

Interactive comment on “Heterogeneous Kinetics of H₂O, HNO₃ and HCl on HNO₃ hydrates (α -NAT, β -NAT, NAD) in the range 175–200 K” by Riccardo Iannarelli and Michel J. Rossi

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General Comments:

Q- However, the organization and motivation needs to be made clearer, both in the introduction and in the atmospheric implications. Both sections read like a “data dump” with little explanation to identify the key discrepancies or limitations in the literature. Why are the authors conducting this study, 20+ years after some of the initial studies were conducted?

A- Referee 2 raises an important point: Why unfold the glory of heterogeneous chemistry once more (or once and for all?) after 20 years of (waning) interest? It may have

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escaped the attention of Referee 2 that we report unique kinetic data secured by a consistency check (called thermochemical kinetics by the late S.W. Benson). There are NO available data in the literature on absolute rates of evaporation, not only for ice, but also for ices contaminated to various degrees by atmospheric trace gases. These data determine the evaporative lifetimes of various ice particles thought to be important in the UT/LS, and we have introduced a synoptic Table (Table 5 in the Discussion Section) in order to demonstrate the usefulness and the atmospheric importance of the kinetic data. Needless to say that we have made the point that in most cases the evaporative lifetimes enable heterogeneous processing to occur in a realistic time frame.

Why have 20 years gone by before coming forth with such seemingly important and useful data? The answer to this is multifactorial. It also has to do with the multidagnostic capabilities of the present instrument that we have built up since 2003 in order to correct for the shortcomings of other experiments (Hanson and Ravishankara – single diagnostics flow tubes; Tolbert and coworkers – spectroscopy in chamber experiments, essentially w/o kinetics capabilities, Aerodyne group Chuck Kolb and Doug Worsnop performing single diagnostic equilibrium experiments for constructing phase diagrams, etc.). We have built an instrument with a decisive improvement in that it provides a unique spot of lowest temperature in a Stirred Flow Reactor w/o extraneous and uncontrolled cold spots that would perturb the reaction kinetics (through condensation of molecule of interest on an unidentified cold spot rather than on an optical support (FTIR, FTRAS, Quartz Crystal MicroBalance (QCMB), optical (HeNe) interferometry, etc.). We believe that the present measurements reveal hitherto unknown kinetic data at an unprecedented level of detail that are checked for mutual consistency by comparing the calculated equilibrium vapor pressure with known literature values.

The Introduction has been curtailed a bit in order to concentrate on the issues at hand. On the other hand, the paper has to be useful also for the non-specialist by providing at least the rudiments of a suitable atmospheric context. The impression of a “data dump”

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is not wrong, except that it is sometimes unavoidable. We have made every effort to “lighten up” the text accordingly. Suffice it to say that we are proud and lucky to be able to present a manifold of hopefully useful data to the scientific community. More often than not papers seem to contain less than meets the eye, we think that we are in the contrary position of “more than meets the eye”!

Q- Instead, the intro leads with a nice (but unnecessary) review of general PSC chemistry, something that is now several decades old and the overview of which is not necessary.

A- See above paragraph in relation to presenting a self-contained account of atmospheric context.

Q- The atmospheric implications section goes on a tangent (incorrectly, at that) on water vapor measurement instruments that really aren't related to the current study results. Both of these aspects distract the reader from the high-quality, laboratory study and their results. While this paper will be eventually publishable, it requires some significant revisions in its current form.

We are heeding the advice of Referee 2 and have cut 90% of the material covering the Cryogenic Mirror Hygrometer. The only thing left is a brief description of the experiments of Gao et al. (2016) and the ramifications of the kinetic results of the present study.

Detailed (key) Points:

Q- Lines 56-129: a review of PSC chemistry has been common knowledge for decades; this section reads like a review article and is not necessary for the manuscript; indeed, it distracts from the critical questions that this study is trying to examine

A- In the interest of presenting a self-contained story we decided to keep this part in the Introduction.

Q- Lines 130-157: While this is a thorough review of the literature, it reads to some

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extent like a “data dump”. The experiments were done under different conditions to some extent. Are there real discrepancies between these results? Perhaps a table of past literature and your results would be more clear/helpful. At the very least, one should summarize the point of this section: e.g. there are discrepancies, there may or may not, too hard to say given the different experimental conditions, etc. and whatever it is, this is the motivation for our study! As written, the reader is left to search through a lot of data with no clear idea on whether there is true disagreement or not. And then explicitly tell what aspect of the study will your work address in this regard.

