

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

Anonymous Referee #2

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Review of Iannarelli and Michel J. Rossi, ACPD

Overall: This laboratory study examines the kinetics of water vapor, nitric acid, and hydrochloric acid on nitric acid trihydrate films using two different approaches to examine surface chemistry. There are some discrepancies or incomplete datasets in the literature, and the strength of this study is the range and complementary techniques in which were used to study the kinetics. Overall, I find the experiments to be well conducted (with one exception, noted below). 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 af-

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ter some of the initial studies were conducted? 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. 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.

Key points: 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.

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

Paragraph 158-162: 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 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

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.

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Line 222-224: Not entirely an apples-to-apples comparison. The RAIR study was most sensitive to very thin films ($< 10\text{s-}100\text{ nm}$) 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.

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 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 H_2O partial/vapor pressures and H_2O 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).

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.

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

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

Line 686-7: Warshawsky et al. GRL 1999 also quantified this process of a sealing NAT layer slowing ice evaporation, and these were done a much lower HNO_3 partial pressures than in the Biermann et al. study. Related to this, what are the partial pressures of HNO_3 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

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HNO₃ partial pressures used in these experiments.

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.

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 measurements” 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

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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.

Syntax/grammar/minor points: Line 135: don't need "respectively"

Line 436: A possible reason (singular)

[Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-247, 2016.](#)

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