The authors would like to thank the reviewers of the manuscript entitled "Evaluation of the accuracy of thermal dissociation CRDS and LIF techniques for atmospheric measurement of reactive nitrogen species" for their helpful comments and suggestions. Our responses are as follows. The reviewer comments are in italics, our responses are in regular font, and changes to the manuscript are in blue.

**Reviewer #1**

*P2L25 Methods that detect some individual components of* $NO_y$ *are listed. How were they selected? Why not include e.g.* $NO_3$ *or HONO etc*
We wanted to highlight the detection of the just the largest components of reactive nitrogen. However, based on the feedback from both Reviewer 1 and 2, we have expanded this section to include references to $NO_3$, HONO, and other detection techniques for organic nitrates. P2L28 now reads: "HONO has been detected by long path differential optical absorption spectroscopy (Perner and Platt, 1979) and $NO_3$ has been detected by CRDS (King et al., 2000)."

*P3L24 "For example, TD-LIF detects* $NO_2$ *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?*
TD-LIF instruments are sometimes operated with the oven at low pressure, but not always. In this sentence, we meant that the $NO_2$ detection (i.e. in the optical cavity, not the oven) always happens at low pressure, but have updated it for clarity. P3L26 now reads: "For example, TD-LIF detects $NO_2$ at low pressure following thermal dissociation. Secondary recombination reactions of the dissociated radicals would thus be suppressed in the detection region, although the thermal dissociation inlet may be operated at either high or low pressures in these instruments. However, it is subject to interferences from ambient levels of NO and $NO_2$…"

*P3L29 "TD-CRDS is an absolute measurement….." Does TD-CRDS being based on a cross-section of* $NO_2$ *really make it absolute? As stated later in the manuscript, the effective optical path-length needs to be calibrated by adding known amounts of* $NO_2$*. Also, the TD-inlet is part of the instrument and its dissociation efficiency needs to be calibrated (the subject of this paper).*
The CRDS measurement does not require calibration of the instrument response; it relates the ringdown time directly to concentration through equation (2), in which the calibration is an absorption cross section, making it an absolute measurement. The instrument is periodically compared to an $NO_2$ standard, but remains absolute. While characterization of the effective optical cavity length, $R_L$, is required, it is not necessary to use $NO_2$ for this process. Any gas-phase species which absorbs at 405 nm would allow us to measure this, it just happens that $NO_2$ is the most convenient. As for the TD-inlet, as long as the temperature setpoint is set correctly, no calibrations are required since the conversion efficiency should be a constant. Standard additions of specific $NO_y$ components would then still be useful for validation of instrument performance. The reviewer raises a good point that perhaps a better word for these steps is "characterization", rather than "calibration". We have updated the lines in the experimental and discussion sections to reflect this. P5L29 now reads: "$\sigma/R_L$ is characterized regularly by filling the cavity with several different known $NO_2$ concentrations." P20L5 now reads: "TD ovens should be characterized with the appropriate reactive nitrogen compounds regularly at the oven set points using the oven residence time and gas pressure that will be used in ambient sampling."

*P4L3 "though this reaction rate depends on the TD inlet pressure and flow rate". What reaction rate is this referring to (NO +* $O_3$ *makes* $NO_2$ *but O +* $NO_2$ *or NO does not)?*
The Wooldridge *et al.* paper was referring to the $O_3$ + NO reaction (among others) when it said these interferences are subject to pressure, so this is the reaction we were referring to. For clarity, we have removed the phrase "(or the O atoms that form in $O_3$ pyrolysis)" from the manuscript to clarify that we

are referring to the $O_3$ + NO reaction. P4L5 now reads: "Likewise, ambient levels of $O_3$ in the sampled air may react in the oven with NO to form $NO_2$, resulting in a positive bias (Pérez et al., 2007), though this reaction rate depends on the TD inlet pressure and flow rate (Wooldridge et al., 2010)"

*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 $NO_2$ 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 effects of radical recombination ($RO_2$ + $NO_2$) or oxidation of NO ($RO_2$ + NO) can bias the detection of peroxy nitrates by factors of 2 or more and is likely the biggest source of uncertainty.*
Thanks to the reviewer for pointing out this sentence was unclear. It was intended to refer to all the interferences described in this paragraph, and it was also intended to refer to after the biases were removed. However, we don't wish to speak for the authors of those papers, and we have therefore deleted that phrase.

