

## ***Interactive comment on “Evaluation of the accuracy of thermal dissociation CRDS and LIF techniques for atmospheric measurement of reactive nitrogen species” by Caroline C. Womack et al.***

### **Anonymous Referee #1**

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Womack et al. present an interesting set of experimental data on the efficiency of conversion of various NO<sub>y</sub> species into NO<sub>2</sub> in TD-inlets as used in CRD and LIF based detectors of e.g. organic nitrates or HNO<sub>3</sub>. The authors have backed up the experimental data with a chemical model which is reasonably successful in reproducing the thermograms they measure. They examined HNO<sub>3</sub>, NH<sub>3</sub> and ammonium nitrate conversion with added trace constituents such as H<sub>2</sub>O or CO or hydrocarbons. What they did NOT do was to examine the efficiency of conversion of mixtures of NO<sub>y</sub> such as HNO<sub>3</sub> in the presence of organic nitrates, NO and NO<sub>2</sub> as will always be the case in ambient air. I appreciate that the experiments are already complex and adding further

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NO<sub>x</sub> containing trace gases components is not trivial. However, the extrapolation of these results to sampling real air needs to be considered. If the authors choose not to do further experiments, it would be interesting to at least predict what the effect of various levels of NO<sub>2</sub> would be on the shape of e.g. the HNO<sub>3</sub> thermogram (if any). For example, would addition of NO or NO<sub>2</sub> change the NH<sub>3</sub> / O<sub>3</sub> thermogram (both NO and NO<sub>2</sub> might react with the NH<sub>2</sub> radical etc etc).

The authors may consider the following specific comments and questions when revising their manuscript.

P2L25 Methods that detect some individual components of NO<sub>y</sub> are listed. How were they selected? Why not include e.g. NO<sub>3</sub> or HONO etc. ....

P3L24 “For example, TD-LIF detects NO<sub>2</sub> at low pressure following thermal dissociation, which minimizes secondary recombination reactions of the dissociated radicals”. Are TD-LIF instruments always operated with the oven at low pressure which would minimise the recombination by reduction of reaction time and rate coefficient?

P3L29 “TD-CRDS is an absolute measurement. ....” Does TD-CRDS being based on a cross-section of NO<sub>2</sub> really make it absolute? As stated later in the manuscript, the effective optical path-length needs to be calibrated by adding known amounts of NO<sub>2</sub>. Also, the TD-inlet is part of the instrument and its dissociation efficiency needs to be calibrated (the subject of this paper).

P4L3 “though this reaction rate depends on the TD inlet pressure and flow rate”. What reaction rate is this referring to (NO + O<sub>3</sub> makes NO<sub>2</sub> but O + NO<sub>2</sub> or NO does not)?

P4L10 “Thieser et al. (2016) parameterized the bias in peroxyacetyl nitrate and 2-propyl nitrate detection in their inlet as a function of ambient NO and NO<sub>2</sub> concentrations, but noted that these parameterizations may vary for other PNs or ANs. These effects are generally considered minor compared to other uncertainties in the measurement”. Is this true? In some TD-instruments, depending on operating temperature, the

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effects of radical recombination ( $\text{RO}_2 + \text{NO}_2$ ) or oxidation of NO ( $\text{RO}_2 + \text{NO}$ ) can bias the detection of peroxy nitrates by factors of 2 or more and is likely the biggest source of uncertainty.

P6L11 Does the temperature probe measure the gas-temperature or the temperature of the inner wall of the quartz tube ? Can there be different due to gradients from the centre of the tube to the wall ?

P6L17 Does addition of 30 ppmv  $\text{O}_3$  have any adverse effects ? Can e.g. ozonolysis of biogenics take place in this volume ? Might this form particles or radicals (Criegees) than can react with  $\text{NO}_2$  ?

P8L7 “A custom-built iodide adduct chemical ionization mass spectrometer (Lee et al., 2014), described in further detail in (Veres et al., 2015), was used to monitor the  $\text{N}_2\text{O}_5$  and  $\text{HNO}_3$  concentrations” How was the CIMS calibrated ? How accurate are the concentration measurements ?

P8L25 What is the pressure in the Berkeley oven? What are the standard operating conditions for this instrument. I believe it has been operated using different pressure configurations.

P8L16 The modelling of this system is not trivial. As the authors state, many rate constants have not been measured at the higher temperatures. Secondly, the authors do not consider surface catalysed thermal decomposition, which is important as the authors mention briefly later when discussing the low temperature  $\text{NO}_y$  instruments with catalytic conversion at the metal surfaces. The wall losses of radicals is probably the biggest uncertainty and can only be assessed by variation of experimental parameters. Thieser et al. 2016 showed that variation of the concentration of the organic nitrates they were using (and thus variation of the  $\text{RO}_2$  concentration) affected the loss rate, which could then be explained using a Langmuir-Hinshelwood type expression. Did you change the concentration (e.g. of  $\text{HNO}_3$ ) significantly to see if the same wall loss rate constant was appropriate ? Do you expect the rate constant for wall loss to be

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independent of temperature (effects of diffusion, turbulent mixing) ?

P9L23 was the  $\text{HNO}_3$  input mixing ratio based on the permeation source or the CIMS signal ?

P9L31 ...”possible due to recombination reactions. . . . .” Which ones ? Be specific.

P10L8 High and low pressure limits have been used to calculate the thermal dissociation rate constant for  $\text{HNO}_3$ . What value for  $F_c$  was used to calculate the rate coefficient at 500 °C. Also, Glänzer and Troe did their study in Argon. Are the results applicable for air (what is the relative collisional stabilisation efficiency) ?

