absence of transport limitations by gas-phase diffusion in the flow system (see below), furthermore, at high HCl partial pressure surface saturation may occur at very short timescales. For example the bombardment rate for a trace gas at 10^{-6} Torr is roughly a monolayer per second, thus within a timescale of a second saturation effects may occur, which will affect already the very initial period of uptake experiments).

In summary, my request to the authors is:

1. The mass accommodation as used in the publication should be clearly defined and related to the various definitions used in previous studies. The authors might consider using a different symbol and name to make clear that their 'α' is not the one used in other studies, unless they can prove that no saturation effects on the surface limit the uptake of HCl onto the growing ice even at very fast growth rates. I suspect that they observe even at fats growth rates still a net uptake coefficient γ.

2. The kinetically limiting step in the uptake process of HCl onto the ice in the presented setup should be identified.

3. The possibility that desorbing HCl from the ice surface affects the experimental analysis should be discussed (quantitatively if possible).

The author's arguments for low mass accommodation coefficients of HCl on ice

I like also to comment on the authors arguments concerning the rather low mass accommodation coefficient for HCl.

The author's argument 1 (page 4725 lines 4-11):

The authors claim that the sticking coefficient of a gas does not have a universal value and argue that the sticking coefficient depends on the surface structure, defect density and the nature of the surface (basal or prismatic).

Comment:

To my understanding, this claim is a possible guess, which needs proof or citation. I'm not aware of a publication, which investigates this effect explicitly for HCl on ice. Without this, the statement is a speculation, which should be marked as such, e.g. by phrasing: “We speculate that the sticking coefficient dependsĚ. “ To the best of my knowledge, practically all previous studies find mass accommodation coefficients for HCl above 0.1. If there was a strong influence of the morphology on the mass accommodation coefficient, it should have been observed before. As these measurements have been performed on various, very different ices, the observed variation of the mass accommodation coefficients should reflect the influence of the morphology on the mass accommodation coefficient. Note that all this is related to the definition of the uptake observed here. May be DR just state that uptake *into* growing the ice is much slower than surface accommodation *onto* the ice observed in the other studies, and everything appears consistent?

One might argue that the mass accommodation coefficient is different during ice growth. I doubt this argument: HCl shows a strong affinity to any kind of ice. During growth the ice surface is renewed all the time, thus bombarding HCl molecules might even easier find sites for accommodation on the growing surface. If the hypothesis is that the mass accommodation coefficient of HCl is lower during growth was correct, it needs experimental or theoretical proof, which I cannot find (or which I have missed?) in presented paper.

The authors refer to the work of Libbrecht, who found rather low mass accommodation coefficients for water molecules during the growth of ice at temperatures of -5 and -40 °C. It is noteworthy that these data were taken under conditions of very slow ice growth, i.e. for supersaturation below 10 %, which is much lower than supersaturations retorted in the presented paper (above 10 % up to 80 %). The study of Libbrecht finds a rise of the mass accommodation coefficient toward higher ice growth rates, for his fastest growth rates he finds a mass accommodation coefficient in the order of 0.1

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and higher, as DR acknowledge themselves on p. 4726, line 19. This is much higher than a value of 1/1000, as suggested in the presented paper. Given the fact, that first growth rates in the presented paper are considerable higher than in the Libbrecht work and secondly the observed mass accommodation coefficient is expected to rise with supersaturation, I find the reference to the Libbrecht work not a convincing argument for the possibility of very low mass accommodation coefficients for HCl on ice. The Libbrecht work rather suggests that the mass accommodation coefficients should be high under the conditions in the presented study.

The author's argument 2 (p. 4725, line 21-26)

The authors note that the mass accommodation coefficient for water increases with increasing growth rate. They furthermore suggest that the mass accommodation of HCl may follow a different trend than the one for water molecules on ice.

Comment:

I cannot see any reason, why the trend should be reversed for HCl. Thus explicit arguments should be given, or this statement should be omitted, or clearly marked as pure speculation. In general, I think that in the whole first part of the results and discussion section (p.4724+4725), the authors rely very much on arguments based on the studies by Libbrecht, while giving less weight to other studies. To justify this weighting, arguments are needed why all other studies are of less importance. The Libbrecht study, might be just one example for other studies, which may show similar results. If this is so, this should be stated explicitly. See for example: J. Chem. Phys., 55, 3624-3635, (1971) citations therein, also see references in the Libbrecht work.

Suggestion: Transport limitation in experimental setup

The most severe objection I have to DR study is related to the issue of transport processes in the growth chamber itself. This objection may become obsolete, once the experiment is describe in better detail. I like to point out that I have already brought

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this point up in the initial review, which was requested prior to posting the paper on the web, hoping the authors would get a chance to comment in this issue in the posted version.

I think that the experimental setup in the presented paper, may underestimate the overall uptake of HCl on ice. To measure high uptake coefficients it must be ensured that the accommodation onto the surface is the kinetically limiting step. In the presented experimental setup, water and HCl are mixed with a carrier gas. This mixture is then flowed into the reactor, where the ice is condensed. The total gas pressure of the system is not given in the experimental description (It should be described in the revised version. I guess the pressure is one atmosphere?). If the experiment is performed at atmospheric pressure and the flow through the growth chamber is laminar, gas phase diffusion will limit the transport to the ice. Typically, in atmospheric pressure flowtubes, only very small mass accommodation (below 1/1000) can be observed. At pressures of one torr the limit is typically in the order of 0.1. It is noteworthy, that the Libbrecht measurements have been performed at pressures around 1-4 torr, to avoid transport limitations by gas phase diffusion.

Clearly, transport processes in the gas phase will affect also the comparison of the data with Eq. (3) in the paper and is thus relevant for the whole analysis. The issue of transport of both water and HCl towards the growing ice surface must be addressed thoroughly in a revised publication, including an error analysis. I think that a thorough discussion of this issue is a prerequisite for publication of this paper.

In summary, I think that the paper presents very interesting data and also treats a topic of major importance in the field of atmospheric science. However, it needs a major revision concerning the understanding of the uptake processes, which are involved in the experimental setup and on the ice surface. The data deserve a deeper analysis, otherwise the conclusion about the total amount of trace gas uptake into growing and the result for the mass accommodation coefficients are probably incorrect.

Minor comments:

p. 4724: line 26.

There are more studies for the determination of α_c for HCl on ice which should be cited. See for example: Hynes et al., GRL, 28, 14, p. 2827 (2001) and citations therein. Technical comments Citations: The citations are ordered alphabetically by name. Within names order should be chronologically, this is not done consistently. If the first author is the same, the ordering should be alphabetically by the second author's name (see for example the list of citations of various papers from the Dominé group.

In my printout, figure 1 is of very low quality.

Misspellings:

Page 4719: The authors name is Dominé and not Domine.

Page 4733, line 22: The authors name should read Brimblecombe and not Brimbelcombe.

Literature

[Ammann 2003] Ammann et al. Phys. Chem. Chem. Phys., 5, 351 (2003) [Hanson, 1997] Hanson, D.R., J. Phys. Chem. B, 101, 4998 (1997) [Hynes 2001] Hynes et al., Geophys. Res. Lett., 28, 14, 2827 (2001) [Jayne, 1991] Jayne et al., J. Phys. Chem., 95, 6369, (1991) [Pruppacher and Klett, 1997] Pruppacher and Klett: Microphysics of clouds and precipitation, Kluwer Academics, Dordrecht, The Netherlands (1997)

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 4719, 2004.

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