*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?*
The temperature probe is mounted on the outside of the quartz. As we point out on P6L12, the effect is that the actual gas temperature is slightly higher than the temperature setpoint, however, we periodically monitor the gas temperature by inserting a temperature probe into the oven, as seen in Fig. S1.

*P6L17 Does addition of 30 ppmv $O_3$ 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 $NO_2$?*
No, we are not concerned with this. Ozonolysis is quite slow, typically on the order of $10^{-17}$ $cm^3$/molec/s. Even though the ozone concentration may be high, the concentration of unsaturated hydrocarbons which may undergo ozonolysis is typically at the level of a few ppbv or less. We would therefore expect less than 0.5% conversion, or an interference on the order of ~20 pptv, which is below the detection limit.

*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 $N_2O_5$ and $HNO_3$ concentrations" How was the CIMS calibrated? How accurate are the concentration measurements?*
As detailed in the paragraph starting on P14L19, the CIMS was calibrated for $HNO_3$ using a permeation tube, but no calibration source was available for $N_2O_5$, so a relative measurement was obtained. The CIMS measurements are accurate to within 20-25%. P8L12 now reads: "This measurement has a detection limit of 4 pptv and 70 pptv and error bars of 25% and 25% ($3\sigma$) for $N_2O_5$ and $HNO_3$, respectively."

*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.*
The Berkeley TD-LIF instrument had an oven operating at ambient pressure, as described in Day et al (2002). P8L27 now reads: "$HNO_3$ and *n*-propyl-nitrate samples were provided by permeation tubes similar to those described in Sect. 2.2, diluted in dry zero air, and passed through 20 cm heated length quartz ovens, held at ambient pressure, at a flow rate of 2 slpm."

*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 NOy 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 $RO_2$ concentration) affected the loss rate, which could then be explained using a Langmuir-Hinshelwood type expression. Did you change the concentration (e.g. of $HNO_3$) significantly to see if the same wall loss rate constant was appropriate? Do you expect the rate constant for wall loss to be independent of temperature (effects of diffusion, turbulent mixing)?*
We did not change the concentration of $HNO_3$, because we were limited by the output of the permeation tube, which, at a flow rate of 1.9 slpm provided a maximum mixing ratio of ~5 ppbv. We used this maximum concentration because it is where we would expect the highest probability of recombination. While we expect the effect of recombination to be even lower at more diluted concentrations, we didn't explicitly test conversion efficiency as a function of $HNO_3$ concentration. We have inserted a line stating this caveat. P10L24 now reads: "No attempt was made to dilute the output of the $HNO_3$ permeation tube any further, as recombination effects would likely only be less important at lower starting $HNO_3$ concentrations."

*P9L23 was the $HNO_3$ input mixing ratio based on the permeation source or the CIMS signal?*
It was based on the output of the permeation source. The CIMS signal is also calibrated on the output of the permeation source, so to base the calculation on CIMS signal would introduce more error into the calculation.

*P9L31..."possible due to recombination reactions......." Which ones? Be specific.*
We have clarified that the recombination reaction is of OH and $NO_2$. P10L5 now reads: "The 0.5 slpm thermogram has a slightly lower maximum conversion efficiency (95%), possibly due to the recombination reaction of OH and $NO_2$ during the extended time in the cool down region prior to detection."

*P10L8 High and low pressure limits have been used to calculate the thermal dissociation rate constant for $HNO_3$. What value for Fc 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)?*
We used a value of $F_c = 0.6$, and have put a note in Table S1 stating this. Following the example of Day et al (2002), we didn't attempt to make any correction for air vs. argon. To our knowledge, no studies of the $HNO_3$ thermal decomposition were conducted in air. Wine et al (JCP 1979) measured the recombination reaction in Ar and $N_2$ and found that although there was a ~30% difference in the rate constant at room temperature (at ~20 Torr), that difference decreased to 10% at 350K. They did not do any experiments at higher temperatures or at ambient pressure. So given the basic nature of the kinetic model, we didn't attempt to make a corrective factor.

