

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

Anonymous Referee #2

Received and published: 8 November 2014

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.

C3630

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

C3631

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 nitrates.

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 8×10^4 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

C3632

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 8×10^4 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.

C3633