A- We have summarized the planned experiments in lines 152-169 by emphasizing at the end the thermochemical as well as the mass balance aspect which are the two novel aspects that make our measurements unique. On the other hand, we have refrained from evaluating the disparate kinetic results in the literature mentioned briefly on lines 116-149 that collect all relevant literature results to date. It is incumbent on reviews such as JPL and IUPAC rather than on original research papers to evaluate kinetic results of atmospheric importance.

TXT- In addition, all experiments have been performed under strict mass balance control by considering how many molecules of HNO₃, HCl and H₂O were present in the gas vs. the condensed phase (including the vessel walls) at any given time. These experiments have been described by Iannarelli and Rossi (2015). Most importantly, the consistency of the accommodation and evaporation kinetics has been checked using the method of thermochemical kinetics (Benson, 1976) by calculating the equilibrium vapor pressure and comparing it with values of published phase diagrams. In addition, the present work is the first to present absolute rates of evaporation of all involved constituents (H₂O, HNO₃, HCl) thus enabling predictions on evaporative lifetimes of ice particles under atmospheric conditions.

Q- Paragraph 158-163: Now suddenly the authors switch their literature review to HNO₃ on pure ice. Only the last two sentences of this paragraph seem relevant to the work, at least for the introduction. And even then, there should be a transitional

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statement such as “The complications/discrepancies of HNO₃ and H₂O uptake on NAT surfaces is also evident when examining HCl uptake on NAT.” or similar.

A- As you guess the single component uptake kinetics of HCl and HNO₃ on pure ice are also important when discussing uptake on binary chemical systems such as HNO₃/H₂O (this work) or HCl/H₂O (Iannarelli and Rossi, 2013).

TXT- In the investigation of the properties of binary chemical systems the behavior of the simple single-component systems is an important stepping stone.

Q- Line 192+: The authors mention that the inlet system was modified but then failed to even provide a brief sentence or two on the actual modification. If it is important to mention at the start, please briefly summarize the modification.

A- Done

TXT- We therefore minimized the volume of the admission system and only retained the absolutely necessary total pressure gauge for measuring the absolute inlet flow rate (molecule s⁻¹).

Q- Line 222-224: Not entirely an apples-to-apples comparison. The RAIR study was most sensitive to very thin films (< 10s-100 nm) and the very near surface properties. At thicker films and higher dose rates, they observed similar results as past studies and even the current study in the manuscript. The technique in the manuscript most likely was not sensitive to the presence of very thin films that were observed in the RAIR study.

A- We intended from the outset to avoid thick films owing to kinetic complications. Very often thin films occur as islands on the substrate or on the ice film such that the kinetics are ill-defined. Therefore, we chose to study the binary systems as thick films using the absorption cross sections that we have measured on thick films.

Q- Line 236-239: This is one of my main concerns experimentally about the study. The excess ice, even if it stabilizes NAT, will impact the vapor pressures of water inside the

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chamber. Is one always on the ice-NAT phase line? If not, to what extent does each phase determine the partial pressure of water observed in the chamber? This has implications for the later results for the accuracy of H₂O partial/vapor pressures and H₂O kinetics. Why not just make a pure NAT film like to past thin film studies? NAT is a pretty stable film to make. The excess ice phase present needs to be discussed in more detail and a logical, reasoned argument why it doesn't complicate the interpretation of the results (or to what extent it does).

A-Figure 2 (introduced as supplemental Figure S5 into the SI section) presents a phase diagram of the binary system HNO₃/H₂O. According to Gibb's Phase Rule we have two components and three phases leading to a single degree of freedom. The dashed lines are isotherms, and as long you keep T constant you see that the equilibrium vapor pressure P_{vap} of H₂O or HNO₃ change within one and 3.5 orders of magnitude, respectively, depending on the composition (mass) of both solid phases, either H₂O or HNO₃ rich. The symbols (red for alpha-, black for beta-NAT) represent experiments characterized by a given value of PHNO₃ and PH₂O depending on the evaporation history of the ice sample. You also see the parameter space for the polar lower stratosphere and the number of points falling into the corresponding phase space of NAT. Riding the coexistence line is only interesting for the construction of the phase diagram in case it is not known. From Figure 2 you can read off both H₂O and HNO₃ vapor pressures and conclude that the present experiments are indeed relevant for the UT/LS as far as the vapor pressures are concerned (see your question below).