*P10 L13 "...the recombination rate for OH + $NO_2$ is quite low..." Be quantitative. What is the rate coefficient at this temperature and wat is the pseudo-first order rate coefficient for recombination for a given $NO_2$ level of e.g. 10 ppbv. This can then be compared to the wall loss rate coefficient.*
The rate constant at 650 °C is on the order of $3 \times 10^{-13}$ $cm^3$ $molec^{-1}$ $s^{-1}$. Therefore, the pseudo-first order rate coefficient for recombination, given an $NO_2$ level of 10 ppbv is ~0.075 $s^{-1}$, nearly three orders of magnitude lower than the wall loss rate coefficient of 46 $s^{-1}$. We have inserted a line which describes this. P10L21 now reads: …OH radicals are far more likely to be lost to the walls of the oven at a diffusion-limited rate determined by Day et al. (2002) of ~46 $s^{-1}$ for 1/4" OD tubing, which is far higher than the pseudo-first order recombination rate coefficient of 0.075 $s^{-1}$ at $[NO_2]$ = 10 ppbv.

*P10L27 Did Sobanski et al. (2016) also present a decomposition efficiency for $HNO_3$? 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.*
They presented a decomposition efficiency curve up to 350 °C, and found the $HNO_3$ conversion efficiency was close to 0% at these temperatures. This is consistent with our results, and we have inserted

that reference into the manuscript. P10L29 now reads: This is in contrast to ANs and PNs, for which the reaction of the dissociated peroxy and alkyl radicals with $NO_2$ is a significant interference (Thieser et al., 2016), but in good agreement with the $HNO_3$ results of Day et al. (2002) and Sobanski et al. (2016).

*P11L9 ".. the onset and final conversion of $HNO_3$ 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 $HNO_3$ but also $NO_2$ to increase the rate of re-formation of $HNO_3$? The authors should consider doing one such experiment to see if elevated $NO_2$ will influence the shape of the $HNO_3$ thermogram. The same applies to the $NH_3$ expeirments.*
Yes, that is our conclusion. If we calculate the pseudo-first order rate coefficient for recombination with $[NO_2]$ = 50 ppbv, which is much higher than typically observed in the field, that rate coefficient is still two orders of magnitude lower than the wall loss rate coefficient, and is still unlikely to compete. We agree that testing this experimentally would be an interesting direction to take these studies in the future, but such tests were not feasible at this time. However, the kinetic box model supports this hypothesis, and we have inserted a line indicating this. P10L26 now reads: "Similarly, increasing the starting $NO_2$ concentration, to mimic conditions in highly polluted environments, was not attempted in this set of experiments, but increasing the starting $NO_2$ concentration in the kinetic model up to 50 ppbv shows that there is no recombination expected even with elevated $NO_2$ in the oven."

*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 $HNO_3$ detection while adding $NO_2$ would have been useful to confirm that the simple model reproduces the thermograms for the right reasons.*
Please see our response to the previous comment.

*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 NOx.*
The purpose of the VOC additions were to test the effect on the secondary chemistry of $HNO_3$ conversion in high VOC environments, such as the recent Uintah Basin Winter Ozone Studies (see Wild 2016), where thermal dissociation inlets were used to measure $NO_y$ and speciated $NO_y$. While the reviewer is correct that adding organic nitrates would also be interesting, the scope this paper was limited to the listed components of reactive nitrogen, $HNO_3$, $N_2O_5$ and ammonium nitrate, to test quantitative conversion at high temperature. However, the study of Thieser *et al*. nicely defines the effect of organic nitrates. We have inserted a line clarifying the intention of these experiments. P12L23 now reads: "Figure 5b shows the measured thermogram with the addition of ~50 ppbv VOCs (described in Sect. 2.2) with and without the addition of 90 ppbv $O_3$, as well as the addition of 5 ppmv of propane, to mimic conditions found in highly polluted wintertime atmospheres."

