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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The rate of water vapor evaporation from ice substrates in the presence of HCl and HBr: Implications for the lifetime of atmospheric ice particles" *by* C. Delval et al.

Anonymous Referee #1

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General comments:

The paper by Delval et al. presents results of a careful experimental study investigating the decrease of ice evaporation rates by small amounts of HCl and HBr. The study nicely combines kinetic, interferometric, and FTIR techniques to measure kinetic parameters of condensation and evaporation and to comprehensively characterize the thickness and composition of the ice films. A mass spectrometric technique is applied to quantitatively analyse the dynamics of gas flows and uptake rates at low molecular concentrations. A nice feature is the combination of a static and steady state approach to independently evaluate evaporation and condensation rates for the same film samples. The implications of the present results for the atmosphere may be important

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(some previous studies carried out under conditions being more realistic for the atmosphere, e.g. by Diehl et al., Atm. Research 47, 235, 1998, also show a decrease of the evaporation rate after HCl exposure), but the conclusion drawn from the present study remain somewhat speculative. After some revisions discussed below the paper can be recommended for publication in ACP.

Specific comments and questions:

First I would like to comment on the film thickness also discussed in the review comment by P. Devlin and in the reply by the authors: As far as I understand, all experiments, at least the period of stirred flow conditions to measure the steady state pressure P_{ss}, have been started at a film thickness around $1\ \mu m$. I guess, the authors mean $1\ \mu m$ instead of $1\ mm$ in referring to Table 1 and Figure 9. Otherwise, something seems to be completely wrong here. The point of film thickness as well as related optical density and IR extinction need to be clarified by the authors.

The paper could be improved by giving more structure to the sections describing the experiments and results. Some statements are repeated several times, others are missing. After the description of the experimental setup including analytical techniques (there is some mismatch of analytical techniques, diagnostics and experimental strategies in *p.2183, l.8 to p.2184, l.18*) I recommend to clearly describe the subsequent steps of a typical experiment including all related processes and experimental techniques applied to get information about the kinetic parameters as well as film width and composition. This could include the discussion of both Figure 3 and 8 to get an idea about the processes controlling the experiment before presenting the experimental results.

It is not clear to me whether HCl deposition to the ice film occurs at static conditions (leak valve closed) or stirred flow conditions (leak valve open). In the first case it would not be able during each deposition step to control the dosage of HCl molecules as described on *p.2184, l.19 to p.2185, l.23*. In the latter case, starting the deposition at

$1\mu m$ film thickness, as stated in *p.2184, l.17*, should lead to complete film evaporation before the kinetic experiments could start. I guess, the dosing control is measured in different experiments or at thicker ice films. The experimental procedures should be described more clearly. Eq. 2 also needs to be clarified: if P is the HCl pressure as stated, P/RT would certainly not give the water concentration of H_2O.

I would also suggest to more clearly explain to the reader the physical nature and units of the evaporation and condensation rates, rate constants, and fluxes used in the manuscript. I assume, R_{ev} is defined as number of evaporating molecules per second and unit volume (or total reactor Volume?), whereas k_{cond} gives the total number of molecules condensing to the ice film per second and thus depends on the water partial pressure in the reactor. If so, the values of k_{cond} differs from each other in both formulas of eq. 4 which should be indicated by respective indices.

During the first reading I was misled by the assumption that evaporation of the pure ice film is lowered by a small amount (submonolayer coverage) of HCl molecules on the surface or a thin surface layer. A closer look to discussion of Figure 3 and, later in the manuscript, Figure 8, told me this is not the case, because poor ice below the doped layer is evaporating at almost the rate of ice without doping (period A to C in Figure 3, phase 1 in Figure 8, *p.2190, l.27 to 29*), and only a minor surface fraction with the mixture of H_2O/HCl is evaporating at significantly lower rates (also depending on the hydrate phase quite nicely analysed by FTIR). This should be clarified already in the abstract (please specify in *p.2180, l.17* the acid concentration or hydrate phase) and before discussing the results of the kinetic experiments (Figures 4 to 7).

In Figures 6 and 7 it would be nice to add at least an estimated uncertainty to get an idea whether the dependence of J_{ev} on the number of HCl and HBr molecules in the ice film is significant. Again please clearly specify, if possible, whether the acid molecules are adsorbed to the surface or not. Because the kinetic results, as far as I understand, critically depend on the steady state pressure P_{ss} measured between points D and E in Figure 3. I suggest to add the measured P_{ss} to Figure 3, which could simplify the discussion. For comparison, it could be added to Table 2 the net evaporation rate obtained from the kinetic and interferometric measurements, at least for pure ice films. Is it possible to translate these numbers, measured under molecular flow conditions, to a typical atmospheric situation at a given temperature and relative humidity?

In the discussion (*p.2198, l.11 to 17*), the authors argue in comparison to effects of NAT layers, that adsorbed acid layers may have similar effects. This seems to be somehow speculative, because the present results show, as far as I understand, that a thin surface layer containing small amounts of HCl or HBr has almost no effect on the evaporation rate of pure ice below. Do the authors think the polar stratosphere or the upper troposphere contains enough HCl or HBr to dope significant ice volume fractions at high enough mole fractions to affect the evaporation rates?

It is stated several times in the manuscript that the Si window is the coldest part of the reactor volume. Please specify the temperatures of e.g. the PTFE thermal insulation on the cold finger or other surfaces to convince the reader that adsorption or desorption effects can be neglected during the experiments.

There is a mismatch of pressure units $mbar$ and $Torr$ in the manuscript. Please use $mbar$ or hPa throughout the whole paper. The paper should also be checked for consistency with respect to the mathematical symbols, fonts used for units and formula, and citation rules.

Minor comments and technical corrections:

p.180, l.25: Wennberg et al., 1996 or 1997?

p.2182, l.3 to 7: If temperatures below $220\ K$ are of interest I do not understand the argument why the temperature range was extended to $240\ K$.

p.2182, l.14: Please explain why two different volumes were used.

p.2182, l.23: ... $100 \leq T/K \leq 250$ ...?

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p.2183, l.13 and l.20: The pressure sensor should either be $1\ hPa$ or $1\ Torr$ full scale.

p.2183, l.22 to 29: Please specify the spectral resolution of the FTIR and its sensitivity to film thickness and composition.

p.2184, l.3: In such a configuration . . . : Please specify what configuration or give reference.

p.2184, l.14: Density unit is missing.

p.2186, l.20: . . . known amounts of HX (X=Cl or Br): In *p.2186, l.12 to 16*, it was stated the only upper limits of HBr can be given!

p.2188, l.11 to 14: When was steady state reached for pure ice films?

p.2189, l.10: . . . the rate constant for condensation, k_{cond} . . . : so far k_{cond} was termed "Condensation rate".

p.2191, l.22: 35 s.

p.2193, l.25: I did not find Kroes et al., 1992 in the list of references.

p.2194, l.10: consistent.

p.2198, l.5: References?

p.2198, l.6: Complete citation Deshler et al.

p.2204, l.26: I didn't find citation of Zondlo et al., 1998 in the text.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 2179, 2003.