

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 #3

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This manuscript reports some tests to characterize the thermal dissociation technique for the detection of reactive nitrogen species using CRDS and LIF detectors. The manuscript is generally well written, and the main results confirm what already known from previous publications. On the other hand, there are some technical details and insights that can be of interest for more selective and precise speciated NO_y measurements. I think that it fits with AMT scopes and I recommend publication, after the authors address the following questions and comments.

Main comments and questions:

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Page 11, lines 4-13: Placing a stainless steel valve in front of the oven is something that I would avoid working with HNO₃ that may be efficiently loss, even if the authors mention a test with the valve fully opened to check if the conversion of HNO₃ changes when it is removed.

Page 12, line 3: Authors tested the effect of RH on the thermograph shape of the HNO₃ with a test at 0% and another at 66%. Since in several sites the RH goes up to 90%, it would be worth to have one more point at high RH.

Page 15, lines 7-19: In this paragraph even if not clearly reported, it is implied that the thermal conversion of NH₄NO₃, reported also in figure 7, is a two step conversion: first from NH₄NO₃ to HNO₃ and then from HNO₃ to NO₂, since the CRDS measures NO₂. In this case it would be important the residence time to allow the double thermal dissociation in the heated tube, but this is not mentioned nor explored.

Page 15, lines 17-19 and figure 7: Here it is reported that the thermograph of NH₄NO₃ agrees with that of HNO₃ reported in fig. 2. In fig. 2 are showed 4 thermographs of HNO₃, but, to me, none of them are the same reported in figure 7.

Page 16, line 18: The NH₃ conversion is unimportant for all the TD-LIFs, since all of them measure directly NO₂: so I would generalize this conclusion to all the TD-LIFs and not only to the Berkeley TD-LIF.

Page 18, lines 22-23: This statement is not correct: 1) there are several campaigns where TD-NO₂ were used during nighttime (i.e. BEACHON-RoMBAS, see Fry et al, 2013; RONOCO, see Di Carlo et al., 2013). 2) There is at least one paper where is described that during nighttime the channel of the TD-LIF instrument that converts

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total peroxy nitrate into NO₂, converts also N₂O₅ (Di Carlo et al., 2013). In that paper is reported also the comparison of nighttime measured peroxy nitrate by TD-LIF with the N₂O₅ measured by CRDS, taking the advantage of a TD-LIF and a CRDS installed on the same aircraft. In that work it is also showed that the TD-LIF measurements of peroxy nitrated, during nighttime and at least in the RONOCO campaign, are dominated by N₂O₅.

Minor comments and questions:

Page 6, line 1: the inlet tube 0.39 cm ID. Seems too small, is it a typo or a conversion error from inch to cm?

Page 15, line 5: Cohen, 2016 is cited as reference here, but it is not reported in the reference list.

Reference

Di Carlo P., E. Aruffo, M. Busilacchio, F. Giammaria, C. Dari-Salisburgo, F. Biancofiore, G. Visconti, J. Lee, S. Moller, C. E. Reeves, S. Bauguitte, G. Forster, R. L. Jones, and B. Ouyang, Aircraft based four-channel thermal dissociation laser induced fluorescence instrument for simultaneous measurements of NO₂, total peroxy nitrate, total alkyl nitrate, and HNO₃, *Atmos. Meas. Tech.*, 6, 971–980, 2013.

Fry, J. L., D. C. Draper, K. J. Zarzana, P. Campuzano-Jost, D. A. Day, J. L. Jimenez, S. S. Brown, R. C. Cohen, L. Kaser, A. Hansel, L. Cappellin, T. Karl, A. Hodzic Roux, A. Turnipseed, C. Cantrell, B. L. Lefer, N. Grossberg, Observations of gas- and aerosol-phase organic nitrates at BEACHON-RoMBAS 2011, *Atmos. Chem. Phys.*, 13, 8585–8605, 2013.

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