*P12L17 ".....The oven is set at sufficiently high temperatures to dissociate ANs and PNs back to $NO_2$ + the organic radical" Not true. At higher temperatures the $RO_2$ formed from thermal dissociation of PNs is unstable (see Thieser et al. 2016).*
The reviewer is correct, $RO_2$ is often unstable at high temperatures. We were intending to say that if some $RO_2$ formed via ozonolysis or other mechanism, it is unlikely that it would scavenge $NO_2$ to reform PNs, since PNs would immediately dissociation. It is true that if the $RO_2$ simply dissociated, then it wouldn't react with $NO_2$ at all. Therefore, we have inserted a line which states that the $RO_2$ molecule would be more likely to dissociate. P12L30 now reads: "Reactions of unsaturated hydrocarbons with O atoms or OH radicals tend to be rapid and would produce organic radicals, but these tend to be unstable, and any stable radicals would likely only react with $NO_2$ to form ANs or PNs. The oven is set at sufficiently high temperatures to dissociate ANs and PNs back to $NO_2$ + the organic radical."

*P12L27 "....The dominant reaction of $O_3$ in the model is the reaction with $NO_2$ to make $NO_3$...." Is this true? I would have thought the pyrolysis will dominate at high temperatures. Is the $O_3$ pyrolysis rate constant in the model correct? What is the O-to-$O_3$ ratio at thermal and kinetic equilibrium?*
We have changed the line to distinguish those reactions from the unimolecular dissociation reaction, which should dominate at higher temperatures. P13L9 now reads: "The dominant bimolecular reaction of $O_3$ in the model is the reaction with $NO_2$ to make $NO_3$, but since these reactions are occurring at high temperature, any $NO_3$ formed will immediately dissociate to $NO_2$ (see Sect. 3.2)."

*P12L30 The reaction between O and $NO_2$ does not form much $NO_3$ but mainly NO + $O_2$. This is especially true at high temperatures.*
Both reactions should be relevant, so we have added both to that line. P13L13 now reads: "Of the O atoms that are not lost to the walls, their primary reaction is also with $NO_2$ to form either NO + $O_2$ or $NO_3$ but NO should be converted back to $NO_2$ after the oven."

*P13L5 That a model with no surface-catalysed reactions cannot reproduce the effect of a surface catalyzed reaction is not surprising. Why do NOy instruments with e.g. gold-surfaces see decomposition at much lower temperature than needed to break the HO-NO2 bond and why do they add CO? It is more than "possible" that surface reactions play a role, it is rather clear.*
We have removed the word possible, and replaced it with the word "likely". P13L25 now reads: "It is likely that there is some surface reaction that affects the $HNO_3$ conversion in the presence of CO."

*P16L25 Are there any other reactions of $NH_2$ that should be considered. Could it react with NO or $NO_2$?*
Thanks for noticing this. Although the $NH_2$ + NO and $NH_2$ + $NO_2$ reactions were included in the model, they were mistakenly omitted from table S1. They have now been included.

*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.*
We have changed the line to be more specific. P17L24 now reads: "This rudimentary simulation predicts the initial signal increase starting at 300 °C, though it has a maximum conversion efficiency of just under 2%, which is below that observed in the experiment."

*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.*
Please see our response to the comment on line P12L11.

*P18L23 "...$N_2O_5$ is not typically considered in the TD-$NO_2$ 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 $N_2O_5$ thermal decomposition (e.g. Thieser et al. 2016)*
That is true, there are some groups which have used TD inlets at night. We have rewritten that paragraph to incorporate this. P19L5 now reads: "TD-$NO_y$ instruments often operate in the daytime when $N_2O_5$ is not a significant fraction of $NO_y$, though some groups have operated at night and have typically assumed complete conversion to $NO_2$ + $NO_3$ at the TD inlet setpoint for PNs (Di Carlo et al., 2013), and complete conversion to $2NO_2$ + O at the setpoint for $HNO_3$ (Wild et al., 2014). These results confirm that there is approximately quantitative conversion at these setpoints, though there are slight deviations from 100% conversion near the PN setpoint. Therefore, care must be taken to select a setpoint carefully and ensure complete conversion at that temperature. However, this interference would only be significant during nighttime or during very cold weather sampling."

