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Atmospheric Measurement Techniques Discussions

Interactive comment on "Measurements of CH₃O₂NO₂ in the upper troposphere" *by* B. A. Nault et al.

Anonymous Referee #2

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Review of Nault et al

Nault et al. report a modification of the Berkeley TD-LIF instrument that enables the selective measurement of methyl peroxy nitrate in the UT. This sounds like a marginal improvement over the instrument described by Murphy et al. (ACP 4, 377-384, 2004) but may nevertheless be an important contribution, as one may hope that the ability to differentiate HO2NO2 from CH3O2NO2 will improve our understanding of nitrogen oxide chemistry in the upper atmosphere.

In general, the paper is written well and straightforward, but perhaps a bit too brief at times. In this reviewer's opinion, it should be published after my comments (below) and those of the other reviewers have been addressed.

General comments

1. It seems like more could have been done to validate the experimental technique. Have there been any laboratory validation experiments? How about in-field comparisons of HO2NO2 measured by TD-LIF and CIMS? Why are only the CIMS data shown?

2. What's lacking in this paper is a prediction of CH3O2NO2 and a comparison of predicted with observed values.

3. The paper could have been made more interesting by showing more of the in-flight data.

Specific comments

page 9454, line 4. In the abstract, it is claimed that these are the first measurements of methyl peroxy nitrate. Considering that this group has published on HO2NO2 and CH3O2NO2 in the past, these are hardly the first measurements of this compound, but perhaps the first selective measurements - certainly not specific, as contributions from HO2NO2 still not to be subtracted.

line 9 "have lower thermal stability" - can you the authors be more quantitative here? Perhaps give (relative) bond dissociation energies?

pg 9455 lines 5-6. It is claimed that ethyl and acetone peroxy nitrate are not abundant enough to interfere, and papers are cited (as if they were fact) in which that assumption was made by the same group. I don't think that the authors are wrong here, but please don't give the wrong impression that this is anything other than an assumption.

pg 9455, line 15/16 (R1 and R2) and Table 2 (pg 9470) The double-headed arrow is used by chemists to denote resonance structures - please replace with the appropriate symbol for equilibrium.

pg 9455, lines 20-23. The authors state lifetimes, but it is not clear on what basis these

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were calculated - based on rates by Sander et al., or are these values derived from observations perhaps?

pg 9456, line 14, and pg 9460, lines 4 and 14. For a chemist, "X" would imply a halide - it would be more appropriate to use RO2NO2 to refer to non-acyl peroxy nitates.

line 20 "... to isolate CH3O2NO2 directly". Since CH3O2NO2 is measured indirectly, consider rephrasing to "... to isolate the CH3O2NO2 signal".

pg 9457, lines 16- pg 9458 line 10. Can the authors comment on the possibility and extent of recombination reactions (e.g., of CH3O2 + NO2) and of the possibility and extent of either HO2 or CH3O2 oxidizing NO and creating a "fake" signal?

pg 9458, line 11. "Interference free NO2" This title is misleading as there always is a water interference with this technique (see pg 9457 - lines 13-15).

pg 9461 line 6. I didn't like that the uncertainty as described as a single number (40%). Shouldn't it be a function of HO2NO2, NO, and NO2? In other words, the uncertainty could be much higher than 40% if there was more HO2NO2 that needed to be subtracted.

pg 9462, line 3 (equation 3) and lines 9-10. "We observe a similar result; therefore, we divide the calculations by 2 to reflect that result". This is interesting. Even with this arbitrary fudging, the predicted values are still quite a bit too high, if I interpret Figure 6 correctly. Earlier (pg 9455, line 20) it is stated that the lifetime of HO2NO2 is typically 7 hours. Under these conditions, it may take more than a day to get a photostationary state. The assumption going into the pss (i.e., equation (3)) may be invalid if the HO2NO2 lifetime really is this long. Couldn't the HO2NO2 concentrations not have been simulated using a simple box model? How about attempting to predict CH3O2NO2 (and comparing to measurements)?

line 11 "the time 7.5 and 8x10^4 s". Please convert to more conventional units of time (hours, minutes). UTC is great, but it would also be helpful to know what time zone you

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were in (and what local time it was then).

pg 9472. Figure 1. Please state in the caption how these lifetimes were calculated.

pg 9477. Why is the predicted data missing after 8x10ˆ4 s? In the caption of Figure 6, please remove the hyphen between ionization and mass.

pg 9479. Please state the r value of the fit.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 9453, 2014.