INSERT Figure 2

Figure 2: Phase diagram for the HNO₃/H₂O system in the range of atmospheric interest. The phase diagram is taken from Chapter 2 “The Probable Role of Stratospheric “Ice” Clouds: Heterogeneous Chemistry of the “Ozone Hole” by M.J. Molina, “The Chemistry of the Atmosphere: Its Impact on Global Change”, J. Calvert (ed.), IUPAC Chemravn 21 Series, Blackwell Scientific Publications.

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Q- Lines 624-633: Report the entropies of evaporation as well – do they make sense with physical principles? If not, why? And elsewhere in the manuscript.

A- Taking $\exp(\Delta S_{0ev}/2.303R) = 10(13.8)$ after conversion from Torr into an atmosphere we obtain $\Delta S_{0ev} = 264.6 \text{ J K}^{-1} \text{ mol}^{-1}$ or $63.25 \text{ cal K}^{-1} \text{ mol}^{-1}$. If we make the assumption that all H₂O comes from NAT we have to divide by three owing to the fact that the decomposition of the trihydrate liberates three moles of H₂O. We therefore have a value of $0.333 \times 63.25 \text{ cal K}^{-1} \text{ mol}^{-1}$ or $21.1 \text{ cal K}^{-1} \text{ mol}^{-1}$ which exactly corresponds to Trouton's rule. However, this may just be fortuitous, also because we have a multicomponent system with several phases, each with its own thermodynamic parameters as we have to contend with the T-dependence of the combined system. The reason we are not discussing entropies of vaporization in this context is that the temperature range over which the measurements were taken is too small to obtain a reliable intercept, or in other words, the extrapolation of $1/T \Rightarrow 0.0$ is too uncertain given the measurement range. This uncertainty owing to extrapolation is much larger than any potential effects of hydrogen bonding of H₂O, HNO₃ or HCl which is known to affect Trouton's rule (towards an increase of Trouton's constant).

Q- Line 660-661: Could a similar explanation be used to invoke discrepancies between your results and those in the literature (JPL recommendations)?

A- We are not sure about your question. Which discrepancies and which JPL recommendations?

Q- Line 681: Can the absolute value of 12 kJ/mole be explained physically in terms of hydrogen bonds? Why or why not?

A- From the point of view of the numerical value 12 kJ/mole is approximately $1/3$ to $1/4$ of a "normal" hydrogen bond. However, this single value is difficult to interpret in the absence of other supporting values. However, we feel that it is related to the fact that α -NAT is not the most stable form of NAT. This primarily concerns the arrangement of H₂O in the lattice which becomes tighter in β -NAT and therefore stabilizes the solid

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hydrate.

Q- Line 686-7: Warshawsky et al. GRL 1999 also quantified this process of a sealing NAT layer slowing ice evaporation, and these were done at much lower HNO₃ partial pressures than in the Biermann et al. study. Related to this, what are the partial pressures of HNO₃ used in these experiments? Are they relevant to the atmosphere at all? They seem like they were much higher than what is expected in the atmosphere based upon the discussion and comparison to other laboratory studies. Please cite the HNO₃ partial pressures used in these experiments.

A- Please see above in conjunction with the binary phase diagram displayed in Figure 2 and/or Figure S5. We would like to affirm that the present conditions indeed are relevant to the UT/LS atmosphere as indicated in Figure 2 above by the symbols. Thank you for the Warshawsky citation that I routinely take from Maggie Tolbert's review article in Annual Rev. Phys. Chem.

TXT- Rev(H₂O) on both α -NAT and β -NAT is smaller compared to Rev(H₂O) on pure ice. This is in agreement with the results of Tolbert and Middlebrook (1990), Middlebrook et al. (1996), Warshawsky et al. (1999) and Delval and Rossi (2005) who showed that ice coated with a number of molecular layers of NAT evaporates H₂O at a slower rate than pure ice. On the other hand, our results are in contrast with the findings of Biermann et al. (1998) who report that no significant decrease of the H₂O evaporation rate was observed in HNO₃-doped ice films. The discrepancy may possibly be caused by the high total pressure of 0.85 mbar in their reactor compared to all other competitive studies cited above that use high-vacuum chambers with total pressures lower by typically a factor of 500 or more. It is very likely that the experiments performed by Biermann et al. (1998) were not sensitive to changes in evaporation rates despite the fact that both the HNO₃ and H₂O concentrations used as well as the thickness of the accumulated NAT layers in their no. 5 experiment were of the same magnitude as in the competing studies. A hint to that effect is the unexpected time dependence of the ice evaporation rate in Biermann et al. (1998) that shows an induction