*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?*
While we agree that organic nitrates are of significant interest, ammonium nitrate, which is in equilibrium with $HNO_3$ in the atmosphere, was the target of this study. We have inserted a line clarifying that we are talking about particulate ammonium nitrate. We have also inserted a line saying that although it's likely that other organic nitrates would behave similarly, further experiments would be required to test this. P19L22 now reads: "These results demonstrate that the volatile portion of the particulate ammonium nitrates will be driven into the gas phase at low oven temperatures, consistent with Rollins et al. (2010), who used a denuder to remove gas phase nitrates and to detect aerosol organic nitrates in a 325 °C oven. Their results indicate it is likely that particulate organic nitrates would be converted to $NO_2$ with 100% efficiency in the NOAA TD-CRDS, but this result has not been explicitly tested here."

Technical / typographical
*P2L20 Techniques that detect the major individual components of NOy include detection....*
See response to P2L20 above

*P4L1/3 negative / positive artefact = negative / positive bias?*
We have changed the word artifact to bias on P4L5 and P4L7.

*P5L4 Inappropriate reference. Fuchs et al were not the first to use CRDS for atmospheric trace gases as this implies.*
The intent was to cite a representative reference, not the first reference. We have added a reference at P5L4 to O'Keefe et al (1988), who were the first that we are aware of to measure ambient $NO_2$ with CRDS.

*P5L18 "light decays" ?*
We have changed "light decays" to "light decay profiles", for clarity. P5L18 now reads: "The measured light decay profiles are summed and fit at a 1 Hz repetition rate to yield the ringdown time $\tau$."

*P5L23 "known NO2 concentrations". How were they determined? Was an "absolute method" used to measure the NO2 concentration?*
The known samples of $NO_2$ were obtained by reacting known amounts of $O_3$ from an ozone generator with an excess of NO. The ozone generator is a commercial ThermoScientific 49i, which measures $O_3$ by UV absorption. This is a technique that has been used by our group, and was described in section 2.2 of Washenfelder et al, EST 2011. We have inserted a new phrase to clarify this. P5L29 now reads: "$\sigma/R_L$ is characterized regularly by filling the cavity with several different known $NO_2$ concentrations (obtained by reacting the output of an $O_3$ standard source with excess NO) and calculating the slope of the measured optical extinction vs $[NO_2]$ as described in Washenfelder et al. (2011)"

*P7L22 "bubbling the dilution zero air through a water bubbler...."*
We have changed "bubbling" to "passing". P7L24 now reads: "Water was added by passing the dilution zero air through a water bubbler prior to mixing with the $HNO_3$ sample."

*P8L31 and at several other places in the manuscript. "rate laws" is the wring term. You refer to "rate constants" or "rate expressions".*
These have all been changed to rate expressions (throughout manuscript).

*References: Several have capitalsed manuscript titles. Nikitas et al spelling of Detector.*
Thank you for noticing. We have fixed these typos.

*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".*
We have changed this to "cooling region" in the Fig 1 and caption, which is consistent with what Day *et al.* (2002) and Wild *et al.* (2014) have called it.

*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.*
We have made these changes.

*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.*
This was a typo/error. We meant to say that only 40% will remain as $O_2$ + O. Figure S4's caption now reads: "These results indicate that $O_3$ dissociates to form O at the entire temperature range relevant for AN and $HNO_3$ TD ovens, but that if allowed to recombine, only ~40% will remain as $O_2$ + O. If wall loss is permitted, nearly all O atoms would be lost to reactions with the wall."

*Table S1. Many/most of the reactions listed contribute little to the thermograms (e.g. does neglecting H + NO3 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 (HNO3 + OH reaction). Please mark those reactions for which experimental data in the range up to 700 celcius was NOT available and inducate which (if any) are estimated or theoretical.*
We have reorganized Table S1. It now includes the rate constant at the minimum and maximum temperature (298K and 950K). We are also now indicating the temperature range, and whether they were experimental or theoretical. References are now directly included. The JPL ** was supposed to be a footnote which was mistakenly omitted, but which is now included. Any reactions at lower than 700 °C were used because reproducible values at higher temperatures were not available.