P10 L13 “. . .the recombination rate for  $\text{OH} + \text{NO}_2$  is quite low. . . .” Be quantitative. What is the rate coefficient at this temperature and what is the pseudo-first order rate coefficient for recombination for a given  $\text{NO}_2$  level of e.g. 10 ppbv. This can then be compared to the wall loss rate coefficient.

P10L27 Did Sobanski et al. (2016) also present a decomposition efficiency for  $\text{HNO}_3$  ? Are the results comparable? Note that Sobanski et al used a radical scavenger with a large surface to reduce radical recombination in the heated inlet.

P11L9 “. . . the onset and final conversion of  $\text{HNO}_3$  are not strongly sensitive to pressure”. Is this because wall losses are invariant with pressure ? is the conclusion that wall losses are so large that recombination never compete ? What if the sample contains not only  $\text{HNO}_3$  but also  $\text{NO}_2$  to increase the rate of re-formation of  $\text{HNO}_3$  ? The authors should consider doing one such experiment to see if elevated  $\text{NO}_2$  will influence the shape of the  $\text{HNO}_3$  thermogram. The same applies to the  $\text{NH}_3$  experiments.

P11L26 This sentence implies that the modelling done in this study (which considers gas-phase processes only) is only a partial representation of the chemistry going on. As mentioned above, the sensitivity  $\text{HNO}_3$  detection while adding  $\text{NO}_2$  would have been useful to confirm that the simple model reproduces the thermograms for the right reasons.

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P12L11 The data shows that the VOCs added had no effect. Not surprising considering their bond-dissociation energies. It would have been more informative to have added VOCs that will decompose, especially organic nitrates as they result in more complex radical chemistry and NO<sub>x</sub>.

P12L17 "...The oven is set at sufficiently high temperatures to dissociate ANs and PNs back to NO<sub>2</sub> + the organic radical" Not true. At higher temperatures the RO<sub>2</sub> formed from thermal dissociation of PNs is unstable (see Thieser et al. 2016).

P12L27 "...The dominant reaction of O<sub>3</sub> in the model is the reaction with NO<sub>2</sub> to make NO<sub>3</sub>..." Is this true? I would have thought the pyrolysis will dominate at high temperatures. Is the O<sub>3</sub> pyrolysis rate constant in the model correct? What is the O-to-O<sub>3</sub> ratio at thermal and kinetic equilibrium?

P12L30 The reaction between O and NO<sub>2</sub> does not form much NO<sub>3</sub> but mainly NO + O<sub>2</sub>. This is especially true at high temperatures.

P13L5 That a model with no surface-catalysed reactions cannot reproduce the effect of a surface catalysed reaction is not surprising. Why do NO<sub>y</sub> instruments with e.g. gold-surfaces see decomposition at much lower temperature than needed to break the HO-NO<sub>2</sub> bond and why do they add CO? It is more than "possible" that surface reactions play a role, it is rather clear.

P16L25 Are there any other reactions of NH<sub>2</sub> that should be considered. Could it react with NO or NO<sub>2</sub>?

P17L6. "However, even this rudimentary simulation predicts the general shape of the experimental data..." What aspect of the "general shape" does it reproduce?. Perhaps you can be more concise here.

P18L3 "ambient levels of a group of representative VOCs". As already mentioned, addition of VOCs that are unstable at the inlet temperatures (organic nitrates) would have been more informative.

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P18L23 "... N<sub>2</sub>O<sub>5</sub> is not typically considered in the TD-NO<sub>2</sub> instrument literature because the existing instruments have largely operated in the daytime..." Perhaps this statement is too general. Some instruments measure day and night and have considered effects of N<sub>2</sub>O<sub>5</sub> thermal decomposition (e.g. Thieser et al. 2016)

P18L32 "...These results demonstrate that the volatile portion of the particulate nitrates will be driven into the gas phase at low oven temperatures..." Particulate nitrate is not only ammonium nitrate but has a large component of organic nitrates. At which efficiency will these be detected?

Technical / typographical

P2L20 Techniques that detect the major individual components of NO<sub>y</sub> include detection...

P4L1/3 negative / positive artefact = negative / positive bias?

P5L4 Inappropriate reference. Fuchs et al were not the first to use CRDS for atmospheric trace gases as this implies.

P5L18 "light decays"?

P5L23 "known NO<sub>2</sub> concentrations". How were they determined? Was an "absolute method" used to measure the NO<sub>2</sub> concentration?

P7L22 "bubbling the dilution zero air through a water bubbler..."

P8L31 and at several other places in the manuscript. "rate laws" is the wrong term. You refer to "rate constants" or "rate expressions".

References: Several have capitalised manuscript titles. Nikitas et al spelling of Detector.

Figure captions: Figure 1: "Instrument schematic of the TD-CRDS instrument" "cool down" (sometimes cooldown" maybe you can find a better expression than "cool down region".

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Figure 3: small dashed line = short dashed line ? Figure 4 "physical oven" ?? Figure 7 "in solid circles" = "as solid circles" ? Figure 8 "shown as red circles" Figure 9 delete preferentially.

Supplementary Info: Caption to Fig. S4. "...but if allowed to recombine, only ~40% will be allowed to recombine, but that nearly all o atoms ....." Not clear what is meant here. Rewrite.

Table S1. Many/most of the reactions listed contribute little to the thermograms (e.g. does neglecting  $H + NO_3$  make any difference at all)? Please highlight those reactions that do have an influence (i.e. those that account for 90 % of the reactive flux). This would make the results of the modelling exercise more transparent. Please add (in a footnote) the original references used for the rate expressions. Just listing the NIST type label (e.g. 1986TSA) is not sufficient. What does JPL \*\* mean ( $HNO_3 + OH$  reaction). Please mark those reactions for which experimental data in the range up to 700 celcius was NOT available and indicate which (if any) are estimated or theoretical.

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