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time of 30 minutes as opposed to the expected linear decrease from the beginning of evaporation (see below). We are unable to attribute the source of the measured H₂O vapor in the presence of two H₂O-containing solid phases in our chemical system, namely pure H₂O ice and NAT. We restate that the partial pressures at constant temperature are controlled by the (relative) composition of the system in agreement with the single degree of freedom resulting from Gibb's Phase Rule and the data displayed in the binary HNO₃/H₂O phase diagrams displayed in Figures 3, 5 and S5.

Q- Atmospheric implications: There is a data dump of numbers here once again, many of which were already described in detail in the discussion section. What are the key points, circling back to the motivation in the introduction and past literature experiments? e.g. Does the JPL kinetic data need to be revised (as suggested in the discussion in several places)? What are the implications of these much different values? How has this study broadened the range of past studies or explained potential discrepancies or unanswered questions in the past literature? What future research is needed? etc.

A- Many of the questions raised by Referee 2 for the "Conclusions and Atmospheric Implications" Section (5) are out of scope for a publication providing fundamental kinetics and thermodynamic data. We are unable to tackle all the suggested questions and do not see it as our task to provide evaluations of rate data on behalf of the JPL or IUPAC panels because this activity is built on consensus. We are happy to provide the best available answers surrounding the HNO₃ hydrates to date. However, we have added Table 5 that is a vivid example and illustration of the usefulness of the obtained data in an atmospheric context, namely absolute rates of evaporation.

TXT- A look at Table 5 reveals evaporative lifetimes of various ice particles with respect to H₂O evaporation. Equation (26) and (27) present the rudiments of a very simple layer-by-layer molecular model used to estimate evaporation lifetimes (θ_{tot}) at atmospheric conditions (Alcala et al., 2002; Chiesa and Rossi, 2013): $\theta_{tot} = (r/a)NML/Jevrh$ (26) $Jevrh = Jevmax(1-rh/100)$ (27) with r , a , rh and NML being the radius of the ice

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particle, shell thickness, relative humidity in % and the number of molecules cm⁻² corresponding to one monolayer. $Jevrh$ and $Jevmax$ are the evaporation fluxes of H₂O at rh and $rh = 0$, the latter corresponding to the maximum value of Jev which we calculate following Equation (2) or (8). The salient feature of this simple evaporation model is the linear rate of change of the radius or diameter of the particle, a well- and widely known fact in aerosol physics in which the shrinking or growing size (diameter) of an aerosol particle is linear with time if the rate of evaporation is zero order, that is independent of a concentration term. Table 5 lists the evaporation life times which are not defined in terms of an e-folding time when dealing with first-order processes. In this example the lifetime is the time span between the cradle and death of the particle, this means from a given diameter $2r$ and "death" at $2r = 0$. The chosen atmospheric conditions correspond to 190 K, $rh = 80\%$, $a = 2.5 \text{ \AA}$ for H₂O and 3.35 \AA for all other systems, $r = 10 \text{ micro m}$ and estimated values 6×10^{14} , 3×10^{14} and $1 \times 10^{15} \text{ molec cm}^{-2}$ for NML of HNO₃, HCl and H₂O. It is immediately apparent that there is a large variation of θ_{tot} values for atmospherically relevant conditions which goes into the direction of increasing opportunities for heterogeneous interaction with atmospheric trace gases, even for pure ice (PSC type II). Table 5 is concerned with the most volatile component, namely H₂O. If we now turn our attention to the least volatile component such as HNO₃ in beta-NAT we obtain $\theta_{tot} = 5.1 \text{ d}$ and 33.9 d for 0 and 85% HNO₃ atmospheric saturation, the former being the maximum possible evaporation rate for 0% HNO₃ saturation. The other boundary conditions are 190 K, polar upper tropospheric conditions at 11 km altitude (226.3 mb at 210 K), 1 ppb HNO₃, 10 ppm H₂O corresponding to 85% HNO₃ saturation. This goes to show that laboratory experiments on gas-condensed phase exchange of lower volatility components in atmospheric hydrates are fraught with complications. It follows as a corollary that both HCl, but especially HNO₃ contamination of H₂O ice is bound to persist for all practical atmospheric conditions.

Q- Also, the discussion on NAT-coated ice impacting field measurements is speculative, unsupported, and shows several large gaps of awareness in UTLS water vapor measurements. First, the authors cite the problems of "reliable and reproducible mea-

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surements” of water vapor in the field UTLS measurements. However, as noted above, I have serious questions on how one can reliably interpret the accuracy of the water vapor measurements in their laboratory setup given that two phases exist at conditions well off the ice/NAT equilibrium line (and higher HNO₃ partial pressures than usually exist in the UTLS) – so it isn’t clear to me how these laboratory results are that representative of the UTLS itself. Second, the CU/NOAA chilled mirror hygrometer has a long measurement history and is best described most recently by the Vömel et al. JGR, 2007 and/or Vömel et al., AMTD, 2016. More importantly, it compared extremely well in recent intercomparison campaigns to the reference standard (see Fahey et al. AMT 2014), an instrument/technique that probably is (in this reviewers’ opinion) the most accurate/uncertainty-documented H₂O measurement in the community. Third, HNO₃ has not been shown in the NOAA tests to impact the frost layer (ice vapor pressure) at relevant HNO₃ concentrations (Thornberry et al., AMT 2011). Fourth, there are numerous diode laser-based hygrometers by many leading groups in the world; in fact, I would argue the NOAA TDL is one of the most recent and, though promising and a quality measurement, has some of the least amount of field data to characterize its strengths and weaknesses. More recent AquaVIT2 UT/LS water vapor intercomparisons showed some improved agreement in general from most of the UTLS hygrometers, whether diode laser-based at any wavelength (1.3, 1.4, 2.6 microns), laser-induced fluorescence, chilled mirrors, or other techniques. Therefore, I’m not sure the authors’ results are applicable to explaining whether or not an instrument may work with the limited knowledge of the measurement instruments themselves and better agreement now being observed. This is especially true since the manuscript’s lab results appear to be at HNO₃ concentrations/thicknesses well above what is possible in the UTLS. The Gao et al. 2016 JPC-A dealt with very small amounts of residual HNO₃ within ice and not related to thick NAT coatings here. For all of these reasons, I suggest removing these paragraphs on H₂O measurements and expanding on the kinetics and the implications thereof/discrepancies.

A- First we agree with Referee 2 that we are in no way specialists in the question of
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H₂O vapor measurements under UT/LS conditions. We therefore take out this section entirely and only mention the Gao et al. (2016) measurements at the very end as they directly relate to the present kinetic results inasmuch as the persistence of the lower volatility components in ice, namely HNO₃, is concerned. We are a bit surprised at the explicit reaction of Referee 2 concerning the atmospheric relevance of the present study. We resolutely take exception to his statements to be “well off the ice/NAT equilibrium line (and higher HNO₃ partial pressures than usually exist in the UTLS)”. Figure 2 (S5 in the SI Section) clearly points out that (1) the UT/LS conditions are in the middle, not the limits of the NAT existence area within the relevant phase diagram, and that (2) the HNO₃ partial pressure are not higher than usually exist in the UT/LS region. If anything, they are a bit lower because we have emphasized lower temperatures. In addition, we assert in contrast to Referee 2 that the NAT layers, typically 300 nm or less thick in the present study, are well representative of “what is possible in the UTLS”! In the end we consider it wise to continue to question measurement concepts for field applications using fundamental research instruments and methods. It is incumbent on us active in the laboratory to alert field scientists to possible shortcomings and artifacts of routinely applied methods and techniques used in the field.

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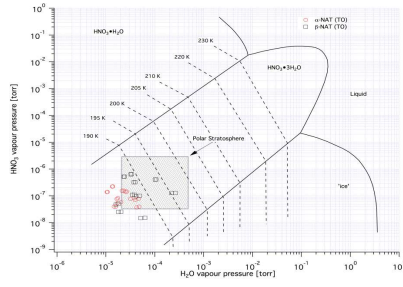


Figure 2 (for Answers to Referee 2)

Fig. 1.

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